

ENTHALPY OF SOLVATION CORRELATIONS FOR ORGANIC SOLUTES AND GASES
DISSOLVED IN 2-PROPANOL, 2-BUTANOL, 2-METHYL-1-PROPANOL AND ETHANOL

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Abstract

Data have been assembled from the published literature on the enthalpies of solvation for 91 organic vapors and gaseous solutes in 2-propanol, for 73 gaseous compounds in 2-butanol, for 85 gaseous compounds in 2-methyl-1-propanol and for 128 gaseous compounds in ethanol. It is shown that an Abraham solvation equation with five descriptors can be used to correlate the experimental solvation enthalpies to within standard deviations of 2.24 kJ/mole, 1.99 kJ/mole, 1.73 kJ/mole and 2.54 kJ/mole for 2-propanol, 2-butanol, 2-methyl-1-propanol and ethanol, respectively. The derived correlations provide very accurate mathematical descriptions of the measured enthalpy of solvation data at 298 K, which in the case of ethanol span a range of 136 kJ/mole. Division of the experimental values into a training set and a test set shows that there is no bias in predictions, and that the predictive capability of the correlations is better than 3.5 kJ/mole.

Key Words: Enthalpy of solvation, enthalpy of transfer, mathematical correlation, partition coefficient, solvation parameter model

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Introduction

This study continues our computational modeling of solute transfer from the gas phase to a condensed phase. Such transfer processes form the basis of chemical separations involving gas-liquid chromatography, absorption of gases onto solid-phase microextraction absorbents, atmospheric transport and redistribution of volatile organic pollutants in the environment, and chemical purifications involving gas stripping methods. To date, we have developed Abraham model correlations for describing the logarithm of the gas-to-organic solvent partition coefficients, $\log K$, [1-7]

$$\log K = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + l \cdot \mathbf{L} \quad (1)$$

of organic vapors and gases into more than 70 different organic solvents of varying polarity and hydrogen-bonding characteristics. Abraham model correlations have also been reported for predicting enthalpies of solvation, $\Delta_{\text{Solv}}H^\circ$,

$$\Delta_{\text{Solv}}H^\circ = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + l \cdot \mathbf{L} \quad (2)$$

$$\Delta_{\text{Solv}}H^\circ = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V} \quad (3)$$

of organic vapors and gases into water [8], and into four alkanes (hexane [9], heptane [10], hexadecane [10] and cyclohexane [10]), into two aromatic hydrocarbons (benzene [10] and toluene [11]), into five alcohols (methanol [12], ethanol [12], 1-butanol [12], 1-octanol [8] and *tert*-butanol [13]), into three chloroalkanes (chloroform [14], carbon tetrachloride [11] and 1,2-dichloroethane [14]), and into seven other organic solvents (dibutyl ether [15], ethyl acetate [15], acetone [16], dimethyl sulfoxide [17], acetonitrile [16], propylene carbonate [17] and *N,N*-dimethylformamide [13]). In total Abraham model $\Delta_{\text{Solv}}H^\circ$ correlations have been reported for a

total of 22 different organic solvents. Expressions have also been developed for estimating enthalpies of solvation of organic vapors and gases into ionic liquid solvents based on the ion-specific equation coefficient [18] and group contribution [19] versions of the Abraham model. Each term in Eqns. 1 – 3 represents a different type of solute-solvent interaction contributing to the solute transfer process. The independent variables are solute descriptors, which are defined as follows: **E** denotes the solute excess molar refraction that reflects the solute's ability to interact with the surrounding solvent molecules through π - and lone-electron pairs, **S** is the solute dipolarity/polarizability parameter, **A** and **B** are measures of the solute's hydrogen-bond acidity and basicity, **V** is the McGowan volume of the solute in units of $(\text{dm}^3 \text{ mol}^{-1})/100$, and **L** is the logarithm of the solute's gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The first four descriptors can be regarded as measures of the tendency of the given compounds to undergo various solute-solvent interactions. The latter two descriptors, **V** and **L**, are both measures of solute size, and so will be measures of the solvent cavity term that will accommodate the dissolved solute. General dispersions are also related to solute size; hence both **V** and **L** will also describe the general solute-solvent interactions. The process coefficients in Eqns. 1 – 3 (c, e, s, a, b, v and l) are determined by regression analysis of the experimental $\log K$ and $\Delta_{\text{Solv}}H^\circ$ data in accordance with the Abraham model. Once the coefficients are known for a given solute transfer process additional partition coefficients and enthalpies of solvation can be calculated for the more than 4000 organic and organometallic compounds for which solute descriptors have been determined.

For the most part, the published gas-to-organic solvent partition coefficients and water-to-organic solvent partition coefficient correlations pertain to 298 K. Not all manufacturing processes occur at 298 K, and there is a need to extrapolate values measured and/or predicted at

298 K to other temperatures. From a thermodynamic standpoint, $\Delta_{\text{Solv}}H^{\circ}$ data can be used to estimate the gas-to-condensed phase partition coefficient, K, and the water-to-organic solvent partition coefficient, P, at other temperatures from measured partition coefficient data at 298.15 K through the van't Hoff equation. The 22 $\Delta_{\text{Solv}}H^{\circ}$ correlations that we have developed thus far allow us to extrapolate log P and log K values measured at 298 K to other temperatures. Eventually we hope to develop mathematical expressions for predicting enthalpies of solvation in most (if not all) of the more than 70 organic solvents for which we have log K and log P correlations.

The present study concerns developing $\Delta_{\text{Solv}}H^{\circ}$ correlations for solutes dissolved in 2-propanol, 2-butanol, 2-methyl-1-propanol and ethanol. Mintz *et al.* [12] previously published $\Delta_{\text{Solv}}H^{\circ}$ expressions for ethanol

$$\begin{aligned} \Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}} \text{ (kJ/mole)} = & -6.558(0.472) - 48.600(1.699) \mathbf{A} - 11.899(1.045) \mathbf{B} \\ & - 8.298(0.153) \mathbf{L} \end{aligned} \quad (4)$$

(N = 111, SD = 2.558, R² = 0.981, F = 1865)

and

$$\begin{aligned} \Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}} \text{ (kJ/mole)} = & 4.411(0.817) - 11.175(1.388) \mathbf{E} - 9.123(1.540) \mathbf{S} \\ & - 55.352(2.425) \mathbf{A} - 12.074(1.714) \mathbf{B} - 32.384(0.934) \mathbf{V} \end{aligned} \quad (5)$$

(N = 111, SD = 3.017, R² = 0.970, F = 589.7)

based on 111 experimental $\Delta_{\text{Solv}}H^{\circ}$ values that covered a range of approximately 89 kJ/mole. Numerical values in parenthesis give the standard errors in the respective equation coefficient. Here and elsewhere, N corresponds to the number of solutes (*i.e.*, data points), R² denotes the squared correlation coefficient, SD is the standard deviation and F represents the Fisher F-

statistic. While the published correlations do describe the measured $\Delta_{\text{Solv}}H^\circ$ data to within standard deviations of $SD = 2.558$ kJ/mole and $SD = 3.017$ kJ/mole, there is a need to update the ethanol correlations to include recent measurements in order to expand the predictive area of chemical space covered by two correlation models. The data set used in obtaining Eqns. 4 and 5 contained benzoic acid ($\mathbf{A} = 0.590$), ethylene glycol ($\mathbf{A} = 0.580$) and 2,2,2-trifluoroethanol ($\mathbf{A} = 0.570$) as the three most acidic solute molecules. Recent solubility measurements for adipic acid ($\mathbf{A} = 1.130$) [20], sebacic acid ($\mathbf{A} = 1.120$) [21], pimelic acid ($\mathbf{A} = 1.100$) [22], azelaic acid ($\mathbf{A} = 1.110$) [23] and succinic acid ($\mathbf{A} = 1.030$) [24] as a function of temperature allow us to include several more highly acidic solute molecules into the data analyses. Moreover, the $\Delta_{\text{Solv}}H^\circ$ values for the five alkanedioic acids, calculated from the temperature dependence of the measured mole fraction solubilities in ethanol and the alkanedioic acids' measured enthalpies of solvation, increases the range covered by the experimental $\Delta_{\text{Solv}}H^\circ$ values from 89 kJ/mole to 136 kJ/mole.

2. Data Sets and Solute Descriptors

A search of the published chemical literature found a large number of papers [25-92] that reported experimental partial molar enthalpies of solution, ΔH_{soln} , of liquid solutes in 2-propanol, 2-butanol and 2-methyl-1-propanol (isobutanol), or excess molar enthalpies of binary mixtures containing either 2-propanol, 2-butanol or 2-methyl-1-propanol. The ΔH_{soln} data for the liquid solutes were determined by either direct calorimetric methods or calculated based on the temperature dependence of the measured infinite dilution activity coefficient data. Calorimetric data was also found for the dissolution of a few crystalline organic solutes, ethylene carbonate [93], benzamide [94], benzoic acid [94], 1-bromoadamantane [95] and 1-adamantanol [96]. Enthalpies of solution of several gas molecules [97-106], anthracene [107], acenaphthene [108,

109], adipic acid [20], succinic acid [24] and sebacic acid [110] were calculated from the variation of mole fraction solubility with temperature. The ΔH_{soln} values were converted to gas-to-organic solvent enthalpies of transfer by

$$\text{Liquid solutes:} \quad \Delta_{\text{Solv}}H^{\circ} = \Delta_{\text{Soln}}H^{\circ} - \Delta_{\text{vap}}H^{\circ}_{298\text{K}} \quad (6)$$

$$\text{Crystalline solutes:} \quad \Delta_{\text{Solv}}H^{\circ} = \Delta_{\text{Soln}}H^{\circ} - \Delta_{\text{Sub}}H^{\circ}_{298} \quad (7)$$

subtracting the solute's standard molar enthalpy of vaporization [111, 112], $\Delta_{\text{vap}}H^{\circ}_{298\text{K}}$, or standard molar enthalpy of sublimation [112, 113], $\Delta_{\text{Sub}}H^{\circ}_{298}$, at 298.15 K.

We eliminated from consideration all experimental data that pertained to temperatures outside the temperature range of 283 K – 318 K. Enthalpies of solvation are temperature-dependent, and we did not want to introduce large errors in the database by including experimental data far removed from 298 K. For several solutes there were multiple, independently determined values. In such cases, we selected direct calorimetric data over indirect values based on the temperature dependence of measured solubilities or infinite dilution activity coefficients. Using the aforementioned criteria, 91 molar enthalpies of solvation in 2-propanol, 73 molar enthalpies of solvation in 2-butanol and 85 molar enthalpies of solvation in 2-methyl-1-propanol were selected for regression analysis. The experimental $\Delta_{\text{Solv}}H^{\circ}_{2\text{-PrOH}}$, $\Delta_{\text{Solv}}H^{\circ}_{2\text{-BuOH}}$, and $\Delta_{\text{Solv}}H^{\circ}_{i\text{-BuOH}}$ values are listed in Tables S1 – S3 (Supplementary Material) along with the values of the solute descriptors of the compounds considered in the present study. The tabulated solute descriptors are of experimental origin and came from our solute descriptor database, which now contains values for more than 5000 different organic and organometallic compounds.

Our search of the chemical and engineering literature also found recently published solubility data for several alkanedioic acids [20 – 24] dissolved in ethanol. The $\Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}}$ database for enthalpy is published elsewhere [12, 114]. In Table S4 we have tabulated the experimental $\Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}}$ values that have been added to the ethanol enthalpy of solvation data set, along with the pertinent literature references [20-24, 28, 36, 60, 93, 96, 107, 115-117] for the added experimental values.

3. Results and Discussion

We have assembled in Table S1 values of $\Delta_{\text{Solv}}H^{\circ}_{2\text{-PrOH}}$ for 91 organic vapors and gases dissolved in 2-propanol covering a reasonably wide range of compound type and descriptor value. Analysis of the experimental data yielded the following two Abraham model correlation equations:

$$\Delta_{\text{Solv}}H^{\circ}_{2\text{-PrOH}} \text{ (kJ/mole)} = -7.669(0.445) + 2.055(1.115) \mathbf{S} - 51.494(1.203) \mathbf{A} - 6.976(1.187) \mathbf{B} - 7.996(0.237) \mathbf{L} \quad (8)$$

(with N = 91, SD = 2.251, R² = 0.989, F = 1972)

$$\Delta_{\text{Solv}}H^{\circ}_{2\text{-PrOH}} \text{ (kJ/mole)} = -10.275(1.133) \mathbf{E} - 5.260(1.594) \mathbf{S} - 53.559(1.583) \mathbf{A} - 8.107(1.707) \mathbf{B} - 28.119(0.699) \mathbf{V} \quad (9)$$

(with N = 91, SD = 2.934, R² = 0.995, F = 3505)

The contribution of the e·E term in Eqn. 8 was negligible, as was the c-coefficient in Eqn. 9. Both terms were removed from the final regression. No loss in descriptive ability as observed by removing the two insignificant terms. All regression analyses were performed using Version 17

of the SPSS statistical software. There is little intercorrelation ($R^2 \leq 0.5$ in all cases) between the descriptors in Eqs. 8 and 9. Both correlations provide a good statistical fit of the observed data with standard deviations of 2.251 and 2.934 kJ/mole for a data set that covers a range of about 118.0 kJ/mole. See Figure 1 for a plot of the calculated values $\Delta_{\text{Solv}}H^{\circ}_{2\text{-PrOH}}$ based on Eqn. 8 against the observed values. Equation 8 is the better equation statistically, and from a thermodynamic standpoint Eqn. 8 is the enthalpic derivative of the Abraham model's gas-to-condensed phase transfer equation. Equation 9 might be more useful in some predictive applications in instances where the **L**-descriptor is not known. Equation 9 uses the McGowan volume, **V**-descriptor, which is easily calculable from the individual atomic sizes and numbers of bonds in the molecule [118].

In order to assess the predictive ability of Eqn. 8 we divided the 91 data points 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 set and the compounds that were left served as the test set. Analysis of the experimental data in the training set gave

$$\Delta_{\text{Solv}}H^{\circ}_{2\text{-PrOH}} \text{ (kJ/mole)} = -8.425(0.516) + 2.994(1.652) \mathbf{S} - 51.452(1.674) \mathbf{A} - 7.811(1.294) \mathbf{B} \\ - 7.693(0.280) \mathbf{L} \tag{10}$$

(with $N = 46$, $SD = 1.939$, $R^2 = 0.992$, $F = 1337$)

Regression analysis showed the $e \cdot E$ term in Eqn. 10 to be negligible, in fact the standard error in the equation coefficients was more than eight times the coefficient itself. There is very little difference in the equation coefficients for the full dataset and the training dataset 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 $\Delta_{\text{Solv}}H^{\circ}_{2\text{-PrOH}}$ values for the 45 compounds in

the test set. For the predicted and experimental values, we find $SD = 2.709$, AAE (average absolute error) = 2.024 and AE (average error) = -0.640 kJ/mole. There is therefore very little bias in using Eqn. 10 with AE equal to -0.640 kJ/mole. The training set and test set analyses were performed two more times with similar results. Training and test validations were also performed for Eqn. 9. To conserve journal space, we give only the test set results. The derived training set correlation for Eqn. 9 predicted the 45 experimental $\Delta_{Solv}H^{\circ}_{2-PrOH}$ values in the test set to within a $SD = 3.512$, $AAE = 2.636$ and $AE = 1.431$ kJ/mole. Again, there is little bias in the predictions using Eqn.9 with AE equal to 1.431 kJ/mole. An error/uncertainty of ± 2 kJ/mole in the enthalpy of solvation results in an error of slightly less than 0.04 log units in extrapolating a log K value measured at 298.15 K to a temperature of 313.15. This level of predictive error will be sufficient for most practical chemical and engineering applications.

In Table S2 we have listed experimental values of the enthalpies of solvation of 73 gaseous solutes in 2-butanol. Analysis of the tabulated $\Delta_{Solv}H^{\circ}_{2-BuOH}$ values yielded the following two mathematical correlations:

$$\Delta_{Solv}H^{\circ}_{2-BuOH} \text{ (kJ/mole)} = -6.883(0.388) + 6.667(1.275) \mathbf{S} - 50.819(1.617) \mathbf{A} - 10.577(1.822) \mathbf{B} - 8.270(0.187) \mathbf{L} \quad (11)$$

(with $N = 73$, $SD = 1.985$, $R^2 = 0.991$, $F = 1891$)

$$\Delta_{Solv}H^{\circ}_{2-BuOH} \text{ (kJ/mole)} = 3.528(0.783) - 11.470(1.303) \mathbf{E} - 51.800(2.276) \mathbf{A} - 13.286(1.806) \mathbf{B} - 32.286(1.110) \mathbf{V} \quad (12)$$

(with $N = 73$, $SD = 2.794$, $R^2 = 0.982$, $F = 946.2$)

Regression analysis showed that the the $e \cdot E$ term and $s \cdot S$ term to be negligible in Eqns. 11 and 12, respectively. Both Eqns. 11 and 12 are statistically very good with standard deviations of 1.985 and 2.794 kJ/mole for a dataset that covers an approximate range of 126 kJ/mole. Figure 2 compares the calculated values of $\Delta_{\text{Solv}}H^{\circ}_{2\text{-BuOH}}$ based on Eqn. 1` against the observed data. To our knowledge there has been no previous attempt to correlate enthalpies of solvation for gaseous solutes in 2-butanol.

The predictive ability of Eqn. 11 was assessed as before by allowing the SPSS software to randomly divide the 73 experimental data points into training and test sets as before. Analyses of the experimental data in the training set gave

$$\Delta_{\text{Solv}}H^{\circ}_{2\text{-BuOH}} \text{ (kJ/mole)} = -7.098(0.631) + 8.831(1.745) \mathbf{S} - 52.721(2.705) \mathbf{A} - 10.620(2.533) \mathbf{B} - 8.494(0.283) \mathbf{L} \quad (13)$$

(with $N = 37$, $SD = 1.960$, $R^2 = 0.986$, $F = 560$)

The $e \cdot E$ term was removed from Eqn. 13 because the term contributed very little to the predicted $\Delta_{\text{Solv}}H^{\circ}$ value, and the standard error in the coefficient was more than twice the coefficient.

There is little difference in the equation coefficients for the full dataset and the training dataset 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 $\Delta_{\text{Solv}}H^{\circ}_{2\text{-BuOH}}$ values for the 36 compounds in the test set. For the predicted and experimental values, we find $SD = 2.195$, $AAE = 1.620$ and $AE = 0.038$ kJ/mole. There is therefore very little bias in using Eqn. 16 with AE equal to 0.038 kJ/mole. The training set and test set analyses were performed two more times with similar results. Training and test validations were also performed for Eqn. 13. To conserve

journal space, we give only the test set results. The derived training set correlation for Eqn. 13 predicted the 36 experimental $\Delta_{\text{Solv}}H^{\circ}_{2\text{-BuOH}}$ values in the test set to within a $SD = 3.100$, $AAE = 2.412$ and $AE = -0.436$ kJ/mole. Again, there is very little bias in the predictions using Eqn. 13 with AE equal to -0.436 kJ/mole.

The data set for 2-methyl-1-propanol (isobutanol) contains experimental $\Delta_{\text{Solv}}H^{\circ}$ values for 85 organic solutes and gases. Regression analysis of the tabulated experimental values in Table S3 gave the following two mathematical expressions:

$$\begin{aligned} \Delta_{\text{Solv}}H^{\circ}_{i\text{-BuOH}} \text{ (kJ/mole)} = & -7.498(0.329) + 3.958(1.105) \mathbf{E} + 2.176(1.320) \mathbf{S} - 53.967(1.809) \mathbf{A} \\ & - 4.610(1.612) \mathbf{B} - 8.602(0.124) \mathbf{L} \end{aligned} \quad (14)$$

(with $N = 85$, $SD = 1.734$, $R^2 = 0.992$, $F = 1920$)

$$\begin{aligned} \Delta_{\text{Solv}}H^{\circ}_{i\text{-BuOH}} \text{ (kJ/mole)} = & 3.427(0.567) - 5.545(1.409) \mathbf{E} - 6.977(1.751) \mathbf{S} - 59.338(2.395) \mathbf{A} \\ & - 4.850(2.127) \mathbf{B} - 33.620(0.642) \mathbf{V} \end{aligned} \quad (15)$$

(with $N = 85$, $SD = 2.288$, $R^2 = 0.986$, $F = 1096$)

Both Eqns. 14 and 15 are statistically very good with standard deviations of $SD = 1.734$ and $SD = 2.288$ kJ/mole for a dataset that covers an approximate range of 86.0 kJ/mole. Figure 3 compares the calculated values of $\Delta_{\text{Solv}}H^{\circ}_{i\text{-BuOH}}$ based on Eqn. 14 against the observed data. The smaller range results because the highly acidic, crystalline alkanedioic acids are absent from the $\Delta_{\text{Solv}}H^{\circ}_{i\text{-BuOH}}$ database. Sebacic acid ($\Delta_{\text{Solv}}H^{\circ} \approx -118$ kJ/mole), adipic acid ($\Delta_{\text{Solv}}H^{\circ} \approx -105$ kJ/mole) and succinic acid ($\Delta_{\text{Solv}}H^{\circ} \approx -94$ kJ/mole) had the larger enthalpies of solvation in the 2-propanol and 2-butanol data sets. The robustness of each correlation was determined through a training set and test set analyses by allowing the SPSS software to randomly split the large data

set in half. The training set correlations predicted the experimental $\Delta_{\text{Solv}}H^{\circ}$ values in the test set to within $SD = 2.062$ and $SD = 2.744$ kJ/mole, $AAE = 1.409$ and $AAE = 2.165$ kJ/mole, and $AE = 0.146$ and $AE = -0.008$ kJ/mole. To our knowledge there has been no previous attempt to correlate enthalpies of solvation for gaseous solutes in 2-methyl-1-propanol.

For information purposes we note that a Reviewer observed that several of the equation coefficients for Eqns. 17 and 18 did change fairly significantly

$$\Delta_{\text{Solv}}H^{\circ}_{i\text{-BuOH}} \text{ (kJ/mole)} = -7.522(0.270) + 4.944(0.981) \mathbf{E} - 0.450(1.351) \mathbf{S} - 48.428(2.007) \mathbf{A} \\ - 1.709(1.701) \mathbf{B} - 8.512(0.103) \mathbf{L} \quad (16)$$

(with $N = 78$, $SD = 1.395$, $R^2 = 0.993$, $F = 2345$)

$$\Delta_{\text{Solv}}H^{\circ}_{i\text{-BuOH}} \text{ (kJ/mole)} = 3.310(0.588) - 4.711(1.567) \mathbf{E} - 8.957(2.243) \mathbf{S} - 55.240(3.322) \mathbf{A} \\ - 2.549(2.808) \mathbf{B} - 33.313(0.675) \mathbf{V} \quad (17)$$

(with $N = 78$, $SD = 2.304$, $R^2 = 0.983$, $F = 850.4$)

when all seven of the alcohol solutes (methanol, 1-butanol, 1-decanol, 2-propanol, 2-butanol, 2-methyl-1-propanol, 2-methoxyethanol and 1-adamantanol) were removed from the data set. The specific coefficient that the Reviewer mentioned was the b coefficient, going from -4.610 (with a standard error of 1.612; see Eqn. 14) to -1.709 (with a standard error of 1.701; see Eqn. 16).

While the **numerical** calculated numerical values are different, the ranges encompassed by the standard errors do overlap. We also note that removal of the seven alcohols from the isobutanol data set resulted in a correlation for which standard errors in two of the equation coefficients were nearly equal to or larger than the coefficient itself (See s and b coefficients in Eqn. 16). With the seven alcohol solvents in the data set, none of the standard errors exceeded the respective equation coefficient (see Eqn. 14). There is no reason to arbitrary remove the seven alcohol solvents.

Our search of the chemical and engineering literature also found recently published solubility data for adipic acid [20], sebacic acid [21], pimelic acid [22], azelaic acid [23] and succinic acid [24] in ethanol as a function of temperature that could be combined with published enthalpy of sublimation data [112, 113] to give $\Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}}$ values for these five highly acidic alkanedioic acids. As noted previously, Mintz *et al.* [12] previously published $\Delta_{\text{Solv}}H^{\circ}$ expressions for ethanol based on 111 experimental $\Delta_{\text{Solv}}H^{\circ}$ values that covered a range of approximately 89 kJ/mole. The experimental values for the five alkanedioic acids expand the $\Delta_{\text{Solv}}H^{\circ}$ range to 136 kJ/mole. We have combined the 111 experimental $\Delta_{\text{Solv}}H^{\circ}$ values compiled by Mintz *et al.* with the 17 additional values listed in Table S4 into a single dataset. Analysis of the 128 experimental values yielded the following two Abraham model correlation equations:

$$\begin{aligned} \Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}} \text{ (kJ/mole)} = & -6.760(0.440) - 0.620(0.899) \mathbf{E} - 0.595(1.070) \mathbf{S} - 50.530(1.079) \mathbf{A} \\ & - 10.468(1.263) \mathbf{B} - 8.165(0.172) \mathbf{L} \end{aligned} \quad (18)$$

(with N = 128, SD = 2.540, R² = 0.989, F = 2267)

$$\begin{aligned} \Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}} \text{ (kJ/mole)} = & 2.611(0.768) - 10.389(1.081) \mathbf{E} - 7.720(1.414) \mathbf{S} - 52.100(1.414) \mathbf{A} \\ & - 13.005(1.651) \mathbf{B} - 30.645(0.865) \mathbf{V} \end{aligned} \quad (19)$$

(with N = 128, SD = 3.342, R² = 0.981, F = 1300)

In order to compare the calculated equation coefficients to those reported previously by Mintz and coworkers [12], the e·**E** and s·**S** terms were moved, to yield:

$$\begin{aligned} \Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}} \text{ (kJ/mole)} = & - 6.711(0.430) - 50.547(1.042) \mathbf{A} - 10.965(0.961) \mathbf{B} \\ & - 8.291(0.137) \mathbf{L} \end{aligned} \quad (20)$$

(N = 128, SD = 2.558, R² = 0.989, F = 3787)

Examination of Eqns. 4 versus 20, and Eqns. 5 versus 19, reveals that the updated equation coefficients are quite comparable (within standard error in the coefficients) to those reported previously. One does note that that the standard errors in the equation coefficients have decreased. In the case of Eqn. 19, the standard error in the a coefficient was significantly reduced when the five alkanedioic acids were added to the data set, standard error of 2.425 for Eqn. 5 versus a standard error of 1.414 for Eqn. 19. Equations 18 and 19 provide a reasonably accurate mathematical description of the observed $\Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}}$ data as evidenced by standard deviations of $SD = 2.540$ and $SD = 3.342$ kJ/mole, respectively. See Figure 4 for a graphical comparison of observed data versus calculated values based on Eqn. 19. Each correlation was validated through a training set and test set analyses as before by having the SPSS split the large data set in half. The training set correlations predicted the experimental $\Delta_{\text{Solv}}H^{\circ}$ values in the test set to within $SD = 2.430$ and $SD = 3.294$ kJ/mole, $AAE = 1.925$ and $AAE = 2.647$ kJ/mole, and $AE = 0.224$ and 0.484 kJ/mole.

As an informational note, Constantinescu and coworkers [119] recently examined the applicability of COSMO-RS models to the prediction of excess enthalpies of mixing for mixtures containing various classes of organic compounds. The authors reported relative standard errors for the various classes of organic compounds. For systems containing alcohols, the relative deviations ranged from about 40 % to 125 %, which we estimate would correspond to an approximate error of about 2.5 to 4.5 kJ/mole in the enthalpy of solvation by the time that one includes the uncertainty in the experimental enthalpy of vaporization (or sublimation in the case of solid solute). The Abraham model predictions fall for 2-propanol, 2-butanol, 2-methyl-1-propanol and ethanol fall in this range.

The correlations presented in this study further document the applicability of the Abraham solvation parameter model to describe enthalpies of solvation for organic vapors and gaseous solutes dissolved in organic solvents. The derived $\Delta_{\text{Solv}}H^\circ$ correlations for 2-propanol, 2-butanol, 2-methyl-1-propanol and ethanol will allow one to extrapolate gas-to-2-PrOH(or 2-BuOH, i-BuOH and EtOH) and water-to-2-PrOH(or 2-BuOH, i-BuOH and EtOH) measured at 298.15 K to other temperatures. Not all manufacturing applications occur at 298.15 K, and there is a growing need in the chemical industry to predict solute transfer and partition properties at other temperatures as well.

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Figure 1.

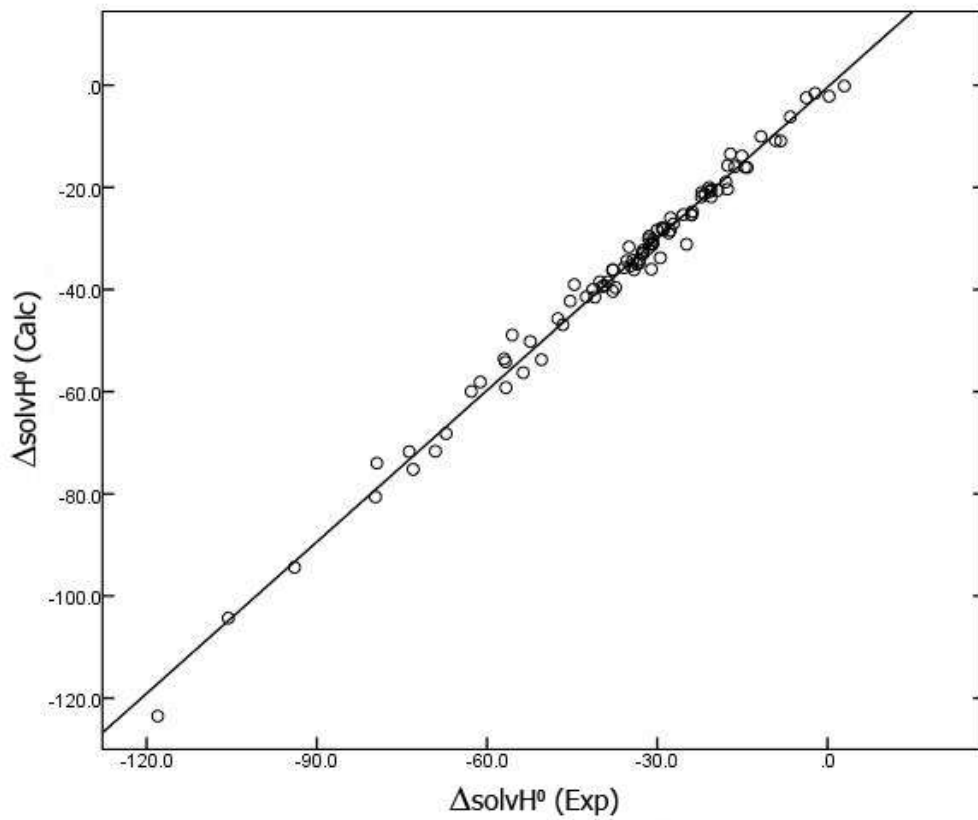


Figure 1. A plot of the calculated values of $\Delta_{\text{Sol}}H^\circ_{2\text{-PrOH}}$ (in kJ/mole) based on eqn 8 against the observed values.

Figure 2

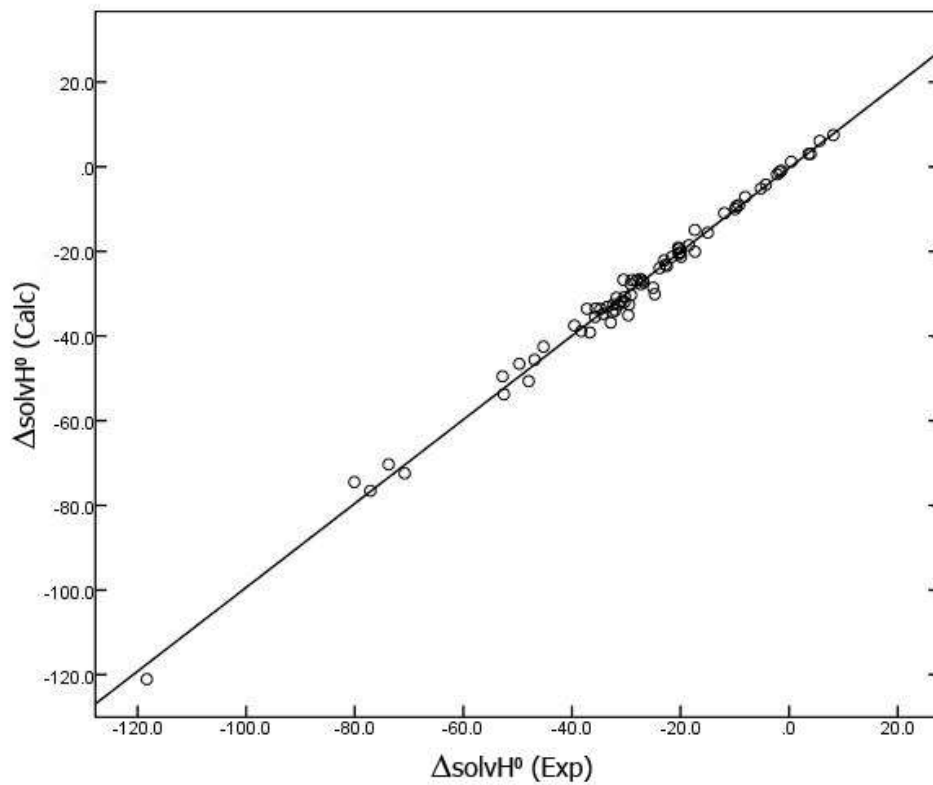


Figure 2. A plot of the calculated values of $\Delta_{\text{Sol}}H^\circ_{2\text{-BuOH}}$ (in kJ/mole) based on eqn 11 against the observed values.

Figure 3.

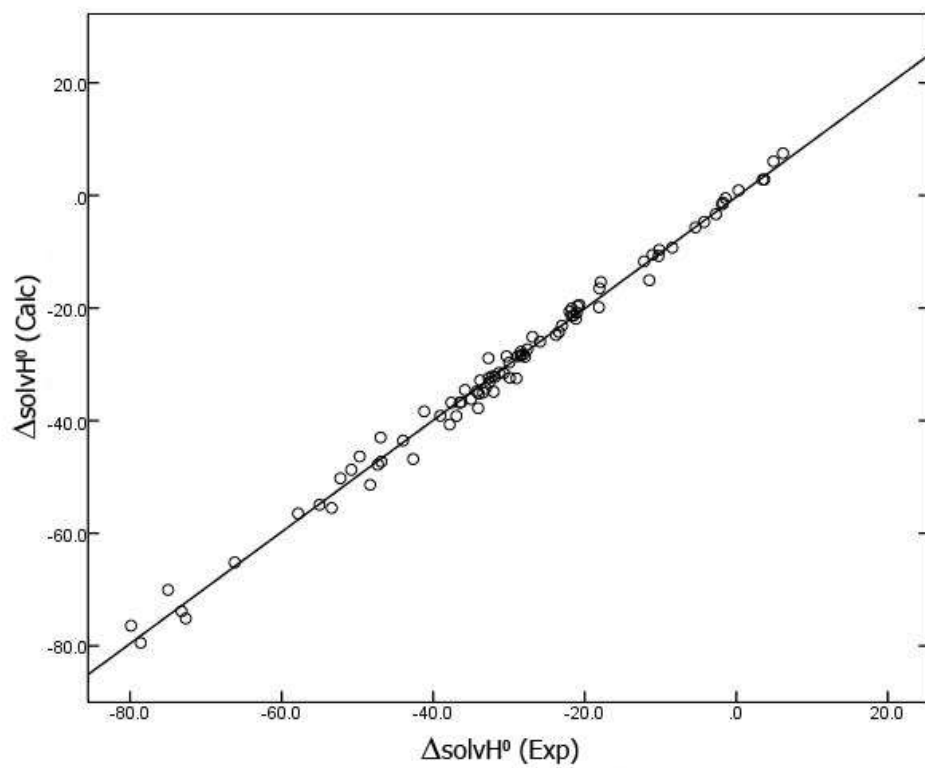


Figure 3. A plot of the calculated values of $\Delta_{\text{Solv}}H^{\circ}_{i\text{-BuOH}}$ (in kJ/mole) based on eqn 14 against the observed values.

Figure 4

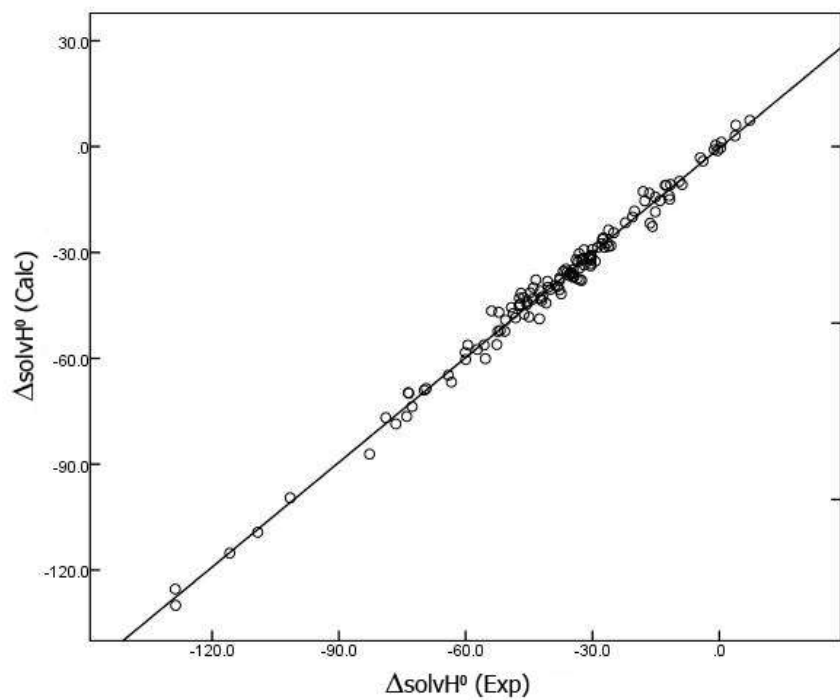


Figure 4. A plot of the calculated values of $\Delta_{\text{Solv}}H^{\circ}_{\text{EtOH}}$ (in kJ/mole) based on eqn 18 against the observed values.