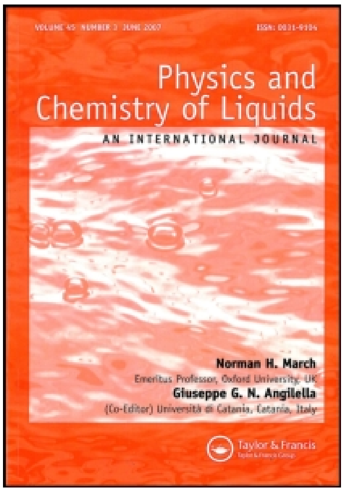

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Linear free energy relationship (LFER) correlations for the solubilising characterisation of room temperature ionic liquids containing triethylsulphonium and 1-butyl-1-methylpyrrolidinium cations

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Gas-to-room temperature ionic liquid (RTIL) partition coefficients have been compiled from the published literature for solutes dissolved in triethylsulphonium *bis*(trifluoromethylsulphonyl)imide, $\{[E_3S]^+[(Tf)_2N]^-\}$, and in 1-butyl-1-methylpyrrolidinium trifluoromethanesulphonate, $\{[BMPyr]^+[Trif]^-\}$. These partition coefficients were converted into water-to-RTIL partition coefficients using the corresponding gas-to-water partition coefficients. Both sets of partition coefficients were analysed using the Abraham model with cation-specific and anion-specific equation coefficients. Equation coefficients are reported for the triethylsulphonium and 1-butyl-1-methylpyrrolidinium cations. The calculated cation coefficients can be combined with our previously determined eight sets of anion-specific equation coefficients to yield expressions capable of predicting the partition coefficients of solutes in 16 different RTILs.

Keywords: activity coefficients; room temperature ionic liquids; partition coefficients; linear free energy relationships

1. Introduction

This study continues our application of the Abraham general solvation model to describe the solubility of organic vapours and gases into room temperature ionic liquids (RTILs). Previous studies [1–5] have examined the feasibility of separating the various solute–RTIL interactions into cation-specific and anion-specific interactions.

$$\log K = c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}}) \cdot \mathbf{E} + (s_{\text{cation}} + s_{\text{anion}}) \cdot \mathbf{S} + (a_{\text{cation}} + a_{\text{anion}}) \cdot \mathbf{A} + (b_{\text{cation}} + b_{\text{anion}}) + (l_{\text{cation}} + l_{\text{anion}}) \cdot \mathbf{L}, \quad (1)$$

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where K is the solute's partition coefficient into the RTIL from the gas phase. The independent variables in Equation (1) are solute descriptors as follows: **E** and **S** refer to the excess molar refraction in units of $(\mathrm{cm}^3\,\mathrm{mol}^{-1})/10$ and dipolarity/polarisability descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and basicity and **L** is the logarithm of the gas-to-hexadecane partition coefficient at 298.15 K. The regression coefficients and constants (i.e. c_{cation}, c_{anion}, e_{cation}, etc.) are determined by regression analyses of the experimental data for a series of organic vapours and gases into a given RTIL. A similar correlation equation has been developed for describing solute partitioning into an RTIL from an aqueous phase, as $\log P$, where P is the water to RTIL partition coefficient.

$$\log P = c_{\mathrm{cation}} + c_{\mathrm{anion}} + (e_{\mathrm{cation}} + e_{\mathrm{anion}}) \cdot \mathbf{E} + (s_{\mathrm{cation}} + s_{\mathrm{anion}}) \cdot \mathbf{S} + (a_{\mathrm{cation}} + a_{\mathrm{anion}}) \cdot \mathbf{A} + (b_{\mathrm{cation}} + b_{\mathrm{anion}}) \cdot \mathbf{B} + (v_{\mathrm{cation}} + v_{\mathrm{anion}}) \cdot \mathbf{V} \tag{2}$$

with the L solute descriptor being replaced by the McGowan volume, V in units of $(\mathrm{cm}^3\,\mathrm{mol}^{-1})/100$. For any fully characterised RTIL (those with calculated values for the c_{cation}, c_{anion}, e_{cation}, etc. equation coefficients) further values of $\log K$ and $\log P$ can be estimated for solutes with known values for the solute descriptors.

To date we have reported Abraham model equation coefficients for 10 cations (4-methyl-*N*-butylpyridinium cation, $[\mathrm{BMPy}]^+$; 1-methyl-3-ethylimidazolium cation, $[\mathrm{MEIm}]^+$; 1,2-dimethyl-3-ethylimidazolium cation, $[\mathrm{M_2EIm}]^+$; 1-methyl-3-butylimidazolium cation, $[\mathrm{MBIm}]^+$; 1-methyl-3-hexylimidazolium cation, $[\mathrm{MHIm}]^+$; trimethylbutylammonium cation, $[\mathrm{M_3BAm}]^+$; 1-methyl-3-octylimidazolium cation, $[\mathrm{MOIm}]^+$; *N*-ethylpyridinium cation, $[\mathrm{NEPy}]^+$; 1-propyl-2,3-dimethyl imidazolium cation, $[\mathrm{PM_2Im}]^+$; and trihexyl(tetradecyl)phosphonium cation, $[\mathrm{H_3TdP}]^+$) and for 8 anions (*bis*(trifluoromethylsulphonyl)imide anion, $[(\mathrm{Tf})_2\mathrm{N}]^-$; tetrafluoroborate anion, $[\mathrm{BF_4}]^-$; hexafluorophosphate anion, $[\mathrm{PF_6}]^-$; ethylsulphate anion, $[\mathrm{EtSO_4}]^-$; the trifluoromethane-sulphonate anion, $[\mathrm{Trif}]^-$; the trifluoroacetate anion, $[\mathrm{F_3Ac}]^-$; octylsulphate anion, $[\mathrm{OtSO_4}]^-$ and thiocyanate anion, $[\mathrm{SCN}]^-$) [1–5]. Our calculated ion-specific equation coefficients were based on 976 $\log K$ and 955 $\log P$ experimental values for solutes dissolved in only 28 RTILs. The major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that one can make predictions for more RTILs. The 10 sets of cation-specific equation coefficients and 8 sets of anion-specific equation coefficients that we have already determined for the Abraham model can be combined to yield predictive $\log K$ and $\log P$ expressions for 80 different RTILs. That is more RTILs than were used in regression analysis when the equation coefficients were determined. Past studies have shown [1,2] that very little loss in predictive ability results from splitting the equation coefficients into separate anion-specific and cation-specific terms.

At the time that we developed Equations (1) and (2) we suggested a computation methodology for calculating additional ion-specific equation coefficients as additional experimental data became available. In the present communication, we report equation coefficients for the triethylsulphonium, $[\mathrm{E_3S}]^+$, and 1-butyl-1-methylpyrrolidinium, $[\mathrm{BMPyr}]^+$, cations based on the recently published infinite dilution activity coefficient data for solutes dissolved in triethylsulphonium *bis*(trifluoromethylsulphonyl)imide, $\{[\mathrm{E_3S}]^+[(\mathrm{Tf})_2\mathrm{N}]^-\}$ [6], and in 1-butyl-1-methylpyrrolidinium trifluoromethanesulphonate, $\{[\mathrm{BMPyr}]^+[\mathrm{Trif}]^-\}$ [7].

2. Database and computation methodology

All the experimental data that we were able to retrieve from the published literature [6,7] for RTILs containing either $[E_3S]^+$ or $[BMPyr]^+$ cations pertained to the infinite dilution activity coefficient, γ^{∞}_{solute}, for solutes dissolved in $\{[E_3S]^+[(Tf)_2N]^-\}$ and $\{[BMPyr]^+[Trif]^-\}$. In order to apply the Abraham model, the infinite dilution activity coefficients needed to be converted to $\log K$ values for gas-to-RTIL partition through Equation (3).

$$\log K = \log\left(\frac{RT}{\gamma^{\infty}_{solute}\ P^{0}_{solute}\ V_{solvent}}\right). \tag{3}$$

Here R is the universal gas constant, T is the system temperature, P^0_{solute} is the vapour pressure of the solute at T and $V_{solvent}$ is the molar volume of the solvent.

Predictive correlations can be developed for water-to-RTIL partition coefficients, $\log P$. In the present case, the values refer to a hypothetic partition in that the RTIL and aqueous phases are not in physical contact with each other. Even so the values are still quite useful. Values of the hypothetical partition coefficients can be used to calculate infinite dilution activity coefficients and the solubilities for solutes dissolved in RTILs. The calculation of $\log P$ values from $\log K$

$$\log P = \log K - \log K_w \tag{4}$$

requires knowledge of the solute's gas phase partition coefficient into water, K_w, which is available for all of the solutes being studied. The experimental values of $\log K$ and $\log P$ for solutes dissolved in $[E_3S]^+[(Tf)_2N]^-$ and $[BMPyr]^+[Trif]^-$ are given in Tables 1 and 2, along with the respective solute descriptors.

3. Results and discussion

In Table 1 we have assembled the $\log P$ and $\log K$ values for 31 solutes dissolved in triethylsulphonium *bis*(trifluoromethylsulphonyl)imide, $\{[E_3S]^+[(Tf)_2N]^-\}$, covering a reasonably wide range of compound type and descriptor values. Analysis of the experimental water-to-RTIL and gas-to-RTIL partition data gave

$$\begin{aligned}\log K = {} & -0.606(0.057) - 0.196(0.142)\cdot\mathbf{E} + 2.992(0.188)\cdot\mathbf{S} + 2.444(0.123)\cdot\mathbf{A}\\ & + 0.355(0.130)\cdot\mathbf{B} + 0.690(0.017)\cdot\mathbf{L}\end{aligned} \tag{5}$$

$$(\text{with } N = 31, \mathrm{SD} = 0.055, R^2 = 0.995, R^2_{adj} = 0.994, F = 1043.5)$$

and

$$\begin{aligned}\log P = {} & -0.062(0.123) - 1.347(0.252)\cdot\mathbf{E} + 2.716(0.332)\cdot\mathbf{S} - 1.550(0.219)\cdot\mathbf{A}\\ & - 5.274(0.236)\cdot\mathbf{B} + 3.242(0.107)\cdot\mathbf{V}\end{aligned} \tag{6}$$

$$(\text{with } N = 31,\ \mathrm{SD} = 0.097,\ R^2 = 0.996,\ R^2_{adj} = 0.995,\ F = 1187.1)$$

where N is the number of data points, that is the number of solutes, R^2 denotes the squared correlation coefficient, R^2_{adj} refers to the adjusted squared correlation coefficient, SD is the standard deviation and F corresponds to the Fisher's F statistic.

Table 1. Logarithms of experimental gas-to-RTIL and water-to-RTIL partition coefficient data for solutes dissolved in triethylsulphonium *bis*(trifluoromethylsulphonyl)imide, $\{[E_3S]^+[(Tf)_2N]^-\}$ at 298.15 K.

Solute	**E**	**S**	**A**	**B**	**L**	**V**	log *K*	log *P*
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	0.789	2.489
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	1.195	3.015
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	1.569	3.529
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	1.912	4.022
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	2.254	4.404
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	2.584	4.844
Cyclopentane	0.263	0.100	0.000	0.000	2.477	0.7045	1.298	2.178
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	1.637	2.537
Cycloheptane	0.350	0.100	0.000	0.000	3.704	0.9863	2.158	2.738
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	2.601	3.231
1-Pentene	0.093	0.080	0.000	0.070	2.047	0.7701	1.084	2.314
1-Hexene	0.078	0.080	0.000	0.070	2.572	0.9110	1.470	2.630
1-Heptene	0.092	0.080	0.000	0.070	3.063	1.0520	1.820	3.040
1-Octene	0.094	0.080	0.000	0.070	3.568	1.1928	2.160	3.570
1-Pentyne	0.172	0.230	0.120	0.120	2.010	0.7271	1.793	1.803
1-Hexyne	0.166	0.230	0.120	0.100	2.510	0.8680	2.140	2.350
1-Heptyne	0.160	0.230	0.120	0.100	3.000	1.0090	2.591	3.031
1-Octyne	0.155	0.230	0.120	0.100	3.521	1.1500	2.828	3.348
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	2.823	2.193
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	3.191	2.541
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	3.468	2.888
σ-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	3.705	3.045
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	3.556	2.946
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	3.541	2.951
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	2.523	−1.217
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	2.727	−0.943
1-Propanol	0.236	0.420	0.370	0.480	2.031	0.5900	3.058	−0.502
1-Butanol	0.224	0.420	0.370	0.480	2.601	0.7309	3.430	−0.030
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6220	2.729	0.179
Thiophene	0.687	0.570	0.000	0.150	2.819	0.6411	2.970	1.930
Methyl tert-butyl ether	0.024	0.210	0.000	0.590	2.380	0.8718	1.970	0.350

The errors in the coefficients are given in parenthesis. The statistics of the derived correlations are quite good given the limited number of data points. Figures 1 and 2 compare the calculated values of log *K* and log *P* based on Equations (5) and (6) against the experimental data.

Each equation coefficient represents the sum of the cation plus anion contribution, i.e. $e_{RTIL} = e_{cation} + e_{anion}$, $s_{RTIL} = s_{cation} + s_{anion}$, etc. In establishing the computation methodology, the equation coefficients for the *bis*(trifluoromethylsulphonyl)imide anion were set equal to zero to provide a convenient reference point from which all other equation coefficients would be calculated. The equation coefficients in Equations (5) and (6) thus correspond to the ion-specific equation coefficients for the triethylsulphonium cation.

Our search of the published chemical and engineering literature also found infinite dilution activity coefficient data for 31 organic solutes dissolved in 1-butyl-1-methylpyrrolidinium trifluoromethanesulphonate, $\{[BMPyr]^+[Trif]^-\}$, covering a reasonably wide range of compound type and descriptor values. The log *P* and log *K*

Table 2. Logarithms of experimental gas-to-RTIL and water-to-RTIL partition coefficient data for solutes dissolved in 1-butyl-1-methylpyrrolidinium trifluoromethanesulphonate, $\{[\mathrm{BMPyr}]^+[\mathrm{Trif}]^-\}$ at 298.15 K.

Solute	**E**	**S**	**A**	**B**	**L**	**V**	log *K*	log *P*
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	0.475	2.175
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	0.973	2.793
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	1.390	3.350
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	1.776	3.886
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	2.133	4.283
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	2.479	4.739
Cyclopentane	0.263	0.100	0.000	0.000	2.477	0.7045	1.117	1.997
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	1.502	2.402
Cycloheptane	0.350	0.100	0.000	0.000	3.704	0.9863	2.096	2.676
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	2.578	3.208
1-Pentene	0.093	0.080	0.000	0.070	2.047	0.7701	0.851	2.081
1-Hexene	0.078	0.080	0.000	0.070	2.572	0.9110	1.300	2.460
1-Heptene	0.092	0.080	0.000	0.070	3.063	1.0520	1.689	2.909
1-Octene	0.094	0.080	0.000	0.070	3.568	1.1928	2.048	3.458
1-Pentyne	0.172	0.230	0.120	0.120	2.010	0.7271	1.850	1.860
1-Hexyne	0.166	0.230	0.120	0.100	2.510	0.8680	2.216	2.426
1-Heptyne	0.160	0.230	0.120	0.100	3.000	1.0090	2.669	3.109
1-Octyne	0.155	0.230	0.120	0.100	3.521	1.1500	2.914	3.434
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	2.776	2.146
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	3.112	2.462
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	3.385	2.805
σ-Xylene	0.663	0.560	0.000	0.160	3.939	0.9982	3.618	2.958
m-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	3.443	2.833
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	3.442	2.852
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	2.945	−0.795
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	3.107	−0.563
1-Propanol	0.236	0.420	0.370	0.480	2.031	0.5900	3.451	−0.109
1-Butanol	0.224	0.420	0.370	0.480	2.601	0.7309	3.821	0.351
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6220	2.554	0.004
Thiophene	0.687	0.570	0.000	0.150	2.819	0.6411	2.996	1.956
Methyl tert-butyl ether	0.024	0.210	0.000	0.590	2.380	0.8718	1.750	0.130

values calculated from the published activity coefficient data (Table 2) were analysed to give

$$\log K = -0.904(0.084) - 0.048(0.210)\cdot\mathbf{E} + 3.016(0.278)\cdot\mathbf{S} + 4.075(0.182)\cdot\mathbf{A} + 0.266(0.192)\cdot\mathbf{B} + 0.732(0.025)\cdot\mathbf{L} \tag{7}$$

$$(\text{with } N = 31,\ \mathrm{SD} = 0.081,\ R^2 = 0.992,\ R^2_{\mathrm{adj}} = 0.990,\ F = 612.6)$$

and

$$\log P = -0.388(0.128) - 1.091(0.262)\cdot\mathbf{E} + 2.691(0.344)\cdot\mathbf{S} + 0.080(0.227)\cdot\mathbf{A} - 5.323(0.245)\cdot\mathbf{B} + 3.386(0.111)\cdot\mathbf{V} \tag{8}$$

$$(\text{with } N = 31,\ \mathrm{SD} = 0.101,\ R^2 = 0.995,\ R^2_{\mathrm{adj}} = 0.994,\ F = 936.5)$$

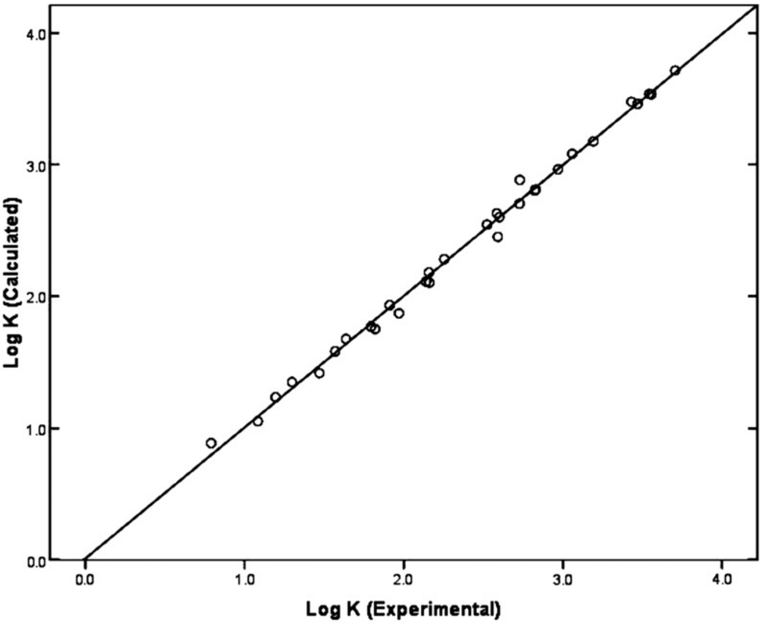

Figure 1. Comparison of experimental log *K* vs. calculated log *K* values based on Equation (5) for solutes dissolved in $\{[E_3S]^+[(Tf)_2N]^-\}$ at 298.15 K.

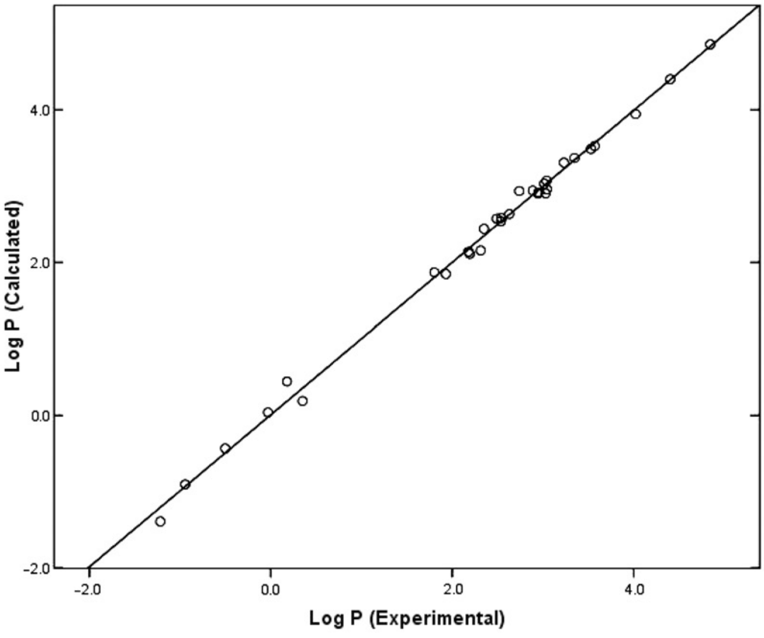

Figure 2. Comparison of experimental log *P* vs. calculated log *P* values based on Equation (6) for solutes dissolved in $\{[E_3S]^+[(Tf)_2N]^-\}$ at 298.15 K.

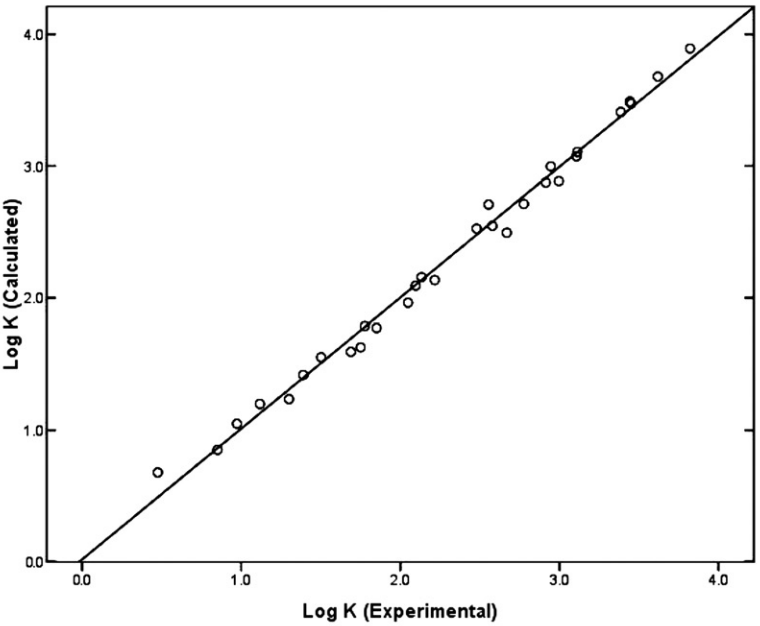

Figure 3. Comparison of experimental log K vs. calculated log K values based on Equation (7) for solutes dissolved in $\{[\mathrm{BMPyr}]^+[\mathrm{Trif}]^-\}$ at 298.15 K.

The statistics of the derived correlations are quite good given the limited number of data points. Figures 3 and 4 compare the calculated values of log K and log P based on Equations (7) and (8) against the experimental data. Using our previously determined values for $[\mathrm{Trif}]^-$, in Table 3 we have calculated and assembled the respective model equation coefficients for the 1-butyl-1-methylpyrrolidinium cation.

The present study increases by two the number of cation-specific equation coefficients for the Abraham model. The 12 sets of cation-specific equation coefficients and 8 sets of anion-specific equation coefficients that we have now determined for both LFER models can be combined to yield predictive log K and log P expressions for 96 different RTILs. The 16 additional RTILs for which partition coefficient predictions are now possible are: triethylsulphonium (*bis*(trifluoromethylsulphonyl)imide; triethylsulphonium tetrafluoroborate; triethylsulphonium hexafluorophosphate; triethylsulphonium ethylsulphate; triethylsulphonium trifluoromethanesulphonate; triethylsulphonium trifluoroacetate; triethylsulphonium octylsulphate; triethylsulphonium thiocyanate; 1-butyl-1-methylpyrrolidinium (*bis*(trifluoromethylsulphonyl)imide; 1-butyl-1-methylpyrrolidinium tetrafluoroborate; 1-butyl-1-methylpyrrolidinium hexafluorophosphate; 1-butyl-1-methylpyrrolidinium ethylsulphate; 1-butyl-1-methylpyrrolidinium trifluoromethanesulphonate; 1-butyl-1-methylpyrrolidinium trifluoroacetate anion; 1-butyl-1-methylpyrrolidinium octylsulphate and 1-butyl-1-methylpyrrolidinium thiocyanate. The anion-specific equation coefficients needed for these predictions are given elsewhere [2–5].

In using these predictive equations, readers are reminded that the predictive area of chemical space is defined by the range of solute descriptors covered. Most of the experimental log K and log P data used in our regression analyses have come from

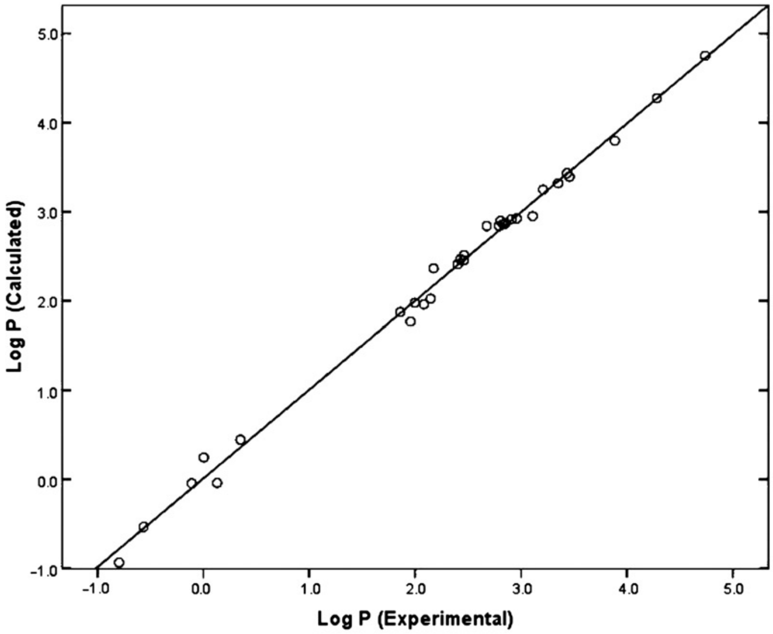

Figure 4. Comparison of experimental log P vs. calculated log P values based on Equation (8) for solutes dissolved in $\{[\mathrm{BMPyr}]^{+}[\mathrm{Trif}]^{-}\}$ at 298.15 K.

Table 3. Compilation of Abraham model equation coefficients for the 1-butyl-1-methylpyrrolidinium cation using experimental data for only $\{[\mathrm{BMPyr}]^{+}[\mathrm{Trif}]^{-}\}$.

	c	e	s	a	b	l	v
Abraham log K model							
RTIL value	−0.904	−0.048	3.016	4.075	0.266	0.732	
$[\mathrm{Trif}]^{-}$ value	−0.283	−0.023	0.391	1.782	−0.446	0.012	
$[\mathrm{BMPyr}]^{+}$ value	−0.621	−0.025	2.625	2.293	0.712	0.720	
Abraham log P model							
RTIL value	−0.388	−1.091	2.691	0.080	−5.323		3.386
$[\mathrm{Trif}]^{-}$ value	−0.178	−0.167	0.412	1.607	−0.362		−0.054
$[\mathrm{BMPyr}]^{+}$ value	−0.210	−0.924	2.279	−1.527	−4.961		3.440

gas solubilities and gas–liquid chromatographic retention measurements. Solutes studied have typically been inert gases, diatomic gas molecules, linear and cyclic alkanes and alkenes (up to dodecane), alkylbenzenes, linear and branched alcohols, linear and cyclic monoethers (plus 1,4-dioxane), chlorinated methanes and a few of the smaller aldehydes and ketones. The solute descriptor space defined by these compounds would be: $\mathbf{E}=0.000$ to $\mathbf{E}=0.850$; $\mathbf{S}=0.000$ to $\mathbf{S}=0.900$; $\mathbf{A}=0.000$ to $\mathbf{A}=0.430$; $\mathbf{B}=0.000$ to $\mathbf{B}=0.650$; $\mathbf{V}=0.109$ to $\mathbf{V}=1.800$; and $\mathbf{L}=-1.200$ to $\mathbf{L}=5.700$. Unfortunately, in the present study we were unable to find experimental data for gaseous solutes like nitrogen gas, oxygen gas and carbon dioxide.

The predictive area of chemical space covered by the $[E_3S]^+$ and $[BMPyr]^+$ equation coefficients is slightly smaller. The smallest solute contained in the two sets is methanol (with $\mathbf{V} = 0.3082$ and $\mathbf{L} = 0.970$). One should be able to make reasonably accurate partition coefficient predictions for most of the solutes having solute descriptors that fall within (or just slightly outside of) the aforementioned ranges.

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