ENTHALPY OF SOLVATION CORRELATIONS FOR GASEOUS SOLUTES DISSOLVED IN CHLOROFORM AND 1,2-DICHLOROETHANE BASED ON THE ABRAHAM MODEL

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Abstract

Enthalpy of solvation data have been compiled from the published literature for more than 80 solutes dissolved in chloroform and 1,2-dichloromethane. Mathematical correlations based on the Abraham general solvation parameter model are developed for describing the experimental solvation enthalpies to within standard deviations of 2.10 kJ/mole (chloroform) and 1.72 kJ/mole (1,2-dichloroethane). Division of the measured values into a training set and a test set shows that there is no bias in predictions, and that the estimative capability of the correlations is better than 2.5 kJ/mole.

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

Short Running Title: Enthalpies of Solvation of Solutes in Chloroform and Dichloroethane

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Introduction

The thermodynamic properties of molecules in various chemical and biological processes are greatly influenced by molecular interactions between the molecule and its solubilizing media. Such interactions may be either non-specific or specific in nature. Nonspecific interactions are described by a random distribution of molecules throughout the entire solution. Specific interactions, on the other hand, are generally much stronger and often result in a specific geometric orientation of one molecule with respect to an adjacent molecule. Even in systems known to contain specific interactions, the need to properly account for nonspecific interactions has been long recognized.

In recent studies we have developed mathematical correlation equations for predicting the enthalpies of solvation of gaseous solutes in water, $\Delta H_{Solv,W}$, [1]

$$\Delta H_{Solv,W} \text{ (kJ/mole)} = -13.310(0.457) + 9.910(0.814)\mathbf{E} + 2.836(0.807)\mathbf{S}$$

$$-32.010(1.102)\mathbf{A} - 41.816(0.781)\mathbf{B} - 6.354(0.200)\mathbf{L} \qquad (1)$$

$$\text{(with N = 368, SD = 3.68, } R^2 = 0.964, R^2_{adj} = 0.964, F = 1950.5)$$

and in several organic solvents, such as carbon tetrachloride, $\Delta H_{Solv,CT}$, [2]

$$\Delta H_{Solv,CT} \text{ (kJ/mole)} = -6.441(0.374) + 3.517(0.703)\ \mathbf{E} - 4.824(0.749)\ \mathbf{S} - 7.045(0.740)\ \mathbf{B}$$

$$-8.886(0.129)\ \mathbf{L}$$

$$\text{(with N = 177, SD = 2.070, } R^2 = 0.984, R^2_{adj} = 0.984, F = 2681.8) \qquad (2)$$

and dimethyl sulfoxide, $\Delta H_{Solv,DMSO}$, [3]

$$\Delta H_{Solv,DMSO} \text{ (kJ/mole)} = -2.546(0.703) - 0.329(0.0.952)\ \mathbf{E} - 18.448(1.139)\ \mathbf{S} -$$

$$47.419(1.653)\ \mathbf{A} - 5.861(1.004)\ \mathbf{B} - 6.380(0.197)\ \mathbf{L}$$

$$\text{(with N = 150, SD = 2.80, } R^2 = 0.967, R^2_{adj} = 0.966, F = 850.6) \qquad (3)$$

based on the Abraham solvation parameter model. Here and elsewhere, N corresponds to the number of solutes, R denotes the correlation coefficient, SD is the standard deviation and F corresponds to the Fisher F-statistic.

The independent variables in Eqns. 1-3 are as follows: **E** and **S** refer to the excess molar refraction and dipolarity/polarizability descriptors of the solute, respectively, **A** and **B** are the solute overall or summation hydrogen bond acidity and basicity, and **L** is the logarithm of the solute's gas phase dimensionless Ostwald partition coefficient into hexadecane at 298.15 K. The first four descriptors can be regarded as measures of the tendency of the given solute to undergo various solute-solvent interactions. The latter descriptor, **L**, is a measure of solute size, and will thus be a measure of the solvent cavity term that will accommodate the dissolved solute. General dispersion interactions are also related to solute size, hence, **L** will also describe the general solute-solvent interactions. The regression coefficients and constants (*c, e, s, a, b,* and *l*) are obtained by regression analysis of experimental data for a given process, which in the case of Eqns. 1-3 was the enthalpic change resulting from the transfer of the gaseous solute into the respective liquid solvent.

Enthalpies of solvation are important in that the numerical values provide valuable information regarding solute-solvent interactions. From a thermodynamic standpoint, ΔH_{Solv} data can be used to estimate the gas-to-condensed phase partition coefficient, K,

$$\ln K(at\,T) - \ln K(at\,298.15\,K) = \frac{-\Delta H_{Solv}}{R}(1/T - 1/298.15) \qquad (4)$$

and the water-to-organic solvent partition coefficient, P,

$$\ln P(at\,T) - \ln P(at\,298.15\,K) = \frac{-\Delta H_{trans}}{R}(1/T - 1/298.15) \tag{5}$$

at other temperatures from measured partition coefficient data at 298.15 K and the

solute's enthalpy of solvation, ΔH_{Solv}, or enthalpy of transfer, ΔH_{trans}, between the two

condensed phases. The enthalpy of transfer needed in Eqn. 5 is defined as

$$\Delta H_{trans} = \Delta H_{Solv,Org} - \Delta H_{Solv,W} \tag{6}$$

the difference in the enthalpy of solvation of the solute in the specified organic solvent

minus its enthalpy of solvation in water. The above equations assume zero heat capacity

changes. There is considerable published experimental partition coefficient data for

solute transfer from water to water-immiscible (or partly miscible) organic solvents, such

as 1-octanol, cyclohexane and heptane.

To date we have derived correlations for estimating the enthalpies of solvation of

gaseous solutes in water, 1-octanol, heptane, hexadecane, cyclohexane, benzene, toluene,

carbon tetrachloride, dimethyl sulfoxide and propylene carbonate [1-4]. Each correlation

was based on experimental data for a minimum of 100 organic and inorganic solutes.

Eventually, we hope to develop mathematical expressions for predicting enthalpies of

solvation in most (if not all) of the organic solvents for which we have log K and log P

correlations. The present study concerns developing a ΔH_{Solv} correlation for two

chloroalkane solvent molecules, chloroform and 1,2-dichloroethane.

Data Correlation and Computation Methods

Our search of the published chemical and engineering literature found a large

number of papers [5-65] that reported experimental partial molar enthalpies of solution of

liquid and crystalline compounds in both chloroform and 1,2-dichloroethane. The

experimental values were determined by either direct calorimetric methods or calculated

based on the temperature dependence of the measured infinite dilution activity

coefficients or solubilities. The retrieved enthalpy of solution values were converted to

gas-to-organic solvent enthalpies of transfer by

Liquid solutes: $\quad\quad \Delta H_{Solv} = \Delta H_{Soln} - \Delta H_{Vap,298K}$ $\quad\quad\quad\quad\quad\quad$ (7)

Crystalline solutes: $\quad \Delta H_{Solv} = \Delta H_{Soln} - \Delta H_{Sub,298}$ $\quad\quad\quad\quad\quad\quad$ (8)

subtracting the solute's standard molar enthalpy of vaporization [66], $\Delta H_{Vap,298K}$, or

standard molar enthalpy of sublimation [67], $\Delta H_{Sub,298K}$, at 298.15 K. For purposes of

the this study we have considered enthalpies of solvation, ΔH_{Solv}, and what will be called

"inner energies", $\Delta U_{Solv,}$ to be equivalent. Goss [68] discusses the difference between the

$\Delta H_{Solv,}$ and $\Delta U_{Solv,}$ in terms of the concentration units used in expressing the gas-phase

concentrations of the Henry's law constant. At 298 K the difference between the

quantities amounts to about 2.5 kJ/mole [68], which is less than the experimental

uncertainty associated with many of the observed values. Given the slight numerical

difference between the two values under normal environmental conditions, we have

combined both sets of numerical values into a single database, as has been done in the

past by most research groups that have developed predictive methods for enthalpies of

solvation. Most of our tabulated values are enthalpies of solvation; however, there may

be a few "inner energies" listed in Tables 1 and 2 that that were mislabeled as enthalpies

in the original data source.

Based on an initial assessment of the available experimental data, we eliminated

from consideration all experimental data that pertained to temperatures outside of 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 fore-mentioned criteria, we obtained 100 molar enthalpies of solvation in chloroform and 88 molar enthalpies of solvation in 1,2-dichloroethane for regression analysis. The experimental $\Delta H_{Solv,CFM}$ and $\Delta H_{Solv,DCE}$ values are listed in Tables 1 and 2, respectively, along with the literature references.

For the analysis of the data, we use the two linear free energy equations of Abraham et al. [69,70]. In Eqn. 10, the descriptor **V** is the McGowan volume.

$$SP = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + l \cdot \mathbf{L} \tag{9}$$

$$SP = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V} \tag{10}$$

Most of our precious studies have dealt with partition processes related to the Gibbs energy of transfer, where the dependent solute property, SP, would be either the logarithm of the gas-to-liquid (Eqn. 9) or the logarithm of the water-to-organic solvent (Eqn. 10) partition coefficient. The basic model can be used to correlate enthalpies of solvation and enthalpies of solute transfer from one condensed phase to a second condensed phase. Equations 1-3 correspond to the temperature derivative of the respective gas-to-liquid partition coefficient correlation; *i.e.*, $\Delta H_{Solv} = R \; \partial \ln K / \partial (1/T)$. From a thermodynamic standpoint, the temperature derivative of the logarithm of the water-to-organic solvent partition coefficient would be related to enthalpy of transfer from water to the organic solvent, *i.e.*, $\Delta H_{trans} = R \; \partial \ln P / \partial (1/T)$. We have also reported

ΔH_{Solv} correlations based on Eqn. 10, which uses the McGowan volume, **V**-descriptor, which is more readily available than the **L**-descriptor. The **V**-descriptor is easily calculable from the individual atomic sizes and numbers of bonds in the molecule [71]. Molecular descriptors for all of the compounds considered in the present study are tabulated in Tables 1 and 2. The numerical values of the solute descriptors came from our solute descriptor database, which now contains values for more than 4000 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, solubility and chromatographic data [70].

Results and Discussion

We have assembled in Table 1 values of $\Delta H_{Solv,CFM}$ for 100 gaseous solutes dissolved in chloroform covering a reasonably wide range of compound type and descriptor values. Analysis of the experimental data yielded the following correlation equations

$\Delta H_{Solv,CFM}$ (kJ/mole) = - 6.516(0.701) + 8.628(0.936) **E** – 13.956(1.160) **S** –

$\qquad$ 2.712(1.666) **A** – 17.334(0.958) **B** – 8.739(0.158) **L** $\qquad$ (11)

(with N = 100, SD = 2.10, R^2 = 0.982, R^2_{adj} = 0.981, F = 1049.5)

$\Delta H_{Solv,CFM}$ (kJ/mole) = - 0.425(0.829) – 0.844(0.916)**E** – 20.735(1.251)**S** –

$\qquad$ 5.817(1.753)**A** - 16.434(1.003)**B** – 31.039(0.587)**V** $\qquad$ (12)

$\qquad$ (with N = 100, SD = 2.19, R^2 = 0.981, R^2_{adj} = 0.980, F = 964.5)

All regression analyses were performed using SPSS statistical software. Both Eqn. 11 and 12 are statistically very good with standard deviations of 2.10 and 2.19 kJ/mole for a data set that covers a range of 106.89 kJ/mole. See Figure 1 for a plot of the calculated values of $\Delta H_{Solv,CFM}$ based on Eqn. 11 against the observed values. Equation 11 is slightly the better equation statistically, and from a thermodynamic standpoint Eqn. 11 is the enthalpic temperature derivative of the Abraham model's gas-to-condensed phase transfer equation. Equation 12 might be more useful in some predictive applications in instances where the **L**-descriptor is not known. Equation 12 uses the McGowan volume, **V**-descriptor, which is easily calculable from the individual atomic sizes and numbers of bonds in the molecule [71]. To our knowledge, equations 11 and 12 are the first expressions that allow one to predict the enthalpy of solvation of gaseous solutes in chloroform.

In order to assess the predictive ability of Eqn. 11 we divided the 100 data points into a training set and a test set by allowing the SPSS software to randomly select half of the experimental data 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

$\Delta H_{Solv,CFM}$ (kJ/mole) = - 6.291(0.775) + 7.456(1.008) **E** – 13.902(1.237) **S** – 4.694(2.179)

$\qquad$ **A** – 15.674(1.082) **B** – 8.734(0.168) **L** $\hphantom{xxxxxxxxxxxxxxxxxx}$ (13)

(with N = 50, SD = 1.66, R^2 = 0.988, R^2_{adj} = 0.987, F = 746.1)

The training set equation, Eqn. 13, was then used to predict $\Delta H_{Solv,CFM}$ for the 50 compounds in the test set. Comparison of the predicted and observed values gave SD = 2.24, Average Absolute Error (AAE) = 1.60 and an Average Error (AE) = - 0.3705.

There is therefore very little bias in the predictions using Eqn. 13 with AE equal to - 0.3705 kJ/mole. To our knowledge there has been no previous attempt to correlate $\Delta H_{Solv,CFM}$ data.

In Table 2 are collected values of the enthalpies of solvation of 88 gaseous solutes in 1,2-dichloroethane. Regression analyses of the experimental $\Delta H_{Solv, DCE}$ data in accordance with the Abraham model yielded

$$\Delta H_{Solv,DCE} = -2.345\ (0.672) + 5.555(0.861)\ \mathbf{E} - 18.328(1.122)\ \mathbf{S} - 9.599(1.794)\ \mathbf{A} -$$
$$7.101(1.013)\ \mathbf{B} - 8.045(0.144)\ \mathbf{L} \tag{14}$$

(with N = 88, SD = 1.72, $R^2 = 0.982$, $R^2_{adj} = 0.980$, F = 875.3.)

$$\Delta H_{Solv,DCE} = 3.623(1.002) - 3.208(1.050)\ \mathbf{E} - 24.665(1.520)\ \mathbf{S} - 11.165(2.348)\ \mathbf{A} -$$
$$6.589(1.322)\ \mathbf{B} - 28.520(0.671)\ \mathbf{V} \tag{15}$$

(with N = 88, SD = 2.24, $R^2 = 0.969$, $R^2_{adj} = 0.967$, F = 509.1)

Both Eqn. (14) and (15) are statistically very good with standard deviations of 1.72 and 2.24 kJ/mole for a data set that covers a range of 71.7 kJ/mole. Figure 2 compares the calculated values of $\Delta H_{Solv,DCE}$ based on Eqn. (14) against the observed values. To our knowledge there has been no previous attempt to correlate $\Delta H_{Solv,DCE}$ data.

In order to assess the predictive ability of Eqn. 14 we divided the 88 data points into a training set and a test set by allowing the SPSS software to randomly select half of the experimental data points. The selected data points became the training set and the remaining compounds that were left served as the test set. Analysis of the experimental data in the training set gave

$$\Delta H_{Solv,DCE}\ (kJ/mole) = -2.972(0.943) + 4.717(1.443)\ \mathbf{E} - 17.267(1.804)\ \mathbf{S} -$$

$$5.233(2.530) \, \mathbf{A} - 8.317(1.984) \, \mathbf{B} - 7.886(0.181) \, \mathbf{L} \tag{16}$$

(with N = 44, SD = 1.48, R^2 = 0.983, R^2_{adj} = 0.980, F = 432.7)

The training set equation, Eqn. 13, was then used to predict $\Delta H_{Solv,DCE}$ for the 44

compounds in the test set. Comparison of the predicted and observed values gave SD =

2.07, Average Absolute Error (AAE) = 1.54 and an Average Error (AE) = - 0.0764.

There is therefore very little bias in the predictions using Eqn. 16 with AE equal to -

0.0764 kJ/mole. An uncertainty/error 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 313.15 K. This level of error will be sufficient for most practical chemical

and engineering applications. To our knowledge there has been no previous attempt to

correlate $\Delta H_{Solv,DCE}$ data.

As noted previously, correlations for predicting enthalpies of solvation in the

various organic solvents can be combined with Eqn. 1 to give enthalpies of solute transfer

from water to the given organic solvent. Enthalpies of solute transfer are particularly

useful in that knowledge of ΔH_{trans} enables one to predict how water-to-organic solvent

partition coefficients vary with temperature. There is considerable published partition

coefficient data for solutes distributed between water and chloroform [72, 73], and

between water and 1,2-dichloroethane [72, 74, 75]. Solutes studied include nonionic

molecules as well as ionizable drugs. Most of the published data pertain to 298 K, and

the correlations presented in the present study will allow one to estimate log P values at

temperatures not too far removed from 298 K.

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TABLE 1. Values of the gas to chloroform solvation enthalpy, $\Delta H_{Solv,CFM}$, in kJ/mole at

298 K for 100 solutes, together with the solute descriptors

Solute	E	S	A	B	L	V	Exp	Ref
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	-24.21	5
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-28.25	5
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-32.95	5
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	-37.57	5
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	-41.95	5
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	-46.12	5
Undecane	0.000	0.000	0.000	0.000	5.191	1.6585	-51.27	5
Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-55.83	5
Tridecane	0.000	0.000	0.000	0.000	6.200	1.9402	-60.03	5
Tetradecane	0.000	0.000	0.000	0.000	6.705	2.0810	-65.37	5
Pentadecane	0.000	0.000	0.000	0.000	7.209	2.2220	-67.72	5
Hexadecane	0.000	0.000	0.000	0.000	7.714	2.3630	-73.95	5
Heptadecane	0.000	0.000	0.000	0.000	8.218	2.5040	-78.09	5
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	-30.29	6
Cycloheptane	0.350	0.100	0.000	0.000	3.704	0.9863	-35.97	7
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	-40.81	7
Benzene	0.610	0.520	0.000	0.140	2.786	0.7176	-35.85	8
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	-41.09	8
1,4-Dimethylbenzene	0.613	0.520	0.000	0.160	3.839	0.9982	-46.20	8
1,3,5-Trimethylbenzene	0.649	0.520	0.000	0.190	4.344	1.1391	-50.29	8
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	-57.18	9
Phenanthrene	2.055	1.290	0.000	0.260	7.632	1.4540	-77.17	9
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4540	-78.45	9
Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	-36.40	8
Dipropyl ether	0.008	0.250	0.000	0.450	2.954	1.0127	-42.20	10
Diisopropyl ether	-0.060	0.160	0.000	0.580	2.530	1.0127	-41.28	10
Dibutyl ether	0.000	0.250	0.000	0.450	3.924	1.2945	-51.00	8
Dipentyl ether	0.000	0.250	0.000	0.450	4.875	1.5763	-57.19	11
Ethoxypropane	0.000	0.250	0.000	0.450	2.493	0.8718	-38.73	10
Ethoxybutane	0.013	0.250	0.000	0.450	2.989	1.0127	-46.90	10
Methyl *tert*-butyl ether	0.024	0.110	0.000	0.630	2.380	0.8718	-38.53	12
Furan	0.369	0.510	0.000	0.130	1.913	0.5363	-29.14	13
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-42.60	8
Tetrahydropyran	0.275	0.470	0.000	0.550	3.057	0.7672	-43.98	14
1,3-Dioxane	0.308	0.720	0.000	0.700	2.519	0.6810	-48.20	14
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-49.70	8
Digylme	0.113	0.760	0.000	1.170	3.920	1.1301	-72.40	8
15-Crown-5	0.410	1.200	0.000	1.750	6.779	1.7025	-105.58	15,18
18-Crown-6	0.400	1.340	0.000	2.130	7.919	2.0430	-131.10	19
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	-39.34	8

2-Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-43.51	16
3-Pentanone	0.154	0.660	0.000	0.510	2.811	0.8288	-47.76	11
4-Heptanone	0.110	0.660	0.000	0.510	3.705	1.1106	-56.07	11
5-Nonanone	0.103	0.660	0.000	0.510	4.698	1.3924	-63.26	11
Cyclohexanone	0.403	0.860	0.000	0.560	3.792	0.8610	-55.90	27
N,N-Dimethylformamide	0.367	1.310	0.000	0.740	3.173	0.6468	-60.00	8
Dimethyl sulfoxide	0.522	1.720	0.000	0.970	3.459	0.6126	-66.69	8
Ethyl formate	0.146	0.660	0.000	0.380	1.845	0.6057	-35.02	20
Propyl formate	0.132	0.630	0.000	0.380	2.433	0.7466	-43.97	21
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-39.68	17
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-43.84	8
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-49.37	22
Ethyl propanoate	0.087	0.580	0.000	0.450	2.807	0.8875	-48.91	23
Propyl propanoate	0.070	0.560	0.000	0.450	3.338	1.0284	-53.24	24
Ethyl butanoate	0.068	0.580	0.000	0.450	3.271	1.0284	-52.85	25
Propyl butanoate	0.05	0.560	0.000	0.450	3.783	1.1693	-56.77	26
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-46.40	8
Aniline	0.955	0.960	0.260	0.410	3.934	0.8162	-56.10	8
N,N-Dimethylaniline	0.957	0.810	0.000	0.410	4.701	1.0980	-58.23	8
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	-48.40	8
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	-36.93	8
Nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237	-37.70	8
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-28.70	8
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-32.80	8
1-Propanol	0.236	0.420	0.370	0.480	2.031	0.5900	-35.20	33
2-Propanol	0.212	0.360	0.330	0.560	1.764	0.5900	-35.10	8
1-Butanol	0.224	0.420	0.370	0.480	2.601	0.7309	-42.00	8
1-Hexanol	0.210	0.420	0.370	0.480	3.610	1.0170	-50.40	8
1-Octanol	0.199	0.420	0.370	0.480	4.619	1.2950	-60.00	8
Dichloromethane	0.387	0.570	0.100	0.050	2.019	0.4943	-30.32	7
Chloroform	0.425	0.490	0.150	0.020	2.480	0.6167	-31.31	66
1-Chlorobutane	0.210	0.400	0.000	0.100	2.722	0.7946	-35.06	30
1,2-Dichloroethane	0.416	0.640	0.100	0.110	2.573	0.6352	-35.65	31
1,1,2,2-Tetrachloroethane	0.595	0.760	0.160	0.120	3.803	0.8800	-45.63	32
Phenol	0.805	0.890	0.600	0.300	3.766	0.7751	-51.00	28
2-Methoxyphenol	0.837	0.910	0.220	0.520	4.449	0.9160	-61.98	28
Anisole	0.710	0.750	0.000	0.290	3.890	0.9160	-50.44	28
Pyrrole	0.613	0.730	0.410	0.290	2.865	0.5770	-41.12	29
N-Methylpyrrole	0.559	0.790	0.000	0.310	2.923	0.7180	-46.73	29
N-Methylaniline	0.948	0.900	0.170	0.430	4.494	0.9571	-56.76	29
N-Ethylaniline	0.945	0.850	0.170	0.430	4.811	1.0980	-60.81	29
Diethyl sulfide	0.373	0.380	0.000	0.320	3.104	0.8357	-43.50	36
Piperidine	0.422	0.460	0.100	0.690	3.304	0.8043	-49.51	38
Nitrobenzene	0.871	1.110	0.000	0.280	4.557	0.8906	-59.20	37
Bromoethane	0.366	0.400	0.000	0.120	2.120	0.5654	-27.90	39
1,2-Diaminobenzene	1.260	1.400	0.240	0.730	4.845	0.9148	-61.40	41

1-Chloropentane	0.208	0.380	0.000	0.090	3.223	0.9355	-40.17	34
1-Chlorohexane	0.201	0.400	0.000	0.100	3.777	1.0770	-44.44	34
1-Chloroheptane	0.194	0.400	0.000	0.100	4.282	1.2178	-48.99	34
1-Chlorooctane	0.191	0.400	0.000	0.100	4.772	1.3585	-53.47	34
Methyl propanoate	0.128	0.600	0.000	0.450	2.431	0.7466	-45.05	35
Methyl butanoate	0.106	0.600	0.000	0.450	2.893	0.8875	-50.40	35
Methyl pentanoate	0.108	0.600	0.000	0.450	3.392	1.0284	-52.59	35
Methyl hexanoate	0.08	0.600	0.000	0.450	3.874	1.1693	-57.93	35
Methyl octanoate	0.065	0.600	0.000	0.450	4.838	1.4511	-67.35	35
Methyl nonanoate	0.056	0.600	0.000	0.450	5.321	1.5920	-70.94	35
Methyl decanoate	0.053	0.600	0.000	0.450	5.803	1.7329	-75.74	35
Additional Indirect values								
1-Pentanol	0.219	0.42	0.37	0.48	3.106	0.8718	-47.67	40
Aniline	0.955	0.96	0.26	0.41	3.934	0.8162	-60.64	40
4-Methylphenol	0.82	0.87	0.57	0.31	4.312	0.9160	-60.64	40

TABLE 2. Values of the gas to 1,2-dichloroethane solvation enthalpy, $\Delta H_{Solv,DCE}$, in

kJ/mole at 298 K for 88 solutes, together with the solute descriptors

Solute	E	S	A	B	L	V	Exp Value	Ref
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	-18.87	42
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-22.80	42
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-26.57	42
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	-30.25	42
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	-34.52	42
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	-38.53	42
Undecane	0.000	0.000	0.000	0.000	5.191	1.6585	-45.70	48
Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-46.02	42
Tridecane	0.000	0.000	0.000	0.000	6.200	1.9402	-54.15	49
Tetradecane	0.000	0.000	0.000	0.000	6.705	2.0810	-57.35	59
Pentadecane	0.000	0.000	0.000	0.000	7.209	2.2220	-61.54	50
Hexadecane	0.000	0.000	0.000	0.000	7.714	2.3630	-61.55	42
Heptadecane	0.000	0.000	0.000	0.000	8.218	2.5040	-71.71	51
3-Ethylpentane	0.000	0.000	0.000	0.000	3.091	0.9540	-27.00	45
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358	-27.13	7
2,2,4,4-Tetramethylpentane	0.000	0.000	0.000	0.000	3.512	1.3767	-28.70	45
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	-25.60	45
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	-32.89	43
2-Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-36.36	43
2-Hexanone	0.136	0.680	0.000	0.510	3.286	0.9697	-46.00	45
2-Heptanone	0.123	0.680	0.000	0.510	3.760	1.1106	-47.49	43
4-Heptanone	0.110	0.660	0.000	0.510	3.705	1.1106	-45.98	43
2-Nonanone	0.119	0.680	0.000	0.510	4.735	1.3924	-55.10	43
5-Nonanone	0.103	0.660	0.000	0.510	4.698	1.3924	-53.14	43
2,2,4,4-Tetramethyl-3-pentanone	0.099	0.560	0.000	0.520	4.370	1.3924	-44.30	43
Cyclohexanone	0.403	0.860	0.000	0.560	3.792	0.8610	-47.15	43
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-23.83	52
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-26.85	52
1-Propanol	0.236	0.420	0.370	0.480	2.031	0.5900	-29.75	52
1-Butanol	0.224	0.420	0.370	0.480	2.601	0.7309	-35.74	52
1-Octanol	0.199	0.420	0.370	0.480	4.619	1.2950	-52.13	46
Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	-27.10	45
Dibutyl ether	0.000	0.250	0.000	0.450	3.924	1.2945	-40.08	46
Butyl methyl Ether	0.045	0.250	0.000	0.440	2.658	0.8718	-31.50	45
Methyl *tert*-butyl ether	0.024	0.210	0.000	0.590	2.380	0.8718	-30.80	45
Methyl heptyl ether	0.048	0.250	0.000	0.450	4.088	1.2945	-43.60	46
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-33.90	45
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-39.30	45
15-Crown-5	0.410	1.200	0.000	1.750	6.779	1.7025	-90.57	53
1-Fluorooctane	-0.020	0.350	0.000	0.100	3.850	1.2538	-44.69	46

1-Chlorooctane	0.191	0.400	0.000	0.090	4.708	1.3580	-48.07	46
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	-54.79	60
Methyl formate	0.192	0.680	0.000	0.380	1.285	0.4648	-28.22	54
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-33.38	44
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-36.00	45
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-39.79	44
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-44.53	44
Pentyl acetate	0.067	0.600	0.000	0.450	3.844	1.1693	-47.30	44
Methyl propanoate	0.128	0.600	0.000	0.450	2.431	0.7466	-36.75	54
Ethyl propanoate	0.087	0.580	0.000	0.450	2.807	0.8875	-37.94	44
Methyl butanoate	0.106	0.600	0.000	0.450	2.893	0.8875	-40.29	54
Ethyl butanoate	0.068	0.580	0.000	0.450	3.271	1.0284	-41.86	44
Methyl pentanoate	0.108	0.600	0.000	0.450	3.392	1.0284	-43.97	54
Ethyl pentanoate	0.049	0.580	0.000	0.450	3.769	1.1693	-47.81	47
Ethyl hexanoate	0.043	0.580	0.000	0.450	4.251	1.3102	-50.46	44
Butyl formate	0.121	0.630	0.000	0.380	2.958	0.8875	-41.21	55
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	-33.10	45
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-33.20	45
Benzene	0.610	0.520	0.000	0.140	2.786	0.7176	-33.50	45
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	-34.70	45
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	-38.90	45
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	-42.70	45
Iodobenzene	1.188	0.820	0.000	0.120	4.502	0.9746	-47.70	45
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	4.518	0.9612	-46.00	45
1,4-Dichlorobenzene	0.825	0.750	0.000	0.020	4.435	0.9612	-45.20	45
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3240	-64.00	45
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4540	-76.60	45
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	-37.70	45
Mesitylene	0.649	0.520	0.000	0.190	4.344	1.1391	-45.20	45
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	-40.60	45
Nitrobenzene	0.871	1.110	0.000	0.280	4.557	0.8906	-54.80	45
Anisole	0.710	0.750	0.000	0.290	3.890	0.9160	-46.90	45
Acetophenone	0.818	1.010	0.000	0.480	4.501	1.0140	-56.50	45
4-Methoxyphenol	0.900	1.170	0.570	0.480	4.773	0.9747	-68.60	65
1,2-Dichloroethane	0.416	0.640	0.100	0.110	2.573	0.6352	-35.10	66
Diethyl carbonate	0.060	0.580	0.000	0.530	3.412	0.9462	-45.02	56
Carbon tetrachloride	0.458	0.380	0.000	0.000	2.823	0.7391	-31.87	58
Sulfur dioxide	0.370	0.660	0.280	0.100	0.778	0.3465	-23.01	61
Dimethyl carbonate	0.142	0.540	0.000	0.570	2.328	0.6644	-38.14	57
1-Chloronaphthalene	1.417	1.000	0.000	0.140	5.856	1.2078	-62.25	56
Nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237	-34.84	39
Nitroethane	0.270	0.950	0.020	0.330	2.414	0.5646	-38.15	39
Propionitrile	0.162	0.900	0.020	0.360	2.082	0.5451	-35.03	39

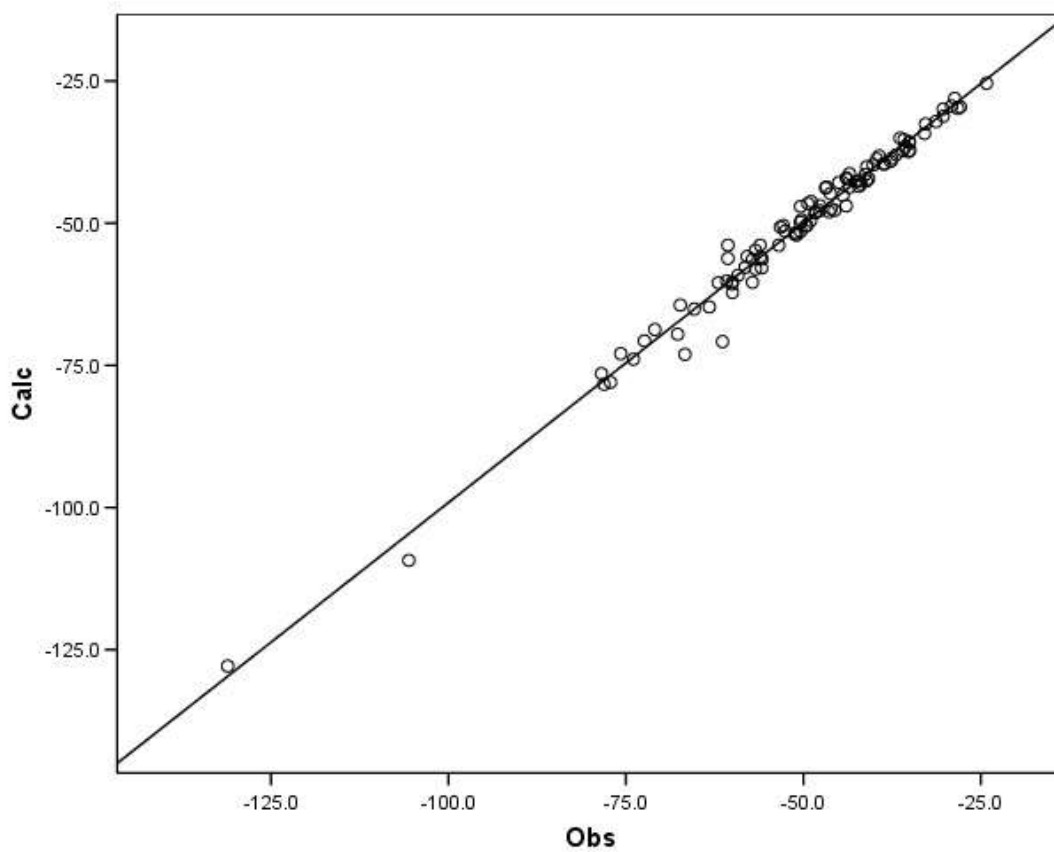| 1-Chlorobutane	0.210	0.400	0.000	0.100	2.722	0.7946	-31.95	62
1,1,1-Trichloroethane	0.369	0.410	0.000	0.090	2.733	0.7576	-31.28	63
trans 1,2-Dichloroethene	0.425	0.410	0.090	0.050	2.278	0.5922	-28.91	64
1,1,2,2-Tetrachloroethane	0.595	0.760	0.160	0.120	3.803	0.8800	-47.03	64
Benzaldehyde	0.820	1.000	0.000	0.390	4.008	0.8730	-50.60	45

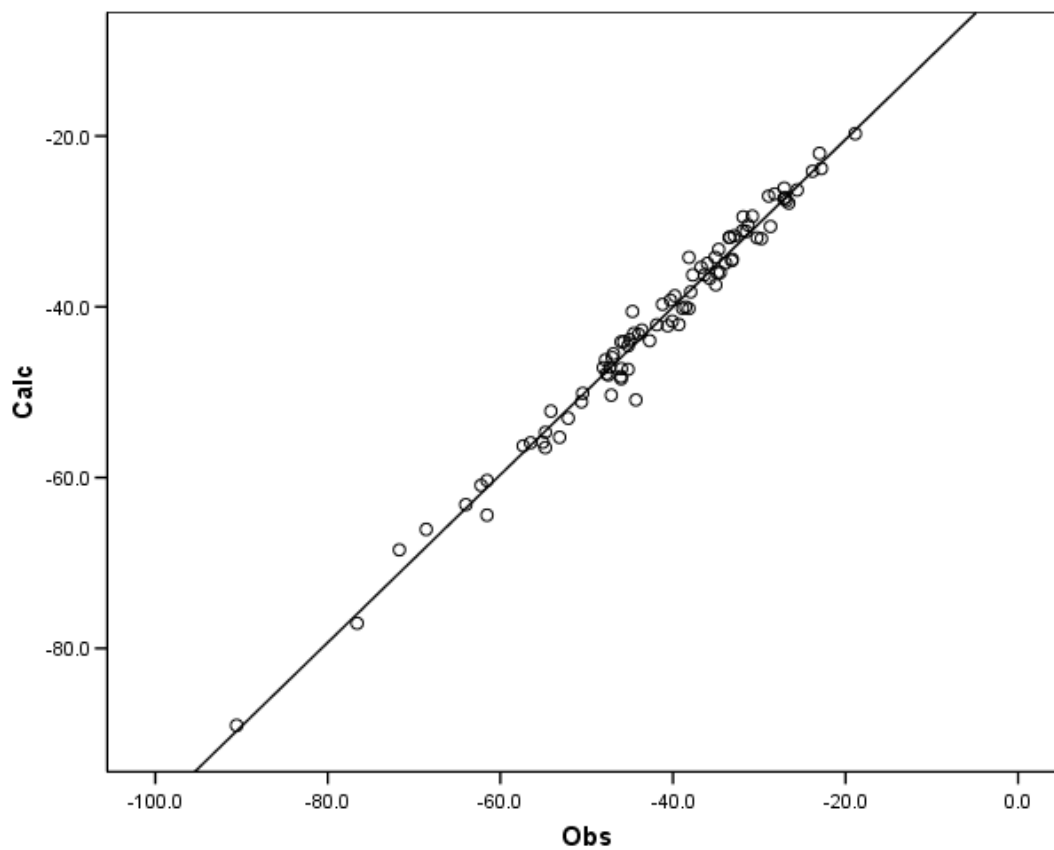Figure 1. A plot of the calculated values of $\Delta H_{Solv,CFM}$ on eqn (11) against the observed values.

Figure 2. A plot of the calculated values of $\Delta H_{Solv,DCE}$ on eqn (14) against the observed values