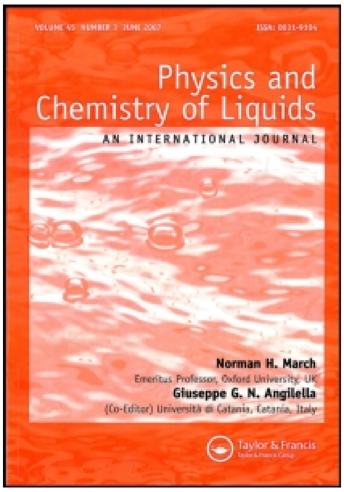

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LFER correlations for the solubilising characterisation of room temperature ionic liquids containing trifluoromethanesulfonate and trifluoroacetate anions

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Gas-to-RTIL (room temperature ionic liquid) partition coefficients have been compiled from the published literature for solutes dissolved in 1-methyl-3-butylimidazolium trifluoromethylsulfonate, $\{[\text{MBIm}]^+[\text{Trif}]^-\}$, and in 1-methyl-3-ethylimidazolium trifluoroacetate, $\{[\text{MEIm}]^+[\text{F}_3\text{Ac}]^-\}$. 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 and Goss modified Abraham models with cation-specific and anion-specific equation coefficients. Equation coefficients are reported for the trifluoromethylsulfonate and trifluoroacetate anions. The calculated anion coefficients can be combined with our previously determined eight sets of cation-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

1. Introduction

Room temperature ionic liquids (RTILs) have received considerable attention in recent years due to their unique physical and chemical properties, and their ability to replace traditional organic solvents in many chemical and manufacturing processes. Physical and chemical properties that make RTILs appealing in commercial manufacturing processes include extremely low vapour pressures, broad liquid temperature ranges and many are non-corrosive and thermally stable even at fairly high temperatures. Immiscibility of ionic liquids with supercritical carbon dioxide, linear hydrocarbons and several acyclic organic solvents makes RTILs ideally suited for synthetic preparations involving biphasic catalysis. Most (if not all) of the classic synthetic methods have been performed in RTILs. Much higher product yields and stereoisomer specificity were reported for RTILs than for the conventional organic solvents.

Currently, synthetic procedures are known for making more than 200 different RTILs. The number continues to increase with the recent preparation of several symmetrical and

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unsymmetrical di-cation ionic liquids [1,2] containing two imidazolium and/or tetra-alkylammonium positively charged moieties. The large number of cation and anion combinations makes it impossible to measure the solubilising properties of every known RTIL, much less than the ones that will be developed in future years. Researchers have thus turned to predictive methods as a means to estimate solubilities and infinite dilution activity coefficients of dissolved organic solutes and gases dissolved in RTILs in the absence of direct experimental values.

The present study continues our characterisation of the solubilising abilities of RTILs. Previously, we have reported linear free energy relationship (LFER) correlations based on the Abraham general solvation parameter model for gas-to-solvent, K, and water-to-solvent partition coefficients, P, for 10 different anhydrous RTILs [3–5] and for two practical water-to-RTIL partition systems [6]. The 10 anhydrous water-to-RTIL correlations describe 'hypothetical' partitions, and the partition coefficient is calculated as the molar solubility ratio for the solute dissolved in both neat solvents. Practical partitions, on the other hand, represent true equilibrium partitioning between the water-saturated organic phase and an aqueous phase that is saturated with the organic solvent. Correlations derived from the Abraham model described the $\log K$ and $\log P$ data for 10 RTILs to within average standard deviations of ±0.086 log units and ±0.129 log units, respectively. The quoted values represent the average value of the standard deviations of the individual $\log K$ and $\log P$ correlations of the 10 RTILs.

In follow-up studies, Sprunger *et al.* [7,8] modified the Abraham solvation parameter model

$$\log P = c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})\mathbf{E} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} \\ + (a_{\text{cation}} + a_{\text{anion}})\mathbf{A} + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (v_{\text{cation}} + v_{\text{anion}})\mathbf{V} \quad (1)$$

$$\log K = c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})\mathbf{E} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} \\ + (a_{\text{cation}} + a_{\text{anion}})\mathbf{A} + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (l_{\text{cation}} + l_{\text{anion}})\mathbf{L} \quad (2)$$

and the Goss modified Abraham model

$$\log P = c_{\text{cation}} + c_{\text{anion}} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} + (a_{\text{cation}} + a_{\text{anion}})\mathbf{A} \\ + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (v_{\text{cation}} + v_{\text{anion}})\mathbf{V} + (l_{\text{cation}} + l_{\text{anion}})\mathbf{L} \quad (3)$$

$$\log K = c_{\text{cation}} + c_{\text{anion}} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} + (a_{\text{cation}} + a_{\text{anion}})\mathbf{A} \\ + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (v_{\text{cation}} + v_{\text{anion}})\mathbf{V} + (l_{\text{cation}} + l_{\text{anion}})\mathbf{L} \quad (4)$$

by rewriting each of the seven solvent equation coefficients as a summation of their respective cation and anion contributions. The independent variables in Equations (1) through (4) are solute descriptors as follows: **E** and **S** refer to the excess molar refraction in units of $(\text{cm}^3\,\text{mol}^{-1})/10$ 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 in units of $(\text{cm}^3\,\text{mol}^{-1})/100$ and **L** is the logarithm of the gas-to-hexadecane partition coefficient at 298 K. As part of the study, the authors calculated equation coefficients for 8 cations and 4 anions using a database that contained 598 experimental $\log K$ and 584 experimental $\log P$ data points. No loss in predictive accuracy was observed by separating the equation coefficients into individual cation-specific and anion-specific values. The calculated coefficients described the 598 experimental $\log K$ and

584 experimental $\log P$ values to within a standard deviation of $\mathrm{SD} = 0.099$ and $\mathrm{SD} = 0.135$ log units, respectively. The descriptive abilities of the Abraham model and Goss modified Abraham model were identical.

The major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that researchers can make predictions for more RTILs. Normally, one needs partition coefficient data for 40–50 solutes dissolved in a given RTIL to develop an Abraham model correlation. By combining all of the experimental data containing RTIL, for example either a 3-methyl-1-ethylimidazolium cation, $[\mathrm{MEIm}]^+$, or tetrafluoroborate, $[\mathrm{BF_4}]^-$, it may be possible to calculate $[\mathrm{MEIm}]^+$-specific and $[\mathrm{BF_4}]^-$-specific equations when there was too few data points for the $[\mathrm{MEIm}]^+[\mathrm{BF_4}]^-$ ionic liquid to develop a meaningful correlation. The computational methodology that we proposed permits us to calculate more ion-specific equation coefficients as more experimental data becomes available in the future.

Since the publication of our last article, experimental activity coefficient data have been reported [9–11] for non-polar and polar organic solutes dissolved in 1-methyl-3-butylimidazolium trifluoromethylsulfonate, $\{[\mathrm{MBIm}]^+[\mathrm{Trif}]^-\}$, and in 1-methyl-3-ethylimidazolium trifluoroacetate, $\{[\mathrm{MEIm}]^+[\mathrm{F_3Ac}]^-\}$. We do not have ion-specific equation coefficients for either the trifluoromethylsulfonate (also called triflate) or trifluoroacetate anions. The recently published infinite dilution activity coefficient data affords us the opportunity to illustrate how one can add coefficients for new cations/anions to our existing database of previously calculated values, without changing the values that have already been determined. As part of the present study, we have also determined the RTIL-specific equation coefficients for $\{[\mathrm{MBIm}]^+[\mathrm{Trif}]^-\}$ and $\{[\mathrm{MEIm}]^+[\mathrm{F_3Ac}]^-\}$ for the $\log P$ and $\log K$ equations of both the Abraham model and Goss modified Abraham model.

2. Database and computation methodology

Most of the experimental data that we were able to retrieve from the published literature [9–11] pertained to the infinite dilution activity coefficient, $\gamma_{\mathrm{solute}}{}^{\infty}$, for solutes dissolved in $\{[\mathrm{MBIm}]^+[\mathrm{Trif}]^-\}$ and $\{[\mathrm{MEIm}]^+[\mathrm{F_3Ac}]^-\}$. In order to apply the Abraham model and Goss modified Abraham model, the infinite dilution activity coefficients needed to be converted to $\log K$ values for gas-to-RTIL partition through Equation (5):

$$\log K = \log\left(\frac{RT}{\gamma^{\infty}_{\mathrm{solute}} P^{\circ}_{\mathrm{solute}} V_{\mathrm{solvent}}}\right). \tag{5}$$

Here R is the universal gas constant, T is the system temperature, $P^{\circ}_{\mathrm{solute}}$ is the vapour pressure of the solute at T and V_{solvent} is the molar volume of the solvent. We did find Henry's law constants, K_{Henry}, for carbon monoxide in 1-methyl-3-butylimidazolium trifluoroacetate, $\{[\mathrm{MBIm}]^+[\mathrm{F_3Ac}]^-\}$ [12], and for both carbon dioxide and ethylene in 1-methyl-3-ethylimidazolium trifluoromethylsulfonate, $\{[\mathrm{MEIm}]^+[\mathrm{Trif}]^-\}$ [13]. These latter values can be used in the determination of the $[\mathrm{F_3Ac}]^-$-specific and $[\mathrm{Trif}]^-$-specific equation coefficients, since the coefficients are known for both respective cations. Henry's constants are converted to gas-to-RTIL partition coefficients using Equation (6):

$$\log K = \log\left(\frac{RT}{K_{\mathrm{Henry}}\ V_{\mathrm{solvent}}}\right). \tag{6}$$

The calculated values were $\log K = 0.251$ for CO_2 in $\{[\mathrm{MEIm}]^+[\mathrm{Trif}]^-\}$, $\log K = -0.228$ for C_2H_4 in $\{[\mathrm{MEIm}]^+[\mathrm{Trif}]^-\}$ and $\log K = -1.298$ for CO in $\{[\mathrm{MBIm}]^+[\mathrm{F_3Ac}]^-\}$.

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 which the RTIL and aqueous phases are not in physical contact with each other. Even then, 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 $\log K$,

$$\log P = \log K - \log K_{\mathrm{w}}, \tag{7}$$

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 $\{[\mathrm{MBIm}]^+\{\mathrm{Trif}]^-\}$and $\{[\mathrm{MEIm}]^+[\mathrm{F_3Ac}]^-\}$are given in Tables 1 and 2,

Table 1. Experimental $\log K$ and $\log P$ partition coefficient data for solutes dissolved in 1-methyl-3-butylimidazolium trifluoromethylsulfonate $\{[\mathrm{MBIm}]^+[\mathrm{Trif}]^-\}$ at 298 K.

Solute	E	S	A	B	V	L	log *K*	log *P*
Pentane	0.000	0.000	0.000	0.000	0.8131	2.162	0.779	2.479
Hexane	0.000	0.000	0.000	0.000	0.9540	2.668	1.148	2.968
Heptane	0.000	0.000	0.000	0.000	1.0949	3.173	1.501	3.461
Octane	0.000	0.000	0.000	0.000	1.2358	3.677	1.816	3.926
Nonane	0.000	0.000	0.000	0.000	1.3767	4.182	2.176	4.326
Decane	0.000	0.000	0.000	0.000	1.5176	4.686	1.800	4.060
Cyclohexane	0.305	0.100	0.000	0.000	0.8454	2.964	1.570	2.470
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	1.2358	3.106	1.461	3.581
Cyclohexene	0.395	0.200	0.000	0.100	0.8024	3.021	1.928	2.198
Styrene	0.849	0.650	0.000	0.160	0.9552	3.908	3.757	2.807
Benzene	0.610	0.520	0.000	0.140	0.7164	2.786	2.692	2.062
Toluene	0.601	0.520	0.000	0.140	0.8573	3.325	3.037	2.387
Ethylbenzene	0.613	0.510	0.000	0.150	0.9982	3.778	3.279	2.699
o-Xylene	0.663	0.560	0.000	0.160	0.9982	3.939	3.544	2.884
m-Xylene	0.623	0.520	0.000	0.160	0.9982	3.839	3.319	2.709
p-Xylene	0.613	0.520	0.000	0.160	0.9982	3.839	3.347	2.757
Methylcyclohexane	0.244	0.060	0.000	0.000	0.9863	3.319	1.764	3.014
Methanol	0.278	0.440	0.430	0.470	0.3082	0.970	2.978	−0.762
Ethanol	0.246	0.420	0.370	0.480	0.4491	1.485	3.085	−0.585
1-Propanol	0.236	0.420	0.370	0.480	0.5900	2.031	3.418	−0.142
1-Butanol	0.224	0.420	0.370	0.480	0.7309	2.601	3.783	0.324
1-Pentanol	0.219	0.420	0.370	0.480	0.8718	3.106	4.093	0.743
2-Propanol	0.212	0.360	0.330	0.560	0.5900	1.764	3.096	−0.383
2-Methyl-1-propnaol	0.217	0.390	0.370	0.480	0.7309	2.413	3.608	0.308
2-Butanol	0.217	0.360	0.330	0.560	0.7309	2.338	3.367	−0.023
3-Methyl-1-butanol	0.192	0.390	0.370	0.480	0.8718	3.011	4.097	0.857
Acetonitrile	0.237	0.900	0.070	0.320	0.4042	1.739	3.062	0.212
Acetone	0.179	0.700	0.040	0.490	0.5470	1.696	2.616	−0.174
1,4-Dioxane	0.329	0.750	0.000	0.640	0.6810	2.892	3.308	−0.402
Tetrahydrofuran	0.289	0.520	0.000	0.480	0.6223	2.636	2.629	0.079
Ethyl acetate	0.106	0.620	0.000	0.450	0.7466	2.314	2.685	0.525
Dichloromethane	0.387	0.570	0.100	0.050	0.4943	2.019	2.337	1.377
Trichloromethane	0.425	0.490	0.150	0.020	0.6167	2.480	2.733	1.943
Tetrachloromethane	0.458	0.380	0.000	0.000	0.7391	2.823	2.308	2.368

along with the respective solute descriptors. The remaining three $\log P$ values are $\log P = 0.331$ for CO_2 in $\{[MEIm]^+[Trif]^-\}$, $\log P = 0.712$ for C_2H_4 in $\{[MEIm]^+[Trif]^-\}$ and $\log P = 0.322$ for CO in $\{[MBIm]^+[F_3Ac]^-\}$.

3. Results and discussion

In Table 1, we have assembled the $\log P$ and $\log K$ values for 34 solutes dissolved in 1-methyl-3-butylimidazolium trifluoromethylsulfonate $\{[MBIm]^+[Trif]^-\}$ 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

Abraham model

$$\log P = 0.043(0.138) + 0.591(0.117)\mathbf{E} - 0.251(0.219)\mathbf{A} - 3.962(0.165)\mathbf{B} + 2.941(0.120)\mathbf{V}$$
$$(\text{with } N = 34, \text{SD} = 0.135, R^2 = 0.992, R^2_{\text{adj}} = 0.991, F = 932) \quad (8)$$

Table 2. Experimental $\log K$ and $\log P$ partition coefficient data for solutes dissolved in 1-methyl-3-ethylimidazolium trifluoroacetate, $\{[MEIm]^+[F_3Ac]^-\}$ at 298 K.

Solute	E	S	A	B	V	L	Log *K*	Log *P*
Pentane	0.000	0.000	0.000	0.000	0.8131	2.162	0.601	2.301
Hexane	0.000	0.000	0.000	0.000	0.9540	2.668	0.922	2.742
Heptane	0.000	0.000	0.000	0.000	1.0949	3.173	1.248	3.208
Octane	0.000	0.000	0.000	0.000	1.2358	3.677	1.597	3.707
Nonane	0.000	0.000	0.000	0.000	1.3767	4.182	1.940	4.090
Decane	0.000	0.000	0.000	0.000	1.5176	4.686	2.271	4.531
Cyclopentane	0.260	0.100	0.000	0.000	0.7045	2.477	1.126	2.006
Cyclohexane	0.310	0.100	0.000	0.000	0.8454	2.964	1.442	2.342
Cycloheptane	0.350	0.100	0.000	0.000	0.9863	3.704	1.953	2.533
Cyclooctane	0.413	0.100	0.000	0.000	1.1272	4.329	2.415	3.045
1-Pentene	0.093	0.080	0.000	0.070	0.7701	2.047	0.848	2.078
1-Hexene	0.080	0.080	0.000	0.070	0.9110	2.572	1.230	2.390
1-Heptene	0.092	0.080	0.000	0.070	1.0519	3.063	1.539	2.759
1-Octene	0.090	0.080	0.000	0.070	1.1928	3.568	1.860	3.270
1-Pentyne	0.172	0.230	0.120	0.120	0.7271	2.010	1.806	1.816
1-Hexyne	0.166	0.220	0.100	0.120	0.8680	2.510	2.121	2.331
1-Heptyne	0.160	0.230	0.090	0.100	1.0089	3.000	2.624	3.064
1-Octyne	0.155	0.220	0.090	0.100	1.1498	3.521	2.730	3.250
Benzene	0.610	0.520	0.000	0.140	0.7164	2.786	2.614	1.984
Toluene	0.601	0.520	0.000	0.140	0.8573	3.325	2.937	2.287
Ethylbenzene	0.613	0.510	0.000	0.150	0.9982	3.778	3.178	2.598
o-Xylene	0.663	0.560	0.000	0.160	0.9982	3.939	3.404	2.744
m-Xylene	0.623	0.520	0.000	0.160	0.9982	3.839	3.232	2.622
p-Xylene	0.613	0.520	0.000	0.160	0.9982	3.839	3.235	2.645
Methanol	0.278	0.440	0.430	0.470	0.3082	0.970	3.613	−0.127
Ethanol	0.246	0.420	0.370	0.480	0.4491	1.485	3.714	0.044
1-Propanol	0.236	0.420	0.370	0.480	0.5900	2.031	4.063	0.503
1-Butanol	0.224	0.420	0.370	0.480	0.7309	2.601	4.482	1.022

$$\log K = -0.449(0.132) + 0.567(0.173)\mathbf{E} + 1.987(0.200)\mathbf{S} + 3.615(0.243)\mathbf{A} + 0.857(0.207)\mathbf{B} + 0.584(0.039)\mathbf{L}$$
$$(\text{with } N = 34,\ \text{SD} = 0.122,\ R^2 = 0.980,\ R^2_{\text{adj}} = 0.976,\ F = 274.8). \qquad (9)$$

Goss modified Abraham model

$$\log P = -0.031(0.170) + 0.461(0.227)\mathbf{S} - 4.318(0.171)\mathbf{B} + 0.123(0.108)\mathbf{L} + 2.672(0.396)\mathbf{V}$$
$$(\text{with } N = 34,\ \text{SD} = 0.150,\ R^2 = 0.990,\ R^2_{\text{adj}} = 0.989,\ F = 748.9), \qquad (10)$$

$$\log K = -0.485(0.175) + 2.356(0.234)\mathbf{S} + 3.797(0.258)\mathbf{A} + 0.526(0.216)\mathbf{B} + 0.729(0.101)\mathbf{L} - 0.354(0.378)\mathbf{L}$$
$$(\text{with } N = 34,\ \text{SD} = 0.136,\ R^2 = 0.975,\ R^2_{\text{adj}} = 0.971,\ F = 221.9), \qquad (11)$$

where N is the number of data points, that is, the number of solutes, R^2 denotes the squared correlation coefficient, $R^2{}_{\text{adj}}$ refers to the adjusted squared correlation coefficient, SD is the standard deviation and F corresponds to the Fisher's F statistic. The errors in the coefficients are given in parentheses. 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 $\log P$ and $\log K$ based on Equations (8) and (9) against the experimental data. In compiling the data, we did notice that the observed $\log K$ value for decane in $\{[\text{MBIm}]^+[\text{Trif}]^-\}$ was out of line with the values for the other *n*-alkane solutes (Table 1).

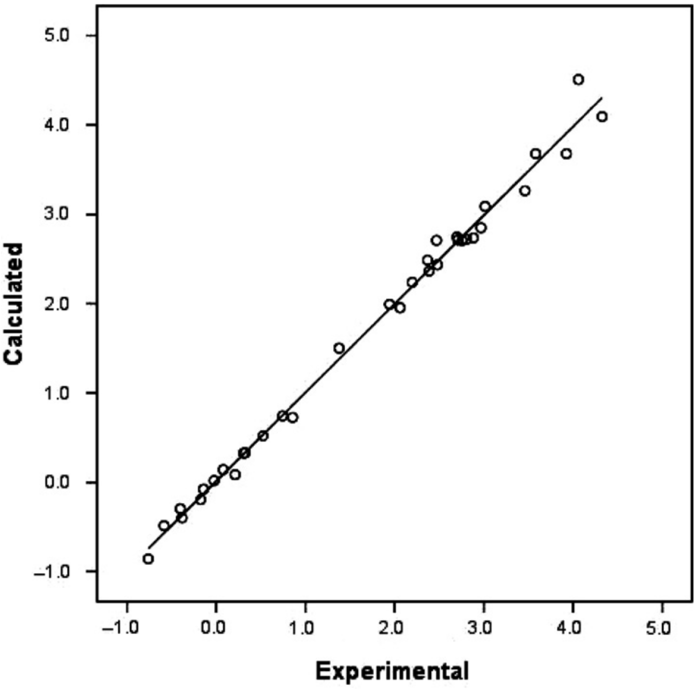

Figure 1. Comparison of the calculated $\log P$ values based on Equation (8) *vs*. observed values for solutes dissolved in $\{[\text{MBIm}]^+[\text{Trif}]^-\}$.

The $\log K$ values for pentane through nonane increase with increasing alkyl chain length; however, the value for decane does not follow the observed trend. Given the small number of experimental data points, we decided not to exclude decane from the regression analysis even though we suspected that the observed value may be a bit too small compared to the other linear alkanes in the series.

Equations (8)–(11) refer to the RTIL-specific Abraham model and Goss modified Abraham model correlations in which the numerical values of all equation coefficients pertain only to the single {[MBIm]$^+$[Trif]$^-$} ionic liquid. Each equation coefficient represents the sum of the cation plus anion contribution, i.e. $e_{\mathrm{RTIL}} = e_{\mathrm{cation}} + e_{\mathrm{anion}}$, $s_{\mathrm{RTIL}} = s_{\mathrm{cation}} + s_{\mathrm{anion}}$, etc. Using our previously determined values for [MBIm]$^+$, we have calculated and assembled in Table 3 the respective model equation coefficients for the trifluoromethylsulfonate anion. Gaseous solutes were absent in the {[MBIm]$^+$[Trif]$^-$} database used in deriving Equations (8)–(11). It is possible to include the $\log P$ and $\log K$ data for both CO_2 and C_2H_4 in {[MEIm]$^+$[Trif]$^-$} by transforming the independent regressed solute property to $\log K - \sum$(cation coefficients x solute descriptors) or $\log P - \sum$(cation coefficients x solute descriptors); i.e. $\log K - c_{\mathrm{cation}} - (e_{\mathrm{cation}} \cdot \mathbf{E}) - (s_{\mathrm{cation}} \cdot \mathbf{S}) - (a_{\mathrm{cation}} \cdot \mathbf{A}) - (b_{\mathrm{cation}} \cdot \mathbf{B}) - (l_{\mathrm{cation}} \cdot \mathbf{L})$, etc. Trifluoromethanesulfonate-specific equation coefficients obtained as the result of this latter computation are tabulated in Table 4. From a predictive standpoint, the second set of equation coefficients are preferred. Inclusion of the two gaseous solutes increased the range of $\log K$ and $\log P$

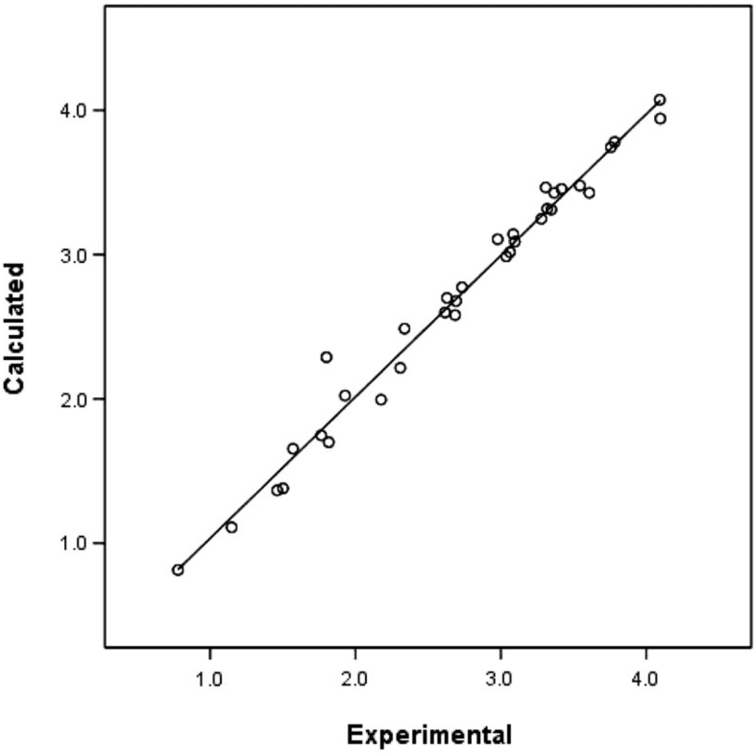

Figure 2. Comparison of the calculated $\log K$ values based on Equation (9) *vs*. observed values for solutes dissolved in {[MBIm]$^+$[Trif]$^-$}.

Table 3. Compilation of Abraham model and Goss modified Abraham model equation coefficients for the trifluoromethylsulfonate anion using experimental data for only {$[MBIm]^+[Trif]^-$}.

	c	*e*	*s*	*a*	*b*	*l*	*v*
Abraham log *P* mode							
RTIL Value	0.043	0.591	0.000	−0.251	−3.962		2.941
$[MBIm]^+$ Value	0.068	0.238	0.090	−1.673	−3.976		3.268
$[Trif]^-$ Value	−0.025	0.353	−0.090	1.422	0.014		−0.327
Abraham log *K* model							
RTIL Value	−0.449	0.567	1.987	3.615	0.857	0.584	
$[MBIm]^+$ Value	−0.422	0.113	2.014	2.125	0.954	0.688	
$[Trif]^-$ Value	−0.027	0.454	−0.027	1.490	−0.097	−0.104	
Goss modified Abraham log *P* model							
RTIL Value	−0.031		0.461	0.000	−4.318	0.123	2.672
$[MBIm]^+$ Value	0.011		0.269	−1.534	−4.105	0.014	3.281
$[Trif]^-$ Value	−0.042		0.192	1.534	−0.213	−0.109	−0.609
Goss modified Abraham log *K* model							
RTIL Value	−0.485		2.356	3.797	0.526	0.729	−0.354
$[MBIm]^+$ Value	−0.463		2.195	2.321	0.750	0.649	0.177
$[Trif]^-$ Value	−0.022		0.161	1.476	−0.224	0.080	−0.531

Table 4. Compilation of Abraham model and Goss modified Abraham model equation coefficients for the trifluoromethylsulfonate anion using experimental data for both {$[MBIm]^+[Trif]^-$} and {$[MEIm]^+[Trif]^-$}.

	c	*e*	*s*	*a*	*b*	*l*	*v*
Abraham log *P* Model							
$[Trif]^-$ Value	−0.1051	0.294	0.044	1.510	−0.064		−0.260
Abraham log *K* model							
$[Trif]^-$ Value	−0.143	0.413	0.038	1.584	−0.107	−0.071	
Goss modified Abraham log *P* model							
$[Trif]^-$ Value	0.012		0.097	1.486	−0.176	0.148	−0.764
Goss modified Abraham log *K* model							
$[Trif]^-$ Value	−0.037		0.136	1.483	−0.207	0.104	−0.592

values used in the regression analysis. Without the two gaseous solutes there were no negative log *K* values in the dataset, and the smallest log *K* value went down only as far as $\log K = 0.78$ for pentane. By having two gases in the database, we have expanded the chemical space that is defined by the solute descriptors, which should enable us to better predict the solubility of gaseous solutes in other RTILs containing $[Trif]^-$ anion.

Our search of the published chemical and engineering literature also found infinite dilution activity coefficient data for 28 organic solutes dissolved in 1-methyl-3-ethylimidazolium trifluoroacetate, {$[MEIm]^+[F_3Ac]^-$} covering a reasonably wide range of compound type and descriptor values. The $\log P$ and $\log K$ values calculated from the published activity coefficient data (Table 2) were analysed to give

Abraham model

$$\log P = -0.129(0.101) - 1.251(0.213)\mathbf{E} + 2.356(0.329)\mathbf{S} + 0.889(0.505)\mathbf{A} - 4.473(0.556)\mathbf{B} + 3.044(0.089)\mathbf{V}$$
$$(\text{with } N = 28,\ \mathrm{SD} = 0.074,\ R^2 = 0.995,\ R^2_{\mathrm{adj}} = 0.994,\ F = 903.1), \qquad (12)$$

$$\log K = -0.810(0.068) + 2.694(0.147)\mathbf{S} + 5.462(0.428)\mathbf{A} + 0.734(0.451)\mathbf{B} + 0.669(0.020)\mathbf{L}$$
$$(\text{with } N = 28,\ \mathrm{SD} = 0.065,\ R^2 = 0.996,\ R^2_{\mathrm{adj}} = 0.995,\ F = 1457.2). \qquad (13)$$

Goss modified Abraham model

$$\log P = -0.456(0.107) + 1.474(0.238)\mathbf{S} + 1.249(0.545)\mathbf{A} - 4.054(0.579)\mathbf{B} - 0.344(0.066)\mathrm{L} + 4.315(0.241)\mathbf{V}$$
$$(\text{with } N = 28,\ \mathrm{SD} = 0.080,\ R^2 = 0.994,\ R^2_{\mathrm{adj}} = 0.993,\ F = 780.1), \qquad (14)$$

$$\log K = -0.810(0.068) + 2.694(0.147)\mathbf{S} + 5.462(0.428)\mathbf{A} + 0.734(0.451)\mathbf{B} + 0.669(0.020)\mathbf{L}$$
$$(\text{with } N = 28,\ \mathrm{SD} = 0.065,\ R^2 = 0.996,\ R^2_{\mathrm{adj}} = 0.995,\ F = 1457.2). \qquad (15)$$

Our preliminary computations showed that the $\mathrm{e}\cdot\mathbf{E}$ term was negligible in the Abraham $\log K$ model, and that the $\mathrm{v}\cdot\mathbf{V}$ term was negligible in the Goss modified Abraham $\log K$ model. The terms were thus eliminated from the respective final derived correlations. The statistics of the derived correlations are quite good. See Figures 3 and 4 for a comparison of the experimental $\log P$ and $\log K$ data versus the calculated values based on the Goss modified Abraham model. No significance is given to the slight differences in descriptive abilities of the two models. Our past experience in comparing the descriptive abilities of the Abraham model versus the Goss modified Abraham model is that both models provide very comparable predictions, and the computations presented here are in accord with these earlier observations. Note that if the $\mathrm{v}\cdot\mathbf{V}$ term is excluded in the Goss modified Abraham $\log K$ model, Equation (15), and if the $\mathrm{e}\cdot\mathbf{E}$ term is excluded in the Abraham $\log K$ model, Equation (13), the two models become identical.

Using our previously determined values for $[\mathrm{MEIm}]^+$, we have calculated and assembled in Table 5 the respective model equation coefficients for the trifluoroacetate anion. Gaseous solutes were absent in the $\{[\mathrm{MEIm}]^+[\mathrm{F_3Ac}]^-\}$ database used in deriving Equations (12)–(15). Ohlin *et al.* [12] measured the solubility of carbon monoxide in several RTILs. Of the RTILs studied by the authors, only 1-methyl-3-butylimidazolium trifluoroacetate contained the $[\mathrm{F_3Ac}]^-$ anion. The $\log K$ and $\log P$ values for carbon monoxide dissolved in $\{[\mathrm{MBIm}]^+[\mathrm{F_3Ac}]^-\}$, $\log K = -1.298$ and $\log P = 0.322$, were included in the regression analysis for the anion-specific equation coefficients by transforming the independent regressed solute property to $\log K - \sum$(cation coefficients x solute descriptors) or $\log P - \sum$(cation coefficients x solute descriptors) as said before. Trifluoroacetate-specific equation coefficients obtained as the result of this latter computation are tabulated in Table 6. From a predictive standpoint, the second set of equation coefficients are preferred. Inclusion of gaseous carbon monoxide increased the range of $\log K$ and $\log P$ values used in the regression analysis. Without carbon monoxide

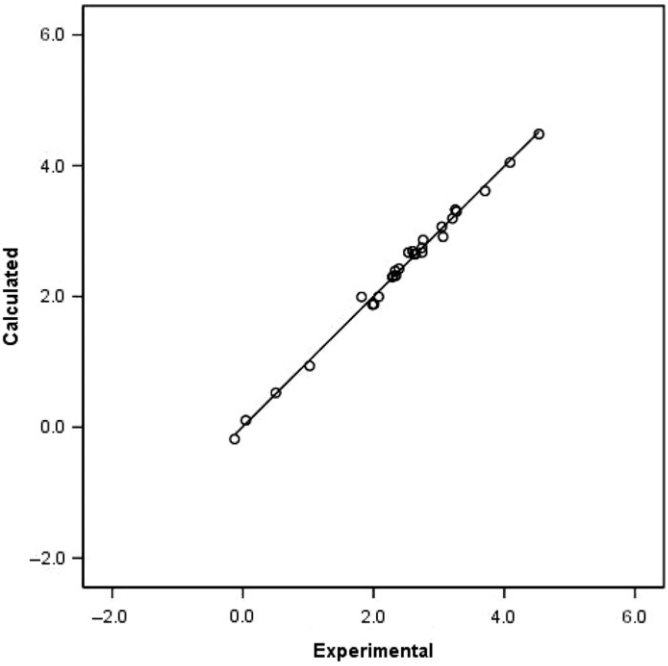

Figure 3. Comparison of the calculated log P values based on Equation (14) *vs*. observed values for solutes dissolved in $\{[\text{MEIm}]^+[\text{F}_3\text{Ac}]^-\}$.

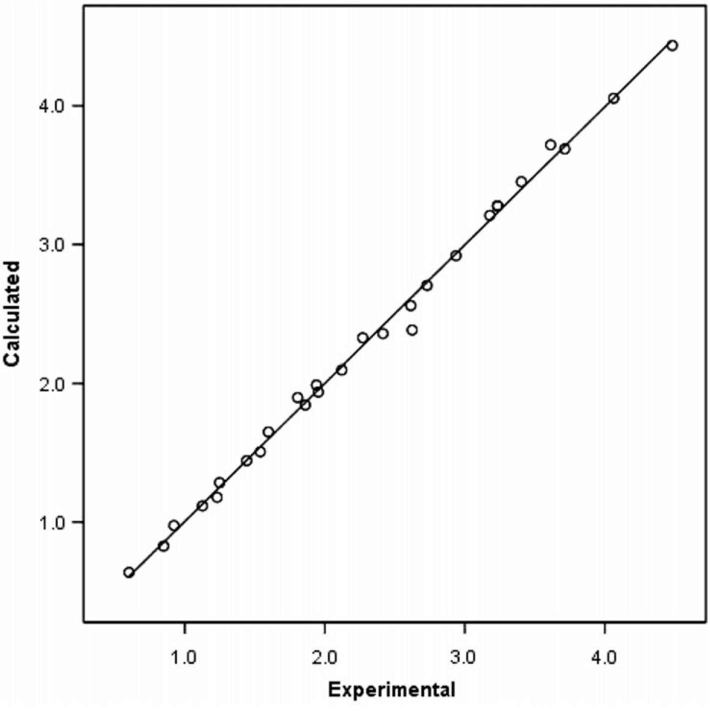

Figure 4. Comparison of the calculated log K values based on Equation (15) *vs*. observed values for solutes dissolved in $\{[\text{MEIm}]^+[\text{F}_3\text{Ac}]^-\}$.

Table 5. Compilation of Abraham model and Goss modified Abraham model equation coefficients for the trifluoroacetate anion using experimental data for only $\{[MEIm]^+[F_3Ac]^-\}$.

	c	*e*	*s*	*a*	*b*	*l*	*v*
Abraham log *P* Model							
RTIL Value	−0.129	−1.251	2.356	0.889	−4.473		3.044
$[MEIm]^+$ Value	−0.026	0.349	0.269	−1.593	−3.649		3.111
$[F_3Ac]^-$ Value	−0.103	−1.600	2.087	2.482	−0.824		−0.067
Abraham log *K* model							
RTIL Value	−0.810	0.000	2.694	5.462	0.734	0.669	
$[MEIm]^+$ Value	−0.533	0.128	2.332	2.349	1.027	0.651	
$[F_3Ac]^-$ Value	−0.277	−0.128	0.362	3.113	−0.293	0.018	
Goss modified Abraham log *P* model							
RTIL Value	−0.456		1.474	1.249	−4.054	−0.344	4.315
$[MEIm]^+$ Value	0.092		0.381	−1.599	−3.765	0.101	2.750
$[F_3Ac]^-$ Value	−0.548		1.093	2.848	−0.289	−0.445	1.565
Goss modified Abraham log *K* model							
RTIL Value	−0.810		2.694	5.462	0.734	0.669	0.000
$[MEIm]^+$ Value	−0.514		2.421	2.397	0.936	0.661	−0.020
$[F_3Ac]^-$ Value	−0.296		0.273	3.065	−0.202	0.008	0.020

Table 6. Compilation of Abraham model and Goss modified Abraham model equation coefficients for the trifluoroacetate anion using experimental data for both $\{[MEIm]^+[F_3Ac]^-\}$and $\{[MBIm]^+[F_3Ac]^-\}$.

	c	*e*	*s*	*a*	*b*	*l*	*v*
Abraham log *P* model							
$[F_3Ac]^-$ Value	−0.103	−1.600	2.088	2.482	−0.824		−0.067
Abraham log *K* model							
$[F_3Ac]^-$ Value	−0.277	−0.121	0.354	3.112	−0.287	0.018	
Goss modified Abraham log *P* model							
$[F_3Ac]^-$ Value	¯0.548		1.093	2.848	−0.289	−0.445	1.565
Goss modified Abraham log *K* model							
$[F_3Ac]^-$ Value	−0.295		0.270	3.062	−0.198	0.010	0.015

there were no negative log *K* values in the dataset, and the smallest log *K* value went down only as far as $\log K = 0.60$ for pentane.

The present study increases by two the number of anion-specific equation coefficients for both the Abraham model and Goss modified Abraham model. The 8 sets of cation-specific equation coefficients and 6 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 48 different RTILs. The 16 additional RTILs for which partition coefficient predictions are now possible are: 4-methyl-*N*-pyridinium trifluoromethylsulfonate, *N*-ethylpyridinium trifluoromethylsulfonate, 1-methyl-3-ethylimidazolium trifluoromethylsulfonate, 1,2-dimethyl-3-ethylimidazolium trifluoromethylsulfonate, 1-methyl-3-butylimidazolium trifluoromethylsulfonate, 1-methyl-3-hexylimidazolium trifluoromethylsulfonate, 1-methyl-3-octylimidazolium trifluoromethylsulfonate, trimethylbutylammonium trifluoromethylsulfonate, 4-methyl-*N*-pyridinium trifluoroacetate, *N*-ethylpyridinium trifluoroacetate, 1-methyl-3-ethylimidazolium trifluoroacetate, 1,2-dimethyl-3-ethylimidazolium trifluoroacetate, 1-methyl-3-butylimidazolium trifluoroacetate, 1-methyl-3-hexylimidazolium trifluoroacetate, 1-methyl-3-octylimidazolium trifluoroacetate and trimethylbutylammonium trifluoroacetate. The cation-specific equation coefficients needed for these predictions are given elsewhere [7,8].

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 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 $\mathbf{L} = 5.700$. A few of the ion-specific databases do span a slightly smaller range of solute descriptors (e.g. both the $[\mathrm{Trif}]^-$ and $[\mathrm{F_3Ac}]^-$ anion databases have decane rather than dodecane as the largest solute). One should be able to make reasonably accurate partition coefficient predictions for most solutes having solute descriptors that fall within the aforementioned ranges.

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