

USING THE ABRAHAM SOLVATION PARAMETER MODEL TO PREDICT
SOLUTE TRANSFER INTO VARIOUS MONO- AND MULTI-
FUNCTIONAL ORGANIC SOLVENTS

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The Abraham solvation parameter model (ASPM) is a linear free energy relationship that can be used to predict various solute properties based on solute-solvent interactions. The ASPM has been used to predict $\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}})$ values, as well as $\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}})$ values for solute transfer into the following organic solvents: 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-isopropoxyethanol and 2-butoxyethanol. The derived $\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}})$ correlations describe the experimental data to within 0.14 log units (or less). The derived $\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}})$ correlations describe the experimental data to within 0.16 log units (or less). The ASPM has also been used to predict the enthalpies of solvation (ΔH_{solv}) of organic solutes dissolved in the following solvents: acetic acid, dimethyl carbonate, diethyl carbonate, 1-butanol, 1-pentanol and 1-hexanol. The derived ΔH_{solv} correlations, using the **L** solute descriptor, describe the experimental to data to within 2.50 log units (or less). The derived ΔH_{solv} correlations, using the **V** solute descriptor, describe the experimental data to within 3.10 log units (or less). Validation analyses have been performed on several of the correlations; and, as long as the solute descriptors fall within the given ranges as reported, the original correlations show good predictive ability for determining 1) solute transfer into, and 2) ΔH_{solv} for the aforementioned solvents.

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By

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TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	iii
LIST OF TABLES.....	viii
LIST OF FIGURES.....	xi
CHAPTER 1. THE ABRAHAM SOLVATION PARAMETER MODEL.....	1
1.1 Introduction.....	1
1.2 Solute Descriptors and Process Coefficients.....	2
1.2.1 E and <i>e</i>	3
1.2.2 S and <i>s</i>	4
1.2.3 A and <i>a</i>	4
1.2.4 B and <i>b</i>	6
1.2.5 L and <i>l</i>	7
1.2.6 V and <i>v</i>	7
1.3 Applications.....	8
1.3.1 Solute Transfer and Solubility.....	9
1.3.2 Enthalpy of Solvation.....	16
1.3.3 “Green Chemistry”.....	18
1.4 Comparison to other predictive models.....	20
1.4.1 Carr’s Model.....	20
1.4.2 Klamt’s Model.....	21
1.4.3 Abraham’s Model.....	22
1.5 References.....	23
CHAPTER 2. STATISTICAL ANALYSIS.....	27
2.1 Introduction.....	27
2.2 SPSS®.....	28
2.2.1 Multiple Linear Regression Analysis.....	28
2.2.2 Validation Process of Regression Analysis.....	34
2.3 Solver®.....	36
2.4 Principal Components Analysis.....	37

2.5	References	40
CHAPTER 3. DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR SOLUTE TRANSFER INTO 2-METHOXYETHANOL FROM WATER AND FROM THE GAS PHASE		
3.1	Introduction	41
3.2	Experimental Methodology	43
3.2.1	Solubility Measurements	43
3.2.2	Gas Chromatographic Headspace Measurements	45
3.3	Results and Discussion.....	46
3.4	Conclusions	53
3.5	References	57
CHAPTER 4. DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR SOLUTE TRANSFER INTO 2-ETHOXYETHANOL FROM WATER AND FROM THE GAS PHASE		
4.1	Introduction	60
4.2	Experimental Methodology	61
4.2.1	Gas Chromatographic Headspace Measurements	61
4.2.2	Solubility Measurements	64
4.3	Results and Discussions.....	65
4.4	Conclusions	75
4.5	References	76
CHAPTER 5. DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR SOLUTE TRANSFER INTO BOTH 2-PROPOXYETHANOL AND 2-ISOPROPOXYETHANOL FROM WATER AND FROM THE GAS PHASE		
5.1	Introduction	79
5.2	Experimental Methodology	82
5.2.1	Gas Chromatographic Headspace Measurements	82
5.2.2	Solubility Measurements	84
5.3	Results and Discussion.....	86
5.4	Conclusions	99
5.5	References	99

CHAPTER 6. DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR SOLUTE TRANSFER INTO 2-BUTOXYETHANOL FROM WATER AND FROM THE GAS PHASE	102
6.1 Introduction	102
6.2 Experimental Methodology	104
6.2.1 Gas Chromatographic Headspace Measurements	104
6.2.2 Solubility Measurements	106
6.3 Results and Discussion.....	107
6.4 Conclusions	115
6.5 References	116
 CHAPTER 7. DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR PREDICTING THE ENTHALPIES OF SOLVATION OF SOLUTES DISSOLVED IN ACETIC ACID	119
7.1 Introduction	119
7.2 Computational Methodology and Data Sets.....	123
7.3 Results and Discussion.....	125
7.4 Conclusions	137
7.5 References	138
 CHAPTER 8. DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR PREDICTING THE ENTHALPIES OF SOLVATION OF SOLUTES DISSOLVED IN BOTH DIMETHYL CARBONATE AND DIETHYL CABONATE	142
8.1 Introduction	142
8.2 Computational Methodology and Data Sets.....	143
8.3 Results and Discussion.....	149
8.4 Conclusions	161
8.5 References	162
 CHAPTER 9. DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR PREDICTING THE ENTHALPIES OF SOLVATION OF SOLUTES DISSOLVED IN 1-ALKANOL SOLVENTS (C ₄ – C ₆).....	165
9.1 Introduction	165
9.2 Computational Methodology and Data Sets.....	166
9.3 Results and Discussion.....	178
9.4 Conclusions	188

9.5	References	189
CHAPTER 10.	CONCLUSIONS.....	195
10.1	Conclusions	195
10.2	References	200

LIST OF TABLES

	Page
Table 1.1. Meanings of process coefficients and solute descriptors.	3
Table 1.2. Atom contributions of select elements to the McGowan volume, in $\text{cm}^3 \text{mol}^{-1}$ [9].	8
Table 1.3. Abraham Solvation Parameter Model $\log K$ process coefficients.	13
Table 1.4. Abraham Solvation Parameter Model $\log P$ process coefficients.	13
Table 1.5. Abraham Solvation Parameter Model ΔH_{solv} process coefficients.	17
Table 1.6. Abraham Solvation Parameter Model ΔH_{solv} process coefficients.	17
Table 2.1. Abraham model process coefficients for predicting enthalpies of solvation of solutes in select organic solvents based on Equation (1.24).	39
Table 3.1. Experimental mole fraction solubilities of crystalline nonelectrolyte solutes dissolved in 2-methoxyethanol at 298.15K.	44
Table 3.2. Experimental infinite dilution activity coefficients, γ_{∞} , of the external test set solutes dissolved in 2-methoxyethanol at 298.15 K.	45
Table 3.3. Experimental $\log (K \text{ or } C_{\text{S,organic}}/C_{\text{S,gas}})$ and $\log (P \text{ or } C_{\text{S,organic}}/C_{\text{S,water}})$ data for solutes dissolved in 2-methoxyethanol at 298.15 K.	48
Table 3.4. Experimental $\log K$ and $\log P$ data for the external test set solutes dissolved in 2-methoxyethanol at 298.15 K.	53
Table 3.5. Coefficients in Equation (1.2) for gas-to-dry solvent partitions.	54
Table 4.1. Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and the Gibbs free energies solvation in 2-ethoxyethanol at 298.15 K ^a	63
Table 4.2. Experimental mole fraction solubilities of crystalline nonelectrolyte solutes dissolved in 2-ethoxyethanol at 298.15 K.	65
Table 4.3. Experimental $\log (K \text{ or } C_{\text{S,organic}}/C_{\text{S,gas}})$ and $\log (P \text{ or } C_{\text{S,organic}}/C_{\text{S,water}})$ data for solutes dissolved in anhydrous 2-ethoxyethanol at 298.15 K.	68
Table 4.4. Statistic test set results for Abraham model training set Equations (4.4) – (4.9).	74
Table 4.5. Regression coefficients of Equation (1.13) for different solvents.	76

Table 5.1. Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and the Gibbs energies of solvation in 2-propoxyethanol at 298.15 K ^a	82
Table 5.2. Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and Gibbs energies of solvation in 2-isopropoxyethanol at 298.15 K ^a	83
Table 5.3. Experimental mole fraction solubilities, X_{Sexp} , of crystalline nonelectrolyte solutes dissolved in 2-propoxyethanol at 298.15 K ^a	85
Table 5.4. Experimental mole fraction solubilities, X_{Sexp} , of crystalline nonelectrolyte solutes dissolved in 2-isopropoxyethanol at 298.15 K ^a	86
Table 5.5. Experimental log (K or $C_{S,organic}/C_{S,gas}$) and log (P or $C_{S,organic}/C_{S,water}$) data for solutes dissolved in 2-propoxyethanol at 298.15 K.	89
Table 5.6. Experimental log (K or $C_{S,organic}/C_{S,gas}$) and log (P or $C_{S,organic}/C_{S,water}$) data for solutes dissolved in 2-isopropoxyethanol at 298.15 K.....	93
Table 6.1. Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and Gibbs free energies of solvation in 2-butoxyethanol at 298.15 K ^a ...	105
Table 6.2. Experimental log (K or $C_{S,organic}/C_{S,gas}$) and log (P or $C_{S,organic}/C_{S,water}$) data for solutes dissolved in 2-butoxyethanol at 298.15 K.	109
Table 7.1. Abraham model process coefficients for predicting enthalpies of solvation of solutes in select organic solvents based on Equation (1.24).....	120
Table 7.2. Abraham model process coefficients for predicting enthalpies of solvation of solutes in select organic solvents based on Equation (1.25).....	121
Table 7.3. Values of the gas-to-acetic acid solvation enthalpy, ΔH_{solv} (in kJ mol ⁻¹), at 298.15 K for 92 solutes together with the solute descriptors.	126
Table 7.4. Values of gas-to-acetic acid partition coefficients, K , gas-to-acetic acid Gibbs energies, ΔG_{solv} (kJ mol ⁻¹), and gas-to-acetic acid enthalpies of solvation, ΔH_{solv} (kJ mol ⁻¹), at 298.15 K for 27 solutes.....	134
Table 8.1. Values of the gas-to-diethyl carbonate solvation enthalpy, $\Delta H_{solv, DEC}$ (in kJ mol ⁻¹), at 298.15 K for 80 solutes together with the solute descriptors.	145
Table 8.2. Values of the gas-to-dimethyl carbonate solvation enthalpy, $\Delta H_{solv, DMC}$ (in kJ mol ⁻¹), at 298.15 K for 57 solutes together with the solute descriptors.	154
Table 8.3. Enthalpies of hydrogen-bond interactions, ΔH_{HB} (in kJ mol ⁻¹) between different proton donors with dimethyl carbonate, diethyl carbonate, propylene carbonate and ethyl acetate based on the Abraham model correlations (Equations (8.10) – (8.13)).	160

Table 9.1. Values of the gas-to-1-pentanol solvation enthalpy, ΔH_{solv} , PtOH for 92 solutes together with the solute descriptors.	168
Table 9.2. Values of the gas-to-1-hexanol solvation enthalpy, ΔH_{solv} , HxOH for 84 solutes together with the solute descriptors.	172
Table 9.3. Values of the gas-to-1-butanol solvation enthalpy, ΔH_{solv} , BtOH for 30 solutes together with the solute descriptors.	177
Table 10.1. Abraham Solvation Parameter Model log K process coefficients.....	198

LIST OF FIGURES

	Page
Figure 1.1. Cavity model of solvation. Adapted from Poole et al. [1].	2
Figure 1.2. Depiction of relationship between partition coefficients and the phases of solute transfer [12].....	10
Figure 1.3. Schematic representation of gas-to-tetraglyme properties [12].	12
Figure 1.4. Schematic representation of water-to-tetraglyme properties [12].	12
Figure 1.5. Pictorial representation of the calculation of enthalpy of solution [39].	17
Figure 2.1. Defining the variables as dependent or independent using IBM® SPSS® 22. Found under the Analyze tab → Regression → Linear[1].	29
Figure 2.2. Submenus under the Linear Regression window to further parameterize the regression in SPSS® 22. [1].	30
Figure 2.3. Output file from SPSS® with highlighted areas showing information of particular interest [1].....	31
Figure 2.4. Visual interpretation of the correlation coefficient and the coefficient of determination [7].	32
Figure 2.5. Description of minimization and calculation process in Solver®. Found under the data tab → Solver.....	38
Figure 2.6. Standard deviation is minimized, and process coefficients and solute property are calculated.....	38
Figure 2.7. Basic PCA plot made using SPSS® with solvents from Table 2.1. [1].....	40
Figure 3.1. Comparison between experimental log <i>K</i> data and calculated values based on Equation (3.2).....	52
Figure 3.2. Comparison between experimental log <i>P</i> data and calculated values based on Equation (3.1).....	52
Figure 3.3. A plot of the scores of PC2 against the scores of PC1. Points numbered as in Table 3.5: ● 2-methoxyethanol and 2-ethoxyethanol; ▲ other alcoholic solvents; ○ non-alcoholic solvents.	56
Figure 4.1. Comparison of the Gibbs free energies of solvation of low polar solutes in 2-ethoxyethanol (EC) and 2-methoxyethanol (MC) at 298.15 K. Triangles are aliphatic, circles are aromatic solutes. Dotted line is $y = x$	64

Figure 4.2. Comparison between experimental log <i>K</i> data and calculated values based on Equation (4.2).....	72
Figure 4.3. Comparison between experimental log <i>P</i> data and calculated values based on Equation (4.1).....	72
Figure 5.1. Comparison of experimental log <i>K</i> data versus back-calculated values based on Equation (5.2) for solutes dissolved in 2-propoxyethanol.	96
Figure 5.2. Comparison of experimental log <i>P</i> data versus back-calculated values based on Equation (5.1) for solutes dissolved in 2-propoxyethanol.	97
Figure 5.3. Comparison of experimental log <i>K</i> data versus back-calculated values based on Equation (5.4) for solutes dissolved in 2-isopropoxyethanol.....	97
Figure 5.4. Comparison of experimental log <i>P</i> data versus back-calculated values based on Equation (5.3) for solutes dissolved in 2-isopropoxyethanol.....	98
Figure 6.1. Comparison between experimental log <i>K</i> data and back-calculated values based on Equation (6.2).....	113
Figure 6.2. Comparison between experimental log <i>P</i> data and back-calculated values based on Equation (6.1).....	113
Figure 7.1. Hydrogenation gas phase and solution phase reactions for converting an alkene to an alkane.	123
Figure 7.2. Comparison between experimental ΔH_{solv} data (in kJ mol^{-1}) for solutes dissolved in acetic acid at 298.15 K and predicted values based on Equation (7.2)...	130
Figure 7.3. Comparison between experimental ΔH_{solv} data (in kJ mol^{-1}) for solutes dissolved in acetic acid at 298.15 K and predicted values based on Equation (7.3)...	131
Figure 7.4. Relationship between the Gibbs energy of solvation and enthalpy of solvation for 27 organic and inorganic solutes dissolved in acetic acid.....	135
Figure 7.5. Comparison of linear structure of acetic acid versus a cyclic dimer formation.	136
Figure 7.6. A plot of the scores of PC2 against the scores of PC1. Solvents numbered as in Table 7.1. Symbols: ● acetic acid; ▲ alcohols.	137
Figure 8.1. Comparison of experimental ΔH_{solv} , DEC data for solutes dissolved in diethyl carbonate and calculated values based on Equation (8.3).	151
Figure 8.2. Comparison of experimental ΔH_{solv} , DEC data for solutes dissolved in diethyl carbonate and calculated values based on Equation (8.4).	151

Figure 8.3. Comparison of experimental ΔH_{solv} , DMC data for solutes dissolved in diethyl carbonate and calculated values based on Equation (8.8).	157
Figure 8.4. Comparison of experimental ΔH_{solv} , DMC data for solutes dissolved in diethyl carbonate and calculated values based on Equation (8.9).	158
Figure 9.1. Comparison of experimental ΔH_{solv} , PtOH (in kJ mol^{-1}) data for solutes dissolved in 1-pentanol and calculated values based on Equation (9.1).	179
Figure 9.2. Comparison of experimental ΔH_{solv} , PtOH (in kJ mol^{-1}) data for solutes dissolved in 1-pentanol and calculated values based on Equation (9.2).	180
Figure 9.3. Comparison of experimental ΔH_{solv} , HxOH (in kJ mol^{-1}) data for solutes dissolved in 1-hexanol and calculated values based on Equation (9.5).	183
Figure 9.4. Comparison of experimental ΔH_{solv} , HxOH (in kJ mol^{-1}) data for solutes dissolved in 1-hexanol and calculated values based on Equation (9.6).	184
Figure 9.5. Comparison of experimental ΔH_{solv} , BtOH (in kJ mol^{-1}) data for solutes dissolved in 1-butanol and calculated values based on Equation (9.9).	186
Figure 9.6. Comparison of experimental ΔH_{solv} , BtOH (in kJ mol^{-1}) data for solutes dissolved in 1-butanol and calculated values based on Equation (9.10).	187
Figure 10.1. PCA plot of solvents listed in Table 10.1.	198

CHAPTER 1

THE ABRAHAM SOLVATION PARAMETER MODEL

1.1 Introduction

The Abraham solvation parameter model (ASPM) is a linear free-energy relationship (LFER) that is used to describe the interactions between solutes and solvents for a given solute property (SP) and is based primarily on the parameterization of the cavity model of solvation [1]. The cavity model of solvation, shown in Figure 1.1, occurs in three steps and describes the process of solute transfer from one phase to another. In the first step, a cavity large enough to accommodate the solute is formed in the phase that is receiving the solute. This process is typically an energetically unfavorable one as it requires the disruption of solvent-solvent interactions; however, it depends upon which phase has stronger solvent-solvent interactions as to whether it truly is energetically unfavorable. In the second step, which is energetically negligible, reorganization of the solvent molecules occurs in order to form a more favorable orientation for the solute molecule. In the third and final step, the solute molecule enters the cavity and various solute-solvent interactions take place. This step is typically energetically favorable and results in the interactions measured by the ASPM: dispersion, orientation, induction and hydrogen-bonding. Through this model, Abraham created measurable, or calculable, parameters for solute transfer from the gas phase to condensed phase (Equation (1.1)) and for solute transfer between condensed phases (Equation (1.2)).

$$SP = c + e\mathbf{E} + s\mathbf{S} + a\mathbf{A} + b\mathbf{B} + l\mathbf{L} \quad (1.1)$$

$$SP = c + e\mathbf{E} + s\mathbf{S} + a\mathbf{A} + b\mathbf{B} + v\mathbf{V} \quad (1.2)$$

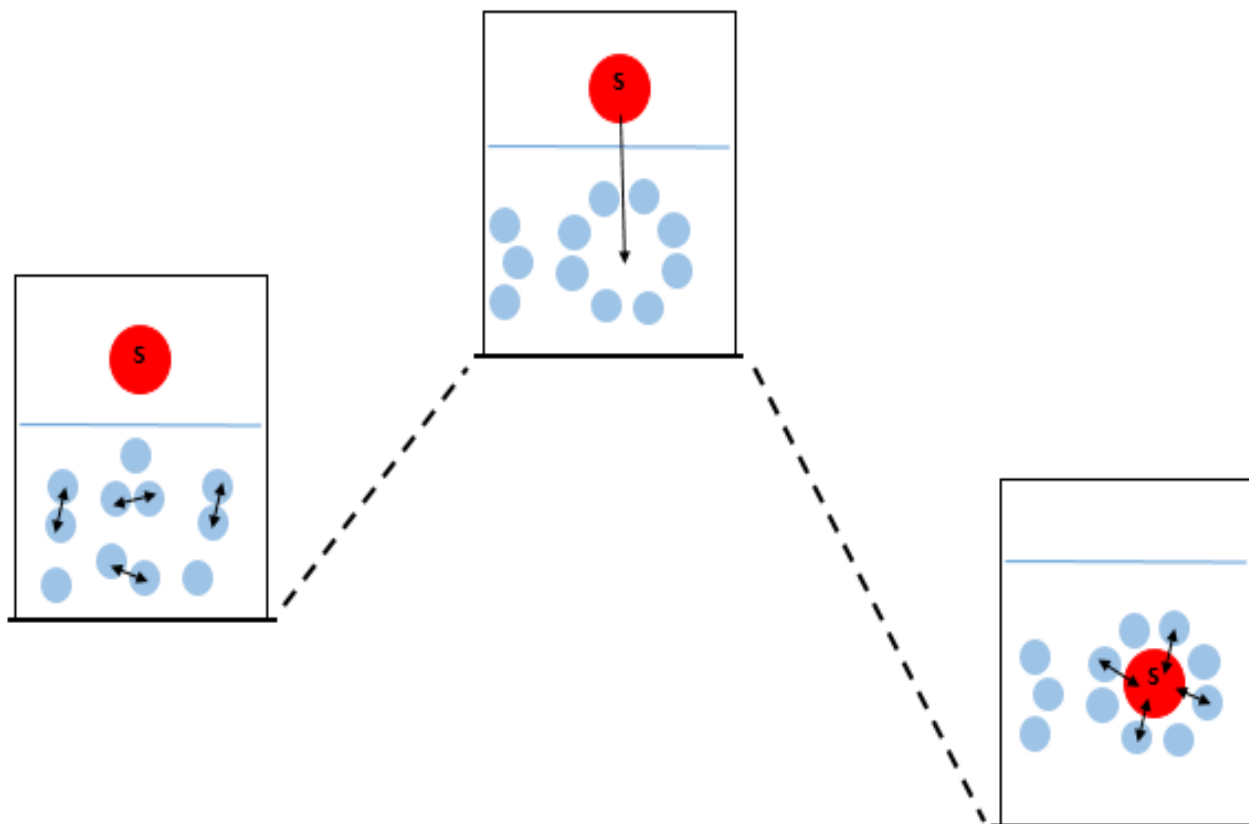


Figure 1.1. Cavity model of solvation. Adapted from Poole et al. [1].

1.2 Solute Descriptors and Process Coefficients

In the general equations above (Equations (1.1) and (1.2)) the lowercase letters (e , s , a , b , l , and v) represent the process coefficients and provide information about the solvent. The uppercase, bolded letters (**E**, **S**, **A**, **B**, **L**, and **V**) are aptly called solute descriptors and provide information about the solute. When multiplied together the process coefficients and the solute descriptors represent complementary processes of solute-solvent interactions. An in-depth description as to the history and meanings of these letters follows, but the summarized version can be found in Table 1.1.

Table 1.1. Meanings of process coefficients and solute descriptors.

Process Coefficients	Solute Descriptors
c: regression constant	
e: measure of lone electron pair interactions	E: solute excess molar refraction
s: measure of dipole-type interactions	S: measure of solute's dipolarity and polarizability
a: measure of hydrogen-bond basicity	A: measure of solute's hydrogen-bond acidity
b: measure of hydrogen-bond acidity	B: measure of solute's hydrogen-bond basicity
l: measure of formation of solvent cavity from gas phase	L: logarithm of gas-to-hexadecane partition coefficient at 298K
v: measure of formation of solvent cavity between condensed phases	V: McGowan characteristic volume

1.2.1 **E** and *e*

Defined as the excess molar refraction, the solute descriptor **E** gives a measure of the electrons that are polarizable in a molecule and is derived from the refractive index. Originally, the molar refraction (MR) was used as a solute descriptor, but it was too closely related to solute size and not independent of McGowan's characteristic volume (solute descriptor **V**), so now it is calculated as follows:

$$\mathbf{E} = (\text{MR}_X) - (\text{MR}_X)_{\text{alkane}} \quad (1.3)$$

where,

$$(\text{MR}_X) = 10 \left[\frac{(\eta^2 - 1)}{(\eta^2 + 2)} \right] V \quad (1.4)$$

$$(\text{MR}_X)_{\text{alkane}} = 2.83195V - 0.52553 \quad (1.5)$$

where η is the refractive index of the compound as a pure liquid at 20 °C for the sodium D-line and V is McGowan's characteristic volume in units of (cm³ mol⁻¹)/100. By

subtracting the molar refraction of an alkane of the same volume, the excess molar refraction is nearly independent of V , can be calculated using software programs such as Absolv and has units of $(\text{cm}^3 \text{mol}^{-1})/10$ [1-3]. McGowan's characteristic volume is discussed in detail in Section 1.2.6. The process coefficient, e , represents the ability of the partitioning system to participate in lone electron pair (non-bonding and π electrons) interactions [4].

1.2.2 **S** and s

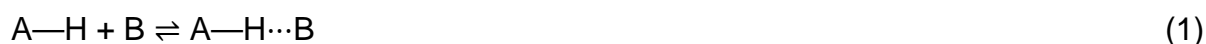
A measure of the solute's dipolarity and polarizability, solute descriptor **S** represents the interactions that are associated with both stable and induced dipoles and has dimensions of free energy. Abraham et al. [5] used extensive sets of gas-liquid chromatography (GLC) data from McReynolds and Pette to be able to develop the **S** solute descriptor scale where it was once believed that the **S** descriptor could only be determined for compounds that already had established **E** and **L** descriptors using polar stationary phases of gas chromatography where hydrogen-bonding interactions could be ignored. Now it is typically determined alongside solute descriptors **A** and **B** by way of water-to-organic solvent partitioning, as well as combining with gas chromatography retention data or through multiple linear regression analysis (MLRA) [1, 6-7]. The complementary process coefficient, s , pertains to the ability of the solvent to participate in dipole-type interactions [4].

1.2.3 **A** and a

The terms $a \cdot \mathbf{A}$ and $b \cdot \mathbf{B}$ together represent the total hydrogen-bond capability

between the solute and solvent for the given system. Presently the history and meaning of **A** and *a* will be discussed, followed by a discussion of **B** and *b* in Section 1.2.4.

The **A** solute descriptor is a measure of the solute's hydrogen-bond acidity and has dimensions of free energy. In a 1993 review, Michael H. Abraham [8] details how the **A** (and **B**) solute descriptor was developed. Abraham and colleagues set a series of acids log *K* values for Reaction (1) in tetrachloromethane against a given reference base and did so for 45 reference bases.



The researchers then plotted the log *K* values for those acids against the reference base versus log *K* values for acids against any other reference base and obtained a series of straight lines that intersected near a point of -1.1 log units when the *K* values were calculated using the molar scale. This allowed them to develop 45 equations of the following form:

$$\log K (\text{series of acids against reference base B}) = L_B \log K_A^H + D_B \quad (1.6)$$

where L_B and D_B characterize the base and $\log K_A^H$ values characterize the series of acids. In order to shift the origin from -1.1 to zero, one needs to convert $\log K_A^H$ to α_2^H using Equation (1.7). It should be pointed out that α_2^H and solute descriptor **A** are one and the same, but due to ease of use **A** is now the preferred label.

$$\alpha_2^H = (\log K_A^H + 1.1)/4.636 \quad (1.7)$$

As for the process coefficient *a*, it represents the complimentary hydrogen-bond basicity of the solvent and it is important to note that in the $a \cdot \mathbf{A}$ term, the solute acts as a hydrogen-bond donor. Typically, the **A** and **B** solute descriptors are determined by

GLC and liquid-liquid partition methods, but it is not uncommon to determine the **A** solute descriptor through NMR spectroscopy [4, 6].

1.2.4 **B** and *b*

The **B** solute descriptor is a measure of the solute's hydrogen-bond basicity and also has dimensions of free energy. According to Abraham [8], the **B** solute descriptor was developed in the same manner described previously for the **A** solute descriptor with the $\log K$ values for a series of bases against a reference acid were plotted versus the $\log K$ values for the bases against any other reference acid. These series formed a set of lines through the same -1.1 point and allowed Abraham to form Equation (1.8) that can be converted to β_2^H through Equation (1.9) to set the origin at zero. It should also be noted that β_2^H and solute descriptor **B** are the same, but **B** is the preferred label used today.

$$\log K (\text{series of bases against reference acid A}) = L_A \log K_B^H + D_A \quad (1.8)$$

$$\beta_2^H = (\log K_B^H + 1.1)/4.636 \quad (1.9)$$

In addition to the **B** solute descriptor, there is also a **B**[°] solute descriptor. This term is used for systems in which the counter solvent or stationary phase (which is not water) is partially miscible with water. For example, this behavior is seen with counter solvents such as octanol and ethyl acetate, and these solute descriptors can be determined using reversed-phase liquid chromatography and micellar electrokinetic chromatography. The process coefficient *b*, represents the solvent's complementary hydrogen-bond acidity and in the term *b* · **B**, the solvent acts as the hydrogen-bond donor [4, 6].

1.2.5 **L** and *l*

The solute descriptor **L**, also known as the Ostwald solubility coefficient, is the logarithm of the gas-to-hexadecane partition coefficient at 298.15 K and is a measure of cavity formation and solute-solvent dispersion interactions for the transfer of a solute from the gas phase to a condensed phase. It is typically determined with other descriptors on a series of stationary phases of differing polarity based on the volatility of the compounds. For compounds with low volatility, the **L** descriptor can be determined by back calculation of retention factors on low-polarity stationary phases at temperatures above 298.15 K. However, for volatile compounds, the **L** descriptor can be directly determined using gas chromatography with n-hexadecane as the stationary phase on a poly(methyloctylsiloxane) SPB-Octyl column [6]. An alternative method of determining the **L** solute descriptor was developed by Abraham and colleagues using Equation (1.10), but it only works if the solute property (*SP*) and **E** solute descriptor are known for a given solute [3].

$$SP = c + eE + lL \quad (1.10)$$

1.2.6 **V** and *v*

Defined as the McGowan characteristic volume, the **V** solute descriptor is the volume of one mole of liquid when the molecules in the solute are at rest, and has units of cm³ mol⁻¹/100. It is the easiest to determine as it can be calculated for any solute whose structure is known by using Equation (1.11).

$$V = \frac{[\Sigma(\text{all atom contributions}) - 6.56(N - 1 + R_g)]}{100} \quad (1.11)$$

where N is the total number of atoms and number of bonds in a molecule and R_g is the total number of ring structures in the solute. In regard to the number of bonds, all bonds count as one, regardless as to whether they are single, double or triple bonds. Included in Table 1.2 below are the atom contributions for select elements. The contributions were calculated using Equation (1.11). It should be noted that there is another equation (Equation (1.12)) that accounts for differences in the characteristic volume of branched alkanes that is based on physical properties such as boiling point.

$$V_{\text{cor}} - V = -0.051N_{\text{br}} + 0.030N_{\text{vic}} \quad (1.12)$$

where V_{cor} is the corrected McGowan characteristic volume, N_{br} is the number of alkyl groups or branches, and N_{vic} is the number of pairs of vicinal branches [3, 6].

Table 1.2. Atom contributions of select elements to the McGowan volume, in $\text{cm}^3 \text{mol}^{-1}$ [9].

Atom	Contribution	Atom	Contribution	Atom	Contribution
C	16.35	N	14.39	O	12.43
Si	26.83	P	24.87	S	22.91
Ge	31.02	As	29.42	Se	27.81
Sn	39.35	Sb	37.74	Te	36.14
Pb	43.44	Bi	42.19		
Atom	Contribution	Atom	Contribution	Atom	Contribution
H	8.71	He	6.76	B	18.32
F	10.48	Ne	8.51	Hg	34.00
Cl	20.95	Ar	19.00		
Br	26.21	Kr	24.60		
I	34.53	Xe	32.90		
		Rn	38.40		

1.3 Applications

The ASPM has numerous applications in biological, chemical and environmental fields, as well as in the manufacturing, pharmaceutical and cosmetic industries. These

applications include but are not limited to: solute transfer or partitioning, enthalpy of solvation and “green chemistry”, to name a few and are discussed below.

1.3.1 Solute Transfer and Solubility

In its most basic terms, solute partitioning involves the transfer of a solute from one phase to another and has been the most widely utilized application of the ASPM. In fact, researchers have calculated gas-to-organic solvent partition coefficients, water-to-organic solvent partition coefficients, organic solvent-to-organic solvent partition coefficients, air-to-body fluid/tissue partition coefficients, blood-to-body fluid/tissue partition coefficients, skin permeability coefficients, and molar solubility ratios [10] using the ASPM. Knowledge of how solutes transfer from one solvent or phase to another, as well as knowing the solubility of a given solute in a certain solvent is important especially in manufacturing processes and in the pharmaceutical industry. Determining this information can be time consuming and costly, yet with the use of the ASPM solute transfer and solubility can be easily predicted and appropriate solvents can be used for drug synthesis, trace removal of impurities, or column selection for liquid-liquid or liquid-gas chromatography. In actuality, the ASPM [1-4, 11] is one of the more successful approaches used in recent years to describe solute partitioning into, and solute solubilities in, organic solvent systems when compared to other methods. Solute partitioning can be between two condensed phases (a biphasic aqueous-organic or organic–organic system) or partitioning into a condensed phase from the gas phase (See Equations (1.13) and (1.14)). In order for the ASPM to fit within the parameters

described in Section 1.2, the relationship between K and P must be linear. Therefore, K and P must be converted to their respective logarithms.

$$\log \left(K \text{ or } \frac{c_{S,\text{organic}}}{c_{S,\text{gas}}} \right) = c_K + e_K \mathbf{E} + s_K \mathbf{S} + a_K \mathbf{A} + b_K \mathbf{B} + l_K \mathbf{L} \quad (1.13)$$

$$\log \left(P \text{ or } \frac{c_{S,\text{organic}}}{c_{S,\text{water}}} \right) = c_P + e_P \mathbf{E} + s_P \mathbf{S} + a_P \mathbf{A} + b_P \mathbf{B} + v_P \mathbf{V} \quad (1.14)$$

where K is the gas-to-organic solvent partition coefficient and P is the water-to-organic partition coefficient. Partition coefficients, K and P , can be calculated as shown in Equations (1.15) and (1.16) and are related to one another as depicted in Figure 1.2, as well as mathematically (See Equation (1.18)). K_w is a special partition coefficient where the condensed phase is water (See Equation (1.17)).

$$\text{Solute}_{(\text{gas phase})} \rightleftharpoons \text{Solute}_{(\text{condensed phase})} \quad \text{or} \quad K = \frac{[\text{solute}]_{\text{organic solvent}}}{[\text{solute}]_{\text{gas}}} \quad (1.15)$$

$$\text{Solute}_{(\text{water})} \rightleftharpoons \text{Solute}_{(\text{condensed phase})} \quad \text{or} \quad P = \frac{[\text{solute}]_{\text{organic solvent}}}{[\text{solute}]_{\text{water}}} \quad (1.16)$$

$$\text{Solute}_{(\text{gas phase})} \rightleftharpoons \text{Solute}_{(\text{water})} \quad \text{or} \quad K_w = \frac{[\text{solute}]_{\text{water}}}{[\text{solute}]_{\text{gas}}} \quad (1.17)$$

$$\log P = \log K - \log K_w \quad (1.18)$$

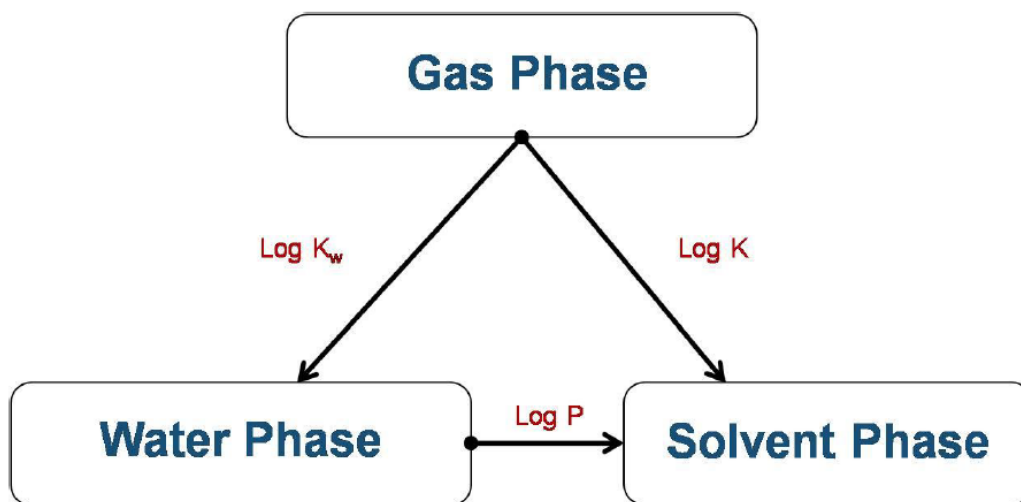


Figure 1.2. Depiction of relationship between partition coefficients and the phases of solute transfer [12].

Figures 1.3 and 1.4 depict the principle of solute transfer in conjunction with the solute descriptors from the ASPM for gaseous and organic solutes dissolved in tetraethylene glycol dimethyl ether (tetraglyme) using the Equations (1.19) and (1.20). Positive numerical values of the product of the process coefficient and solute descriptor terms facilitate solute transfer into the destination phase, whereas negative product terms retain the solute in the origination phase. Based on molecular structural considerations, tetraglyme cannot act as a hydrogen-bond donor because the molecule does not possess an acidic hydrogen. Therefore, the b_k coefficient in the $\log K$ expression will equal zero and solute transfer will depend upon the $a_k \cdot \mathbf{A}$ term [13]. As a general example, a positive $a_p \cdot \mathbf{A} + b_p \cdot \mathbf{B}$ sum term in Equation (1.2) would result in a larger water-to-organic solvent partition coefficient, P , as would be the case when solute–organic solvent hydrogen-bond interactions are stronger than solute–water hydrogen-bond interactions. Conversely, when solute–water hydrogen-bond interactions are stronger, then the solute remains in the aqueous phase, leading to a smaller $\log P$ value.

$$\log K = -0.296(0.022) - 0.290(0.064)\mathbf{E} + 2.005(0.058)\mathbf{S} + 3.555(0.098)\mathbf{A} + 0.882(0.011)\mathbf{L} \quad (1.19)$$

$$\log P = -0.158(0.040) + 0.119(0.092)\mathbf{E} + 0.374(0.102)\mathbf{S} + 0.192(0.126)\mathbf{A} - 5.114(0.108)\mathbf{B} + 4.144(0.061)\mathbf{V} \quad (1.20)$$

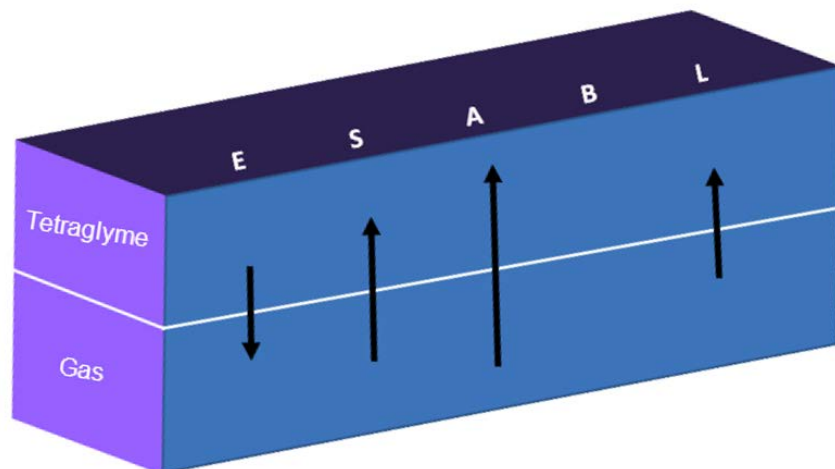


Figure 1.3. Schematic representation of gas-to-tetraglyme properties [12].

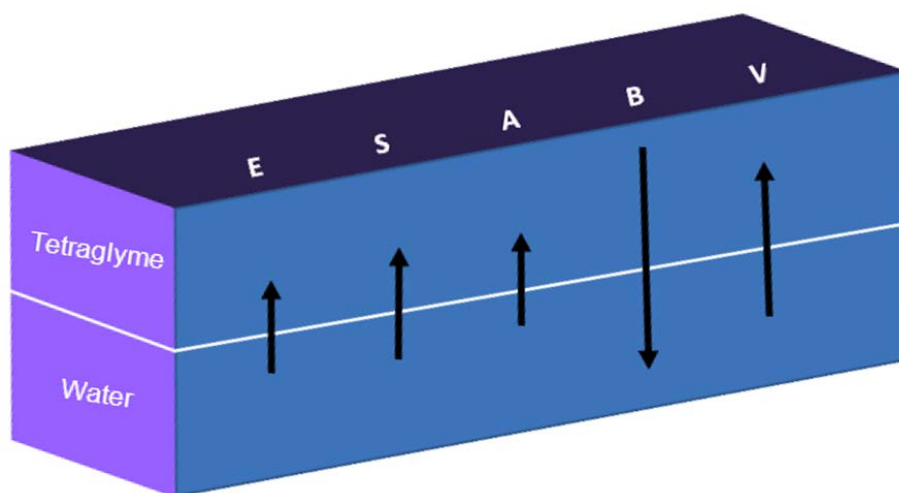


Figure 1.4. Schematic representation of water-to-tetraglyme properties [12].

To date, there are over 190 correlations used to predict $\log K$ values (Table 1.3) and over 175 correlations used to predict $\log P$ values (Table 1.4). Stephens (2014) has compiled the values for 184 $\log K$ correlations and 164 $\log P$ correlations [14], so there is no need to reproduce those tables here. Instead, included in Tables 1.3 and 1.4 are the values for the correlations developed during the course of this dissertation. Values for $\log K$ and $\log P$ calculated for this dissertation are for the following organic solvents:

2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-isopropoxyethanol and 2-butoxyethanol.

Table 1.3. Abraham Solvation Parameter Model log *K* process coefficients.

Solvent	c_k	e_k	s_k	a_k	b_k	l_k	SD	Ref.
2-methoxyethanol	-0.141	-0.265	1.810	3.641	0.590	0.790	0.139	[15]
2-ethoxyethanol	-0.064	-0.257	1.452	3.672	0.662	0.843	0.126	[16]
2-propoxyethanol	-0.091	-0.288	1.265	3.566	0.390	0.902	0.094	[17]
2-isopropoxyethanol	-0.045	-0.264	1.296	3.646	0.352	0.880	0.099	[17]
2-butoxyethanol	-0.109	-0.304	1.126	3.407	0.660	0.914	0.103	[18]

Table 1.4. Abraham Solvation Parameter Model log *P* process coefficients.

Solvent	c_p	e_p	s_p	a_p	b_p	v_p	SD	Ref.
2-methoxyethanol	0.175	0.326	-0.140	-	-4.086	3.630	0.158	[15]
2-ethoxyethanol	0.133	0.392	-0.419	0.125	-4.200	3.888	0.149	[16]
2-propoxyethanol	0.053	0.419	-0.569	-	-4.327	4.095	0.100	[17]
2-isopropoxyethanol	0.107	0.391	-0.525	0.071	-4.439	4.051	0.113	[17]
2-butoxyethanol	-0.055	0.377	-0.607	-0.080	-4.371	4.234	0.134	[18]

The ASPM was also used to calculate molar solubility ratios for several of the aforementioned compounds. In order to calculate the molar solubility ratios one first needs to convert measured mole fraction solubilities (X_S^{exp}) into molar solubility (C_S^{exp}) using Equation (1.21).

$$C_S^{\text{exp}} \approx X_S^{\text{exp}} / [X_S^{\text{exp}} V_{\text{solute}} + (1 - X_S^{\text{exp}}) V_{\text{solvent}}] \quad (1.21)$$

Molar solubility ratios and partition coefficients are related through Equations (1.13) and (1.14), where $C_{S,\text{organic}}$ and $C_{S,\text{water}}$ represent the molar solubility of the solute in the organic solvent and in water, respectively. The term $C_{S,\text{gas}}$ is the molar concentration of the solute in the gas phase and can be determined two ways: (1) it can be calculated from experimental vapor pressure data, or (2) it can be determined as part

of the solute descriptor computations when treated as an adjustable parameter [11]. Because solubility and partitioning are often researched simultaneously, there is much overlap between the equations.

Published articles pertaining to solute transfer and solubility are presented in Chapters 3-6 and include transfer of various solutes into the following five solvents: 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-isopropoxyethanol and 2-butoxyethanol. Described below is the general procedure as to how solubility measurements and gas chromatographic headspace measurements were performed for the papers described in Chapters 3-6.

1.3.1.1 Experimental Methodology for Determining Solubility Measurements

Excess solute and solvent under investigation are placed in amber glass bottles and allowed to equilibrate in a constant temperature water bath at 298.15 ± 0.1 K for at least 3 days with periodic agitation. After equilibrium, the samples stand unagitated for several hours in the constant temperature bath to allow any finely dispersed particles to settle to the bottom of the container. Attainment of equilibrium is verified by both repetitive measurements the following day (or after 2 days) and by approaching equilibrium from supersaturation by pre-equilibrating the solution at a slightly higher temperature.

Aliquots of the respective saturated solutions are transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with 2-propanol for spectrophotometric analysis on a Milton Roy Spectronic 1001 Plus spectrophotometer. Molar concentrations of the diluted solutions

are determined from a Beer–Lambert law absorbance versus concentration working curve for eight or nine standard solutions of known concentration. The analysis wavelengths and concentration ranges used for each solute have been reported in earlier solubility publications [19-37].

The molar concentrations obtained from the Beer–Lambert law working curve are converted to mass fraction solubilities by multiplying by the molar mass of the solute, volume(s) of the volumetric flasks used and any dilutions required to place the measured absorbances on the Beer–Lambert law absorbance versus concentration working curve, and then dividing by the mass of the saturated solution analyzed. Mole fraction solubilities are calculated from solubility mass fractions using the molar masses of the solvent under investigation and the respective organic solutes.

1.3.1.2 Experimental Methodology for Determining Gas Chromatographic Headspace Measurements

This method involves equilibrating sealed vials containing the dilute solutions of the studied compounds dissolved in the solvent under investigation at 298.15 K. A PerkinElmer Clarus 580 chromatograph with a headspace autosampler removes portions of the equilibrated vapor sample from the thermostated vial and transfers it through a heated quartz glass line into the injector of a gas chromatograph. The area of a peak S corresponding to a solute is calculated. Such measurements are performed at 3–4 different solute concentrations in the range 0.1–1.5 vol.%. The peak area of the pure solute, S_{solute} , is measured three times in similar fashion. The ratio of the areas of the peaks corresponding to the dilute solution and that of the pure solute is equal to the ratio of the solute vapor pressure over this solution p to saturated vapor pressure

p_{solute}^o : $S/S_{solute} = p/p_{solute}^o$. The activity coefficient, γ , of a solute is calculated by $\gamma = p/(p_{solute}^o \cdot x)$, where x is the equilibrium mole fraction of the given solute in the liquid phase. The values of p_{solute}^o were taken from literature [38].

The mole fraction composition of the equilibrated dilute solutions, taking into account partial evaporation of a solute, x , was calculated using a formula $x = x_0 - \frac{p_{solute}^o V_{free} S}{RT S_{solute} v_{solvent}}$, where x_0 is the initial quantity of a solute in a vial, $v_{solvent}$ is the number of moles of solvent in a vial and $V_{free} = 17$ mL is a volume of the head space. For all the studied systems γ is found to be virtually independent of x , and it is concluded that at such concentrations $\gamma = \gamma_\infty$, where γ_∞ is the limiting activity coefficient.

1.3.2 Enthalpy of Solvation

Enthalpy of solvation (ΔH_{solv}) is defined as the energy released when one mole of solute is dissolved in a solvent and is calculated differently depending on whether the solute is liquid or crystalline (See Equations (1.22) and (1.23)). Figure 1.5 shows how enthalpy of solution is measured.

$$\text{Liquid solutes: } \Delta H_{solv} = \Delta H_{soln} - \Delta H_{vap, 298.15 K} \quad (1.22)$$

$$\text{Crystalline solutes: } \Delta H_{solv} = \Delta H_{soln} - \Delta H_{sub, 298.15 K} \quad (1.23)$$

where ΔH_{soln} is the enthalpy of solution, $\Delta H_{vap, 298.15 K}$ is the enthalpy of vaporization at 298.15 K and $\Delta H_{sub, 298.15 K}$ is the enthalpy of sublimation at 298.15 K.

For the purposes of this dissertation, enthalpy of solvation correlations were obtained for the following solvents: acetic acid, dimethyl carbonate, diethyl carbonate, 1-butanol, 1-pentanol and 1-hexanol, using Equations (1.24) and (1.25) below.

$$\Delta H_{solv} = c_{h,l} + e_{h,l} \mathbf{E} + s_{h,l} \mathbf{S} + a_{h,l} \mathbf{A} + b_{h,l} \mathbf{B} + l_{h,l} \mathbf{L} \quad (1.24)$$

$$\Delta H_{\text{soln}} = c_{h,v} + e_{h,v}\mathbf{E} + s_{h,v}\mathbf{S} + a_{h,v}\mathbf{A} + b_{h,v}\mathbf{B} + v_{h,v}\mathbf{V} \quad (1.25)$$

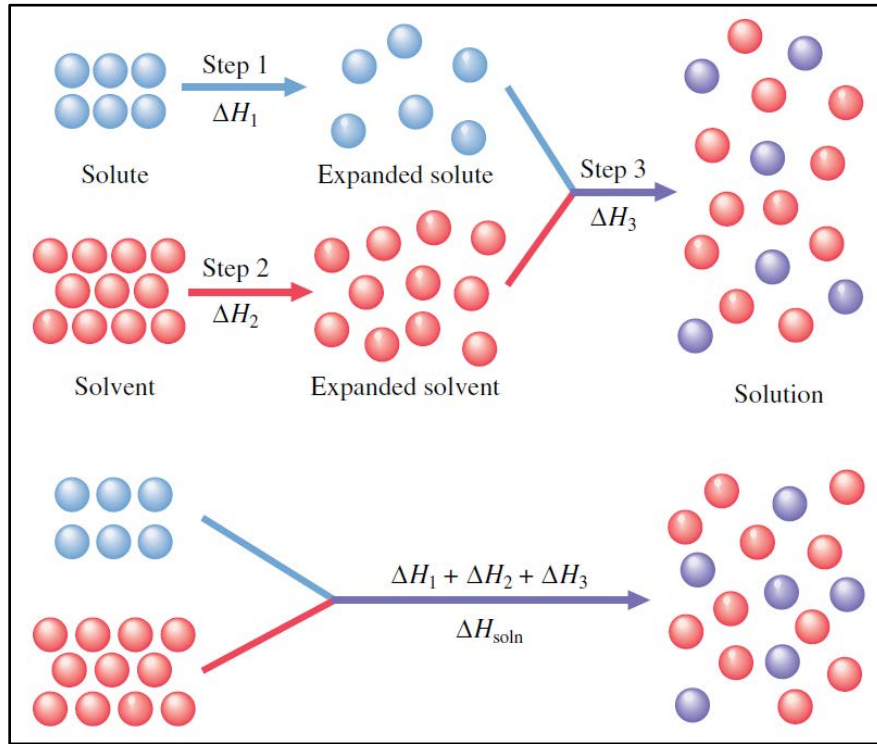


Figure 1.5. Pictorial representation of the calculation of enthalpy of solution [39].

Table 1.5. Abraham Solvation Parameter Model ΔH_{soln} process coefficients.

Solvent	$c_{h,l}$	$e_{h,l}$	$s_{h,l}$	$a_{h,l}$	$b_{h,l}$	$l_{h,l}$	SD	Ref.
acetic acid	-3.219	6.719	-11.448	-38.283	-12.175	-8.461	1.980	[40]
dimethyl carbonate	-3.030	7.749	-18.894	-30.719	-	-8.390	2.258	[41]
diethyl carbonate	-4.499	6.558	-15.966	-25.537	-	-8.767	1.651	[41]
1-butanol	-7.490	-	1.597	-52.542	-6.831	-8.585	2.457	[42]
1-pentanol	-6.160	4.452	1.737	-54.432	-8.673	-9.170	2.394	[42]
1-hexanol	-4.614	-	1.614	-45.975	-11.256	-9.269	2.348	[42]

Table 1.6. Abraham Solvation Parameter Model ΔH_{soln} process coefficients.

Solvent	$c_{h,v}$	$e_{h,v}$	$s_{h,v}$	$a_{h,v}$	$b_{h,v}$	$v_{h,v}$	SD	Ref.
acetic acid	4.695	-8.305	-14.668	-40.667	-15.426	-30.958	2.16	[40]
dimethyl carbonate	5.749	-3.022	-28.852	-32.746	-	-29.655	3.092	[41]
diethyl carbonate	5.957	-4.458	-25.925	-29.492	-	-32.549	2.522	[41]
1-butanol	2.649	-12.088	-6.767	-57.593	-5.521	-32.814	2.855	[42]
1-pentanol	2.444	-7.713	-6.397	-58.906	-6.866	-32.673	2.671	[42]
1-hexanol	3.383	-12.657	-5.599	-50.238	-10.949	-33.033	2.890	[42]

A search of SciFinder Scholar shows that there are about 49 correlations utilizing the ASPM to predict ΔH_{solv} values. Of these correlations, only the six tabulated in Tables 1.5 and 1.6 were used as part of this dissertation. It is important to note that the ASPM can be used with any solute property that is related to Gibbs energy, including, but not limited to, Gibbs energy of transfer (ΔG_{trans}), Gibbs energy of solvation (ΔG_{solv}) and entropy of solvation (ΔS_{solv}).

Published articles involving the enthalpy of solvation are presented in Chapters 7-9 and pertain to the following solvents: acetic acid, dimethyl carbonate, diethyl carbonate, 1-butanol, 1-pentanol and 1-hexanol.

1.3.3 “Green Chemistry”

The term “green chemistry” refers to the “design of chemical products or processes that reduce or eliminate the generation of hazardous substances” [43]. The ASPM has applications in this field due to its: (1) ability to predict more environmentally-friendly solvents in the use of organic and drug synthesis; (2) ability to aid in trace removal of impurities from the environment; and (3) development of ionic liquids.

According to Poole et al. (2013), the ASPM can be used to predict the environmental distribution and fate of frequently used compounds based on their solubility in water, their octanol-water partition coefficient (K_{OW}), their air-octanol partition coefficient (K_{OA}) and their vapor pressure. For some compounds these properties are easy to measure; for others, such as those with low solubility or vapor pressure, the properties are difficult to measure or are time and cost intensive. The ASPM is one solution to overcoming these challenges as it can be used to help predict

these properties, in addition to being able to provide information as to which chromatographic method would work best for a given compound [3]. Acree et al. (2012) have used various properties named above in conjunction with the ASPM to determine toxicity of pharmaceuticals in several aquatic species, as well as to determine biological responses of volatile organic compounds (VOCs) in rats, mice and tadpoles [9].

Ionic liquids (ILs) are a class of compounds that are salts composed of a cation and an anion and are liquid at temperatures below 100 °C. According to Holbrey and Seddon (1999) there are 10^{18} possible cation/anion combinations of ILs that have a myriad of applications, including, but not limited to: electrochemistry, organic synthesis, liquid-liquid extraction, and catalysis with transition metal complexes. Most notably, ILs are known for being “green” because of their physical and chemical properties, such as low melting points, no measurable vapor pressure and variable densities [44-45]. As far as the ASPM is concerned, ILs have been studied in order to provide the scientific community with the process coefficients for several different cations and anions, which can be used in conjunction with known solute descriptors or known solute properties to predict partitioning ability, enthalpy of solvation and other free energy related properties through the use of Equations (1.26) and (1.27) that breaks each pair of molecular interactions into a cation part and an anion part.

$$SP = (c_{\text{cation}} + c_{\text{anion}}) + (e_{\text{cation}} + e_{\text{anion}})\mathbf{E} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} + (a_{\text{cation}} + a_{\text{anion}})\mathbf{A} + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (l_{\text{cation}} + l_{\text{anion}})\mathbf{L} \quad (1.26)$$

$$SP = (c_{\text{cation}} + c_{\text{anion}}) + (e_{\text{cation}} + e_{\text{anion}})\mathbf{E} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} + (a_{\text{cation}} + a_{\text{anion}})\mathbf{A} + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (v_{\text{cation}} + v_{\text{anion}})\mathbf{V} \quad (1.27)$$

1.4 Comparison to Other Predictive Models

The ASPM is just one of many similar models that use solute descriptors to predict properties of various systems, but many of the creators of these models tend to use the ASPM as part of their model or as a guide. This is an indication that the ASPM tends to be the best, most comprehensive LFER and can be used in a variety of situations. A comparison of the ASPM to models by Carr and Klamt follows, finishing with a justification as to when and why the ASPM should be utilized.

1.4.1 Carr's Model

The model used by Carr and colleagues is based on linear solvation energy relationships (LSER) where the solute descriptors, defined by Kamlet, Taft and Abboud [46] were determined by solvent properties generally in conjunction with gas or liquid chromatography. The solute descriptors used in Carr's model (See Equation (1.28)) include two already-determined solute descriptors: (1) the $\log L^{16}$ descriptor that Abraham et al. defined [47]; and, (2) the δ descriptor, which is a polarizability correction descriptor defined by Kamlet et al. [48] where aromatic compounds have a δ of one, polychlorinated aliphatic compounds have a δ of 0.5 and all other compounds have a δ of zero. The other three descriptors in Carr's model (π_2^c , α_2^c , and β_2^H) are determined experimentally via chromatography. Carr et al. were able to develop new scales for the solute dipolarity/polarizability descriptor, π_2^c , as well as the overall solute hydrogen-bond acidity descriptor, α_2^c using the retention data of 200 solutes on a variety of stationary phases. It is important to note that the scales for π_2^c and α_2^c did not differ significantly

from those Abraham developed (π_2^H and $\Sigma\alpha_2^H$) and all of the solutes tested by Carr et al. were mono-functional, and therefore may be considered redundant.

$$\log SP = c + d\delta_2 + s\pi_2^c + a\alpha_2^c + b\beta_2^H + l\log L^{16} \quad (1.28)$$

However, Carr and colleagues noted that since the $b\beta_2^H$ term was quite small, Equation (1.28) was not recommended for setting up a new hydrogen-bond basicity scale, and so they decided to develop a new scale for the overall hydrogen-bond basicity, which they denoted as β_2^c . To accomplish this, Carr et al. ran a set of 84 solutes with known retention factors through two stationary phases to determine a ratio of partitioning of the solutes between the two phases in order to calculate the values of the solute hydrogen-bond basicity. Once this was completed, Carr et al. ran a set of 59 additional solutes through the stationary phases and compared the β_2^c values to both β_2^H and $\Sigma\beta_2^H$ of Abraham. According to Carr et al., the scales of Abraham correspond to the free energy formation of 1:1 complexes, which is not necessarily the case for all solutes that can act as hydrogen-bond acceptors. Therefore, the values for some solutes did not correlate well with either hydrogen-bond basicity scale devised by Abraham et al. and a new hydrogen-bond basicity scale was developed [49].

1.4.2 Klamt's Model

The model developed by Klamt et al. (1998), known as COSMO-RS, is a linear free energy relationship (LFER)-based computational model that combines quantum theory, dielectric continuum models, surface interactions and statistical thermodynamics [49]. It has been used for the prediction of various chemical and physical properties of neutral solutes in a variety of organic solvents with an accuracy of approximately 0.4

kcal/mol when using DFT (density functional theory) methods. The COSMO-RS theory has eight general parameters or COSMOments: (1) r_{av} – averaging radius for the screening charge density, (2) a_{eff} - effective contact area, (3) α' - electrostatic interaction coefficient, (4) c_{hb} and (5) σ_{hb} - two hydrogen-bonding parameters, (6) ω - a ring correction term, (7) λ - the degeneracy difference between the gas phase and the liquid phase, (8) f_{corr} – a correction term dealing with polarizability, and a constant – η , which corresponds to the entropy difference between the standard state in the gas phase and in the liquid phase. With the use of this parameterization, chemists and engineers now have the ability to predict nearly any chemical equilibrium in both the gas-to-condensed phase system, as well as the condensed phase-to-condensed phase system without any additional experimental data for solutes or solvents [50].

Zissimos and colleagues (2002) compared the ASPM to COSMO-RS and discovered that there is “considerable overlap” between Abraham’s solute descriptors (**E**, **S**, **A**, **B**, and **V**) and five of the COSMOments (α' , c_{hb} , σ_{hb} , r_{av} and a_{eff}), but they noted that the **E** solute descriptor contains additional information not accounted for in any of the COSMOments. Furthermore, there was no discussion as to a correlation to the **L** solute descriptor and so a complete comparison is not represented [51].

1.4.3 Abraham’s Model

The model developed by Abraham, as described previously, appears to be the most comprehensive and seemingly the best to use because the solute descriptors are free energy related, the current database has descriptors for over 7 000 solutes [52], and wet and dry processes have the same mathematical form for solute transfer (i.e.,

they have the same general Abraham model equation (See Equations (1.1) and (1.2)), though they may have different process coefficients. These aspects make this model easier to use. If there is a broad range of functional groups for the various solutes, Abraham's model gives one the best chances at predicting various solute properties. In fact, there are three main applications of the general equation (See Equation (1.1)):

- (1) If the process coefficients (lowercase letters) and the solute descriptors (uppercase letters) are known, then the solute property can be predicted.
- (2) If the process coefficients and the solute property are known, then the solute descriptors can be calculated.
- (3) If the solute descriptors and the solute property are known, then the process coefficients can be calculated.

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CHAPTER 2

STATISTICAL ANALYSIS

2.1 Introduction

Multiple linear regression analysis has been performed throughout the research done for this dissertation, specifically to calculate the process coefficients, the solute descriptors and the solute properties, as described in Chapter 1, using version 22 of the IBM® statistical software package SPSS® [1], as well as the 10.0 version Microsoft® Excel® with an add-in called Solver®. In addition to the aforementioned values, the coefficient of determination value, the Fisher F-statistic value and the value of the standard deviation of the correlation have also been calculated (R^2 , F , and SD , respectively).

In order to use these programs, it is first necessary to make sure that all the data to be analyzed is in the same solvation process. Most of the processes studied dealt with values either in the logarithm of the partition coefficients (K and P) or in the concentration of the solute (C_S). At times, the literature was searched for infinite activity dilution coefficients ($\gamma_{\text{solute}}^\infty$) or for gas solubility data in terms of Henry's law constant (K_{Henry}) to transform the data into $\log K$ or $\log P$ values via the following equations:

$$\log K = \log \left(\frac{RT}{\gamma_{\text{solute}}^\infty P_{\text{solute}}^\circ V_{\text{solvent}}} \right) \quad (2.1)$$

$$\log K = \log \left(\frac{RT}{K_{\text{Henry}} V_{\text{solvent}}} \right) \quad (2.2)$$

$$\log P = \log K - \log K_w \quad (2.3)$$

where R is the universal gas constant in units of $\frac{L \cdot kPa}{mol \cdot K}$; T is the system temperature in units of K ; P_{solute}° is the saturated vapor pressure of a pure solute in its standard state at

temperature T in units of kPa ; V_{solvent} is the molar volume of the organic solvent, which is the molecular weight divided by its density in units of $\frac{L}{mol}$. The infinite activity dilution coefficient, $\gamma_{\text{solute}}^{\infty}$, is unitless and can be measured using the following equation:

$$\gamma_{\text{solute}}^{\infty} = \frac{P}{P_{\text{solute}}^{\circ} \cdot x} \quad (2.4)$$

where x is the equilibrium molar fraction of a solute in the liquid phase, and the ratio,

$\frac{P}{P_{\text{solute}}^{\circ}}$, can be determined experimentally via gas chromatography and is the ratio of the peak areas for two samples of the same volume taken from the equilibrium vapor phase of solution and of pure solute thermostatted in sealed vials [2-3].

If $K = \frac{C_{\text{S,organic}}}{C_{\text{S,gas}}}$ and $P = \frac{C_{\text{S,organic}}}{C_{\text{S,water}}}$, then to calculate $C_{\text{S,organic}}$, use the following equation:

$$C_{\text{S,organic}}^{\text{exp}} = \frac{X_{\text{S,organic}}^{\text{exp}}}{[X_{\text{S,organic}}^{\text{exp}} \cdot V_{\text{solute}} + (1 - X_{\text{S,organic}}^{\text{exp}})V_{\text{solvent}}]} \quad (2.5)$$

Other research required the calculation of the enthalpy of solvation (ΔH_{solv}). This was accomplished using the following two equations depending on whether the solutes were liquid or crystalline (Equations (2.6) and (2.7), respectively):

$$\Delta H_{\text{solv}} = \Delta H_{\text{soln}} - \Delta H_{\text{Vap},298.15 \text{ K}} \quad (2.6)$$

$$\Delta H_{\text{solv}} = \Delta H_{\text{soln}} - \Delta H_{\text{Sub},298.15 \text{ K}} \quad (2.7)$$

where ΔH_{soln} is the enthalpy of solution in units of $\frac{kJ}{mol}$, $\Delta H_{\text{Vap},298.15 \text{ K}}$ is the enthalpy of vaporization at 298.15 K in units of $\frac{kJ}{mol}$, and $\Delta H_{\text{Sub},298.15 \text{ K}}$ is the enthalpy of sublimation at 298.15 K in units of $\frac{kJ}{mol}$ [4].

2.2 SPSS®

2.2.1 Multiple Linear Regression Analysis

Multiple linear regression analysis is an important tool to analyze the relationship

between dependent and independent variables, such as how a change in one of the independent variables causes a change in one of the dependent variables. The solute property of the ASPM described in Chapter 1 is the dependent variable, with the solute descriptors or process coefficients representing the independent variables as shown in Figure 2.1. Figure 2.2 shows how to define the parameters of the linear regression which are found in the submenus of the Linear Regression window.

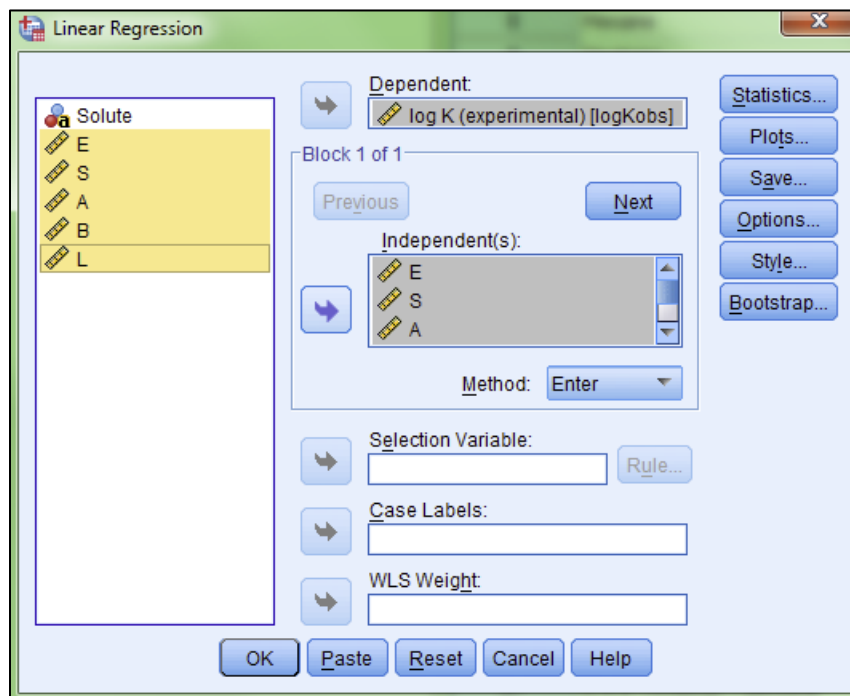


Figure 2.1. Defining the variables as dependent or independent using IBM® SPSS® 22. Found under the Analyze tab → Regression → Linear[1].

Once these parameters have been input, the program yields an output file as shown in Figure 2.3. The highlighted areas are of importance for the purpose of this dissertation, which include: the number of data points (N), the R value, the R^2 value, the adjusted R^2 value, the Fisher F-statistic, the process coefficients or solute descriptors along with their standard error, and the standard deviation, all of which will be explained in detail in sections 2.2.1.1-2.2.1.3

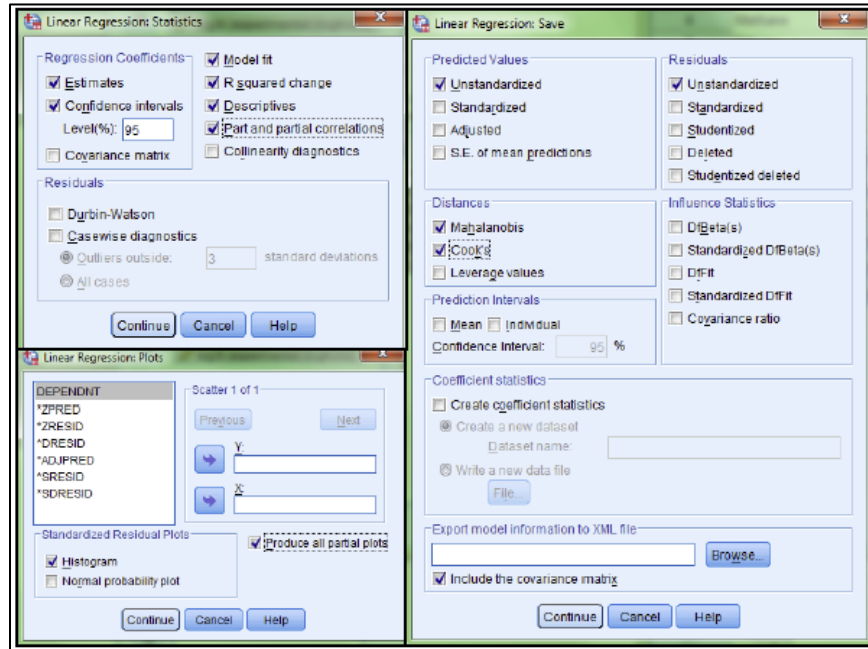


Figure 2.2. Submenus under the Linear Regression window to further parameterize the regression in SPSS® 22. [1].

2.2.1.1 Correlation Coefficient, Coefficient of Determination and Adjusted Coefficient of Determination

The correlation coefficient, R, is a value between negative one and positive one and measures the degree to which two variables or sets of data are related or dependent upon one another. An R value close to positive one indicates a positive correlation where the values are strongly related. An R value close to negative one is indicative of a negative correlation and suggests that the variables or data sets are inversely proportional to one another. A value of zero indicates that there is no relationship or correlation between the two variables or sets of data. The correlation coefficient can be calculated as follows:

$$R = \frac{N(\sum xy) - (\sum x)(\sum y)}{\sqrt{[N\sum x^2 - (\sum x)^2][N\sum y^2 - (\sum y)^2]}} \quad (2.8)$$

where N is the number of data points, x is the individual data on the x-axis and y is the individual data on the y-axis [5-6].

Model Summary ^b											
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics						
					R Square Change	F Change	df1	df2	Sig. F Change		
1	.999 ^a	.999	.998	.1229535007	.999	10344.227	5	76	.000		
a. Predictors: (Constant), L, A, B, E, S											
b. Dependent Variable: log K (experimental)											
ANOVA ^a											
Model		Sum of Squares	df	Mean Square	F	Sig.					
1	Regression	781.898	5	156.380	10344.227	.000 ^b					
	Residual	1.149	76	.015							
	Total	783.046	81								
a. Dependent Variable: log K (experimental)											
b. Predictors: (Constant), L, A, B, E, S											
Coefficients ^a											
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B		Correlations		
		B	Std. Error	Beta			Lower Bound	Upper Bound	Zero-order	Partial	Part
1	(Constant)	-.469	.032		-14.466	.000	-.534	-.405			
	E	.235	.069	.040	3.410	.001	.098	.373	.852	.364	.015
	S	2.079	.083	.382	25.125	.000	1.914	2.244	.940	.945	.110
	A	3.824	.073	.290	52.291	.000	3.679	3.970	.658	.986	.230
	B	.775	.125	.056	6.219	.000	.527	1.023	.782	.581	.027
	L	.626	.012	.425	51.735	.000	.601	.650	.873	.986	.227
a. Dependent Variable: log K (experimental)											
Residuals Statistics ^a											
	Minimum	Maximum	Mean	Std. Deviation	N						
Predicted Value	-.671132267	12.64726067	4.060499903	3.106936795	82						
Std. Predicted Value	-1.523	2.764	.000	1.000	82						
Standard Error of Predicted Value	.017	.068	.031	.011	82						
Adjusted Predicted Value	-.642368793	12.68182087	4.061541862	3.109999843	82						
Residual	-.315867752	.3279969394	.0000000000	.1190981966	82						
Std. Residual	-2.569	2.668	.000	.969	82						
Stud. Residual	-2.683	2.863	-.004	1.020	82						
Deleted Residual	-.344631165	.3776822984	-.001041959	.1322055284	82						
Stud. Deleted Residual	-2.802	3.011	-.003	1.036	82						
Mahal. Distance	.528	24.146	4.939	4.371	82						
Cook's Distance	.000	.207	.019	.035	82						
Centered Leverage Value	.007	.298	.061	.054	82						
a. Dependent Variable: log K (experimental)											

Figure 2.3. Output file from SPSS® with highlighted areas showing information of particular interest [1].

The value of the coefficient of determination, R^2 , lies between zero and one and shows a goodness of fit from the calculated data to the experimental data. An R^2 value of one indicates that the dependent variable(s) can be predicted from the independent variable(s), whereas a value of zero suggests that the dependent variable(s) cannot be predicted. An R^2 value that lies between zero and one shows the degree to which the dependent variable(s) can be predicted by the independent variable(s). For example, an R^2 value of 0.25 says that 25% of the dependent variable(s) can be predicted by the independent variable(s), where an R^2 value of 0.90 states that 90% of the variance can be predicted. The coefficient of determination is calculated by squaring the correlation coefficient. Figure 2.4 shows a visual representation of the relationship between the correlation coefficient and the coefficient of determination.







Correlation Coefficient	Coefficient of Determination	Experimental Values	Calculated Values
$R = 0$	$R^2 = 0$ or 0%		 0% shared variance
$R = 0.5$	$R^2 = 0.25$ or 25%		 25% shared variance
$R = 1.0$	$R^2 = 1.0$ or 100%		 100% shared variance

Figure 2.4. Visual interpretation of the correlation coefficient and the coefficient of determination [7].

The adjusted R^2 value, or the adjusted coefficient of determination, also lies between zero and one and is a modified version of R^2 that considers the number of predictors in a model. If useful terms are added, the adjusted R^2 value increases. Alternatively, if useless terms are added, the adjusted R^2 value decreases. This shows that the dependent and independent variable(s) are not just related by chance. The adjusted R^2 value can be calculated as follows:

$$R_{\text{adj}}^2 = 1 - \left[\frac{(1 - R^2)(N - 1)}{N - k - 1} \right] \quad (2.9)$$

where N is the number of data points and k is the number of variables in the model, excluding the constant [8].

2.2.1.2 Fisher F-statistic

Named in honor of Sir Robert Fisher, the Fisher F-statistic is used to determine if two populations or sets of data are significantly different. The larger the value of the F-statistic, the more the two sets of data are related and the data did not occur by chance. The smaller the value, the less correlation exists between the two data sets. Furthermore, larger numbers of data within the sets leads to larger F-statistic values, as can be seen in Equation (2.10), which is used to calculate the Fisher F-statistic.

$$F = \frac{\text{explained or between group variability}}{\text{unexplained or within group variability}} \quad \text{or} \quad F = \frac{R^2(N - k - 1)}{k(1 - R^2)} \quad (2.10)$$

where R^2 is the coefficient of determination, N is the number of data points and k represents the degrees of freedom [7-8].

2.2.1.3 Standard Deviation

The standard deviation, SD, is a statistical measure of the nearness of the data points to the mean. The closer to the mean a set of data is, the smaller the value of the standard deviation. Alternatively, the further from the mean a set of data is, the larger the value of the standard deviation. Standard deviation can be an important statistic because it has the same units as the data, and therefore is easy to understand. It can be calculated using the following equation:

$$SD = \sqrt{\frac{\sum(x_i - \bar{x})^2}{N-1}} \quad (2.11)$$

where x_i is each individual data point, \bar{x} is the mean of the data points and N is the number of data points [5].

2.2.2 Validation Process of Regression Analysis

In order to determine whether or not the regression performed is valid one can choose from a myriad of validation methods. The method of validation used during the process of this dissertation is called “Test and Training.”

2.2.2.1 “Test and Training”

To perform “Test and Training”, split at least 80 data points of chemically diverse compounds in two – a test set and a training set. For sets that have an odd number of data points, the odd number is added to the training set. A linear regression is run on the training set and the values of the coefficients for the correlation are used to predict the test set. From the test set, statistics of interest are obtained. These statistics are: the absolute error, the average absolute error and the standard deviation (AE, AAE and SD, respectively). It can be done with as few as 60 data points, but that method is a little more involved. First, split the full data set into three different sets (A, B and C) and then combine two for a training set (e.g., AB, AC, and BC), run a linear regression and use the correlation to predict the test set for the letter not included (i.e., using training set AB with test set C, training set AC with test set B and training set BC with test set A).

2.2.2.2 Average Error and Average Absolute Error

The average error (AE) is a measure of accuracy of the regression and gives an indication of whether or not there is inherent bias in the regression. The AE can be positive, negative or zero. An AE value close to zero is ideal because a value of zero indicates no bias. The further from zero a value is, the more bias exists in the regression. A positive AE value is indicative of the regression consistently predicting a calculated value greater than the experimental value for the dependent variable. A negative AE value indicates the opposite (i.e., the regression consistently predicts a calculated value less than the experiment value for the dependent variable). The average error can be calculated as follows:

$$AE = \frac{\sum(\hat{Y}_i - Y_i)}{N} \quad (2.12)$$

where \hat{Y}_i is the calculated value, Y_i is the experimental value and N is the number of data points [7].

The average absolute error (AAE) is also a measure of accuracy in the regression, but is more closely related to the standard deviation in that it is the average absolute deviation between the calculated and experimental values. The AAE will always be a positive number and will be slightly smaller than the standard deviation that corresponds to the same equation, not the overall standard deviation. Using Equation (2.13) below, one can calculate the AAE.

$$AAE = \frac{\sum |\hat{Y}_i - Y_i|}{N} \quad (2.13)$$

where \hat{Y}_i is the calculated value, Y_i is the experimental value and N is the number of data points [7].

2.2.2.3 Standard Deviation

Of the descriptive statistics that are calculated, standard deviation of the residual is important to determine the spread of the data from the test and training sets. Like all standard deviations, the smaller the value, the better the data fit.

2.2.2.4 Determination of Validity

It is important to note that the regression will be considered valid if: (1) the process coefficients from the training set show good agreement to the experimental values (i.e., if the values of the process coefficients from the training set are within the margins of error to those from the experimental values of the full data set); and, (2) the test sets show little or no bias (i.e., $AE \cong 0$ and $AAE \cong 0$), then the training set is a good representation of the entire data set and the correlation is likely to be have good predictive ability if the solute descriptors of a new compound are within the ranges determined for that specific solute property.

2.3 Solver[®]

The process of calculating the process coefficients, solute descriptors, solute properties, as well as the additional information that determines the accuracy of the calculated data to the experimental data is quite similar in Solver[®] as it is in SPSS[®]. To start, all data must be in the same units as described previously. For the majority of the work done for this dissertation, the solute property and the process coefficients were calculated and since one cannot calculate the solute property without knowing both the

process coefficients and the solute descriptors, it is necessary to use several functions in Excel®.

Using if/then functions, one can set up the empty calculated solute property column ($\log K_{\text{calc}}$ or $\log P_{\text{calc}}$) and the empty process coefficients cells. In another cell, a formula can be used to calculate the standard deviation. Without the calculated solute property or process coefficients, this value will be quite large. To minimize the standard deviation, which will also simultaneously calculate the solute property, as well as the process coefficients see Figures 2.5 and 2.6. For 'Set Objective', put in the cell for the standard deviation. For process coefficients, use the "solver" add-in with the following information as shown in 'To', click the circle for minimization (min). For 'By Changing Variable Cells:', put in the cells for the process coefficients. If one knows that a process coefficient equals zero, that information may be included in the 'Subject to the Constraints' area. Lastly, unmark the box 'Make Unconstrained Variables Non-Negative' and click 'Solve'. Figure 2.6 shows how the standard deviation has decreased from 3.75 to 0.141, and there are values for the process coefficients and the calculated solute property.

2.4 Principal Components Analysis

Principal components analysis (PCA) is a statistical technique that converts a set of possibly correlated variables into a set of linearly uncorrelated variables using an orthogonal transformation. This allows one to visually compare and assess data.

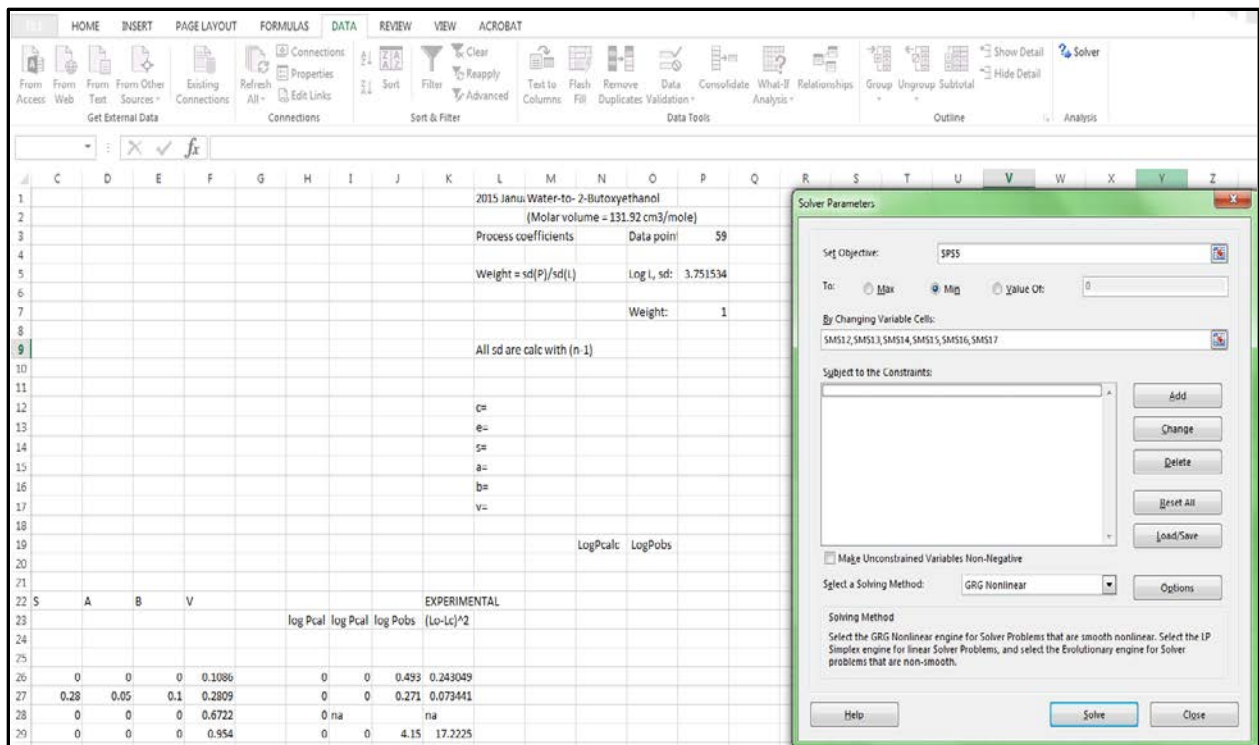


Figure 2.5. Description of minimization and calculation process in Solver®. Found under the data tab → Solver.

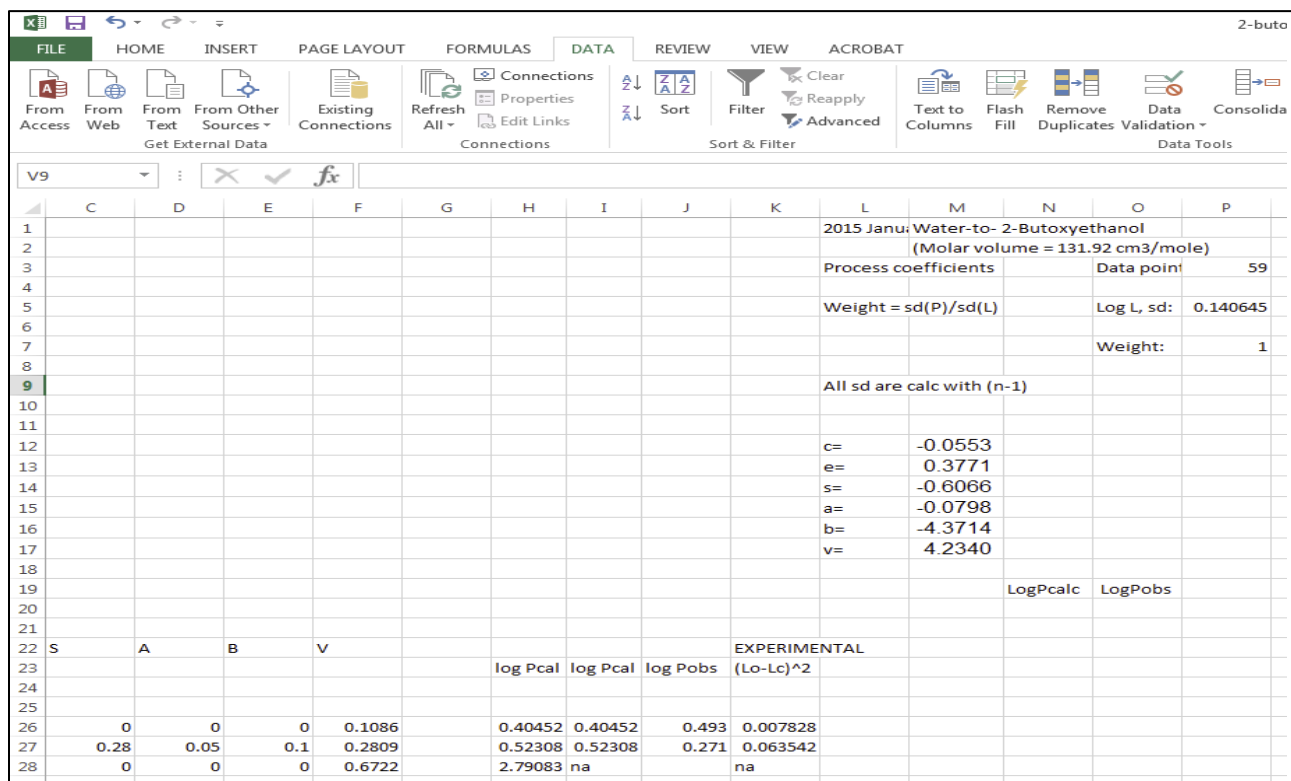


Figure 2.6. Standard deviation is minimized, and process coefficients and solute property are calculated.

The five sets of process coefficients (e , s , a , b and l or v) are transformed into five new sets of principal components (PCs) that contain all the information from the five original sets of coefficients. The first two PCs (PC1 and PC2) contain most of the total data in the original coefficients and the scores of PC2 are plotted against PC1. The nearness of any two points is a measure of how near the corresponding solvents are in term of their solute properties and solute-solvent interactions [9]. Figure 2.7 shows a basic PCA plot of solvents from Table 2.1. As can be easily seen, solvents numbered 2, 3, and 4 (hydrocarbons) are similar to one another based on their nearness, while solvents 5, 6, 7 and 8 (alcohols) are similar to one another, yet different from solvents 2, 3, and 4. Solvent number 1, water, is unlike any of the other solvents depicted due to the differences in the $e_{h,l}$ and the $b_{h,l}$ process coefficients.

Table 2.1. Abraham model process coefficients for predicting enthalpies of solvation of solutes in select organic solvents based on Equation (1.24).

No.	Solvent	$c_{h,l}$	$e_{h,l}$	$s_{h,l}$	$a_{h,l}$	$b_{h,l}$	$l_{h,l}$
1	Water	-13.310	9.910	2.836	-32.010	-41.816	-6.354
2	Hexane	-6.458	3.610	0.000	0.000	0.000	-9.399
3	Heptane	-7.018	4.036	0.000	0.000	0.000	-9.209
4	Hexadecane	-6.097	2.305	0.000	0.000	0.000	-9.364
5	1-Propanol	-8.713	-2.593	5.190	-53.042	-7.852	-8.108
6	2-Propanol	-7.669	0.000	2.055	-51.494	-6.976	-7.996
7	1-Butanol	-7.490	0.000	1.597	-52.542	-6.831	-8.585
8	2-Butanol	-6.883	0.000	6.667	-50.819	-10.577	-8.270
9	Ethyl acetate	-7.063	4.671	-15.141	-28.763	0.000	-7.691
10	Acetone	-4.965	4.290	-17.026	-36.672	-3.794	-7.307
11	Acetonitrile	-4.148	3.304	-18.430	-26.104	-7.535	-6.727

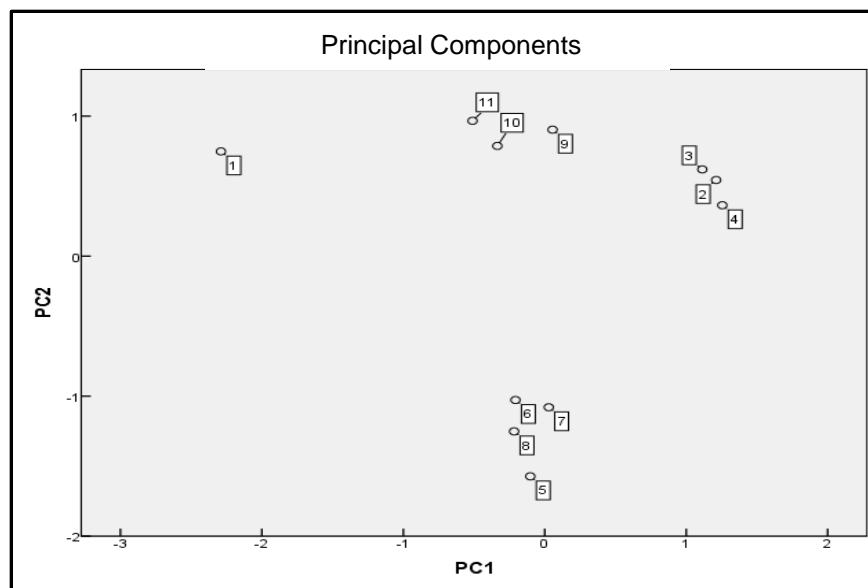


Figure 2.7. Basic PCA plot made using SPSS[®] with solvents from Table 2.1. [1].

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CHAPTER 3

DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR SOLUTE TRANSFER INTO 2-METHOXYETHANOL FROM WATER AND FROM THE GAS PHASE*

3.1 Introduction

Organic solvents are used extensively in manufacturing processes involving chemical syntheses and purifications. The selection of an appropriate solvent for a given process requires knowledge of the solvent's physical properties and solubilizing abilities, as well as the solvent's toxicity, purchase price and disposal cost. Physical properties are largely governed by solvent–solvent interactions, which are determined by molecular size and shape, and by the functional groups present in the solvent molecule. Solubilizing ability, on the other hand, depends more on the strength of the solute–solvent interactions relative to the strengths of both solvent–solvent and solute–solute interactions. Strong solute–solvent interactions tend to favor dissolution of the solute into the organic solvent media. Conversely, weak solute–solvent interactions result in very low solute solubility.

During the past 50 years, researchers have studied molecular interactions in fluid solutions using various spectroscopic, calorimetric and computational methods in order to achieve a better quantitative understanding of how these interactions affect chemical reaction rates and product yields, solute partitioning behavior between two completely immiscible (or partly miscible) phases, and solute solubility. The more successful of the

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proposed descriptive/predictive approaches include terms to represent contributions from both stronger interaction types (e.g., dipole–dipole and hydrogen-bonding) and weaker interaction types (e.g., dipole-induced dipole and nonspecific dispersion forces). Even in systems known to contain solute–solvent complexation and solvent/solute self-association, the need to include weaker molecular interactions has been recognized. For example, Bertrand [1] showed that neglect of nonspecific molecular interactions can lead to significant errors in calculating thermodynamic association properties, particularly in the case of weak molecular complexes, such as the chloroform–triethylamine complex.

A major advantage that the Abraham model has over many of the other methods developed in recent years for describing solute transfer is that once the process coefficients (c_p , e_p , s_p , a_p , b_p , v_p , c_k , e_k , s_k , a_k , b_k and l_k) are calculated, then one can easily make predictions for the more than 7 000 different organic, inorganic and organometallic compounds for which solute descriptors are known. To date, process coefficients have been published for more than 100 different organic solvents including several alkanes, alkanols, haloalkanes, substituted benzenes, alkyl alkanoates, dialkyl and cyclic ethers, alkanones, and other miscellaneous organic compounds of varying polarity and hydrogen-bonding character [2-7]. We are continually reporting process coefficients for additional solvents and partitioning systems.

Considerations are extended here to include solute transfer into an alkoxyalcohol solvent. Experimental solubilities have been determined for acenaphthene, biphenyl, benzoic acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid, 2-methoxybenzoic acid, 4-methoxybenzoic acid, 3,4-dimethoxybenzoic acid, 4-aminobenzoic acid, 4-

chlorobenzoic acid, 3,5-dinitro-2-methylbenzoic acid, 2- methylbenzoic acid, 3- methylbenzoic acid, 4-chloro-3-nitrobenzoic acid, 2-chloro-5-nitrobenzoic acid, 2- hydroxybenzoic acid, acetylsalicylic acid, 3,4-dichlorobenzoic acid, benzil, salicylamide, trans-stilbene, benzoin, and 9-fluorenone dissolved in 2-methoxyethanol at 298.15 K. Abraham model $\log P$ and $\log K$ correlations have been derived by combining measured molar solubilities with published activity coefficients [8-10], gas-to-liquid partition coefficients [11], and solubility data for hydrogen gas [12], carbon dioxide [13], anthracene [14], pyrene [15], 2- nitrobenzoic acid [16], 2-chlorobenzoic acid [16], 3- chlorobenzoic acid [16], and 4-nitroaniline [17]. The derived Abraham model correlations were validated using an external test set of $\log P$ and $\log K$ values for acetone, methanol, acetonitrile, butyl acetate, pyridine, 2-propanol, and dichloromethane that were measured as part of the current study. The derived Abraham model correlations describe the experimental data to within 0.16 log units (or less).

3.2 Experimental Methodology

3.2.1 Solubility Measurements

Experimental mole fraction solubilities, X_S^{exp} , are listed in Table 3.1 for the 23 different organic solutes for which solubility measurements were performed as described in Chapter 1 Section 1.3.1.1 using 2-methoxyethanol as the solvent. The tabulated numerical values correspond to the average of between four and eight independent determinations and were reproducible to within ± 1.5 relative percent.

Table 3.1. Experimental mole fraction solubilities of crystalline nonelectrolyte solutes dissolved in 2-methoxyethanol at 298.15K.

Solute	$X_{S,organic}^{exp}$
Acenaphthene	0.03291
Biphenyl	0.1150
Benzoic acid	0.2810
3-Nitrobenzoic acid	0.2931
4-Nitrobenzoic acid	0.03999
2-Methoxybenzoic acid	0.1462
4-Methoxybenzoic acid	0.03856
3,4-Dimethoxybenzoic acid	0.03133
4-Aminobenzoic acid	0.1932
2-Chloro-5-nitrobenzoic acid	0.2226
4-Chloro-3-nitrobenzoic acid	0.1134
2-Methylbenzoic acid	0.2194
3-Methylbenzoic acid	0.2180
4-Chlorobenzoic acid	0.03168
3,4-Dichlorobenzoic acid	0.04819
3,5-Dinitro-2-methylbenzoic acid	0.1299
Acetylsalicylic acid	0.1658
2-Hydroxybenzoic acid	0.2761
Benzil	0.06133
Salicylamide	0.1565
trans-Stilbene	0.01442
9-Fluorenone	0.1204
Benzoin	0.01484

Published literature values do exist for the solubility of benzoic acid, 4-chlorobenzoic acid and 4-nitrobenzoic acid in 2-methoxyethanol. Our [18] measured solubilities, when converted to molarities using the ideal molar volume approximation, are in reasonably good agreement with the molar solubilities of Ghosh and Hazra [19]:

for benzoic acid, $C_{s,organic} = 3.257$ M (ours) versus $C_{s,organic} = 3.054$ M [19]; for 4-chlorobenzoic acid, $C_{s,organic} = 0.3941$ M (ours) versus $C_{s,organic} = 0.4031$ M [19]; and for 4-nitrobenzoic acid, $C_{s,organic} = 0.4953$ M (ours) versus $C_{s,organic} = 0.4884$ M [19]. The maximum difference between the two sets of experimental values is 6.5%. As an informational note Ghosh and Hazra determined the concentrations of the three carboxylic acids in the saturated solutions by volumetric titration with standard caustic soda using phenolphthalein as indicator. Differences in chemical purities and experimental methodologies can lead to differences of a few percent in independently measured solute solubilities.

3.2.2 Gas Chromatographic Headspace Measurements

Provided by Dr. Igor Sedov's research group from Kazan Federal University, gas chromatographic headspace measurements were performed as described in Chapter 1 Section 1.3.1.2 with the solutes being dissolved in 2-methoxyethanol. The experimental infinite dilution activity coefficients are given in Table 3.2 for the seven solutes studied.

Table 3.2. Experimental infinite dilution activity coefficients, γ_{∞} , of the external test set solutes dissolved in 2-methoxyethanol at 298.15 K.

Solute	γ_{∞}
Acetone	1.68
Methanol	1.42
Acetonitrile	1.85
Butyl acetate	3.21
Pyridine	1.18
2-Propanol	2.00
Dichloromethane	0.99

3.3 Results and Discussion

Development of the Abraham model correlations for solute transfer into 2-methoxyethanol from both water and the gas phase is relatively straightforward. First, the experimental mole fraction solubilities given in Table 3.1 are converted to molar solubilities by using Equation (1.21) as described in Chapter 1. The molar solubility ratios of $(C_{S,organic}/C_{S,water})$ and $(C_{S,organic}/C_{S,gas})$ are obtained by dividing the solute's molar solubility in 2-methoxyethanol by the solute's molar solubility in water, $C_{S,water}$, and by the solute's gas phase molar concentration, $C_{S,gas}$. Numerical values of $C_{S,water}$ and $C_{S,gas}$ are available in earlier publications [20-38] for all of the crystalline solutes considered in the current study.

Second, the published infinite dilution activity coefficient data of Sedov et al. [8-9] and Matteoli et al. [10] that was retrieved from the published literature is converted to gas-to-2-methoxyethanol partition coefficients and water-to-2-methoxyethanol using the standard thermodynamic relationships described in Chapter 2 using Equations (2.1) and (2.3).

The experimental $\log P$, $\log K$, $\log (C_{S,organic}/C_{S,water})$ and $\log (C_{S,organic}/C_{S,gas})$ values obtained in this manner are tabulated in the eighth and ninth columns of Table 3.3. For solid solutes the tabulated values represent molar solubility ratios, except for naphthalene. The molecular solute descriptors for the 62 solutes that will be used in deriving the Abraham model correlations are given in Table 3.3. The tabulated values came from a solute descriptor database that contains over 7 000 compounds.

The experimental $\log (K$ or $C_{S,organic}/C_{S,gas})$ values in the eighth column of Table 3.3 give a second set 62 Abraham model equations containing six process coefficients

(c_k , e_k , s_k , a_k , b_k and l_k), and the experimental log (P or $C_{S,organic}/C_{S,water}$) values in the ninth column of Table 3.3 give a set of 62 Abraham model equations containing six process coefficients (c_p , e_p , s_p , a_p , b_p , v_p). Each set of equations is solved simultaneously for the optimal set of process coefficients that best describes the respective experimental log (K or $C_{S,organic}/C_{S,gas}$) and log (P or $C_{S,organic}/C_{S,water}$) data. Preliminary regression analysis of the experimental data in Table 3.3 showed that the a_p coefficient in the log (P or $C_{S,organic}/C_{S,water}$) correlation was small ($a_p = 0.032$), and that the error in the coefficient (standard error = 0.096) was larger than the coefficient itself.

Table 3.3. Experimental log (K or $C_{S,organic}/C_{S,gas}$) and log (P or $C_{S,organic}/C_{S,water}$) data for solutes dissolved in 2-methoxyethanol at 298.15 K.

Table 3.3. Experimental $\log (K$ or $C_{S,organic}/C_{S,gas}$) and $\log (P$ or $C_{S,organic}/C_{S,water}$) data for solutes dissolved in 2-methoxyethanol at 298.15 K.

Solute	E	S	A	B	L	V	$\log K^a$	$\log P^a$	Ref.
Hydrogen	0.000	0.000	0.000	0.000	-1.200	0.1086	-1.346	0.674	[12]
Carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.2809	0.478	0.558	[13]
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	1.985	3.805	[8]
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	2.363	4.323	[8]
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	2.781	4.891	[8]
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	3.111	5.261	[8]
Decane	0.000	0.000	0.000	0.000	4.686	1.5180	3.466	5.786	[8]
Undecane	0.000	0.000	0.000	0.000	5.191	1.6590	3.785	6.165	[8]
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	2.333	3.233	[8]
Methylcyclopentane	0.225	0.100	0.000	0.000	2.907	0.8454	2.195	3.365	[8]
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	2.546	3.756	[8]
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	3.332	3.962	[8]
Cyclohexene	0.395	0.200	0.000	0.070	3.021	0.8024	2.557	2.827	[8]
1,7-Octadiene	0.191	0.200	0.000	0.100	3.415	1.1498	2.999	3.959	[8]
4-Vinyl-1-cyclohexene	0.450	0.330	0.000	0.170	3.708	1.0412	3.246	3.316	[8]
2-Chloro-2-methylpropane	0.142	0.300	0.000	0.030	2.273	0.7946	2.426	3.226	[9]
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	3.550	-0.120	[11]
2-Methoxyethanol	0.269	0.500	0.300	0.840	2.490	0.6487	4.371	-0.589	Unity
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	2.877	0.327	[10]
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	3.625	-0.085	[11]
Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	3.165	0.445	[11]

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref.
Nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237	3.644	0.694	[11]
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	3.019	2.389	[8]
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	3.366	2.716	[8]
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	3.704	3.124	[8]
o-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	3.857	3.197	[8]
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	3.741	3.131	[8]
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	3.714	3.124	[8]
4-Isopropyltoluene	0.607	0.490	0.000	0.190	4.590	1.2800	4.213	3.713	[8]
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	5.405	3.675	[8]
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4544	7.901	4.871	[14]
Pyrene	2.808	1.710	0.000	0.280	8.833	1.5846	8.974	5.474	[15]
Acenaphthene	1.604	1.050	0.000	0.220	6.469	1.2586	6.508	4.148	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	6.400	4.450	This work
trans-Stilbene	1.450	1.050	0.000	0.340	7.520	1.5630	7.833	5.053	This work
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	3.233	2.643	[8]
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	3.834	3.014	[8]
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	4.211	3.141	[8]
Benzoic acid	0.730	0.900	0.590	0.400	4.657	0.9317	7.202	2.062	This work
2-Nitrobenzoic acid	0.990	1.480	0.820	0.530	5.900	1.1059	9.926	1.836	[16]
3-Nitrobenzoic acid	0.990	1.180	0.730	0.520	5.601	1.1059	9.121	2.191	This work
4-Nitrobenzoic acid	0.990	1.520	0.680	0.400	5.770	1.1059	9.575	2.675	This work
2-Methoxybenzoic acid	0.899	1.410	0.450	0.620	5.636	1.1313	8.586	1.786	This work
4-Methoxybenzoic acid	0.899	1.250	0.620	0.520	5.741	1.1313	9.178	2.478	This work
3,4-Dimethoxybenzoic acid	0.950	1.646	0.570	0.755	6.746	1.3309	10.526	2.079	This work

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref.
4-Aminobenzoic acid	1.075	1.650	0.940	0.600	5.916	1.0315	11.159	1.729	This work
2-Chlorobenzoic acid	0.840	1.010	0.680	0.400	4.840	1.0541	7.770	2.270	[16]
3-Chlorobenzoic acid	0.840	0.950	0.630	0.320	5.197	1.0541	8.073	2.923	[16]
4-Chlorobenzoic acid	0.840	1.020	0.630	0.270	4.947	1.0541	7.956	3.156	This work
3,5-Dinitro-2-methylbenzoic acid	1.310	2.120	0.750	0.650	8.040	1.4210	12.724	2.768	This work
2-Methylbenzoic acid	0.730	0.840	0.420	0.440	4.677	1.0726	6.754	2.454	This work
3-Methylbenzoic acid	0.730	0.890	0.600	0.400	4.819	1.0726	7.512	2.532	This work
4-Chloro-3-nitrobenzoic acid	1.250	1.470	0.700	0.440	6.685	1.2283	10.335	3.125	This work
2-Chloro-5-nitrobenzoic acid	1.250	1.400	0.670	0.460	6.513	1.2283	9.929	2.979	This work
2-Hydroxybenzoic acid	0.900	0.850	0.730	0.370	4.732	0.9904	7.780	2.430	This work
Acetylsalicylic acid	0.781	1.690	0.710	0.670	6.279	1.2879	10.447	1.947	This work
3,4-Dichlorobenzoic acid	0.950	0.920	0.670	0.260	5.623	1.1766	8.491	3.751	This work
Benzoin	1.585	2.115	0.196	0.841	9.159	1.6804	11.666	2.935	This work
Benzil	1.445	1.590	0.000	0.620	7.611	1.6374	8.775	3.905	This work
Salicylamide	1.160	1.650	0.630	0.480	5.910	1.0315	9.689	2.004	This work
4-Nitroaniline	1.220	1.920	0.460	0.350	6.042	0.9904	9.713	2.533	[17]
9-Fluorenone	1.600	1.490	0.000	0.350	7.474	1.3722	8.312	4.120	This work

^a For solid solutes the tabulated values represent molar solubility ratios, except for naphthalene.

The $a_p \cdot \mathbf{A}$ term was deleted, and the final regressions yielded the following two Abraham model correlations:

$$\log P = 0.175(0.076) + 0.326(0.073)\mathbf{E} - 0.140(0.094)\mathbf{S} - 4.086(0.159)\mathbf{B} + 3.630(0.078)\mathbf{V}$$

(with N = 62, SD= 0.158, R²=0.988, F = 1163) (3.1)

$$\log K = -0.141(0.052) - 0.265(0.076)\mathbf{E} + 1.810(0.096)\mathbf{S} + 3.641(0.085)\mathbf{A} +$$

$$0.590(0.141)\mathbf{B} + 0.790(0.018)\mathbf{L}$$
(3.2)

(with N = 62, SD = 0.139, R² = 0.998, F = 6044)

where the standard error in each calculated equation coefficient is given in parenthesis immediately after the respective coefficient. The statistical information associated with each correlation includes the number of experimental data points used in the regression analysis (N), the standard deviation (SD), the squared correlation coefficient (R²) and the Fisher F-statistic (F). No loss in descriptive ability resulted from setting the a_p coefficient equal to zero, SD = 0.158 log units ($a_p \neq 0$) versus SD = 0.158 log units (with $a_p = 0$).

The Abraham model correlations given by Equations (3.1) and (3.2) are statistically very good with standard deviations of 0.158 log units and 0.139 log units, respectively. Figure 3.1 compares the observed log (K or $C_{S,organic}/C_{S,gas}$) values against the back-calculated values based on Equation (3.2). The experimental data covers a range of approximately 14.1 log units, from log $K = -1.346$ for hydrogen gas to log ($C_{S,organic}/C_{S,gas}$) = 12.724 for 3,5-dinitro-2-methylbenzoic acid. A comparison of the back-calculated versus measured log (P or $C_{S,organic}/C_{S,water}$) data is depicted in Figure 3.2. As expected, the standard deviation for the log (P or $C_{S,organic}/C_{S,water}$) correlation is slightly larger than that of the log (K or $C_{S,organic}/C_{S,gas}$) correlations because the log (P

or $C_{S,organic}/C_{S,water}$) values contain the additional experimental uncertainty in the gas-to-water partition coefficients used in the $\log(K \text{ or } C_{S,organic}/C_{S,gas})$ to $\log(P \text{ or } C_{S,organic}/C_{S,water})$ conversion for the liquid organic solutes.

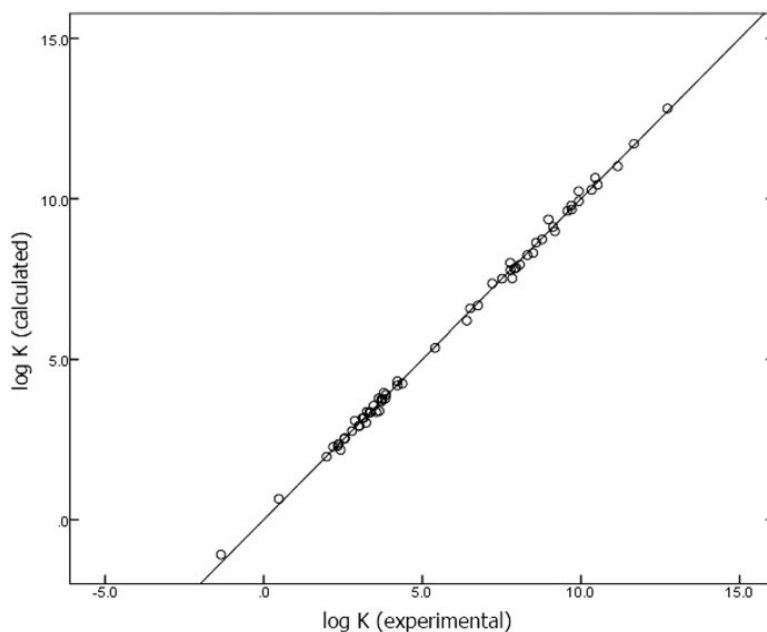


Figure 3.1. Comparison between experimental $\log K$ data and calculated values based on Equation (3.2).

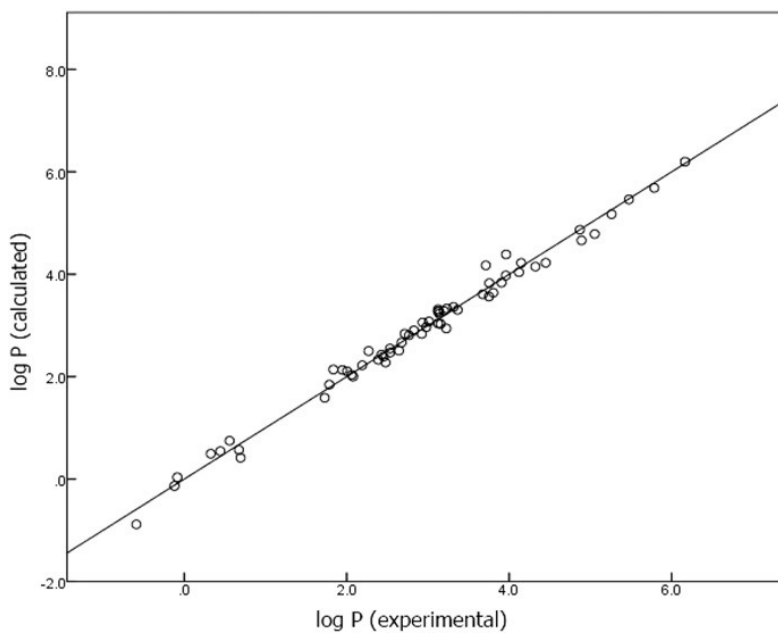


Figure 3.2. Comparison between experimental $\log P$ data and calculated values based on Equation (3.1).

There is insufficient experimental data to perform a meaningful training set and test set validation analyses; however, the experimental data for acetone, methanol, acetonitrile, butyl acetate, pyridine, 2-propanol, and dichloromethane that was measured in this study can be used as an external test set. The experimental $\log K$ and $\log P$ values for the aforementioned seven solutes were not used in deriving Equations (3.1) and (3.2) above. Tabulated in Table 3.4 are the solute descriptors and experimental $\log K$ and $\log P$ values for the seven compounds used in the external test set. Equations (3.1) and (3.2) provide very accurate mathematical predictions of the $\log K$ and $\log P$ values. The average absolute differences between the experimental data and predicted values were 0.060 and 0.078 log units for $\log K$ and $\log P$, respectively. The average absolute differences for the test set analyses were less than the calculated standard deviations associated with Equations (3.1) and (3.2).

Table 3.4. Experimental $\log K$ and $\log P$ data for the external test set solutes dissolved in 2-methoxyethanol at 298.15 K.

Solute	E	S	A	B	L	V	$\log K$	$\log P$
Propanone	0.179	0.700	0.040	0.490	1.696	0.5470	2.781	-0.049
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	3.116	-0.624
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	3.157	0.307
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	3.805	1.865
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	3.982	0.542
2-Propanol	0.212	0.360	0.330	0.560	1.764	0.5900	3.414	-0.066
Dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943	2.738	1.778

3.4 Conclusions

In an earlier paper on correlations of solute transfer into 2-ethoxyethanol [39], which will be presented in Chapter 4, process coefficients for 2-ethoxyethanol are compared with those for the solvents 1-butanol and ethylene glycol. Now that

coefficients for 2-methoxyethanol are known, as well as those for 2-ethoxyethanol, it is of some interest to compare coefficients for these 2-alkoxyethanols with those for a wider selection of solvents. The coefficients in Equation (3.1) refer to differences between solubility properties of 2-methoxyethanol and water, whereas the coefficients in Equation (3.2) refer to the solubility properties of 2-methoxyethanol itself and hence are easier to interpret. Therefore, the general Equation (1.2) was used to analyze coefficients.

A useful visual method of comparison is that of Principal Components Analysis, PCA, which is described in detail in Chapter 2 Section 4. Coefficients for all the solvents studied were not used because the PC plot would be far too busy. Therefore, a representative selection of solvents was chosen, as given in Table 3.5 [2, 37-38, 40-42]. A PCA on the coefficients for the 33 solvents showed that the first two PCs contained 71% of the total data. A plot of the scores of PC2 against the scores of PC1 is given in Figure 3.5. The points for 2-methoxyethanol and 2-ethoxyethanol (No. 10 and No. 11) are quite close to those for most of the hydroxylic solvents (Nos. 1–8) with only the point for ethylene glycol (No. 9) being far away.

Table 3.5. Coefficients in Equation (1.2) for gas-to-dry solvent partitions.

Solvent	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>	<i>N</i>
Methanol	-0.039	-0.338	1.317	3.826	1.396	0.773	1
Ethanol	0.017	-0.232	0.867	3.894	1.192	0.846	2
Propan-1-ol	-0.042	-0.246	0.749	3.888	1.076	0.874	3
Octan-1-ol	-0.147	-0.214	0.561	3.507	0.749	0.943	4
Decan-1-ol	-0.139	-0.090	0.356	3.547	0.727	0.958	5
Propan-2-ol	-0.048	-0.324	0.713	4.036	1.055	0.884	6

(table continues)

Solvent	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>	<i>N</i>
tert-Butanol	0.053	-0.443	0.699	4.026	0.882	0.907	7
Trifluoroethanol	-0.092	-0.547	1.339	2.213	3.807	0.645	8
Ethylene glycol	-0.887	0.132	1.657	4.457	2.355	0.565	9
2-Methoxyethanol	-0.141	-0.265	1.810	3.641	0.590	0.790	10
2-Ethoxyethanol	-0.064	-0.257	1.452	3.672	0.662	0.843	11
Diethyl ether	0.288	-0.379	0.904	2.937	0.000	0.963	12
Dioxane	-0.034	-0.354	1.674	3.021	0.000	0.919	13
Ethyl acetate	0.182	-0.352	1.316	2.891	0.000	0.916	14
Propanone	0.127	-0.387	1.733	3.060	0.000	0.866	15
Butanone	0.112	-0.474	1.671	2.878	0.000	0.916	16
Dimethylformamide	-0.391	-0.869	2.107	3.774	0.000	1.011	17
N-Methylformamide	-0.249	-0.142	1.661	4.147	0.817	0.739	18
Formamide	-0.800	0.310	2.292	4.130	1.933	0.442	19
Acetonitrile	-0.007	-0.595	2.461	2.085	0.418	0.738	20
Dimethyl sulfoxide	-0.556	-0.223	2.903	5.037	0.000	0.719	21
Tributyl phosphate	0.097	-0.098	1.103	2.411	0.588	0.844	22
Propylene carbonate	-0.356	-0.413	2.587	2.207	0.455	0.719	23
Dichloromethane	0.192	-0.572	1.492	0.460	0.847	0.965	24
Trichloromethane	0.157	-0.560	1.259	0.374	1.333	0.976	25
Tetrachloromethane	0.217	-0.435	0.554	0.000	0.000	1.069	26
Octane	0.219	0.000	0.000	0.000	0.000	0.960	27
Cyclohexane	0.163	-0.110	0.000	0.000	0.000	1.013	28
Toluene	0.085	-0.400	1.063	0.501	0.154	1.011	29
Fluorobenzene	0.181	-0.621	1.432	0.647	0.000	0.986	30
Bromobenzene	-0.064	-0.326	1.261	0.323	0.292	1.002	31
Iodobenzene	-0.171	-0.192	1.197	0.245	0.245	1.002	32
Nitrobenzene	-0.296	0.092	1.707	1.147	0.443	0.912	33

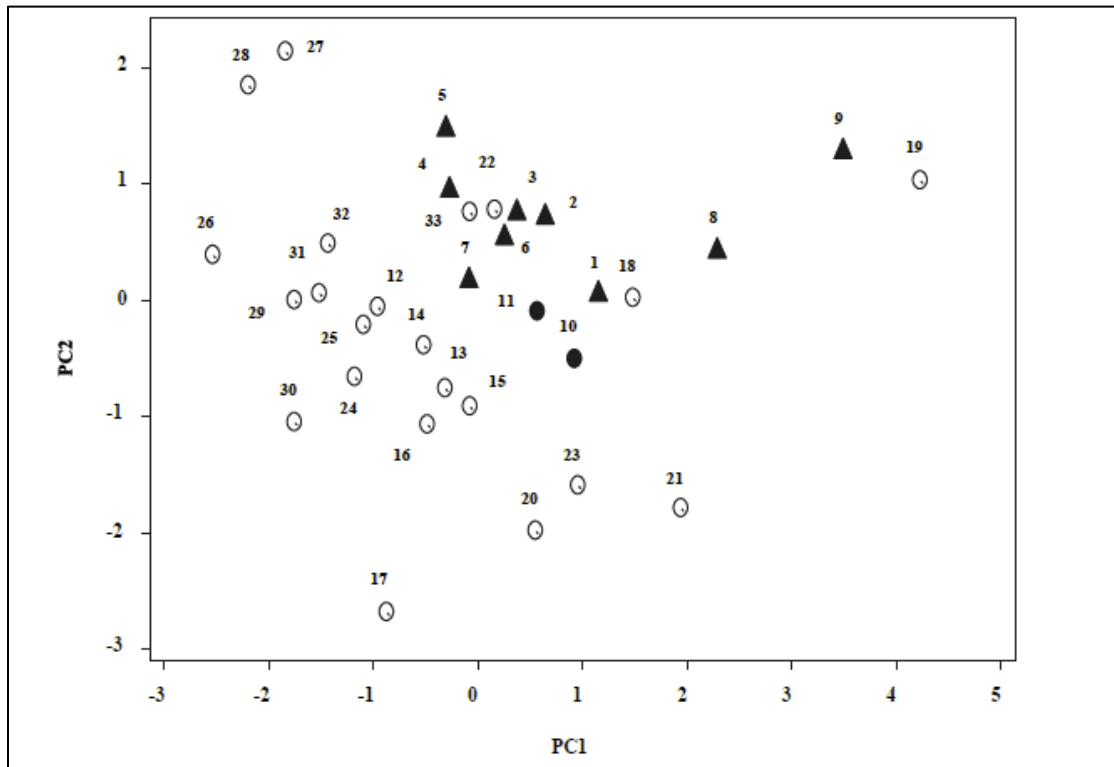


Figure 3.3. A plot of the scores of PC2 against the scores of PC1. Points numbered as in Table 3.5: ● 2-methoxyethanol and 2-ethoxyethanol; ▲ other alcoholic solvents; ○ non-alcoholic solvents.

By and large, solvents in the top left hand corner are characterized as ‘non-polar’ and those towards the bottom right hand corner are the more ‘polar’ solvents. In addition, going from left to right across the plot, solvents start off as poor hydrogen-bond acids, poor hydrogen-bond bases and of low polarity on the left, and finish as strong hydrogen-bond bases, strong hydrogen-bond acids and of high polarity on the right. The strongest such solvents are ethylene glycol (No. 9) and formamide (No. 19). The two alkoxyethanols are slightly more ‘polar’ than the aliphatic alcohols yet in the overall pattern of solvent behavior are actually quite similar to many of the aliphatic alcohols as regards solubility related properties. Apart from solvents trifluoroethanol (No. 8) and ethylene glycol (No. 9) the hydroxylic solvents including the alkoxyethanols form a

distinct cluster in the PC plot, so that by comparison to the solvents listed in Table 3.5, they all have similar influences on properties such as gas-to-solvent partition coefficients.

The mathematical correlations derived in this study for solute transfer to 2-methoxyethanol from both water and the gas phase further illustrate the applicability of the Abraham model. Moreover, the external test set analysis suggests that the derived Abraham model equations should be capable of providing reasonably accurate predictions of gas-to-2-methoxyethanol partition coefficients and water-to-2-methoxyethanol partition coefficients for additional solutes, as well as solubilities of both gases and crystalline nonelectrolyte solutes in 2-methoxyethanol, provided that the solute descriptors of the additional solutes fall within the range numerical values used in deriving Equations (3.1) and (3.2). Solutes used in deriving the aforementioned expressions cover a fairly wide range of descriptor numerical values as shown in Table 3.3.

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CHAPTER 4

DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR SOLUTE TRANSFER INTO 2-ETHOXYETHANOL FROM WATER AND FROM THE GAS PHASE[†]

4.1 Introduction

Hydrogen-bonding has received considerable attention over the years due to its role in determining solubilities, molecular shapes and spectral properties of biomolecules dissolved in fluid solution. Differences in hydrogen-bonding interactions are important considerations in predicting solute transfer between water and hydrogen-bonding solvents such as alcohols and alkoxyalcohols. If the water–solute hydrogen-bonds are stronger than the organic solvent–solute hydrogen-bonds then solute transfer into the organic solvent is generally not favored. If, on the other hand, the organic solvent–solute interactions are the stronger of the hydrogen-bonding interactions, then one would predict a greater molar solute concentration in the organic solvent relative to that in the aqueous phase. Over the past two decades the applicability of the Abraham Solvation Parameter Model (ASPM) to describe solute transfer into organic solvents of varying polarities and hydrogen-bonding character from both water and the gas phase has been demonstrated. The Abraham model includes the effects from hydrogen-bonding interactions, as well as contributions from the other types of solute–solute, solute–solvent and solvent–solvent interactions. Neglect of these contributions can lead to significant errors in predicting solute transfer, particularly in the case of weak hydrogen-bonded molecular solute–solvent complexes. In the present communication

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considerations are extended to include 2-ethoxyethanol, which contains both an ether (R–O–R) and hydroxyl (R–OH) functional group. Infinite dilution activity coefficients (γ_∞) were measured at 298.15 K for 13 different aliphatic hydrocarbons (alkanes, cycloalkanes, alkenes), 12 different aromatic compounds (benzene, alkylbenzenes, halobenzenes, naphthalene), and 2-chloro-2-methylpropane dissolved in 2-ethoxyethanol using a gas chromatographic headspace analysis method, and gas-to-liquid partition coefficients (K) were calculated using these results, as well as saturated vapor pressures of solutes taken from literature. As part of this study solubilities were also measured for xanthene, phenothiazine, acenaphthene, diphenyl sulfone, 3,5-dinitro-2-methylbenzoic acid, 3-chlorobenzoic acid, 2-methylbenzoic acid, 4-chloro-3-nitrobenzoic acid, 3,5-dinitrobenzoic acid, benzil, and thioxanthen-9-one dissolved in 2-ethoxyethanol at 298.15 K. The measured partition coefficients, combined with published infinite dilution activity coefficient data for liquid organic compounds [1-13], gas solubility data for 2-methylpropane [14] and hydrogen gas [15], and solubility data for crystalline nonelectrolyte organic compounds [16-17] dissolved in 2-ethoxyethanol, were used to derive Abraham model correlations for both water-to-2-ethoxyethanol partition coefficients ($\log P$) and gas-to-2-ethoxyethanol partition coefficients ($\log K$).

4.2 Experimental Methodology

4.2.1 Gas Chromatographic Headspace Measurements

Provided by Dr. Igor Sedov's group from Kazan Federal University, limiting activity coefficients of low polar liquid organic compounds in 2-ethoxyethanol were measured with a headspace autosampler as described in Chapter 1 Section 1.3.1.2. To

determine the limiting activity coefficient, γ_∞ , activity coefficients at 3–4 different concentrations of a solute in the range of 0.1–1.5 vol.% were measured and repeated 2 times for each concentration. Since the considered solutes form no dimers or other associates, it is likely that at such concentrations the solutions behave like infinitely diluted ones. This was confirmed experimentally by the absence of concentration dependence of the activity coefficients. Gas-to-liquid partition coefficients, K , can be calculated using Equation (2.1) as shown in Chapter 2. The Gibbs free energy of solvation is calculated according to the equation: $\Delta G_{\text{solv}} = RT \ln(\gamma_\infty p_{\text{sat}})$, where R is the universal gas constant, T is the temperature in K, γ_∞ is the limiting activity coefficient and p_{sat} is the saturated vapor pressure. Average values of $\log K$ and ΔG_{solv} calculated from all measurements for the same system were taken and are presented in Table 4.1.

Comparison with the vapor-liquid equilibrium (VLE) data for the mixtures of hexane, heptane, and cyclohexane with 2-ethoxyethanol at 303 and 323 K [1] shows that the limiting activity coefficients of Sedov et al. [18] are 7–12% lower than the values extrapolated to 298.15 K using the results of that study. However, the lowest concentrations of hydrocarbons at which Carmona et al. [1] conducted their measurements were 3 and 6 mol%. This corresponds to 3.3–9 vol.% of a hydrocarbon and is certainly not at infinite dilution. Extrapolation to zero concentration made by authors [1] is likely to lead to the overestimation of γ_∞ .

Comparison with the previously reported Gibbs free energies of solvation in 2-methoxyethanol at 298.15 K ($\Delta G_{\text{solv}}^{\text{A/MC}}$) [19] shows a good correlation between the data in two solvents:

$$\Delta G_{\text{solv}}^{\text{A/EC}} = 0.951 \Delta G_{\text{solv}}^{\text{A/MC}} - 1.712 \quad (4.1)$$

(with $N = 25$, $\sigma = 0.62$ kJ/mol, $R^2 = 0.9780$)

Table 4.1. Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and the Gibbs free energies solvation in 2-ethoxyethanol at 298.15 K^a.

Solute	γ_∞	$u(\gamma_\infty)$	Log K	ΔG_{solv}^b /(kJ/mol)
n-Hexane	7.65	0.4	2.22	1.1
n-Heptane	9.63	0.3	2.64	-1.3
n-Octane	12.16	0.3	3.05	-3.7
n-Nonane	14.70	0.6	3.47	-6.0
n-Decane	20.80	0.9	3.81	-8.0
n-Undecane	30.40	0.6	4.19	-10.1
Cyclohexane	5.47	0.3	2.56	-0.9
Methylcyclopentane	5.52	0.6	2.40	0.0
Methylcyclohexane	6.93	0.4	2.78	-2.1
Cyclooctane	8.70	0.2	3.60	-6.8
Cyclohexene	3.98	0.2	2.73	-1.9
1,7-Octadiene	5.38	0.5	3.20	-4.5
4-Vinyl-1-cyclohexene	4.53	0.2	3.43	-5.8
Benzene	1.91	0.1	3.03	-3.5
Toluene	2.42	0.15	3.45	-5.9
Fluorobenzene	1.52	0.1	3.21	-4.6
Chlorobenzene	1.69	0.1	3.98	-8.9
Bromobenzene	2.01	0.2	4.36	-11.1
o-Dichlorobenzene	2.00	0.4	4.85	-13.9
o-Xylene	3.18	0.15	3.96	-8.9
m-Xylene	3.36	0.2	3.84	-8.2
p-Xylene	3.38	0.15	3.81	-8.0
Ethylbenzene	3.16	0.1	3.80	-7.9
p-Cymene	5.46	0.3	4.38	-11.3
Naphthalene	9.97	1.4	5.36	-16.8
tert-Butyl chloride	2.30	0.55	2.43	-0.1

^a Standard uncertainty for temperature $u(T) = 0.2$ K. ^b Standard state for the ΔG_{solv} is a hypothetical ideal solution at unit mole fraction and a gas at 1 bar fugacity. ΔG_{solv} calculated in this fashion are not the same as values calculated as $\Delta G_{\text{solv}} = -RT \ln K$ where K is the equilibrium constant in the table.

This correlation is shown in Figure 4.1. For all the considered solutes the Gibbs free energy of solvation in 2-ethoxyethanol is lower than in 2-methoxyethanol, and for

aliphatic compounds this difference is larger than for aromatic.

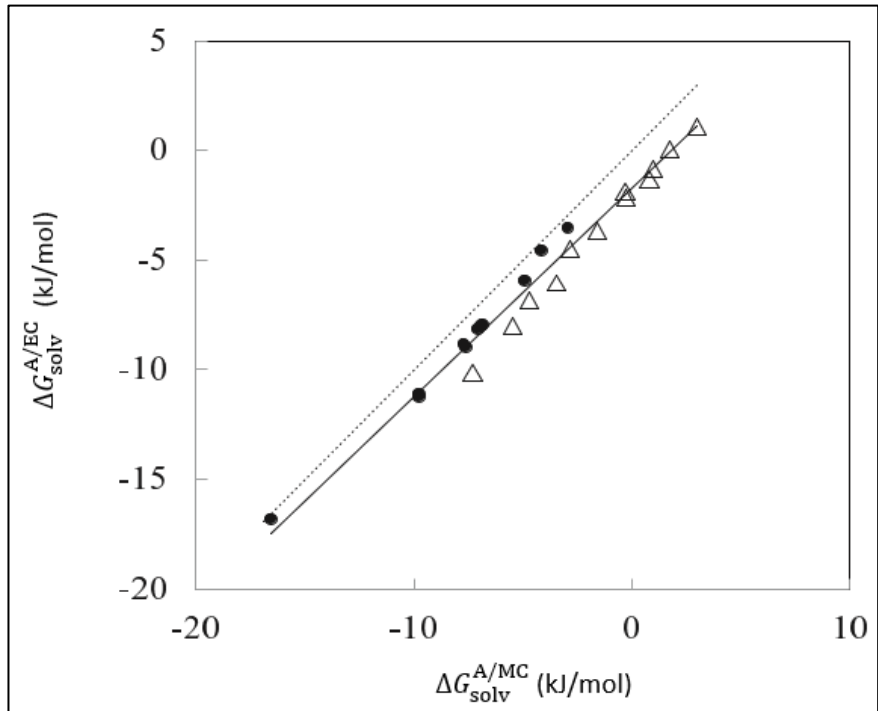


Figure 4.1. Comparison of the Gibbs free energies of solvation of low polar solutes in 2-ethoxyethanol (EC) and 2-methoxyethanol (MC) at 298.15 K. Triangles are aliphatic, circles are aromatic solutes. Dotted line is $y = x$.

4.2.2 Solubility Measurements

Solubility measurements were performed as described in Chapter 1 Section 1.3.1.1 using 2-ethoxyethanol as the solvent. Experimental mole fraction solubilities, X_S^{exp} , are tabulated in Table 4.2 for the 11 organic solutes for which solubility measurements were made. Numerical values represent the average of between four and eight independent determinations and were reproducible to within $\pm 1.5\%$.

Table 4.2. Experimental mole fraction solubilities of crystalline nonelectrolyte solutes dissolved in 2-ethoxyethanol at 298.15 K.

Solute	X_S^{exp}
Xanthene	0.04299
Acenaphthene	0.04561
Thioxanthen-9-one	0.002795
Phenothiazine	0.08050
Diphenyl sulfone	0.03087
3,5-Dinitrobenzoic acid	0.1361
4-Chloro-3-nitrobenzoic acid	0.08320
2-Methylbenzoic acid	0.2194
3-Chlorobenzoic acid	0.1612
3,5-Dinitro-2-methylbenzoic acid	0.09944
Benzil	0.06654

4.3 Results and Discussions

Assembled in Table 4.3 are the experimental partition coefficients and solubility ratios for a chemically diverse set of 76 solutes dissolved in 2-ethoxyethanol. For hexane, heptane, and cyclohexane log K values measured at 298.15 K in the data treatment have been used rather than the extrapolated values based on the published log K data of Carmona et al. [1]. As noted above, the data of Carmona et al. were measured at a slightly higher temperature, and to remove any uncertainty associated with extrapolating the values to a slightly lower temperature, the values that were measured at 298.15 K have been chosen. In the case of the liquid solutes, the experimental partition coefficients were calculated from measured infinite dilution activity coefficient data ($\gamma_{\text{solute}}^{\infty}$) using the standard thermodynamic relationships of Equations (2.1) and (2.3) as described in Chapter 2. The calculation of log P requires

knowledge of the solute's gas phase partition coefficient into water, K_w , which is available for all of the liquid organic compounds considered in the present communication.

In the case of crystalline solutes, the tabulated numerical values in Table 4.2 represent the logarithm of the molar solubility ratios, $\log (C_{S,organic}/C_{S,water})$ (Equation (1.14)) and $\log (C_{S,organic}/C_{S,gas})$ (Equation (1.13)). Several authors [3-16, 20-21, 24-29] reported their experimental solubility data in units of mole fraction. Measured mole fraction solubilities were converted to molar solubilities as described in Chapter 1 using Equation (1.21). The experimental $\log (P \text{ or } (C_{S,organic}/C_{S,water}))$ and $\log (K \text{ or } (C_{S,organic}/C_{S,gas}))$ values at 298.15 K for solutes dissolved in 2-ethoxyethanol are listed in the last two columns of Table 4.3. Also given in Table 4.3 are the molecular solute descriptors for all solutes considered in this study. The tabulated values came from our solute descriptor database and are all based on experimental partition coefficient, molar solubility ratios, and chromatographic retention factor data.

Regression analysis of the 76 experimental $\log P$ values and 76 $\log K$ values in Table 4.3 yielded the following two Abraham model correlations as seen in Equations (4.2) and (4.3):

$$\log (P \text{ or } C_{S,organic}/C_{S,water}) = 0.133(0.049) + 0.392(0.050)E - 0.419(0.056)S + 0.125(0.068)A - 4.200(0.073)B + 3.888(0.056)V \quad (4.2)$$

(with $N = 76$, $SD = 0.149$, $R^2 = 0.994$, $F = 2153$)

$$\log (K \text{ or } C_{S,organic}/C_{S,gas}) = -0.064(0.032) - 0.257(0.049)E + 1.452(0.047)S + 3.672(0.055)A + 0.662(0.060)B + 0.843(0.012)L \quad (4.3)$$

(with $N = 76$, $SD = 0.126$, $R^2 = 0.999$, $F = 17838$)

where the standard error in each calculated equation coefficient is given in parentheses immediately after the respective coefficient. The statistical information associated with each correlation includes the number of experimental data points used in the regression analysis (N), the standard deviation (SD), the squared correlation coefficient (R^2) and the Fisher F-statistic (F).

The Abraham model correlations given by Equations (4.2) and (4.3) are statistically very good with standard deviations of 0.149 log units and 0.126 log units, respectively. Figure 4.2 compares the observed log (K or $C_{S,organic}/C_{S,gas}$) values against the back-calculated values based on Equation (4.3). The experimental data covers a range of approximately 25.51 log units, from $\log K = -1.24$ for hydrogen gas to $\log (C_{S,organic}/C_{S,gas}) = 24.27$ for hexaphenoxycyclotriphosphazene. A comparison of the back-calculated versus measured log (P or $C_{S,organic}/C_{S,water}$) data is depicted in Figure 4.3 for values that cover a range of about 11.04 log units. As expected, the standard deviation for the log (P or $C_{S,organic}/C_{S,water}$) correlation is slightly larger than that of the log (K or $C_{S,organic}/C_{S,gas}$) correlations because the log (P or $C_{S,organic}/C_{S,water}$) values contain the additional experimental uncertainty in the gas-to-water partition coefficients used in the log (K or $C_{S,organic}/C_{S,gas}$) to log (P or $C_{S,organic}/C_{S,water}$) conversion.

Table 4.3. Experimental $\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}})$ and $\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}})$ data for solutes dissolved in anhydrous 2-ethoxyethanol at 298.15 K.

Solute	E	S	A	B	L	V	$\log K^a$	$\log P^a$	Ref.
Hydrogen	0.000	0.000	0.000	0.000	-1.200	0.1086	-1.243	0.477	[15]
2-Methylpropane	0.000	0.000	0.000	0.000	1.409	0.6722	1.061	2.761	[14]
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	2.220	4.040	This work
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	2.640	4.600	This work
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	3.050	5.160	This work
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	3.470	5.620	This work
Decane	0.000	0.000	0.000	0.000	4.686	1.5180	3.810	6.130	This work
Undecane	0.000	0.000	0.000	0.000	5.191	1.6590	4.190	6.570	This work
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	2.560	3.460	This work
Methylcyclopentane	0.225	0.100	0.000	0.000	2.907	0.8454	2.400	3.570	This work
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	2.780	3.990	This work
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	3.600	4.370	This work
Cyclohexene	0.395	0.200	0.000	0.070	3.021	0.8024	2.730	3.000	This work
1,7-Octadiene	0.191	0.200	0.000	0.100	3.415	1.1498	3.200	4.160	This work
4-Vinyl-1-cyclohexene	0.450	0.330	0.000	0.170	3.708	1.0412	3.430	3.500	This work
tert-Butyl chloride	0.142	0.300	0.000	0.030	2.273	0.7946	2.430	3.230	This work
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	3.179	-0.561	[3,13]
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	3.346	-0.324	[4,13]
1-Propanol	0.236	0.420	0.370	0.480	2.031	0.5900	3.910	0.350	[5,13]
2-Propanol	0.212	0.360	0.330	0.560	1.764	0.5900	3.571	0.091	[6,13]
Methyl formate	0.192	0.680	0.000	0.380	1.285	0.4648	2.256	0.216	[7,12]

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref.
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	2.703	0.403	[8,12]
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	3.037	0.877	[9,12]
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	3.450	1.400	[10,12]
Ethyl propanoate	0.087	0.580	0.000	0.450	2.807	0.8875	3.360	1.390	[11,12]
2-Ethoxyethanol	0.237	0.550	0.290	0.820	2.719	0.7896	4.569	-0.341	Unity
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	3.030	2.400	This work
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	3.450	2.800	This work
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	3.800	3.220	This work
o-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	3.960	3.300	This work
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	3.840	3.230	This work
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	3.810	3.220	This work
4-Isopropyltoluene	0.607	0.490	0.000	0.190	4.590	1.2800	4.380	3.880	This work
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	5.360	3.630	This work
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4544	7.864	4.834	[22]
Pyrene	2.808	1.710	0.000	0.280	8.833	1.5846	9.135	5.635	[23]
Acenaphthene	1.604	1.050	0.000	0.220	6.469	1.2586	6.562	4.202	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	6.409	4.459	[16]
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	3.210	2.620	This work
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	3.980	3.160	This work
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	4.518	0.9612	4.850	3.950	This work
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	4.360	3.290	This work
Xanthene	1.502	1.070	0.000	0.230	7.153	1.4152	7.344	4.844	This work
Phenothiazine	1.890	1.560	0.310	0.300	8.389	1.4789	10.399	4.996	This work
4-Nitrobenzoic acid	0.990	1.520	0.680	0.400	5.770	1.1059	9.366	2.466	[16]

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref.
2-Methoxybenzoic acid	0.899	1.410	0.450	0.620	5.636	1.1313	8.427	1.627	[16]
4-Methoxybenzoic acid	0.899	1.250	0.620	0.520	5.741	1.1313	9.120	2.420	[16]
3,4-Dimethoxybenzoic acid	0.950	1.646	0.570	0.755	6.746	1.3309	10.429	1.982	[16]
4-Hydroxyacetanilide	1.060	1.630	1.040	0.860	6.430	1.1724	12.034	1.134	[16]
4-Chlorobenzoic acid	0.840	1.020	0.630	0.270	4.947	1.0541	7.895	3.095	[16]
3,5-Dinitro-2-methylbenzoic acid	1.310	2.120	0.750	0.650	8.040	1.4210	12.543	2.587	This work
3-Chlorobenzoic acid	0.840	0.950	0.630	0.320	5.197	1.0541	8.004	2.854	This work
2-Methylbenzoic acid	0.730	0.840	0.420	0.440	4.677	1.0726	6.689	2.389	This work
3-Methylbenzoic acid	0.730	0.890	0.600	0.400	4.819	1.0726	7.432	2.452	[16]
4-Chloro-3-nitrobenzoic acid	1.250	1.470	0.700	0.440	6.685	1.2283	10.129	2.919	This work
3,5-Dinitrobenzoic acid	1.250	1.630	0.700	0.590	6.984	1.2801	10.842	2.542	This work
4-Aminobenzoic acid	1.075	1.650	0.940	0.600	5.916	1.0315	11.105	1.675	[25]
Diphenyl sulfone	1.570	2.150	0.000	0.700	8.902	1.6051	10.522	3.132	This work
Benzoin	1.585	2.115	0.196	0.841	9.159	1.6804	11.544	2.813	[21]
3,4-Dichlorobenzoic acid	0.950	0.920	0.670	0.260	5.623	1.1766	8.373	3.633	[20]
2,3-Dimethyl-2,3-dinitrobutane	0.430	1.410	0.040	0.590	5.717	1.3624	7.089	2.389	[24]
Benzil	1.445	1.590	0.000	0.620	7.611	1.6374	8.729	3.859	This work
Thioxanthen-9-one	1.940	1.441	0.000	0.557	8.436	1.5357	9.065	3.997	This work
Salicylamide	1.160	1.650	0.630	0.480	5.910	1.0315	9.543	1.858	[16]
Methyl 4-hydroxybenzoate	0.930	1.460	0.710	0.460	5.914	1.1313	9.461	2.221	[25]
Testosterone	1.540	2.560	0.320	1.170	11.690	2.3827	14.949	3.759	[25]
Phosphorous compound 1b	2.080	2.440	0.000	1.860	13.672	2.6903	15.595	2.465	[27]
Phosphorous compound 2c	1.130	1.070	1.210	1.160	6.175	1.2380	11.950	0.380	[27]

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref.
Phosphorous compound 3d	2.020	2.100	0.000	1.170	13.536	2.7354	15.130	6.240	[27]
Phosphorous compound 4e	2.070	2.780	0.000	1.900	14.442	2.7941	16.980	2.880	[27]
Phosphorous compound 5f	2.330	2.180	0.360	1.910	11.644	2.3127	14.890	1.250	[28]
Phosphorous compound 6g	1.040	1.250	0.860	0.860	5.543	1.0384	9.760	0.440	[29]
Phosphorous compound 7h	0.930	1.390	0.750	0.960	6.010	1.1793	10.040	0.460	[29]
Phosphorous compound 8i	0.850	1.180	0.000	0.500	7.236	1.6676	7.950	4.460	[29]
Phosphorous compound 9j	4.290	2.290	0.000	2.200	24.707	4.9122	24.270	10.480	[29]
Phosphorous compound 10k	1.500	1.500	0.870	1.230	8.380	1.6462	12.605	1.565	[26]

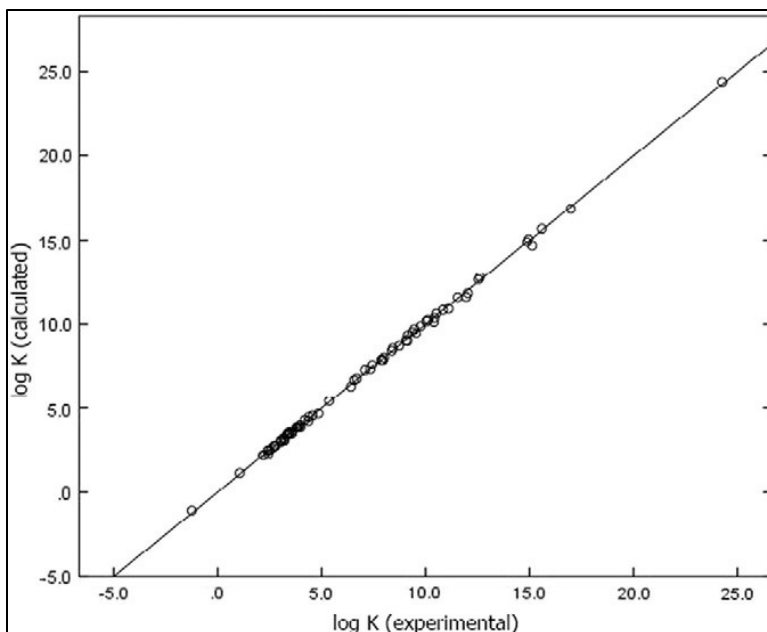


Figure 4.2. Comparison between experimental log K data and calculated values based on Equation (4.2).

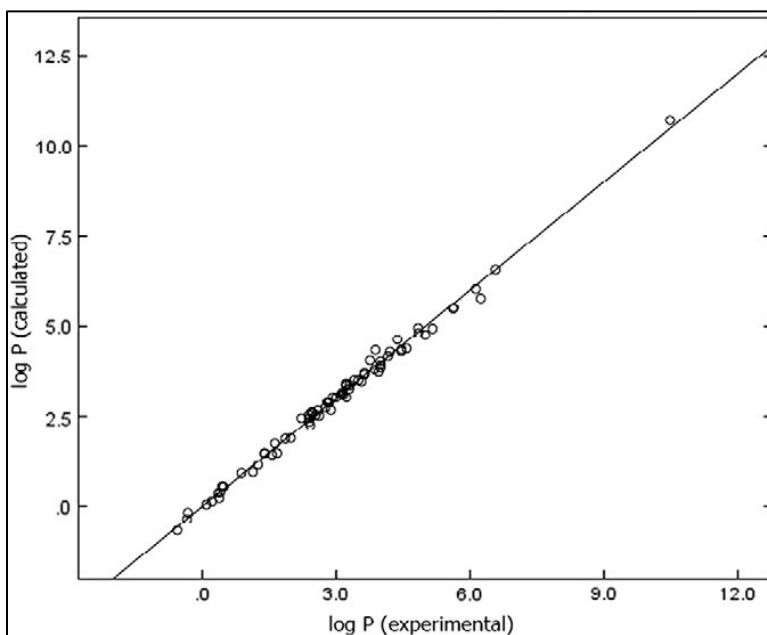


Figure 4.3. Comparison between experimental log P data and calculated values based on Equation (4.1).

The log (P or $C_{S,organic}/C_{S,water}$) and log (K or $C_{S,organic}/C_{S,gas}$) databases for 2-ethoxyethanol contain experimental values for only 76 different solutes. It would be

difficult to obtain a good training set correlation by using only half of the experimental values. To assess the predictive ability of Equations (4.2) and (4.3) the parent data points were divided into three subsets (A, B, and C) as described in detail in Chapter 2.

Three training sets were prepared as combinations of two subsets (A and B), (A and C), and (B and C). For each training set, a correlation was derived:

(Training sets A and B)

$$\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}}) = 0.092(0.057) + 0.316(0.061)\mathbf{E} - 0.363(0.064)\mathbf{S} + 0.157(0.077)\mathbf{A} - 4.277(0.086)\mathbf{B} + 3.964(0.065)\mathbf{V} \quad (4.4)$$

(with N = 51, SD= 0.138, R²=0.995, F = 1931)

$$\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.079(0.041) - 0.229(0.070)\mathbf{E} + 1.462(0.060)\mathbf{S} + 3.722(0.071)\mathbf{A} + 0.628(0.082)\mathbf{B} + 0.842(0.016)\mathbf{L} \quad (4.5)$$

(with N = 51, SD = 0.133, R² = 0.999, F = 11191)

(Training sets A and C)

$$\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}}) = 0.126(0.061) + 0.392(0.063)\mathbf{E} - 0.399(0.070)\mathbf{S} + 0.124(0.089)\mathbf{A} - 4.227(0.099)\mathbf{B} + 3.880(0.071)\mathbf{V} \quad (4.6)$$

(with N = 51, SD = 0.153, R² = 0.993, F = 1331)

$$\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.087(0.038) - 0.317(0.059)\mathbf{E} + 1.508(0.056)\mathbf{S} + 3.644(0.068)\mathbf{A} + 0.599(0.077)\mathbf{B} + 0.851(0.014)\mathbf{L} \quad (4.7)$$

(with N = 51, SD = 0.122, R² = 0.999, F = 13882)

(Training sets B and C)

$$\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}}) = 0.128(0.070) + 0.472(0.063)\mathbf{E} - 0.490(0.080)\mathbf{S} + 0.128(0.085)\mathbf{A} - 4.118(0.085)\mathbf{B} + 3.864(0.077)\mathbf{V} \quad (4.8)$$

(with N = 50, SD = 0.146, R² = 0.992, F = 1147)

$$\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.049(0.042) - 0.219(0.055)\mathbf{E} + 1.430(0.070)\mathbf{S} + 3.669(0.065)\mathbf{A} + 0.693(0.067)\mathbf{B} + 0.836(0.016)\mathbf{L} \quad (4.9)$$

(with N = 50, SD = 0.116, R² = 0.999, F = 10238)

Each validation computation gave a training set correlation equation having coefficients not too different from that obtained from the parent 76 compound database. The training set equations were then used to predict log (*P* or $C_{S,\text{organic}}/C_{S,\text{water}}$) and log (*K* or $C_{S,\text{organic}}/C_{S,\text{gas}}$) values for the compounds in the respective test sets (A, B and C). The standard deviations, average absolute errors (AAEs) and average errors (AEs) for the test set computations are reported in Table 3.9 for Equations (4.4) – (4.9).

Examination of the numerical AE values in the last column of Table 4.4 shows that there is very little bias associated with the derived training set correlations. The training and test set analyses were performed three more times with very similar results. Each time the large 76 compound database was randomized prior to separating the compounds into the smaller A, B, and C datasets.

Table 4.4. Statistic test set results for Abraham model training set Equations (4.4) – (4.9).

Property	Test set	N	SD	AAE	AE
log (<i>P</i> or $C_{S,\text{organic}}/C_{S,\text{water}}$)	A	26	0.171	0.123	-0.013
log (<i>K</i> or $C_{S,\text{organic}}/C_{S,\text{gas}}$)	A	26	0.146	0.106	-0.011
log (<i>P</i> or $C_{S,\text{organic}}/C_{S,\text{water}}$)	B	25	0.136	0.110	0.035
log (<i>K</i> or $C_{S,\text{organic}}/C_{S,\text{gas}}$)	B	25	0.136	0.099	0.041
log (<i>P</i> or $C_{S,\text{organic}}/C_{S,\text{water}}$)	C	25	0.175	0.139	-0.030
log (<i>K</i> or $C_{S,\text{organic}}/C_{S,\text{gas}}$)	C	25	0.114	0.093	-0.031

4.4 Conclusions

It is expected that Abraham model Equations (4.2) and (4.3) will provide reasonably accurate predictions of the water-to-2-ethoxyethanol partition coefficients, gas-to-2-ethoxyethanol partition coefficients, and molar solubilities of additional solutes dissolved in anhydrous 2-ethoxyethanol provided that the solutes stay within the predictive area of chemical space defined by the compounds used in determining Equations (4.2) and (4.3). The numerical values of the solute descriptors for the 76 compounds in the 2-ethoxyethanol database ranged from: **E** = 0.000 to **E** = 4.290; **S** = 0.000 to **S** = 2.780; **A** = 0.000 to **A** = 1.210, **B** = 0.000 to **B** = 2.200; **V** = 0.1086 to **V** = 4.9122 and **L** = -1.200 and **L** = 24.707. As noted previously the 76 compounds were chemically diverse and included several liquid and crystalline nonelectrolyte organic compounds, plus hydrogen gas and 2-methylpropane gas. Experimental-based solute descriptors have been determined for more than 7 000 different organic, organometallic and inorganic compounds, plus several ions and ionic species.

It is possible to compare the regression coefficients of Equation (4.3) for 2-ethoxyethanol with the previously reported coefficients in similar equations for other solvents. 1-Butanol has the same number of carbon atoms and one OH-group as 2-ethoxyethanol, but differs from it by one oxygen atom. As can be seen from Table 4.5, five of the six coefficients of Equation (4.3) are very similar for 1-butanol and 2-ethoxyethanol; the only one that is significantly different is the *s*-coefficient, which corresponds to polar interactions. It is obvious that addition of electronegative oxygen atom increases these polar interactions. On the other hand, 2-ethoxyethanol is a derivative of ethylene glycol, which has a hydroxyl group instead of ethoxy group in its

molecule. The a - and b -coefficients are much larger for ethylene glycol than for 2-ethoxyethanol, which means that the diol engages in much stronger hydrogen-bonding interactions than 2-ethoxyethanol with both solute hydrogen-bond acids and solute hydrogen-bond bases, because of the additional OH-group.

Table 4.5. Regression coefficients of Equation (1.13) for different solvents.

Solvent	c_k	e_k	s_k	a_k	b_k	l_k
2-Ethoxyethanol	-0.064	-0.257	1.452	3.672	0.662	0.843
1-Butanol [30]	-0.004	-0.285	0.768	3.705	0.879	0.800
Ethylene glycol [31]	-0.887	0.132	1.657	4.457	2.355	0.500

The mathematical correlations derived in this study further document the applicability of the Abraham Solvation Parameter Model to describe the solute transfer between two condensed phases and solute transfer to a condensed phase from the vapor phase. The derived $\log K$ and $\log P$ expressions for solutes dissolved in anhydrous 2-ethoxyethanol should provide reasonably accurate solubility ratio and partition coefficient predictions for additional organic solutes that fall in the area of predictive chemical space defined by hydrogen gas and the various organic solutes given in Table 4.3. Solutes used in deriving the two Abraham model correlations cover a wide range of chemical diversity as evidenced by the different functional groups present on the molecules, and the range of numerical values encompassed by the solute descriptors.

4.5 References

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CHAPTER 5

DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR SOLUTE TRANSFER INTO BOTH 2-PROPOXYETHANOL AND 2-ISOPROPOXYETHANOL FROM WATER AND FROM THE GAS PHASE*

5.1 Introduction

Organic solvents represent a significant quantity of the chemicals used in industrial manufacturing processes. Increased chemical and disposal costs, coupled with environmental concerns and governmental regulations controlling the release of hazardous materials into the environment, have prompted the manufacturing sector to find ways to reduce organic solvent consumption. Implementation of solvent-free processes provides one solution to the problem; however, from a practical standpoint it is not feasible to completely eliminate organic solvents from all synthetic methods and chemical separations. Organic solvents provide a critical role in dissolving organic starting materials, in facilitating heat and mass transfer, and serve as mobile phases for chemical separations involving high-performance liquid chromatography. A more viable and practical solution to the problem is to replace expensive solvents derived from petroleum with solvents made from renewable resources, and to replace hazardous solvents with ones that exhibit better environmental, health and safety properties.

Solvent selection includes economical, toxicological and chemical considerations. The authors' [1] contributions in the area of solvent selection have

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focused on chemical considerations and specifically on the solubilizing properties of potential solvent candidates. For organic synthesis the solvent must be able to dissolve the starting material(s) and provide for the convenient isolation of the synthesized product from the reaction solvent media. This can either be accomplished by selecting a solvent in which the product is not soluble or by evaporation of the solvent once the reaction is complete. In the case of purification by extraction one needs to find a two-phase partitioning system (usually water and an organic solvent) where the compounds to be separated have vastly different relative solubilities in the respective immiscible liquid phases. Purification by recrystallization is also based on solubility differences of the compound in the hot versus cold solvent, or in the dissolving solvent versus precipitating anti-solvent. The solubility of a dissolved solute in different solvents is controlled by molecular interactions between the solute and surrounding solvent molecules, as well as by solvent–solvent and solute–solute interactions.

In the past several years, mathematical correlations for describing measured partition coefficient and solubility data for solutes dissolved in both traditional organic solvents and in ionic liquid solvents have reported based on the Abraham Solvation Parameter Model [2–8] that is described in detail in Chapter 1. In the present communication considerations are extended to include 2-propoxyethanol and 2-isopropoxyethanol. Alkoxyalcohols contain both an ether functional group (R-O-R) and a hydroxyl functional group (R-OH). This will allow one to search for possible synergistic effects between adjacent ether and hydroxyl groups once the search for methods to predict the solvent/process coefficients begins.

Infinite dilution activity coefficients (γ^∞) were measured at 298.15 K for a series of organic solutes containing up to nine different aliphatic hydrocarbons (alkanes, cycloalkanes, alkenes), up to nine different aromatic compounds (benzene, alkylbenzenes, halobenzenes), two cyclic ethers (tetrahydrofuran, 1,4-dioxane), chloroalkanes (dichloromethane, 1,2-dichloropropane), acetone, acetonitrile, 2-propanol, and butyl acetate (in 2-isopropoxyethanol only) dissolved in both 2-propoxyethanol and 2-isopropoxyethanol using a gas chromatographic headspace analysis method. Gas-to-liquid partition coefficients, K , were calculated using these results and saturated vapor pressures of solutes taken from the published literature. As part of this study, solubilities were measured at 298.15 K for acetylsalicylic acid, acenaphthene, benzil, benzoic acid, 1-chloroanthraquinone, 4-chloro-3-nitrobenzoic acid, 3,5-dinitrobenzoic acid, 3,5-dinitro-2-methylbenzoic acid, diphenyl sulfone, fluorene, 2-hydroxybenzoic acid, 3-hydroxybenzoic acid, 2-methylbenzoic acid, phenothiazine, trans-stilbene, thioxanthen-9-one, and xanthene dissolved in the two 2-alkoxyethanol solvents as well. Solubilities were also determined for 3-chlorobenzoic acid, 2-ethylanthraquinone and pyrene dissolved in 2-isopropoxyethanol and for 3,4-dimethoxybenzoic acid dissolved in 2-propoxyethanol. The measured gas-to-liquid partition coefficient and solubility data, combined with published solubility data for anthracene [9-10], benzoin [11], pyrene [12], 4-nitrobenzoic acid [13], 2-methoxybenzoic acid [13], 4-methoxybenzoic acid [13], 4-hydroxyacetanilide [13], 4-chlorobenzoic acid [13], 3-methylbenzoic acid [13], 3,4-dimethoxybenzoic acid [14], 3,4-dichlorobenzoic acid [15], biphenyl [13], and salicylamide [13], were used to derive Abraham model $\log(P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}})$ and $\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}})$ correlations for

describing solute transfer into 2-propoxyethanol and 2-isopropoxyethanol both from water and from the gas phase.

5.2 Experimental Methodology

5.2.1 Gas Chromatographic Headspace Measurements

Provided by Dr. Igor Sedov's research group from Kazan Federal University, the 25 compounds listed in Tables 5.1 and 5.2 were dissolved in 2-propoxyethanol and 2-isopropoxyethanol (with methylcyclohexane, 1,7-octadiene, and toluene only being dissolved in 2-propoxyethanol, and 1-octyne and butyl acetate only being dissolved in 2-isopropoxyethanol). Gas chromatograms of all the substances show no peaks with the area exceeding 0.5% of that of the peak corresponding to the main substance.

Table 5.1. Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and the Gibbs energies of solvation in 2-propoxyethanol at 298.15 K^a.

Solute	γ_{∞}	$u(\gamma_{\infty})$	$\log K$	$\Delta G_{\text{solv}}/(\text{kJ/mol})$
Hexane	5.11	0.14	2.323	0.1
Heptane	6.12	0.22	2.761	-2.4
Nonane	8.63	0.25	3.626	-7.4
Cyclohexane	3.85	0.10	2.639	-1.7
Methylcyclohexane	4.55	0.10	2.890	-3.2
1,7-Octadiene	3.48	0.11	3.316	-5.6
1-Heptyne	2.25	0.06	3.138	-4.6
Benzene	1.62	0.04	3.024	-3.9
Fluorobenzene	1.41	0.04	3.173	-4.8
Chlorobenzene	1.61	0.07	3.924	-9.1
Bromobenzene	1.79	0.05	4.336	-11.4
Toluene	2.03	0.10	3.449	-6.4
Ethylbenzene	2.56	0.08	3.820	-8.5

(table continues)

Solute	γ_∞	$u(\gamma_\infty)$	$\log K$	$\Delta G_{\text{solv}}/(\text{kJ/mol})$
o-Xylene	2.52	0.09	3.989	-9.4
m-Xylene	2.71	0.10	3.859	-8.7
p-Xylene	2.58	0.07	3.852	-8.7
Dichloromethane	0.70	0.02	2.727	-2.2
1,2-Dichloropropane	1.46	0.06	3.319	-5.6
Acetone	1.53	0.02	2.660	-1.9
Acetonitrile	2.18	0.03	2.923	-3.4
1,4-Dioxane	1.52	0.04	3.447	-6.3
2-Propanol	1.47	0.03	3.386	-6.0
Tetrahydrofuran	1.03	0.03	2.988	-3.7

^a Standard uncertainty for temperature $u(T) = 0.2$ K.

Table 5.2. Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and Gibbs energies of solvation in 2-isopropoxyethanol at 298.15 K^a.

Solute	γ_∞	$u(\gamma_\infty)$	$\log K$	$\Delta G_{\text{solv}}/(\text{kJ/mol})$
Hexane	5.08	0.11	2.322	0.1
Heptane	6.00	0.32	2.766	-2.5
Octane	6.77	0.20	3.227	-5.1
Nonane	8.72	0.17	3.618	-7.3
Cyclohexane	3.95	0.09	2.624	-1.7
1-Heptyne	2.23	0.07	3.139	-4.6
1-Octyne	2.99	0.08	3.598	-7.2
Benzene	1.60	0.05	3.026	-4.0
Fluorobenzene	1.33	0.05	3.196	-4.9
Chlorobenzene	1.62	0.05	3.919	-9.0
Bromobenzene	1.76	0.10	4.341	-11.5
Ethylbenzene	2.68	0.13	3.797	-8.4
o-Xylene	2.67	0.06	3.960	-9.3
m-Xylene	2.46	0.08	3.898	-8.9
p-Xylene	2.60	0.08	3.846	-8.6
Dichloromethane	0.63	0.02	2.769	-2.5
1,2-Dichloropropane	1.52	0.07	3.299	-5.5

(table continues)

Solute	γ_{∞}	$u(\gamma_{\infty})$	$\log K$	$\Delta G_{\text{solv}}/(\text{kJ/mol})$
Acetone	1.48	0.03	2.672	-1.9
Acetonitrile	2.04	0.05	2.949	-3.5
Butyl acetate	2.70	0.12	3.715	-7.9
1,4-Dioxane	1.26	0.04	3.526	-6.8
2-Propanol	1.19	0.04	3.475	-6.5
Tetrahydrofuran	1.01	0.04	2.993	-3.8

^a Standard uncertainty for temperature $u(T) = 0.2$ K.

In a typical experiment, for each solute–solvent pair six solutions containing different concentrations of a solute in the range 0.1–0.8 volume percent were prepared. At such concentrations, solutions are thought to behave as infinitely diluted ones, which was confirmed by the absence of dependence of the results from concentration. The activity coefficient of a solute at infinite dilution γ_{∞} , as well as the procedure for the gas chromatographic headspace measurements are described in detail in Chapter 1 Section 1.3.1.2.

Gas-to-liquid partition coefficients, K , can be calculated using Equation (2.1) as described in Chapter 2. The values of $p_{\text{solute}}^{\circ}$ were taken from literature [16]. The Gibbs energy of solvation with the standard states defined as a hypothetical ideal solution at unit mole fraction and a gas at 1 bar fugacity is given by $\Delta G_{\text{solv}} = RT \ln(\gamma_{\infty} p_{\text{solute}}^{\circ})$.

Results are presented in Tables 5.1 and 5.2.

5.2.2 Solubility Measurements

The 21 compounds listed in Tables 5.3 and 5.4 were purchased and solubility measurements were performed as described in Chapter 1 Section 1.3.1.1. To ensure that there was no solvate formation, the melting point temperature was determined for

the equilibrated solid phases that were recovered from the saturated solutions after the solubility measurements were performed. For each crystalline solute–solvent combination studied, the melting point temperature of the equilibrated solid phase was within ± 0.5 K of the melting point temperature of the commercial sample or recrystallized solute prior to contact with 2-propoxyethanol and 2-isopropoxyethanol.

The experimental mole fraction solubilities of the crystalline organic solutes dissolved in 2-propoxyethanol and 2-isopropoxyethanol are reported in Tables 5.3 and 5.4, respectively. The numerical values represent the average of four to eight independent experimental measurements. The reproducibility of the replicate measurements was $\pm 1.5\%$ (relative error).

Table 5.3. Experimental mole fraction solubilities, X_S^{exp} , of crystalline nonelectrolyte solutes dissolved in 2-propoxyethanol at 298.15 K^a.

Solute	X_S^{exp}
Xanthene	0.05649
Acenaphthene	0.06082
Fluorene	0.05161
trans-Stilbene	0.02164
Thioxanthen-9-one	0.003447
Phenothiazine	0.07241
Diphenyl sulfone	0.02622
1-Chloroanthraquinone	0.003717
3,5-Dinitrobenzoic acid	0.1058
4-Chloro-3-nitrobenzoic acid	0.07763
2-Methylbenzoic acid	0.1975
3,5-Dinitro-2-methylbenzoic acid	0.08413
3,4-Dimethoxybenzoic acid	0.02158
Benzil	0.06887
2-Hydroxybenzoic acid	0.2734
3-Hydroxybenzoic acid	0.1621
Acetylsalicylic acid	0.1127
Benzoic acid	0.2673

^a Standard uncertainty for temperature $u(T) = 0.05$ K.

Table 5.4. Experimental mole fraction solubilities, X_S^{exp} , of crystalline nonelectrolyte solutes dissolved in 2-isopropoxyethanol at 298.15 K^a.

Solute	X_S^{exp}
Xanthene	0.05285
Acenaphthene	0.05996
Pyrene	0.02919
Fluorene	0.04574
trans-Stilbene	0.01884
Thioxanthen-9-one	0.002827
Phenothiazine	0.07122
Diphenyl sulfone	0.02538
1-Chloroanthraquinone	0.003156
2-Ethylantraquinone	0.01829
3,5-Dinitrobenzoic acid	0.1226
4-Chloro-3-nitrobenzoic acid	0.09291
2-Methylbenzoic acid	0.1798
3-Chlorobenzoic acid	0.1795
3,5-Dinitro-2-methylbenzoic acid	0.0997
Benzil	0.06612
2-Hydroxybenzoic acid	0.2864
3-Hydroxybenzoic acid	0.1600
Acetylsalicylic acid	0.1182
Benzoic acid	0.2765

^a Standard uncertainty for temperature $u(T) = 0.05$ K.

5.3 Results and Discussion

The log K values for the organic liquid solutes were determined from the gas chromatographic headspace measurements and are given in Tables 5.1 and 5.2, along with the respective infinite dilution activity coefficients and Gibbs energies of solvation. Water-to-liquid and gas-to-liquid partition coefficients are interrelated through the thermodynamic relationship shown in Equation (1.18) as described in Chapter 1.

The gas-to-water partition coefficients, $\log K_w$, required for the calculation of $\log P$ are available for all of the liquid solutes considered in the present study.

Headspace chromatographic measurements provide a convenient experimental method for determining $\log K$ values for volatile organic liquid solutes having quantifiable partial pressures at low solute concentrations. Headspace measurements are more difficult in the case of crystalline organic solutes as the vapor pressure is often extremely small. For crystalline solutes one can use the logarithm of the molar solubility ratios as the measured solute property. The mole fraction solubility data in Tables 5.3 and 5.4 were converted to molar solubilities following the procedure as described in Chapter 1 Section 1.3.1. The experimental mole fraction solubility data in Tables 5.3 and 5.4 gave $\log (C_{S,\text{organic}}/C_{S,\text{water}})$ and $\log (C_{S,\text{organic}}/C_{S,\text{gas}})$ values for 18 and 20 solutes dissolved in 2-propoxyethanol and 2-isopropoxyethanol, respectively. The number of experimental data points was increased by including published solubility data from several earlier solubility studies [9-15]. Numerical values of $C_{S,\text{water}}$ and $C_{S,\text{gas}}$ were taken from published papers [11,14-15,17-34] for all of the crystalline solutes considered in the current study.

Our experimental measurements and search of the chemical literature yielded nearly 55 data points for each solvent. This is sufficient chemical diversity and more than enough experimental values in each of the solvent data sets to develop meaningful Abraham model $\log P$ and $\log K$ correlations. Each data set contains several nonpolar alkane solutes, several polycyclic aromatic hydrocarbons (anthracene, $E = 2.290$; pyrene, $E = 2.808$; acenaphthene, $E = 1.604$) and polycyclic aromatic hetero-atom compounds (xanthene, $E = 1.502$; phenothiazine, $E = 1.890$) having large E solute

descriptors, several carboxylic acid solutes possessing strong H-bond donor capability (3,5-dinitrobenzoic acid, **A** = 0.700; acetylsalicylic acid, **A** = 0.710; 2-hydroxybenzoic acid, **A** = 0.730; 3-hydroxybenzoic acid, **A** = 0.860; 3,5-dinitro-2-methylbenzoic acid, **A** = 0.750), and several organic solutes possessing fairly strong H-bond acceptor character (benzoin, **B** = 0.841; 4-hydroxyacetanilide, **B** = 0.860; diphenyl sulfone, **B** = 0.700). As documented in Tables 5.5 and 5.6 the organic solutes considered in the present study cover a fairly large range in the numerical values of their solute descriptors.

Preliminary regression analysis of the experimental $\log(P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}})$ and $\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}})$ values in Table 5.5 revealed that the $a_p \cdot \mathbf{A}$ term in the $\log(P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}})$ made a negligible contribution in the case of 2-propoxyethanol. The calculated numerical of a_p coefficient was small and the standard error in the coefficient was larger than the coefficient itself. The $a_p \cdot \mathbf{A}$ term was removed from the $\log P$ correlation for 2-propoxyethanol, and reanalysis of the experimental data gave the following Abraham model expressions for 2-propoxyethanol:

$$\log(P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}}) = 0.053(0.059) + 0.419(0.049)\mathbf{E} - 0.569(0.062)\mathbf{S} - 4.327(0.098)\mathbf{B} + 4.095(0.070)\mathbf{V} \quad (5.1)$$

(with $N = 54$, $SD = 0.100$, $R^2 = 0.996$, $F = 2810$)

$$\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.091(0.042) - 0.288(0.57)\mathbf{E} + 1.265(0.066)\mathbf{S} + 3.566(0.055)\mathbf{A} + 0.390(0.094)\mathbf{B} + 0.902(0.017)\mathbf{L} \quad (5.2)$$

(with $N = 54$, $SD = 0.094$, $R^2 = 0.999$, $F = 10,096$)

Table 5.5. Experimental $\log (K$ or $C_{S,organic}/C_{S,gas}$) and $\log (P$ or $C_{S,organic}/C_{S,water}$) data for solutes dissolved in 2-propanol at 298.15 K.

Solute	E	S	A	B	L	V	$\log K^a$	$\log P^a$	Ref
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	2.323	4.143	This work
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	2.761	4.721	This work
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	3.626	5.776	This work
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	2.639	3.539	This work
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	2.890	4.140	This work
1,7-Octadiene	0.191	0.200	0.000	0.100	3.415	1.1498	3.316	4.276	This work
1-Heptyne	0.160	0.230	0.090	0.100	3.000	1.0089	3.138	3.578	This work
Dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943	2.727	1.767	This work
1,2-Dichloropropane	0.370	0.630	0.000	0.170	2.836	0.7761	3.319	2.349	This work
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	3.024	2.394	This work
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	3.449	2.799	This work
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	3.820	3.240	This work
o-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	3.989	3.329	This work
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	3.859	3.249	This work
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	3.852	3.262	This work
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	2.988	0.438	This work
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	3.447	-0.263	This work
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	2.660	-0.170	This work
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	2.923	0.073	This work
2-Propanol	0.212	0.360	0.330	0.560	1.764	0.5900	3.386	-0.094	This work
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4544	7.924	4.894	[9]

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref
Pyrene	2.808	1.710	0.000	0.280	8.833	1.5846	9.114	5.614	[12]
Acenaphthene	1.604	1.050	0.000	0.220	6.469	1.2586	6.618	4.258	This work
Fluorene	1.588	1.060	0.000	0.250	6.922	1.3565	7.096	4.646	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	6.424	4.474	[13]
trans-Stilbene	1.450	1.050	0.000	0.340	7.520	1.5630	7.850	5.070	This work
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	3.173	2.583	This work
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	3.924	3.104	This work
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	4.336	3.266	This work
Xanthene	1.502	1.070	0.000	0.230	7.153	1.4152	7.394	4.894	This work
Phenothiazine	1.890	1.560	0.310	0.300	8.389	1.4789	10.291	4.888	This work
Benzoic acid	0.730	0.900	0.590	0.400	4.657	0.9317	7.067	1.927	This work
4-Nitrobenzoic acid	0.990	1.520	0.680	0.400	5.770	1.1059	9.213	2.313	[13]
3,5-Dinitrobenzoic acid	1.250	1.630	0.700	0.590	6.984	1.2801	10.675	2.375	This work
2-Methoxybenzoic acid	0.899	1.410	0.450	0.620	5.636	1.1313	8.304	1.504	[13]
4-Methoxybenzoic acid	0.899	1.250	0.620	0.520	5.741	1.1313	8.961	2.261	[13]
3,4-Dimethoxybenzoic acid	0.950	1.646	0.570	0.755	6.746	1.3309	10.213	1.766	This work
4-Hydroxyacetanilide	1.060	1.630	1.040	0.860	6.430	1.1724	11.778	0.878	[13]
4-Chlorobenzoic acid	0.840	1.020	0.630	0.270	4.947	1.0541	7.790	2.990	[13]
3,5-Dinitro-2-methylbenzoic acid	1.310	2.120	0.750	0.650	8.040	1.4210	12.410	2.454	This work
2-Methylbenzoic acid	0.730	0.840	0.420	0.440	4.677	1.0726	6.590	2.290	This work
3-Methylbenzoic acid	0.730	0.890	0.600	0.400	4.819	1.0726	7.378	2.398	[13]
4-Chloro-3-nitrobenzoic acid	1.250	1.470	0.700	0.440	6.685	1.2283	10.035	2.826	This work
2-Hydroxybenzoic acid	0.900	0.850	0.730	0.370	4.732	0.9904	7.668	2.308	This work
3-Hydroxybenzoic acid	0.910	0.880	0.860	0.580	4.860	0.9904	8.423	1.423	This work

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref
Acetylsalicylic acid	0.781	1.690	0.710	0.670	6.279	1.2879	10.160	1.630	This work
3,4-Dichlorobenzoic acid	0.950	0.920	0.670	0.260	5.623	1.1766	8.327	3.587	[15]
Diphenyl sulfone	1.570	2.150	0.000	0.700	8.902	1.6051	10.384	2.994	This work
Benzoin	1.585	2.115	0.196	0.841	9.159	1.6804	11.382	2.651	[11]
Benzil	1.445	1.590	0.000	0.620	7.611	1.6374	8.680	3.810	This work
Thioxanthen-9-one	1.940	1.441	0.000	0.557	8.436	1.5357	9.084	4.016	This work
Salicylamide	1.160	1.650	0.630	0.480	5.910	1.0315	9.409	1.724	[13]
2-Propoxyethanol	0.212	0.500	0.300	0.830	3.310	0.9305	4.815	0.115	Unity ^b
1-Chloroanthraquinone	1.900	1.790	0.000	0.570	9.171	1.6512	10.083	4.049	This work

^a For solid solutes the tabulated values represent molar solubility ratios. ^b Activity coefficient is unity.

Regression analysis of the experimental $\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}})$ and $\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}})$ values in Table 5.6 gave the following Abraham model expressions for For 2-isopropoxyethanol:

$$\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}}) = 0.107(0.065) + 0.391(0.056)\mathbf{E} - 0.525(0.082)\mathbf{S} + 0.071(0.063)\mathbf{A} - 4.439(0.131)\mathbf{B} + 4.051(0.073)\mathbf{V} \quad (5.3)$$

(with $N = 55$, $SD = 0.113$, $R^2 = 0.994$, $F = 1676$)

$$\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.045(0.043) - 0.264(0.057)\mathbf{E} + 1.296(0.075)\mathbf{S} + 3.646(0.054)\mathbf{A} + 0.352(0.115)\mathbf{B} + 0.880(0.017)\mathbf{L} \quad (5.4)$$

(with $N = 55$, $SD = 0.099$, $R^2 = 0.999$, $F = 9143$)

where N represents the number of experimental data points used in the regression analysis, SD refers to the standard deviation of the correlation, R^2 corresponds to the squared correlation coefficient, and F denotes the Fisher F -statistic. The standard error in the calculated process coefficients is given in parentheses after the respective coefficient.

Table 5.6. Experimental $\log (K$ or $C_{S,organic}/C_{S,gas}$) and $\log (P$ or $C_{S,organic}/C_{S,water}$) data for solutes dissolved in 2-isopropoxyethanol at 298.15 K.

Solute	E	S	A	B	L	V	$\log K^a$	$\log P^a$	Ref
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	2.322	4.142	This work
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	2.766	4.726	This work
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	3.227	5.337	This work
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	3.618	5.768	This work
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	2.624	3.524	This work
1-Heptyne	0.160	0.230	0.090	0.100	3.000	1.0089	3.139	3.579	This work
1-Octyne	0.155	0.220	0.090	0.100	3.521	1.1498	3.598	4.118	This work
Dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943	2.769	1.809	This work
1,2-Dichloropropane	0.370	0.630	0.000	0.170	2.836	0.7761	3.299	2.329	This work
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	3.026	2.396	This work
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	3.797	3.217	This work
o-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	3.960	3.300	This work
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	3.898	3.288	This work
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	3.846	3.256	This work
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	2.993	0.443	This work
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	3.526	-0.184	This work
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	2.672	-0.158	This work
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	2.949	0.099	This work
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	3.715	1.775	This work
2-Propanol	0.212	0.360	0.330	0.560	1.764	0.5900	3.475	-0.005	This work
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4544	7.885	4.855	[10]

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref
Pyrene	2.808	1.710	0.000	0.280	8.833	1.5846	9.045	5.545	This work
Acenaphthene	1.604	1.050	0.000	0.220	6.469	1.2586	6.608	4.248	This work
Fluorene	1.588	1.060	0.000	0.250	6.922	1.3565	7.040	4.590	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	6.403	4.453	[13]
trans-Stilbene	1.450	1.050	0.000	0.340	7.520	1.5630	7.785	5.005	This work
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	3.196	2.606	This work
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	3.919	3.099	This work
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	4.341	3.271	This work
Xanthene	1.502	1.070	0.000	0.230	7.153	1.4152	7.361	4.861	This work
Phenothiazine	1.890	1.560	0.310	0.300	8.389	1.4789	10.280	4.877	This work
Benzoic acid	0.730	0.900	0.590	0.400	4.657	0.9317	7.079	1.939	This work
4-Nitrobenzoic acid	0.990	1.520	0.680	0.400	5.770	1.1059	9.264	2.364	[13]
3,5-Dinitrobenzoic acid	1.250	1.630	0.700	0.590	6.984	1.2801	10.734	2.434	This work
2-Methoxybenzoic acid	0.899	1.410	0.450	0.620	5.636	1.1313	8.209	1.409	[13]
4-Methoxybenzoic acid	0.899	1.250	0.620	0.520	5.741	1.1313	8.991	2.291	[13]
3,4-Dimethoxybenzoic acid	0.950	1.646	0.570	0.755	6.746	1.3309	10.066	1.796	[14]
4-Hydroxyacetanilide	1.060	1.630	1.040	0.860	6.430	1.1724	11.810	0.910	[13]
3-Chlorobenzoic acid	0.840	0.950	0.630	0.320	5.197	1.0541	7.988	2.838	This work
4-Chlorobenzoic acid	0.840	1.020	0.630	0.270	4.947	1.0541	7.844	3.044	[13]
3,5-Dinitro-2-methylbenzoic acid	1.310	2.120	0.750	0.650	8.040	1.4210	12.478	2.522	This work
2-Methylbenzoic acid	0.730	0.840	0.420	0.440	4.677	1.0726	6.556	2.246	This work
3-Methylbenzoic acid	0.730	0.890	0.600	0.400	4.819	1.0726	7.408	2.428	[13]
4-Chloro-3-nitrobenzoic acid	1.250	1.470	0.700	0.440	6.685	1.2283	10.108	2.898	This work
2-Hydroxybenzoic acid	0.900	0.850	0.730	0.370	4.732	0.9904	7.686	2.326	This work

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref
3-Hydroxybenzoic acid	0.910	0.880	0.860	0.580	4.860	0.9904	8.413	1.413	This work
Acetylsalicylic acid	0.781	1.690	0.710	0.670	6.279	1.2879	10.176	1.676	This work
3,4-Dichlorobenzoic acid	0.950	0.920	0.670	0.260	5.623	1.1766	8.336	3.596	[15]
Diphenyl sulfone	1.570	2.150	0.000	0.700	8.902	1.6051	10.365	2.975	This work
Benzoin	1.585	2.115	0.196	0.841	9.159	1.6804	11.346	2.615	[11]
Benzil	1.445	1.590	0.000	0.620	7.611	1.6374	8.659	3.789	This work
Thioxanthen-9-one	1.940	1.441	0.000	0.557	8.436	1.5357	8.994	3.926	This work
Salicylamide	1.160	1.650	0.630	0.480	5.910	1.0315	9.383	1.698	[13]
1-Chloroanthraquinone	1.900	1.790	0.000	0.570	9.171	1.6512	10.007	3.973	This work
2-Ethylanthraquinone	1.410	1.540	0.000	0.550	8.876	1.8106	9.536	4.722	This work

^a For solid solutes the tabulated values represent molar solubility ratios.

The derived Abraham model correlations provide a reasonably accurate mathematical description of the observed solubility ratios and partition coefficient data. The standard deviations were $SD = 0.094$ log units and $SD = 0.099$ log units for the log K correlations for 2-propoxyethanol and 2-isopropoxyethanol, respectively. Slightly larger standard deviations of $SD = 0.100$ log units (2-propoxyethanol) and $SD = 0.113$ log units (2-isopropoxyethanol) were calculated for the two log P correlations. Figures 5.1 - 5.4 depict a graphical comparison of the observed experimental solubility ratios and partition coefficients and back-calculated values based on Equations (5.1) - (5.4). There is not sufficient experimental data to perform training set and test set analyses. In the past we have performed many such analyses on other organic solvents that had larger log P and log K datasets. Our past experience has been that the analyses, when they could be performed, gave very similar standard deviations to the parent data sets.

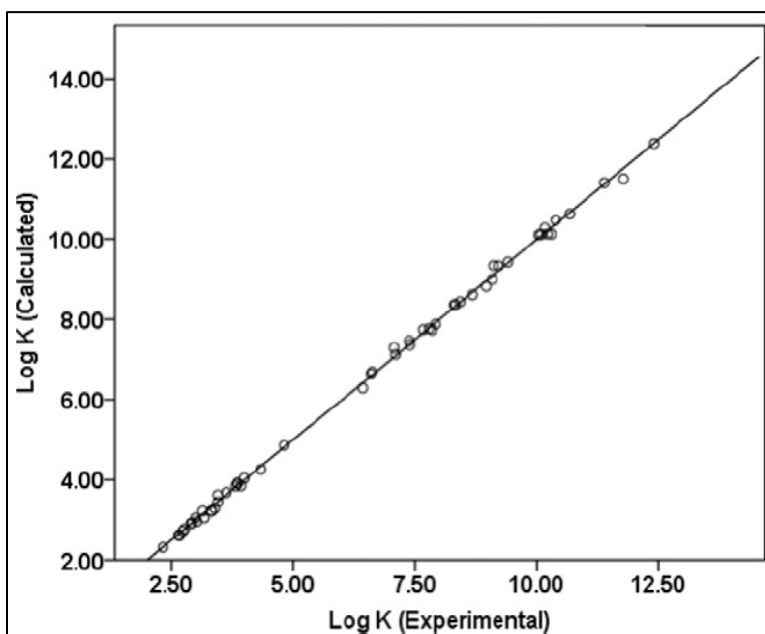


Figure 5.1. Comparison of experimental log K data versus back-calculated values based on Equation (5.2) for solutes dissolved in 2-propoxyethanol.

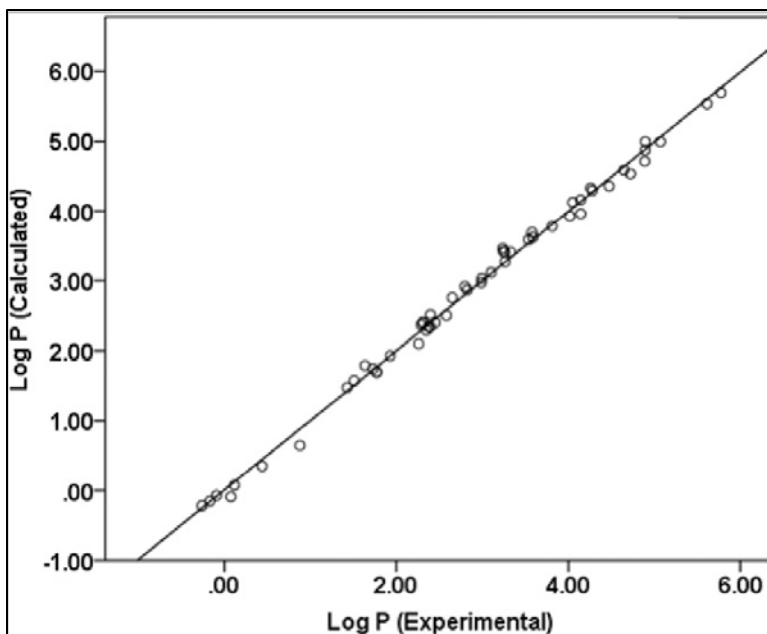


Figure 5.2. Comparison of experimental log P data versus back-calculated values based on Equation (5.1) for solutes dissolved in 2-propoxyethanol.

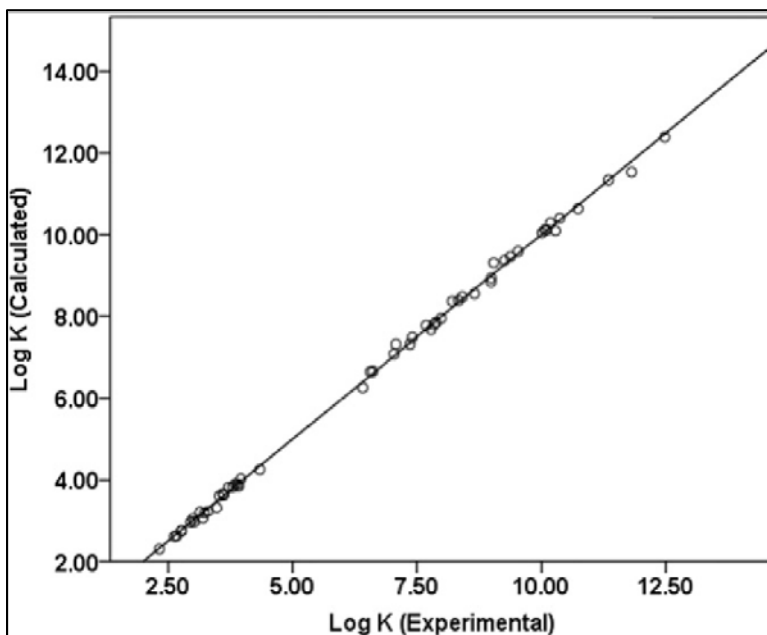


Figure 5.3. Comparison of experimental log K data versus back-calculated values based on Equation (5.4) for solutes dissolved in 2-isopropoxyethanol.

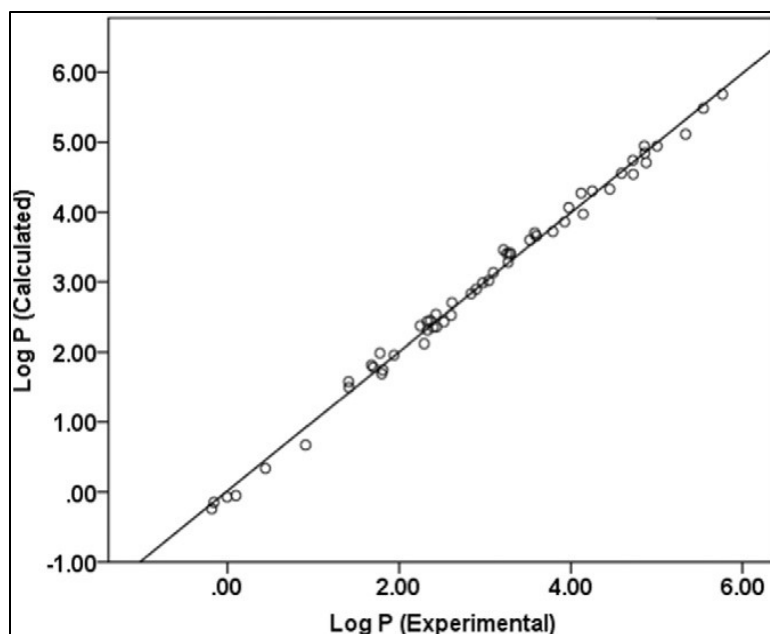


Figure 5.4. Comparison of experimental log P data versus back-calculated values based on Equation (5.3) for solutes dissolved in 2-isopropoxyethanol.

Process coefficients are reasonable and in line with expectations based on earlier studies involving 2-methoxyethanol [35], 2-ethoxyethanol [36] and 2-butoxyethanol [37]. For example, the estimated process coefficients for 2-propoxyethanol [37] as the arithmetic average of the coefficients for the 2-ethoxyethanol and 2-butoxyethanol correlations. The predicted correlations for 2-propoxyethanol are given by Equations (5.5) and (5.6). The derived log P correlation for 2-propoxyethanol (see Equation (5.3) above) is nearly identical to what was predicted earlier, and in the case of the log K , five of the six predicted process coefficients fall within the confidence interval of the coefficients given in Equation (5.4). Only the predicted b_k -coefficient falls slightly outside of the confidence interval.

$$\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}}) = 0.039 + 0.385\mathbf{E} - 0.513\mathbf{S} + 0.022\mathbf{A} - 4.285\mathbf{B} + 4.061\mathbf{V} \quad (5.5)$$

$$\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.087 - 0.281\mathbf{E} + 1.289\mathbf{S} + 3.540\mathbf{A} + 0.661\mathbf{B} + 0.878\mathbf{L} \quad (5.6)$$

5.4 Conclusions

Mathematical expressions have been derived for predicting the solubility and partitioning behavior of neutral, nonelectrolyte solutions into both 2-propoxyethanol and 2-isopropoxyethanol at 298.15 K based on the Abraham Solvation Parameter Model. The derived mathematical expressions are expected to predict the solute transfer properties to alkoxyethanol solvents ($\log P$, $\log K$, $\log (C_{S,\text{organic}}/C_{S,\text{water}})$, and $\log (C_{S,\text{organic}}/C_{S,\text{gas}})$) for additional solutes to within 0.12 log units, provided that the solute descriptors fall within the following range of numerical values: from $\mathbf{E} = 0.000$ to $\mathbf{E} = 2.808$; from $\mathbf{S} = 0.000$ to $\mathbf{S} = 2.150$; from $\mathbf{A} = 0.000$ to $\mathbf{A} = 1.040$; from $\mathbf{B} = 0.000$ to $\mathbf{B} = 0.860$; from $\mathbf{V} = 0.4042$ to $\mathbf{V} = 1.6804$; and from $\mathbf{L} = 1.696$ to $\mathbf{L} = 9.171$.

This study has shown that two solvents, 2-propoxyethanol and 2-isopropoxyethanol, have very similar solvation properties. The confidence intervals for the respective coefficients of Equations (5.1) and (5.3) or (5.2) and (5.4) overlap. The root mean square (RMS) is between the values of $\log K$ in the two solvents for 50 studied solutes is 0.046, the largest deviation by absolute value is 0.147 $\log K$ units for 3,4-dimethoxybenzoic acid and the second largest is 0.095 for 2-methoxybenzoic acid.

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CHAPTER 6

DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR SOLUTE TRANSFER INTO 2-BUTOXYETHANOL FROM WATER AND FROM THE GAS PHASE*

6.1 Introduction

Organic solvents and ionic liquids are used extensively in analytical chemistry for two-phase extractions and chemical separations based on both gas–liquid chromatography (GLC) and high-performance liquid chromatography (HPLC). Solvent selection is determined largely by the solvent's physical and chemical properties, and by the molecular interactions between the solvent and analyte molecule(s) present in the sample being analyzed. Differences in solvent–analyte interactions govern analyte transfer between the various phases present, and play an important role in determining solubilities, chemical selectivities and recovery factors. For liquid–liquid extractions the organic solvent and/or ionic liquid must be partly miscible with the sample solvent media in order to establish a two-phase partitioning system. In the past, the trial-and-error methods used were time consuming and costly. Now, mathematical approaches based on empirical solution models, linear free energy relationships (LFERs), and quantitative structure–property relationships (QSPRs), have facilitated solvent selection in the modern chemical separation methods.

The authors' [1] contributions in the area of solvent selection have been to characterize numerous organic solvents and ionic liquids in terms of their solubilizing abilities using both measured partition coefficient and solubility data. The model that we

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have been using in our studies has been the Abraham Solvation Parameter Model [2-8], which allows one to describe solute transfer between two condensed phases (a biphasic aqueous-organic or organic–organic system) or solute transfer to a condensed phase from the vapor phase.

In the present communication, considerations are extended to include 2-butoxyethanol, which contains both an ether (R-O-R) and a hydroxyl (R-OH) functional group. This is the fifth alkoxyalcohol that these authors [1] have studied. 2-Methoxyethanol [9], 2-ethoxyethanol [10], 2-propoxyethanol [11] and 2-isopropoxyethanol [11] were studied previously. 2-Butoxyethanol is an industrial solvent widely used to dissolve cleaning products, enamels, paints and surface coatings. It has weak surfactant properties, moderate polarity and the ability to be both a hydrogen-bond donor, as well as a hydrogen-bond acceptor. Both polar and nonpolar organic substances are well-soluble in it.

Infinite dilution activity coefficients (γ_∞) were measured at 298.15 K for 12 different aliphatic hydrocarbons (alkanes, cycloalkanes, alkenes), 11 different aromatic compounds (benzene, alkylbenzenes, halobenzenes, naphthalene), and 2-chloro-2-methylpropane dissolved in 2-butoxyethanol using a gas chromatographic headspace analysis method, and gas-to-liquid partition coefficients, K , were calculated using these results and saturated vapor pressures of solutes taken from literature. As part of this study, solubilities were also measured for 2-hydroxybenzoic acid, acetylsalicylic acid, 3,5-dinitro-2-methylbenzoic acid, acenaphthene, fluoranthene, trans-stilbene, xanthene, phenothiazine, 3,5-dinitrobenzoic acid, 3-chlorobenzoic acid, 2-methylbenzoic acid, 4-chloro-3-nitrobenzoic acid, 2-chloro-5-nitrobenzoic acid, benzoic acid, 4-aminobenzoic

acid, benzil, thioxanthen-9-one, 3-nitrobenzoic acid, and diphenyl sulfone dissolved in 2-butoxyethanol at 298.15 K. The measured partition coefficients and solubilities, combined with published gas solubility data for carbon dioxide [12] and hydrogen gas [13], and our previously reported solubility data for anthracene [14], pyrene [15], benzoin [16], 3,4-dichlorobenzoic acid [17], 3,4-dimethoxybenzoic acid [18], 3-methylbenzoic acid [19], salicylamide [19], 4-nitrobenzoic acid [19], 2-methoxybenzoic acid [19], 4-methoxybenzoic acid [19], 4-chlorobenzoic acid [19], biphenyl [19] and 4-hydroxyacetanilide [19] dissolved in 2-butoxyethanol, were used to derive Abraham model correlations for both water-to-2-butoxyethanol partition coefficients ($\log P$) and gas-to-2-butoxyethanol partition coefficients ($\log K$).

6.2 Experimental Methodology

6.2.1 Gas Chromatographic Headspace Measurements

Provided by Dr. Igor Sedov's research group from Kazan Federal University, measurements of activity coefficients at infinite dilution for a set of low-polar volatile organic substances were made using headspace analysis technique as discussed in Chapter 1 Section 1.3.1.2 for the 25 compounds listed in Table 6.1, which were dissolved in 2-butoxyethanol.

Since the considered solutes form no dimers or other associates and the activity coefficient, γ , is found to be virtually independent of mole fraction solubility, x , it is concluded that at such concentrations $\gamma = \gamma^\infty$, where γ^∞ is the limiting activity coefficient. The values of p_{solute}° were taken from literature [20]. Gas-to-liquid partition coefficients, K , can be calculated using Equation (2.1) as described in Chapter 2. The Gibbs energy

of solvation with the standard states defined as a hypothetical ideal solution at unit mole fraction and a gas at 1 bar fugacity is given by $\Delta G_{\text{solv}} = RT \ln(\gamma_{\infty} p_{\text{solute}}^{\circ})$. The measured infinite dilution activity coefficients, average values of $\log K$ and ΔG_{solv} , are presented in Table 6.1 for 12 different aliphatic hydrocarbons, 11 different aromatic compounds, and 2-chloro-2-methylpropane, along with the standard uncertainty in the measured infinite dilution activity coefficient, $u(\gamma_{\infty})$.

Table 6.1. Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and Gibbs free energies of solvation in 2-butoxyethanol at 298.15 K^a.

Solute	γ_{∞}	$u(\gamma_{\infty})$	$\log K$	$\Delta G_{\text{solv}}/(\text{kJ/mol})$
Hexane	4.41	0.20	2.33	-0.3
Heptane	4.55	0.12	2.83	-3.2
Octane	5.34	0.15	3.27	-5.7
Nonane	6.14	1.00	3.71	-8.2
Decane	7.78	0.30	4.10	-10.4
Undecane	10.41	1.40	4.52	-12.8
Cyclohexane	2.95	0.13	2.69	-2.4
Methylcyclopentane	2.95	0.12	2.54	-1.5
Methylcyclohexane	3.54	0.09	2.94	-3.8
Cyclooctane	4.24	0.40	3.78	-8.6
Cyclohexene	2.32	0.08	2.84	-3.2
1,7-Octadiene	2.30	0.10	3.44	-6.6
Benzene	1.50	0.05	3.00	-4.1
Toluene	1.81	0.05	3.44	-6.6
Fluorobenzene	1.29	0.05	3.15	-5.0
Chlorobenzene	1.46	0.10	3.91	-9.3
Bromobenzene	1.89	0.20	4.25	-11.3
o-Dichlorobenzene	1.90	0.20	4.74	-14.0
m-Xylene	2.20	0.10	3.89	-9.2
p-Xylene	3.37	0.20	3.68	-8.0
Ethylbenzene	2.17	0.20	3.83	-8.9
p-Cymene	2.24	0.15	4.64	-13.5
Naphthalene	6.49	0.70	5.41	-17.9
<i>tert</i> -Butyl chloride	1.76	0.05	2.42	-0.8

^a Standard uncertainty for temperature $u(T) = 0.2$ K.

6.2.2 Solubility Measurements

Reported in Table 6.2 are the mole fraction solubilities of the 19 crystalline nonelectrolyte solutes dissolved in 2-butoxyethanol that were measured as part of the present study. The numerical values tabulated in Table 6.2 represent the average of between four and eight independent experimental measurements. The reproducibility of the measured values was $\pm 1.5\%$ (relative error). The solubility measurements were performed as described in Chapter 1 Section 1.3.1.1. To ensure that there was no solvate formation, the melting point temperature was determined for the equilibrated solid phases that were recovered from the saturated solutions after the solubility measurements were performed. For each crystalline solute–solvent combination studied, the melting point temperature of the equilibrated solid phase was within ± 0.5 K of the melting point temperature of the commercial sample or recrystallized solute prior to contact with 2-butoxyethanol.

Table 6.2. Experimental mole fraction solubilities, X_S^{exp} , of crystalline nonelectrolyte solutes dissolved in 2-butoxyethanol at 298.15 K.

Solute	X_S^{exp}
Xanthene	0.05288
Acenaphthene	0.06484
Fluoranthene	0.04991
trans-Stilbene	0.01862
Thioxanthen-9-one	0.004036
Phenothiazine	0.05625
Diphenyl sulfone	0.03016
3,5-Dinitrobenzoic acid	0.08966
4-Chloro-3-nitrobenzoic acid	0.06793
2-Chloro-5-nitrobenzoic acid	0.1562

(table continues)

Solute	x_s^{exp}
2-Methylbenzoic acid	0.1959
3-Chlorobenzoic acid	0.1411
3,5-Dinitro-2-methylbenzoic acid	0.07014
Benzil	0.06671
2-Hydroxybenzoic acid	0.2430
Acetylsalicylic acid	0.09255
3-Nitrobenzoic acid	0.2081
4-Aminobenzoic acid	0.04336
Benzoic acid	0.2582

6.3 Results and Discussion

The published mole fraction solubility data [17-19] and mole fraction solubility data in Table 6.2 are converted to molar solubilities as described in Chapter 1 using Equation (1.21). The molar solubility ratios of $(C_{S,\text{organic}}/C_{S,\text{water}})$ and $(C_{S,\text{organic}}/C_{S,\text{gas}})$ are obtained by dividing the solute's molar solubility in 2-butoxyethanol by the solute's molar solubility in water, $C_{S,\text{water}}$, and by the solute's gas phase molar concentration, $C_{S,\text{gas}}$. Numerical values of $C_{S,\text{water}}$ and $C_{S,\text{gas}}$ are available in earlier publications [16-18,21-34] for all of the crystalline solutes considered in the current study. The measured $\log K$ data given in Table 6.1 are converted $\log P$ values using Equation (1.18) as described in Chapter 1. The calculation of $\log P$ requires knowledge of the solute's gas phase partition coefficient into water, K_w , which is available for all of the liquid organic compounds considered in the present communication. After performing the indicated conversions, there are 59 experimental $\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}})$ and 59 experimental $\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}})$ values to use in developing Abraham model correlations for describing solute transfer into 2-butoxyethanol. The 59 experimental $\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}})$

$C_{S,organic}/C_{S,gas}$) and $\log (P \text{ or } C_{S,organic}/C_{S,water})$ values are tabulated in the eighth and ninth columns of Table 6.3, respectively. Also given in Table 6.3 are the molecular solute descriptors for the 59 solutes that will be used in deriving the Abraham model correlations. The descriptors are of experimental origin and were obtained from measured water-to-organic solvent partitions, gas-to-organic solvent partitions, molar solubility ratios and chromatographic retention factor data as described in several earlier publications [2, 4, 7, 21-28].

The experimental $\log (K \text{ or } C_{S,organic}/C_{S,gas})$ values in the eighth column of Table 6.3 give a set of 59 Abraham model equations containing six process coefficients ($\alpha_k, e_k, s_k, a_k, b_k$ and l_k), and the experimental $\log (P \text{ or } C_{S,organic}/C_{S,water})$ values in the ninth column of Table 6.3 give a second set of 59 Abraham model equations containing six process coefficients ($c_p, e_p, s_p, a_p, b_p, v_p$). Each set of 59 equations was solved simultaneously for the optimal set of processes coefficients that best describes the respective experimental $\log (K \text{ or } C_{S,organic}/C_{S,gas})$ and $\log (P \text{ or } C_{S,organic}/C_{S,water})$ data.

Table 6.2. Experimental $\log (K$ or $C_{S,organic}/C_{S,gas}$) and $\log (P$ or $C_{S,organic}/C_{S,water}$) data for solutes dissolved in 2-butoxyethanol at 298.15 K.

Solute	E	S	A	B	L	V	$\log K^a$	$\log P^a$	Ref.
Hydrogen	0.000	0.000	0.000	0.000	-1.200	0.1086	-1.227	0.493	[13]
Carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.2809	0.191	0.271	[12]
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	2.330	4.150	This work
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	2.830	4.790	This work
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	3.270	5.380	This work
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	3.710	5.860	This work
Decane	0.000	0.000	0.000	0.000	4.686	1.5180	4.100	6.420	This work
Undecane	0.000	0.000	0.000	0.000	5.191	1.6590	4.520	6.900	This work
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	2.690	3.590	This work
Methylcyclopentane	0.225	0.100	0.000	0.000	2.907	0.8454	2.540	3.710	This work
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	2.940	4.150	This work
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	3.780	4.410	This work
Cyclohexene	0.395	0.200	0.000	0.070	3.021	0.8024	2.840	3.110	This work
1,7-Octadiene	0.191	0.200	0.000	0.100	3.415	1.1498	3.440	4.400	This work
2-Chloro-2-methylpropane	0.142	0.300	0.000	0.030	2.273	0.7946	2.420	3.220	This work
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	3.000	2.370	This work
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	3.440	2.790	This work
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	3.830	3.250	This work
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	3.890	3.280	This work
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	3.680	3.090	This work

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref.
4-Isopropyltoluene	0.607	0.490	0.000	0.190	4.590	1.2800	4.640	4.140	This work
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	5.410	3.680	This work
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4544	7.918	4.888	[14]
Pyrene	2.808	1.710	0.000	0.280	8.833	1.5846	9.104	5.604	[15]
Acenaphthene	1.604	1.050	0.000	0.220	6.469	1.2586	6.590	4.230	This work
Fluoranthene	2.377	1.550	0.000	0.240	8.827	1.5850	8.943	5.493	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	6.341	4.391	[19]
trans-Stilbene	1.450	1.050	0.000	0.340	7.520	1.5630	7.727	4.947	This work
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	3.150	2.560	This work
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	3.910	3.090	This work
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	4.518	0.9612	4.740	3.840	This work
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	4.250	3.180	This work
Xanthene	1.502	1.070	0.000	0.230	7.153	1.4152	7.310	4.810	This work
Phenothiazine	1.890	1.560	0.310	0.300	8.389	1.4789	10.128	4.725	This work
Benzoic acid	0.730	0.900	0.590	0.400	4.657	0.9317	7.006	1.866	This work
3-Nitrobenzoic acid	0.990	1.180	0.730	0.520	5.601	1.1059	8.818	1.888	This work
4-Nitrobenzoic acid	0.990	1.520	0.680	0.400	5.770	1.1059	9.160	2.260	[19]
3,5-Dinitrobenzoic acid	1.250	1.630	0.700	0.590	6.984	1.2801	10.550	2.250	This work
2-Methoxybenzoic acid	0.899	1.410	0.450	0.620	5.636	1.1313	8.351	1.551	[19]
4-Methoxybenzoic acid	0.899	1.250	0.620	0.520	5.741	1.1313	8.965	2.265	[19]
3,4-Dimethoxybenzoic acid	0.950	1.646	0.570	0.755	6.746	1.3309	9.993	1.546	[18]
4-Aminobenzoic acid	1.075	1.650	0.940	0.600	5.916	1.0315	10.320	0.890	This work
4-Hydroxyacetanilide	1.060	1.630	1.040	0.860	6.430	1.1724	11.603	0.703	[19]
3-Chlorobenzoic acid	0.840	0.950	0.630	0.320	5.197	1.0541	7.836	2.686	This work

(table continues)

Solute	E	S	A	B	L	V	log K^a	log P^a	Ref.
4-Chlorobenzoic acid	0.840	1.020	0.630	0.270	4.947	1.0541	7.717	2.917	[19]
3,5-Dinitro-2-methylbenzoic acid	1.310	2.120	0.750	0.650	8.040	1.4210	12.278	2.322	This work
2-Methylbenzoic acid	0.730	0.840	0.420	0.440	4.677	1.0726	6.538	2.238	This work
3-Methylbenzoic acid	0.730	0.890	0.600	0.400	4.819	1.0726	7.342	2.362	[19]
4-Chloro-3-nitrobenzoic acid	1.250	1.470	0.700	0.440	6.685	1.2283	9.922	2.712	This work
2-Chloro-5-nitrobenzoic acid	1.250	1.400	0.670	0.460	6.513	1.2283	9.612	2.662	This work
2-Hydroxybenzoic acid	0.900	0.850	0.730	0.370	4.732	0.9904	7.556	2.206	This work
Acetylsalicylic acid	0.781	1.690	0.710	0.670	6.279	1.2879	10.023	1.523	This work
3,4-Dichlorobenzoic acid	0.950	0.920	0.670	0.260	5.623	1.1766	8.201	3.461	[17]
Diphenylsulfone	1.570	2.150	0.000	0.700	8.902	1.6051	10.386	2.996	This work
Benzoin	1.585	2.115	0.196	0.841	9.159	1.6804	11.310	2.579	[16]
Benzil	1.445	1.590	0.000	0.620	7.611	1.6374	8.613	3.743	This work
Thioxanthen-9-one	1.940	1.441	0.000	0.557	8.436	1.5357	9.093	4.025	This work
Salicylamide	1.160	1.650	0.630	0.480	5.910	1.0315	9.266	1.581	[19]
2-Butoxyethanol	0.201	0.530	0.260	0.830	3.656	1.0714	5.215	0.625	Unity

^a For solid solutes the tabulated values represent molar solubility ratios, except for naphthalene.

Regression analysis of the experimental data in Table 6.3 yielded the following two mathematical expressions as can be seen in Equations (6.1) and (6.2):

$$\log (P \text{ or } C_{S,\text{organic}}/C_{S,\text{water}}) = -0.055(0.075) + 0.377(0.069)\mathbf{E} - 0.607(0.104)\mathbf{S} - 0.080(0.087)\mathbf{A} - 4.371(0.166)\mathbf{B} + 4.234(0.077)\mathbf{V} \quad (6.1)$$

(with N = 59, SD = 0.134, R² = 0.992, F = 1278)

$$\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.109(0.043) - 0.304(0.057)\mathbf{E} + 1.126(0.081)\mathbf{S} + 3.407(0.065)\mathbf{A} + 0.660(0.126)\mathbf{B} + 0.914(0.015)\mathbf{L} \quad (6.2)$$

(with N = 59, SD = 0.103, R² = 0.999, F = 9908)

where the standard error in each calculated process coefficients is given in parenthesis immediately following the respective coefficient. The statistical information pertaining to each derived correlation is given below the respective equation and includes the number of experimental data points used in the regression analysis (N), the standard deviation (SD), the squared correlation coefficient (R²) and the Fisher F-statistic (F).

The Abraham model Equations (6.1) and (6.2) provide a reasonably accurate mathematical description of the solubility and partitioning behavior of organic solutes into 2-butoxyethanol as documented by the relatively small standard deviations of 0.134 and 0.103 log units, respectively. Figures 6.1 and 6.2 graphically compare the experimental data to the back-calculated values based on Equations (6.2) and (6.1). In the case of the log (K or C_{S,organic}/C_{S,gas}) comparison of the experimental values span a range of approximately 13.51 log units, from log K = -1.23 for hydrogen gas to log (C_{S,organic}/C_{S,gas}) = 12.28 for 3,5-dinitro-2-methylbenzoic acid. The log (P or C_{S,organic}/C_{S,water}) comparison spans a much smaller range, from log P = 0.27 for carbon dioxide gas to log P = 6.90 for undecane.

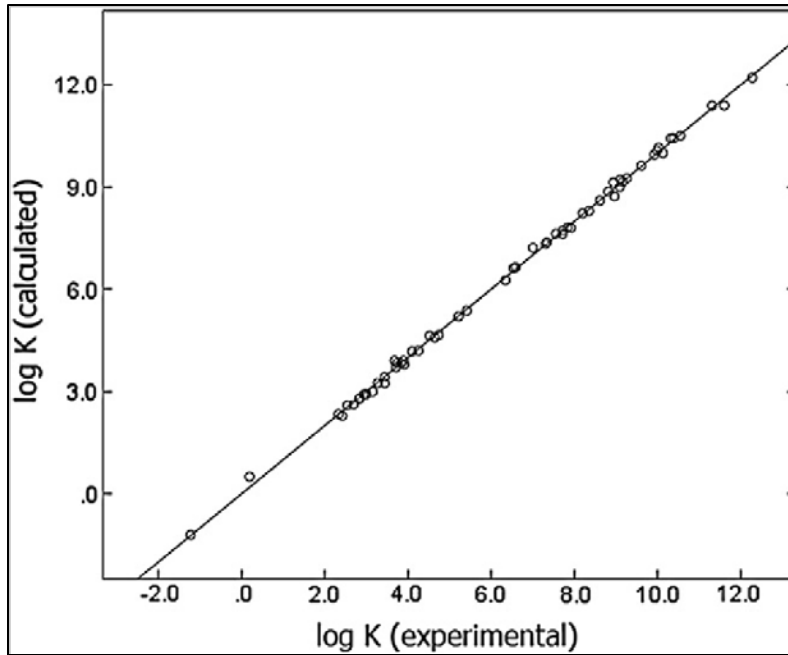


Figure 6.1. Comparison between experimental $\log K$ data and back-calculated values based on Equation (6.2).

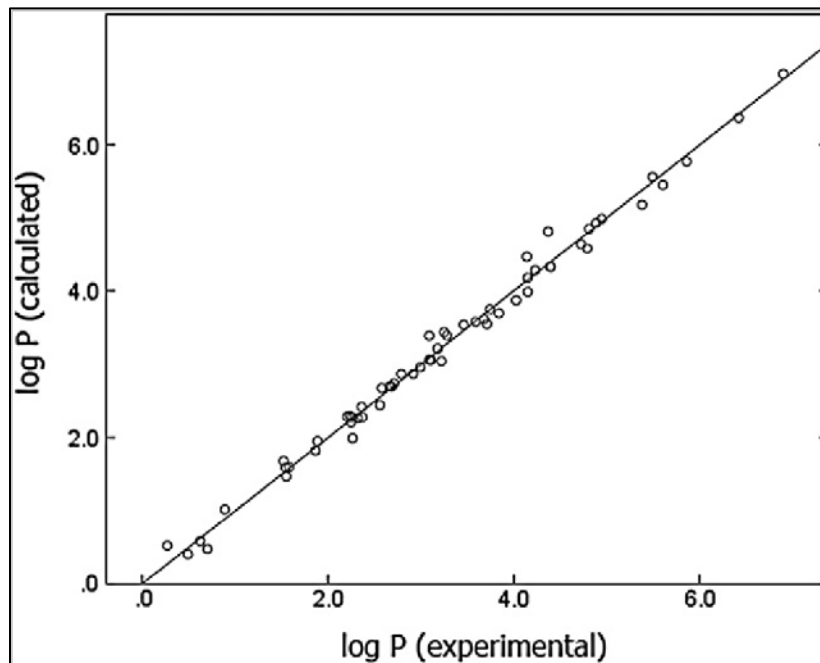


Figure 6.2. Comparison between experimental $\log P$ data and back-calculated values based on Equation (6.1).

Unfortunately, there is insufficient experimental data to perform training set and

test set analyses to assess the predictive ability of the derived expressions. Based on past experience with Abraham model, and having performed many training set and test analyses on derived Abraham model correlations when there were a sufficient number of experimental data points [10, 35-37], it is expected that Equations (6.1) and (6.2) should be capable of predicting molar solubility ratios and partition coefficients of additional solutes dissolved in 2-butoxyethanol to within 0.14 log units. The standard deviations of the training set correlations and test set calculations performed in the past have always been very similar to the standard deviations of the derived correlations for the full data set.

Similar solubilizing properties of the three alkoxyalcohol solvents can also be seen in the process coefficients for the log *K* correlations, which are given by Equations (6.3) - (6.4) for 2-methoxyethanol and 2-ethoxyethanol, respectively.

For 2-methoxyethanol: [9]

$$\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.141(0.052) - 0.265(0.076)\mathbf{E} + 1.810(0.096)\mathbf{S} + 3.641(0.085)\mathbf{A} + 0.590(0.141)\mathbf{B} + 0.790(0.018)\mathbf{L} \quad (6.3)$$

(with N = 62, SD = 0.139, R² = 0.998, F = 6044)

For 2-ethoxyethanol: [10]

$$\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.064(0.032) - 0.257(0.049)\mathbf{E} + 1.452(0.047)\mathbf{S} + 3.672(0.055)\mathbf{A} + 0.662(0.060)\mathbf{B} + 0.843(0.012)\mathbf{L} \quad (6.4)$$

(with N = 76, SD = 0.126, R² = 0.999, F = 17838)

Careful examination of Equations (6.2) – (6.4), reveals that five of the six process coefficients are very similar. To within the standard uncertainty in the calculated process coefficients for the hydrogen-bond donor (as reflected in the *b_k* coefficient) and

hydrogen-bond acceptor (as reflected in the a_k coefficient) properties are nearly the same. It is only the s_k coefficient in the correlations that differs significantly between the three alkoxyalcohols. The s_k coefficient decreases with increasing length of the alkoxy-chain, from $s_k = 1.810$ for 2-methoxyethanol to $s_k = 1.452$ for 2-ethoxyethanol to $s_k = 1.126$ for 2-butoxyethanol. This tendency is similar to that observed for the $\log K$ correlations for normal aliphatic alcohols in which the s_k coefficient also decreases rapidly with the growing alkyl chain length [38].

6.4 Conclusions

Mathematical expressions have been derived for predicting the solubility and partitioning behavior of neutral, nonelectrolyte solutions into 2-butoxyethanol based on the Abraham Solvation Parameter Model. The derived mathematical expressions are expected to predict the solute transfer properties to 2-butoxyethanol ($\log P$, $\log K$, $\log (C_{S,\text{organic}}/C_{S,\text{water}})$, and $\log (C_{S,\text{organic}}/C_{S,\text{gas}})$) for additional solutes to within 0.14 log units, provided that the numerical values of the solute descriptors fall within the range of values used in obtaining the predictive expressions. Comparison of the derived $\log K$ correlations for 2-butoxyethanol to correlations derived previously for 2-methoxyethanol and 2-ethoxyethanol indicates that the solubilizing properties of the three 2-alkoxyethanol solvents are very similar. To within the standard uncertainty in the calculated process coefficients for the hydrogen-bond donor (b_k coefficient) and hydrogen-bond acceptor (a_k coefficient) properties are nearly the same. It is only the s_k coefficient in the three correlations that differs significantly between the three alkoxyalcohols.

6.5 References

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CHAPTER 7

DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR PREDICTING THE ENTHALPIES OF SOLVATION OF SOLUTES DISSOLVED IN ACETIC ACID*

7.1 Introduction

Thermodynamic properties pertaining to solute transfer between two immiscible phases (or partly miscible phases) are of interest from both a theoretical and practical point of view. Transfer properties provide valuable information concerning solute–solvent and solvent–solvent interactions in fluid solution, particularly at low solute concentrations where interactions between two solute molecules are negligible. Solute transfer between phases forms the basis of gas-liquid chromatographic and high-performance liquid chromatographic chemical separations. Solute transfer between two phases is mathematically described in terms of partition coefficients that enable one to calculate the equilibrium concentrations of the solute and chemical impurities in both phases of the partition/extraction system.

This study continues our development of Abraham model correlations for estimating the enthalpies of solvation of solutes (ΔH_{solv}) dissolved in water [1] and in organic solvents at 298.15 K [1-15]. Most of our derived Abraham model $\log P$ and $\log K$ correlations are for 298.15 K. Industrial chemical separation processes may occur at other temperatures; however, Equations (1.24) and (1.25) presented in Chapter 1 may be used as a means for extrapolating $\log P$ and $\log K$ values measured or calculated at 298.15 K to slightly higher temperatures and/or slightly lower temperatures. Coefficients

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for several biphasic organic partition systems are available in publications by Poole and co-workers [16-17]. For convenience, the organic solvents for which there are published ΔH_{solV} correlations are listed along with their respective process coefficients, in Tables 7.1 and 7.2.

Table 7.1. Abraham model process coefficients for predicting enthalpies of solvation of solutes in select organic solvents based on Equation (1.24).

No	Solvent	$c_{h,l}$	$e_{h,l}$	$s_{h,l}$	$a_{h,l}$	$b_{h,l}$	$l_{h,l}$
1	Water	-13.310	9.910	2.836	-32.010	-41.816	-6.354
2	Hexane	-6.458	3.610	0.000	0.000	0.000	-9.399
3	Heptane	-7.018	4.036	0.000	0.000	0.000	-9.209
4	Hexadecane	-6.097	2.305	0.000	0.000	0.000	-9.364
5	Cyclohexane	-6.507	3.375	0.000	0.000	0.000	-9.078
6	Benzene	-4.637	4.446	-12.599	-9.775	-4.023	-8.488
7	Toluene	-5.291	3.511	-12.943	-6.317	-4.434	-8.382
8	1,4-Dimethylbenzene	-6.265	6.460	-9.862	-10.775	0.000	-9.318
9	1,3,5-Trimethylbenzene	-5.488	6.646	-9.602	-10.828	0.000	-9.538
10	Dichloromethane	-4.691	4.948	-14.616	-3.187	-10.683	-7.920
11	Trichloromethane	-6.516	8.628	-13.956	-2.712	-17.334	-8.739
12	Tetrachloromethane	-6.441	3.517	-4.824	0.000	-7.045	-8.886
13	1,2-Dichloroethane	-2.345	5.555	-18.328	-9.599	-7.101	-8.045
14	Dibutyl ether	-6.366	3.943	-5.105	-33.970	0.000	-9.325
15	Tetrahydrofuran	-6.040	3.640	-14.478	-40.652	0.000	-8.537
16	1,4-Dioxane	-3.845	5.825	-19.873	-35.905	0.000	-7.842
17	Methanol	-6.366	-2.506	-1.807	-37.692	-15.466	-7.674
18	Ethanol	-6.711	0.000	0.000	-50.547	-10.965	-8.291
19	1-Propanol	-8.713	-2.593	5.190	-53.042	-7.852	-8.108
20	2-Propanol	-7.669	0.000	2.055	-51.494	-6.976	-7.996
21	1-Butanol	-7.490	0.000	1.597	-52.542	-6.831	-8.585
22	2-Butanol	-6.883	0.000	6.667	-50.819	-10.577	-8.270
23	2-Methyl-1-propanol	-7.498	3.958	2.176	-53.967	-4.610	-8.602

(table continues)

No	Solvent	$C_{h,l}$	$E_{h,l}$	$S_{h,l}$	$a_{h,l}$	$b_{h,l}$	$l_{h,l}$
24	2-Methyl-2-propanol	-3.179	4.379	2.563	-57.447	-12.008	-8.881
25	1-Pentanol	-6.160	4.452	1.737	-54.432	-8.673	-9.170
26	1-Hexanol	-4.614	0.000	1.614	-45.975	-11.256	-9.269
27	1-Octanol	-6.490	-1.040	5.890	-53.990	-8.990	-9.180
28	Ethyl acetate	-7.063	4.671	-15.141	-28.763	0.000	-7.691
29	Acetone	-4.965	4.290	-17.026	-36.672	-3.794	-7.307
30	Acetonitrile	-4.148	3.304	-18.430	-26.104	-7.535	-6.727
31	N,N-Dimethylformamide	-4.324	0.000	-15.168	-42.211	-8.223	-7.121
32	Propylene carbonate	-4.377	0.478	-13.370	-17.898	-12.596	-6.685
33	Dimethyl carbonate	-3.030	7.749	-18.894	-30.719	0.000	-8.390
34	Diethyl carbonate	-4.499	6.558	-15.966	-25.537	0.000	-8.767
35	Dimethyl sulfoxide	-2.546	-0.329	-18.448	-47.419	-5.861	-6.380
36	Acetic acid ^a	-3.219	6.719	-11.448	-38.283	-12.175	-8.461

^a Coefficients were determined as part of the present study.

Table 7.2. Abraham model process coefficients for predicting enthalpies of solvation of solutes in select organic solvents based on Equation (1.25).

No	Solvent	$C_{h,v}$	$E_{h,v}$	$S_{h,v}$	$a_{h,v}$	$b_{h,v}$	$v_{h,v}$
1	Water	-6.952	1.415	-2.859	-34.086	-42.686	-22.720
2	Hexane	4.894	-8.916	-8.463	-1.168	0.773	-36.769
3	Heptane	3.368	-8.941	-7.065	-2.836	0.657	-35.595
4	Hexadecane	4.696	-9.621	-7.902	-2.933	1.102	-36.610
5	Cyclohexane	3.046	-8.735	-6.353	-1.264	-2.449	-33.550
6	Benzene	4.391	-5.422	-21.268	-11.797	-3.118	-31.674
7	Toluene	4.199	-7.143	-20.440	-10.006	-3.439	-32.235
8	1,4-Dimethylbenzene	1.703	-3.466	-18.074	-14.109	0.000	-33.618
9	1,3,5-Trimethylbenzene	2.940	-3.805	-18.981	-14.011	0.000	-34.238
10	Dichloromethane	4.540	-3.986	-22.068	-6.411	-12.589	-30.113
11	Trichloromethane	-0.425	-0.844	-20.735	-5.817	-16.434	-31.039
12	Tetrachloromethane	3.281	-6.024	-14.130	-3.383	-4.729	-34.154
13	1,2-Dichloroethane	3.623	-3.208	-24.665	-11.165	-6.589	-28.520
14	Dibutyl ether	0.324	-6.480	-14.644	-37.094	4.354	-32.989

(table continues)

No	Solvent	$C_{h,v}$	$E_{h,v}$	$S_{h,v}$	$a_{h,v}$	$b_{h,v}$	$V_{h,v}$
15	Tetrahydrofuran	4.777	-6.642	-23.110	-43.222	0.000	-33.683
16	1,4-Dioxane	5.087	-1.871	-28.459	-38.323	0.000	-29.845
17	Methanol	1.636	-11.797	-9.336	-41.378	-15.984	-27.891
18	Ethanol	2.611	-10.389	-7.720	-52.100	-13.005	-30.645
19	1-Propanol	-0.114	-12.428	-2.052	-55.258	-7.964	-30.202
20	2-Propanol	0.000	-10.275	-5.260	-53.559	-8.107	-28.119
21	1-Butanol	2.649	-12.088	-6.767	-57.593	-5.521	-32.814
22	2-Butanol	3.528	-11.470	0.000	-51.800	-13.286	-32.286
23	2-Methyl-1-propanol	3.427	-5.545	-6.977	-59.338	-4.850	-33.620
24	2-Methyl-2-propanol	3.637	-6.914	-3.098	-60.220	-14.133	-30.934
25	1-Pentanol	2.444	-7.713	-6.397	-58.906	-6.866	-32.673
26	1-Hexanol	3.383	-12.657	-5.599	-50.238	-10.949	-33.033
27	1-Octanol	1.570	-13.340	0.320	-58.760	-7.630	-34.050
28	Ethyl acetate	0.679	-4.403	-20.424	-32.125	-1.299	-28.598
29	Acetone	4.411	-3.436	-25.312	-39.209	-4.076	-27.314
30	Acetonitrile	2.650	-3.000	-25.559	-30.397	-6.797	-24.961
31	N,N-Dimethylformamide	2.301	-7.377	-23.129	-45.258	-6.463	-25.733
32	Propylene carbonate	1.409	-7.886	-18.776	-20.632	-11.636	-24.199
33	Dimethyl carbonate	5.749	-3.022	-28.852	-32.746	0.000	-29.655
34	Diethyl carbonate	5.957	-4.458	-25.925	-29.492	0.000	-32.549
35	Dimethyl sulfoxide	2.184	-7.233	-24.071	-50.992	-5.182	-22.301
36	Acetic acid ^b	4.695	-8.305	-14.668	-40.677	-15.426	-30.958

^b Coefficients were determined as part of the present study.

In the present communication, considerations are extended to include enthalpies of solvation of organic vapors and inorganic gases in acetic acid. Abraham model enthalpy of solvation correlations are developed for acetic acid using published enthalpy data gathered from the published chemical and engineering literature. Acetic acid is an important solvent in hydrogenation studies involving alkenes and alkynes. Enthalpy data for the hydrogenation reactants and products are needed to correct the observed

solution phase hydrogenation enthalpy, $\Delta H_{\text{hydrogenation,soln}}$, to the gas phase hydrogenation reaction as shown in Figure 7.1.

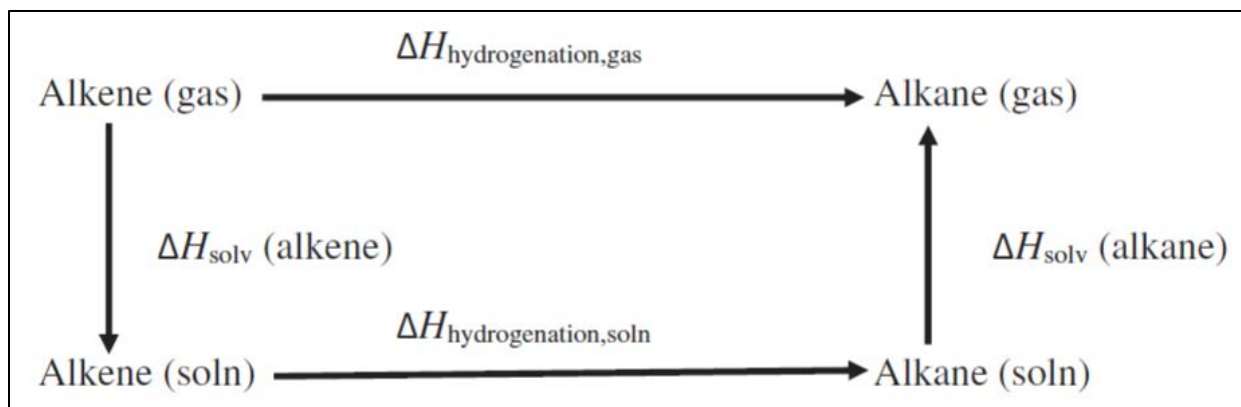


Figure 7.1. Hydrogenation gas phase and solution phase reactions for converting an alkene to an alkane.

This process is also represented by Equation (7.1), as the experimental procedure involves measuring the enthalpy associated with breaking an ampoule containing the alkene (alkyne) in acetic acid and the subsequent introduction of the hydrogen gas into the reaction zone of the calorimetric device until no further gas absorption occurs [18]. The derived ΔH_{solv} correlations provide a method for estimating the enthalpies of solvation of both the unsaturated hydrocarbon and the alkane product that is formed in the acetic acid solvent media.

$$\Delta H_{\text{hydrogenation,gas}} = \Delta H_{\text{hydrogenation,soln}} + \Delta H_{\text{solv,alkene}} - \Delta H_{\text{solv,alkane}} \quad (7.1)$$

7.2 Computational Methodology and Data Sets

A search of the published literature found several papers that reported calorimetrically determined enthalpies of solution, ΔH_{soln} , of linear and branched alkanes [19-21], cycloalkanes [19,21], alkenes [21], benzene [22], toluene [22], N-methylpyrrole [22], pyrrole [22], 2-chloro-2-methylpropane [23], and 2-bromo-2-

methylpropane [23] dissolved in acetic acid at 298.15 K, as well as integral excess enthalpy of mixing data for binary systems containing acetic acid as one of the mixture components [24-43]. In the case of the integral enthalpy data the measured values were extrapolated to infinite dilution by standard thermodynamic methods. For hexane [18-19,21,29], heptane [19,28], cyclohexane [19,21,27], and benzene [22,26], both enthalpy of solution and integral excess enthalpy of mixing data was found. For these four compounds the measured enthalpy of solution data was used, rather than the enthalpy of mixing data, as this eliminated any uncertainties associated with extrapolating the values to infinite dilution. Enthalpies of solution of xenon [44], carbon dioxide [45], benzoic acid [46], 4-methylbenzoic acid [47], 2-hydroxybenzoic acid [48], oxalic acid [49], malonic acid [49], succinic acid [49], glutaric acid [49], adipic acid [49], pimelic acid [49], suberic acid [49], azelaic acid [49], and sebacic acid [49] were calculated from the variation of mole fraction solubility with temperature.

In total, enthalpy of solution data was obtained for 92 different organic solutes in acetic acid measured at 298.15 K or at temperatures very near 298.15 K. The ΔH_{soln} values were converted to gas-to-organic solvent enthalpies of transfer by using Equations (1.22) and (1.23) as described in Chapter 1 for both liquid and crystalline solutes. The experimental ΔH_{solv} values are listed in Table 7.3 along with the numerical values of the solute descriptors of the 92 organic and inorganic compounds considered in the present study. It is estimated the experimental uncertainty in the tabulated ΔH_{solv} values to be approximately 2–4 kJ mol⁻¹ based on the combined uncertainties in the published enthalpy of solution and enthalpy of vaporization/sublimation data. The tabulated solute descriptors are of experimental origin and came from our solute

descriptor database. Large tabulations of solute descriptors are available in several earlier publications [1, 50-53].

7.3 Results and Discussion

Development of a meaningful Abraham model correlation for enthalpies of solvation of organic solutes dissolved in acetic acid requires the regression analysis of experimental ΔH_{solv} data for solutes having known descriptor values. The set of solutes should be chemically diverse and span as wide a range of descriptor values as possible. The ΔH_{solv} database that has been constructed contains both liquid and crystalline nonelectrolyte organic compounds, as well as two inorganic gases. Both volatile and non-volatile solutes are included in the data set, as well as several compounds (such as ethylene glycol, 4-methylbenzoic acid, 2-hydroxybenzoic acid, oxalic acid, malonic acid, adipic acid, succinic acid, pimelic acid, sebacic acid, and azelaic acid) possessing the ability to act as both hydrogen-bond donors and hydrogen-bond acceptors during hydrogen-bond formation. Regression analysis of the experimental ΔH_{solv} data in the next to last column of Table 7.3 using Version 22 of the IBM[®] SPSS[®] Statistical Software yielded the following two Abraham model correlations:

$$\Delta H_{\text{solv}} (\text{kJ mol}^{-1}) = -3.219(0.670) + 6.719(1.273)\mathbf{E} - 11.448(1.470)\mathbf{S} - 38.283(0.988)\mathbf{A} - 12.175(1.857)\mathbf{B} - 8.461(0.081)\mathbf{L} \quad (7.2)$$

(with $N = 92$, $SD = 1.98$, $R^2 = 0.994$, $F = 2703$)

$$\Delta H_{\text{solv}} (\text{kJ mol}^{-1}) = 4.695(0.882) - 8.305(1.428)\mathbf{E} - 14.668(1.593)\mathbf{S} - 40.677(1.067)\mathbf{A} - 15.426(2.025)\mathbf{B} - 30.958(0.699)\mathbf{V} \quad (7.3)$$

(with $N = 92$, $SD = 2.16$, $R^2 = 0.993$, $F = 2284$)

Table 7.3. Values of the gas-to-acetic acid solvation enthalpy, ΔH_{solv} (in kJ mol^{-1}), at 298.15 K for 92 solutes together with the solute descriptors.

Solute	E	S	A	B	L	V	ΔH_{solv}	Ref.
Xenon	0.000	0.000	0.000	0.000	0.378	0.3290	-5.72	[44]
Carbon monoxide	0.000	0.000	0.000	0.040	-0.836	0.2220	1.28	[45]
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	-21.76	[19]
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-25.88	[19]
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-30.34	[19]
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	-34.28	[19]
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	-38.82	[19]
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	-43.10	[19]
Undecane	0.000	0.000	0.000	0.000	5.191	1.6585	-47.28	[19]
Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-52.00	[19]
Tridecane	0.000	0.000	0.000	0.000	6.200	1.9403	-56.20	[19]
2-Methylpentane	0.000	0.000	0.000	0.000	2.503	0.9540	-25.34	[20]
3-Methylpentane	0.000	0.000	0.000	0.000	2.581	0.9540	-25.74	[20]
2,2-Dimethylbutane	0.000	0.000	0.000	0.000	2.352	0.9540	-23.65	[20]
2-Methylhexane	0.000	0.000	0.000	0.000	3.001	1.0949	-29.35	[20]
3-Methylhexane	0.000	0.000	0.000	0.000	3.044	1.0949	-29.63	[20]
2,3-Dimethylpentane	0.000	0.000	0.000	0.000	3.016	1.0949	-29.33	[20]
2,4-Dimethylpentane	0.000	0.000	0.000	0.000	2.809	1.0949	-27.57	[20]
2,2,3-Trimethylpentane	0.000	0.000	0.000	0.000	3.325	1.2358	-32.30	[20]
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358	-29.75	[20]

(table continues)

Solute	E	S	A	B	L	V	ΔH_{solv}	Ref.
2,3,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.481	1.2358	-32.16	[20]
Cyclopentane	0.260	0.100	0.000	0.000	2.477	0.7045	-23.66	[19]
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	-27.41	[19]
Cycloheptane	0.350	0.100	0.000	0.000	3.704	0.9863	-32.04	[19]
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	-36.18	[19]
Cyclodecane	0.474	0.100	0.000	0.000	5.258	1.4090	-46.12	[19]
Methylcyclopentane	0.225	0.100	0.000	0.000	2.907	0.8454	-26.24	[21]
Ethylcyclopentane	0.227	0.100	0.000	0.000	3.324	0.9863	-30.14	[21]
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	-29.08	[21]
Ethylcyclohexane	0.263	0.100	0.000	0.000	3.877	1.1272	-33.55	[21]
1-Methylcyclopentene	0.330	0.200	0.000	0.100	2.864	0.8024	-29.29	[21]
1-Ethylcyclopentene	0.330	0.330	0.000	0.210	3.300	0.9433	-34.48	[21]
Methylenecyclohexane	0.385	0.260	0.000	0.100	3.352	0.9433	-31.46	[21]
Ethylidenecyclohexane	0.435	0.190	0.000	0.100	3.981	1.0842	-36.94	[21]
Cyclohexene	0.395	0.200	0.000	0.100	3.021	0.8024	-29.31	[21]
Cyclohepta-1,3,5-triene	0.764	0.460	0.000	0.200	3.442	0.8573	-36.06	[21]
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-36.69	[30]
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-38.73	[30]
1-Propanol	0.236	0.420	0.370	0.480	2.031	0.5900	-45.18	[30]
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7309	-48.94	[30]
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	0.8718	-54.01	[30]
Hexan-1-ol	0.210	0.420	0.370	0.480	3.610	1.0127	-57.41	[30]
Heptan-1-ol	0.211	0.420	0.370	0.480	4.115	1.1536	-63.28	[30]

(table continues)

Solute	E	S	A	B	L	V	ΔH_{solv}	Ref.
Octan-1-ol	0.199	0.420	0.370	0.480	4.619	1.2945	-66.52	[30]
Nonan-1-ol	0.193	0.420	0.370	0.480	5.124	1.4354	-72.66	[30]
Decan-1-ol	0.191	0.420	0.370	0.480	5.610	1.5763	-75.84	[30]
Ethylene glycol	0.404	0.900	0.580	0.780	2.661	0.5078	-63.32	[39]
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-32.90	[43]
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-35.99	[35]
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-34.92	[41]
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-43.84	[33]
Ethyl propanoate	0.087	0.580	0.000	0.450	2.807	0.8875	-39.00	[35]
Ethyl butanoate	0.068	0.580	0.000	0.450	3.271	1.0284	-43.12	[35]
Ethyl pentanoate	0.049	0.580	0.000	0.450	3.769	1.1693	-46.10	[35]
Ethyl hexanoate	0.043	0.580	0.000	0.450	4.251	1.3102	-50.20	[35]
Ethyl heptanoate	0.027	0.580	0.000	0.450	4.733	1.4511	-53.83	[35]
Ethyl octanoate	0.024	0.580	0.000	0.450	5.215	1.5920	-57.46	[35]
Ethyl decanoate	0.013	0.580	0.000	0.450	6.180	1.8738	-67.13	[35]
Dibutyl ether	0.000	0.250	0.000	0.450	3.924	1.2945	-42.81	[40]
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-35.99	[25]
Tetrahydropyran	0.296	0.490	0.000	0.480	3.013	0.7632	-37.93	[25]
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-39.85	[24]
1,3-Dioxolane	0.298	0.510	0.000	0.620	1.830	0.5401	-35.05	[24]
1-Butanenitrile	0.188	0.900	0.000	0.360	2.548	0.6860	-37.73	[38]
Dimethyl carbonate	0.142	0.610	0.000	0.550	2.447	0.6644	-36.84	[34]
Diethyl carbonate	0.061	0.580	0.000	0.530	3.412	0.9462	-42.91	[34]
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	-31.99	[22]

(table continues)

Solute	E	S	A	B	L	V	ΔH_{solv}	Ref.
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	-36.58	[22]
o-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	-40.46	[32]
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	-40.01	[32]
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	-40.21	[32]
Benzonitrile	0.742	1.110	0.000	0.330	4.039	0.8711	-48.69	[37]
Benzoic acid	0.730	0.900	0.590	0.400	4.657	0.9317	-73.50	[46]
4-Methylbenzoic acid	0.730	0.930	0.620	0.420	4.890	1.0726	-84.67	[47]
2-Hydroxybenzoic acid	0.900	0.850	0.730	0.370	4.732	0.9904	-77.33	[48]
Acetic acid	0.265	0.640	0.620	0.440	1.816	0.4648	-51.60	ΔH_{vap}
Propanoic acid	0.233	0.650	0.600	0.450	2.290	0.6057	-54.74	[18,42]
Butanoic acid	0.210	0.640	0.610	0.450	2.750	0.7466	-56.84	[42]
2-Methylpropanoic acid	0.200	0.600	0.610	0.450	2.693	0.7466	-54.24	[18]
Oxalic acid	0.400	1.210	0.750	0.510	2.835	0.5392	-70.18	[49]
Malonic acid	0.380	1.460	0.990	0.590	3.616	0.6801	-96.37	[49]
Succinic acid	0.370	1.320	1.030	0.710	3.951	0.8210	-98.26	[49]
Glutaric acid	0.360	1.280	1.050	0.750	4.207	0.9619	-104.71	[49]
Adipic acid	0.350	1.210	1.130	0.760	4.457	1.1028	-109.32	[49]
Pimelic acid	0.350	1.260	1.100	0.840	5.277	1.2437	-110.21	[49]
Suberic acid	0.350	1.360	1.100	0.870	5.926	1.3846	-118.21	[49]
Azelaic acid	0.340	1.360	1.110	0.870	6.420	1.5277	-126.31	[49]
Sebacic acid	0.350	1.400	1.100	0.900	6.910	1.6664	-126.20	[49]
2-Chloro-2-methylpropane	0.142	0.300	0.000	0.030	2.273	0.7946	-27.39	[23]
2-Bromo-2-methylpropane	0.305	0.290	0.000	0.070	2.609	0.8472	-29.76	[23]
N-Methylpyrrole	0.559	0.790	0.000	0.310	2.923	0.7180	-39.01	[22]
Pyrrole	0.613	0.730	0.410	0.290	2.865	0.5570	-44.16	[22]

The statistical information associated with the correlation includes the number of experimental data points used in the regression analysis (N), the standard deviation (SD), the squared correlation coefficient (R^2), and the Fisher F-statistic and is provided below Equations (7.2) and (7.3). The standard error in each calculated process coefficient is provided in parenthesis immediately after the respective coefficient.

Equations (7.2) and (7.3) provide a very good mathematical description of the observed enthalpy of solvation data for solutes dissolved in anhydrous acetic acid as evidenced by SDs of 1.98 kJ mol^{-1} and 2.16 kJ mol^{-1} , respectively. The SDs compare favorably with the estimated uncertainties in the measured ΔH_{solv} data used in the regression analyses. Graphical comparisons of the observed experimental ΔH_{solv} data vs. back-calculated values based on the two derived Abraham model correlations are depicted in Figures 7.2 and 7.3. The experimental ΔH_{solv} values cover a range of approximately $127.6 \text{ kJ mol}^{-1}$, from $\Delta H_{\text{solv}} = 1.28 \text{ kJ mol}^{-1}$ for carbon monoxide to $\Delta H_{\text{solv}} = -126.31 \text{ kJ mol}^{-1}$ for azelaic acid.

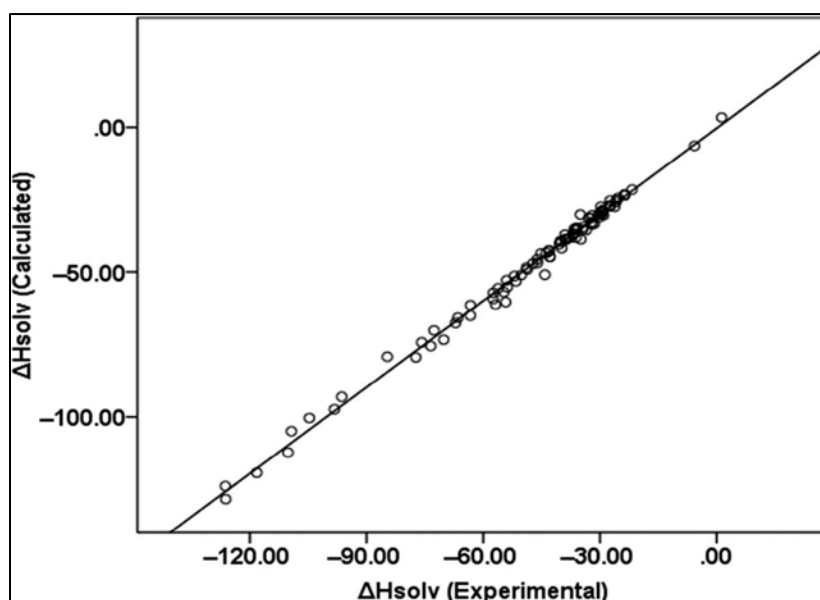


Figure 7.2. Comparison between experimental ΔH_{solv} data (in kJ mol^{-1}) for solutes dissolved in acetic acid at 298.15 K and predicted values based on Equation (7.2).

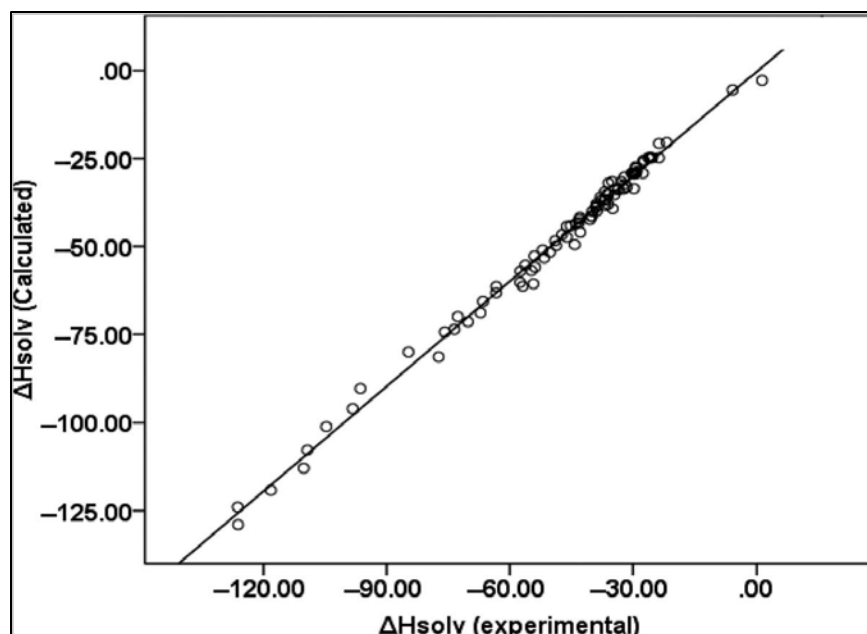


Figure 7.3. Comparison between experimental ΔH_{solv} data (in kJ mol^{-1}) for solutes dissolved in acetic acid at 298.15 K and predicted values based on Equation (7.3).

To assess the predictive ability of Equations (7.2) and (7.3), the 92 data points were divided into a training set and a test set by allowing the IBM® SPSS® software to randomly select half of the experimental points. The selected data points became the training set, and the compounds that were left served as the test set. Analysis of the experimental data in the training set gave the following equations:

$$\Delta H_{\text{solv}} (\text{kJ mol}^{-1}) = -2.652(0.447) + 7.948(1.654)\mathbf{E} - 10.557(2.034)\mathbf{S} - 37.032(1.295)\mathbf{A} - 15.605(2.625)\mathbf{B} - 8.627(0.227)\mathbf{L} \quad (7.4)$$

(with $N = 46$, $SD = 1.84$, $R^2 = 0.995$, $F = 1451$)

$$\Delta H_{\text{solv}} (\text{kJ mol}^{-1}) = 4.581(1.069) - 6.764(1.720)\mathbf{E} - 13.605(2.072)\mathbf{S} - 39.895(1.305)\mathbf{A} - 18.058(2.673)\mathbf{B} - 31.271(0.839)\mathbf{V} \quad (7.5)$$

(with $N = 46$, $SD = 1.88$, $R^2 = 0.994$, $F = 1400$)

There is very little difference in the process coefficients for the full data set and the training data set correlations, thus showing that the training set of compounds is a representative sample of the total data set. Each training set equation was then used to predict the ΔH_{solv} values for the 46 compounds in the test set. For the predicted and experimental values, the SD = 2.45 kJ mol⁻¹ (Equation (7.4)) and SD = 2.74 kJ mol⁻¹ (Equation (7.5)), average absolute error (AAE) = 1.67 kJ mol⁻¹ (Equation (7.4)) and AAE = 1.83 kJ mol⁻¹ (Equation (7.5)), and average error (AE) = -0.12 kJ mol⁻¹ (Equation (7.4)) and AE = -0.37 kJ mol⁻¹ (Equation (7.5)). There is, therefore, very little bias in using Equations (7.4) and (7.5) with AE = -0.12 kJ mol⁻¹ and AE = -0.37 kJ mol⁻¹, respectively. The training set and test set analyses were performed two more times with similar results. In each repetition the data set was split into new training and test sets using the SPSS randomization software. The ranges of solute descriptors covered by the respective training and test sets were approximately the same. It is expected that Equations (7.2) and (7.3) should be capable of predicting enthalpies of solvation of additional compounds dissolved in acetic acid to within 2.2 kJ mol⁻¹ provided that the compound's descriptors solute descriptors fall within the area of chemical space defined by: **E** = 0.000 to **E** = 0.900; **S** = 0.000 to **S** = 1.460; **A** = 0.000 to **A** = 1.130; **B** = 0.000 to **B** = 0.900; **L** = -0.836 to **L** = 6.910; and **V** = 0.2220 to **V** = 1.9403.

There are several organic compounds for which solute descriptors and/or enthalpies of vaporization/sublimation may not be readily available. Enthalpies of vaporization/sublimation are needed to convert the measured ΔH_{soln} data to ΔH_{solv} values through Equations (1.22) and (1.23). For these compounds the possibility of estimating enthalpies of solvation from other measured solute properties, such as

estimating ΔH_{solv} from the solute's measured gas-to-organic solvent partition coefficient or Gibbs energy of solvation, ΔG_{solv} , is being explored. During a search of the published literature, experimental gas-to-acetic acid partition coefficient data, K , was found for five alkanes (pentane, hexane, heptane, octane, and 2,2,4-trimethylpentane), two aromatic hydrocarbons (benzene and toluene), ethanol, 1,4-dioxane, xenon, and carbon monoxide, infinite dilution activity coefficient for 2-chloro-2-methylpropane and 2-bromo-2-methylpropane, and solubility data for several carboxylic acids (benzoic acid, 4-methylbenzoic acid, 2-hydroxybenzoic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid) all of which are listed in Table 7.3. The infinite dilution activity coefficient data, $\gamma_{\text{solute}}^{\infty}$, for the two 2-methylpropane halides was converted to a log K value through standard thermodynamic relationships as defined in Chapter 2 in Equations (2.1) and (2.3). In the case of crystalline compounds the gas-to-liquid partition coefficient, K , is estimated as a molar solubility ratio of the solute solubility in the organic solvent, $C_{\text{S,organic}}$ divided by the solute's molar concentration in the gas phase, $C_{\text{S,gas}}$ (e.g., $K = C_{\text{S,organic}}/C_{\text{S,gas}}$).

Information needed to calculate $C_{\text{S,gas}}$ is available in earlier publications [51-56] in the form of the solute's gas-to-water partition coefficient, K_w , and aqueous molar solubility, $C_{\text{s,water}}$. Measured mole fraction solubilities were converted to molar solubilities as described in Chapter 1 using Equation (1.21). In total there are log K and ΔH_{solv} data for 27 common organic and inorganic solutes. The experimental log K and ΔH_{solv} values are listed in Table 7.4, along with the literature references [47-49,57-59] for the log K data and the Gibbs energies of solvation calculated as $\Delta G_{\text{solv}} = -2.303 RT \log K$.

Table 7.4. Values of gas-to-acetic acid partition coefficients, K , gas-to-acetic acid Gibbs energies, ΔG_{solv} (kJ mol^{-1}), and gas-to-acetic acid enthalpies of solvation, ΔH_{solv} (kJ mol^{-1}), at 298.15 K for 27 solutes.

Solute	$\log K$	ΔG_{solv}	ΔH_{solv}	$\log K$ (Ref.)
Xenon	0.215	-1.23	-5.72	[51]
Carbon monoxide	-0.771	4.40	1.28	[66]
Pentane	1.509	-8.61	-21.76	[66]
Hexane	1.957	-11.17	-25.88	[66]
Heptane	2.337	-13.34	-30.34	[66]
Octane	2.939	-16.78	-34.28	[64]
Isooctane	2.268	-12.95	-29.75	[66]
Cyclopentane	1.921	-10.97	-23.66	[66]
Cyclohexane	2.357	-13.46	-27.41	[66]
Ethanol	3.810	-21.75	-38.73	[64]
1,4-Dioxane	4.296	-24.53	-39.85	[64]
Benzene	2.824	-16.12	-31.99	[66]
Toluene	3.357	-19.16	-36.58	[66]
Benzoic acid	7.098	-40.52	-73.50	[65]
4-Methylbenzoic acid	7.605	-43.42	-84.67	[54]
2-Hydroxybenzoic acid	7.234	-41.30	-77.33	[55]
Oxalic acid	6.992	-39.92	-70.18	[56]
Malonic acid	8.367	-47.77	-96.37	[56]
Succinic acid	8.825	-50.38	-98.26	[56]
Glutaric acid	9.131	-52.13	-104.71	[56]
Adipic acid	9.787	-55.87	-109.32	[56]
Pimelic acid	10.196	-58.21	-110.21	[56]
Suberic acid	11.260	-64.28	-118.21	[56]
Azelaic acid	11.770	-67.19	-126.31	[56]
Sebacic acid	12.220	-69.76	-126.20	[56]
2-Chloro-2-methylpropane	2.243	-12.81	-27.39	[30]
2-Bromo-2-methylpropane	2.513	-14.35	-29.76	[30]

Analysis of the experimental values in the last two columns of Table 7.4 yielded the following linear mathematical expression:

$$\Delta H_{\text{solv}} (\text{kJ mol}^{-1}) = 1.815(0.031)\Delta G_{\text{solv}} (\text{kJ mol}^{-1}) - 3.805(1.174) \quad (7.6)$$

(with $N = 27$, $SD = 3.45$, $R^2 = 0.993$, $F = 3327$)

which could be used to predict ΔH_{solv} from the measured ΔG_{solv} values and vice versa.

See Figure 7.4 for a graph of ΔH_{solv} vs. ΔG_{solv} . The $SD = 3.45 \text{ kJ mol}^{-1}$ for Equation (7.6) is a bit larger than that obtained from the two derived Abraham model correlations.

For predictive purposes, it is recommended that estimating ΔH_{solv} involve the use of Equations (7.2) and (7.3) if the solute descriptors are known. Equation (7.6) is offered as possible alternative predictive expression for those instances where ΔG_{solv} is known and the solute descriptors are not readily available.

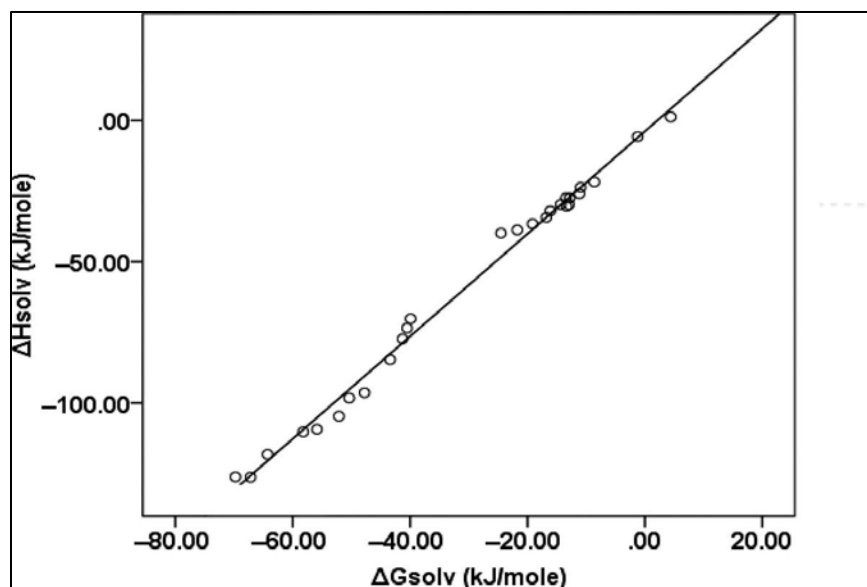


Figure 7.4. Relationship between the Gibbs energy of solvation and enthalpy of solvation for 27 organic and inorganic solutes dissolved in acetic acid.

The structure of acetic acid is often portrayed as a cyclic dimer, with the OH groups intramolecularly hydrogen-bonded, and no longer available for interaction with an external hydrogen-bond base. This would lead to acetic acid having little or no

hydrogen-bond acidity. However, the cyclic dimer is probably only formed in solutions of acetic acid in non-polar solvents, and neat liquid acetic acid has been shown to exist as linear associates [60-62] in which there are free OH-groups (although not as many as if acetic acid was non-associated). See Figure 7.5 for a pictorial representation of this concept. On this basis, liquid acetic acid would be expected to have some hydrogen-bond acidity, as evidenced by significant numerical values of the coefficients

$b_{h,l}$ in Equation (1.24) and $b_{h,v}$ in Equation (1.25). These coefficients are given in Tables 7.1 and 7.2 for acetic acid and for the other solvents that have been studied but are not very informative. Thus $b_{h,l}$ for acetic acid, Table 7.1, is just as large as that for many alcohols, but about the same as $b_{h,l}$ for propylene carbonate, a solvent expected to have no hydrogen-bond acidity at all.

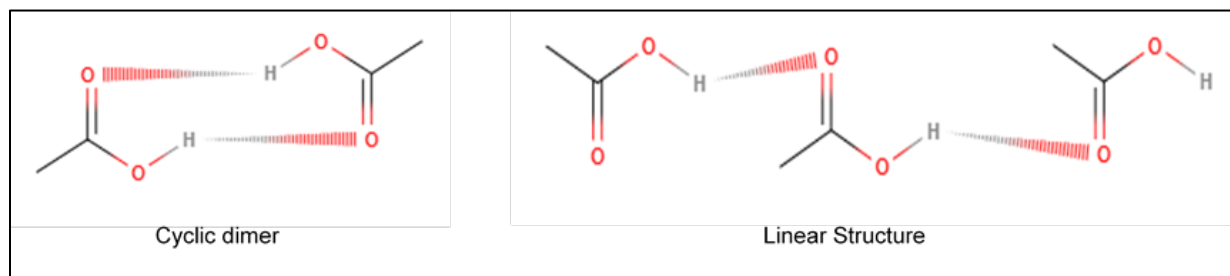


Figure 7.5. Comparison of linear structure of acetic acid versus a cyclic dimer formation.

To compare the properties of solvent acetic acid with those for the other solvents in Table 7.1, in general terms, a Principal Component Analysis (PCA) was performed on the five coefficients $e_{h,l}$, $s_{h,l}$, $a_{h,l}$, $b_{h,l}$, and $h_{h,l}$ in Equation (1.24). From the PCA, the first two PCs contain 68% of the total information, which is rather less than normal. The plot of the PC scores is shown as in Figure 7.6, and it is clear that acetic acid, as a solvent, (No. 36) does not resemble hydroxylic solvents in terms of enthalpic interactions but is

more akin to moderately polar solvents such as ethyl acetate (No. 28) or acetone (No. 29).

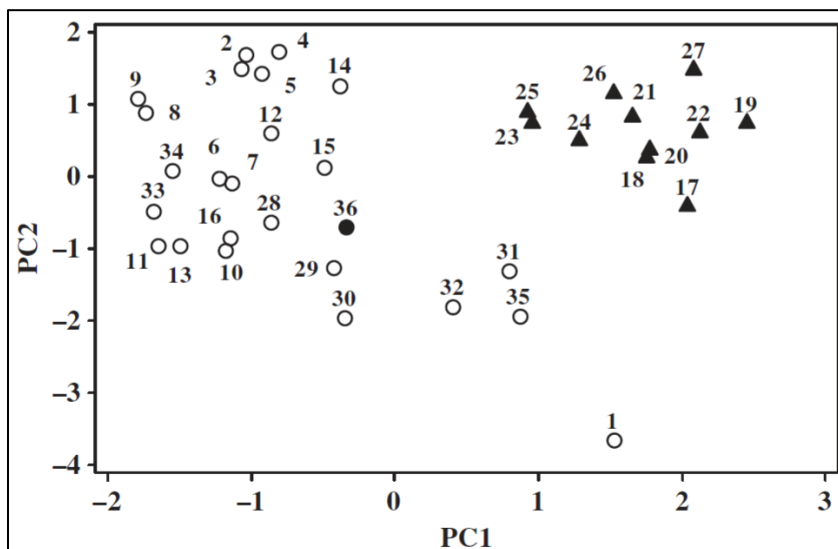


Figure 7.6. A plot of the scores of PC2 against the scores of PC1. Solvents numbered as in Table 7.1. Symbols: ● acetic acid; ▲ alcohols.

7.4 Conclusions

Mathematical expressions are derived for correlating enthalpies of solvation of inorganic gases and organic solutes dissolved in acetic acid based on the Abraham Solvation Parameter Model. The correlations presented in this paper should allow one to predict ΔH_{solv} values for additional solutes at 298.15 K to within $\pm 2.2 \text{ kJ mol}^{-1}$ provided one stays within the chemical space defined by the solute descriptors used in determining Abraham model Equations (7.2) and (7.3). In cases where numerical values of the solute descriptors are not available, a predictive expression for ΔH_{solv} that uses the measured ΔG_{solv} as the sole required input parameter is provided. The SD of this latter predictive expression is larger than the SD of the derived Abraham model equations, $\text{SD} = 3.5 \text{ kJ mol}^{-1}$ vs. $\text{SD} = 2.2 \text{ kJ mol}^{-1}$. For predictive purposes, it is

recommended that one estimate ΔH_{solv} using Abraham model equations if the solute descriptors are known and offer the linear ΔH_{solv} vs. ΔG_{solv} equation as a possible alternative predictive expression for those instances where ΔG_{solv} is known and the solute descriptors are not readily available. PCA on the five process coefficients $e_{h,l}$, $s_{h,l}$, $a_{h,l}$, $b_{h,l}$, and $l_{h,l}$ in Equation (1.24) shows that acetic acid does not resemble hydroxylic solvents in terms of enthalpic interactions, but is more akin to moderately polar solvents such as ethyl acetate or acetone.

7.5 References

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CHAPTER 8

DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR PREDICTING THE ENTHALPIES OF SOLVATION OF SOLUTES DISSOLVED IN BOTH DIMETHYL CARBONATE AND DIETHYL CARBONATE⁶

8.1 Introduction

Enthalpies of solvation provide valuable information regarding molecular interactions in solution. Enthalpy data are often needed in the design and development of industrial processes involving chemical syntheses and separations. In previous publications, mathematical correlations for describing the enthalpic interactions of both non-complexing and complexing solutes based on the Abraham Solvation Parameter Model (ASPM) has been reported. The basic model has been used successfully to describe both enthalpy of solvation, ΔH_{solv} , for solute transfer into condensed phases from the gas phase, as well as, solute transfer between two condensed phases (See Equations (1.24) and (1.25)).

In the present communication, considerations are extended to include enthalpies of solvation of organic vapors and gases in dimethyl carbonate (DMC) and diethyl carbonate (DEC). These two solvents, along with propylene carbonate (PC), are used in the manufacture of lithium ion batteries. Abraham model enthalpy of solvation correlations are developed for both solvents using published enthalpy data gathered from the published chemical and engineering literature. The derived process coefficients are used to examine hydrogen-bonding interactions between the two dialkyl carbonate solvents and various proton donor solute molecules.

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8.2 Computational Methodology and Data Sets

A search of the literature found a large number of published papers [1-31] that reported experimental excess molar enthalpies of mixing of binary mixtures containing dimethyl carbonate or diethyl carbonate, and partial molar enthalpies of solution of inorganic and organic compounds in the two solvents of interest. The compiled enthalpy data for the liquid and solid organic compounds were converted to gas-to-dialkyl carbonate solvent enthalpies of solvation using Equations (1.22) and (1.23) as discussed in Chapter 1.

Based on an initial assessment of the available experimental data, all experimental data that pertained to temperatures outside of the temperature range of 288–313 K were eliminated. Enthalpies of solvation are temperature dependent, and the introduction of large errors in the database by including experimental data far removed from 298.15 K was not wanted. For several of the organic solutes, there were multiple, independently determined enthalpy values. In such cases, direct calorimetric enthalpy of solution data were selected over values calculated from excess molar enthalpy of mixing data. Partial molar enthalpies of solution can be easily calculated from enthalpy of mixing data using standard thermodynamic relationships as described in Chapter 2 [32]. Excess enthalpy of mixing data was used only if experimental measurements had been performed at solute concentrations of less than 0.06 mole fraction. Using the aforementioned criteria, 80 molar enthalpies of solvation in diethyl carbonate and 57 molar enthalpies of solvation in dimethyl carbonate were selected for regression analysis. The experimental $\Delta H_{\text{solv,DEC}}$ and $\Delta H_{\text{solv,DMC}}$ values are listed in Tables 8.1 and 8.2, respectively. It is estimated the uncertainty in many of the measured values to be in

the range of ± 1.0 to ± 2.0 kJ mol⁻¹ based on the experimental uncertainties reported by the authors [32] who measured the enthalpy of solution and excess enthalpy of mixing data, combined with the experimental uncertainties reported in the enthalpy of vaporization and enthalpy of sublimation data needed to convert ΔH_{soln} values to ΔH_{solv} .

Also tabulated in Tables 8.1 and 8.2 are the numerical values of the solute descriptors for the compounds considered in the present study. The tabulated values came from a solute descriptor database which now contains values for more than 7 000 different organic and organometallic compounds. The descriptors were obtained exactly as described before using various types of experimental data, including water-to-solvent partitions, gas-to-solvent partitions, solubility and chromatographic data [33-38]. Solute descriptors used in the present study are all based on experimental data.

Table 8.1. Values of the gas-to-diethyl carbonate solvation enthalpy, $\Delta H_{\text{solv,DEC}}$ (in kJ mol^{-1}), at 298.15 K for 80 solutes together with the solute descriptors.

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv,DEC}}$	Ref.
Helium	0.000	0.000	0.000	0.000	-1.741	0.0680	13.71	[1]
Neon	0.000	0.000	0.000	0.000	-1.575	0.0850	10.85	[1]
Argon	0.000	0.000	0.000	0.000	-0.688	0.1900	2.07	[1]
Krypton	0.000	0.000	0.000	0.000	-0.211	0.2460	-2.63	[1]
Xenon	0.000	0.000	0.000	0.000	0.378	0.3290	-6.77	[1]
Carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.2809	-11.93	[24]
Sulfur hexafluoride	-0.600	-0.200	0.000	0.000	-0.120	0.4643	-2.39	[1]
Methane	0.000	0.000	0.000	0.000	-0.323	0.2495	-1.80	[1]
Ethane	0.000	0.000	0.000	0.000	0.492	0.3904	-8.66	[1]
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358	-32.76	[12]
Ethene	0.107	0.100	0.000	0.070	0.289	0.3470	-8.33	[1]
1,2-Dichloroethane	0.420	0.640	0.100	0.110	2.573	0.6352	-36.60	[17]
1,1,1-Trichloroethane	0.370	0.410	0.000	0.090	2.733	0.7576	-32.96	[17]
1,2-Dichloropropane	0.370	0.630	0.000	0.170	2.836	0.7761	-37.20	[17]
1,3-Dichloropropane	0.408	0.800	0.050	0.120	3.106	0.7761	-41.25	[17]
1,4-Dichlorobutane	0.413	0.950	0.000	0.170	3.501	0.9170	-47.15	[17]
1,1,2,2-Tetrachloroethane	0.600	0.760	0.160	0.120	3.803	0.8800	-53.57	[17]
<i>trans</i> 1,2-Dichloroethene	0.430	0.410	0.090	0.050	2.278	0.5922	-31.03	[15]
Trichloroethene	0.520	0.370	0.080	0.030	2.997	0.7146	-35.47	[15]
Tetrachloroethene	0.640	0.440	0.000	0.000	3.584	0.8370	-38.67	[15]
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-29.56	[22]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solV,DEC}}$	Ref.
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-32.97	[3]
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7310	-41.80	[8]
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	0.8718	-46.41	[9]
Hexan-1-ol	0.210	0.420	0.370	0.480	3.610	1.0127	-49.27	[22]
Octan-1-ol	0.199	0.420	0.370	0.480	4.619	1.2945	-59.45	[22]
2-Butanol	0.217	0.360	0.330	0.560	2.338	0.7310	-38.60	[8]
2-Methyl-1-propanol	0.217	0.390	0.370	0.480	2.413	0.7310	-40.06	[8]
2-Methyl-2-propanol	0.180	0.300	0.310	0.600	1.963	0.7310	-35.99	[8]
2-Pentanol	0.195	0.360	0.330	0.560	2.840	0.8718	-43.12	[9]
3-Pentanol	0.218	0.360	0.330	0.560	2.860	0.8718	-41.96	[9]
2-Methyl-1-butanol	0.219	0.390	0.370	0.480	3.011	0.8718	-43.40	[9]
2-Methyl-2-butanol	0.194	0.300	0.310	0.600	2.630	0.8718	-40.49	[9]
3-Methyl-1-butanol	0.192	0.390	0.370	0.480	3.011	0.8718	-44.12	[9]
3-Methyl-2-butanol	0.194	0.330	0.330	0.560	2.793	0.8718	-41.02	[9]
2-Ethoxyethanol	0.237	0.520	0.310	0.810	2.792	0.7896	-42.46	[7]
2-Butoxyethanol	0.201	0.530	0.260	0.830	3.656	1.0714	-50.13	[7]
Methyl <i>tert</i> -butyl ether	0.024	0.210	0.000	0.590	2.372	0.8720	-29.36	[11]
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-32.00	[18]
Tetrahydropyran	0.275	0.470	0.000	0.550	3.057	0.7632	-37.87	[18]
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-37.65	[18]
Dimethyl carbonate	0.142	0.540	0.000	0.570	2.328	0.6644	-37.40	[16]
Diethyl carbonate	0.060	0.580	0.000	0.530	3.412	0.9462	-45.12	ΔH_{vap}
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	-30.30	[13]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solV,DEC}}$	Ref.
2-Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-34.15	[13]
2-Pentanone	0.143	0.680	0.000	0.510	2.755	0.8288	-37.80	[13]
2-Hexanone	0.136	0.680	0.000	0.510	3.286	0.9697	-42.25	[13]
2-Octanone	0.108	0.680	0.000	0.510	4.257	1.2515	-51.07	[13]
2-Undecanone	0.101	0.680	0.000	0.510	5.732	1.6742	-64.89	[13]
Cyclohexanone	0.403	0.860	0.000	0.560	3.792	0.8610	-44.10	[14]
2-Methylcyclohexanone	0.372	0.830	0.000	0.560	4.050	1.0020	-45.12	[14]
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-32.26	[10]
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-35.56	[10]
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-39.71	[10]
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-43.51	[10]
Pentyl acetate	0.067	0.600	0.000	0.450	3.844	1.1693	-46.49	[10]
Hexyl acetate	0.056	0.600	0.000	0.450	4.290	1.3102	-51.38	[10]
Methyl propanoate	0.128	0.600	0.000	0.450	2.431	0.7466	-35.74	[10]
Ethyl propanoate	0.087	0.580	0.000	0.450	2.807	0.8875	-39.30	[10]
Propyl propanoate	0.070	0.560	0.000	0.450	3.338	1.0284	-43.20	[10]
Methyl butanoate	0.106	0.600	0.000	0.450	2.893	0.8875	-40.10	[10]
Ethyl butanoate	0.068	0.580	0.000	0.450	3.271	1.0284	-41.90	[10]
Propyl butanoate	0.050	0.560	0.000	0.450	3.783	1.1693	-43.52	[10]
Benzene	0.610	0.520	0.000	0.140	2.786	0.7160	-33.80	[19]
Toluene	0.601	0.520	0.000	0.140	3.325	0.8570	-38.00	[20]
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	-41.79	[4]
1,2-Dimethylbenzene	0.663	0.560	0.000	0.160	3.939	0.9982	-43.13	[4]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solV,DEC}}$	Ref.
1,3-Dimethylbenzene	0.623	0.520	0.000	0.160	3.839	0.9982	-42.21	[4]
1,4-Dimethylbenzene	0.613	0.520	0.000	0.160	3.839	0.9982	-42.08	[4]
1,1,1,2-Tetrafluoroethane	-0.390	0.160	0.160	0.050	0.403	0.4612	-19.43	[23]
Benzyl alcohol	0.803	0.870	0.330	0.560	4.221	0.9160	-57.68	[2]
2-Phenylethanol	0.811	0.860	0.310	0.650	4.628	1.0569	-58.12	[2]
Ethyl benzoate	0.689	0.850	0.000	0.460	5.075	1.2140	-60.97	[4]
alpha-Pinene	0.438	0.200	0.000	0.140	4.256	1.2574	-40.62	[5]
beta-Pinene	0.515	0.190	0.000	0.150	4.515	1.2574	-42.53	[5]
<i>p</i> -Cymene	0.607	0.490	0.000	0.190	4.590	1.2800	-49.11	[5]
Anisole	0.708	0.750	0.000	0.290	3.890	0.9160	-46.92	[6]
Phenetole	0.681	0.700	0.000	0.320	4.242	1.0569	-50.27	[6]
4-Fluorophenol	0.670	0.970	0.630	0.230	3.844	0.7928	-66.33	[21]
4-Fluoroanisole	0.571	0.740	0.000	0.280	3.904	0.9337	-49.96	[21]

8.3 Results and Discussion

Assembled in Table 8.1 are the values of $\Delta H_{\text{solv,DEC}}$ for 80 gaseous solutes dissolved in diethyl carbonate covering a reasonably wide range of compound types and descriptor values. Preliminary regression analysis of the experimental data gave a small positive numerical value for the b -equation coefficient in Equation (1.24) of $b = 0.64$. The b -coefficient in this Abraham model equation represents the ability of the solvent to act as a hydrogen-bond donor, and when multiplied by the **B** solute descriptor gives the contribution to the enthalpy of solvation resulting from the formation of a hydrogen-bond. Contributions to ΔH_{solv} from hydrogen-bond formation should be negative, not positive as would be the case if the b -coefficient were positive. Based on the molecular structure of diethyl carbonate, one would not expect the solvent molecule to act as a hydrogen-bond donor. The $b \cdot \mathbf{B}$ terms were removed from both enthalpy of solvation equations and the final regression analyses were performed to yield the following Abraham model correlations as can be seen in Equations (8.3) and (8.4):

$$\Delta H_{\text{solv,DEC}} (\text{kJ mol}^{-1}) = - 4.499(0.448) + 6.558(0.954)\mathbf{E} - 15.966(1.083)\mathbf{S} - 25.537(1.213)\mathbf{A} - 8.767(0.191)\mathbf{L} \quad (8.3)$$

(with $N = 80$, $SD = 1.651$, $R^2 = 0.989$, $F = 1729$)

$$\Delta H_{\text{solv,DEC}} (\text{kJ mol}^{-1}) = 5.957(0.879) - 4.458(1.378)\mathbf{E} - 25.925(1.507)\mathbf{S} - 29.492(1.854)\mathbf{A} - 32.549(1.109)\mathbf{V} \quad (8.4)$$

(with $N = 80$, $SD = 2.522$, $R^2 = 0.975$, $F = 730.1$)

where the numerical values in parenthesis give the standard error for the respective process coefficient. Here as elsewhere, N corresponds to the number of solutes, SD denotes the standard deviation, R^2 is the squared correlation coefficient and F

corresponds to Fisher's F-statistic. The SDs associated with Equations (8.3) and (8.4) are slightly larger than the estimated uncertainties in the measured experimental ΔH_{solv} values.

As stated above, the *b*-equation coefficient was set equal to zero because diethyl carbonate should not be capable of acting as a hydrogen-bond donor. There was very little decrease in descriptive ability resulting from setting the *b*-coefficients equal to zero. The SD increased very slightly from 1.648 kJ mol⁻¹ (*b* ≠ 0) to 1.651 kJ mol⁻¹ (*b* = 0) for Equation (8.3) and from 2.519 kJ mol⁻¹ (*b* ≠ 0) to 2.522 kJ mol⁻¹ (*b* = 0) for Equation (8.4), which is less than the estimated uncertainty associated with the experimental data. Both Equations (8.3) and (8.4) are statistically very good with SDs of 1.651 and 2.522 kJ mol⁻¹ for a data set that covers a range of about 80 kJ mol⁻¹ from $\Delta H_{\text{solv,DEC}} = 13.7$ kJ mol⁻¹ for helium to $\Delta H_{\text{solv,DEC}} = -66.3$ kJ mol⁻¹ for 4-fluorophenol. See Figures 8.1 and 8.2 for the plots of the calculated values of $\Delta H_{\text{solv,DEC}}$ based on the derived Abraham model correlations against the observed values. Equation (8.3) is a slightly better equation statistically, and from a thermodynamic standpoint it is the enthalpic temperature derivative of the Abraham model's gas-to-condensed phase transfer equation. The Abraham solute descriptors are taken to be independent of temperature [39-40]. Equation (8.4) might be more useful in some predictive applications in instances where the **L**-descriptor is not known. Equation (8.4) uses the McGowan volume, **V**-descriptor, which can be easily calculated from the individual atomic sizes and numbers of bonds in the molecule [41].

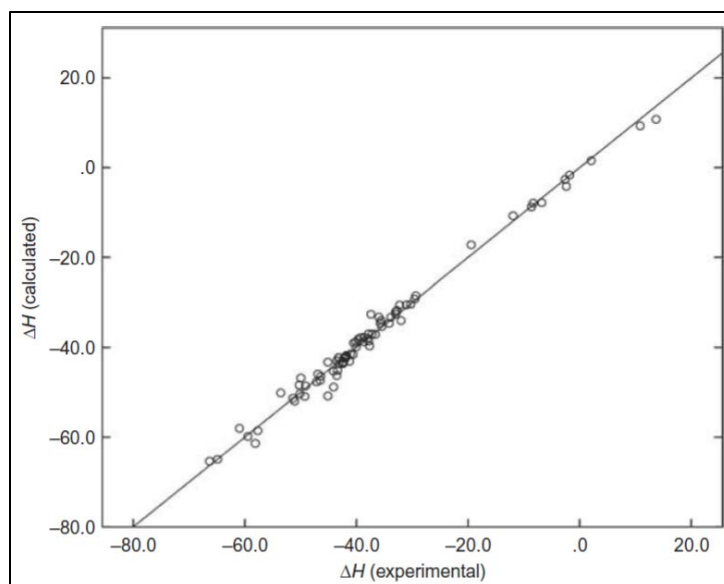


Figure 8.1. Comparison of experimental $\Delta H_{\text{solv,DEC}}$ data for solutes dissolved in diethyl carbonate and calculated values based on Equation (8.3).

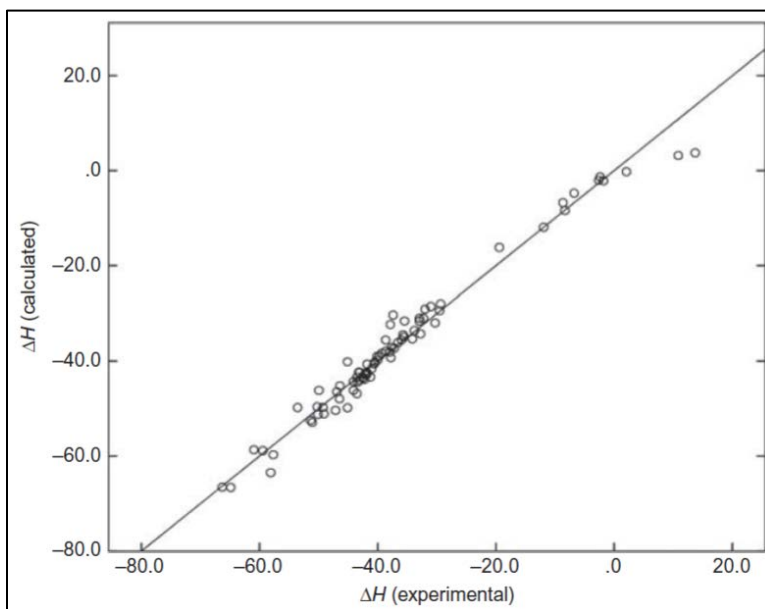


Figure 8.2. Comparison of experimental $\Delta H_{\text{solv,DEC}}$ data for solutes dissolved in diethyl carbonate and calculated values based on Equation (8.4).

Since the enthalpy of solvation database for diethyl carbonate contains experimental values for only 80 different solutes it would be difficult to obtain a good training set correlation by using only half of the experimental values. Therefore, to

assess the predictive ability of Equation (8.3), the parent data points were divided into three subsets (A, B and C) as described in Chapter 2. For each training set, a correlation was derived according to Equations (8.5) – (8.7):

(Training set A and B)

$$\Delta H_{\text{solv,DEC}} \text{ (kJ mol}^{-1}\text{)} = - 4.115(0.462) + 6.480(1.013)\mathbf{E} - 16.601(1.135)\mathbf{S} - 25.113(1.293)\mathbf{A} - 8.848(0.201)\mathbf{L} \quad (8.5)$$

(with N = 54, SD = 1.458, R² = 0.993, F = 1677)

(Training set A and C)

$$\Delta H_{\text{solv,DEC}} \text{ (kJ mol}^{-1}\text{)} = - 4.549(0.575) + 6.946(1.169)\mathbf{E} - 16.089(1.397)\mathbf{S} - 25.431(1.467)\mathbf{A} - 8.775(0.238)\mathbf{L} \quad (8.6)$$

(with N = 53, SD = 1.652, R² = 0.989, F = 1078)

(Training set B and C)

$$\Delta H_{\text{solv,DEC}} \text{ (kJ mol}^{-1}\text{)} = - 4.937(0.631) + 6.310(1.375)\mathbf{E} - 15.135(1.484)\mathbf{S} - 25.999(1.753)\mathbf{A} - 8.665(0.270)\mathbf{L} \quad (8.7)$$

(with N = 53, SD = 1.780, R² = 0.986, F = 840.0)

Each validation computation gave a training set correlation equation having coefficients not too different from that obtained from the parent 80 compound database. The training set equations were then used to predict $\Delta H_{\text{solv,DEC}}$ values for the compounds in the respective test sets (A, B and C). Computations on the three test sets yielded SD = 2.062 (test set C), SD = 1.686 (test set B) and SD = 1.458 kJ mol⁻¹ (test set A); average absolute errors (AAE) = 1.456 (test set C), AAE = 1.162 (test set B) and AAE = 1.141 kJ mol⁻¹ (test set A); and average errors (AE) = 0.371 (test set C), AE = 0.051 (test set B) and AE = -0.388 kJ mol⁻¹ (test set A). There is therefore very little

bias in the predictions based on Equations (8.4)–(8.6). Equation (8.4) was validated in a similar fashion. To conserve space, reported are only the statistical results for the three test set calculations: SD = 2.654 (test set C), SD = 2.341 (test set B) and SD = 2.965 (test set A); AAE = 1.919 (test set C), AAE = 1.535 (test set B) and AAE = 1.958 (test set A); and AE = 0.299 (test set C), AE = -0.050 (test set B) and AE = -0.376 (test set A). Again, there is very little bias in predictions based on the Abraham model correlations.

Presented in Table 8.2 are the collected experimental enthalpies of solvation for 57 inorganic gases and organic compounds dissolved in dimethyl carbonate. Regression analysis of the 57 $\Delta H_{\text{solv,DMC}}$ data points in accordance with the Abraham model gave the following two mathematical correlations as can be seen in Equations (8.8) and (8.9):

$$\Delta H_{\text{solv,DMC}} (\text{kJ mol}^{-1}) = -3.030(0.696) + 7.749(1.532)\mathbf{E} - 18.894(1.687)\mathbf{S} - 30.719(2.063)\mathbf{A} - 8.390(0.360)\mathbf{L} \quad (8.8)$$

(with N = 57, SD = 2.258, R² = 0.981, F = 660.0)

$$\Delta H_{\text{solv,DMC}} (\text{kJ mol}^{-1}) = 5.749(1.243) - 3.022(1.904)\mathbf{E} - 28.852(2.074)\mathbf{S} - 32.746(2.863)\mathbf{A} - 29.655(1.635)\mathbf{V} \quad (8.9)$$

(with N = 57, SD = 3.092, R² = 0.964, F = 346.3)

Table 8.2. Values of the gas-to-dimethyl carbonate solvation enthalpy, $\Delta H_{\text{solv,DMC}}$ (in kJ mol^{-1}), at 298.15 K for 57 solutes together with the solute descriptors.

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv,DMC}}$	Ref.
Neon	0.000	0.000	0.000	0.000	-1.575	0.0850	15.31	[1]
Argon	0.000	0.000	0.000	0.000	-0.688	0.1900	7.62	[1]
Krypton	0.000	0.000	0.000	0.000	-0.211	0.2460	-2.53	[1]
Xenon	0.000	0.000	0.000	0.000	0.378	0.3290	-5.64	[1]
Sulfur hexafluoride	-0.600	-0.200	0.000	0.000	-0.120	0.4643	-3.34	[1]
Methane	0.000	0.000	0.000	0.000	-0.323	0.2495	-1.27	[1]
Ethane	0.000	0.000	0.000	0.000	0.492	0.3904	-7.85	[1]
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358	-30.34	[12]
Ethene	0.107	0.100	0.000	0.070	0.289	0.3470	-9.17	[1]
1,2-Dichloroethane	0.420	0.640	0.100	0.110	2.573	0.6352	-35.41	[31]
1,1,1-Trichloroethane	0.370	0.410	0.000	0.090	2.733	0.7576	-31.76	[31]
<i>trans</i> 1,2-Dichloroethene	0.430	0.410	0.090	0.050	2.278	0.5922	-30.29	[15]
Trichloroethene	0.520	0.370	0.080	0.030	2.997	0.7146	-34.18	[15]
Tetrachloroethene	0.640	0.440	0.000	0.000	3.584	0.8370	-37.07	[15]
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-32.06	[28]
Propan-1-ol	0.236	0.420	0.370	0.480	2.031	0.5900	-36.12	[28]
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7310	-39.78	[26]
2-Butanol	0.217	0.360	0.330	0.560	2.338	0.7310	-36.84	[26]
2-Methyl-1-propanol	0.217	0.390	0.370	0.480	2.413	0.7310	-38.70	[26]
2-Methyl-2-propanol	0.180	0.300	0.310	0.600	1.963	0.7310	-34.72	[26]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solV,DMC}}$	Ref.
Methyl <i>tert</i> -butyl ether	0.024	0.210	0.000	0.590	2.372	0.8720	-28.25	[11]
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-32.55	[18]
Tetrahydropyran	0.275	0.470	0.000	0.550	3.057	0.7632	-37.06	[18]
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-38.05	[18]
Dimethyl carbonate	0.142	0.540	0.000	0.570	2.328	0.6644	-37.70	ΔH_{vap}
Diethyl carbonate	0.060	0.580	0.000	0.530	3.412	0.9462	-43.60	[16]
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	-30.45	[13]
2-Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-33.35	[13]
2-Pentanone	0.143	0.680	0.000	0.510	2.755	0.8288	-36.77	[13]
2-Hexanone	0.136	0.680	0.000	0.510	3.286	0.9697	-40.88	[13]
2-Octanone	0.108	0.680	0.000	0.510	4.257	1.2515	-47.97	[13]
2-Undecanone	0.101	0.680	0.000	0.510	5.732	1.6742	-60.77	[13]
Cyclohexanone	0.403	0.860	0.000	0.560	3.792	0.8610	-43.03	[14]
2-Methylcyclohexanone	0.372	0.830	0.000	0.560	4.050	1.0020	-44.25	[14]
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-32.30	[27]
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-35.42	[27]
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-36.48	[27]
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-42.34	[27]
Pentyl acetate	0.067	0.600	0.000	0.450	3.844	1.1693	-47.34	[27]
Hexyl acetate	0.056	0.600	0.000	0.450	4.290	1.3102	-49.61	[27]
Vinyl acetate	0.223	0.640	0.000	0.430	2.152	0.7036	-34.48	[27]
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	-39.25	[25]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv,DMC}}$	Ref.
1,2-Dimethylbenzene	0.663	0.560	0.000	0.160	3.939	0.9982	-40.56	[25]
1,3-Dimethylbenzene	0.623	0.520	0.000	0.160	3.839	0.9982	-39.73	[25]
1,4-Dimethylbenzene	0.613	0.520	0.000	0.160	3.839	0.9982	-39.49	[25]
1,1,1,2-Tetrafluoroethane	-0.390	0.160	0.160	0.050	0.403	0.4612	-19.57	[23]
Benzyl alcohol	0.803	0.870	0.330	0.560	4.221	0.9160	-55.75	[2]
2-Phenylethanol	0.811	0.860	0.310	0.650	4.628	1.0569	-66.70	[2]
Ethyl benzoate	0.689	0.850	0.000	0.460	5.075	1.2140	-59.28	[25]
alpha-Pinene	0.438	0.200	0.000	0.140	4.256	1.2574	-37.35	[5]
beta-Pinene	0.515	0.190	0.000	0.150	4.515	1.2574	-39.40	[5]
<i>p</i> -Cymene	0.607	0.490	0.000	0.190	4.590	1.2800	-45.72	[5]
Anisole	0.708	0.750	0.000	0.290	3.890	0.9160	-45.48	[6]
Phenetole	0.681	0.700	0.000	0.320	4.242	1.0569	-48.56	[6]
Acetic acid	0.265	0.640	0.620	0.440	1.816	0.4648	-49.03	[29]
Propanoic acid	0.233	0.650	0.600	0.450	2.290	0.6057	-51.49	[29]
1,2-Epoxybutane	0.222	0.560	0.030	0.350	2.226	0.6223	-32.91	[30]

As before, the $b \cdot \mathbf{B}$ terms were eliminated from both correlations because the calculated process coefficients were small and dimethyl carbonate has no acidic hydrogen-bonding character. Both Equations (8.8) and (8.9) are statistically very good with SDs of 2.258 and 3.092 kJ mol^{-1} for a data set that covers a range of about 82 kJ mol^{-1} from $\Delta H_{\text{solv,DMC}} = 15.3 \text{ kJ mol}^{-1}$ for helium to $\Delta H_{\text{solv,DMC}} = -66.7 \text{ kJ mol}^{-1}$ for 2-

phenylethanol. Figures 8.3 and 8.4 compare the calculated values of $\Delta H_{\text{solv,DMC}}$ based on Equations (8.8) and (8.9) against the observed values. The SDs associated with Equations (8.8) and (8.9) are slightly larger than the estimated uncertainties in the measured experimental ΔH_{solv} values. There is insufficient experimental $\Delta H_{\text{solv,DMC}}$ to perform a training set and test set analysis.

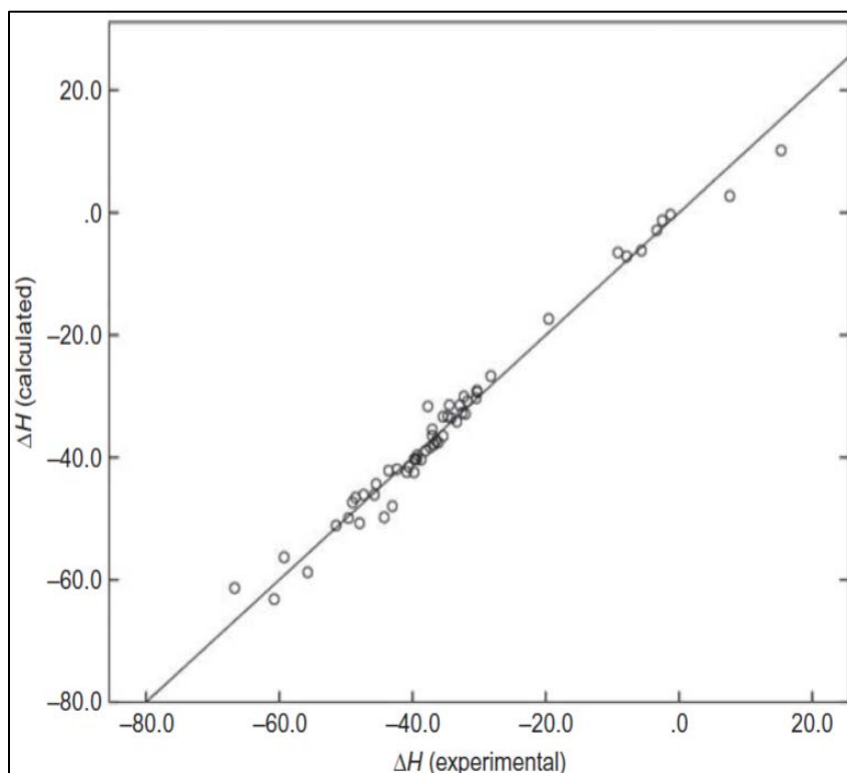


Figure 8.3. Comparison of experimental $\Delta H_{\text{solv,DMC}}$ data for solutes dissolved in diethyl carbonate and calculated values based on Equation (8.8).

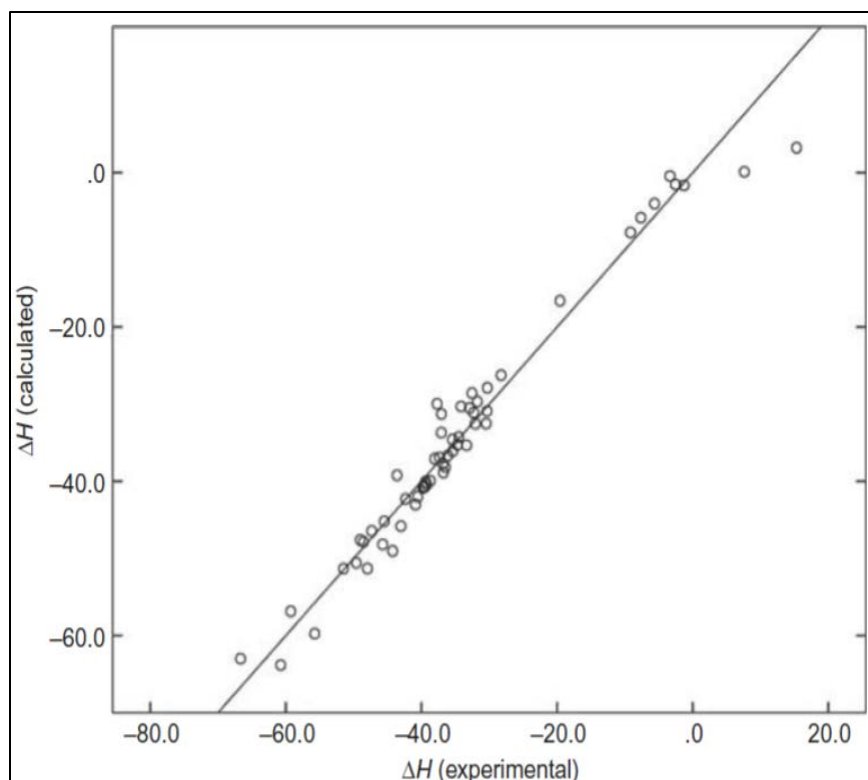


Figure 8.4. Comparison of experimental $\Delta H_{\text{solvent,DMC}}$ data for solutes dissolved in diethyl carbonate and calculated values based on Equation (8.9).

Each term in the Abraham model represents a different type of solute–solvent interaction. The total contribution of the hydrogen-bonding interactions would be given by the sum of the $a_{h,l} \cdot \mathbf{A} + b_{h,l} \cdot \mathbf{B}$ and $a_{h,v} \cdot \mathbf{A} + b_{h,v} \cdot \mathbf{B}$ terms in Equations (1.24) and (1.25). It should be possible now to compare the hydrogen-bonding interactions of select proton–donor solutes in both alkyl carbonate solvents (R–O–C(=O)–O–R) and dialkyl ester solvents (R–C(=O)–O–R). The two solvent classes have several similar structural features. Both have a C=O carbon double and at least one C–O single bond, but the carbonates have an additional C–O single bond. Abraham model correlations have been developed for two dialkyl carbonates, for one cycloalkyl carbonate (PC) and for one dialkyl ester solvent (ethyl acetate (EA)). The hydrogen-bonding contributions to

the enthalpies of solvation, ΔH_{HB} , in the aforementioned solvents would be given by the following Equations (8.10) – (8.13):

$$\Delta H_{\text{HB,DMC}} \text{ (in kJ mol}^{-1}\text{)} = -30.719(2.063)\mathbf{A} \quad (8.10)$$

$$\Delta H_{\text{HB,DEC}} \text{ (in kJ mol}^{-1}\text{)} = -25.537(1.213)\mathbf{A} \quad (8.11)$$

$$\Delta H_{\text{HB,PC}} \text{ (in kJ mol}^{-1}\text{)} = -17.898(2.185)\mathbf{A} - 12.596(1.362)\mathbf{B} \quad (8.12)$$

$$\Delta H_{\text{HB,EA}} \text{ (in kJ mol}^{-1}\text{)} = -28.763(1.423)\mathbf{A} \quad (8.13)$$

The Abraham model correlations containing the **L** solute descriptor are focused on because this form of the Abraham model enthalpy of solvation correlation is the $1/T$ derivative of the Abraham model gas-to-organic solvent $\log K$ correlation. Equation (1.25), which contains the **V** solute descriptor, is not the $1/T$ derivative of the Abraham model water-to-organic solvent $\log P$ correlation. Numerical values of the $a_{\text{h,l}}$ process coefficients for PC and EA were taken from the work of Mintz and coworkers [42-43]. The non-zero value in the b -coefficient in Equation (8.12) for PC suggests that the solvent does exhibit some hydrogen-bond acidic character. This is consistent with the fact that the Abraham model correlation (Equation (8.14)) for the gas-to-anhydrous partition coefficient [44] does have a small non-zero b -equation coefficient, which is indicative of a weakly acidic solvent. This is further supported by the practical partition coefficient measurements of solutes distributed between heptane and PC [45].

$$\log K = -0.366 - 0.413\mathbf{E} + 2.587\mathbf{S} + 2.207\mathbf{A} + 0.455\mathbf{B} + 0.719\mathbf{L} \quad (8.14)$$

Values of ΔH_{HB} for several acidic solutes with dimethyl carbonate, diethyl carbonate, PC and EA are given in Table 8.3. The Abraham model calculated ΔH_{HB} values for 4-fluorophenol are in reasonably good agreement with the published literature values of Arnett and coworkers [21]: $\Delta H_{\text{HB,EA}} = -18.1 \pm 0.9 \text{ kJ mol}^{-1}$ vs $\Delta H_{\text{HB,EA}} = -19.8$

kJ mol⁻¹ for EA; $\Delta H_{\text{HB,PC}} = -14.2 \pm 1.7$ kJ mol⁻¹ vs $\Delta H_{\text{HB,PC}} = -19.0$ kJ mol⁻¹ for PC; and $\Delta H_{\text{HB,DEC}} = -16.1 \pm 0.8$ kJ mol⁻¹ vs $\Delta H_{\text{HB,DEC}} = -17.6$ kJ mol⁻¹ for diethyl carbonate. The published literature values were based on the ‘pure base’ method which involved measuring the enthalpy associated with injecting a small quantity of the hydrogen-bonding acid into a large excess of the pure base solvent.

Table 8.3. Enthalpies of hydrogen-bond interactions, ΔH_{HB} (in kJ mol⁻¹) between different proton donors with dimethyl carbonate, diethyl carbonate, propylene carbonate and ethyl acetate based on the Abraham model correlations (Equations (8.10) – (8.13)).

Solute	$\Delta H_{\text{HB,DMC}}$	$\Delta H_{\text{HB,DEC}}$	$\Delta H_{\text{HB,PC}}$	$\Delta H_{\text{HB,EA}}$
Chloroform (A = 0.150; B = 0.020)	-4.6	-3.8	-2.9	-4.3
Methanol (A = 0.430; B = 0.470)	-13.2	-11.0	-13.6	-12.4
Ethanol (A = 0.370; B = 0.480)	-11.4	-9.5	-12.7	-10.6
1-Propanol (A = 0.370; B = 0.480)	-11.4	-9.5	-12.7	-10.6
1-Butanol (A = 0.370; B = 0.480)	-11.4	-9.5	-12.7	-10.6
1-Pentanol (A = 0.370; B = 0.480)	-11.4	-9.5	-12.7	-10.6
1-Hexanol (A = 0.370; B = 0.480)	-11.4	-9.5	-12.7	-10.6
1-Heptanol (A = 0.370; B = 0.480)	-11.4	-9.5	-12.7	-10.6
1-Octanol (A = 0.370; B = 0.480)	-11.4	-9.5	-12.7	-10.6
2-Ethoxyethanol (A = 0.310; B = 0.810)	-9.5	-7.9	-15.8	-8.9
2-Butoxyethanol (A = 0.260; B = 0.830)	-8.0	-6.6	-15.1	-7.5
Benzyl alcohol (A = 0.330; B = 0.560)	-10.1	-8.4	-13.0	-9.5
Phenol (A = 0.600; B = 0.300)	-18.4	-15.3	-14.5	-17.3
3-Methylphenol (A = 0.570; B = 0.340)	-17.5	-14.6	-14.5	-16.4
4-Fluorophenol (A = 0.630; B = 0.230)	-19.4	-16.1	-14.2	-18.1
2-Methoxyphenol (A = 0.220; B = 0.520)	-6.8	-5.6	-10.5	-6.3
4-Methoxyphenol (A = 0.570; B = 0.480)	-17.5	-14.6	-16.2	-16.4
Propylamine (A = 0.160; B = 0.610)	-4.9	-4.1	-10.5	-4.6
Butylamine (A = 0.160; B = 0.610)	-4.9	-4.1	-10.5	-4.6
Diethylamine (A = 0.080; B = 0.690)	-2.5	-2.0	-10.1	-2.3
Dipropylamine (A = 0.080; B = 0.690)	-2.5	-2.0	-10.1	-2.3

(table continues)

Solute	$\Delta H_{\text{HB,DMC}}$	$\Delta H_{\text{HB,DEC}}$	$\Delta H_{\text{HB,PC}}$	$\Delta H_{\text{HB,EA}}$
Aniline (A = 0.260; B = 0.410)	-8.0	-6.6	-9.8	-7.5
2-Methylaniline (A = 0.230; B = 0.450)	-7.1	-5.9	-9.8	-6.6
3-Chloroaniline (A = 0.300; B = 0.300)	-9.2	-7.7	-9.1	-8.6
N-Methylaniline (A = 0.170; B = 0.430)	-5.2	-4.3	-8.5	-4.9
Indole (A = 0.440; B = 0.180)	-13.5	-11.2	-10.1	-12.7
Imidazole (A = 0.420; B = 0.780)	-12.9	-10.7	-17.3	-12.1

As an informative note, the pure base method gives the total hydrogen-bonding interactions between the solute and the solvent. The Abraham model correlations, on the other hand, enable one to calculate the separate interactions for the solvent acting as a hydrogen-bond donor and as a hydrogen-bond acceptor.

8.4 Conclusions

Mathematical expressions are derived for correlating enthalpies of solvation of inorganic gases and organic solutes dissolved in dimethyl carbonate and diethyl carbonate based on the Abraham Solvation Parameter Model. The correlations presented in this paper should allow one to predict $\Delta H_{\text{HB,DMC}}$ and $\Delta H_{\text{HB,DEC}}$ values for additional solutes at 298.15 K to within $\pm 3 \text{ kJ mol}^{-1}$ provided that one stays within the chemical space defined by the solute descriptors used in determining the Abraham model correlations (Equations (8.3), (8.4), (8.8) and (8.9)). The Abraham model can also be useful for analysis of intermolecular solute–solvent interactions, such as hydrogen-bonding interactions between a proton donor solute and an alkyl carbonate (e.g., dimethyl carbonate, diethyl carbonate and PC) or alkyl ethanoate (e.g., EA) solvent.

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CHAPTER 9

DEVELOPMENT OF ABRAHAM SOLVATION PARAMETER MODEL EXPRESSIONS FOR PREDICTING THE ENTHALPIES OF SOLVATION OF SOLUTES DISSOLVED IN 1-ALKANOL SOLVENTS (C₄ – C₆)*

9.1 Introduction

Molecular interactions play an important role in governing the equilibrium distribution of a solute between two immiscible liquid phases and in determining the solubility of crystalline nonelectrolyte solutes in different organic solvents of varying polarity and hydrogen-bonding character. Strong solute–solvent interactions favor solute transfer into the phase/solvent, while weak solute–solvent interactions would not favor the solubilization of solute into a strongly self-associating solvent media.

In the present communication, earlier [1-14] enthalpy of solvation, ΔH_{solv} , studies of solutes dissolved in organic solvents are extended to include two more solvents capable of self-associating through hydrogen-bond formation, namely 1-pentanol and 1-hexanol. These two solvents can act as both a hydrogen-bond donor and a hydrogen-bond acceptor. Reasonably accurate predictive expressions for enthalpies of solvation have been obtained for all types of organic solvents studied thus far. Abraham model ΔH_{solv} correlations are derived for 1-pentanol and 1-hexanol based on 92 and 84 experimental ΔH_{solv} values compiled from the published chemical and engineering literature. As part of the current study, previously published ΔH_{solv} correlations for 1-butanol are updated by including additional 28 data points in the regression analysis.

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The added data points increase the chemical diversity of the 1-butanol data set and include more alkylamine and alkyl alkanoate solutes in the regression analysis.

9.2 Computational Methodology and Data Sets

A search of the literature found a large number of published papers [15-79] that reported experimental excess molar enthalpies of mixing of binary mixtures containing 1-pentanol or 1-hexanol and partial molar enthalpies of solution of inorganic and organic compounds in the two solvents of interest. The compiled enthalpy data for the liquid and solid organic compounds were converted to gas-to-1-alkanol solvent enthalpies of solvation using Equations (1.22) and (1.23) as described in Chapter 1.

Based on an initial assessment of the available experimental data, all experimental data that pertained to temperatures outside of the temperature range 288 K–313 K have been eliminated. Enthalpies of solvation are temperature-dependent, and the introduction of large errors in the database by including experimental data far removed from 298.15 K was not wanted. For several of the organic solutes, there were multiple, independently determined enthalpy values. In such cases, direct calorimetric enthalpy of solution data were selected over values calculated from excess molar enthalpy of mixing data. Partial molar enthalpies of solution can easily be calculated from enthalpy of mixing data using standard thermodynamic relationships [80]. Excess enthalpy of mixing data was used only if experimental measurements had been performed at solute concentrations of less than 0.06 mole fraction. Using the aforementioned criteria, 92 molar enthalpies of solvation in 1-pentanol and 84 molar enthalpies of solvation in 1-hexanol were selected for regression analysis. The

experimental $\Delta H_{\text{solv,PtOH}}$ and $\Delta H_{\text{solv,HxOH}}$ values are listed in Tables 9.1 and 9.2, respectively. In Table 9.3, the $\Delta H_{\text{solv,BtOH}}$ values are listed for the 28 additional solutes that were added to the 1-butanol data set. The initial $\Delta H_{\text{solv,BtOH}}$ data set was published as supporting data that accompanied an earlier paper [14] reporting enthalpy of solvation correlations for methanol, ethanol and 1-butanol.

Table 9.1. Values of the gas-to-1-pentanol solvation enthalpy, $\Delta H_{\text{solv,PtOH}}$ for 92 solutes together with the solute descriptors.

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv}}^{\text{exp}}$	Ref
Xenon	0.000	0.000	0.000	0.000	0.378	0.3290	-9.75	[21]
Carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.2809	-9.30	[58]
Methane	0.000	0.000	0.000	0.000	-0.323	0.2495	-2.51	[17]
Ethane	0.000	0.000	0.000	0.000	0.492	0.3904	-10.00	[17]
Propane	0.000	0.000	0.000	0.000	1.050	0.5313	-18.43	[30]
Butane	0.000	0.000	0.000	0.000	1.615	0.6722	-21.95	[30]
2-Methylpropane	0.000	0.000	0.000	0.000	1.409	0.6722	-21.00	[30]
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	-26.03	[19]
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-30.42	[15]
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-35.21	[23]
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	-40.46	[56]
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	-44.72	[15]
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	-49.24	[18]
Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-58.97	[15]
Hexadecane	0.000	0.000	0.000	0.000	7.714	2.3630	-77.39	[15]
3-Ethylpentane	0.000	0.000	0.000	0.000	3.091	1.0949	-33.95	[15]
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358	-33.78	[15]
Methylcyclopentane	0.225	0.100	0.000	0.000	2.907	0.8454	-29.81	[31]
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	-31.50	[15]
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	-33.32	[25]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv}}^{\text{exp}}$	Ref
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	-41.57	[15]
Bicyclohexyl	0.523	0.450	0.000	0.040	6.044	1.5822	-56.07	[15]
1-Propene	0.100	0.080	0.000	0.070	0.946	0.4883	-18.50	[30]
1-Butene	0.100	0.080	0.000	0.070	1.491	0.6292	-19.57	[30]
<i>cis</i> -2-Butene	0.140	0.080	0.000	0.050	1.737	0.6292	-21.65	[29]
<i>trans</i> -2-Butene	0.126	0.080	0.000	0.050	1.664	0.6292	-21.30	[30]
2-Methylprop-1-ene	0.120	0.080	0.000	0.080	1.579	0.6292	-19.80	[30]
1,3-Butadiene	0.320	0.230	0.000	0.100	1.543	0.5862	-20.50	[30]
1-Hexene	0.080	0.080	0.000	0.070	2.572	0.9110	-33.17	[31]
1-Heptene	0.092	0.080	0.000	0.070	3.063	1.0519	-34.49	[15]
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-35.04	[31]
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	0.8718	-56.90	ΔH_{vap}
Heptan-1-ol	0.211	0.420	0.370	0.480	4.115	1.1536	-66.60	[20]
Octan-1-ol	0.199	0.420	0.370	0.480	4.619	1.2945	-70.72	[20]
Nonan-1-ol	0.193	0.420	0.370	0.480	5.120	1.4354	-76.44	[20]
Decan-1-ol	0.191	0.420	0.370	0.480	5.628	1.5763	-80.84	[20]
1-Adamantanol	0.940	0.900	0.310	0.660	5.634	1.2505	-74.82	[57]
Dimethyl ether	0.000	0.270	0.000	0.410	1.285	0.4491	-17.65	[29]
Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	-26.41	[31]
Dibutyl ether	0.000	0.250	0.000	0.450	3.924	1.2945	-42.77	[53]
Diisopropyl ether	-0.060	0.160	0.000	0.580	2.530	1.0127	-31.25	[54]
Methyl <i>tert</i> -butyl ether	0.024	0.210	0.000	0.590	2.380	0.8718	-29.69	[52]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv}}^{\text{exp}}$	Ref
Carbon tetrachloride	0.458	0.380	0.000	0.000	2.823	0.7391	-32.55	[15]
Dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943	-25.98	[31]
Chloroethane	0.227	0.400	0.000	0.100	1.678	0.5128	-22.85	[29]
1-Chlorobutane	0.210	0.400	0.000	0.100	2.722	0.7946	-31.45	[32]
1-Chlorohexane	0.201	0.390	0.000	0.090	3.708	1.0764	-40.41	[42]
1-Chlorooctane	0.191	0.400	0.000	0.090	4.708	1.3582	-49.77	[43]
2-Methyl-2-bromopropane	0.305	0.290	0.000	0.070	2.609	0.8472	-29.18	[26]
2-Methyl-2-chloropropane	0.142	0.300	0.000	0.030	2.273	0.7946	-26.42	[66]
2-Methyl-2-iodopropane	0.589	0.350	0.000	0.190	3.439	0.9304	-32.81	[50]
2-Chloro-2-methylbutane	0.171	0.270	0.000	0.150	2.858	0.9355	-32.09	[45]
2-Chloro-2-methylpentane	0.207	0.390	0.000	0.130	3.520	1.0764	-37.30	[45]
2-Methyl-2-bromobutane	0.343	0.400	0.000	0.150	3.400	0.9881	-35.18	[49]
1,3-Dichloropropane	0.408	0.800	0.050	0.120	3.106	0.7761	-37.29	[46]
1,5-Dichloropentane	0.421	0.960	0.000	0.170	4.251	1.0579	-45.97	[46]
1,6-Dichlorohexane	0.397	0.960	0.000	0.170	4.723	1.1988	-51.08	[46]
1-Bromoadamantane	1.070	0.900	0.000	0.200	6.130	1.3668	-55.70	[75]
Trichloroethene	0.520	0.370	0.080	0.030	2.997	0.7146	-34.02	[55]
1,1,2,2-Tetrachloroethane	0.600	0.760	0.160	0.120	3.803	0.8800	-47.34	[22]
1,1-Difluoroethane	-0.250	0.470	0.040	0.070	0.570	0.4258	-16.70	[29]
Dimethyl carbonate	0.142	0.540	0.000	0.570	2.328	0.6644	-25.84	[48]
Diethyl carbonate	0.060	0.580	0.000	0.530	3.412	0.9462	-36.24	[44]
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	-28.42	[31]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{sol}}^{\text{exp}}$	Ref
2-Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-28.15	[33]
4-Methyl-2-pentanone	0.111	0.650	0.000	0.510	3.089	0.9697	-37.33	[33]
2-Heptanone	0.123	0.680	0.000	0.510	3.760	1.1106	-41.44	[35]
Cyclohexanone	0.403	0.860	0.000	0.560	3.792	0.8611	-38.50	[28]
Butanal	0.187	0.650	0.000	0.450	2.270	0.6879	-26.32	[31]
Aniline	0.955	0.960	0.260	0.410	3.934	0.8162	-52.93	[34]
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-26.49	[31]
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-29.04	[31]
Propyl formate	0.132	0.630	0.000	0.380	2.433	0.7466	-31.61	[27]
1-Butylamine	0.224	0.350	0.160	0.610	2.618	0.7720	-45.60	[16]
1-Heptylamine	0.197	0.350	0.160	0.610	4.153	1.1947	-59.90	[16]
<i>N</i> -Ethyl- <i>N</i> -butylamine	0.124	0.320	0.080	0.650	3.269	1.0538	-51.70	[16]
Dipropylamine	0.124	0.300	0.080	0.690	3.351	1.0538	-50.41	[24]
Dibutylamine	0.107	0.300	0.080	0.690	4.349	1.3356	-60.70	[16]
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-43.69	[16]
Benzene	0.610	0.520	0.000	0.140	2.786	0.7176	-31.49	[15]
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	-35.86	[37]
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	-38.84	[34]
<i>N,N</i> -Dimethylformamide	0.367	1.310	0.000	0.740	3.173	0.6468	-41.79	[51]
Tetramethylsilicon	-0.057	0.080	0.000	0.000	1.812	0.9179	-23.20	[41]
Ethylene carbonate	0.381	1.250	0.000	0.580	2.670	0.5558	-35.00	[38]
Diethyl malonate	0.112	0.900	0.000	0.810	4.470	1.2437	-48.73	[40]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv}}^{\text{exp}}$	Ref
beta-Pinene	0.515	0.190	0.000	0.150	4.515	1.2574	-44.21	[47]
D-Limonene	0.501	0.310	0.000	0.230	4.688	1.3230	-47.03	[39]
1,8-Cineole	0.383	0.330	0.000	0.760	4.688	1.4250	-53.20	[36]
1,1,2-Trifluoroethane	0.010	0.130	0.000	0.000	2.210	0.8107	-24.22	[31]
1,3-Diaminopropane	0.446	0.610	0.430	1.140	2.852	0.7309	-65.20	[16]
N-Methylformamide	0.405	1.300	0.400	0.550	2.687	0.5059	-50.86	[51]

Table 9.2. Values of the gas-to-1-hexanol solvation enthalpy, $\Delta H_{\text{solv,HxOH}}$ for 84 solutes together with the solute descriptors.

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv}}^{\text{exp}}$	Ref
Methane	0.000	0.000	0.000	0.000	-0.323	0.2945	-2.09	[17]
Ethane	0.000	0.000	0.000	0.000	0.492	0.3904	-8.79	[17]
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	-25.89	[19]
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-30.68	[15]
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	-44.90	[15]
Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-58.79	[15]
Hexadecane	0.000	0.000	0.000	0.000	7.714	2.3630	-77.80	[15]
2-Methylpentane	0.000	0.000	0.000	0.000	2.503	0.9540	-28.87	[62]
3-Methylpentane	0.000	0.000	0.000	0.000	2.581	0.9540	-29.30	[62]
2,2-Dimethylbutane	0.000	0.000	0.000	0.000	2.352	0.9540	-26.67	[62]
2,3-Dimethylbutane	0.000	0.000	0.000	0.000	2.495	0.9540	-28.14	[62]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv}}^{\text{exp}}$	Ref
3-Ethylpentane	0.000	0.000	0.000	0.000	3.091	1.0949	-34.20	[15]
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358	-33.95	[15]
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	-31.53	[15]
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	-33.63	[25]
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	-41.70	[15]
Bicyclohexyl	0.523	0.450	0.000	0.040	6.044	1.5822	-56.40	[15]
1-Heptene	0.092	0.080	0.000	0.070	3.063	1.0519	-34.57	[15]
Propan-1-ol	0.236	0.420	0.370	0.480	2.031	0.5900	-47.08	[78]
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7309	-52.00	[61]
Hexan-1-ol	0.210	0.420	0.370	0.480	3.610	1.0170	-61.60	ΔH_{vap}
Octan-1-ol	0.199	0.420	0.370	0.480	4.619	1.2950	-70.89	[61]
Decan-1-ol	0.191	0.420	0.370	0.480	5.628	1.5763	-81.06	[77]
Dibutyl ether	0.000	0.250	0.000	0.450	3.924	1.2945	-42.82	[53]
Dipropyl ether	0.008	0.250	0.000	0.450	2.954	1.0127	-33.61	[59]
Diisopropyl ether	-0.060	0.160	0.000	0.580	2.530	1.0127	-31.16	[54]
1,2-Dimethoxyethane	0.116	0.670	0.000	0.680	2.654	0.7896	-31.95	[59]
2-Methyl-2-bromopropane	0.305	0.290	0.000	0.070	2.609	0.9304	-28.97	[41]
Chloroform	0.425	0.490	0.150	0.020	2.480	0.6167	-34.60	[68]
Carbon tetrachloride	0.458	0.380	0.000	0.000	2.823	0.7391	-32.28	[15]
1-Chlorobutane	0.210	0.400	0.000	0.100	2.722	0.7946	-31.30	[32]
1-Chlorohexane	0.201	0.400	0.000	0.100	3.777	1.0764	-40.39	[42]
1-Chlorooctane	0.191	0.400	0.000	0.090	4.708	1.3582	-49.89	[43]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{sol}}^{\text{exp}}$	Ref
2-Methyl-2-chloropropane	0.142	0.300	0.000	0.030	2.273	0.7946	-26.28	[41]
1,3-Dichloropropane	0.408	0.800	0.050	0.120	3.106	0.7761	-36.46	[46]
1,4-Dichlorobutane	0.413	0.950	0.000	0.170	3.501	0.9170	-41.65	[46]
1,5-Dichloropentane	0.421	0.960	0.000	0.170	4.251	1.0579	-45.77	[46]
1,6-Dichlorohexane	0.397	0.960	0.000	0.170	4.723	1.1988	-50.90	[46]
Trichloroethene	0.520	0.370	0.080	0.030	2.997	0.7146	-34.08	[55]
1,1,2,2-Tetrachloroethane	0.600	0.760	0.160	0.120	3.803	0.8800	-46.77	[22]
2-Methyl-2-iodopropane	0.589	0.350	0.000	0.190	3.439	0.9304	-32.78	[41]
Xenon	0.000	0.000	0.000	0.000	0.378	0.3290	-9.89	[21]
Diethyl carbonate	0.060	0.580	0.000	0.530	3.412	0.9462	-36.27	[74]
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	-23.52	[59]
2-Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-28.03	[33]
2-Hexanone	0.136	0.680	0.000	0.510	3.286	0.9697	-35.20	[60]
4-Methyl-2-pentanone	0.111	0.650	0.000	0.510	3.089	0.9697	-38.86	[33]
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-28.49	[59]
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-37.07	[76]
Methyl pentanoate	0.108	0.600	0.000	0.450	3.392	1.0284	-37.23	[63]
Methyl heptanoate	0.079	0.600	0.000	0.450	4.356	1.3102	-46.82	[63]
Methyl nonanoate	0.056	0.600	0.000	0.450	5.321	1.5920	-55.79	[63]
Methyl undecanoate	0.051	0.630	0.000	0.450	6.296	1.8738	-65.03	[63]
Methyl tridecanoate	0.042	0.640	0.000	0.450	7.271	2.1566	-76.43	[63]
Methyl pentadecanoate	0.035	0.680	0.000	0.450	8.242	2.4374	-86.88	[63]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{sol}}^{\text{exp}}$	Ref
Propyl propanoate	0.070	0.560	0.000	0.450	3.338	1.0284	-37.27	[72]
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	-23.81	[69]
Butyronitrile	0.188	0.900	0.000	0.360	2.548	0.6860	-30.78	[71]
Dimethyl sulphoxide	0.522	1.740	0.000	0.880	3.459	0.6126	-47.60	[64]
Butylamine	0.244	0.350	0.160	0.610	2.618	0.7720	-44.50	[16]
1-Heptylamine	0.197	0.350	0.160	0.610	4.153	1.1947	-59.90	[16]
<i>N</i> -Ethyl- <i>N</i> -butylamine	0.124	0.320	0.080	0.650	3.269	1.0538	-51.40	[16]
Dibutylamine	0.107	0.300	0.080	0.690	4.349	1.3356	-60.40	[16]
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-43.40	[16]
Tributylamine	0.051	0.150	0.000	0.790	5.983	1.8992	-66.10	[67]
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	-40.30	[70]
2-Methylpyridine	0.598	0.750	0.000	0.580	3.422	0.8162	-46.09	[79]
3-Methylpyridine	0.631	0.810	0.000	0.540	3.631	0.8162	-45.91	[79]
Benzene	0.610	0.520	0.000	0.140	2.786	0.7176	-31.43	[15]
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	-42.66	[59]
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	-38.85	[34]
Benzonitrile	0.742	1.110	0.000	0.330	4.039	0.8711	-42.47	[59]
Anisole	0.710	0.750	0.000	0.290	3.890	0.9160	-41.70	[59]
Nitrobenzene	0.871	1.110	0.000	0.280	4.557	0.8906	-48.10	[59]
Tetramethylsilicon	-0.057	0.080	0.000	0.030	1.812	0.9179	-23.30	[41]
Ethylene carbonate	0.381	1.250	0.000	0.580	2.670	0.5558	-35.60	[38]
Hexanoic acid	0.174	0.630	0.620	0.440	3.697	1.0284	-69.50	[66]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{sol}}^{\text{exp}}$	Ref
Octanoic acid	0.150	0.650	0.620	0.450	4.680	1.3102	-79.03	[66]
2-Methylphenol	0.840	0.860	0.520	0.300	4.218	0.9160	-64.58	[65]
<i>N,N</i> -Dimethylformamide	0.367	1.310	0.000	0.740	3.173	0.6468	-40.72	[73]
Quinoline	1.268	0.970	0.000	0.540	5.457	1.0443	-58.94	[59]
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	-52.78	[59]
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	-62.18	[59]
1-Nitronaphthalene	1.600	1.590	0.000	0.290	7.056	1.2600	-71.50	[59]

Also provided in Tables 9.1 – 9.3 are the numerical values of the solute descriptors for the compounds considered in the present study. The tabulated values came from our solute descriptor database, which now contains values for more than 7000 different organic and organometallic compounds. The descriptors were obtained exactly as described before, using various types of experimental data, including water-to-organic solvent partitions, gas-to-organic solvent partitions, molar solubility ratios and chromatographic retention factor data [81-86]. Solute descriptors used in the present study are all based on experimental data.

Table 9.3. Values of the gas-to-1-butanol solvation enthalpy, $\Delta H_{\text{solv,BtOH}}^{\text{exp}}$ for 30 solutes together with the solute descriptors.

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv}}^{\text{exp}}$	Ref
3-Ethylpentane	0.000	0.000	0.000	0.000	3.091	1.0949	-33.77	[15]
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	-41.41	[15]
1-Heptene	0.092	0.080	0.000	0.070	3.063	1.0519	-34.39	[15]
2-Butanol	0.217	0.360	0.330	0.560	2.338	0.7309	-50.09	[91]
2-Methyl-1-propanol	0.217	0.390	0.370	0.480	2.413	0.7309	-50.80	[91]
Dibutyl ether	0.000	0.250	0.000	0.450	3.924	1.2945	-42.49	[53]
Tetrahydropyran ^a	0.296	0.490	0.000	0.480	3.013	0.7632	-34.94	[92]
2-Methyl-2-bromobutane	0.343	0.400	0.000	0.150	3.400	0.9881	-35.28	[49]
2-Chloro-2-methylbutane	0.171	0.270	0.000	0.150	2.858	0.9355	-32.36	[45]
2-Chloro-2-methylpentane	0.207	0.390	0.000	0.130	3.520	1.0764	-37.56	[45]
Propyl formate	0.132	0.630	0.000	0.380	2.433	0.7466	-31.33	[27]
Methyl heptanoate	0.079	0.600	0.000	0.450	4.356	1.3102	-45.60	[63]
Methyl nonanoate	0.056	0.600	0.000	0.450	5.321	1.5920	-55.66	[63]
Methyl undecanoate	0.051	0.630	0.000	0.450	6.296	1.8738	-64.78	[63]
Ethyl propanoate	0.087	0.580	0.000	0.450	2.807	0.8875	-30.66	[93]
Ethyl butanoate	0.068	0.580	0.000	0.450	3.271	1.0284	-36.74	[93]
Ethyl pentanoate	0.049	0.580	0.000	0.450	3.769	1.1693	-41.63	[93]

(table continues)

Solute	E	S	A	B	L	V	$\Delta H_{\text{solv}}^{\text{exp}}$	Ref
Ethyl hexanoate	0.043	0.580	0.000	0.450	4.251	1.3102	-45.99	[93]
1-Heptylamine	0.197	0.350	0.160	0.610	4.153	1.1947	-59.70	[16]
Dibutylamine	0.107	0.300	0.080	0.690	4.349	1.3356	-60.80	[16]
Triethylamine ^b	0.101	0.150	0.000	0.790	3.040	1.0538	-43.14	[16]
Tributylamine	0.051	0.150	0.000	0.790	5.983	1.8992	-65.90	[67]
1,3-Diaminopropane	0.446	0.610	0.430	1.140	2.852	0.7309	-65.30	[16]
2-Methylpyridine	0.598	0.750	0.000	0.580	3.422	0.8162	-46.19	[79]
3-Methylpyridine	0.631	0.810	0.000	0.540	3.631	0.8162	-46.11	[79]
Fluoromethane	0.070	0.350	0.000	0.090	0.057	0.2672	-11.03	[94]
Difluoromethane	-0.320	0.490	0.060	0.050	0.040	0.2849	-7.53	[94]
1,8-Cineole	0.383	0.330	0.000	0.760	4.688	1.4250	-53.30	[36]
Ethylene carbonate	0.381	1.250	0.000	0.580	2.670	0.5558	-33.90	[38]
Linalool	0.398	0.550	0.200	0.670	4.794	1.4903	-65.92	[95]

^a Solute was inadvertently left out of the tabulation given by Mintz et al. [14]. ^b The experimental $\Delta H_{\text{solv,BtOH}}$ value in the Mintz et al. database [14] is replaced by the $\Delta H_{\text{solv,BtOH}}$ based on the calorimetric measurements of Widner [16].

9.3 Results and Discussion

In Table 9.1, values of $\Delta H_{\text{solv,PtOH}}$ have been assembled for 92 organic vapors and gases dissolved in 1-pentanol covering a reasonably wide range of compound type and descriptor value. An analysis of the experimental data yielded the following two Abraham model correlations as seen in Equations (9.1) and (9.2):

$$\Delta H_{\text{solv,PtOH}} \text{ (in kJ mol}^{-1}\text{)} = -6.160(0.642) + 4.452(1.529)\mathbf{E} + 1.737(1.198)\mathbf{S} - 54.432(2.531)\mathbf{A} - 8.673(1.294)\mathbf{B} - 9.170(0.202)\mathbf{L} \quad (9.1)$$

(with N = 92, SD = 2.394, R² = 0.977, F = 752.9)

$$\Delta H_{\text{solv,PtOH}} \text{ (in kJ mol}^{-1}\text{)} = 2.444(0.895) - 7.713(1.619)\mathbf{E} - 6.397(1.377)\mathbf{S} - 58.906(2.829)\mathbf{A} - 6.866(1.477)\mathbf{B} - 32.673(0.840)\mathbf{V} \quad (9.2)$$

(with N = 92, SD = 2.671, R² = 0.972, F = 587.0)

where N corresponds to the number of solutes (i.e., data points), R^2 denotes the squared correlation coefficient, SD is the standard deviation, and F represents the Fisher F -statistic. All regression analyses were performed using the IBM® SPSS® statistical software. Both correlations provide a good statistical fit of the observed $\Delta H_{\text{solv,PtOH}}$ data with standard deviations of $2.394 \text{ kJ mol}^{-1}$ and $2.671 \text{ kJ mol}^{-1}$ for a data set that covers a range of about 78.3 kJ mol^{-1} . See Figures 9.1 and 9.2 for plots of the calculated values based on Equations (9.1) and (9.2) against the observed values. Equation (9.1) is the better equation statistically, and from a thermodynamic standpoint, Equation (9.1) is the enthalpic derivative of the Abraham model's gas-to-condensed phase transfer equation. Equation (9.2) might be more useful in some predictive applications in instances where the L -descriptor is not known. Equation (9.2) uses the McGowan volume, V -descriptor, which is easily calculable from the individual atomic sizes and numbers of bonds in the molecule [89].

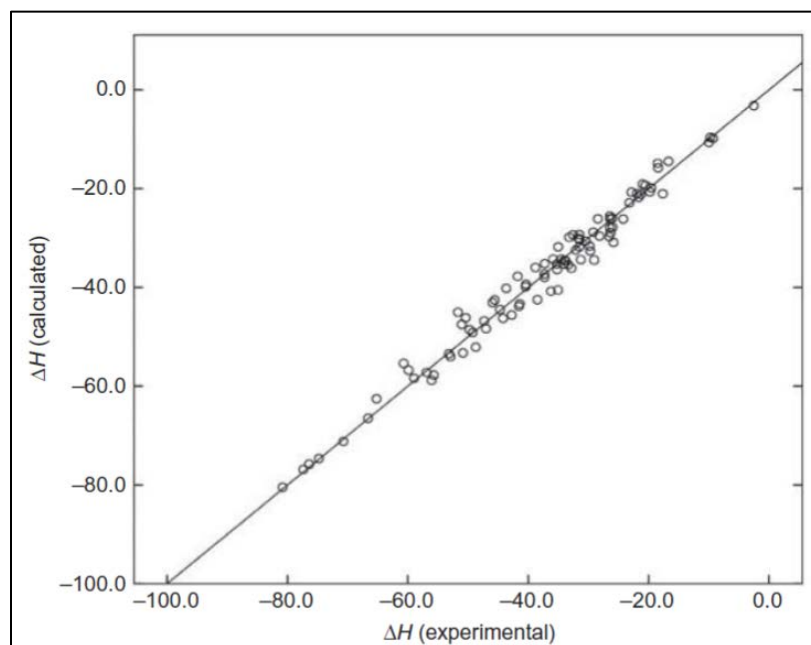


Figure 9.1. Comparison of experimental $\Delta H_{\text{solv,PtOH}}$ (in kJ mol^{-1}) data for solutes dissolved in 1-pentanol and calculated values based on Equation (9.1).

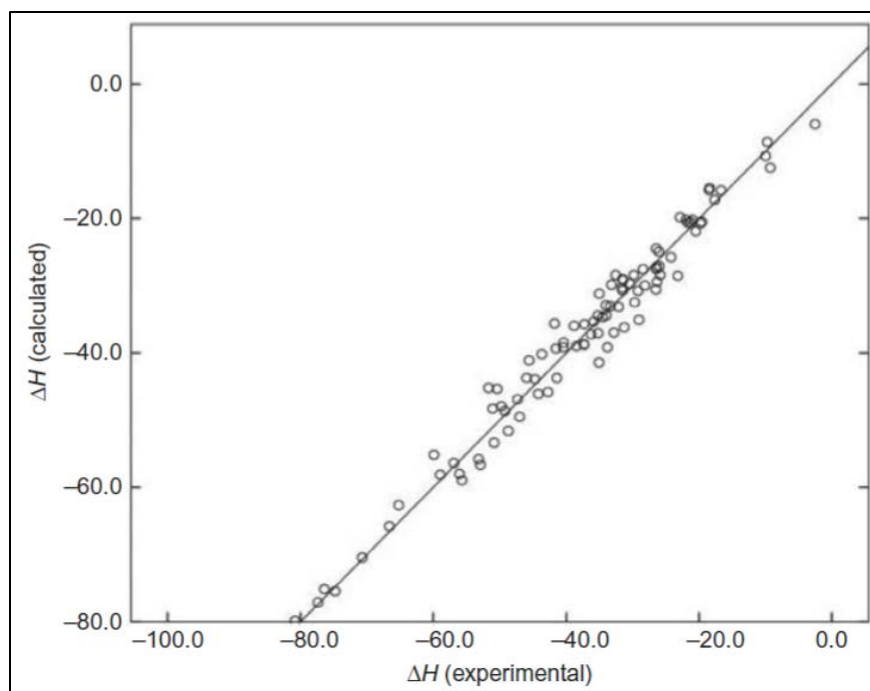


Figure 9.2. Comparison of experimental $\Delta H_{\text{solv,PtOH}}$ (in kJ mol^{-1}) data for solutes dissolved in 1-pentanol and calculated values based on Equation (9.2).

In order to assess the predictive ability of both derived Abraham correlations, the 92 data points were divided into a training set and a test set by allowing the SPSS software to randomly select half of the experimental points. The selected data points became the training sets and the compounds that were left served as the respective test sets. The analysis of the experimental data in the training sets gave the following Equations (9.3) and (9.4):

$$\Delta H_{\text{solv,PtOH}} \text{ (in } \text{kJ mol}^{-1}\text{)} = -6.582(1.186) + 4.975(2.570)\mathbf{E} + 1.551(1.979)\mathbf{S} - 60.400(4.545)\mathbf{A} - 8.548(2.177)\mathbf{B} - 9.029(0.377)\mathbf{L} \quad (9.3)$$

(with $N = 46$, $SD = 2.463$, $R^2 = 0.972$, $F = 288.3$)

$$\Delta H_{\text{solv,PtOH}} \text{ (in } \text{kJ mol}^{-1}\text{)} = 1.694(1.757) - 7.974(2.688)\mathbf{E} - 6.310(2.309)\mathbf{S} - 67.618(5.610)\mathbf{A} - 5.867(2.591)\mathbf{B} - 32.936(1.663)\mathbf{V} \quad (9.4)$$

(with $N = 46$, $SD = 2.714$, $R^2 = 0.958$, $F = 176.7$)

There is very small difference in the process coefficients for the full data set and the training data set correlations, thus showing that the training set of compounds is a representative sample of the total data set. The training set equation was then used to predict values for the 46 compounds in the test set. For the experimental and predicted $\Delta H_{\text{solv,PtOH}}$ values based on Equation (9.3), the SD = 2.523, AAE (average absolute error) = 1.997, and AE (average error) = 0.451 kJ mol⁻¹. There is, therefore, very little bias in using Equation (9.3) with AE equal to 0.451 kJ mol⁻¹. Test set calculations for Equation (9.4) gave SD = 2.960, AAE = 2.245, and AE = 0.571 kJ mol⁻¹. The small AE of AE = 0.571 kJ mol⁻¹ shows that there is very little bias associated with Equation (9.4). The training set and test set analyses were performed two more times with very similar results. It is expected that Equations (9.1) and (9.2) should be able to provide reasonably accurate predictions of the enthalpy of solvation for additional solutes, provided that one stays within the area of predictive space determined by the solute descriptor values used in deriving these predictive equations. The numerical values of the descriptors of the solutes listed in Table 9.1 cover the range of **E** = -0.250 to **E** = 1.070, **S** = 0.000 to **S** = 1.310, **A** = 0.000 to **A** = 0.430, **B** = 0.000 to **B** = 1.140, **V** = 0.2495 to **V** = 2.3630, and **L** = -0.323 to **L** = 7.714. The data set used in deriving Equations (9.1) and (9.2) does not contain any of the really acidic solute molecules like carboxylic acids or substituted phenols, which have the larger **A**-values.

As an informational note, an error/uncertainty of ± 2 kJ mol⁻¹ in the enthalpy of solvation results in an error of slightly less than 0.04 log units in extrapolating a measured gas-to-1-pentanol partition coefficient measured or predicted at 298.15 K to a temperature of 313.15. This level of predictive error will be sufficient for the most

practical chemical and engineering applications. Abraham model correlations have been published previously for predicting both water-to-1-pentanol partition coefficients and gas-to-1-pentanol partition coefficients at 298.15 K [90]. The derived Abraham model correlations for $\Delta H_{\text{solV,PtOH}}$ allow one to project the partitioning behavior and solubility behavior of solutes dissolved in 1-pentanol to slightly higher and/or slightly lower temperatures using standard thermodynamic relationships.

In Table 9.2, experimental values of the enthalpies of solvation have been listed for 84 gaseous solutes in 1-hexanol. Preliminary regression analysis yielded a very small numerical value of $e_{h,l} = -0.300$ for the $e_{h,l}$ -coefficient in the Equation (1.24) correlation, and the standard error in the coefficient was much larger than the actual numerical value. The $e_{h,l} \cdot \mathbf{E}$ term was removed from Equation (1.24), and the analysis of the tabulated $\Delta H_{\text{solV,HxOH}}$ values yielded the following two mathematical correlations as seen in Equations (9.5) and (9.6):

$$\Delta H_{\text{solV,HxOH}} \text{ (in kJ mol}^{-1}\text{)} = -4.614(0.717) + 1.614(0.795)\mathbf{S} - 45.975(1.950)\mathbf{A} - 11.256(1.222)\mathbf{B} - 9.269(0.182)\mathbf{L} \quad (9.5)$$

(with $N = 84$, $SD = 2.348$, $R^2 = 0.980$, $F = 961.7$)

$$\Delta H_{\text{solV,HxOH}} \text{ (in kJ mol}^{-1}\text{)} = 3.383(1.051) - 12.657(1.383)\mathbf{E} - 5.599(1.413)\mathbf{S} - 50.238(2.421)\mathbf{A} - 10.949(1.711)\mathbf{B} - 33.033(0.829)\mathbf{V} \quad (9.6)$$

(with $N = 84$, $SD = 2.890$, $R^2 = 0.970$, $F = 496.3$)

There was very small decrease in descriptive ability resulting from setting the $e_{h,l}$ coefficients equal to zero. For all practical purposes, the standard deviation remained the same, $SD = 2.347 \text{ kJ mol}^{-1}$ ($e_{h,l} \neq 0$) vs. $SD = 2.348 \text{ kJ mol}^{-1}$ ($e_{h,l} = 0$), for Equation

(9.5). Both Equations (9.5) and (9.6) are statistically very good with standard deviations of $2.348 \text{ kJ mol}^{-1}$ and $2.890 \text{ kJ mol}^{-1}$ for a data set that covers an approximate range of 84.8 kJ mol^{-1} . It is noted that the data used in determining the $\Delta H_{\text{solV,HxOH}}$ correlations do contain two carboxylic acid solutes (hexanoic acid with $\mathbf{A} = 0.620$ and octanoic acid with $\mathbf{A} = 0.620$) and one substituted phenolic compound (2-methylphenol with $\mathbf{A} = 0.520$). Figures 9.3 and 9.4 compare the calculated values of $\Delta H_{\text{solV,HxOH}}$ based on Equations (9.5) and (9.6) against the observed data.

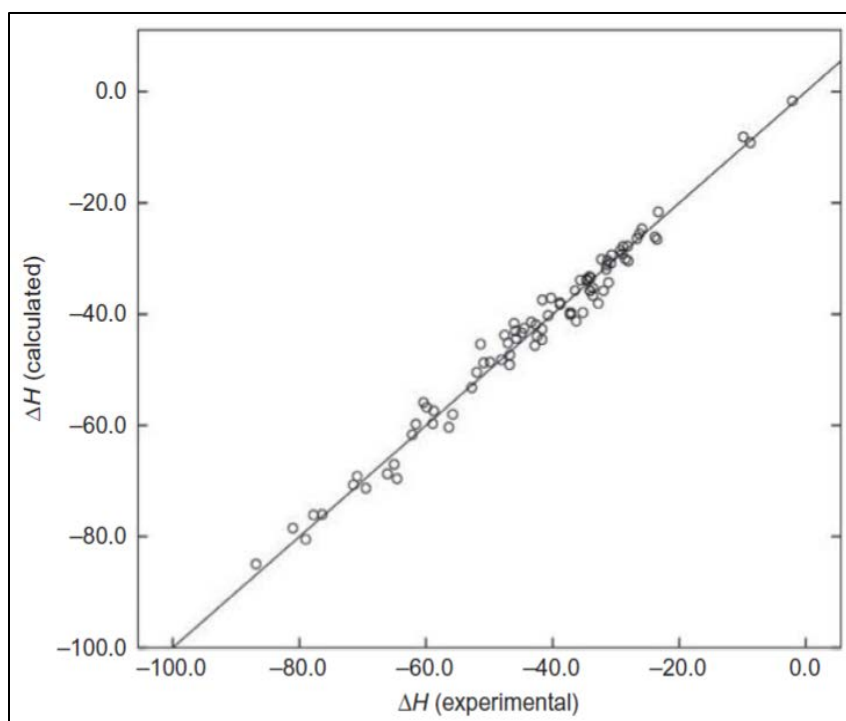


Figure 9.3. Comparison of experimental $\Delta H_{\text{solV,HxOH}}$ (in kJ mol^{-1}) data for solutes dissolved in 1-hexanol and calculated values based on Equation (9.5).

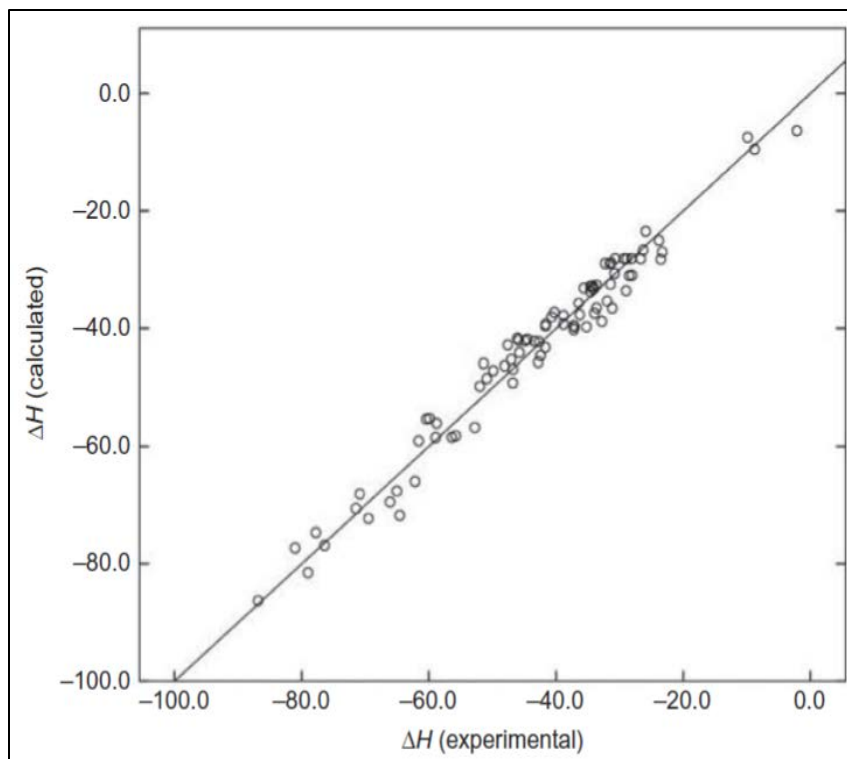


Figure 9.4. Comparison of experimental $\Delta H_{\text{solV,HxOH}}$ (in kJ mol^{-1}) data for solutes dissolved in 1-hexanol and calculated values based on Equation (9.6).

The predictive abilities of Equations (9.5) and (9.6) were assessed as before by allowing the SPSS software to randomly divide the 84 experimental data points into training and test sets. The analysis of the experimental data in the training set gave the following Equations (9.7) and (9.8):

$$\Delta H_{\text{solV,HxOH}} \text{ (in } \text{kJ mol}^{-1}\text{)} = -3.536(1.303) + 2.791(1.452)\mathbf{S} - 44.843(3.987)\mathbf{A} - 13.252(2.327)\mathbf{B} - 9.596(0.359)\mathbf{L} \quad (9.7)$$

(with $N = 42$, $SD = 2.581$, $R^2 = 0.976$, $F = 289.9$)

$$\Delta H_{\text{solV,HxOH}} \text{ (in } \text{kJ mol}^{-1}\text{)} = 4.606(1.807) - 15.383(2.167)\mathbf{E} - 3.326(2.195)\mathbf{S} - 49.747(4.522)\mathbf{A} - 13.679(2.783)\mathbf{B} - 33.952(1.549)\mathbf{V} \quad (9.8)$$

(with $N = 42$, $SD = 2.880$, $R^2 = 0.971$, $F = 178.6$)

The $e_{h,l} \cdot \mathbf{E}$ term again proved to be negligible and was eliminated from Equation (9.7). The training set equation was then used to predict $\Delta H_{\text{solv,HxOH}}$ values for the 42 compounds in the test set. For the predicted and experimental values, the SD = 2.370 kJ mol⁻¹ (Equation (9.7)) and SD = 3.099 kJ mol⁻¹ (Equation (9.8)), AAE = 1.884 kJ mol⁻¹ (Equation (9.7)) and AAE = 2.589 kJ mol⁻¹ (Equation (9.8)) and AE = -0.051 kJ mol⁻¹ (Equation (9.7)) and AE = 0.269 kJ mol⁻¹ (Equation (9.8)). Again, there is very little bias in the predictions using Equations (9.7) and (9.8) with AE equal to -0.051 kJ mol⁻¹ and 0.269 kJ mol⁻¹, respectively. Predictive Abraham model correlations have been previously reported for partition coefficients and molar solubility ratios for solutes dissolved in 1-hexanol at 298.15 K [90]. Equations (9.5) and (9.6) will allow us to obtain predicted values for slightly higher and/or slightly lower temperatures.

Mintz et al. [14] previously published Abraham model $\Delta H_{\text{solv,BtOH}}$ correlations for 1-butanol. Combining the 103 experimental $\Delta H_{\text{solv,BtOH}}$ values used in deriving the previous correlations with the additional $\Delta H_{\text{solv,BtOH}}$ data, which is tabulated in Table 9.3, gives 131 data points to use in updating our Abraham model correlations for the enthalpy of solvation for solutes dissolved in 1-butanol. The additional data points increase the data set by slightly more than 27 %. Preliminary regression analysis yielded a very small numerical value for the $e_{h,l}$ -coefficient in Equation (1.24) correlation, and the standard error in the coefficient was much larger than the actual numerical value itself. The $e_{h,l} \cdot \mathbf{E}$ term was removed from Equation (1.24), and reanalysis of the tabulated $\Delta H_{\text{solv,BtOH}}$ values yielded the following two mathematical expressions as seen in Equations (9.9) and (9.10):

$$\Delta H_{\text{solv,BtOH}} \text{ (in kJ mol}^{-1}\text{)} = -7.490(0.420) + 1.597(0.821)\mathbf{S} - 52.542(1.824)\mathbf{A} - 6.831(0.951)\mathbf{B} - 8.585(0.137)\mathbf{L} \quad (9.9)$$

(with N = 131, SD = 2.457, R² = 0.982, F = 1760.0)

$$\Delta H_{\text{solv,BtOH}} \text{ (in kJ mol}^{-1}\text{)} = 2.649(0.642) - 12.088(1.330)\mathbf{E} - 6.767(1.321)\mathbf{S} - 57.593(2.204)\mathbf{A} - 5.521(1.255)\mathbf{B} - 32.814(0.654)\mathbf{V} \quad (9.10)$$

(with N = 131, SD = 2.855, R² = 0.976, F = 1028.1)

There was very small decrease in descriptive ability resulting from setting the $e_{h,l}$ coefficients equal to zero. For all practical purposes, the standard deviation remained the same, SD = 2.454 kJ mol⁻¹ ($e_{h,l} \neq 0$) vs. SD = 2.457 kJ mol⁻¹ ($e_{h,l} = 0$), for Equation (9.9). Both Equations (9.9) and (9.10) are statistically very good with standard deviations of 2.457 kJ mol⁻¹ and 2.855 kJ mol⁻¹ for a data set that covers an approximate range of 87.6 kJ mol⁻¹. See Figures 9.5 and 9.6 for graphs of the calculated values based on Equations (9.9) and (9.10) against the measured enthalpy of solvation data.

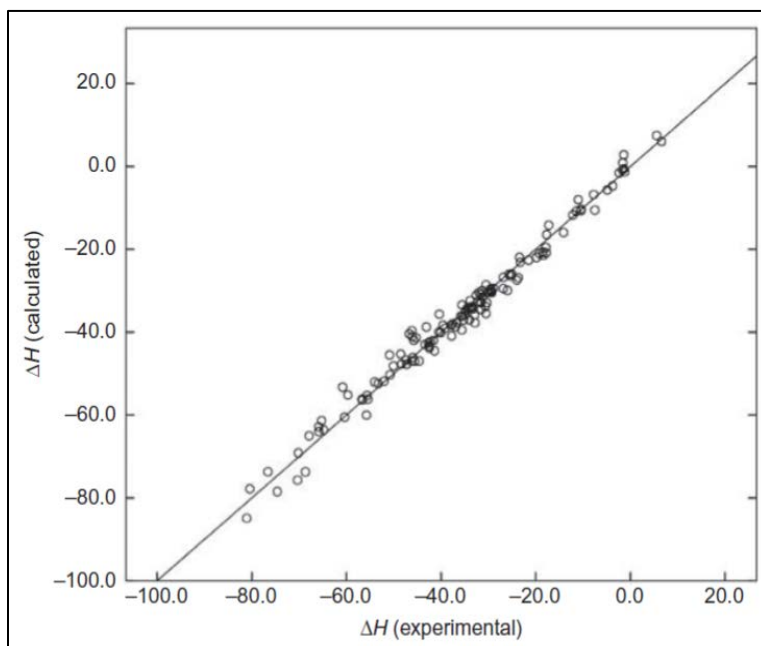


Figure 9.5. Comparison of experimental $\Delta H_{\text{solv,BtOH}}$ (in kJ mol⁻¹) data for solutes dissolved in 1-butanol and calculated values based on Equation (9.9).

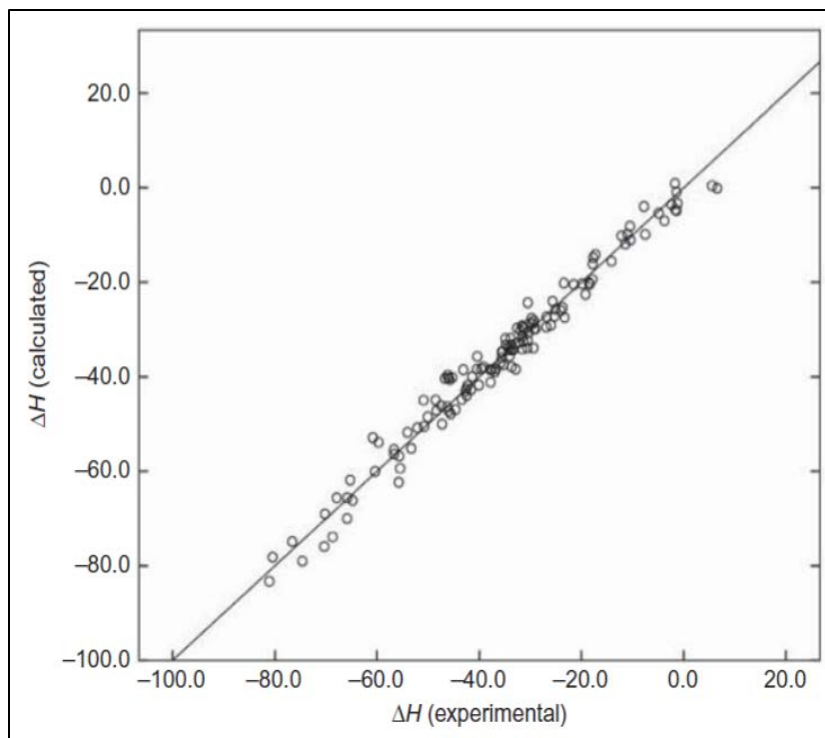


Figure 9.6. Comparison of experimental $\Delta H_{\text{solV,BtOH}}$ (in kJ mol^{-1}) data for solutes dissolved in 1-butanol and calculated values based on Equation (9.10).

The comparison of the updated (Equations (9.9) and (9.10)) and the initial sets of correlations by Mintz et al. [14] reveals very small change in the actual numerical values of the process coefficients. Within the combined standard errors in the process coefficients, the respective values are the same. The observation is important so that one knows how many data points are needed in a regression analysis so that the calculated process coefficients do not significantly change whenever additional experimental values are included in the data set. In the present case, the data set was increased from 103 to 131 compounds, and there was only a small difference between the new and old process coefficients.

The robustness of both 1-butanol correlations was verified by a training set and test set analysis. To conserve space, only the test set computations are reported. The training set correlation for $\Delta H_{\text{solV,BtOH}}$ (**L**-solute descriptor) predicted the 65 experimental

values in the test set to within $SD = 2.662 \text{ kJ mol}^{-1}$, $AAE = 1.883 \text{ kJ mol}^{-1}$, and $AE = -0.222 \text{ kJ mol}^{-1}$. The corresponding statistics for the test predictions based on the $\Delta H_{\text{solv,BtOH}}$ (**V**-solute descriptor) training set equation were: $SD = 3.122 \text{ kJ mol}^{-1}$, $AAE = 2.452 \text{ kJ mol}^{-1}$, and $AE = -0.046 \text{ kJ mol}^{-1}$. The validation studies were repeated three times with similar results obtained each time. The built-in SPSS software was used each time to randomly divide the parent data set into half.

It is of some interest that the **B**-coefficient in Equations (9.1), (9.5) and (9.9) is numerically much smaller than the **A**-coefficient. This suggests that in terms of enthalpic interactions these alcohol solvents behave as rather poor hydrogen-bond acids, but reasonably strong hydrogen-bond bases. Exactly the same phenomenon is seen with equations for gas-to-alcohol partition coefficients, as $\log K$, where the **B**-coefficients are also numerically much smaller than the **A**-coefficients [90,96].

9.4 Conclusions

Mathematical expressions are derived for correlating enthalpies of solvation of inorganic gases and organic solutes dissolved in 1-butanol, 1-pentanol and 1-hexanol based on the Abraham Solvation Parameter Model. The correlations presented in this article should allow one to predict $\Delta H_{\text{solv,BtOH}}$, $\Delta H_{\text{solv,PtOH}}$ and $\Delta H_{\text{solv,HxOH}}$ values for additional solutes at 298.15 K to within $\pm 3 \text{ kJ mol}^{-1}$ provided that one stays within the chemical space defined by the solute descriptors used in the determination of Abraham model Equations (9.1), (9.2), (9.5), (9.6), (9.9) and (9.10). The derived enthalpy of solvation equations provides a convenient method for extrapolating partition coefficients data measured at 298.15 K for solutes dissolved in 1-butanol, 1-pentanol and 1-hexanol

to slightly higher and slightly lower temperatures. Not all chemical and manufacturing processes take place at 298.15 K, and there is a growing need in the engineering sector to extrapolate the measured data to other temperatures.

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CHAPTER 10

CONCLUSIONS

10.1 Conclusions

The Abraham Solvation Parameter Model (ASPM) has been used extensively in various areas of biology, biochemistry and chemistry. Its applications span from toxicology to trace removal of impurities for organic syntheses, and it is one of the most widely used models to predict solute properties in a variety of solvents [1]. The ASPM have proven itself to be one of the most consistent predictive models that allows researchers to save time and money. With a solute descriptor database [2] of over 7 000 organic, inorganic and organometallic compounds, as well as data for the process coefficients for hundreds of organic solvents and ionic liquids, the predictive capabilities of these models are endless.

As part of the work for this dissertation, Abraham model correlations have been derived for solute transfer into five 2-alkoxyalcohols from water and from the gas phase. These five solvents are: 2-methoxyethanol [1], 2-ethoxyethanol [3], 2-propoxyethanol [4], 2-isopropoxyethanol [4] and 2-butoxyethanol [5]. When one compares the experimental gas-to-liquid partition ($\log K$) data for the same solutes in the five different alkoxyalcohol solvents, one observes that there is a good intercorrelation between the solvents. The intercorrelations can be expressed by the following Equations (10.1) – (10.4):

$$\log K(2 - \text{butoxyethanol}) = 0.928(0.008) \log K(2 - \text{methoxyethanol}) + 0.431(0.055)$$

(with $N = 62$, $SD = 0.202$, $R^2 = 0.996$) (10.1)

$$\log K(2\text{-butoxyethanol}) = 0.956(0.006) \log K(2\text{-ethoxyethanol}) + 0.229(0.043)$$

(with N = 50, SD = 0.145, R² = 0.998) (10.2)

$$\log K(2\text{-butoxyethanol}) = 0.986(0.005) \log K(2\text{-propoxyethanol}) + 0.037(0.040)$$

(with N = 41, SD = 0.101, R² = 0.999) (10.3)

$$\log K(2\text{-butoxyethanol}) = 0.984(0.007) \log K(2\text{-isopropoxyethanol}) + 0.056(0.050)$$

(with N = 41, SD = 0.118, R² = 0.998) (10.4)

The solutes include both liquid and crystalline nonelectrolyte compounds, both hydrogen-bonding and nonhydrogen-bonding compounds, and both polar and nonpolar organic compounds. High correlation coefficients speaks to similar solvation properties of the five solvents and the absence of large experimental errors in the data sets. This is further shown when comparing the log *K* correlations for the five alkoxyalcohols as shown below in Equations (10.5) to (10.9).

For 2-methoxyethanol: [1]

$$\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.141(0.052) - 0.265(0.076)\mathbf{E} + 1.810(0.096)\mathbf{S} +$$

$$3.641(0.085)\mathbf{A} + 0.590(0.141)\mathbf{B} + 0.790(0.018)\mathbf{L} \quad (10.5)$$

(with N = 62, SD = 0.139, R² = 0.998, F = 6044)

For 2-ethoxyethanol: [3]

$$\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.064(0.032) - 0.257(0.049)\mathbf{E} + 1.452(0.047)\mathbf{S} +$$

$$3.672(0.055)\mathbf{A} + 0.662(0.060)\mathbf{B} + 0.843(0.012)\mathbf{L} \quad (10.6)$$

(with N = 76, SD = 0.126, R² = 0.999, F = 17838)

For 2-propoxyethanol: [4]

$$\log(K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.091(0.042) - 0.288(0.057)\mathbf{E} + 1.265(0.066)\mathbf{S} +$$

$$3.566(0.055)\mathbf{A} + 0.390(0.094)\mathbf{B} + 0.902(0.017)\mathbf{L} \quad (10.7)$$

(with N = 54, SD = 0.094, R² = 0.999, F = 10,096)

For 2-isopropoxyethanol: [4]

$$\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.045(0.043) - 0.264(0.057)\mathbf{E} + 1.296(0.075)\mathbf{S} + \\ 3.646(0.054)\mathbf{A} + 0.352(0.115)\mathbf{B} + 0.880(0.017)\mathbf{L} \quad (10.8)$$

(with N = 55, SD = 0.099, R² = 0.999, F = 9143)

For 2-butoxyethanol: [5]

$$\log (K \text{ or } C_{S,\text{organic}}/C_{S,\text{gas}}) = -0.109(0.043) - 0.304(0.057)\mathbf{E} + 1.126(0.081)\mathbf{S} + \\ 3.407(0.065)\mathbf{A} + 0.660(0.126)\mathbf{B} + 0.914(0.015)\mathbf{L} \quad (10.9)$$

(with N = 59, SD = 0.103, R² = 0.999, F = 9908)

As mentioned in Chapter 6, careful examination of the above equations (Equations (10.5) – (10.9)), reveals that five of the six process coefficients are very similar. To within the standard uncertainty in the calculated process coefficients for the hydrogen-bond donor (as reflected in the b_k coefficient) and hydrogen-bond acceptor (as reflected in the a_k coefficient) properties are nearly the same. It is only the s_k coefficient in the correlations that differs significantly between the five alkoxyalcohols. The s_k coefficient decreases with increasing length of the alkoxy-chain, from $s_k = 1.810$ for 2-methoxyethanol to $s_k = 1.452$ for 2-ethoxyethanol to $s_k = 1.265$ for 2-propoxyethanol to $s_k = 1.126$ for 2-butoxyethanol. The outlier to this trend is in the s_k coefficient for 2-isopropoxyethanol, which has a value between those of the straight chain alkoxyalcohols, 2-propoxyethanol and 2-butoxyethanol.

Figure 10.1 shows a Principal Components Analysis (PCA) plot of the five alkoxyalcohols, along with other solvents which are listed in Table 10.1. As can be seen the five alkoxyalcohols are near each other, further confirming their similarities in

solvent properties. It is also clear from the PCA, that the alkoxyalcohols have similar solvent properties as their normal aliphatic alcoholic counterparts. With the use of the ASPM, one should be able to predict the given solute properties (i.e., $\log K$, $\log P$, $C_{S,organic}/C_{S,gas}$ or $C_{S,organic}/C_{S,water}$) for a solute with solute descriptors between the values as given in Chapters 3-6.

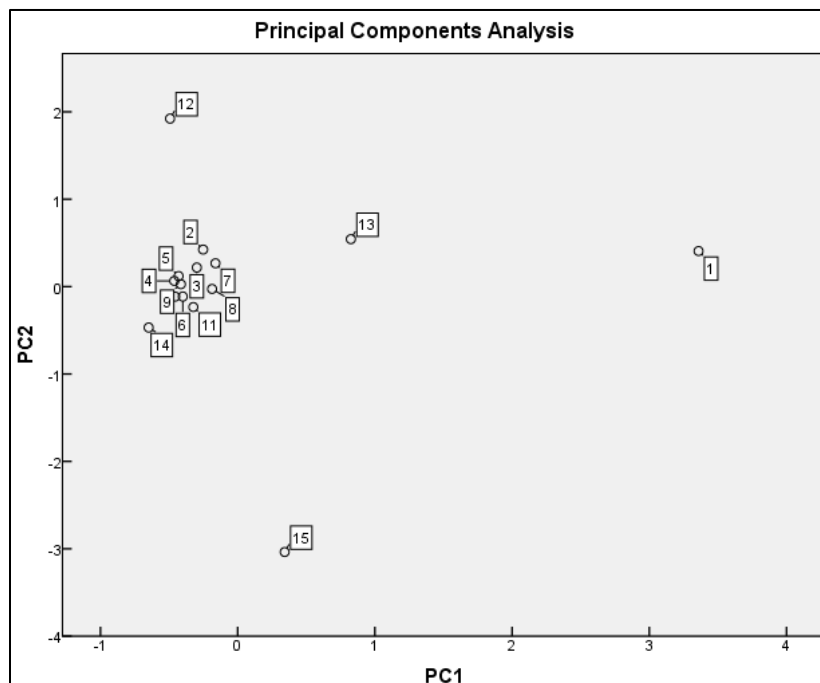


Figure 10.1. PCA plot of solvents listed in Table 10.1.

Table 10.1. Abraham Solvation Parameter Model $\log K$ process coefficients.

No.	Solvent	c_k	e_k	s_k	a_k	b_k	l_k	Ref.
1	water	-1.2710	0.822	2.743	3.904	4.814	-0.213	[6]
2	2-methoxyethanol	-0.1410	-0.265	1.810	3.641	0.590	0.790	[1]
3	2-ethoxyethanol	-0.0640	-0.257	1.452	3.672	0.662	0.843	[3]
4	2-propoxyethanol	-0.0910	-0.288	1.265	3.566	0.390	0.902	[4]
5	2-isopropoxyethanol	-0.0450	-0.264	1.296	3.646	0.352	0.880	[4]
6	2-butoxyethanol	-0.1090	-0.304	1.126	3.407	0.660	0.914	[5]
7	methanol	-0.0390	-0.338	1.317	3.826	1.396	0.773	[6]

(table continues)

No.	Solvent	c_k	e_k	s_k	a_k	b_k	l_k	Ref.
8	ethanol	0.0170	-0.232	0.867	3.894	1.192	0.846	[6]
9	2-propanol	-0.0480	-0.324	0.713	4.036	1.055	0.884	[6]
10	2-butanol	-0.0340	-0.387	0.719	3.736	1.088	0.905	[6]
11	2-methyl-1-propanol	-0.0030	-0.357	0.699	3.595	1.247	0.881	[6]
12	dimethyl sulfoxide	-0.5560	-0.223	2.903	5.037	0.000	0.719	[6]
13	ethylene glycol	-0.8870	0.132	1.657	4.457	2.355	0.565	[6]
14	diethyl ether	0.2880	-0.379	0.904	2.937	0.000	0.963	[6]
15	octane	0.2190	0.000	0.000	0.000	0.000	0.960	[6]

Chapters 7-9 show the application of the ASPM towards predicting the enthalpy of solvation, ΔH_{solv} , for organic solutes in the solvents: acetic acid, dimethyl carbonate, diethyl carbonate, 1-butanol, 1-pentanol and 1-hexanol. This information is important in terms of chemical synthesis and separations, as well as hydrogenation studies.

In Chapter 7 it was determined that, as a solvent, acetic acid formed linear chains instead of the previously held belief that it existed as dimers. This was confirmed by the large b -coefficients, indicating that the solvent acetic acid has a strong hydrogen-bond acidity. As a dimer, one would expect a small b -coefficient which would signify an inability to participate in hydrogen-bonds [7].

In Chapter 8 the correlations for the prediction of the enthalpies of solvation were developed for dimethyl carbonate (DMC) and diethyl carbonate (DEC). Being able to predict this information can aid in the synthesis of these two carbonates [8]. DMC can be substituted for methyl halides and dimethyl sulfate that are toxic and corrosive chemicals used in the production of isocyanates [9]. DEC, on the other hand, is used in the synthesis of carbamates, which are pesticides that have low mammalian oral and dermal toxicity [10-11].

In Chapter 9 correlations for the prediction of the enthalpies of solvation were determined for the 1-alkanol solvents of: 1-butanol, 1-pentanol and 1-hexanol [12]. These solvents have a wide range of applications from the cosmetics and food industries to coatings for CDs and DVDs. They are also widely used as solvents for various synthetic reactions, as well as being intermediaries themselves in certain reactions [13-15].

Future work in the use of the ASPM will include adding more solutes and solvents to the ever-growing database, as well as predicting various solute properties in the hopes of achieving a cleaner, “greener” and smaller impact on our planet in regards to chemical synthesis, production and use.

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