Abraham Model Correlations for Estimating Solute Transfer of Neutral Molecules into Anhydrous Acetic Acid from Water and from the Gas Phase

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Abstract

Experimental infinite dilution activity coefficient data, gas-to-liquid partition coefficient data, and solubility data have been combined from the published literature for neutral organic molecules and inert gases dissolved in anhydrous acetic acid. The compiled experimental data were transformed into molar solubility ratios, water-to-acetic acid (*P*) and gas-to-acetic acid (*K*) using standard thermodynamic relationships. The derived Abraham model correlations described the observed solubility and partition coefficient data of neutral organic compounds to within 0.18 log units (or less). Our analysis further showed that acetic acid solvent has considerable hydrogen-bond acidity, in agreement with the proposed linear structure for the solvent, and in terms of solubility related properties is not an unusual solvent at all.

Keywords: Partition coefficients, Solute transfer, Solubility ratios, Activity coefficients, Acetic acid solvent, Hydrogen-bonding

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1 Introduction

More than twenty tons of organic solvents are consumed annually by chemical industries in applications involving chemical syntheses, chemical separations, pharmaceutical formulations, cosmetic products, lubricants, paints and varnishes, food processing, petroleum products, and cleaning materials [1]. The increasing consumption of organic solvents, combined with growing environmental awareness, has led to new governmental policies and regulations regarding the progressive replacement of environmentally harmful compounds with less harmful chemical alternatives having more favorable environmental, health and safety hazard profiles. Selection of a suitable replacement solvent requires knowledge of the chemical and physical properties not only of the solvent that is to be replaced, but also knowledge of the properties of the solvents that are being considered as safer alternative candidates.

Over the years there have been several methods developed to characterize the solubilizing properties of organic solvents so that researchers can have this information at hand when selecting possible replacement solvents. The Hildebrand solubility parameter approach [2] allows one to compare the solubility of a given solute in a series of organic solvents. Solute solubility is expected to increase as the difference between the solubility parameters of the solute, δ_{solute}, and the solvent, $\delta_{solvent}$, decreases. Hansen [3] extended the application of the model by dividing the intermolecular forces into dispersion, polar, and hydrogen-bonding interactions. This modification enabled the construction of a three-dimensional space in which solvents and solutes could be conveniently situated. The solute is visualized as a point surrounded by a solubilization sphere. Organic solvents and solvent mixtures residing within the solubilization sphere are predicted to be able to solubilize the solute under consideration.

The Abraham solvation parameter model [4-8] affords a second means to compare the solubilization properties of organic solvents. The model is composed of two linear free energy relationships that contain terms to mathematically describe the various solute-solvent interactions that are believed to be present. The interactions are described as the product of a solute properties (called solute descriptors) and solvent properties (called equation or process coefficients). For solubility and partition coefficients the Abraham model correlations are given as [4-8]:

$$\log (P \text{ or } C_{S,organic}/C_{S,water}) = c_p + e_p \cdot \mathbf{E} + s_p \cdot \mathbf{S} + a_p \cdot \mathbf{A} + b_p \cdot \mathbf{B} + v_p \cdot \mathbf{V} \quad (1)$$

$$\log (K \text{ or } C_{S,organic}/C_{S,gas}) = c_k + e_k \cdot \mathbf{E} + s_k \cdot \mathbf{S} + a_k \cdot \mathbf{A} + b_k \cdot \mathbf{B} + l_k \cdot \mathbf{L} \quad (2)$$

where P and K refer to the solute's water-to-organic solvent and gas-to-organic solvent partition coefficients, and C_s refers to the solute's molar solubility with the subscripts "organic", "water" and "gas" indicating the phase to which the solute molar concentrations pertain. In Eqns. (1) and (2) the solute descriptors are defined as follows: **E** denotes to the solute excess molar refractivity in units of (cm^3 mol^{-1})/10, **S** corresponds to the solute dipolarity/polarizability, **A** and **B** quantify the overall or total hydrogen-bond acidity and basicity, **V** refers to the McGowan volume in units of (cm^3 mol^{-1})/100, and **L** is defined as the logarithm of the dimensionless gas-to-hexadecane partition coefficient at 298 K. The complementary solvent process constants/coefficients pertain to the ability of the partitioning system to participate in lone electron pair interactions (e), and in dipole-type interactions (s), to act as a hydrogen-bond type base (a) and as a hydrogen-bond type acid (b), and to break solvent-solvent interactions that lead to the formation of the solvent cavity needed for solute transfer between condensed phases (v) or for solute transfer from the gas phase (l). The last term in each equation, the $v_p \cdot \mathbf{V}$ term in eqn. (1) and the $l_k \cdot \mathbf{L}$ term in eqn. (2), may also contain dispersion interactions that do not cancel in the respective solute transfer process.

Comparison of the solubilizing properties of the different organic solvents can be achieved through the calculated numerical values of the equation coefficients (c_p, e_p, s_p, a_p, b_p, v_p, c_k, e_k, s_k, a_k, b_k, and l_k). One such method [9] would be to consider the five coefficients of each individual solvent as representing a point in five-dimensional space. The distance between any two points (or in this case two solvents) could be calculated by straightforward geometry through eqn. (3):

$$\text{Distance} = [(e_{\text{solvent 1}} - e_{\text{solvent 2}})^2 + (s_{\text{solvent 1}} - s_{\text{solvent 2}})^2 + (a_{\text{solvent 1}} - a_{\text{solvent 2}})^2 + (b_{\text{solvent 1}} - b_{\text{solvent 2}})^2 + (v_{\text{solvent 1}} - v_{\text{solvent 2}})^2]^{0.5} \quad (3)$$

The smaller the distance, the closer are the two solvents in terms of solubilizing properties. Principal Component Analysis (PCA) provides a second and more visual method of comparing the solubilizing properties of different organic solvents using calculated Abraham Model solvent coefficients [10-13]. Here a selection of solvents to be compared is made, and their respective five sets of equation coefficients (e, s, a, b and v/l) are transformed into five new sets of principal components, PCs. These five PCs contain all of the information in the five sets of coefficients, however, the information yields five orthogonal sets of PC scores. Since the first two PCs (PC1 and PC2) generally contain most of the total data in the original coefficients, one can analyze the data by plotting the scores of PC2 against the scores of PC1. The resulting plot would be set of points, one point for each of the different solvents. The nearness of any two points is then a measure of how near are the corresponding two solvents in terms of the solubilizing properties.

Thus far we have reported Abraham model equation coefficients for more than 80 different organic solvents for log *P* and log *K* partitioning systems, including several systems containing linear and cyclic alkanes [6,14,15], alkylbenzenes [6,16,17], chloroalkanes [18,19], dialkyl ethers [6,20] and cyclic ethers [21], halobenzenes [22], alkanones [23], alkyl alkanoates

[24], amides [25], mono-functional alcohols [6,26,27], several miscellaneous organic solvents (dimethyl sulfoxide, acetonitrile, benzonitrile, nitrobenzene, propylene carbonate, sulfolane, 1-hexadecene, 1,9-decadiene) [6,28-32] and ionic liquid solvents [33-38]. Our most recent solvent additions have included tributyl phosphate [39], diisopropyl ether [40], 1,2-propylene glycol [41], 2-methoxyethanol [13], 2-ethoxyethanol [42], and 2-butoxyethanol [43]. In the present communication we extend our considerations to include solute transfer into anhydrous acetic acid, which is used as a solvent used in the manufacture of terephthalic acid and in non-aqueous acid-base titrations for determining the concentrations of weakly alkaline substances (e.g., organic amides). This is the first carboxylic acid that we have studied as a solvent. Abraham model log (P or $C_{S,organic}/C_{S,water}$) and log ($K$ or $C_{S,organic}/C_{S,gas}$) correlations are derived from published gas-to-liquid partition coefficient data and solubility data for 68 organic and inorganic solutes dissolved in acetic acid.

2. Dataset and Computation Methodology

The experimental data used in deriving the log P and log K correlations came from various sources [44-79]. Rudakov et al. [44] reported equilibrium distribution coefficients, $\alpha = C_{s,gas}/C_{s,solvent}$, for methane, ethane, propane, butane, pentane, hexane, heptane, octane, 2-methylpropane, 2,2,4-trimethylpentane, cyclopentane, cyclohexane, and benzene determined by measuring the solute concentration in both the gas phase and in acetic acid using a gas-liquid chromatographic method. Park et al. [45] determined the infinite dilution activity coefficients and gas-to-liquid partition coefficients of octane, toluene, ethanol, 2-butanone, nitromethane and 1,4-dioxane dissolved in acetic acid based on headspace gas chromatographic measurements. Banipal and coworkers [46] studied the vapor-liquid equilibria of binary mixtures containing acetonitrile with acetic acid, propionic acid, isobutryic acid and trimethylmethylacetic acid over

the entire range of mixture compositions. The authors calculated the activity coefficients of both mixture components from the observed total vapor pressures. Abraham and coworkers [47] published infinite dilution activity coefficient data for 2-chloro-2-methylpropane and 2-bromo-2-methylpropane in water and in 37 different organic solvents as part of their investigation of solvent effects regarding *tert*-butyl halide solvolysis reactions. Acetic acid was one of the solvents considered by Abraham et al. The infinite dilution activity coefficient data, γ_{solute}^{∞}, from Banipal et al. and Abraham et al. was converted to a log *K* value through eqn. (4):

$$\log K = \log \left(\frac{RT}{\gamma_{solute}^{\infty} P_{solute}^{o} V_{solvent}}\right) \quad (4)$$

where R is the universal gas constant, *T* is the system temperature, P_{solute}^{o} is the vapor pressure of the solute at *T*, and $V_{solvent}$ is the molar volume of the solvent.

Our search of the published literature did find solubility data for several organic and inorganic gases dissolved in acetic acid. Pollack et al. [48] measured the solubility of xenon in acetic acid from 293 K to 313 K, Kunerth [49] determined the solubility of carbon dioxide and nitrous oxide in acetic acid in 2 K increments from 291 K to 309 K, and Barton and Hsu [50] reported the solubility of cyclopropane in acetic acid in the temperature range of 273 K to 313 K. Experimental data for hydrogen sulfide, propene, *trans*-2-butane, 2-methyl-1-propene and 1,3-butadiene came from solubility studies by Hayduk and coworkers [51-54]. In each case, the experimental data was expressed as both the mole fraction solubility and the Ostwald Coefficient, *K*. The experimental log *K* values were converted to log *P* values:

$$\text{Log } P = \log K - \log Kw \quad (5)$$

using the solute's measured gas-to-water partition coefficients, *Kw*, which are available for all of liquid and gaseous compounds considered in the present communication.

Experimental mole fraction solubility data was also found for several crystalline nonelectrolyte solutes, including two polycyclic aromatic hydrocarbons (naphthalene [66] and phenanthrene [73]), four nonsteroidal anti-inflammatory drugs (2-hydroxybenzoic acid [65], naproxen [72], ibuprofen [74], diclofenac [76]) and two other drug molecules (niflumic acid [77] and salicylamide [64]), nine alkanedioic acids (oxalic acid through sebacic acid) [63], and benzoic acid [70] and three substituted benzoic acid derivatives (4-hydroxybenzoic acid [69], 4-methylbenzoic acid [71], and isophthalic acid [79]). Measured mole fraction solubilities were converted to molar solubilities by dividing $X_{S,organic}^{exp}$ by the ideal molar volume of the saturated solution (i.e., $C_{S,organic}^{exp} \approx X_{S,organic}^{exp}/[X_{S,organic}^{exp}\ V_{Solute} + (1 - X_{S,organic}^{exp})\ V_{Solvent}]$). The numerical values used for the molar volumes of the hypothetical subcooled liquid solutes were obtained by summing group values for the functional groups contained in the solute molecules. The experimental log (P or ($C_{S,organic}/C_{S,water}$)) and log ($K$ or ($C_{S,organic}/C_{S,gas}$)) values at 298.15 K for solutes dissolved in acetic acid are listed in Table 1. In total there are 68 log (P or ($C_{S,organic}/C_{S,water}$)) and 68 log ($K$ or ($C_{S,organic}/C_{S,gas}$)) values for solutes covering a fairly wide range of solute polarities and hydrogen-bonding capability. Both volatile and nonvolatile solutes are included in the dataset, as well as several strong H-bond donors (isophthalic acid, **A** = 0.960; adipic acid, **A** = 1.130; azelaic acid, **A** = 1.110; hydroquinone, **A** = 1.060) and strong H-bond acceptors (diphenylphosphinic acid, **B** = 1.230; sebacic acid, **B** = 0.900; 2-carboxyethylphenylphosphinic acid, CEPPA, **B** = 1.450). The aqueous molar solubility data needed to calculate ($C_{S,organic}/C_{S,water}$), is available elsewhere [80-85].

3. Results and Discussion

The 68 different organic and inorganic solutes listed in Table 1 represent a chemically diverse of compounds as reflected in the range covered by the numerical values of their solute

descriptors: from **E** = 0.000 to **E** = 2.055; from **S** = 0.000 to **S** = 2.022; from **A** = 0.000 to **A** = 1.130; from **B** = 0.000 to **B** = 1.450; from **V** = 0.0680 to **V** = 2.0250; and from **L** = –1.741 to **L** = 11.025. The data set includes both liquid and crystalline nonelectrolyte organic compounds, as well as several inorganic and organic gas molecules. The chemical diversity of the solutes should be more than sufficient for developing meaningful Abraham model correlations having good predictive capability.

Development of Abraham model correlations for solute transfer into acetic acid is relatively straightforward and involves solving simultaneously the series of 68 log (P or $C_{S,organic}/C_{S,water}$) and 68 log ($K$ or $C_{S,organic}/C_{S,gas}$) equations constructed from the solute descriptors and experimental data given in Table 1. The 68 log (P or $C_{S,organic}/C_{S,water}$) equations are solved for the optimal set of equation coefficients (c_p, e_p, s_p, a_p, b_p, v_p) that best describes respective experimental log (P or $C_{S,organic}/C_{S,water}$) partition coefficient data and molar solubility ratios. The optimal set of equation coefficients (c_k, e_k, s_k, a_k, b_k, and l_k) is obtained in similar fashion using the 68 experimental log (K or $C_{S,organic}/C_{S,gas}$) values. Regression analysis of the experimental data using Version 22 of the IBM SPSS Statistical Software yielded the following two Abraham model correlations:

$$\log (P \text{ or } C_{S,organic}/C_{S,water}) = 0.175(0.049) + 0.174(0.086)\,\mathbf{E} - 0.454(0.115)\,\mathbf{S} - 1.073(0.123)\,\mathbf{A} - 2.789(0.163)\,\mathbf{B} + 3.725(0.081)\,\mathbf{V} \quad (6)$$

(with N = 68, SD = 0.182, R^2 = 0.980, F = 612.4)

$$\log (K \text{ or } C_{S,organic}/C_{S,gas}) = -0.070(0.030) - 0.366(0.084)\,\mathbf{E} + 1.300(0.098)\,\mathbf{S} + 2.736(0.105)\,\mathbf{A} + 2.117(0.139)\,\mathbf{B} + 0.796(0.018)\,\mathbf{L} \quad (7)$$

(with N = 68, SD = 0.159, R^2 = 0.999, F = 9435)

The statistical information associated with the correlation is given below Eqns. (6) and (7), and the standard error in each calculated equation coefficient is given in parenthesis immediately after the respective coefficient. The statistical information includes: the number of experimental data points used in the regression analysis (N); the standard deviation (SD); the squared correlation coefficient (R^2); and the Fisher F-statistic.

Equations (6) and (7) provide a very good mathematical description of the observed partitioning and solubility behavior of solutes dissolved in anhydrous acetic acid as evidenced by standard deviations of 0.182 log units and 0.159 log units, respectively. Graphical comparisons of the observed experimental data versus back-calculated log (P or $C_{S,organic}/C_{S,water}$) and log ($K$ or $C_{S,organic}/C_{S,gas}$) values based on the two derived Abraham model correlations are depicted in Figures 1 and 2. The experimental log (P or $C_{S,organic}/C_{S,water}$) values cover a range of approximately 5.68 log units, from log (P or $C_{S,organic}/C_{S,water}$) = –0.633 log units for malonic acid to log (P or $C_{S,organic}/C_{S,water}$) = 5.049 for octane. The log (K or $C_{S,organic}/C_{S,gas}$) values cover a much larger range of 14.58 log units. To our knowledge this is the first time that mathematical correlations have been reported for predicting partition coefficients and solubility ratios for solutes dissolved in acetic acid.

The predictive ability of Eqns. (6) and (7) was assessed through a training set and test set analysis. The large 68 compound data sets were divided into three smaller subsets by labeling three consecutive solutes A, B and C. The 23 solutes that were labeled A were gathered together into solute subset A, the 23 solutes that were labeled B were placed into solute subset B, and the remaining 22 solutes became solute subset C. Three training sets were prepared as combinations of two of the created smaller subsets (A and B), (A and C), and (B and C). For each training set, a correlation was derived:

Training Set (A and B):

$$\log (P \text{ or } C_{S,organic}/C_{S,water}) = 0.154(0.062) + 0.090(0.101)\,\mathbf{E} - 0.378(0.151)\,\mathbf{S} - 1.092(0.142)\,\mathbf{A} - 2.963(0.158)\,\mathbf{B} + 3.829(0.107)\,\mathbf{V} \quad (8)$$

(with N = 46, SD = 0.182, R^2 = 0.981, F = 415.3)

$$\log (K \text{ or } C_{S,organic}/C_{S,gas}) = -0.056(0.037) - 0.408(0.099)\,\mathbf{E} + 1.389(0.131)\,\mathbf{S} + 2.763(0.122)\,\mathbf{A} + 1.963(0.156)\,\mathbf{B} + 0.794(0.022)\,\mathbf{L} \quad (9)$$

(with N = 46, SD = 0.157, R^2 = 0.999, F = 9435)

Training Set (A and C):

$$\log (P \text{ or } C_{S,organic}/C_{S,water}) = 0.218(0.059) + 0.216(0.103)\,\mathbf{E} - 0.529(0.132)\,\mathbf{S} - 1.032(0.162)\,\mathbf{A} - 2.624(0.216)\,\mathbf{B} + 3.627(0.096)\,\mathbf{V} \quad (10)$$

(with N = 45, SD = 0.180, R^2 = 0.979, F = 365.9)

$$\log (K \text{ or } C_{S,organic}/C_{S,gas}) = -0.073(0.038) - 0.322(0.104)\,\mathbf{E} + 1.237(0.117)\,\mathbf{S} + 2.731(0.143)\,\mathbf{A} + 2.217(0.191)\,\mathbf{B} + 0.792(0.022)\,\mathbf{L} \quad (11)$$

(with N = 45, SD = 0.159, R^2 = 0.999, F = 5735)

Training Set (B and C):

$$\log (P \text{ or } C_{S,organic}/C_{S,water}) = 0.146(0.064) + 0.209(0.121)\,\mathbf{E} - 0.452(0.149)\,\mathbf{S} - 1.101(0.162)\,\mathbf{A} - 2.744(0.217)\,\mathbf{B} + 3.729(0.100)\,\mathbf{V} \quad (12)$$

(with N = 45, SD = 0.189, R^2 = 0.982, F = 419.9)

$$\log (K \text{ or } C_{S,organic}/C_{S,gas}) = -0.084(0.039) - 0.366(0.114)\,\mathbf{E} + 1.285(0.122)\,\mathbf{S} + 2.667(0.134)\,\mathbf{A} + 2.232(0.177)\,\mathbf{B} + 0.800(0.021)\,\mathbf{L} \quad (13)$$

(with N = 45, SD = 0.156, R^2 = 0.999, F = 6198)

Each regression analysis gave a training set correlation equation having coefficients not too different from that obtained from the parent 68 compound database. The training set equations were then used to calculate log (P or $C_{S,organic}/C_{S,water}$) and log ($K$ or $C_{S,organic}/C_{S,gas}$) values for the

compounds in the respective test sets (A, B and C). The test set computations are summarized in Table 2 as the standard deviations (SD), Average Absolute Errors (AAE) and Average Errors (AE). The training set and test set validations were repeated three additional times by first scrambling the experimental data points in the parent dataset, and then dividing the data points into three subsets as before. Similar results were obtained each time. To conserve journal space only one set of validations is reported. The small AE values in the last column of Table 2 show that there is very little bias in Eqns. (8) - (13).

Acetic acid is well known to exist as a cyclic dimer, but this is usually restricted to solutions of acetic acid in non-polar solvents. The structure of neat acetic acid has been studied several times, with agreement that liquid acetic acid exists as linear associates [86-88]. Unlike the cyclic dimer, there are free –OH groups in the linear associates, see Figure 3, that are free to interact with external solutes that are hydrogen-bond bases. Hence on this basis, acetic acid solvent would be expected to act as a hydrogen-bond acid. Eqn (2) is easier to interpret than eqn. (1), and in Table 3 are listed the coefficients in eqn, (2) for acetic acid solvent and for a selection of solvents that we have studied previously. The coefficient b_k refers to the hydrogen-bond acidity of the solvent (because hydrogen-bond basic solutes interact with hydrogen-bond acidic solvents). From Table 3 it can be seen that acetic acid solvent has a considerable hydrogen-bond acidity (b_k = 2.117), even larger than that of methanol (b_k = 1.396), in agreement with the linear associated structure of liquid acetic acid, and contrary to what would be expected if liquid acetic acid was composed of cyclic dimers.

In order to compare the general solubility properties of acetic acid with those of other solvents, especially those with hydroxyl functional groups, we have carried out a PCA of the coefficients listed in Table 3, exactly as detailed above. The first two PCs contain 79% of the

total information, and a plot of PC2 against PC1 is shown in Figure 4. Of the hydroxylic solvents water (No 2) is quite exceptional, but the point for acetic acid (No 1) is quite close to those for many of the other hydroxylic solvents. Perhaps counter intuitively, it seems as though the solubility properties of acetic acid are not unusual and are not very different to the solubility properties of solvents such as octan-1ol (No 4). Compounds such as acetic acid, water, alcohols, formamide and N-methylformamide act as hydrogen-bond acids both as solvents, as shown by the b_k-coefficient in eqn (2), and as solutes, as shown by the **A**-descriptor. Although the b_k-coefficient and the **A**-descriptor are on different scales, it is of some interest to see how transformation from a solute to a solvent results in change in hydrogen-bond acidity. In Figure 5 is a plot of the b_k –coefficient for solvents against the **A**-descriptor for solutes. Water solvent has (a relatively) very large increase in hydrogen-bond acidity over monomeric water solute, trifluoroethanol solvent has a substantial increase but acetic acid is again not very different to several other solvents. In terms of hydrogen-bond acidity and general solution properties acetic acid is not an unusual solvent.

4. Conclusion

Mathematical expressions based on the Abraham solvation parameter model are derived for describing molar solubility ratios and solute partition coefficients for neutral organic molecules and inorganic gases dissolved in acetic acid at 298 K. The derived mathematical expressions provide a reasonably accurate mathematical description of the observed solubility and partition coefficient data. Our analysis further showed that acetic acid solvent has considerable hydrogen-bond acidity, in agreement with the proposed linear structure for the solvent, and in terms of solubility related properties is not an unusual solvent at all.

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Table 1. Logarithm of the experimental water-to-acetic acid partition coefficients, log *P*, and logarithm of the gas-to-acetic acid partition coefficient, log *K*, for solutes dissolved in acetic acid at 298 K along with the numerical values of the solute descriptors

Solute	**E**	**S**	**A**	**B**	**L**	**V**	log K^a	log P^a	Ref
Hydrogen	0.000	0.000	0.000	0.000	-1.741	0.0680	-1.199	0.821	58
Argon	0.000	0.000	0.000	0.000	-0.688	0.1900	-0.663	0.807	44
Krypton	0.000	0.000	0.000	0.000	-0.211	0.2460	-0.380	0.830	44
Xenon	0.000	0.000	0.000	0.000	0.378	0.3290	0.215	1.185	48
Radon	0.000	0.000	0.000	0.000	0.877	0.3840	0.646	1.296	56
Nitrogen	0.000	0.000	0.000	0.000	-0.978	0.2222	-0.924	0.876	59
Oxygen	0.000	0.000	0.000	0.000	-0.723	0.1830	-0.710	0.800	62
Ozone	0.000	0.100	0.090	0.000	0.039	0.2417	0.262	0.782	62
Nitrous oxide	0.068	0.350	0.000	0.100	0.164	0.2810	0.658	0.888	49
Carbon monoxide	0.000	0.000	0.000	0.040	-0.836	0.2220	-0.771	0.849	44
Carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.2809	0.681	0.761	49
Hydrogen sulfide	0.350	0.310	0.100	0.070	0.723	0.2721	1.096	0.696	51
Chlorine	0.360	0.320	0.100	0.000	1.193	0.3534	1.472	1.292	55
Phosphine	0.200	0.110	0.000	0.050	0.340	0.3132	0.504	1.204	57
Methane	0.000	0.000	0.000	0.000	-0.323	0.2495	-0.380	1.080	44
Ethane	0.000	0.000	0.000	0.000	0.492	0.3904	0.276	1.616	44
Propane	0.000	0.000	0.000	0.000	1.050	0.5313	0.699	2.139	44
Butane	0.000	0.000	0.000	0.000	1.615	0.6722	0.886	2.406	44
2-Methylpropane	0.000	0.000	0.000	0.000	1.409	0.6722	0.959	2.659	44
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	1.509	3.209	44
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	1.957	3.777	44
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	2.337	4.297	44
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	2.939	5.049	45
Isooctane	0.000	0.000	0.000	0.000	3.106	1.2358	2.268	4.388	44
Cyclopropane	0.408	0.230	0.000	0.000	1.314	0.4227	1.227	1.777	50
Cyclopentane	0.260	0.100	0.000	0.000	2.477	0.7045	1.921	2.801	44
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	2.357	3.257	44
Ethene	0.110	0.100	0.000	0.070	0.289	0.3474	0.547	1.487	60
Propene	0.100	0.080	0.000	0.070	0.946	0.4883	0.981	1.951	54
trans-2-Butene	0.126	0.080	0.000	0.050	1.664	0.6292	1.672	2.652	52
2-Methyl-1-propene	0.120	0.080	0.000	0.080	1.579	0.6292	1.537	2.397	53
1,3-Butadiene	0.320	0.230	0.000	0.100	1.543	0.5862	1.788	2.238	52
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	3.810	0.140	45
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	4.296	0.586	45

Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	3.585	0.865	45
Nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237	3.547	0.597	45
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	2.940	0.090	46
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	2.824	2.194	44
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	3.357	2.707	44
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	5.372	3.612	66
Phenanthrene	2.055	1.290	0.000	0.290	7.632	1.4544	7.600	4.800	73
Benzoic acid	0.730	0.900	0.590	0.400	4.657	0.9317	7.098	1.958	70
4-Methylbenzoic acid	0.730	0.930	0.620	0.420	4.890	1.0726	7.605	2.304	71
2-Hydroxybenzoic acid	0.900	0.850	0.730	0.370	4.732	0.9904	7.234	1.844	65
4-Hydroxybenzoic acid	0.930	0.900	0.810	0.560	4.867	0.9904	8.125	1.345	69
Isophthalic acid	1.100	1.210	0.960	0.590	5.988	1.1470	9.544	1.284	79
Salicylamide	1.160	1.650	0.630	0.480	5.910	1.0315	9.549	1.864	64
Methyl 4-hydroxybenzoate	0.900	1.370	0.690	0.450	5.665	1.1313	8.612	1.762	69
Oxalic acid	0.400	1.210	0.750	0.510	2.835	0.5392	6.992	-0.178	63
Malonic acid	0.380	1.460	0.990	0.590	3.616	0.6801	8.367	-0.633	63
Succinic acid	0.370	1.320	1.030	0.710	3.951	0.8210	8.825	-0.405	63
Glutaric acid	0.360	1.280	1.050	0.750	4.207	0.9619	9.131	-0.189	63
Adipic acid	0.350	1.210	1.130	0.760	4.457	1.1028	9.787	0.357	63
Pimelic acid	0.350	1.260	1.100	0.840	5.277	1.2437	10.196	0.546	63
Suberic acid	0.350	1.360	1.100	0.870	5.926	1.3846	11.260	1.330	63
Azelaic acid	0.340	1.360	1.110	0.870	6.420	1.5277	11.770	1.940	63
Sebacic acid	0.350	1.400	1.100	0.900	6.910	1.6664	12.220	2.200	63
Diphenylphosphinic acid	1.500	1.300	0.870	1.230	8.380	1.6462	12.636	1.596	67
Hydroquinone	1.063	1.270	1.060	0.570	4.827	0.8338	8.891	-0.159	68
Naproxen	1.510	2.022	0.600	0.673	9.207	1.7821	12.368	3.568	72
Iodine	1.398	0.670	0.280	0.000	3.681	0.6250	3.839	1.979	78
Diclofenac	1.810	1.850	0.550	0.770	11.025	2.0250	13.380	4.110	76
Ibuprofen	0.730	0.700	0.570	0.790	7.184	1.7771	9.800	3.940	74
Niflumic acid	1.540	1.710	0.750	0.790	9.277	1.7922	12.540	3.130	77
CEPPA[b]	1.090	1.530	0.900	1.450	7.655	1.5355	13.080	0.340	75
Fluoroethane	0.052	0.340	0.000	0.050	0.751	0.4081	1.030	1.330	61
2-Chloro-2-methylpropane	0.142	0.300	0.000	0.030	2.273	0.7946	2.243	3.043	47
2-Bromo-2-methylpropane	0.305	0.290	0.000	0.070	2.609	0.8472	2.513	3.113	47

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

[b] CEPPA is 2-carboxyethylphenylphosphinic acid.

Table 2. Summary of Test Set Analysis for the Derived Abraham Model Correlations

Correlation	Training Set	Test Set	SD of Test Set	AAE of Test Set	AE of Test Set
log (P or $C_{S,organic}/C_{S,water}$)	A and B	C	0.207	0.171	-0.043
	A and C	B	0.212	0.164	0.001
	B and C	A	0.186	0.147	0.030
log (K or $C_{S,organic}/C_{S,gas}$)	A and B	C	0.173	0.146	-0.017
	A and C	B	0.187	0.122	-0.020
	B and C	A	0.196	0.154	0.005

Table 3. Equation coefficients for the transfer of solutes from the gas phase to solvents, Eqn. (2)

Solvent	N	c_k	e_k	s_k	a_k	b_k	l_k
Acetic acid	1	-0.070	-0.366	1.300	2.736	2.117	0.796
Water	2	-1.271	0.822	2.743	3.904	4.814	-0.213
Methanol	3	-0.039	-0.338	1.317	3.826	1.396	0.773
Octan-1-ol	4	-0.147	-0.214	0.561	3.507	0.749	0.943
Trifluoroethanol	5	-0.092	-0.547	1.339	2.213	3.807	0.645
Ethylene glycol	6	-0.887	0.132	1.657	4.457	2.355	0.565
2-Methoxyethanol	7	-0.141	-0.265	1.810	3.641	0.590	0.790
2-Ethoxyethanol	8	-0.064	-0.257	1.452	3.672	0.662	0.843
Trichloromethane	9	0.157	-0.560	1.259	0.374	1.333	0.976
Hexane	10	0.320	0.000	0.000	0.000	0.000	0.945
Toluene	11	0.085	-0.400	1.063	0.501	0.154	1.011
Nitrobenzene	12	-0.296	0.092	1.707	1.147	0.443	0.912
Diethylether	13	0.288	-0.379	0.904	2.937	0.000	0.963
Ethyl acetate	14	0.182	-0.352	1.316	2.891	0.000	0.916
Propanone	15	0.127	-0.387	1.733	3.060	0.000	0.866
Dimethylformamide	16	-0.391	-0.869	2.107	3.774	0.000	1.011
N-Methylformamide	17	-0.249	-0.142	1.661	4.147	0.817	0.739
Formamide	18	-0.800	0.310	2.292	4.130	1.933	0.442
Acetonitrile	19	-0.007	-0.595	2.461	2.085	0.418	0.738
Nitromethane	20	-0.340	-0.297	2.689	2.193	0.514	0.728
Dimethylsulfoxide	21	-0.556	-0.223	2.903	5.037	0.000	0.719

Figure 1

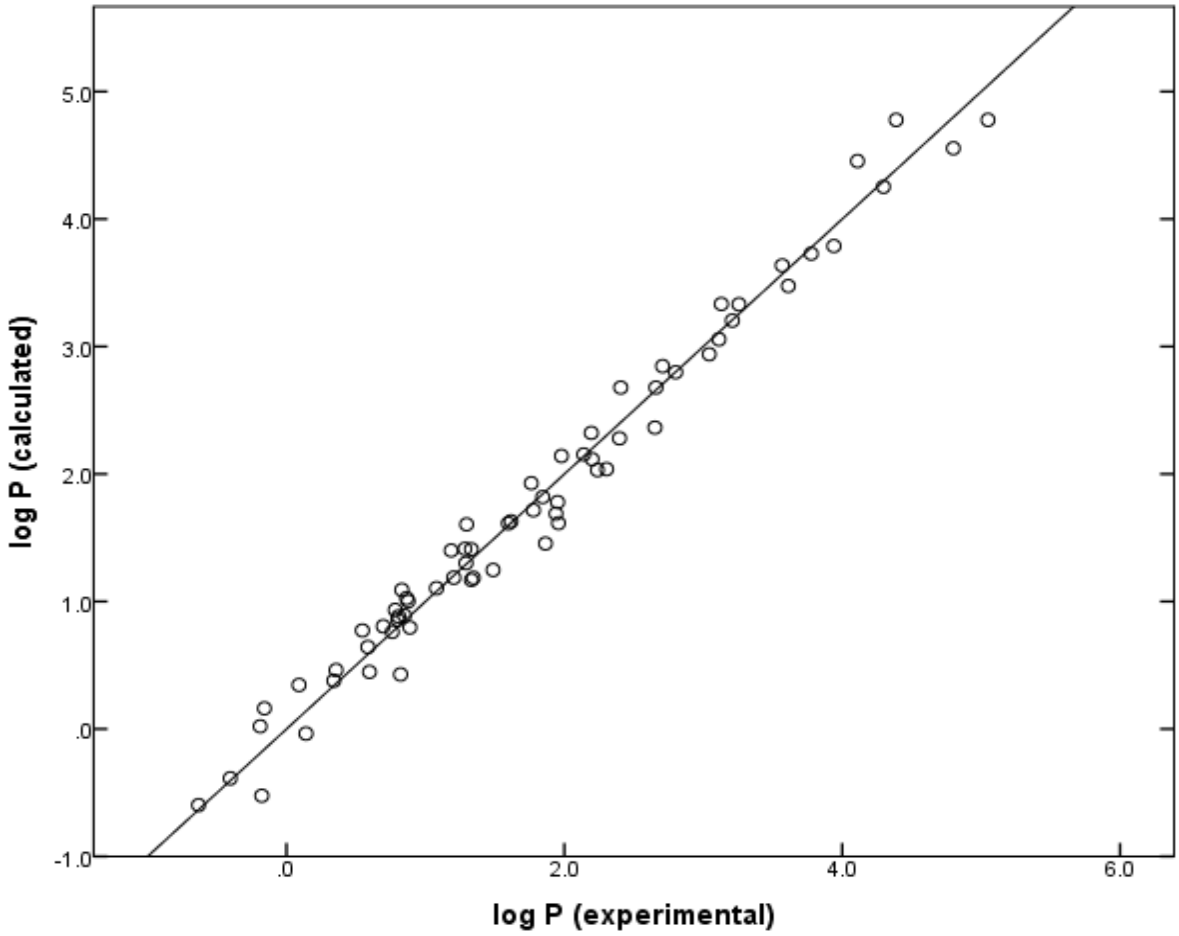

Figure 1. Comparison between experimental log (P or $C_{S,organic}/C_{S,water}$) data and back-calculated values based on Eqn. (6)

Figure 2

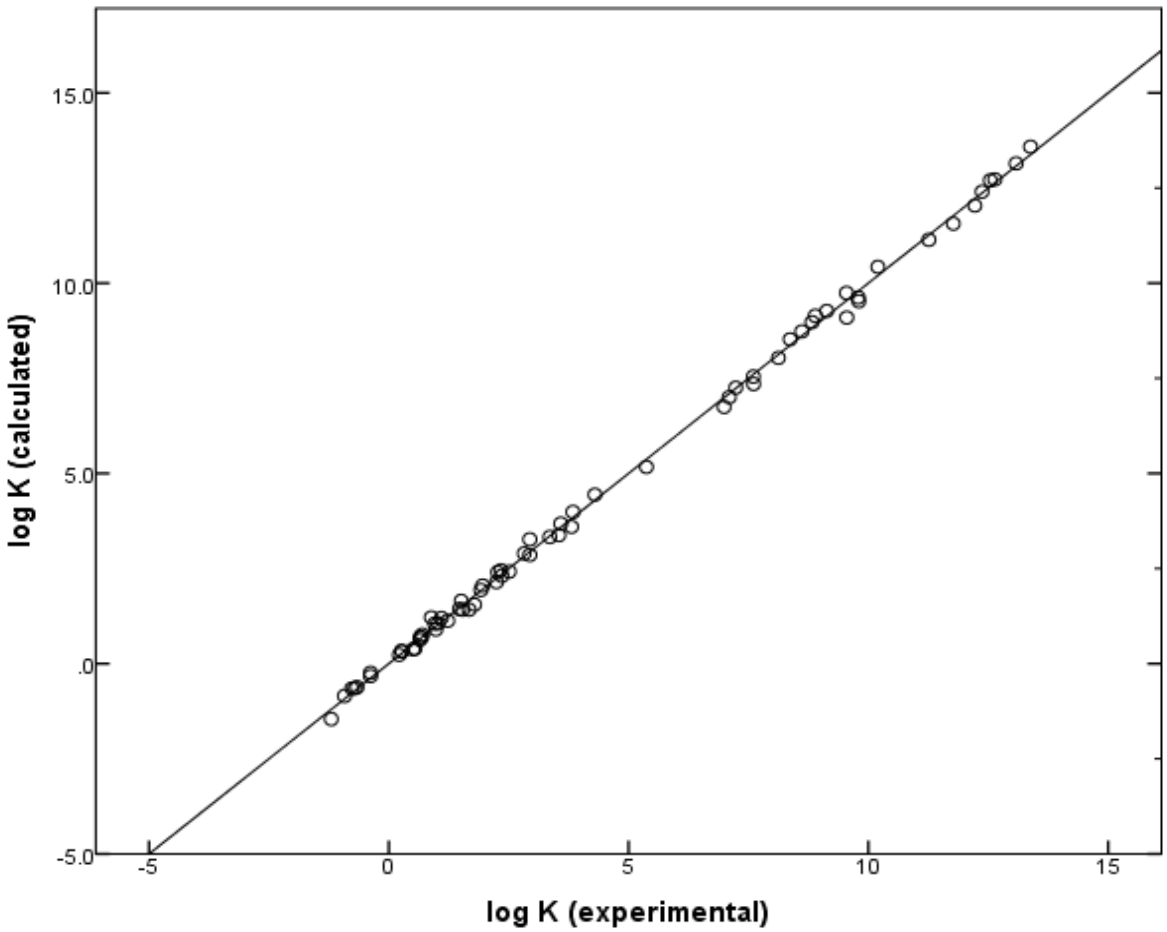

Figure 2. Comparison between experimental log (K or $C_{S,organic}/C_{S,gas}$) data and back-calculated values based on Eqn. (7)

Figure 3.

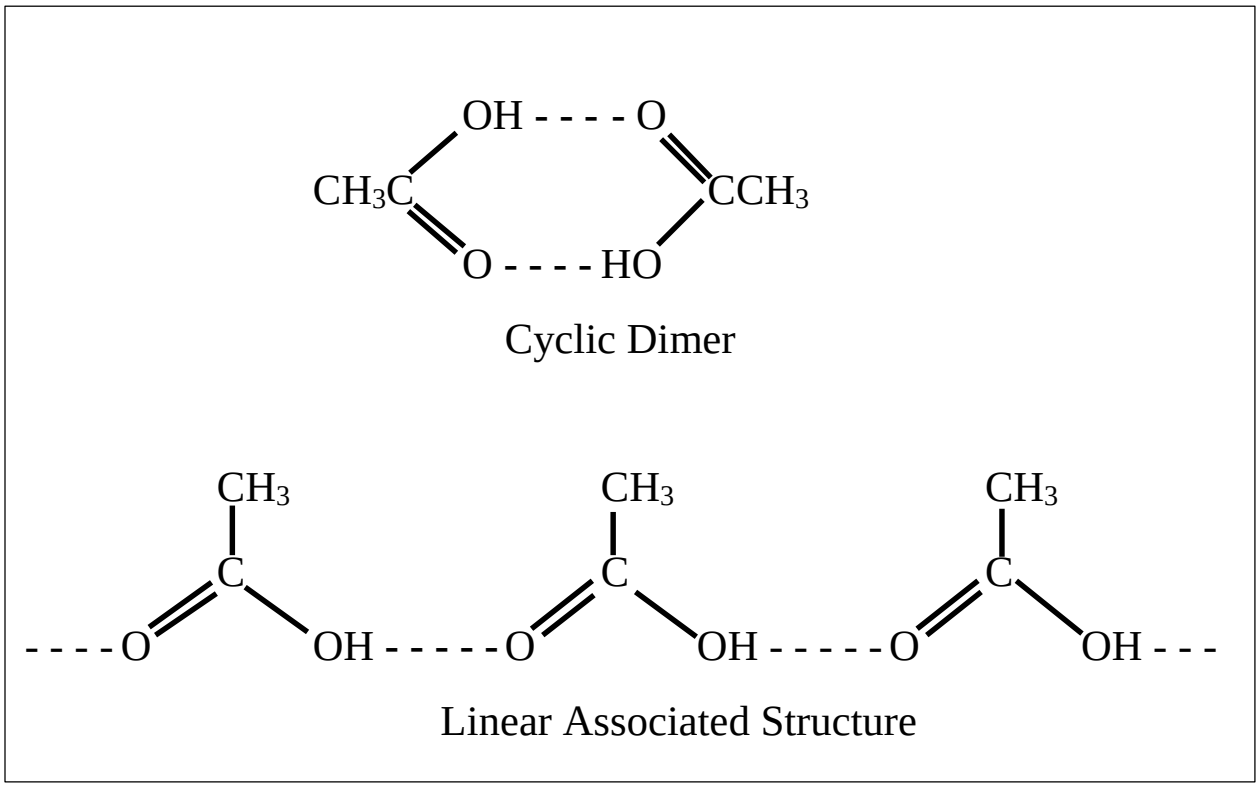

Figure 3. The cyclic dimer and linear associated structure of acetic acid.

Figure 4

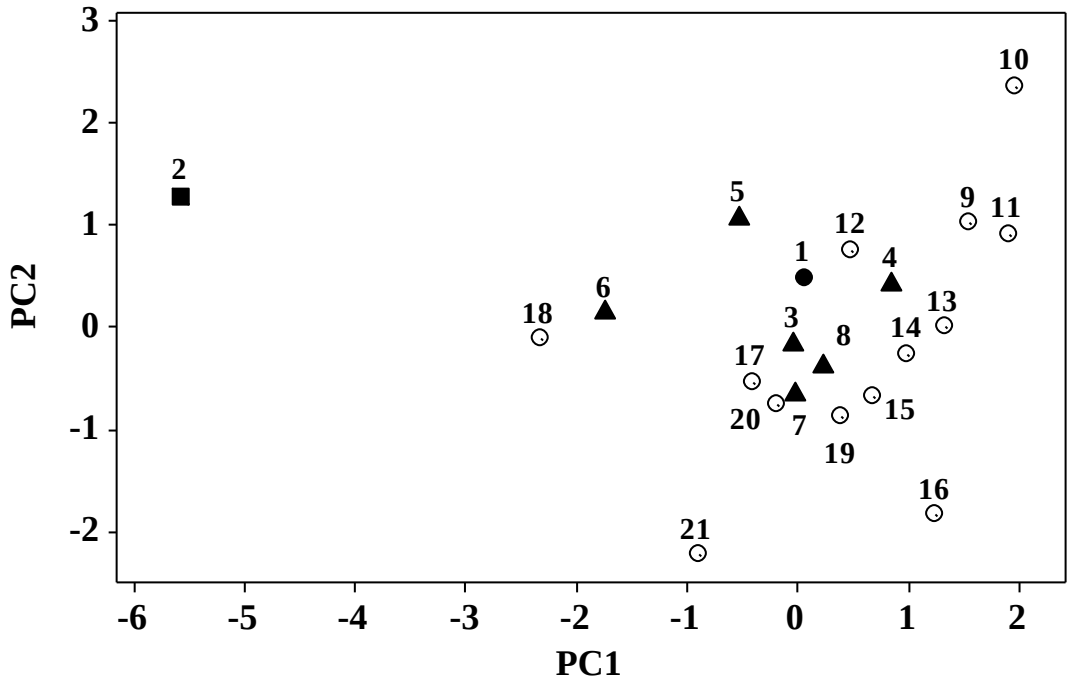

Figure 4. A plot of the scores of PC2 against the scores of PC1. Solvents numbered as in Table 3: ● acetic acid; ■ water; ▲ hydroxylic solvents, formamide and N-methylformamide.

Figure 5

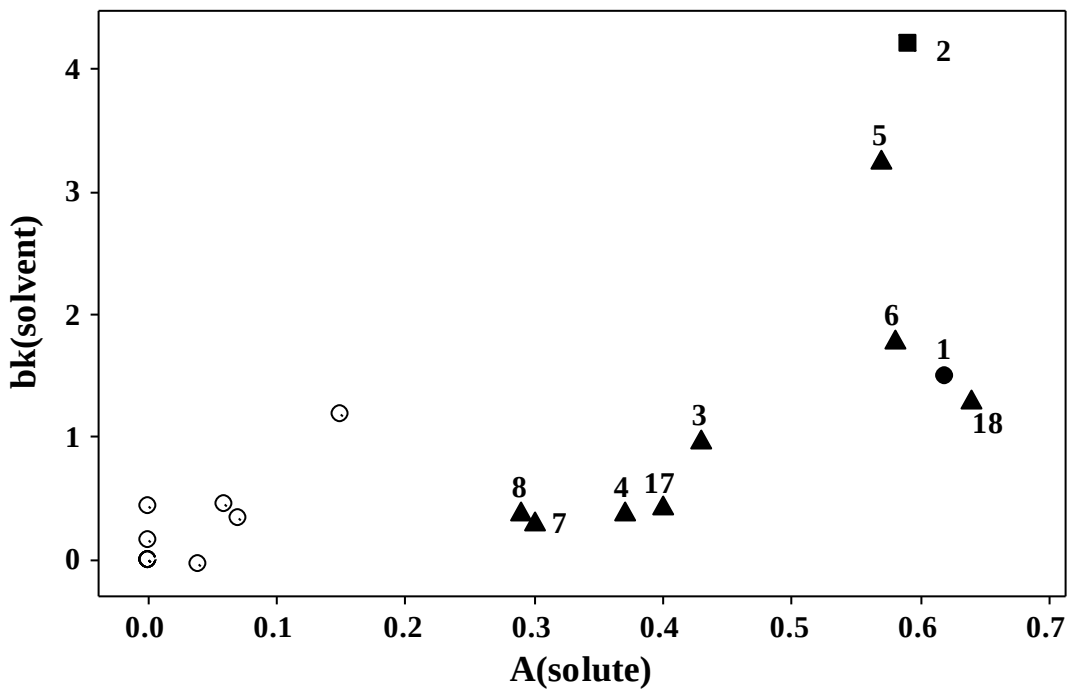

Figure 5. A plot of b_k for solvents against **A** values for solutes. Solvents numbered as in Table 4: ● acetic acid; ■ water; ▲ hydroxylic solvents, formamide and N-methylformamide.

GRAPHIC ABSTRACT

SOLUTE TRANSFER PROCESSES

ABRAHAM MODEL CORRELATIONS

$$\log (P \text{ or } C_{S,organic}/C_{S,water}) = c_p + e_p \cdot E + s_p \cdot S + a_p \cdot A + b_p \cdot B + v_p \cdot V$$

SOLUTE IN H_2O → **SOLUTE IN CH_3COOH**

$$\log (K \text{ or } C_{S,organic}/C_{S,gas}) = c_k + e_k \cdot E + s_k \cdot S + a_k \cdot A + b_k \cdot B + l_k \cdot L$$

SOLUTE IN GAS → **SOLUTE IN CH_3COOH**