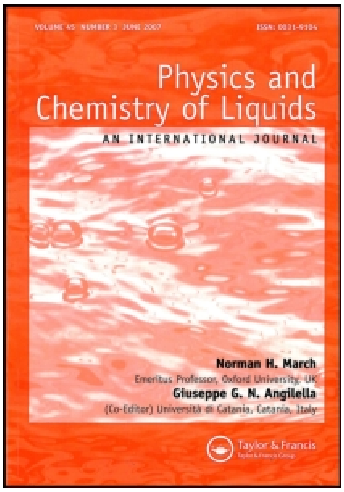

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Characterisation of room temperature ionic liquid chromatographic stationary phases by combining experimental retention factor and partition coefficient data into a single model

Laura M. Sprunger[a], Jennifer Gibbs[a], Quinner Q. Baltazar[b], William E. Acree Jr.[a]*, Michael H. Abraham[c] and Jared L. Anderson[b]

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Experimental gas-to-liquid partition coefficients, *K*, and chromatographic retention factors, *k*, have been compiled from the published literature for gases and organic solutes in 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl) imide. In total, 102 experimental values were collected. It is shown that an Abraham solvation equation with five solute descriptors and one experimental data-type indicator can be used to correlate the combined $\log K$ and $\log k$ values. The derived correlation described the experimental data two within 0.1 log units. Training and test set analyses were used to validate the derived correlation model.

Keywords: room temperature ionic liquids; retention factors; gas-to-liquid partition coefficients; solvation parameter model

1. Introduction

Room temperature ionic liquids (RTILs) have generated considerable interest recently because of their unique physical and chemical properties, high-thermal stability, negligible vapour pressure and high-solvent capacity. New generation RTILs have increasingly become a solvent choice for applications involving organic synthesis and electrochemistry, extraction and chromatographic separations, and gas absorption. The main advantage that ionic liquids offer over the more conventional organic solvents is that it is possible to modify the physical and chemical properties of RTILs simply by changing the cation and anion combination. Ionic liquids are often referred to as *designer solvents* in published chemical literature. While our understanding of the properties of ionic liquids has improved considerably in recent years, we are not yet to the point of being able to 'tailor make' ionic liquids having specific physical and chemical properties.

The present study continues our characterisation of the solubilising properties of RTILs. Previously, we have reported linear free energy relationship (LFER) correlations

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based on the Abraham solvation parameter model for gas chromatographic retention factors, k, [1–3]

$$\log k = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + l \cdot L, \tag{1}$$

for the gas-to-solvent partition coefficients, K, for gases and organic vapours dissolved in RTILs [3–8]

$$\log K = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + l \cdot L, \tag{2}$$

and for the partitioning of solutes between water and an RTIL, P, [3–9]

$$\log P = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + v \cdot V. \tag{3}$$

The independent variables, or descriptors, are solute properties as follows: E and S refer to the excess molar refraction and dipolarity/polarisability descriptors of the solute, respectively, A and B are measures of the solute hydrogen-bond acidity and basicity, V is the McGowan volume of the solute and L is the logarithm of the solute gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The first four descriptors can be regarded as measures of the tendency of the given solute to undergo various solute–solvent interactions. The latter two descriptors, V and L, are both measures of solute size, and so will be measures of the solvent cavity term that will accommodate the dissolved solute. General dispersion interactions are also related to solute size, hence, both V and L will also describe the general solute–solvent interactions.

The usefulness of Equations (1)–(3) in the characterisation of solvent phases is that the coefficients e, s, a, b, l and v are not just curve fitting constants, but rather reflect particular solute–solvent interactions that correspond to chemical properties of the solvent phase. The excess molar refraction, E, is derived from the solute refractive index, and hence the e coefficient gives a measure of general solute–solvent dispersion interactions. The V and L descriptors were set up as measures of the endoergic effect of disrupting solvent–solvent bonds. However, solute volume is always well correlated with polarisability and so the v and l coefficients will include not only an endoergic cavity effect but also exoergic solute–solvent effects that arise through solute polarisability. The S descriptor is a measure of dipolarity and polarisability and hence the s coefficient will reflect the ability of the solvent to undergo dipole and dipole-induced interactions with a solute. The A descriptor is a measure of solute hydrogen bond acidity, and hence the a coefficient will reflect the complementary solvent hydrogen bond basicity. Similarly, the b coefficient will be a measure of the solvent hydrogen bond acidity. This is straightforward for gas-to-solvent partitions because there are no interactions to consider in the gas phase. For partitioning between solvents, the coefficients in Equation (3) then refer to the differences between properties of the two respective immiscible phases.

Our individual research groups have studied more than 30 different neat RTILs, as well as several binary RTIL mixtures. For several RTILs, such as 3-methyl-1-butylimidazolium bis(trifluoromethylsulfonyl)imide ($[\mathrm{MBIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$), we have developed correlation equations for gas chromatographic retention factors

$$\begin{aligned} Log\, k \text{ (at } 40^\circ\text{C)} &= -2.70 + 0.22(0.08)E + 1.89(0.10)S + 2.16(0.11)A \\ &\quad + 0.57(0.13)B + 0.59(0.02)L \\ &\quad (N = 38, \mathrm{SD} = 0.09, R^2 = 0.987 \text{ and } F = 381) \end{aligned} \tag{4}$$

and for partition of solutes to the RTIL from both the water and the gas phases

$$\log K \text{ (at } 25^{\circ}\text{C)} = -0.407(0.024) + 0.040(0.068)E + 2.158(0.089)S + 2.478(0.111)A + 0.665(0.116)B + 0.697(0.007)L \quad (5)$$
$$(N = 59, \mathrm{SD} = 0.068, R^2 = 0.997 \text{ and } F = 3772.3)$$

$$\log P \text{ (at } 25^{\circ}C) = 0.041(0.042) + 0.088(0.098)E + 0.381(0.129)S - 1.146(0.159)A - 4.421(0.165)B + 3.336(0.037)V \quad (6)$$
$$(N = 61, \mathrm{SD} = 0.095, R^2 = 0.997 \text{ and } F = 3935.6),$$

where N is the number of data points, SD denotes the standard deviation, R^2 gives the squared correlation coefficient and F denotes the Fisher F-statistic. The statistics of Equations (4)–(6) are quite good and the derived expressions allow one to predict retention factors and partition coefficients for additional solutes into ($[\mathrm{MBIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$). For any fully characterised system/process (those with calculated values for the equation coefficients), further values of $\log \mathrm{k}$, $\log K$ and $\log P$ can be estimated for solutes with known values for the solute descriptors.

Retention factors and gas-to-liquid partition coefficients are thermodynamically interrelated; however, no attempt has been made to combine experimental $\log k$ and $\log K$ data for a RTIL into a single correlation. In the present communication, we show how the $\log k$ and $\log K$ data can be combined into a single correlation model through the use of an experimental data-type indicator variable. Our proposed methodology provides a means to increase the number of experimental data points available for regression analyses. Determination of a meaningful Abraham model correlation requires experimental data for 40 or more compounds spanning a large range of solute descriptor numerical values, and it is difficult for us to find sufficient gas-to-liquid partition coefficients for many of the newly synthesised RTIL solvents. The combined $\log k$ and $\log K$ datasets contain a more diverse set of compounds, and include both gas solutes (e.g. H_2, CO, CO_2 and N_2O) and organic vapours (hydrocarbons, aromatic compounds, ketones, alcohols, esters and alkanoic acids). Gases and alkane solutes were absent in the $\log k$ dataset, and the $\log K$ dataset had no alkanoic acids or polar aromatic solutes. Predictive equations derived from the combined datasets should provide better predictions for a much wider range of chemical solutes than our existing $\log k$ and $\log K$ equations.

2. Datasets and computation methodology

The majority of the experimental gas-to-($[\mathrm{MBIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$) partition coefficient values, K, came from tabulations given in earlier papers [5, 7]. The experimental $\log K$ values were calculated from published experimental infinite dilution activity coefficients, $\gamma^{\infty}_{\mathrm{solute}}$, or Henry's law constants, K_{Henry}, through Equations (7) and (8).

$$\log K = \log\left(\frac{RT}{\gamma^{\infty}_{\mathrm{solute}} P^{0}_{\mathrm{solute}} V_{\mathrm{solvent}}}\right) \quad (7)$$

$$\log K = \log\left(\frac{RT}{K_{\mathrm{Henry}} V_{\mathrm{solvent}}}\right), \quad (8)$$

where R is the universal gas constant, T is the system temperature, $P^{\circ}_{\text{solute}}$ is the vapour pressure of the solute at T and V_{solvent} is the molar volume of the RTIL solvent. One additional experimental value for hydrogen sulfide, $\log K = 1.119$, has been added to the dataset based on the recent solubility measurements of O'Mahony *et al.* [10]. For convenience we give in Table 1 the $\log K$ values, as well as the solute descriptors of the listed compounds.

Experimental gas chromatographic retention factors were from an earlier study [3] that explored the feasibility of using binary ionic liquid mixtures as chromatographic stationary phases for improving the separation selectivity of alcohols and aromatic compounds. The earlier chromatographic were performed at slightly higher temperatures of 40°C, 70°C and 100°C. Numerical values at 25°C were obtained through a linear $\log K$ versus $1/T$ (with T in Kelvin) plot of the measured $\log k$ data at 40°C and 70°C. The calculated $\log k$ values at 25°C, along with the solute descriptors of the compounds, are tabulated in Table 2. The solute descriptors in Tables 1 and 2 are of experimental origin, and were taken from the Abraham database. The numerical values were obtained from gas–liquid chromatographic measurements and water-to-solvent partition measurements as described in detail elsewhere [11].

3. Results and discussion

We have assembled in Tables 1 and 2 experimental gas-to-liquid partition coefficient data for 64 compounds and chromatographic retention factors for 38 compounds, respectively. The experimental $\log K$ and $\log k$ values can be regressed separately as was done in deriving Equations (4) and (5). Alternatively, the two datasets can be combined into a single regression analyses

$$\begin{aligned}\text{Log }(K \text{ and } k, \text{at } 25^{\circ}C) = {} & -0.366(0.029) + 0.148(0.067)E + 1.946(0.085)S \\ & + 2.261(0.098)A + 0.872(0.107)B + 0.688(0.008)L \\ & - 2.495(0.028)I_{\text{RF}} \\ & (N = 102, \text{SD} = 0.102, R^2 = 0.994 \text{ and } F = 2446.8),\end{aligned} \tag{9}$$

by introducing a single experimental data-type indicator (denoted as I_{RF} in Equation (9)). The indicator variable is assigned a numerical value of zero, $I_{\text{RF}} = 0$ for the $\log K$ data, and a numerical value of $I_{\text{RF}} = 1$ for the gas chromatographic retention factor data. There is thermodynamic justification for the indicator variable. The gas-to-liquid partition coefficient can be obtained from isothermal chromatographic measurements through $K = V_{\text{N}}/V_{\text{L}}$, where V_{N} is the volume of gas required to elute a solute and V_{L} is the volume of liquid present as the stationary phase. The retention factor, k, is given by [3] $k = (t_{\text{r}}–t_{\text{m}})/t_{\text{m}}$, where t_{r} is the retention time of a solute and t_{m} is the 'void' retention time. Since $t_{\text{r}}–t_{\text{m}}$, the corrected retention time, is proportional to V_{N}, the corrected elution volume, it follows that gas-to-liquid partition coefficients and retention factors are interrelated

$$K = P' \cdot k \text{ or } \log K = \log P' + \log k. \tag{10}$$

That is, a regression of $\log K$ or of $\log k$ against the same set of independent variables should lead to exactly the same regression coefficients, except for the c-constant which will correspond to $\log P'$. To a first approximation, the proportionality constant, P', is the phase ratio and depends only on chromatographic conditions that should remain constant

Table 1. Logarithm of the experimental gas-to-liquid partition coefficient data, $\log K$, for gases and organic vapours dissolved in ([MBIm]$^+$[(Tf)$_2$N]$^-$) at 25°C.

Solute	*E*	*S*	*A*	*B*	*L*	Log *K*
Carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.410
Nitrous oxide	0.068	0.350	0.000	0.100	0.164	0.403
Ethane	0.000	0.000	0.000	0.000	0.492	−0.058
Propane	0.000	0.000	0.000	0.000	1.050	0.292
Butane	0.000	0.000	0.000	0.000	1.615	0.691
Pentane	0.000	0.000	0.000	0.000	2.162	1.090
Hexane	0.000	0.000	0.000	0.000	2.668	1.435
Heptane	0.000	0.000	0.000	0.000	3.130	1.785
Octane	0.000	0.000	0.000	0.000	3.677	2.128
Nonane	0.000	0.000	0.000	0.000	4.182	2.470
Decane	0.000	0.000	0.000	0.000	4.686	2.862
Undecane	0.000	0.000	0.000	0.000	5.191	3.218
Dodecane	0.000	0.000	0.000	0.000	5.696	3.573
Cyclopentane	0.263	0.100	0.000	0.000	2.477	1.517
Cyclohexane	0.305	0.100	0.000	0.000	2.964	1.845
Cyclopentene	0.335	0.200	0.000	0.070	2.402	1.678
Cyclohexene	0.395	0.200	0.000	0.070	3.021	2.130
1,3-Cyclohexadiene	0.515	0.300	0.000	0.070	2.917	2.398
Ethene	0.107	0.100	0.000	0.070	0.289	0.084
Propene	0.103	0.080	0.000	0.070	0.946	0.581
1-Butene	0.100	0.080	0.000	0.070	1.529	0.925
1-Pentene	0.093	0.080	0.000	0.070	2.047	1.300
1-Hexene	0.078	0.080	0.000	0.070	2.572	1.652
1-Heptene	0.092	0.080	0.000	0.070	3.063	1.996
1-Octene	0.094	0.080	0.000	0.070	3.568	2.337
1-Nonene	0.090	0.080	0.000	0.070	4.073	2.680
1-Decene	0.093	0.080	0.000	0.070	4.554	3.038
1-Undecene	0.091	0.080	0.000	0.070	5.023	3.398
1-Dodecene	0.089	0.080	0.000	0.070	5.515	3.639
Benzene	0.610	0.520	0.000	0.140	2.786	2.883
Toluene	0.601	0.520	0.000	0.140	3.325	3.203
Ethylbenzene	0.613	0.510	0.000	0.150	3.788	3.474
Propylbenzene	0.604	0.500	0.000	0.150	4.230	3.754
Butylbenzene	0.600	0.510	0.000	0.150	4.730	4.099
Pentylbenzene	0.594	0.510	0.000	0.150	5.230	4.466
Methanol	0.278	0.440	0.430	0.470	0.970	2.589
Ethanol	0.246	0.420	0.370	0.480	1.485	2.756
1-Propanol	0.236	0.420	0.370	0.480	2.031	3.052
1-Butanol	0.224	0.420	0.370	0.480	2.601	3.507
1-Pentanol	0.219	0.420	0.370	0.480	3.106	3.910
1-Hexanol	0.210	0.420	0.370	0.480	3.610	4.306
1-Heptanol	0.210	0.420	0.370	0.480	4.115	4.764
2-Propanol	0.212	0.360	0.330	0.560	1.764	2.831
2-Methyl-1-propanol	0.217	0.390	0.370	0.480	2.413	3.324
tert-Butanol	0.180	0.300	0.310	0.600	1.963	2.902
2-Butanol	0.217	0.360	0.330	0.560	2.338	3.150
2-Methyl-2-butanol	0.194	0.300	0.310	0.600	2.630	3.286
Cyclohexanol	0.460	0.540	0.320	0.570	3.758	4.462
Propanal	0.196	0.650	0.000	0.450	1.815	2.602
Butanal	0.187	0.650	0.000	0.450	2.270	2.922

(*continued*)

Table 1. Continued.

Solute	E	S	A	B	L	Log K
Pentanal	0.163	0.650	0.000	0.450	2.770	3.101
Hexanal	0.146	0.650	0.000	0.450	3.370	3.651
Heptanal	0.140	0.650	0.000	0.450	3.860	4.028
Octanal	0.160	0.650	0.000	0.450	4.380	4.350
Acetonitrile	0.237	0.900	0.070	0.320	1.739	3.164
Acetone	0.179	0.700	0.040	0.490	1.696	2.873
Methyl propanoate	0.128	0.600	0.000	0.450	2.431	2.969
Methyl butanoate	0.106	0.600	0.000	0.450	2.943	3.271
Methyl pentanoate	0.108	0.600	0.000	0.450	3.442	3.598
Methyl hexanoate	0.080	0.600	0.000	0.450	3.874	3.865
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	3.506
Carbon monoxide	0.000	0.000	0.000	0.040	−0.836	−1.048
Hydrogen	0.000	0.000	0.000	0.000	−1.200	−1.211
Hydrogen sulfide	0.350	0.310	0.100	0.070	0.723	1.119

Table 2. Logarithm of the gas chromatographic retention factor data, log k, for organic solutes dissolved in ($[MBIm]^+[(Tf)_2N]^-$) at 25°C.

Solute	E	S	A	B	L	Log k
Acetic acid	0.265	0.640	0.620	0.440	1.816	1.402
Acetophenone	0.818	1.010	0.000	0.480	4.501	2.889
Aniline	0.955	0.960	0.260	0.410	3.934	3.076
Benzaldehyde	0.820	1.000	0.000	0.390	4.008	2.316
Benzene	0.610	0.520	0.000	0.140	2.786	0.425
Benzonitrile	0.742	1.110	0.000	0.330	4.039	2.511
Benzyl alcohol	0.803	0.870	0.330	0.560	4.221	3.252
1-Bromooctane	0.339	0.400	0.000	0.120	5.143	1.559
1-Butanol	0.224	0.420	0.370	0.480	2.601	0.966
Butanal	0.187	0.650	0.000	0.450	2.270	0.490
2-Chloroaniline	1.050	1.100	0.300	0.360	4.674	3.236
1-Chlorohexane	0.201	0.400	0.000	0.100	3.777	0.653
1-Chlorooctane	0.191	0.400	0.000	0.100	4.772	1.256
Cyclohexanone	0.403	0.860	0.000	0.560	3.792	1.870
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	4.518	1.708
N,*N*-Dimethylformamide	0.367	1.310	0.000	0.740	3.173	2.357
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	1.052
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.504
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.968
Methyl hexanoate	0.080	0.600	0.000	0.450	3.874	1.391
Naphthalene	1.340	0.920	0.000	0.200	5.161	2.907
Nitrobenzene	0.871	1.110	0.000	0.280	4.557	2.629
1-Nitropropane	0.242	0.950	0.000	0.310	2.894	1.309
1-Octanol	0.199	0.420	0.370	0.480	4.619	2.208
Octanal	0.160	0.650	0.000	0.450	4.361	1.777
1-Pentanol	0.219	0.420	0.370	0.480	3.106	1.237
2-Pentanone	0.143	0.680	0.000	0.510	2.755	0.951
Phenetole	0.681	0.700	0.000	0.320	4.242	1.830
Propionitrile	0.162	0.900	0.020	0.360	2.082	0.885
Pyridine	0.631	0.840	0.000	0.520	3.022	1.149
Pyrrole	0.613	0.730	0.410	0.290	2.865	1.898
Toluene	0.601	0.520	0.000	0.140	3.325	0.753

(*continued*)

Table 2. Continued.

Solute	E	S	A	B	L	Log k
m-Xylene	0.623	0.520	0.000	0.160	3.839	1.113
o-Xylene	0.663	0.560	0.000	0.160	3.939	1.235
p-Xylene	0.613	0.520	0.000	0.160	3.839	1.100
2-Propanol	0.212	0.360	0.330	0.560	1.764	0.422
1-Bromohexane	0.349	0.400	0.000	0.120	4.130	0.975
1-Decanol	0.191	0.420	0.370	0.480	5.610	3.142

for a given column during the time the experimental measurements are performed. The numerical value of −2.495 in Equation (9) corresponds to the negative logarithm of this proportionality constant, that is, to $\log P'$ in Equation (10). The proportionality constant can be evaluated directly in which both $\log K$ and $\log k$ values have been measured for 10 organic solutes: benzene $(-\log P' = -2.458)$; 1-butanol $(-\log P = -2.541)$; butanal $(-\log P' = -2.432)$; 1,4-dioxane $(-\log P' = -2.454)$; ethylbenzene $(-\log P' = -2.506)$; methyl hexanoate $(-\log P' = -2.414)$; octanal $(-\log P' = -2.573)$; 1-pentanol $(-\log P' = -2.673)$; toluene $(-\log P' = -2.450)$; and 2-propanol $(-\log P' = -2.409)$. The average offset in the $\log K$ and $\log k$ values for the 10 compounds is −2.482, which is in excellent agreement with the offset of $I_{\mathrm{RF}} = -2.495$ determined from regression analyses of the 102 $\log K$ and $\log k$ values.

Equation (9) provides a reasonably accurate mathematical description of the observed $\log K$ and $\log k$ data for gases and organic vapours dissolved in ($[\mathrm{MBIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$). See Figure 1 for a graphical comparison between the observed data and back-calculated values based on Equation (9). The experimental data covers a range of about six log units. Careful examination of Equations (4), (5) and (9) show that the equation coefficients of all three mathematical correlations are identical to within the standard errors of the respective calculated values, as required by Equation (10). The standard deviations and squared correlation coefficients are comparable for all three models, indicating that there was no loss in descriptive/predictive ability resulting from combining the two datasets. Equation (9) is based on a dataset having greater chemical diversity and spanning a larger range of solute descriptors. Readers are reminded that in using predictive correlations it is important to stay within the predictive area of chemical space defined by the range of solute descriptors covered. By combining the $\log K$ and k datasets into a single correlation we were able increase the solute descriptor range to: $E = 0.00$ to $E = 1.34$; $S = 0.00$ to $S = 1.31$; $A = 0.00$ to $A = 0.61$; $B = 0.00$ to $B = 0.74$ and $L = -1.21$ to $L = 5.70$.

In order to assess the predictive ability of Equation (9), we divided the 102 data points into a training set and a test set by selecting every other data point in the combined $\log K$ and $\log k$ datasets. The 51 selected data points became the training set and the remaining compounds were served as the test set. Analysis of the experimental data in the training set gave

$$\begin{aligned}\mathrm{Log}\,(K\ \text{and}\ k;\ \text{at}\ 25^\circ C) = {} & -0.361(0.044) + 0.127(0.089)E + 1.951(0.113)S \\ & + 2.271(0.133)A + 0.893(0.138)B + 0.685(0.013)L \\ & - 2.470(0.045)I_{\mathrm{RF}} \\ & (N = 51, \mathrm{SD} = 0.105, R^2 = 0.993 \text{ and } F = 1079.7). \qquad (11)\end{aligned}$$

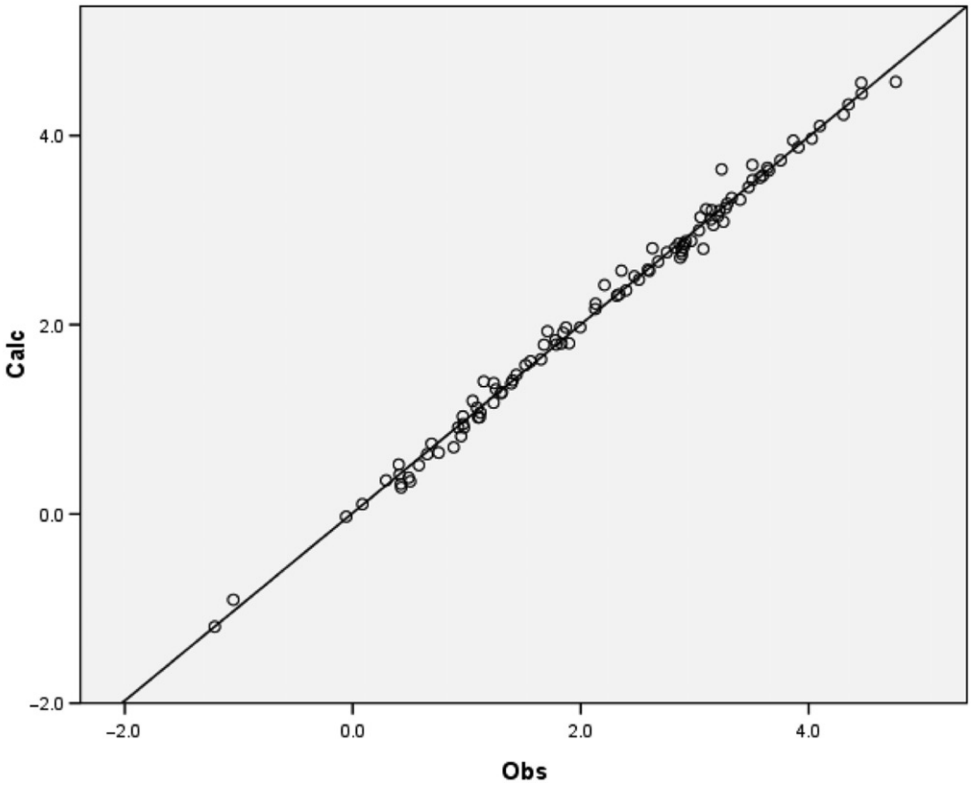

Figure 1. Comparison of measured log K and log k data for solutes dissolved in ($[\mathrm{MBIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$) versus back-calculated values based on Equation (9).

The validation computation gave a training set correlation equation not too different from that obtained from the parent 102 compound database. The training set equation was then used to predict log K and log k values for the 51 compounds in the test set. Comparison of the predicted and observed values gave SD = 0.101, average absolute error (AAE) = 0.075 and average error (AE) = −0.014. There is very little bias in the predictions based on Equation (11) with AE = −0.014.

Retention factors and gas-to-liquid partition coefficients fit the same Abraham model correlation. The log k data can be used as a test set in an external validation of the equation coefficients that we previously reported for the $[\mathrm{MBIm}]^+$ and $[(\mathrm{Tf})_2\mathrm{N}]^-$ ions. Equation (12), developed by Sprunger *et al.* [7]

$$\begin{aligned}\mathrm{Log}\ K = {} & c_{\mathrm{cation}} + c_{\mathrm{anion}} + (e_{\mathrm{cation}} + e_{\mathrm{anion}})E + (s_{\mathrm{cation}} + s_{\mathrm{anion}})S \\ & + (a_{\mathrm{cation}} + a_{\mathrm{anion}})A + (b_{\mathrm{cation}} + b_{\mathrm{anion}})B + (l_{\mathrm{cation}} + l_{\mathrm{anion}})L\end{aligned} \tag{12}$$

expresses the Abraham model equation coefficients as the sum of the respective cation and anion contributions. To date [7, 12] coefficients have been determined for eight cations and six anions. Substitution of the numerical values that have been calculated for the $[\mathrm{MBIm}]^+$ and $[(\mathrm{Tf})_2\mathrm{N}]^-$ ions into Equation (12) gives the following:

$$\mathrm{Log}\ K = -0.422 + 0.133\,E + 2.014\,S + 2.125\,A + 0.954\,B + 0.688\,L, \tag{13}$$

which predicts the $\log K$ values of the 38 compounds in the $\log k$ dataset within $SD = 0.166$, $AAE = 0.163$ and $AE = 0.112$. The standard deviation of Equation (13) for just the $\log K$ data is $SD = 0.133$ log units. There is a slight loss in predictive ability in going from a RTIL-specific correlation model to the form of the Abraham model that employs ion-specific equation coefficients. The slight loss in predictive ability is offset by the ability to make predictions for more RTILs. The experimental $\log k$ data were converted into the respective $\log K$ values by adding 2.482 to each $\log k$ value. The numerical value of 2.482 corresponds to the average difference between $\log K$ and $\log k$ for the 10 common compounds in the retention factor and gas-to-liquid partition coefficient datasets. Predictions based on Equation (13) are very good, given that several compounds in the retention factor database fell outside of the predictive area of chemical space defined by the range of solute descriptors that were used in calculating the ion-specific equation coefficients. The four compounds having the larger deviations between predicted and observed values were aniline, naphthalene, benzyl alcohol and acetophenone. These four compounds had E descriptors, and sometimes S descriptors, that were outside the predictive area of Equation (13). It is possible to expand the predictive area of chemical space by including the chromatographic retention factor data (more specifically the $\log K$ values calculated from the retention factors) in a re-determination of the equation coefficients for the $[MBIm]^+$ and $[(Tf)_2N]^-$ ions. Revision of the $[MBIm]^+$ and $[(Tf)_2N]^-$ equation coefficients will wait until there are sufficient new experimental values to warrant a reanalysis of the equation coefficients that have been determined for the other seven cations and five anions as well.

4. Conclusion

Experimental gas-to-liquid partition coefficients, K, and chromatographic retention factors, k, for gases and organic solutes dissolved in 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide can be combined into a single database, and correlated through the Abraham solvation parameter model. A single experimental-type indicator is added to allow the experimental $\log K$ and $\log k$ data to fit on a single correlation. Our proposed methodology of combining $\log K$ and $\log k$ data into a single correlation model provides a means to increase the number of experimental data points available for regression analyses, and enlarges the predictive area of chemical space defined by the range of solute descriptors covered.

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