Effect of halogen substitution on the enthalpies of solvation and hydrogen bonding of organic solutes in chlorobenzene and 1,2-dichlorobenzene derived using multi-parameter correlations

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Abstract

Enthalpies of solution at infinite dilution at 298 K, $\Delta_{soln}H^{A/Solvent}$, have been measured by isothermal solution calorimetry for 43 and 72 organic solutes dissolved in chlorobenzene and 1,2-dichlorobenzene, respectively. The measured $\Delta_{soln}H^{A/Solvent}$ data, along with published $\Delta_{soln}H^{A/Solvent}$ values taken from the published literature for solutes dissolved in both chlorobenzene solvents, were converted to enthalpies of solvation, $\Delta_{solv}H^{A/Solvent}$, using standard thermodynamic equations. Abraham model correlations were developed from the experimental $\Delta_{solv}H^{A/Solvent}$ data. The best derived correlations describe the experimental gas-to-chlorobenzene and gas-to-1,2-dichlorobenzene enthalpies of solvation to within standard deviations of 1.5 kJ mol^{-1} and 1.9 kJ mol^{-1}, respectively. Enthalpies of X-H…π (X – O, N, and C) hydrogen bond formation of proton donor solutes (alcohols, amines, chlorinated hydrocarbons and etc.) with chlorobenzene and 1,2-dichlorobenzene were calculated based on the Abraham solvation equation. Obtained values are in good agreement with the results determined using conventional methods.

Key Words: Enthalpy of solution; enthalpy of solvation; chlorobenzene; 1,2-dichlorobenzene; molecular interactions; hydrogen bonding

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Introduction

This study continues our combined experimental and theoretical examination of gas-to-organic solvent transfer processes for nonelectrolyte solutes [1-19]. Such processes govern chemical separations by gas-liquid chromatography, measurement of solubilities and activity coefficients by inert-gas stripping methods, and the removal and pre-concentration of volatile organic solutes from aqueous analytical samples using headspace single drop micro-extraction methods. The latter extraction process involves two partition coefficients, the first for solute transfer to the gas phase from the aqueous solution being analyzed, and the second for solute transfer into the suspended liquid drop of the micro-extraction device. A complete understanding of the solute transfer process requires not only examining how the equilibrium partition coefficient depends on the polarity and hydrogen-bonding character of the solute and solvent molecules, but also on understanding the enthalpic effects that determine how the gas-to-organic solvent partition coefficients of the different solute-solvent combinations vary with temperature.

In previous publications [1-15] we have developed Abraham model correlations:

$$\Delta_{solv}H^{A/Solvent} = c_{h,l} + e_{h,l}\cdot\mathbf{E} + s_{h,l}\cdot\mathbf{S} + a_{h,l}\cdot\mathbf{A} + b_{h,l}\cdot\mathbf{B} + l_{h,l}\cdot\mathbf{L} \qquad (1)$$

$$\Delta_{solv}H^{A/Solvent} = c_{h,v} + e_{h,v}\cdot\mathbf{E} + s_{h,v}\cdot\mathbf{S} + a_{h,v}\cdot\mathbf{A} + b_{h,v}\cdot\mathbf{B} + v_{h,v}\cdot\mathbf{V} \qquad (2)$$

for mathematically describing experimental enthalpies of solvation, $\Delta_{solv}H^{A/Solvent}$, of inert gases and organic vapors dissolved in water and in a wide range of organic solvents of varying polarity and hydrogen bonding character. The organic solvents included several saturated hydrocarbons [1,2] and aromatic hydrocarbons [1,3,4], chlorinated alkanes [4-6], several primary, secondary and tertiary alcohols [7-11], two dialkyl carbonates [12], one alkyl acetate solvent [13], one dialkyl ether [13] and two cyclic ethers [6,8], as well as several miscellaneous organic solvents [9,14,15]. In each case eqns. (1) and (2) were found to provide a reasonably accurate mathematical description of the experimental enthalpy of solvation data. For each solvent the differences between the experimental and back-calculated $\Delta_{\mathrm{solv}}H^{\mathrm{A/Solvent}}$ values were on the order of ± 3 kJ mol^{-1} or less.

The Abraham model is a linear free energy relationship that has been used to describe a large number of solute transfer processes involving two liquid phases [20-24], blood and body fluids/organs/tissues [25-29], water and molecularly organized solvent media (micellar solutions) [30, 31], and gas and condensed liquid or solid phases [20-25, 27, 28, 30-32]. The same mathematical form is used to describe each solute transfer process, the only difference being that $\Delta_{\mathrm{solv}}H^{\mathrm{A/Solvent}}$ is replaced by the solute transfer property being described (*e.g.*, gas-to-liquid partition coefficient, water-to-liquid partition coefficient, blood-to-brain partition coefficient, gas-to-brain partition coefficient, *etc*.). Each term in eqns. (1) and (2) represents a different type of molecular interaction involving the solute and its solubilizing media. The interactions are expressed as the product of a solute property times the complimentary solvent property. Molecular solute descriptors contain important information regarding the ability of the dissolved solute to interact with its surrounding solubilizing media. Solute descriptors are defined as follows: **E** is the solute excess molar refractivity in units of (cm^3 mol^{-1})/10, **S** is the solute dipolarity/polarizability, **A** and **B** are the overall or summation hydrogen-bond acidity and basicity, **V** is the McGowan volume in units of (cm^3 mol^{-1})/100, and **L** is the logarithm of the gas-to-hexadecane partition coefficient at 298 K. The complimentary solubilizing media properties are identified in eqns. (1) and (2) by the lower case alphabetic letters that immediately precede the solute descriptors. Numerical values of the solvent properties are determined by solving a series of equations generated from measured solute transfer properties for solutes with known solute descriptors. The $a_{h,l}$ equation coefficients for benzene, mesitylene and p-xylene were recently used [3] to examine weak X-H…π (X – O,N, and C) hydrogen bonding of aromatic solvents with different proton donors. Hydrogen-bonding enthalpies calculated as the product of $a_{h,l} \cdot \mathbf{A}$ (*e.g.*, $\Delta_{HB}H^0 = a_{h,l} \cdot \mathbf{A}$) were in good agreement with values calculated using the Solomonov et al method [33]. Two independent models, the Abraham model and Solomonov et al. model, yielded comparable hydrogen-bonding enthalpies.

In the present study we extended our enthalpic considerations to include both chlorobenzene and 1,2-dichlorobenzene. Enthalpies of solution have been measured calorimetrically for 43 different organic solutes dissolved in chlorobenzene, and for 72 different organic solutes dissolved in 1,2-dichlorobenzene at 298.15 K. The measured enthalpies of solution, $\Delta_{soln}H^0$, are converted into enthalpies of solvation by subtracting the solute's molar enthalpy of vaporization or molar enthalpy of sublimation, $\Delta_{solv}H^{A/Solvent} = \Delta_{soln}H^{A/Solvent} - \Delta_{vap}H^0$ and $\Delta_{solv}H^{A/Solvent} = \Delta_{soln}H^{A/Solvent} - \Delta_{sub}H^0$, depending on whether measured $\Delta_{soln}H^{A/Solvent}$ value pertained to a liquid or crystalline solute. Abraham model $\Delta_{solv}H^{A/Solvent}$ correlations for both chlorobenzene and 1,2-dichlorobenzene were derived by combining our measured experimental data with published $\Delta_{soln}H^{A/Solvent}$ and $\Delta_{solv}H^{A/Solvent}$ data taken from the chemical literature [34-65].

Thermodynamic studies in chloroaromatic hydrocarbon solvents can be informative in that halogen-bond formation may occur [66-68]. Halogen bonds can be represented as RX ⋯⋯**:**YZ type specific interactions where RX is generally either an alkyl halide or aromatic halide (X = Cl, Br, I) and YZ is a Lewis base (Y = an atom having one or more lone electron pairs). Halogen bonds are considered to be analogous to hydrogen bonds, RH ⋯⋯**:**YZ. The same terminology is used for both halogen bonds and hydrogen bonds. RX and RH are described as halogen-bond and hydrogen-bond donors, and the YZ base is the halogen-bond or hydrogen-bond acceptor. In halogen-bonded complexes the X ⋯⋯ Y halogen-bond distance is typically shorter than the sum of the van der Waals radii of the respective X and Y atoms. Questions have been raised concerning whether fluorine compounds can participate in halogen bonding. Eskandari and Lesani [69] noted that RF molecules could interact with electron donors; however, there were fundamental differences between RF ⋯⋯**:**YZ type interactions and the interactions generally regarded as halogen bonds. Solvation effects due to a halogen atom acting as a Lewis acid, above, will be reflected in the A value for a solute and the b-coefficient for a solvent. For the more common case of a halogen atom acting as a base, this will be reflected in the **B** value for solute and the a-coefficient for a solvent. Interactions of the type AH ⋯⋯ **:**RX where the halogen atom acts as a hydrogen bond base are classified as hydrogen-bonding, as opposed to halogen-bonding, in this paper. From a mathematical standpoint it will be informative to ascertain how halogen-bond type interactions and/or halogen aromatic ring substituents might affect the other calculated equation coefficients in the Abraham model. To date we have reported Abraham model enthalpy of solvation correlations for benzene, and for three methyl-substituted benzenes (toluene, *p*-xylene and mesitylene).

Experimental

Chlorobenzene and 1,2-dichlorobenzene supplied by Sigma Aldrich (mass fraction purity min. 0.995) were used in calorimetric experiments without further purification. All organic solutes were of commercial origin (mass fraction purity more than 0.98). Before usage they were purified by repeated distillation or recrystallization in according to standards methods [70]. The content of impurities was controlled by Agilent 7890 B gas chromatograph and their mass fraction was not exceeded 0.005 after purification. Karl Fisher titration technique was used for analysis water content in studied samples. Detailed information about studied samples, their purity and water content is presented in Table 1.

Heat effects of dissolution of organic solutes in chlorobenzene and 1,2-dichlorobenzene were measured by commercial semi-adiabatic solution calorimeter TAM III (TA-Instruments). Temperature of all dissolution experiments was kept constant at 298.15±0.01 K. Solvent was thermostated in 100 mL glass cell equipped with a gold stirrer. Two different input systems were used for heat effect measurements: ampoule breaking technique for solid samples and titration technique for liquids. Calorimeter was calibrated separately for these two types of input techniques by dissolving the potassium chloride and propan-1-ol in pure water, respectively. In both cases our experimental results ($\Delta_{\rm soln}H^{\rm KCl/H_2O}$) = (17.41±0.04 kJ·mol^{-1}) and ($\Delta_{\rm soln}H^{\rm KCl/H_2O}$) = (-10.16±0.03 kJ·mol^{-1}) were in good agreement with recommended literature data ($\Delta_{\rm soln}H^{\rm KCl/H_2O}$) = (17.47±0.07 kJ·mol^{-1}) [71] and ($\Delta_{\rm soln}H^{\rm KCl/H_2O}$) = (-10.16±0.02 kJ·mol^{-1}) [72]. The detailed procedure of calorimetric measurements was published elsewhere [73,74]. Dissolution experiments for each solute-solvent system were reproduced at least 4 times at different concentrations of solute (see Table S1 and S2). All values of solution enthalpies were constant in studied range of concentrations. This fact confirms the assumption that each studied solute dissolves in sufficient amount of solvent to give a solution of infinite dilution.

Average values of the solution enthalpies of the organic solutes at infinite dilution in chlorobenzene and 1,2-dichlorobenzene are listed in Tables 2 and 3, respectively. Enthalpies of solution were converted to $\Delta_{\rm solv}H^{A/Solvent}$ values by subtracting the solute's measured enthalpy of vaporization (for liquid solutes) or measured enthalpy of sublimation (for solid solutions). The $\Delta_{\rm vap}H$ and $\Delta_{\rm sub}H$ values adjusted to 298 K used in the calculations came from a compilation by Acree and Chickos [75] and from Ref. [76]. Our measured $\Delta_{\rm solv}H^{A/Solvent}$ data was combined with published data taken from the chemical literature. In total we have 126 experimental $\Delta_{solv}H^{A/C_6H_5Cl}$ data points for solutes dissolved in chlorobenzene (see Table 4) and 94 experimental $\Delta_{solv}H^{A/C_6H_4Cl_2}$ values for solutes dissolved in 1,2-dichlorobenzene (see Table 5). For convenience we have also tabulated in Tables 4 and 5 the numerical values of the solute descriptors for all compounds considered in the present study.

Results and Discussion

Much of the experimental enthalpic data that is available in the published literature for solutions containing either chlorobenzene or dichlorobenzene pertain to excess enthalpies for binary mixtures. Normally the enthalpic measurements are made over the entire binary composition range. There are a few data sets [61, 64, 77-80] that we found which provide experimental measurements at sufficient low mole fraction compositions where extrapolations to infinite dilution could be made to obtain enthalpies of solution of solutes dissolved in chlorobenzene and 1,2-dichlorobenzene at 298.15 K. In Table 6 we compare our measured $\Delta_{\text{soln}}H^{\text{A/C}_6\text{H}_5\text{Cl}}$ and $\Delta_{\text{soln}}H^{\text{A/C}_6\text{H}_4\text{Cl}_2}$ to values extrapolated to infinite dilution based on published excess enthalpy data. Our measured $\Delta_{\text{soln}}H^{\text{A/C}_6\text{H}_5\text{Cl}}$ and $\Delta_{\text{soln}}H^{\text{A/C}_6\text{H}_4\text{Cl}_2}$ data are in reasonably good agreement with the published literature values.

The chlorobenzene database is the larger of the two data sets having numerical $\Delta_{solv}H^{A/C_6H_5Cl}$ values for 126 different compounds for solutes spanning a fairly wide range of descriptor values and hydrogen-bonding character. The database includes both liquid and crystalline nonelectrolyte organic compounds, as well as several inert and organic gases. Strong H-bond donors are represented in the database by 3-methoxyphenol (**A** = 0.590), 4-methoxyphenol (**A** = 0.570), and pyrazole (**A** = 0.540). Dimethyl sulfoxide (**B** = 0.880), *N*,*N*-dimethylformamide (**B** = 0.800), *N*-methylimidazole (**B** = 0.800), trimethylamine (**B** = 0.790), and tri-*n*-butylamine (**B** = 0.790) are the strongest H-bond bases in the database. The chemical diversity of the solutes in Table 4 should be more than sufficient for developing meaningful Abraham model correlations having good predictive capability.

The 126 experimental $\Delta_{solv}H^{A/C_6H_5Cl}$ data points in Table 4 provide two sets of 126 mathematical expressions. The first set expressions pertain to eqn. (1) and the second set of expressions pertain to eqn. (2). Each set of mathematical equations is solved simultaneously to yield the optimized numerical values of the equation coefficients, ($c_{h,l}$, $e_{h,l}$, $s_{h,l}$, $a_{h,l}$, $b_{h,l}$, and $l_{h,l}$) for eqn. (1) and ($c_{h,v}$, $e_{h,v}$, $s_{h,v}$, $a_{h,v}$, $b_{h,v}$, and $l_{h,v}$) for eqn. (2), that minimizes the collective differences between the experimental $\Delta_{solv}H^{A/C_6H_5Cl}$ data and the back-calculated values based on the respective Abraham model equation. The derived Abraham model correlations:

$$\Delta_{solv}H^{A/C_6H_5Cl}\ (\text{kJ mol}^{-1}) = -5.377(0.320) + 5.383(0.646)\,\mathbf{E} - 10.333(0.733)\,\mathbf{S} - 11.478(1.005)\,\mathbf{A} - 5.038(0.847)\,\mathbf{B} - 9.041(0.098)\,\mathbf{L} \qquad (3)$$

(with N = 126, $SD = 1.52$, $R^2 = 0.993$, $F = 3452$)

$$\Delta_{solv}H^{A/C_6H_5Cl}\ (\text{kJ mol}^{-1}) = 5.534(0.640) - 4.164(0.984)\,\mathbf{E} - 20.543(1.212)\,\mathbf{S} - 16.252(1.639)\,\mathbf{A} - 4.832(1.275)\,\mathbf{B} - 34.675(0.615)\,\mathbf{V} \qquad (4)$$

(with N = 126, $SD = 2.46$, $R^2 = 0.982$, $F = 1298$)

provide a very reasonable mathematical description of the measured $\Delta_{solv}H^{A/C_6H_5Cl}$ values as evidenced by the low standard deviations of $SD = 1.52$ kJ mol^{-1} and $SD = 2.46$ kJ mol^{-1} for eqns. (1) and (2), respectively. The uncertainties in the measured enthalpies of solvation are estimated to be on the order 0.5 – 2 kJ mol^{-1} based on an error propagation analysis of the uncertainties in the enthalpy of solution data, combined with the uncertainties in the measured enthalpy of sublimation and vaporization needed to convert $\Delta_{soln}H^{A/Solvent}$ to $\Delta_{solv}H^{A/Solvent}$ values. Enthalpies of sublimation and vaporization for several of the nonvolatile solutes were measured at much higher temperatures and there was a fair amount of uncertainty in extrapolating the measured values back to 298 K. Standard errors in the equation coefficients are given in parenthesis immediately following the calculated coefficient, and the relevant statistical information is given below the correlation equation, where *N* is the number of experimental data points used in the regression analyses, R^2 denotes the squared correlation coefficient, and *F* refers to the Fisher F-statistic.

The goodness-of-fit of eqns. (3) and (4) is further documented in Figures 1 and 2. The experimental data ranges from an enthalpy of solvation of $\Delta_{solv}H^{A/C_6H_5Cl}$ = 10.04 kJ mol^{-1} for helium dissolved in chlorobenzene to $\Delta_{solv}H^{A/C_6H_5Cl}$ = –78.22 kJ mol^{-1} for 2,6-dimethoxyphenol dissolved in chlorobenzene. Note that the back-calculated values in each figure are distributed uniformly about the diagonal line indicating a "perfect" fit. This is the first time that expressions have been reported for estimating enthalpies of solvation of solutes dissolved in chlorobenzene. Abraham and coworkers [81] have published Abraham model correlations for predicting the logarithm of the gas-to-chlorobenzene partition coefficient, log *K*, and the logarithm of the water-to-chlorobenzene partition coefficient, log *P*, at 298 K. The derived $\Delta_{solv}H^{A/C_6H_5Cl}$ correlations given above will expand the predictive capability of the published partition coefficients by allow researchers to extrapolate predicted log *K* and log *P* values to slightly higher and slightly lower temperatures. 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 log *K* value measured at 298.15 K to a temperature of 313.15. This level of predictive error will be sufficient for most design applications involving chemical extractions and separations.

In order to assess the predictive ability of eqns. 3 and 4 we divided the 126 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

$$\Delta_{solv}H^{A/C_6H_5Cl}\ (\text{kJ mol}^{-1}) = -\ 5.898(0.447) + 4.947(0.888)\ \mathbf{E} - 8.438(1.019)\ \mathbf{S} - 8.703(1.639)\ \mathbf{A} - 6.079(1.281)\ \mathbf{B} - 9.083(0.141)\ \mathbf{L} \qquad (5)$$

(with N = 63, *SD* = 1.36, R^2 = 0.993, *F* = 1679)

$$\Delta_{solv}H^{A/C_6H_5Cl}\ (\text{kJ mol}^{-1}) = 4.451(0.834) - 4.701(1.262)\ \mathbf{E} - 20.777(1.463)\ \mathbf{S} - 17.519(2.2337)\ \mathbf{A} - 2.462(1.665)\ \mathbf{B} - 33.914(0.749)\ \mathbf{V} \qquad (6)$$

(with N = 63, *SD* = 2.25, R^2 = 0.984, *F* = 711.5)

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. Each training set equation was then used to predict the $\Delta_{solv}H^{A/C_6H_5Cl}$ values for the 63 compounds in the test set. For the predicted and experimental values, we find *SD* = 1.91 kJ mol^{-1} (eqn. (5)) and *SD* = 2.85 kJ mol^{-1} (eqn. (6)), *AAE* (average absolute error) = 1.23 kJ mol^{-1} (eqn. (5)) and *AAE* = 1.92 kJ mol^{-1} (eqn. (6)), and *AE* (average error) = –0.27 kJ mol^{-1} (eqn. (5)) and AE = 0.31 kJ mol^{-1} (eqn. (6)). There is therefore very little bias in using eqns. (5) and (6) with *AE* equal to –0.27 kJ mol^{-1} and AE = 0.31 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.

The Abraham model correlations for enthalpies of solvation of solutes dissolved in 1,2-dichlorobenzene were derived in similar fashion by analyzing the 94 experimental $\Delta_{solv}H^{A/C_6H_4Cl_2}$ tabulated in Table 5. The derived mathematical expressions:

$$\Delta_{solv}H^{A/C_6H_4Cl_2}\ (\text{kJ mol}^{-1}) = -\ 4.609(0.714) + 3.975(0.920)\ \mathbf{E} - 8.947(0.961)\ \mathbf{S} - 8.518(1.148)\ \mathbf{A} - 5.928(1.140)\ \mathbf{B} - 9.182(0.186)\ \mathbf{L} \qquad (7)$$

(with N = 94, *SD* = 1.86, R^2 = 0.979, *F* = 802.8)

$\Delta_{solv}H^{A/C_6H_4Cl_2}$ (kJ mol^{-1}) = 1.234(1.047) – 5.635(1.082) **E** – 16.692(1.290) **S**

– 12.033(1.492) **A** – 5.196(1.469) **B** – 32.033(0.845) **V** (8)

(with N = 94, *SD* = 2.39, R^2 = 0.982, *F* = 478.4)

described the measured $\Delta_{solv}H^{A/C_6H_4Cl_2}$ values to within standard deviations of 1.86 kJ mol^{-1} and 2.39 kJ mol^{-1} as shown in Figures 3 and 4. The experimental values range from a value of $\Delta_{solv}H^{A/C_6H_4Cl_2}$ = – 23.00 kJ mol^{-1} for methanol to a value of $\Delta_{solv}H^{A/C_6H_4Cl_2}$ = – 79.54 kJ mol^{-1} for anthracene. As an informational note the dataset used in regression analysis contains mainly moderately volatile liquid organic solutes and nonvolatile crystalline organic solutes. There is only a single organic gas molecule, dimethylamine, in the data set. While we expect eqns. (7) and (8) to provide reasonably accurate estimations of the enthalpies of solvation of helium, hydrogen, oxygen, nitrogen and other inert gases, we would be remiss in not mentioning that such predictions would fall outside of the range of descriptor values used in deriving eqns. (7) and (8) as none of the solutes had negative **L**-descriptor values or really small **V**-descriptor values.

There are a sufficient number of $\Delta_{solv}H^{A/C_6H_4Cl_2}$ values in the 1,2-dichlorobenzene database to permit training set and test set analyses to be performed. The 94 experimental values in the large database were split into smaller training set and test sets of 47 data points each using the built-in randomization function of the SPSS software. Analysis of the 47 values in the training set gave the following two Abraham model correlations:

$\Delta_{solv}H^{A/C_6H_4Cl_2}$ (kJ mol^{-1}) = – 4.395(1.106) + 3.308(1.333) **E** – 6.695(1.561) **S** – 11.700(2.260) **A**

– 7.873(2.089) **B** – 9.388(0.316) **L** (9)

(with N = 47, *SD* = 1.98, R^2 = 0.979, *F* = 382.9)

$\Delta_{solv}H^{A/C_6H_4Cl_2}$ (kJ mol^{-1}) = 0.963(1.229) – 3.546(1.442) **E** – 18.988(1.608) **S** – 11.848(1.877) **A**

– 3.969(1.685) **B** – 32.365(0.952) **V** (10)

(with N = 47, $SD = 1.90$, $R^2 = 0.977$, $F = 345.2$)

Comparison of the training set equations to eqns. (7) and (8) reveals that there is very little difference in the numerical values of the equation coefficients. The training set equations were then used to predict the enthalpies of solvation for the 47 solutes in the test sets. For the predicted and experimental values, we find $SD = 2.00$ kJ mol^{-1} (eqn. (9)) and $SD = 2.96$ kJ mol^{-1} (eqn. (10)), $AAE = 1.48$ kJ mol^{-1} (eqn. (9)) and $AAE = 2.02$ kJ mol^{-1} (eqn. (10)), and $AE = 0.62$ kJ mol^{-1} (eqn. (9)) and AE = – 0.74 kJ mol^{-1} (eqn. (10)). There is therefore very little bias in using eqns. (9) and (10) with *AE* equal to 0.62 kJ mol^{-1} and AE = – 0.74 kJ mol^{-1}, respectively. As before the training set and test set computations were repeated two more times with very similar results.

Each term in the Abraham model describes a different type of solute-solvent intermolecular interactions. The hydrogen bonding interactions would be given by $a_h \cdot \mathbf{A} + b_h \cdot \mathbf{B}$ terms. In Table 5 we have compiled numerical values of the Abraham model solvent coefficients for both eqn. (1) and eqn. (2) for benzene [3], methylbenzene [4], 1,4-dimethylbenzene [3], 1,3,5-trimethylbenzene [3], chlorobenzene and 1,2-dichlorobenzene. In the case of 1,4-dimethylbenzene and 1,3,5-trimethylbenzene the b coefficients were set equal to zero because the calculated numerical values were very small and the standard error in the coefficient exceeded the coefficient itself. Examination of the numerical entries in Table 7 reveals that chlorobenzene is the best H-bond acceptor as reflected by its larger a-coefficient. Chlorobenzene interactions with acidic H-bond donor solutes likely occur through the aromatic ring system and the lone electron pairs on the chlorine ring substituent. In the case of RX ······:YZ halogen bonding the halogen atom (atom X) interacts with Lewis bases rather than Lewis acids. There is nothing unusual in the equation coefficients for either chlorobenzene or 1,2-dichlorobenzene to suggest strong halogen bonding. From our analysis we deduce that the interaction of halogen in chlorobenzene or 1,2-dichlorobenzene with basic solutes is quite small. The $b_h \cdot \mathbf{B}$ term in the Abraham model describes enthalpic hydrogen-bonding interactions between the solvent as a Lewis acid and basic solutes. 1,2-Dichlorobenzene having a slightly more negative b_h coefficient is the stronger Lewis acid of the two solvents studied here. The numerical value of the $b_h \cdot \mathbf{B}$ term (eqn. (7)) for 1,2-dichlorobenzene halogen-bonding interactions with 1-alkanols ($\mathbf{B}$ = 0.480) would be about –2.85 kJ mol^{-1}; for interactions with 2-alkanones ($\mathbf{B}$ = 0.510) would be about – 3.02 kJ mol^{-1}, and for interactions with alkyl alkanoates ($\mathbf{B}$ = 0.450) would be about – 2.67 kJ mol^{-1}. Interactions with chlorobenzene would be slightly weaker.

In an earlier study [3] we examined the weak X-H…π (X – O,N, and C) hydrogen-bonding interactions between acidic solutes and alkylbenzenes (benzene, toluene, 1,4-dimethylbenzene and 1,3,5-trimethylbenzene). H-bonds play an important role in understanding how different solvents affect both the reactivity and solubility of dissolved solute molecules. In accordance with the Abraham model correlations derived above, the enthalpy of hydrogen bond associated with an acidic H-bond donor solute interacting with the π-donor site(s) or with the lone electron pairs on the chlorine atom in chlorobenzene, $\Delta_{HB}H^{A...C_6H_5Cl}$, would be calculated by:

$$\Delta_{HB}H^{A...C_6H_5Cl}\,(\text{kJ mol}^{-1}) = -11.478\,\mathbf{A} \qquad (11)$$

$$\Delta_{HB}H^{A...C_6H_5Cl}\,(\text{kJ mol}^{-1}) = -16.252\,\mathbf{A} \qquad (12)$$

and with the π-donor site(s) or with the lone electron pairs on the two chlorine atoms in dichlorobenzene, $\Delta_{HB}H^{A....C_6H_4Cl_2}$, would be calculated by:

$$\Delta_{HB}H^{A....C_6H_4Cl_2}\,(\text{kJ mol}^{-1}) = -8.518\,\mathbf{A} \qquad (13)$$

$$\Delta_{HB}H^{A....C_6H_4Cl_2}\,(\text{kJ mol}^{-1}) = -12.033\,\mathbf{A} \qquad (14)$$

Data on $\Delta_{HB}H^{A...C_6H_5Cl}$ and $\Delta_{HB}H^{A....C_6H_4Cl_2}$ for several hydrogen bond acidic solutes calculated using eqns. (11) - (14) are presented in Table 8, along with corresponding enthalpy of hydrogen bond formation of the same organic substances with benzene, $\Delta_{HB}H^{A/C_6H_6}$.

Another independent method [33] for determination of hydrogen bond enthalpies based on the Solomonov et al eqn. (15) was used to verify obtained results. Previously, Solomonov et al method was used for determination of hydrogen bond enthalpies in various solute-solvent systems including different proton acceptors and proton donors [6,16,33], self-associated solvents [16-19,74], systems with weak and strong intermolecular and intramolecular hydrogen bonds [3,76,82] (totally more than 500 solute-solvent systems). Values of $\Delta_{HB}H^{A...S}$ obtained by this method were coincided well with the available literature data. Consequently, Solomonov et al method can be a useful tool for determination or validation of hydrogen bond enthalpies.

$$\Delta_{\mathrm{HB}}H^{\mathrm{A/S}} = \Delta_{\mathrm{soln}}H^{\mathrm{A/S}} - (\delta_{\mathrm{cav}}h^{\mathrm{S}} - \delta_{\mathrm{cav}}h^{\mathrm{C_6H_{12}}})\cdot \mathrm{V}^{\mathrm{A}} - \Delta_{\mathrm{soln}}H^{\mathrm{A/C_6H_{12}}} - (a_R + b_R \cdot \sqrt{\delta_{\mathrm{cav}}h^{\mathrm{S}}})\cdot$$

$$\cdot\left[(\Delta_{\mathrm{soln}}H^{\mathrm{A/S_R}} - \Delta_{\mathrm{soln}}H^{\mathrm{A/C_6H_{12}}}) - (\delta_{\mathrm{cav}}h^{\mathrm{S_R}} - \delta_{\mathrm{cav}}h^{\mathrm{C_6H_{12}}})\cdot \mathrm{V}^{\mathrm{A}}\right], \qquad (13)$$

Here $\Delta_{\mathrm{soln}}H^{\mathrm{A/S}}$, $\Delta_{\mathrm{soln}}H^{\mathrm{A/S_R}}$, $\Delta_{\mathrm{soln}}H^{\mathrm{A/C_6H_{12}}}$ are enthalpies of solution of solute *A* in studied solvent S, standard solvent S_R, and in cyclohexane, respectively; $\delta_{\mathrm{cav}}h^{\mathrm{S}}$, $\delta_{\mathrm{cav}}h^{\mathrm{S_R}}$, and $\delta_{\mathrm{cav}}h^{\mathrm{C_6H_{12}}}$ are the specific relative cavity formation enthalpies for each solvent; V^{A} is the characteristic volume of solute. Carbon tetrachloride was selected as a standard solvent S_R, because it does not form hydrogen bonds with any studied proton donor solutes. The specific relative cavity formation enthalpy $\delta_{\mathrm{cav}}h^{\mathrm{S}}$ is the enthalpy of transfer of an alkane from imaginary solvent S_0, where the solution enthalpy of an alkane is zero ($\Delta_{\mathrm{soln}}H^{\mathrm{C_nH_{2n+2}/S}}$), to the solvent *S*, divided by the alkane's characteristic volume $\mathrm{V}^{\mathrm{C_nH_{2n+2}}}$. Experimental data required for application of eqn. (15) were collected in Supplementary material (Table S3).

Hydrogen bond enthalpies of proton donor solutes with chlorobenzene and 1,2-dichlorobenzene determined by eqn. (15) are also presented in Table 8. These results and values obtained using eqns. (11)-(14) are in good agreement. It proves applicability of enthalpies of solvation correlations based on the Abraham model for calculation of the energies of intermolecular hydrogen bonds in aprotic media.

Conclusion

The enthalpy of solvation correlations reported in this paper for solutes dissolved in both chlorobenzene and 1,2-dichlorobenzene at 298 K further illustrates the applicability of the Abraham general solvation model for describing solute transfer into condensed phases from the gas phase. The derived Abraham model correlations provide a very accurate mathematical description of the measured $\Delta_{\rm solv}H^{\rm A/Solvent}$ data as evidenced by standard deviations between measured and calculated values of 1.5 and 2.5 kJ mol^{-1} and 1.9 and 2.4 kJ mol^{-1} for solutes dissolved in chlorobenzene and 1,2-dichlorobenzene, respectively. Equation coefficients calculated from regression analysis of experimental $\Delta_{\rm solv}H^{\rm A/Solvent}$ data in accordance with the Abraham model are used to estimate the hydrogen-bonding interactions of proton donor solute molecules with both chlorobenzene and 1,2-dichlorobenzene. The calculated hydrogen-bonding enthalpies based on the Abraham model correlations are in good agreement with calculated values based on the Solomonov et al. method [33].

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Table 1. Characteristics of the chemicals studied in this work

Chemical Name	Source	Initial Mass Fraction Purity	Purification Method	Final Mass Fraction Purity	Analysis Method	Mass fraction of Water
Acetonitrile (l)	Sigma Aldrich	0.99	Distillation	0.998	GC	0.0002
Acetone (l)	Sigma Aldrich	0.99	Distillation	0.997	GC	0.0002
Acetophenone (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0005
Anisole (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0003
Aniline (l)	Sigma Aldrich	0.99	Distillation	0.998	GC	0.0003
Anthracene (cr)	Sigma Aldrich	0.99	None	-	-	-
Benzonitrile (l)	Sigma Aldrich	0.98	Distillation	0.999	GC	0.0002
Benzophenone (cr)	Sigma Aldrich	0.99	None	-	-	-
Biphenyl (cr)	Sigma Aldrich	0.99	None	-	-	-
Bromobenzene (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0003
Butanone (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0002
Butan-1-ol (l)	Sigma Aldrich	0.99	Distillation	0.997	GC	0.0004
Butyl acetate (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0003
Butyl benzoate (l)	Sigma Aldrich	0.99	Distillation	0.996	GC	0.0002
Butyronitrile (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0002
Chlorobenzene (l)	Sigma Aldrich	≥ 0.995	None	-	-	-

1-Chlorobutane (l)	Sigma Aldrich	0.98	Distillation	0.995	GC	0.0004
2-Chlorophenol (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0002
n-Decane (l)	Sigma Aldrich	0.99	None	-	-	-
Decan-1-ol (l)	Sigma Aldrich	0.98	Distillation	0.995	GC	0.0004
Di-*n*-butyl ether (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0001
1,2-Dichlorobenzene (l)	Sigma Aldrich	≥ 0.995	None	-	-	-
1,2-Dichloropropane (l)	Sigma Aldrich	0.98	Distillation	0.995	GC	0.0003
1,4-Dioxane (l)	Sigma Aldrich	0.98	Distillation	0.995	GC	0.0003
n-Dodecane (l)	Sigma Aldrich	0.99	None	-	-	-
Dichloromethane (l)	Sigma Aldrich	0.99	Distillation	0.996	GC	0.0002
Diethyl ether (l)	Ekos	0.98	Distillation	0.997	GC	0.0001
2,6-Dimethoxyphenol (cr)	Sigma Aldrich	0.97	Sublimation	0.998	GC	0.0004
N,N-Dimethylacetamide (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0002
N,N-Dimethylformamide (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0002
Ethanol (l)	Sigma Aldrich	0.98	Distillation	0996	GC	0.0004
Ethyl acetate (l)	Sigma Aldrich	0.99	None	-	-	-
Ethyl benzoate (l)	Sigma Aldrich	0.98	Distillation	0.995	GC	0.0002
Ethyl salicylate (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0003
Fluorobenzene (l)	Sigma Aldrich	0.99	Distillation	0.998	GC	0.0002
n-Heptane (l)	Sigma Aldrich	0.99	None	-	-	-

Heptan-2-one (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0002
n-Hexane (l)	Sigma Aldrich	0.99	None	-	-	-
Hexan-1-ol (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0003
2-Hydroxyacetophenone (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0003
Indole (cr)	Sigma Aldrich	0.98	Sublimation	0.998	GC	0.0004
Methanol (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0004
2-Methoxyphenol (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0002
3-Methoxyphenol (l)	Sigma Aldrich	0.97	Distillation	0.997	GC	0.0002
4-Methoxyphenol (cr)	Sigma Aldrich	0.97	Recrystallization	0.995	GC	0.0004
Methyl acetate (l)	Sigma Aldrich	0.99	None	-	-	-
Methyl benzoate (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
Mesitylene (l)	Sigma Aldrich	0.97	Distillation	0.997	GC	0.0002
Methyl propionate (l)	Sigma Aldrich	0.99	Distillation	0.997	GC	0.0002
Methyl salicylate (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0002
Naphthalene (cr)	Sigma Aldrich	0.98	Recrystallization	0.996	GC	0.0005
n-Nonane (l)	Sigma Aldrich	0.99	None	-	-	-
Nonan-2-one (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
n-Octane (l)	Sigma Aldrich	0.99	None	-	-	-
Octan-1-ol (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0003
Octan-2-one (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002

Pentan-2-one (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
Pentan-1-ol (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0004
2-Picoline (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
3-Picoline (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0002
4-Picoline (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
Propan-1-ol (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0004
Propionitrile (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
Propyl acetate (l)	Sigma Aldrich	0.98	Distillation	0.999	GC	0.0002
Propyl benzoate (l)	Sigma Aldrich	0.97	Distillation	0.999	GC	0.0002
Pyrazole (cr)	Sigma Aldrich	0.98	Sublimation	0.998	GC	0.0004
Pyridine (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
Tetrachloromethane (l)	Ekos	≥0.995	None	-	=	0.0001
Tetrahydrofuran (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
Tri-*n*-butylamine (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
Trichloromethane (l)	Sigma Aldrich	0.98	Distillation	0.999	GC	0.0002
o-Xylene (l)	Sigma Aldrich	0.99	Distillation	0.998	GC	0.0002
m-Xylene (l)	Sigma Aldrich	0.98	Distillation	0.998	GC	0.0002
p-Xylene (l)	Sigma Aldrich	0.99	Distillation	0.998	GC	0.0002

Table 2. Enthalpies of solution (kJ · mol^{-1}) at infinite dilution of different organic solutes in chlorobenzene, measured in this work at 298.15±0.01 K and 0.1 MPa.[a]

N	Solute	$\Delta_{\mathrm{soln}}H^{\mathrm{A/C_6H_5Cl}}$
1	Acetone (l)	-0.01 ± 0.004[b]
2	Benzonitrile (l)	0.52 ± 0.04
3	Butyl acetate (l)	-1.61 ± 0.04
4	Butan-1-ol (l)	15.87 ± 0.05
5	Butyl benzoate (l)	-0.64 ± 0.02
6	Butyronitrile (l)	0.08 ± 0.01
7	2-Chlorophenol (l)	-4.84 ± 0.07
8	*n*-Decane (l)	3.62 ± 0.04
9	Decan-1-ol (l)	15.27 ± 0.10
10	Dichloromethane (l)	0.32 ± 0.01
11	*N*,*N*-Dimethylacetamide (l)	-2.55 ± 0.02
12	2,6-Dimethoxyphenol (cr)	20.18 ± 0.11
13	*n*-Dodecane (l)	4.27 ± 0.04
14	Ethyl acetate (l)	-0.78 ± 0.01
15	Ethyl benzoate (l)	-0.44 ± 0.02
16	Ethyl salicylate (l)	0.09 ± 0.02
17	*n*-Heptane (l)	2.77 ± 0.03
18	Heptan-2-one (l)	-1.64 ± 0.02
19	Hexan-1-ol (l)	15.19 ± 0.14
20	Indole (cr)	13.62 ± 0.42
21	Mesitylene (l)	-0.09 ± 0.02
22	2-Methoxyphenol (l)	4.69 ± 0.03
23	3-Methoxyphenol (l)	6.95 ± 0.12

24	4-Methoxyphenol (cr)	26.43 ± 0.11
25	Methyl acetate (l)	0.16 ± 0.02
26	Methyl benzoate (l)	0.09 ± 0.01
27	Methyl propionate (l)	-0.34 ± 0.02
28	Methyl salicylate (l)	1.03 ± 0.06
29	*n*-Nonane (l)	3.39 ± 0.02
30	Nonan-2-one (l)	-1.43 ± 0.02
31	*n*-Octane (l)	3.08 ± 0.01
32	Octan-2-one (l)	-1.43 ± 0.02
33	Octan-1-ol (l)	15.11 ± 0.18
34	Pentan-1-ol (l)	15.22 ± 0.05
35	Pentan-2-one (l)	-1.24 ± 0.02
36	3-Picoline (l)	-0.39 ± 0.01
37	4-Picoline (l)	0.06 ± 0.01
38	Propionitrile (l)	0.73 ± 0.01
39	Propyl acetate (l)	-1.25 ± 0.02
40	Propyl benzoate (l)	-0.66 ± 0.01
41	Pyrazole (cr)	26.60 ± 0.06
42	Tetrachloromethane (l)	-0.25 ± 0.02
43	Trichloromethane (l)	-0.60 ± 0.01

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[a] Standard uncertainties u are u(T) = 0.01 K, u(p) = 10 kPa.

[b] Uncertainties of solution enthalpies are calculated as an experimental standard deviation.

Table 3. Enthalpies of solution (kJ·mol^{-1}) at infinite dilution of different organic solutes in 1,2-dichlorobenzene, measured in this work at 298.15±0.01 K and 0.1 MPa.[a]

N	Solute	$\Delta_{soln}H^{A/C_6H_4Cl_2}$
1	Acetonitrile (l)	3.23 ± 0.03[b]
2	Acetone (l)	0.55 ± 0.01
3	Acetophenone (l)	0.78 ± 0.02
4	Anisole (l)	0.42 ± 0.03
5	Aniline (l)	2.51 ± 0.02
6	Anthracene (cr)	22.37 ± 0.14
7	Benzonitrile (l)	0.62 ± 0.02
8	Benzophenone (cr)	16.73 ± 0.05
9	Biphenyl (cr)	16.17 ± 0.27
10	Bromobenzene (l)	0.33 ± 0.01
11	Butanone (l)	-0.46 ± 0.02
12	Butan-1-ol (l)	15.86 ± 0.06
13	Butyl acetate (l)	-1.00 ± 0.05
14	Butyl benzoate (l)	-0.71 ± 0.02
15	Butyronitrile (l)	0.82 ± 0.01
16	Chlorobenzene (l)	0.26 ± 0.03
17	1-Chlorobutane (l)	0.10 ± 0.01
18	2-Chlorophenol (l)	-3.21 ± 0.03
19	*n*-Decane (l)	3.50± 0.03
20	Decan-1-ol (l)	15.60 ± 0.06
21	Di-*n*-butyl ether (l)	-0.10 ± 0.02
22	1,2-Dichloropropane (l)	1.16 ± 0.03
23	1,4-Dioxane (l)	-0.80 ± 0.03
24	*n*-Dodecane (l)	3.98 ± 0.04

25	Dichloromethane (l)	0.95 ± 0.01
26	Diethyl ether (l)	0.92 ± 0.01
27	2,6-Dimethoxyphenol (cr)	20.65 ± 0.10
28	*N*,*N*-Dimethylacetamide (l)	-2.21 ± 0.06
29	*N*,*N*-Dimethylformamide (l)	-0.37 ± 0.01
30	Ethanol (l)	15.96 ± 0.02
31	Ethyl acetate (l)	-0.30 ± 0.03
32	Ethyl benzoate (l)	-0.28± 0.02
33	Ethyl salicylate (l)	0.10 ± 0.03
34	Fluorobenzene (l)	0.69 ± 0.02
35	*n*-Heptane (l)	2.83 ± 0.03
36	Heptan-2-one (l)	-1.31 ± 0.02
37	*n*-Hexane (l)	2.64 ± 0.03
38	Hexan-1-ol (l)	15.40 ± 0.17
39	2-Hydroxyacetophenone (l)	0.88 ± 0.05
40	Indole (cr)	12.52 ± 0.08
41	Methanol (l)	15.00 ± 0.02
42	2-Methoxyphenol (l)	4.53 ± 0.02
43	3-Methoxyphenol (l)	9.14 ± 0.08
44	4-Methoxyphenol (cr)	27.43 ± 0.26
45	Methyl acetate (l)	0.46 ± 0.02
46	Methyl benzoate (l)	0.15 ± 0.01
47	Mesitylene (l)	-0.22 ± 0.02
48	Methyl propionate (l)	-0.39 ± 0.02
49	Methyl salicylate (l)	0.65 ± 0.02
50	Naphthalene (cr)	17.35 ± 0.10
51	*n*-Nonane (l)	3.27 ± 0.02
52	Nonan-2-one (l)	-1.32 ± 0.05
53	*n*-Octane (l)	3.00 ± 0.02

54	Octan-1-ol (l)	15.47 ± 0.03
55	Octan-2-one (l)	-1.30 ± 0.03
56	Pentan-2-one (l)	-0.92 ± 0.02
57	Pentan-1-ol (l)	15.31 ± 0.09
58	2-Picoline (l)	1.11 ± 0.05
59	3-Picoline (l)	1.05 ± 0.04
60	4-Picoline (l)	1.53 ± 0.04
61	Propan-1-ol (l)	15.96 ± 0.09
62	Propionitrile (l)	1.56 ± 0.01
63	Propyl acetate (l)	-0.76 ± 0.05
64	Propyl benzoate (l)	-0.52 ± 0.02
65	Pyrazole (cr)	24.39 ± 0.03
66	Pyridine (l)	1.62 ± 0.01
67	Tetrahydrofuran (l)	-0.91 ± 0.01
68	Tri-*n*-butylamine (l)	2.17 ± 0.03
69	Trichloromethane (l)	0.05 ± 0.02
70	*o*-Xylene (l)	-0.34 ± 0.01
71	*m*-Xylene (l)	-0.27 ± 0.03
72	*p*-Xylene (l)	-0.29 ± 0.01

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[a] Standard uncertainties u are $u(\mathrm{T}) = 0.01$ K, $u(\mathrm{p}) = 10$ kPa.

[b] Uncertainties of solution enthalpies are calculated as an experimental standard deviation.

Table 4. Values of the gas to chlorobenzene solvation enthalpies in kJ·mol^{-1} at 298 K, $\Delta_{solv}H^{A/C_6H_5Cl}$, for 126 solutes together with the solute descriptors

Solute (A)	**E**	**S**	**A**	**B**	**L**	**V**	$\Delta_{solv}H^{A/C_6H_5Cl}$	Ref
Helium	0.000	0.000	0.000	0.000	-1.741	0.0680	10.04	49
Neon	0.000	0.000	0.000	0.000	-1.575	0.0850	9.62	49
Argon	0.000	0.000	0.000	0.000	-0.688	0.1900	0.46	49
Krypton	0.000	0.000	0.000	0.000	-0.211	0.2460	-3.05	49
Xenon	0.000	0.000	0.000	0.000	0.378	0.3290	-8.70	49
Hydrogen	0.000	0.000	0.000	0.000	-1.200	0.1086	4.98	49
Nitrogen	0.000	0.000	0.000	0.000	-0.978	0.2222	2.42	49
Oxygen	0.000	0.000	0.000	0.000	-0.723	0.1830	0.63	49
Carbon monoxide	0.000	0.000	0.000	0.000	-0.836	0.2220	0.96	49
Methane	0.000	0.000	0.000	0.000	-0.323	0.2495	-2.56	49
Ethane	0.000	0.000	0.000	0.000	0.492	0.3904	-9.87	49
Propane	0.000	0.000	0.000	0.000	1.050	0.5313	-15.77	49
n-Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-29.04	49
n-Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-33.83	This work
n-Octane	0.000	0.000	0.000	0.000	3.677	1.2358	-38.42	This work
n-Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	-43.21	This work
n-Decane	0.000	0.000	0.000	0.000	4.686	1.5176	-47.79	This work
n-Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-57.13	This work
n-Hexadecane	0.000	0.000	0.000	0.000	7.714	2.3630	-75.54	34
Tetradecane	0.000	0.000	0.000	0.000	6.705	2.0812	-65.95	35
Cyclohexane	0.310	0.100	0.000	0.000	2.964	0.8454	-30.58	49
Dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943	-28.48	This work
Trichloromethane	0.430	0.490	0.150	0.020	2.480	0.6167	-31.70	This work
Tetrachloromethane	0.460	0.380	0.000	0.000	2.823	0.7391	-32.65	This work
Tetrachloroethene	0.639	0.440	0.000	0.000	3.584	0.8370	-39.06	36
Trichloroethene	0.520	0.370	0.080	0.030	2.997	0.7146	-34.79	36

Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	-28.88	50
Dipropyl ether	0.008	0.250	0.000	0.450	2.954	1.0127	-37.15	50
Methyl *tert*-butyl ether	0.024	0.210	0.000	0.590	2.372	0.8720	-32.10	37
Dimethoxymethane	0.099	0.460	0.000	0.520	1.894	0.6487	-29.66	51
1,2-Dimethoxyethane	0.116	0.670	0.000	0.680	2.654	0.7896	-38.95	51
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-34.71	51
Tetrahydropyran	0.296	0.490	0.000	0.480	3.013	0.7632	-39.89	51
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-39.13	51
2-Methyltetrahydrofuran	0.241	0.480	0.000	0.530	2.820	0.7632	-33.56	52
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	-31.31	This work
Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-35.80	53
Pentan-2-one	0.143	0.680	0.000	0.510	2.755	0.8288	-39.64	This work
Heptan-2-one	0.123	0.680	0.000	0.510	3.760	1.1106	-49.04	This work
Octan-2-one	0.108	0.680	0.000	0.510	4.257	1.2515	-53.43	This work
Nonan-2-one	0.113	0.680	0.000	0.510	4.735	1.3924	-57.83	This work
Acetophenone	0.818	1.010	0.000	0.480	4.501	1.0140	-55.12	38
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-32.14	This work
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-35.78	This work
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-38.95	This work
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-44.31	This work
Methyl propionate	0.128	0.600	0.000	0.450	2.431	0.7466	-35.94	This work
Propyl propionate	0.070	0.560	0.000	0.450	3.338	1.0284	-45.38	58
Methyl salicylate	0.850	0.840	0.020	0.470	5.025	1.1313	-56.27	This work
Ethyl salicylate	0.802	0.910	0.030	0.430	5.509	1.2722	-62.31	This work
Methyl benzoate	0.733	0.850	0.000	0.460	4.704	1.0726	-56.31	This work
Ethyl benzoate	0.689	0.850	0.000	0.460	5.075	1.2135	-59.24	This work
Propyl benzoate	0.675	0.800	0.000	0.460	5.718	1.3544	-65.46	This work
Butyl benzoate	0.668	0.800	0.000	0.460	6.210	1.4953	-69.04	This work
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	-30.68	56
Propionitrile	0.162	0.900	0.020	0.360	2.082	0.5451	-35.97	This work
Butyronitrile	0.188	0.900	0.000	0.360	2.548	0.6860	-39.12	This work
Benzonitrile	0.742	1.110	0.000	0.330	4.039	0.8710	-49.58	This work

Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-35.65	39
Tri-*n*-butylamine	0.051	0.150	0.000	0.790	6.050	1.8998	-61.70	39
N,*N*-Dimethylformamide	0.367	1.310	0.000	0.740	3.173	0.6468	-47.32	40
N,*N*-Dimethylacetamide	0.363	1.380	0.000	0.800	3.639	0.7877	-53.25	This work
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-26.13	56
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-30.40	56
Propan-1-ol	0.236	0.420	0.370	0.480	2.031	0.5900	-33.90	57
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7309	-35.83	This work
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	0.8718	-42.18	This work
Hexan-1-ol	0.210	0.420	0.370	0.480	3.610	1.0127	-46.31	This work
Octan-1-ol	0.199	0.420	0.370	0.480	4.619	1.2945	-56.49	This work
Decan-1-ol	0.191	0.420	0.370	0.480	5.628	1.5763	-66.43	This work
2-Propanol	0.212	0.360	0.330	0.560	1.764	0.5900	-31.83	57
2-Chlorophenol	0.853	0.880	0.320	0.310	4.178	0.8976	-57.14	This work
2-Methoxyphenol	0.837	0.910	0.220	0.520	4.449	0.9747	-56.72	This work
3-Methoxyphenol	0.879	1.170	0.590	0.380	4.803	0.9747	-67.85	This work
4-Methoxyphenol	0.900	1.170	0.570	0.480	4.773	0.9747	-63.37	This work
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	-33.82	41
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	-38.45	41
Ethylbenzene	0.613	0.510	0.000	0.150	3.788	0.9982	-43.00	55
o-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	-43.83	55
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	-43.12	55
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	-42.85	55
Anisole	0.710	0.750	0.000	0.290	3.890	0.9160	-46.63	42
Mesitylene	0.649	0.520	0.000	0.190	4.344	1.1391	-47.59	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	-64.90	34
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4540	-77.80	34
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	-55.10	34
1-Chloronaphthalene	1.417	1.000	0.000	0.140	5.856	1.2078	-63.47	34
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	-41.00	34
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	-34.65	34
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	-44.04	34

Iodobenzene	1.188	0.820	0.000	0.120	4.502	0.9746	-49.37	34
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	4.518	0.9612	-49.34	34
1,3-Dichlorobenzene	0.847	0.730	0.000	0.020	4.410	0.9612	-46.69	34
1,4-Dichlorobenzene	0.825	0.750	0.000	0.020	4.435	0.9612	-47.10	34
1,2,4,5-Tetrachlorobenzene	1.160	0.860	0.000	0.000	5.926	1.4164	-59.70	34
Hexachlorobenzene	1.490	0.990	0.000	0.000	7.624	1.4508	-76.96	34
1,3,5-Trichlorobenzene	0.980	0.730	0.000	0.000	5.045	1.0836	-51.04	34
1,3,5-Tribromobenzene	1.450	1.020	0.000	0.000	6.307	1.2410	-63.84	34
Pyrrole	0.613	0.730	0.410	0.290	2.865	0.5570	-40.20	42
N-Methylpyrrole	0.559	0.790	0.000	0.310	2.923	0.7180	-40.80	42
Aniline	0.955	0.960	0.260	0.410	3.934	0.8160	-52.82	43
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	-40.18	48
2-Picoline	0.598	0.750	0.000	0.580	3.422	0.8162	-43.43	48
3-Picoline	0.631	0.810	0.000	0.540	3.631	0.8162	-44.99	This work
4-Picoline	0.630	0.820	0.000	0.540	3.640	0.8162	-44.74	This work
2,4-Dimethylpyridine	0.634	0.760	0.000	0.630	4.006	0.9571	-48.53	44
2,6-Dimethylpyridine	0.607	0.700	0.000	0.630	3.760	0.9571	-46.61	44
2-Chloropyridine	0.738	1.040	0.000	0.370	3.875	0.7977	-50.28	48
3-Chloropyridine	0.732	0.830	0.000	0.400	3.783	0.7977	-46.94	48
3-Cyanopyridine	0.750	1.260	0.000	0.620	4.164	0.8300	-53.90	48
4-Cyanopyridine	0.750	1.210	0.000	0.590	4.033	0.8300	-52.50	48
N-Methylimidazole	0.589	0.950	0.000	0.800	3.805	0.6772	-52.89	45
Indole	1.200	1.260	0.440	0.180	5.310	0.9464	-63.98	This work
Tetramethyltin	0.324	0.110	0.000	0.100	2.651	1.0431	-30.71	49
Iodine	1.398	0.670	0.280	0.000	3.681	0.6250	-40.20	46
Pyrazole	0.620	1.000	0.540	0.450	3.151	0.5363	-47.40	This work
N-Methylpyrazole	0.521	0.970	0.000	0.550	3.215	0.6722	-44.52	45
Dimethyl sulfoxide	0.522	1.740	0.000	0.880	3.459	0.6126	-51.10	54
2,6-Dimethoxyphenol	0.840	1.410	0.130	0.710	5.677	1.1743	-78.22	This work
N-Methyl-2-pyrrolidone	0.491	1.300	0.000	0.790	3.832	0.8200	-57.01	47
Isoquinoline	1.211	1.000	0.000	0.540	5.595	1.0443	-60.28	44
cis-1,2-Dichloroethene	0.440	0.610	0.110	0.050	2.439	0.5922	-30.27	36

trans-1,2-Dichloroethene	0.430	0.410	0.090	0.050	2.278	0.5922	-30.30	36
Ammonia	0.140	0.390	0.160	0.560	0.319	0.2084	-14.90	59
Hydrogen sulfide	0.350	0.310	0.100	0.070	0.723	0.2721	-12.10	59
1,2-Propylene oxide	0.243	0.740	0.070	0.350	1.775	0.4814	-28.69	50

Table 5. Values of the gas to 1,2-dichlorobenzene solvation enthalpies in kJ·mol^{-1} at 298 K, $\Delta_{solv}H^{A/C_6H_4Cl_2}$, for 94 solutes together with the solute descriptors

Solute (A)	**E**	**S**	**A**	**B**	**L**	**V**	$\Delta_{solv}H^{A/C_6H_4Cl_2}$	Ref
n-Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-28.86	This work
n-Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-33.77	This work
n-Octane	0.000	0.000	0.000	0.000	3.677	1.2358	-38.50	This work
n-Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	-43.33	This work
n-Decane	0.000	0.000	0.000	0.000	4.686	1.5176	-47.90	This work
n-Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-57.42	This work
n-Tetradecane	0.000	0.000	0.000	0.000	6.705	2.0812	-67.42	60
Cyclohexane	0.310	0.100	0.000	0.000	2.964	0.8454	-30.07	34
Dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943	-27.84	This work
1-Chlorobutane	0.210	0.400	0.000	0.100	2.722	0.7946	-33.40	This work
1-Chlorohexane	0.201	0.400	0.000	0.100	3.777	1.0770	-42.55	61
1,2-Dichloropropane	0.369	0.630	0.000	0.170	2.836	0.7761	-35.04	This work
Trichloroethene	0.520	0.370	0.080	0.030	2.997	0.7146	-35.71	36
Trichloromethane	0.430	0.490	0.150	0.020	2.480	0.6167	-31.05	This work
Tetrachloroethene	0.639	0.440	0.000	0.000	3.584	0.8370	-38.47	36
Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	-26.19	This work
Di-*n*-butyl ether	0.000	0.250	0.000	0.450	3.924	1.2950	-44.80	This work
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-33.81	This work
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-39.41	This work
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	-30.74	This work
Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-35.26	This work
Pentan-2-one	0.143	0.680	0.000	0.510	2.755	0.8288	-39.32	This work
Heptan-2-one	0.123	0.680	0.000	0.510	3.760	1.1106	-48.71	This work
Octan-2-one	0.108	0.680	0.000	0.510	4.257	1.2515	-53.30	This work
Nonan-2-one	0.113	0.680	0.000	0.510	4.735	1.3924	-57.72	This work
Acetophenone	0.818	1.010	0.000	0.480	4.501	1.014	-54.62	This work
Benzophenone	1.447	1.500	0.000	0.500	6.852	1.4810	-78.38	This work
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-31.84	This work

Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-35.30	This work
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-38.46	This work
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-43.70	This work
Methyl propionate	0.128	0.600	0.000	0.450	2.431	0.7466	-35.99	This work
Methylsalicylate	0.850	0.840	0.020	0.470	5.025	1.1313	-56.65	This work
Ethylsalicylate	0.802	0.910	0.030	0.430	5.509	1.2722	-62.30	This work
Methyl benzoate	0.733	0.850	0.000	0.460	4.704	1.0726	-56.25	This work
Ethyl benzoate	0.689	0.850	0.000	0.460	5.075	1.2135	-59.08	This work
Propyl benzoate	0.675	0.800	0.000	0.460	5.718	1.3544	-65.32	This work
Butyl benzoate	0.668	0.800	0.000	0.460	6.210	1.4953	-69.11	This work
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	-29.76	This work
Propionitrile	0.162	0.900	0.020	0.360	2.082	0.5451	-35.14	This work
Butyronitrile	0.188	0.900	0.000	0.360	2.548	0.6860	-38.38	This work
Benzonitrile	0.742	1.110	0.000	0.330	4.039	0.8710	-49.48	This work
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-36.195	62
Tri-*n*-butylamine	0.051	0.150	0.000	0.790	6.050	1.8998	-60.53	This work
N-Methylpyrrole	0.559	0.790	0.000	0.310	2.923	0.7180	-40.50	41
N,*N*-Dimethylformamide	0.367	1.310	0.000	0.740	3.173	0.6468	-47.07	This work
N,*N*-Dimethylacetamide	0.363	1.380	0.000	0.800	3.639	0.7877	-52.91	This work
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-23.00	This work
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-26.44	This work
Propan-1-ol	0.236	0.420	0.370	0.480	2.031	0.5900	-31.54	This work
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7309	-35.84	This work
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	0.8718	-42.10	This work
Hexan-1-ol	0.210	0.420	0.370	0.480	3.610	1.0127	-46.10	This work
Octan-1-ol	0.199	0.420	0.370	0.480	4.619	1.2945	-56.13	This work
Decan-1-ol	0.191	0.420	0.370	0.480	5.628	1.5763	-66.10	This work
2-Chlorophenol	0.853	0.880	0.320	0.310	4.178	0.8976	-55.11	This work
2-Methoxyphenol	0.837	0.910	0.220	0.520	4.449	0.9750	-56.86	This work
3-Methoxyphenol	0.879	1.170	0.590	0.380	4.803	0.9747	-65.67	This work
4-Methoxyphenol	0.900	1.170	0.570	0.480	4.773	0.9747	-62.37	This work
4-Fluorophenol	0.670	0.970	0.630	0.230	3.844	0.7928	-48.96	63

Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	-33.20	41
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	-38.18	41
o-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	-43.74	This work
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	-42.87	This work
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	-42.69	This work
Anisole	0.710	0.750	0.000	0.290	3.890	0.9160	-46.18	This work
Mesitylene	0.649	0.520	0.000	0.190	4.344	1.1391	-47.72	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	-65.64	This work
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	-55.25	This work
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4540	-79.54	This work
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	-40.76	This work
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	-34.21	This work
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	-44.17	This work
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	4.518	0.9612	-49.60	34
Pyrrole	0.613	0.730	0.410	0.290	2.865	0.5570	-40.14	41
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	-38.88	This work
2-Picoline	0.598	0.750	0.000	0.580	3.422	0.8162	-41.89	This work
3-Picoline	0.631	0.810	0.000	0.540	3.631	0.8162	-43.55	This work
4-Picoline	0.630	0.820	0.000	0.540	3.64	0.8162	-43.27	This work
N-Methylimidazole	0.589	0.950	0.000	0.800	3.805	0.6772	-52.27	45
Indole	1.200	1.260	0.440	0.180	5.310	0.9464	-65.07	This work
Pyrazole	0.620	1.000	0.540	0.450	3.151	0.5363	-49.61	This work
Dimethyl sulfoxide	0.522	1.740	0.000	0.880	3.459	0.6126	-49.66	62
N-Methylpyrazole	0.521	0.970	0.000	0.550	3.215	0.6722	-43.94	45
N-Methyl-2-pyrrolidone	0.491	1.300	0.000	0.790	3.832	0.8200	-56.78	47
cis-1,2-Dichloroehtene	0.440	0.610	0.110	0.050	2.439	0.5922	-29.77	36
trans-1,2- Dichloroehtene	0.430	0.410	0.090	0.050	2.278	0.5922	-30.01	36
4-Fluoroanisole	0.571	0.740	0.000	0.280	3.904	0.9337	-48.08	63
3-Fluorophenol	0.667	0.976	0.680	0.170	3.844	0.7928	-49.01	63
2,6-Dimethoxyphenol	0.840	1.410	0.130	0.710	5.677	1.1743	-77.75	This work
2-Hydoxyacetophenone	0.948	1.320	0.000	0.370	5.341	1.0726	-57.42	This work
1,3-Dichlorobenzene	0.847	0.730	0.000	0.020	4.410	0.9612	-46.97	64

Aniline	0.955	0.960	0.260	0.410	3.934	0.8160	-51.69	This work
Dimethylamine	0.189	0.300	0.080	0.660	1.600	0.4902	-29.52	65

Table 6. Comparison Between Our Measured $\Delta_{soln}H^{A/Solvent}$ (in kJ mol^{-1}) Values for Solutes Dissolved in Chlorobenzene and 1,2-Dichlorobenzene at 298 K and Published Literature Data

Solute	$\Delta_{soln}H^{A/Solvent}$ (our)	$\Delta_{soln}H^{A/Solvent}$ (lit)	Ref.
Solvent = Chlorobenzene			
1-Butanol	15.87	13.10	77
1-Pentanol	15.22	14.87	78
1-Hexanol	15.22	14.44	78
Benzonitrile	0.52	0.41	79
Solvent = 1,2-Dichlorobenzene			
Hexane	2.64	3.41	61
o-Xylene	-0.35	-0.31	80
m-Xylene	-0.27	-0.26	80
p-Xylene	-0.30	-0.28	80
Chlorobenzene	0.26	0.25	64

Table 7. Regression coefficients (solvent parameters) of Eqs. (1) and (2) for benzene and its chlorine derivatives.

Solvent	c	e	s	a	b	l (v)
Benzene	-4.637	4.446	-12.599	-9.775	-4.023	-8.488
Benzene (V)	4.391	-5.422	-21.268	-11.797	-3.118	-31.674[a]
Methylbenzene	-5.291	3.511	-12.943	-6.317	-4.434	-8.382
Methylbenzene (V)	4.199	-7.143	-20.440	-10.006	-3.439	-32.235[a]
1,4-Dimethylbenzene	-6.265	6.460	-9.862	-10.775	0	-9.318
1,4-Dimethylbenzene (V)	1.703	-3.466	-18.074	-14.109	0	-33.618[a]
1,3,5-Trimethylbenzene	-5.488	6.646	-9.602	-10.828	0	-9.538
1,3,5-Trimethylbenzene (V)	2.940	-3.805	-18.981	-14.011	0	-34.238[a]
Chlorobenzene	-5.377	5.383	-10.333	-11.478	-5.038	-9.041
Chlorobenzene (V)	5.534	-4.164	-20.543	-16.252	-4.832	-34.675[a]
1,2-Dichlorobenzene	-4.609	3.975	-8.947	-8.518	-5.928	-9.182
1,2-Dichlorobenzene (V)	1.234	-5.635	-16.692	-12.033	-5.196	-32.033[a]

[a] value of "v" coefficient in Eqn. (2)

Table 8. Enthalpies of weak hydrogen bonding of benzene and chlorobenzenes with different proton donor solutes calculated by Abraham-Acree and Solomonov methods.

Solute (A)	$\Delta_{HB}H^{A...S}$			$\Delta_{HB}H^{A...S}$			$\Delta_{HB}H^{A...S}$		
	Benzene			Chlorobenzene			1,2-Dichlorobenzene		
	L[a]	V[b]	S[c]	L[a]	V[b]	S[c]	L[a]	V[b]	S[c]
Methanol	-4.2	-5.1	-3.0	-4.9	-7.0	-4.9	-3.7	-5.2	-1.8
Ethanol	-3.6	-4.4	-3.4	-4.2	-6.0	-5.1	-3.2	-4.5	-1.2
Propan-1-ol	-3.6	-4.4	-	-4.2	-6.0	-3.3	-3.2	-4.5	-1.0
Butan-1-ol	-3.6	-4.4	-0.9	-4.2	-6.0	-2.0	-3.2	-4.5	-2.1
Pentan-1-ol	-3.6	-4.4	-0.4	-4.2	-6.0	-2.8	-3.2	-4.5	-2.7
Hexan-1-ol	-3.6	-4.4	-0.7	-4.2	-6.0	-2.2	-3.2	-4.5	-2.1
Octan-1-ol	-3.6	-4.4	0.2	-4.2	-6.0	-2.3	-3.2	-4.5	-1.9
Decan-1-ol	-3.6	-4.4	-	-4.2	-6.0	-1.4	-3.2	-4.5	-1.0
2-Methoxyphenol	-2.2	-2.6	-	-2.5	-3.6	-2.6	-1.9	-2.7	-2.7
3-Methoxyphenol	-5.8	-7.0	-	-6.8	-9.6	-6.0	-5.0	-7.2	-3.9
4-Methoxyphenol	-5.6	-6.7	-	-6.5	-9.3	-7.3	-4.9	-6.9	-6.3
2-Chlorophenol	-3.1	-3.8	-	-3.8	-5.2		-2.7	-3.9	
Pyrrole	-4.0	-4.8	-3.2	-4.7	-6.7	-2.6	-3.5	-5.0	-2.6
Indole	-4.3	-5.2	-	-5.1	-7.2	-3.5	-3.7	-5.3	-4.6
Pyrazole	-5.3	-6.4	-5.5	-6.2	-8.8	-5.2	-4.6	-6.6	-7.5
Dichloromethane	-1.0	-1.2	-	-1.1	-1.6	-0.8	-0.9	-1.2	-0.2
Trichloromethane	-1.5	-1.8	-2.5	-1.7	-2.4	-1.2	-1.3	-1.8	-0.5
Acetonitrile	-0.7	-0.8	-0.6	-0.8	-1.1	-1.4	-0.6	-0.8	-1.5

Aniline	-2.5	-3.1	-0.8	-3.0	-4.2	-5.6	-2.2	-3.2	-4.5

[a] Calculated from the Abraham-Acree multiparameter correlations with L descriptor

[b] Calculated from the Abraham-Acree multiparameter correlations with V descriptor

[c] Calculated using Solomonov method

Figure 1

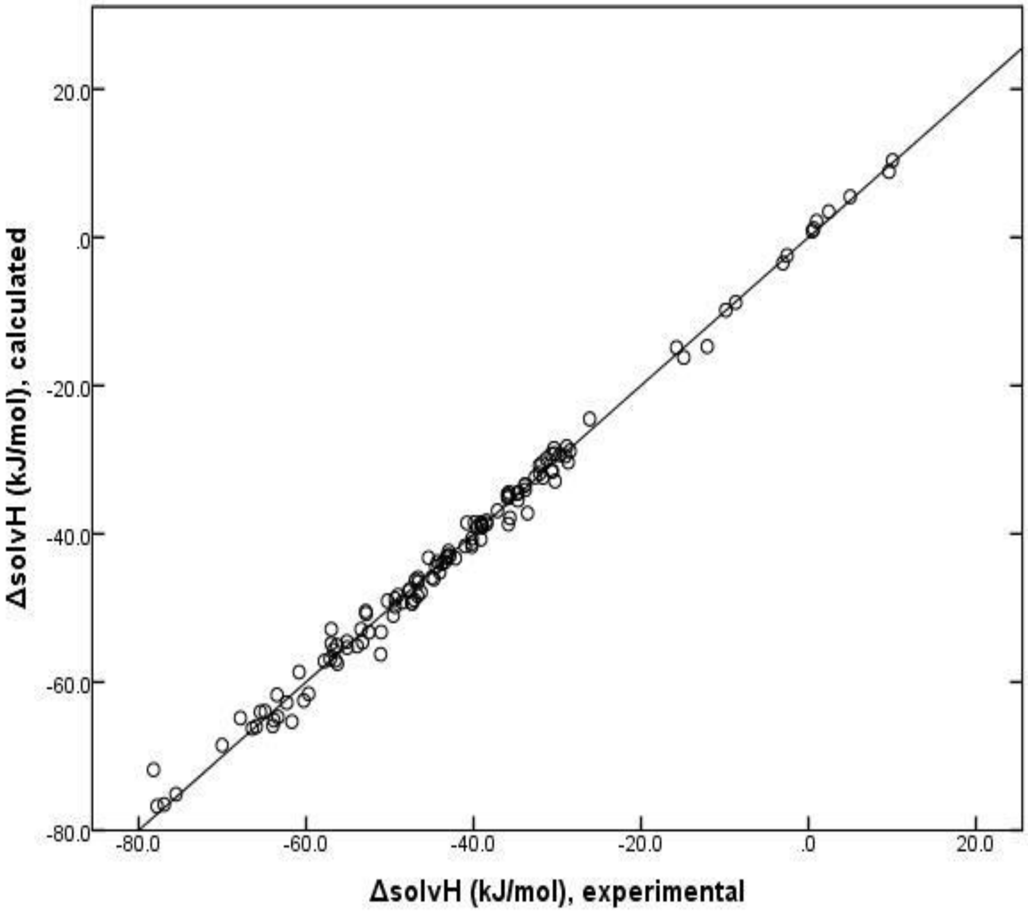


Figure 1. Comparison of experimental $\Delta_{solv}H^{A/C_6H_5Cl}$ data and back-calculated values based on eqn. (3).

Figure 2

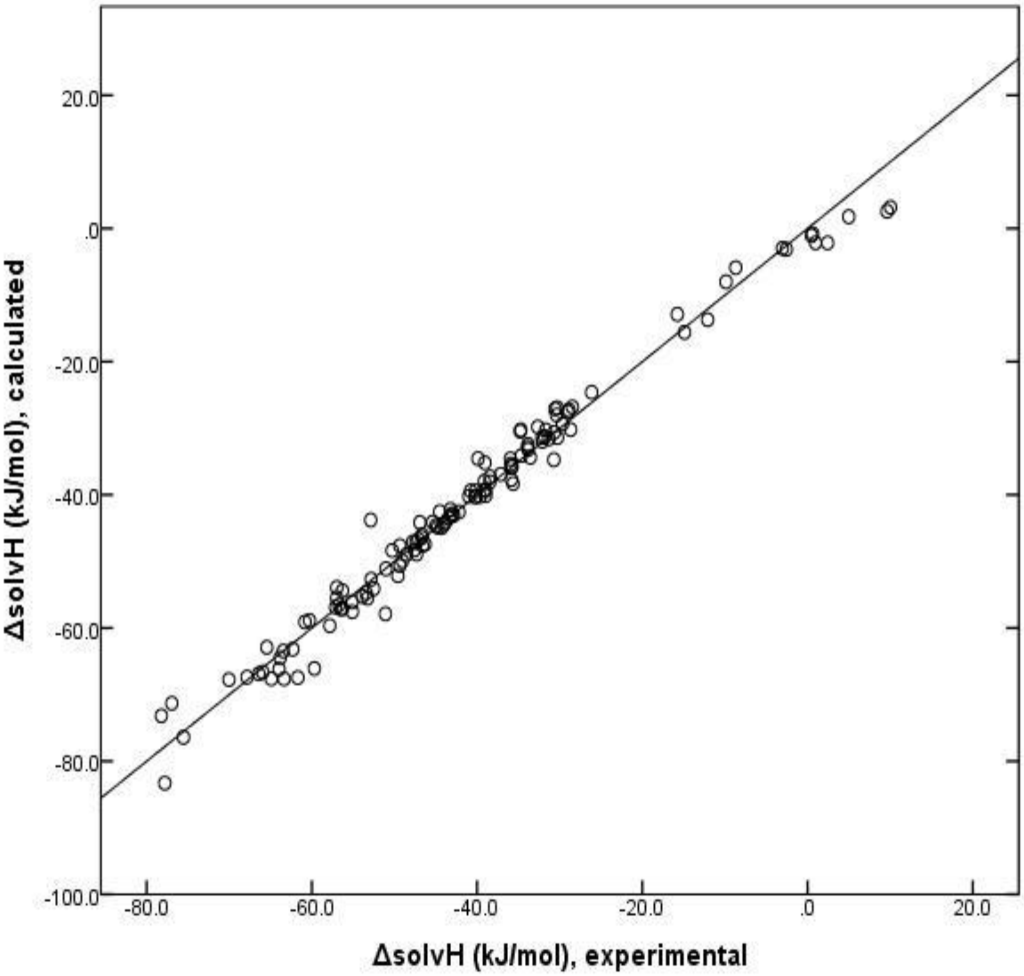


Figure 2. Comparison of experimental $\Delta_{solv}H^{A/C_6H_5Cl}$ data and back-calculated values based on eqn. (4).

Figure 3

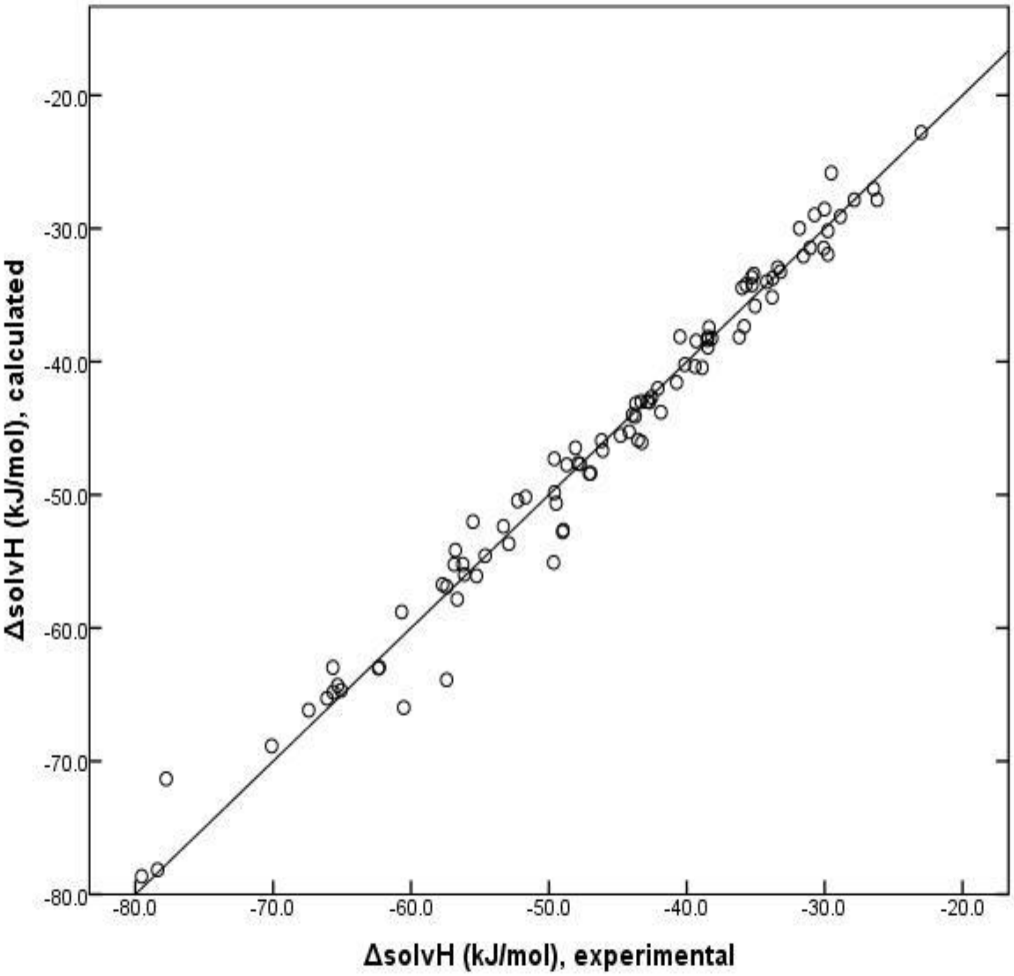


Figure 3. Comparison of experimental $\Delta_{solv}H^{A/C_6H_4Cl_2}$ data and back-calculated values based on eqn. (7).

Figure 4

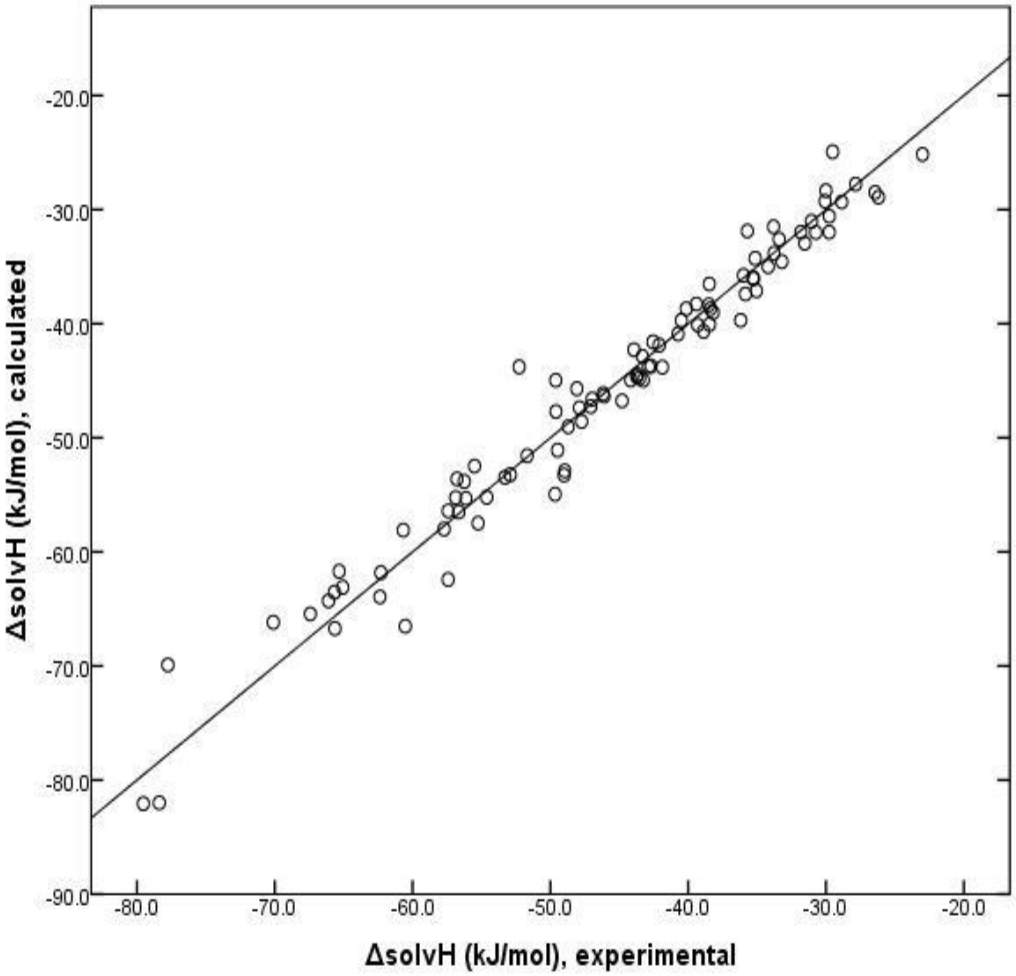
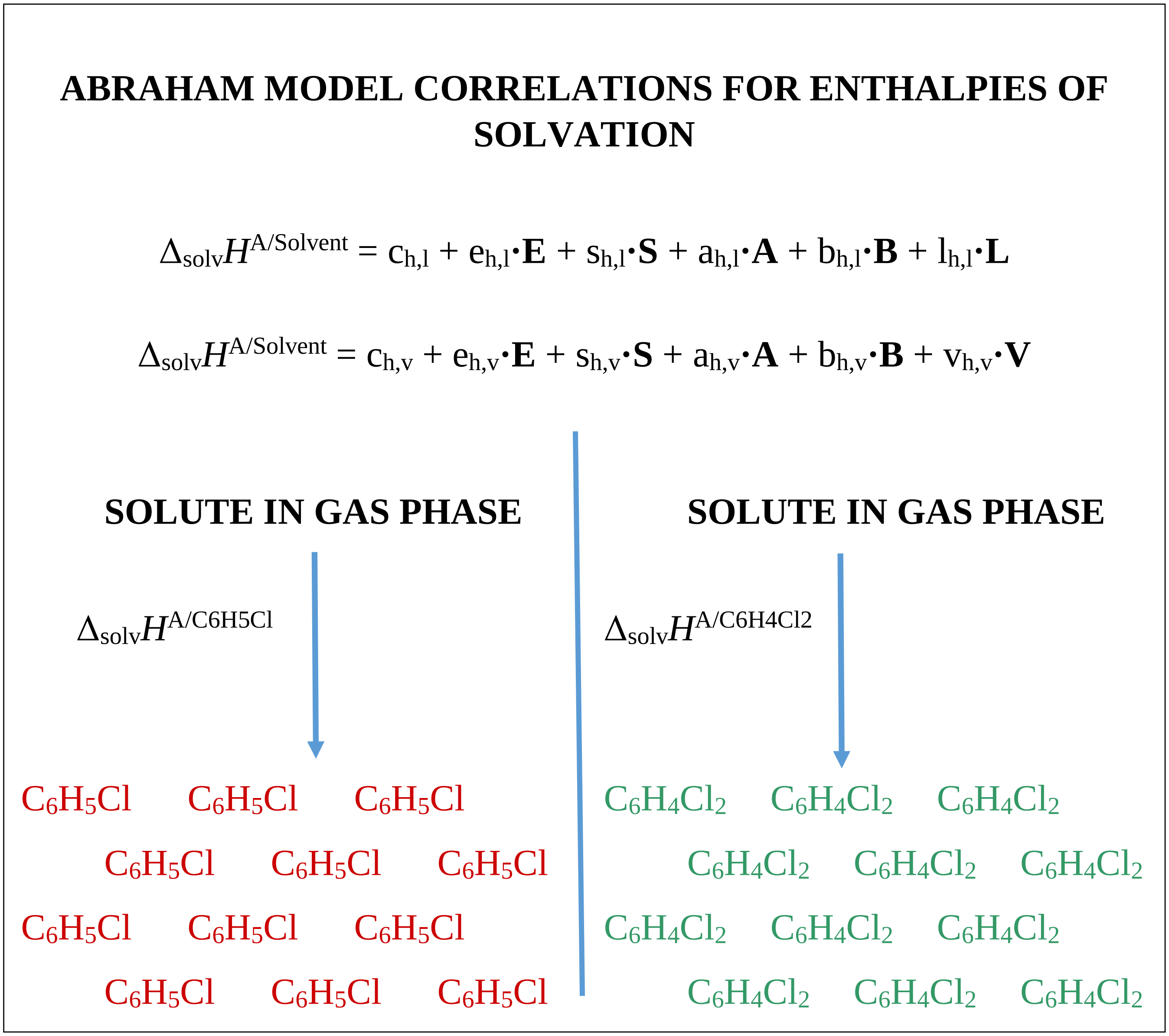


Figure 4. Comparison of experimental $\Delta_{solv}H^{A/C_6H_4Cl_2}$ data and back-calculated values based on eqn. (8).

HIGHLIGHTS

- Enthalpies of solution measured for 43 solutes dissolved in chlorobenzene
- Enthalpies of solution measured for 72 solutes dissolved in 1,2-dichlorobenzene
- Mathematical expressions derived for predicting enthalpies of solvation of solutes in chlorobenzene
- Mathematical expressions derived for predicting enthalpies of solvation of solutes in 1,2-chlorobenzene

GRAPHICAL ABSTRACT



ABRAHAM MODEL CORRELATIONS FOR ENTHALPIES OF SOLVATION

$$\Delta_{\mathrm{solv}}H^{\mathrm{A/Solvent}} = \mathrm{c_{h,l}} + \mathrm{e_{h,l}}\cdot\mathbf{E} + \mathrm{s_{h,l}}\cdot\mathbf{S} + \mathrm{a_{h,l}}\cdot\mathbf{A} + \mathrm{b_{h,l}}\cdot\mathbf{B} + \mathrm{l_{h,l}}\cdot\mathbf{L}$$

$$\Delta_{\mathrm{solv}}H^{\mathrm{A/Solvent}} = \mathrm{c_{h,v}} + \mathrm{e_{h,v}}\cdot\mathbf{E} + \mathrm{s_{h,v}}\cdot\mathbf{S} + \mathrm{a_{h,v}}\cdot\mathbf{A} + \mathrm{b_{h,v}}\cdot\mathbf{B} + \mathrm{v_{h,v}}\cdot\mathbf{V}$$

SOLUTE IN GAS PHASE

$\Delta_{\mathrm{solv}}H^{\mathrm{A/C6H5Cl}}$

C_6H_5Cl C_6H_5Cl C_6H_5Cl
C_6H_5Cl C_6H_5Cl C_6H_5Cl
C_6H_5Cl C_6H_5Cl C_6H_5Cl
C_6H_5Cl C_6H_5Cl C_6H_5Cl

SOLUTE IN GAS PHASE

$\Delta_{\mathrm{solv}}H^{\mathrm{A/C6H4Cl2}}$

$C_6H_4Cl_2$ $C_6H_4Cl_2$ $C_6H_4Cl_2$
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