ABRAHAM MODEL CORRELATIONS FOR TRANSFER OF NEUTRAL MOLECULES AND IONS TO SULFOLANE

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Abstract

Data have been compiled from the published literature on the partition coefficients of solutes and vapors into anhydrous sulfolane. The logarithms of the water-to-sulfolane partition coefficients, log P, and gas-to-sulfolane partition coefficients, log K, were correlated with the Abraham solvation parameter model. The derived correlations described the observed log P and log K values for solutes dissolved in sulfolane to within average standard deviations of 0.14 log units or less. The log P correlation was extended to include the partition of ions by inclusion of a cation-solvent and an anion-solvent term.

Key words and phrases

Partition coefficients, sulfolane, nonelectrolyte solutes, ionic solutes, Abraham model correlations

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1. Introduction

Removal of aromatic hydrocarbons (benzene, methylbenzene, ethylbenzene and dimethylbenzenes) from aliphatic hydrocarbon mixtures (hexanes, heptanes and octanes) is a challenging chemical separation problem encountered in petrochemical processing. Distillation is often not a viable separation method due to the narrow range covered by the boiling point temperatures of the mixture components. Moreover, several combinations of aromatic and aliphatic hydrocarbons form azeotropic mixtures. Liquid-liquid extraction has proved to be a convenient means for aromatic hydrocarbon removal from such mixtures containing up to 65 % aromatic hydrocarbon content by mass. Extractive distillation is used for mixtures containing 65 % to 90 % aromatic hydrocarbon content, and for larger amounts of aromatic compounds, one employs methods based on azeotropic distillation. Sulfolane, N-methylpyrrolidin-2-one, ethylene glycol, propylene carbonate and other polar organic solvents have served as the extraction solvent or as an additive to prevent azeotrope formation. The published chemical and engineering literature [1-14] report experimental liquid-liquid equilibrium data for ternary, quaternary and quinary aromatic hydrocarbon(s) + aliphatic hydrocarbon(s) + polar organic solvent mixtures to facilitate the design of extraction processes for aromatic hydrocarbon removal. Choice of the extraction solvent is an important design consideration.

The solvation parameter model of Abraham [15-17] is an useful approach for quantifying the solubilizing ability of organic solvents. The method relies on two linear free energy relationships (LFERs); the first for describing the solute water-to-organic solvent partition coefficient, P,

$$\log P = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V} \tag{1}$$

and the second for describing the solute partition coefficient into the organic solvent from the gas phase, K,

$$\log K = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + l \cdot \mathbf{L} \qquad (2)$$

The independent variables, or solute descriptors, in Eqns. 1 and 2 are properties of the neutral solutes as follows: [9,10] $\mathbf{E}$ is the solute excess molar refraction in cm^3 $mol^{-1}/10$, $\mathbf{S}$ is the solute dipolarity/polarizability, $\mathbf{A}$ is the overall solute hydrogen bond acidity, $\mathbf{B}$ is the overall solute hydrogen bond basicity, $\mathbf{V}$ is McGowan's characteristic molecular volume in cm^3 $mol^{-1}/100$ and L is the logarithm of the gas to hexadecane partition coefficient measured at 298 K. The regression coefficients and constants (c, e, s, a, b, v and l) are obtained by multiple linear regression analysis of experimental partition coefficient data for a specific biphasic system. For any fully characterized partitioning system (those with calculated values for the equation coefficients), further values of log P and log K can be estimated with known values for the solute descriptors. To date, we have reported equation coefficients for more than 70 different organic solvents [17], including several of the polar organic solvents (ethylene glycol [18], propylene carbonate [18], N-methylpyrrolidin-2-one [19] and N-formylmorpholine [19]) in the separation of aromatic hydrocarbons from aliphatic hydrocarbons.

We recently extended our Abraham model log P equations to include partition coefficients of ions and ionic species [18, 20-24]:

$$\log P = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V} + j^+ \cdot \mathbf{J}^+ + j^- \cdot \mathbf{J}^- \qquad (3)$$

we use the latter term to describe anions derived from acids by loss of a proton, and cations derived from bases by acceptance of a proton. The descriptors for anions and cations are $\mathbf{E}$, $\mathbf{S}$, $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{V}$ on exactly the same scales as for neutral molecules together with an additional descriptor, $\mathbf{J}^-$, for anions and an additional descriptor, $\mathbf{J}^+$, for cations. The complementary

solvent coefficients in Eqn. 3 are j$^-$ and j$^+$. For anions j$^+$ = 0, for cations j$^-$ = 0, and for neutral

solutes j$^+$ = j$^-$ = 0 so that Eqn 3 then reverts to Eqn 1. Note that the coefficients c, e, s, a, b and v

in Eqn 3 are taken to be exactly the same as the coefficients in the corresponding Eqn 1, so that

only one new coefficient, j$^+$, has to be determined for cations and only one new coefficient, j$^-$,

has to be determined for anions. Numerical values of j$^+$ and j$^-$ have been determined for the

partition of ions from water to the solvents methanol, ethanol, 1-propanol, 1-butanol, 1-hexanol,

1-octanol, 2-propanol, *tert*-butanol, ethylene glycol, 1,2-dichloroethane, tetrahydrofuran,

propylene carbonate, propanone, dimethyl sulfoxide, formamide, N-methylpyrrolidin-2-one,

acetonitrile, and nitrophenyl octyl ether so far [18, 20-24]. Anion coefficients have been

reported also for N,N-dimethylformamide, N,N-dimethylacetamide, nitrobenzene and

nitromethane. [20]

Sulfolane is an important extraction solvent for which we have now developed an

Abraham model correlation. The aim of the present work is to collect experimental data from

the published literature on the partition coefficients of neutral solutes from water and from air

into sulfolane, and to derive Abraham model log *P* and log *K* correlations. As part of the present

work we have calculated the j$^+$ and j$^-$ equation coefficients for sulfolane from published single

ion transfer properties computed from electrochemical measurements and solubility data.

2. Data Sets and Computation Methodology

Most of the experimental data that we were able to retrieve from the published literature

pertained to the Raoult's law infinite dilution activity coefficient, $\gamma_{\text{solute}}^{\infty}$, for solutes dissolved in

anhydrous sulfolane [25-31]. The activity coefficients were determined by an inverse gas

chromatographic method from retention time measurements of solutes on a liquid sulfolane

stationary phase. Measurements were performed at 298 K or at slightly higher temperatures. In

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the latter case, each research group made measurements at two or more column temperatures. The measured γ_{solute}^{∞} values were extrapolated back to 298 K assuming a ln γ_{solute}^{∞} versus 1/T linear relationship. Henry's law constants were also found for carbon dioxide [32, 33], nitrous oxide [32], sulfur dioxide [34], ethane [35] and hydrogen sulfide [33] in sulfolane.

In order to apply the Abraham model, the infinite dilution activity coefficients and Henry's law constants needed to be converted to log K values through Eqns. 4 and 5

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

$$\log K = \log \left(\frac{RT}{K_{Henry} V_{solvent}} \right) \tag{5}$$

or to log P values for partition from water to solvent through Eqn. 6 where Kw is the gas to water partition coefficient.

$$\log P = \log K - \log Kw \tag{6}$$

In Eqns. 4 and 5, 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. The calculation of log P requires knowledge of the solute's gas phase partition coefficient into water, K_w, which is available for all of the solutes being studied [36-38]. The experimental log K and log P values at 298 K for anhydrous sulfolane are listed in Table 1, along with the corresponding literature references. As an informational note, the calculated log P values for anhydrous sulfolane refer to a hypothetical partition coefficient. Even though hypothetical, these log P correlations are still quite useful in that predicted log P values can be used to estimate the solute's infinite dilution activity coefficient or molar solubility in anhydrous sulfolane for those solutes for which the solute descriptors are known

During our search of the published literature we also found experimental solubility data for several crystalline carboxylic acid solutes (benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 2-chlorobenzoic acid, 4-chlorobenzoic acid, 2-nitrobenzoic acid, 4-nitrobenzoic acid and 4-aminobenzoic acid) dissolved in both anhydrous sulfolane and in water [39]. In the case of crystalline solutes, the partition coefficient between water and the anhydrous organic solvent is calculated as a solubility ratio

$$P = C_S/C_W \tag{7}$$

of the solute's molar solubilities in the organic solvent, C_S, and in water, C_W. The calculated log P value is converted to log K through Eqn. 6.

Molecular descriptors for all of the compounds considered in the present study are also tabulated in Table 1. The tabulated values came from our solute descriptor database, and were obtained using various types of experimental data, including water-to-solvent partitions, gas-to-solvent partitions, solubility and chromatographic data. [15-19]

3. Results and Discussion

We have assembled in Table 1 log K and log P values for the partitioning of 77 solutes between the gas phase and sulfolane, and between water and sulfolane. The solutes considered are mostly simple volatile aliphatic compounds, plus eight substituted benzoic acid derivatives. Numerical values of the solute descriptors covered by the data set range from: $E = -0.060$ to $E = 1.075$; $S = 0.000$ to $S = 1.650$; $A = 0.000$ to $A = 0.940$; $B = 0.000$ to $B = 0.600$; $V = 0.281$ to $V = 1.518$; and $L = -0.836$ to $L = 5.916$. Regression analysis of the tabulated experimental values in Table 1 gave the following two mathematical expressions:

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log P = 0.147(0.123) **E** + 0.601(0.106) **S** − 0.318(0.112) **A** − 4.541(0.116) **B** + 3.290(0.065) **V**

(8)

(N = 77, SD = 0.140, R^2 = 0.989, F = 1269)

and

log K = −0.414(0.040) + 0.084(0.109) **E** + 2.396(0.085) **S** + 3.144(0.093) **A** + 0.420(0.095) **B**

+ 0.684(0.014) **L** (9)

(N = 77, SD = 0.115, R^2 = 0.997, F = 4486)

The c-coefficient in the log P correlation was found to be negligible (c = −0.008), and was removed from the final correlation. All regression analyses were performed using SPSS statistical software. The standard errors in the calculated coefficients are given in parenthesis. Here and elsewhere, N corresponds to the number of solutes, R denotes the correlation coefficient, SD is the standard deviation and F corresponds to the Fisher F-statistic. Both correlations describe the experimental water-to-sulfolane partition coefficient data (Eqn. 8) and gas-to-sulfolane partition coefficient data (Eqn. 9) to within a standard deviation of SD = 0.14 log units for experimental values that cover ranges of about 6.0 and 11.2 log units, respectively. Graphical comparisons of predicted versus observed values are given in Figures 1 and 2.

We note that the descriptor **E** plays little part in the analyses in the two correlations, and the major cross-correlation amongst the other descriptors is that between **S** and **A** with R^2 = 0.472. In the correlation for log K, when the term s·**S** or a·**A** is removed the equation collapses and the F-statistic decreases from 4486 to 466 or 323. Hence both **S** and **A** must be retained. The situation is different for the correlation for log P. If the term s·**S** is removed, the F-statistic decreases from 1262 to 1094, but if the term a·**A** is removed the F-statistic increases to1421; then if the term e·**E** is also left out, F increases to 1918, the resulting equation being,

$$\log P = 0.022(0.060) + 0.585(0.059)\ \mathbf{S} - 4.614(0.100)\ \mathbf{B} + 3.288(0.064)\ \mathbf{V} \qquad (10)$$

$$N = 76,\ SD = 0.152,\ R^2 = 0.987,\ F = 1918.2$$

Although this is statistically the best equation for log P, as judged by the F-statistic, it is very useful to retain all five descriptors for purposes of comparison with equations for other processes.

In order to assess the predictive ability of Eqns. 8 and 9 we divided the data points into a training set and a test set by allowing the SPSS software to randomly select half of the experimental data points. The selected data points became the training sets and the remaining compounds that were left served as the test sets. Analysis of the experimental data in the log P and log K training sets gave:

$$\log P = 0.113(0.184)\ \mathbf{E} + 0.742(0.162)\ \mathbf{S} - 0.397(0.169)\ \mathbf{A} - 4.634(0.172)\ \mathbf{B} + 3.286(0.042)\ \mathbf{V}$$

$$(11)$$

$$(N = 39,\ SD = 0.144,\ R^2 = 0.997,\ F = 189.0)$$

and

$$\log K = -0.435(0.050) + 0.233(0.153)\ \mathbf{E} + 2.290(0.141)\ \mathbf{S} + 3.182(0.135)\ \mathbf{A} + 0.467(0.135)\ \mathbf{B}$$

$$+ 0.694(0.017)\ \mathbf{L} \qquad (12)$$

$$(N = 39,\ SD = 0.110,\ R^2 = 0.997,\ F = 2484)$$

There is little difference in the equation coefficients for the full dataset and the training dataset correlations, thus showing that both training sets of compounds are representative samples of the total log P and log K data sets. The derived training set equations were then used to predict the respective partition coefficients for the compounds in the test sets. For the predicted and experimental values, we found SD = 0.141 (Eqn. 11) and SD = 0.136 (Eqn. 12), AAE (average

absolute error) = 0.115 (Eqn. 11) and AAE = 0.101 (Eqn. 12), and AE (average error) = –0.045 (Eqn. 11) and AE = –0.037 (Eqn. 12). There is therefore little bias in using Eqns. 11 and 12 with AE equal to –0.045 and –0.037 log units. The training and test set analyses were performed three more times with similar results.

Now that we have the coefficients in Eqn 8 for partition between water and sulfolane of neutral solutes, we can attempt to fit log P values for single ions to an extension of Eqn 8 using just the two additional terms $j^+ \cdot \mathbf{J}^+$ and $j^- \cdot \mathbf{J}^-$ in Eqn 3. Single ion values based on the convention that log $P(Ph_4P^+$ or $Ph_4As^+) = $ log $P(Ph_4B^-)$ have been determined by Cox et al. [40] and reviewed by Marcus [41]. The former are the more consistent and are the ones we shall use. These single ion values refer to 303 K rather than to 298 K [42]. Single ion enthalpies of transfer are no more than about 20 kJ mol^{-1} [40], and our inclusion of the 303 K data in the data set should lead to an error of no greater than 0.06 in log P, probably less than the experimental error. Ludwig et al. [43] have determined pK_a values for a large number of benzoic acids in sulfolane and in water. These can be used to calculate values of log P for the benzoate ions, log $P(A^-)$, through Eqn 13,

$$\text{Log } P(A^-) = \log P(HA) - \log P(H^+) + pK_a(aq) - pK_a(s) \tag{13}$$

In Eqn 13, $P(HA)$ and $P(H^+)$ are the water to sulfolane partition coefficients of the neutral benzoic acid and of H$^+$, pK_a(aq) is the acid dissociation constant in water, and pK_a(s) is the acid dissociation constant in sulfolane. Log $P(HA)$ can be estimated from Eqn 8 and known descriptors for the neutral benzoic acids, but log $P(H^+)$ is not well established. We therefore

used log $P(H^+)$ as a fitting parameter, and with log $P(H^+)$ = -11.55 we obtained the results shown in Table 2. With j^+ = -1.200 and j^- = -0.792 we could fit 41 log P values for ions with SD = 0.225 log units; as noted above, all the other coefficients are the same as those in Eqn 9. Of the 33 benzoic acids studied by Ludwig *et al*. [43], we left out benzoic acid itself and 4-nitrobenzoic acid which were outliers by 0.84 and 0.80 log units respectfully. Our fitted value of -11.55 for log $P(H^+)$ compares reasonably well with the only literature value available of -12.08 log units [43]. Use of the latter would not affect the results significantly. For the five anions (other than the benzoates) in Table 2, the standard deviation between observed and calculated values is 0.29 with log $P(H^+)$ = -11.55 and 0.50 with log $P(H^+)$ = -12.08. We use our fitted value to get the final result for transfer of neutral molecules, ions and ionic species from water to sulfolane,

$$\log P = 0.147\ \mathbf{E} + 0.601\ \mathbf{S} - 0.318\ \mathbf{A} - 4.541\ \mathbf{B} + 3.290\ \mathbf{V} - 1.200\ \mathbf{J^+} - 0.792\ \mathbf{J^-} \qquad (14)$$

The present study shows that the correlations derived from the Abraham solvation parameter model describe the transfer of neutral molecules and ions into sulfolane from both water and from the gas phase to within standard deviations of 0.14 log units (neutral molecules) and 0.22 log units (ions), respectively. The derived correlations are expected to provide reasonable predictions of log P and log K for those solute molecules and ions for which Abraham solute descriptors are known, provided that the molecule's (or ion's) solute descriptors fall within the range of values used in deriving Eqns. 8, 9 and 14.

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Table 1. Solute Descriptors and Experimental log P and log K Data for Solutes Dissolved in Sulfolane at 298 K

Solute	E	S	A	B	L	V	log K_{obs}	Log P_{obs}	Ref
Carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.2809	0.474	0.554	32, 33
Nitrous Oxide	0.068	0.350	0.000	0.100	0.164	0.2810	0.346	0.576	32
Sulfur dioxide	0.370	0.660	0.280	0.100	0.778	0.3465	2.401	0.871	34
Hydrogen sulfide	0.350	0.310	0.100	0.070	0.723	0.2721	1.173	0.773	33
Ethane	0.000	0.000	0.000	0.000	0.492	0.3904	-0.248	1.092	35
Butane	0.000	0.000	0.000	0.000	1.615	0.6722	0.590	2.110	30
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	1.020	2.720	25
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	1.414	3.234	25
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	1.817	3.777	25, 27
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	2.000	4.110	27
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	2.340	4.490	27
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	2.713	5.051	27
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358	1.706	3.826	28
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	1.805	2.705	25
Cycloheptane	0.350	0.100	0.000	0.000	3.704	0.9863	2.302	2.882	26
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	2.796	3.426	26
Methylcyclopentane	0.225	0.100	0.000	0.000	2.907	0.8454	1.618	2.788	28
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	1.977	3.227	25
1-Butene	0.100	0.080	0.000	0.070	1.529	0.6292	0.903	1.913	29
Isobutene	0.120	0.080	0.000	0.080	1.579	0.6292	0.930	1.790	29
trans-2-Butene	0.126	0.080	0.000	0.050	1.664	0.6292	0.993	1.973	29
cis-2-butene	0.142	0.080	0.000	0.050	1.737	0.6292	1.085	2.075	29
1,3-Butadiene	0.320	0.230	0.000	0.100	1.543	0.5862	1.324	1.774	29
1-Hexene	0.078	0.080	0.000	0.070	2.572	0.9110	1.527	2.687	26
1-Heptene	0.092	0.080	0.000	0.070	3.063	1.0520	1.899	3.119	26
1-Octene	0.094	0.080	0.000	0.070	3.568	1.1930	2.251	3.661	26
Cyclohexene	0.395	0.280	0.000	0.090	2.952	0.8024	2.201	2.471	25

1-Hexyne	0.166	0.220	0.100	0.120	2.510	0.8680	2.402	2.612	26
1-Heptyne	0.160	0.230	0.090	0.100	3.000	1.0090	2.867	3.307	26
1-Octyne	0.155	0.220	0.090	0.100	3.521	1.1500	3.089	3.609	26
Dichloromethane	0.387	0.570	0.100	0.050	2.019	0.4943	2.703	1.743	25
Chloroform	0.425	0.490	0.150	0.020	2.480	0.6167	3.035	2.245	25
Carbon tetrachloride	0.458	0.380	0.000	0.000	2.823	0.7391	2.569	2.759	25
Chloroethane	0.227	0.400	0.000	0.100	1.678	0.5128	1.789	1.329	30
1,2-Dichloroethane	0.416	0.640	0.100	0.110	2.573	0.6352	3.346	2.076	25
Trichloroethene	0.520	0.370	0.080	0.030	2.997	0.7146	2.901	2.581	25
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	3.307	0.457	25
Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	1.740	0.570	25
Diisopropyl ether	-0.060	0.160	0.000	0.580	2.530	1.0127	1.946	0.896	25
Methyl *tert*-butyl ether	0.024	0.210	0.000	0.590	2.380	0.8718	2.025	0.405	25
Ethyl tert-butyl ether	0.000	0.160	0.000	0.570	2.652	1.0127	2.077	0.897	25
Methyl *tert*-amyl ether	0.050	0.250	0.000	0.540	2.799	1.0127	2.422	1.112	25
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	2.710	0.160	25
Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	3.444	-0.266	25
Methyl formate	0.192	0.680	0.000	0.380	1.285	0.4648	2.366	0.326	25
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	2.668	0.368	25
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	2.871	0.711	25
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	3.173	1.123	25
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	3.533	1.593	25
Acetaldehyde	0.208	0.670	0.000	0.450	1.230	0.4061	2.143	-0.427	25
Isobutyraldehyde	0.144	0.62	0.00	0.45	2.120	0.6879	2.670	0.570	25
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	2.712	-0.078	25
Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	3.031	0.311	25
4-Methyl-2-pentanone	0.111	0.650	0.000	0.510	3.089	0.9697	3.421	1.181	25
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	2.803	-0.937	25
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	2.975	-0.695	25
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7309	3.707	0.247	25

2-Propanol	0.212	0.360	0.330	0.560	1.764	0.5900	2.964	-0.516	25
2-Methyl-1-propanol	0.217	0.390	0.370	0.480	2.413	0.7309	3.576	0.276	25
Allyl alcohol	0.342	0.46	0.38	0.48	1.951	0.5470	3.698	0.008	25
Nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237	3.870	0.920	31
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	2.936	2.306	25, 27
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	3.273	2.623	25, 27
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	3.570	2.990	25, 27
o-Xylene	0.663	0.560	0.000	0.160	3.939	0.9980	3.738	3.078	27
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9980	3.564	2.954	27
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9980	3.523	2.933	27
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	3.768	2.948	25
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	3.830	0.390	25
Benzoic acid	0.730	0.900	0.590	0.400	4.657	0.9317	6.991	1.891	39
2-Methylbenzoic acid	0.730	0.840	0.420	0.440	4.677	1.0726	6.514	2.214	39
3-Methylbenzoic acid	0.730	0.890	0.600	0.400	4.819	1.0726	7.240	2.260	39
2-Chlorobenzoic acid	0.840	1.010	0.680	0.400	4.840	1.0541	7.692	2.192	39
4-Chlorobenzoic acid	0.840	1.020	0.630	0.270	4.947	1.0540	7.488	2.688	39
2-Nitrobenozic acid	0.990	1.480	0.820	0.530	5.900	1.1059	9.751	1.661	39
4-Nitrobenzoic acid	0.990	1.520	0.680	0.400	5.770	1.1059	9.636	2.736	39
4-Aminobenzoic acid	1.075	1.650	0.940	0.600	5.916	1.0315	10.953	1.523	39

Table 2. Descriptors for ions[a], and calculated and observed log P values.

Ion	E	S	A	B	V	J$^+$	J$^-$	Log P	
								Calc	Obs
Na+	-0.02	2.31	1.22	0.00	0.0330	0.316	0.000	0.72	0.51
K+	0.00	2.56	1.21	0.00	0.0920	0.358	0.000	1.02	0.73
Rb+	0.02	2.55	1.05	0.00	0.1300	0.477	0.000	1.05	1.54
Cs+	0.10	2.60	1.17	0.00	0.1770	0.438	0.000	1.25	1.76
Ph$_4$As+	2.22	3.15	0.07	0.88	2.8110	0.630	0.000	6.69	6.23
Cl-	0.10	3.52	0.00	2.32	0.2280	0.000	2.363	-9.53	-9.24
Br-	0.17	2.74	0.00	1.82	0.3070	0.000	1.567	-6.83	-6.96
I-	0.38	3.52	0.00	1.33	0.4080	0.000	1.231	-3.51	-3.59
N$_3$-	0.16	3.04	0.00	1.82	0.2820	0.000	1.718	-6.85	-6.96
Ph$_4$B-	1.95	2.72	0.18	1.15	2.7000	0.000	-0.188	5.67	6.23
Benzoate	0.88	3.64	0.00	2.88	0.9102	0.000	2.395	-9.67	-8.83[b]
3-Methylbenzoate	0.88	3.25	0.00	2.85	1.0511	0.000	2.228	-9.17	-9.10
4-Methylbenzoate	0.88	3.10	0.00	2.88	1.0511	0.000	2.167	-9.35	-9.37
4-tert-Butylbenzoate	0.88	3.16	0.00	2.88	1.4738	0.000	2.229	-7.97	-8.04
3-CF$_3$-benzoate	0.45	2.99	0.00	2.52	1.1042	0.000	2.119	-7.63	-7.69
3-Cyanobenzoate	1.01	3.70	0.00	2.82	1.0649	0.000	2.192	-8.67	-8.74
4-Cyanobenzoate	1.01	3.96	0.00	2.78	1.0649	0.000	2.248	-8.38	-8.49
3-Acetylbenzoate	1.09	3.66	0.00	3.04	1.2077	0.000	2.201	-9.22	-9.25
4-Acetylbenzoate	1.09	3.99	0.00	3.02	1.2077	0.000	2.280	-9.00	-9.14
Terephthalic acid [c]	1.25	3.90	0.41	2.92	1.1255	0.000	2.323	-9.01	-9.01
4-Aminobenzoate	1.23	4.07	0.25	3.26	1.0100	0.000	2.357	-10.81	-10.60
3-HO-benzoate	1.06	3.65	0.13	3.07	0.9689	0.000	2.344	-10.31	-10.81
4-HO-benzoate	1.08	3.78	0.04	3.05	0.9689	0.000	2.382	-10.14	-10.44
3-MeO-benzoate	0.98	3.32	0.00	3.00	1.1098	0.000	2.254	-9.63	-9.44
3-PhO-benzoate	1.54	3.54	0.00	2.78	1.5767	0.000	2.088	-6.74	-6.70
4-PhO-benzoate	1.54	3.91	0.00	2.61	1.5767	0.000	2.108	-5.77	-5.80
3-SH-benzoate	1.37	3.36	0.01	2.77	1.0737	0.000	2.227	-8.60	-8.46
4-SH-benzoate	1.37	3.44	0.00	2.85	1.0737	0.000	2.191	-8.88	-8.79
4-SMe-benzoate	1.33	3.37	0.00	2.90	1.1946	0.000	2.215	-8.78	-8.84
3-SO$_2$Me-benzoate	1.21	4.00	0.00	3.23	1.3320	0.000	2.121	-9.39	-9.38
4-SO$_2$Me-benzoate	1.21	4.15	0.00	3.26	1.3320	0.000	2.188	-9.49	-9.53
3-SO$_2$NH$_2$-benzoate	1.50	3.99	0.04	3.39	1.2909	0.000	2.205	-10.30	-10.14
4-SO$_2$NH$_2$-benzoate	1.50	3.65	0.15	3.38	1.2909	0.000	2.102	-10.41	-10.19
3-Fluorobenzoate	0.95	2.96	0.00	2.73	0.9279	0.000	2.175	-9.16	-9.06
4-Fluorobenzoate	0.95	2.82	0.00	2.82	0.9275	0.000	2.174	-9.65	-9.58
3-Chlorobenzoate	0.99	3.13	0.00	2.57	1.0326	0.000	2.034	-7.87	-8.16

4-Chlorobenzoate	0.99	3.37	0.00	2.60	1.0326	0.000	2.179	-7.97	-8.03
3-Bromobenzoate	1.15	3.47	0.00	2.56	1.0852	0.000	2.197	-7.55	-7.53
4-Bromobenzoate	1.15	3.25	0.00	2.60	1.0852	0.000	2.148	-7.82	-7.67
3-Iodobenzoate	1.46	3.31	0.00	2.57	1.1684	0.000	2.082	-7.28	-7.07
4-Iodobenzoate	1.46	3.29	0.00	2.61	1.1684	0.000	2.059	-7.45	-7.42
3-Nitrobenzoate	1.14	3.60	0.00	2.79	1.0844	0.000	2.217	-8.53	-8.47
4-Nitrobenzoate	1.14	3.50	0.00	2.79	1.0844	0.000	2.212	-8.59	-7.79 [b]

[a] Solute descriptors for the ions were taken from Abraham and Acree [20]. [b]Not used. [c] Mono-anion.

Figure 1

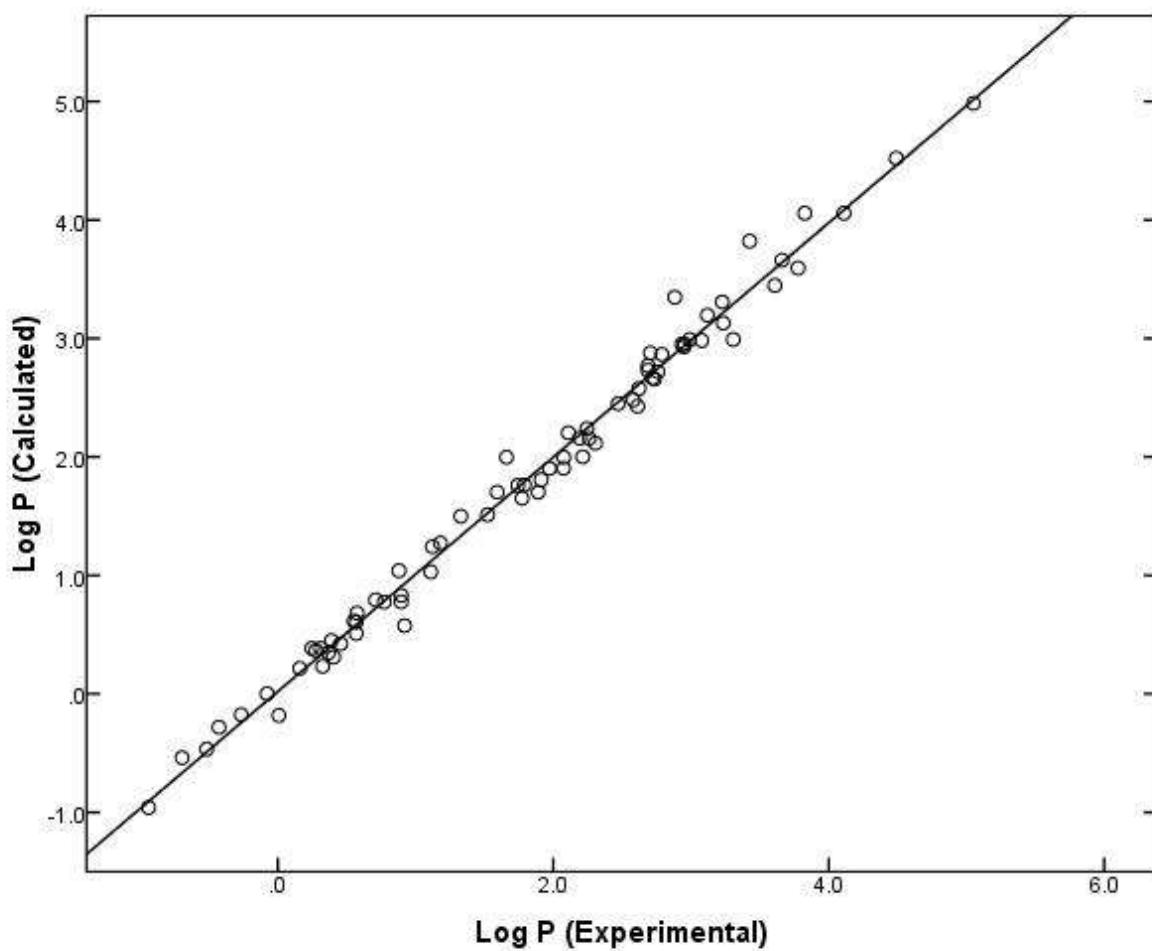

Figure 1. Comparison of the experimental log *P* data for solutes dissolved in sulfolane against
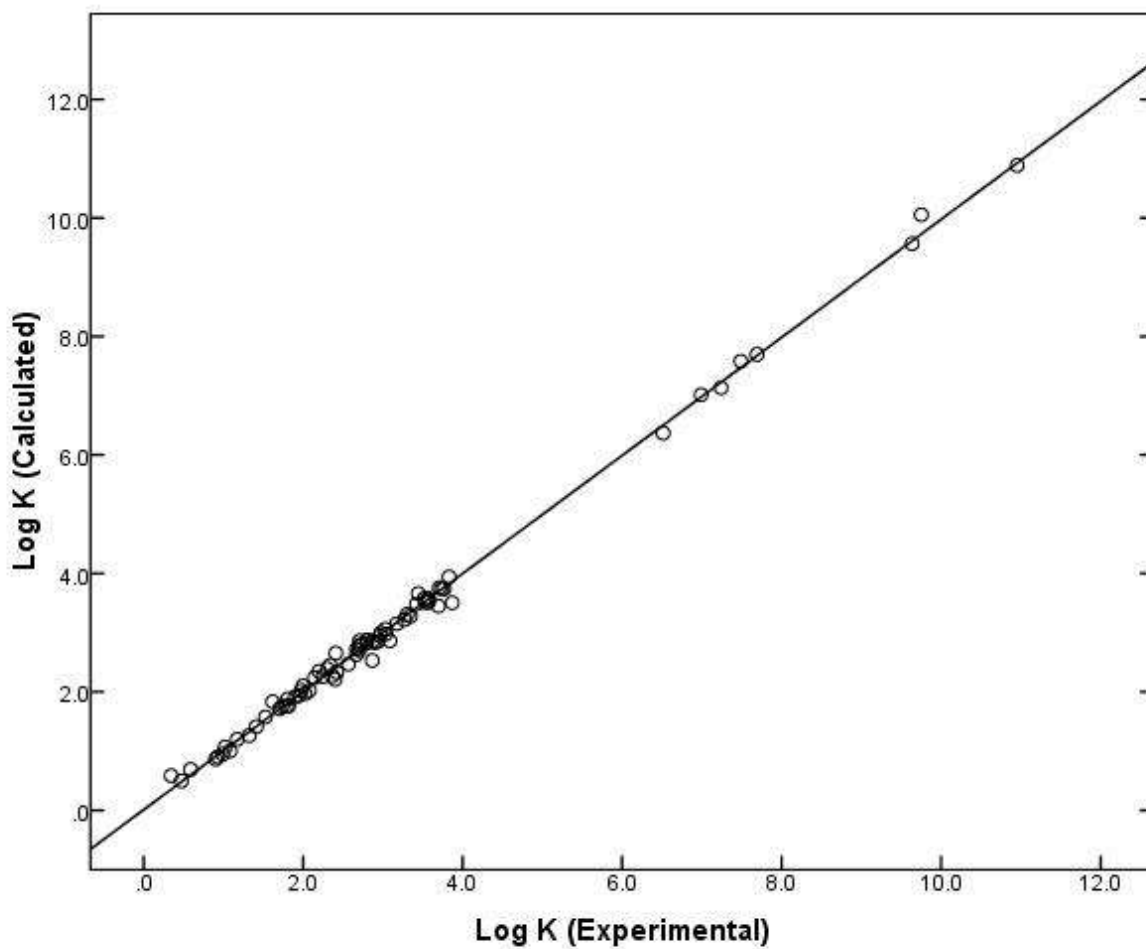
calculated values based on Eqn. 8.

Figure 2

Figure 2. Comparison of the experimental log *K* data for solutes dissolved in sulfolane against calculated values based on Eqn. 9.