

Cation-specific and anion-specific Abraham model correlations for solute transfer into ionic liquid solvents

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Received 19 Mar 2010; Accepted 26 Apr 2010; Available Online 31 Aug 2010

Abstract

Data have been assembled from the published literature on the infinite dilution activity coefficients and gas solubilities of solutes dissolved in ionic liquid (IL) solvents. In total data for more than 1790 solute-IL pairs were compiled. The published experimental data were converted to gas-to-IL and water-to-IL partition coefficients, and correlated with the ion-specific equation coefficient version of the Abraham general solvation model. Ion-specific equation coefficients were calculated for 19 different cations and 12 different anions. The calculated ion-specific equation coefficients describe the experimental gas-to-IL and water-to-IL partition coefficient data to within 0.114 and 0.139 log units, respectively. Reported for the first time are equation coefficients for diethylphosphate, tris(pentafluoroethyl)trifluorophosphate and tetracyanoborate anions.

Keywords: Ionic liquid; Partition coefficient; Activity coefficients linear solvation energy relationship; Solvation energy; Chemical separation

1. Introduction

New generation ionic liquids (ILs) have become a popular solvent choice for manufacturing applications involving organic synthesis, electrochemistry, extractive distillation and chromatographic separations, and gas adsorption. Select alkylimidazolium-based ILs have exhibited large carbon dioxide versus nitrogen gas selectivities [1], large carbon dioxide versus methane gas selectivities [1], and benzene versus cyclohexane vapor selectivities [2]. The main advantage that ILs offer over the more conventional organic solvents and polymeric sorption materials is that the physical properties and solvating characteristics of ILs can be tuned simply by changing the cation and anion combinations. Presently more than 1000 different ILs are commercially available. The number of cation-anion combinations is significantly larger (more than 10^{14}) [3, 4]. It is not feasible to experimentally study every possible cation-anion combination, and

predictive methods need to be developed to aid researchers in selecting the most appropriate IL for a given application.

The present study continues our examination of the solubilizing properties of ionic liquids using the Abraham liner solvation energy relationship (LSER) model. Previously we have reported [5-13] LSERs for solute transfer to ILs from the gas phase

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

and for the partitioning of solutes between water and an IL

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

The dependent variables in Eqns. 1 and 2 are the logarithm of the gas-to-IL partition coefficient ($\log K$) and logarithm of the water-to-

IL partition coefficient (log P). The independent variables in the log K and log P correlations are solute descriptors as follows: A and B are measures of the solute hydrogen-bond acidity and basicity solute descriptors of the solute, respectively, E and S refer to the excess molar refraction in units of $(\text{cm}^3 \text{mol}^{-1})/10$ and dipolarity/polarizability descriptors, 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 298.15 K. The cation-specific and anion-specific regression coefficients and constants (lowercase letters) are determined by regression analyses of the experimental data for the given partition process. In the case of partition coefficients involving two condensed solvent phases, the lower case equation coefficients represent differences in the solvent phase properties. For any fully characterized system/process (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.

Currently we have published equation coefficients for nineteen cations and nine anions [5-13]. Most of the experimental log K and log P values used in our regression analyses have come from gas solubilities and infinite dilution activity coefficients determined by gas-liquid chromatographic measurements. Solutes studied have typically been inert gases, diatomic gas molecules, linear, branched and cycloalkanes, linear and branched alcohols, linear and cyclic monoethers (plus 1,4-dioxane), alkanoates, chlorinated methanes, several aldehydes and ketones, and several polar aromatic compounds. Solubility data for caffeine and acetaminophen in 1-methyl-3-octylimidazolium tetrafluoroborate, $([\text{MOIm}]^+[\text{BF}_4]^-)$, in 1-methyl-3-octylimidazolium hexafluorophosphate, $([\text{MOIm}]^+[\text{PF}_6]^-)$, in $([\text{BMIm}]^+[\text{PF}_6]^-)$, and in 1-butyl-3-methylimidazolium tetrafluoroborate, $([\text{BMIm}]^+[\text{BF}_4]^-)$ were also included in the regression analysis. The area of predictive chemical space defined by these compounds would be $E = 0.000$ to $E = 1.500$; $S = 0.000$ to $S = 1.720$; $A = 0.000$ to $A = 1.040$; $B = 0.000$ to $B = 1.280$; $V = 0.109$ to $V = 1.799$; and $L = -1.200$ to $L = 7.833$. A few of the ion-specific data sets spanned a slightly smaller range of solute descriptors. The ion-specific equation coefficients that we have determined should allow one to make reasonably accurate partition coefficient predictions for most solutes having solute descriptors that fall within the aforementioned ranges.

The major advantage of splitting the equation coefficients into individual cation-

specific and anion-specific contribution is that one can make predictions for many more ILs. The 19 cation and 9 anion coefficients that we have calculated thus far were based on experimental partition coefficient data for 36 different ILs. It takes approximately 40 to 50 experimental log K values (or log P values) to develop an Abraham model specifically for a given IL. We have developed very few IL-specific Abraham model correlations. On the other hand, the 19 cation and 9 anion coefficients that we have calculated can be combined to give predictive LSERs for 171 ILs (19×9). Revelli *et al.* [3] recently extended the Abraham model's predictive capability for IL solvents by further splitting the cation-specific equation coefficient into functional group values

$$\begin{aligned} \log K = & \sum_{\text{group}} c_i n_i + \sum_{\text{group}} e_i n_i E + \sum_{\text{group}} s_i n_i S \\ & + \sum_{\text{group}} a_i n_i A + \sum_{\text{group}} b_i n_i B + \sum_{\text{group}} l_i n_i L \\ & + (c_{\text{anion}} + e_{\text{anion}} E + s_{\text{anion}} S \\ & + a_{\text{anion}} A + b_{\text{anion}} B + l_{\text{anion}} L) \end{aligned} \quad (3)$$

and

$$\begin{aligned} \log P = & \sum_{\text{group}} c_i n_i + \sum_{\text{group}} e_i n_i E + \sum_{\text{group}} s_i n_i S \\ & + \sum_{\text{group}} a_i n_i A + \sum_{\text{group}} b_i n_i B + \sum_{\text{group}} v_i n_i V \\ & + (c_{\text{anion}} + e_{\text{anion}} E + s_{\text{anion}} S \\ & + a_{\text{anion}} A + b_{\text{anion}} B + v_{\text{anion}} V) \end{aligned} \quad (4)$$

where n_i is the number of times a particular functional group appears in the cation. The authors were able to mathematically describe the 1450 available gas-to-IL partition coefficients (log K values) and 1410 water-to-IL partition coefficients (log P values) with 21 groups: 12 functional groups characterizing the cations (CH_3 , CH_2 , N_{cyclic} , C_{cyclic} , *etc.*) and 9 individual anions ($[\text{PF}_6]^-$, $[\text{BF}_4]^-$, $[\text{SCN}]^-$, *etc.*) to within 0.15 and 0.17 log units, respectively. The standard deviations noted for Eqns. 3 and 4 were comparable in magnitude to the standard deviations for the IL-specific Abraham model correlations and for the cation-specific and anion-specific equation coefficient version of the Abraham model. Sprunger *et al.* [14] had earlier proposed a similar fragmentation scheme to describe solute transfer into acyclic monofunctional alcohol solvents.

It has been several years since the publication of many of IL-specific Abraham model correlations. A large number of new experimental data points have been added to our log K and log P databases. The databases used in obtaining the benchmark IL-specific correlations contained far fewer experimental data points than is currently available for each individual ionic liquid. There are sufficient new experimental log K and log P values for compounds outside of the chemical space of our existing IL-specific correlations to warrant a redetermination. Numerical values computed from the reanalysis should give much better predictions, particularly for the more acidic and/or polarizable compounds that were added to the database in the last two years. The predictive area of chemical space defined by the benchmark IL-specific correlations must be comparable to the space defined by the log P and log K databases used in Eqns. 1 – 4 in order to properly assess how much predictive accuracy might be lost in using the ion-specific equation coefficients and/or functional group-specific equation coefficients. As part of the present we also updated the numerical values of the cation-specific and anion-specific equation coefficients using our larger database containing 1790 log K and 1760 log P values, and have reported for the first time equation coefficients for the diethylphosphate anion, $[\text{Et}_2\text{PO}_4]^-$. The last major revision of the ion coefficients occurred at 976 log K and 955 log P values in the regression database. Following this last major recalculation of equation coefficients, we have determined [8-13] values for several additional ions based on suggested computational methodology described elsewhere [6]. The calculation allows additional ions to be added without affecting the ion-specific equation coefficients that have already been determined.

2. Experimental

The majority of experimental log K and log P data considered in the present study were taken from the supporting information that accompanied our three earlier papers [5-7] and from six followup studies [8-13] concerning the computation of ion-specific equation coefficients of several additional cations and anions. Notable additions and corrections to the previously reported values are as follows. The log K and log P values for solutes dissolved in 1-methyl-3-butylimidazolium hexafluorophosphate, $([\text{MBIm}]^+[\text{PF}_6]^-)$, were recalculated using a

density of 1.366 g/cm^3 [15] for the IL solvent. Domanska and coworkers [16-18] published infinite dilution activity coefficient data, $\gamma_{\text{solute}}^\infty$, for solutes dissolved in 4-methyl-N-butylpyridinium bis(trifluoromethylsulfonyl)imide $([\text{BMPy}]^+[(\text{TF})_2\text{N}]^-)$, 1-methyl-3-butylimidazolium thiocyanate $([\text{MBIm}]^+[\text{SCN}]^-)$, 1-methyl-3-hexylimidazolium thiocyanate $([\text{MHIm}]^+[\text{SCN}]^-)$, based on chromatographic measurements. Olivier *et al.* [19] measured infinite dilution activity coefficients of organic solutes in 1-methyl-3-octylimidazolium hexafluorophosphate $([\text{MOIm}]^+[\text{PF}_6]^-)$. Revelli *et al.* [3, 20] reported $\gamma_{\text{solute}}^\infty$ values for solutes dissolved in 1-ethanol-3-methylimidazolium hexafluorophosphate, $([\text{EtOHMIm}]^+[\text{PF}_6]^-)$, 1-methyl-3-ethylimidazolium diethylphosphate, $([\text{MEIm}]^+[\text{E}_2\text{PO}_4]^-)$, and 1-ethanol-3-methylimidazolium tetrafluoroborate, $([\text{EtOHMIm}]^+[\text{BF}_4]^-)$. The 43 ILs considered in the present study are listed in Table 1.

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 Eqn. 5 and 6

$$\log K = \log \left(\frac{RT}{\gamma_{\text{solute}}^\infty P_{\text{solute}}^o V_{\text{solvent}}} \right) \quad (5)$$

$$\log K = \log \left(\frac{RT}{K_{\text{Henry}} V_{\text{solvent}}} \right) \quad (6)$$

or log P values for partition from water to the ionic liquid through Eqn. (7)

$$\log P = \log K - \log K_w \quad (7)$$

In equations 5 - 7 P_{solute}^o is the vapor pressure of the solute at the system temperature (T), V_{solvent} is the molar volume of the solvent, and R is the universal gas constant. The conversion of log K data to log P requires knowledge of the solute's gas phase partition coefficient into water, K_w , which is available for most of the solutes being studied. As an informational note, water to IL partition coefficients (more formally called Gibbs energy of solute transfer when multiplied by -2.303 RT) calculated through Eqn. 7 refer to a hypothetical partitioning process involving solute transfer from water to the anhydrous IL. Log P values calculated in this fashion are still useful in that predicted log P values can be used to estimate the solute's infinite dilution activity coefficient in the IL.

Table 1. Ionic liquids solvents represented in the log K and log P database.

Ionic liquid name	Abbreviation
1-methyl-3-ethylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide	([MEIm] ⁺ [(Tf) ₂ N] ⁻)
1,2-dimethyl-3-ethylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide	([M ₂ EIm] ⁺ [(Tf) ₂ N] ⁻)
1-methyl-3-butylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide	([MBIm] ⁺ [(Tf) ₂ N] ⁻)
1-methyl-3-hexylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide	([MHIm] ⁺ [(Tf) ₂ N] ⁻)
1-methyl-3-octylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide	([MOIm] ⁺ [(Tf) ₂ N] ⁻)
trimethylbutylammonium <i>bis</i> (trifluoromethylsulfonyl)imide	([M ₃ BAm] ⁺ [(Tf) ₂ N] ⁻)
hexyltrimethylammonium <i>bis</i> (trifluoromethylsulfonyl)imide	([HexM ₃ Am] ⁺ [(Tf) ₂ N] ⁻)
N-ethylpyridinium <i>bis</i> (trifluoromethylsulfonyl)imide	[NEPy] ⁺ [(Tf) ₂ N] ⁻)
4-methyl-N-butylpyridinium <i>bis</i> (trifluoromethylsulfonyl)imide	([BMPy] ⁺ [(Tf) ₂ N] ⁻)
1-hexyloxymethyl-3-methylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide,	([HxomMIm] ⁺ [(Tf) ₂ N] ⁻)
1,3-dihexyloxymethylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide	(Hxom) ₂ Im] ⁺ [(Tf) ₂ N] ⁻)
1,3-dimethoxyimidazolium <i>bis</i> ((trifluoromethyl)sulfonyl)imide	([(Meo) ₂ Im] ⁺ [(Tf) ₂ N] ⁻)
1-ethanol-3-methylimidazolium <i>bis</i> (trifluoromethyl)sulfonylimide	([EtOHMIm] ⁺ [(Tf) ₂ N] ⁻)
trihexyltetradecylphosphonium <i>bis</i> (trifluoromethylsulfonyl)imide	([H ₃ TdP] ⁺ [(Tf) ₂ N] ⁻)
1-methylethylether-3-methylimidazolium <i>bis</i> ((trifluoromethyl)sulfonyl)imide	([MeoeMIm] ⁺ [(Tf) ₂ N] ⁻)
1-methyl-3-ethylimidazolium tetrafluoroborate	([MEIm] ⁺ [BF ₄] ⁻)
1-methyl-3-butylimidazolium tetrafluoroborate	([MBIm] ⁺ [BF ₄] ⁻)
1-methyl-3-hexylimidazolium tetrafluoroborate	([MHIm] ⁺ [BF ₄] ⁻)
1-methyl-3-octylimidazolium tetrafluoroborate	([MOIm] ⁺ [BF ₄] ⁻)
1-hexadecyl-3-methylimidazolium tetrafluoroborate	([HexdMIm] ⁺ [BF ₄] ⁻)
1-propyl-2,3-dimethyl-imidazolium tetrafluoroborate	([PM ₂ Im] ⁺ [BF ₄] ⁻)
4-methyl-N-butylpyridinium tetrafluoroborate	([BMPy] ⁺ [BF ₄] ⁻)
1-ethanol-3-methylimidazolium tetrafluoroborate	([EtOHMIm] ⁺ [BF ₄] ⁻)
1-methyl-3-butylimidazolium hexafluorophosphate	([MBIm] ⁺ [PF ₆] ⁻)
1-methyl-3-hexylimidazolium hexafluorophosphate	([MHIm] ⁺ [PF ₆] ⁻)
1-methyl-3-octylimidazolium hexafluorophosphate	([MOIm] ⁺ [PF ₆] ⁻)
1-ethanol-3-methylimidazolium hexafluorophosphate	([EtOHMIm] ⁺ [PF ₆] ⁻)
1-methyl-3-ethylimidazolium ethylsulfate	([MEIm] ⁺ [EtSO ₄] ⁻)
1-methyl-3-ethylimidazolium octylsulfate	([MEIm] ⁺ [OtSO ₄] ⁻)
1-methyl-3-butylimidazolium octylsulfate	([MBIm] ⁺ [OtSO ₄] ⁻)
1-methyl-3-ethylimidazolium thiocyanate	([MEIm] ⁺ [SCN] ⁻)
1-methyl-3-butylimidazolium thiocyanate	([MBIm] ⁺ [SCN] ⁻)
1-methyl-3-hexylimidazolium thiocyanate	([MHIm] ⁺ [SCN] ⁻)
1-methyl-3-ethylimidazolium trifluoromethanesulfonate	([MEIm] ⁺ [Trif] ⁻)
1-methyl-3-butylimidazolium trifluoromethanesulfonate	([MBIm] ⁺ [Trif] ⁻)
1-methyl-3-hexylimidazolium trifluoromethanesulfonate	([MHIm] ⁺ [Trif] ⁻)
1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate,	([BMPyrr] ⁺ [Trif] ⁻)
1-methyl-3-ethylimidazolium trifluoroacetate	([MEIm] ⁺ [F ₃ Ac] ⁻)
1-methyl-3-butylimidazolium trifluoroacetate	([MBIm] ⁺ [F ₃ Ac] ⁻)
1-methyl-3-ethylimidazolium dicyanamide	([MEIm] ⁺ [C(CN) ₂] ⁻)
1-(3-cyanopropyl)-3-methylimidazolium dicyanamide	([CNPrMIm] ⁺ [C(CN) ₂] ⁻)
1-methyl-3-ethylimidazolium diethylphosphate	([MEIm] ⁺ [E ₂ PO ₄] ⁻)

Experimental gas chromatographic retention factors on 1-ethanol-3-methylimidazolium *bis*((trifluoromethyl)sulfonyl)imide, ([EtOHMIm]⁺[(Tf)₂N]⁻), were from a study by the Anderson group [21] concerning characterizing solute interactions with functionalized ionic liquids containing the

tris(pentafluoroethyl)trifluorophosphate anion, [FAP]⁻. For comparison purposes, the authors provided data for three ILs containing the *bis*((trifluoromethyl)sulfonyl)-imide anion. The 1-ethanol-3-methylimidazolium *bis*((trifluoromethyl)sulfonyl)imide column was prepared by coating the ionic liquid on an

Table 2. Logarithm of the gas chromatographic retention factors of solutes on a 1-ethanol-3-methylimidazolium *bis*(trifluoromethyl)sulfonylimide stationary phase at 298.15 K.

Solute	log k
Acetic acid	1.319
Acetophenone	2.637
Aniline	2.956
Benzaldehyde	2.097
Benzene	-0.047
Benzonitrile	2.206
Benzyl alcohol	3.233
1-Bromooctane	0.952
1-Butanol	0.978
Butyraldehyde	0.236
2-Chloroaniline	2.952
1-Chlorooctane	0.694
p-Cresol	3.352
Cyclohexanol	1.863
Cyclohexanone	1.786
1,2-Dichlorobenzene	1.276
Ethyl Acetate	0.382
Ethyl benzene	0.601
Methyl Caproate	1.140
Naphthalene	2.431
1-Nitropropane	1.225
1-Octanol	2.153
Octylaldehyde	1.399
1-Pentanol	1.287
2-Pentanone	0.805
Ethyl phenyl ether	1.512
Phenol	3.054
Propionitrile	0.832
m-Xylene	0.658
o-Xylene	0.826
p-Xylene	0.654
2-Propanol	0.454
1-Bromohexane	0.349
Decyl alcohol	2.713

untreated glass column. The chromatographic experiments were performed at slightly higher temperatures of 50 °C, 80 °C and 110 °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 50 °C and 80 °C. The calculated log k values at 25 °C are tabulated in Table 2. The gas to liquid partition coefficient

can be obtained from isothermal chromatographic measurements through $K = V_N/V_L$ 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 [22] $k = (t_r - t_m)/t_m$ where t_r is the retention time of a solute and t_m is the 'void' retention time. Since $t_r - t_m$, 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,

$$K = P^* \cdot k \quad \text{or} \quad \log K = \log P^* + \log k. \quad (8)$$

To a first approximation, the proportionality constant, P^* , is the phase ratio and depends only on chromatographic conditions that should remain constant for a given column during the time the experimental measurements are performed. The proportionality constant used in conversion, $\log P^* = 2.415$ was the calculated average difference between the measured $\log k$ [21] and $\log K$ [13] data for 9 common compounds (benzene, 1-butanol, ethylbenzene, 1-nitropropane, 2-pentanone, o-xylene, m-xylene, p-xylene and 2-propanol) in the $\log k$ and $\log K$ data sets. The chromatographic retention factor data for the *tris*(pentafluoroethyl) trifluorophosphate ILs is not useable at the present time because thermodynamic $\log K$ data is not available for determining the phase ratio. The only [FAP]⁻ IL for which infinite dilution activity coefficient data has been reported for is 1-methyl-3-ethylimidazolium *tris*(pentafluoroethyl)trifluorophosphate ([MEIm]⁺[FAP]⁻) [23]. This was not one of the seven [FAP]⁻ ILs studied by the Anderson group.

In total our search of the published chemical literature found experimental gas-to-IL partition coefficients for 1790 solute-IL pairs and water-to-IL partition coefficients for 1760 solute-IL pairs. The experimental values, along with the solute descriptors for all of the compounds considered in the present study, are available upon request from the corresponding author. The solute descriptors are of experimental origin, and came from our solute descriptor database, which

now contains values for more than 4500 different organic, organometallic and inorganic compounds.

3. Results and Discussion

Several of the Abraham model correlations that we have for the individual ionic liquids were developed years ago when experimental data was much more limited. To provide better benchmark correlations we have reanalyzed the experimental $\log K$ and $\log P$ data for solutes dissolved in ([MEIm]⁺[(Tf)₂N]⁻), ([MBIm]⁺[(Tf)₂N]⁻), ([MHIm]⁺[(Tf)₂N]⁻), ([M₃BAm]⁺[(Tf)₂N]⁻), ([EtOHMIm]⁺[(Tf)₂N]⁻), ([MBIm]⁺[BF₄]⁻), and ([MBIm]⁺[PF₆]⁻) using the solvent-specific forms of the basic Abraham model

$$\log K = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + l \cdot L \quad (9)$$

$$\log P = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + v \cdot V \quad (10)$$

The calculated equation coefficients for the $\log K$ and $\log P$ correlations are listed in Tables 3 and 4, respectively. Standard errors in the coefficients are given in parenthesis below the respective coefficients. Here and elsewhere N corresponds to the number of data points, that is the number of solutes dissolved in the given IL, R^2 denotes the squared correlation coefficient, SD is the standard deviation and F corresponds to the Fisher's F statistic. All regression analyses were performed using the SPSS statistic software. The derived Abraham model correlations are statistically very good as evidenced by the small standard deviations and near unity values of squared correlation coefficient. The Abraham model was to describe the experimental gas-to-IL and water-to-IL

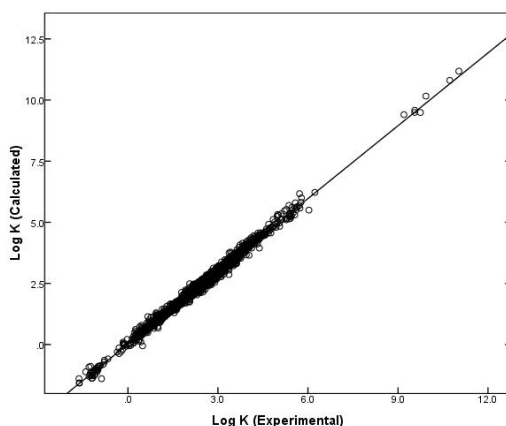


Figure 1. Comparison of experimental $\log K$ data to calculated values based on Equation 11.

Table 3. Abraham model correlation equation coefficients for the transfer of solutes from gas to the anhydrous (dry) ionic liquid solvents (log K correlation).

Solvent	c	e	s	a	b	l	N	SD	R ²	F
([M _B Im] ⁺ [BF ₄] ⁻)	-0.600 (0.026)	0.356 (0.075)	2.534 (0.068)	3.312 (0.100)	0.284 (0.074)	0.604 (0.011)	66	0.099	0.997	3481
([EtOHM _{Im}] ⁺ [(Tf) ₂ N] ⁻)	-0.793 (0.047)	0.139 (0.061)	2.404 (0.065)	2.587 (0.074)	1.353 (0.077)	0.581 (0.011)	81	0.100	0.993	2096
([M _B Im] ⁺ [PF ₆] ⁻)	-0.460 (0.033)	-0.191 (0.081)	2.747 (0.086)	2.228 (0.097)	0.363 (0.101)	0.663 (0.015)	91	0.154	0.994	3071
([M _B Im] ⁺ [(Tf) ₂ N] ⁻)	-0.394 (0.029)	0.089 (0.068)	1.969 (0.085)	2.283 (0.104)	0.873 (0.113)	0.696 (0.009)	104	0.111	0.994	5490
([M _H Im] ⁺ [(Tf) ₂ N] ⁻)	-0.348 (0.032)	-0.240 (0.102)	2.060 (0.102)	2.184 (0.136)	0.561 (0.113)	0.754 (0.010)	77	0.117	0.993	2021
([M _O Im] ⁺ [BF ₄] ⁻)	-0.409 (0.050)	-0.049 (0.115)	1.562 (0.135)	2.911 (0.125)	0.803 (0.155)	0.778 (0.013)	61	0.140	0.987	427.5
([M _E Im] ⁺ [(Tf) ₂ N] ⁻)	-0.486 (0.041)	0.068 (0.058)	2.296 (0.052)	2.278 (0.052)	0.988 (0.126)	0.651 (0.067)	65	0.094	0.996	3203
([M ₃ BA _m] ⁺ [(Tf) ₂ N] ⁻)	-0.457 (0.048)	0.000	2.188 (0.150)	2.375 (0.198)	0.663 (0.197)	0.668 (0.013)	58	0.120	0.990	990.5

Table 4. Abraham model correlation equation coefficients for the transfer of solutes from water to the anhydrous (dry) ionic liquid solvents (log P correlation).

Solvent	c	e	s	a	b	v	N	SD	R ²	F
([MBIm] ⁺ [BF ₄] ⁻)	-0.082 (0.049)	0.454 (0.092)	0.541 (0.095)	-0.427 (0.134)	-4.583 (0.099)	2.961 (0.057)	66	0.132	0.992	1403
([EtOHIm] ⁺ [(Tf) ₂ N] ⁻)	-0.402 (0.078)	0.304 (0.078)	0.470 (0.091)	-1.082 (0.099)	-3.510 (0.103)	2.977 (0.063)	79	0.133	0.990	1489
([MBIm] ⁺ [PF ₆] ⁻)	-0.056 (0.046)	0.193 (0.080)	0.737 (0.087)	-1.351 (0.100)	-4.526 (0.102)	3.109 (0.059)	86	0.154	0.988	1274
([MBIm] ⁺ [(Tf) ₂ N] ⁻)	-0.018 (0.044)	0.416 (0.084)	0.153 (0.105)	-1.312 (0.131)	-4.187 (0.139)	3.347 (0.039)	101	0.131	0.994	3033
([MHIm] ⁺ [(Tf) ₂ N] ⁻)	-0.065 (0.042)	0.010 (0.105)	0.260 (0.103)	-1.476 (0.135)	-4.313 (0.111)	3.587 (0.039)	75	0.115	0.996	3433
([MOIm] ⁺ [BF ₄] ⁻)	-0.115 (0.076)	0.210 (0.130)	0.000	-0.511 (0.143)	-4.338 (0.177)	3.617 (0.063)	59	0.159	0.994	1792
([MEIm] ⁺ [(Tf) ₂ N] ⁻)	0.029 (0.048)	0.351 (0.103)	0.202 (0.121)	-1.684 (0.163)	-3.585 (0.137)	3.059 (0.055)	64	0.119	0.993	1543
([M ₃ BAm] ⁺ [(Tf) ₂ N] ⁻)	0.047 (0.060)	-0.051 (0.133)	0.356 (0.154)	-1.262 (0.202)	-4.400 (0.198)	3.209 (0.049)	57	0.120	0.996	2484

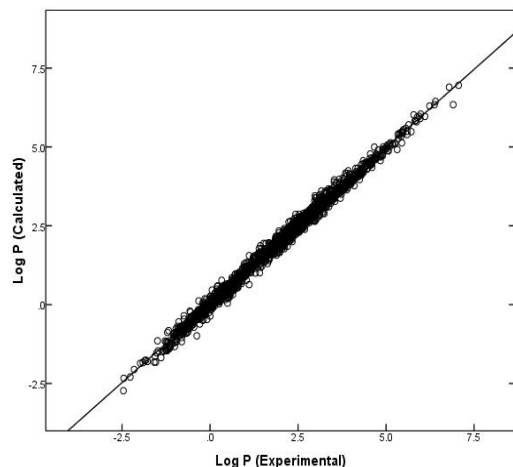


Figure 2. Comparison of experimental log P data to calculated values based on Equation 12.

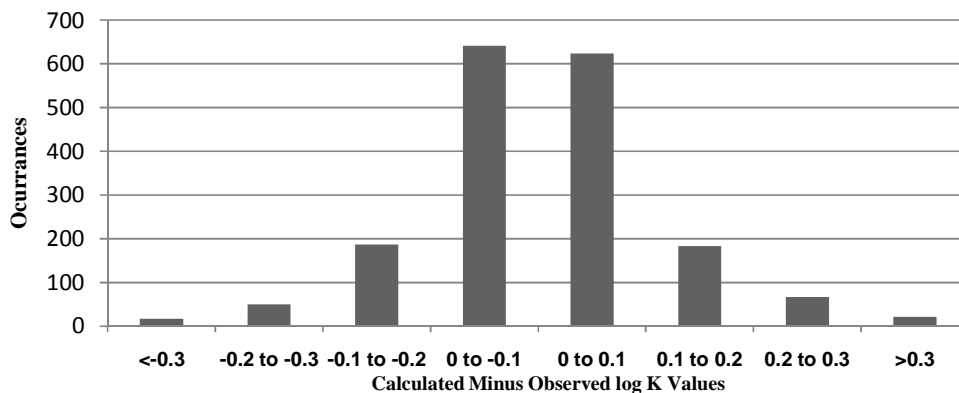


Figure 3. Differences between the experimental log K data and backcalculated values based on Eqn. 11.

partition coefficient to within overall standard deviations of 0.117 and 0.133 log units, respectively. The correlations reported in Tables 3 and 4 serve as the benchmark IL-specific correlations that will be used in determining how much predictive accuracy might be lost by splitting the equation coefficients into cation and anion contributions (present study), or into cation functional group values and anion values, as Revelli et al. [3] recently suggested.

Updated values of the cation-specific and anion-specific equation coefficients were determined by regression analysis of the 1790 log K values and 1760 log P values to yield the following LSERS

$$\begin{aligned} \log K = & \sum_{cation} (c_{cation} + e_{cation} E + s_{cation} S \\ & + a_{cation} A + b_{cation} B + l_{cation} L) \\ & + \sum_{anion} (c_{anion} + e_{anion} E + s_{anion} S \\ & + a_{anion} A + b_{anion} B + l_{anion} L) \end{aligned} \quad (11)$$

(N = 1790, R² = 0.998, R²_{adj} = 0.997, SD = 0.114, F = 6012)
and

$$\log P = \sum_{\text{cation}} (c_{\text{cation}} + e_{\text{cation}} E + s_{\text{cation}} S) + a_{\text{cation}} A + b_{\text{cation}} B + v_{\text{cation}} V + \sum_{\text{anion}} (c_{\text{anion}} + e_{\text{anion}} E + s_{\text{anion}} S) + a_{\text{anion}} A + b_{\text{anion}} B + v_{\text{anion}} V \quad (12)$$

(N = 1760, $R^2 = 0.997$, $R^2_{\text{adj}} = 0.996$, SD = 0.139, F = 2855). In accordance with the computational methodology that we recommended in our earlier papers [1-3] we have set all six anion-specific equation coefficients of $[(\text{Tf})_2\text{N}]^-$ equal to zero.

The calculated cation-specific and anion-specific equation coefficients for Eqns. 11 and 12 are listed in Tables 5 and 6, respectively. Reported for the first time equation coefficients for the diethylphosphate anion, $[\text{Et}_2\text{PO}_4]^-$. The standard errors in the coefficients again are given again in parenthesis directly below the respective values. For the most part, the larger standard errors are noted in the equation coefficients for those ions for which experimental data is limited. The number of data points for the individual ions ranges from a minimum of 31 log K values for the $[\text{NEP}]^+$, $[\text{HexdMIm}]^+$ and $[\text{MBPyrr}]^+$ cations to more than 795 log K values for the $[(\text{Tf})_2\text{N}]^-$ anion, which is sufficient for the regression analyses.

Both LSERs are statistically very good, and describe experimental log K and log P databases that cover a 12.5 log unit and 8.7 log unit range to within standard deviations of 0.114 log units (Eqn. 11) and 0.139 log units (Eqn. 12) as shown in Figures 1 and 2. Based on the

limited number of replicate independent activity coefficient measurements that have been performed for solutes dissolved in ILs we believe that 0.05 to 0.15 log units would be a reasonable guesstimate of the uncertainty associated with the experimental log K values. Slightly larger standard deviations are expected for the log P correlation which also includes the experimental uncertainties in the log K_w data used to convert the log K values to log P.

Careful examination of the individual residuals between the calculated and observed values revealed that Equation 11 described 70.7 % (1265 of 1790 values) of the gas-to-IL partition coefficient data to within 0.1 log units, 91.3 % (1635 of 1790 values) to within 0.2 log units, and 97.9 % (1752 of 1790 values) to within 0.3 log units of observed values. Only 2.1 % of the predicted log K values fell more than 0.3 log units from the experimental value, with the largest residual being -0.55 log units. The residual analysis is depicted graphically in Figure 3. Similar results were noted for Eqn. 12; 56.1 % of the back-calculated water-to-IL partition coefficients differed from the observed value by less than 0.1 log units, 85.9 % differed by less than 0.2 log units, and 95.6 % differed by less than 0.3 log units. Less than 4.4 % of the predicted log P values were more than 0.3 log units from the observed value (See Figure 4 for a graphical summary). The largest residual for the log P calculations is -0.61 log units. We expect these values would be reflect the predictive ability that Eqns. 11 and 12 would exhibit in terms of predicting partition coefficients for new compounds dissolved in ILs containing the 19 cations and 10 anions given in Tables 5 and 6, provided that the solute descriptors of the compounds fall within the area of predictive chemical space defined by the calculated

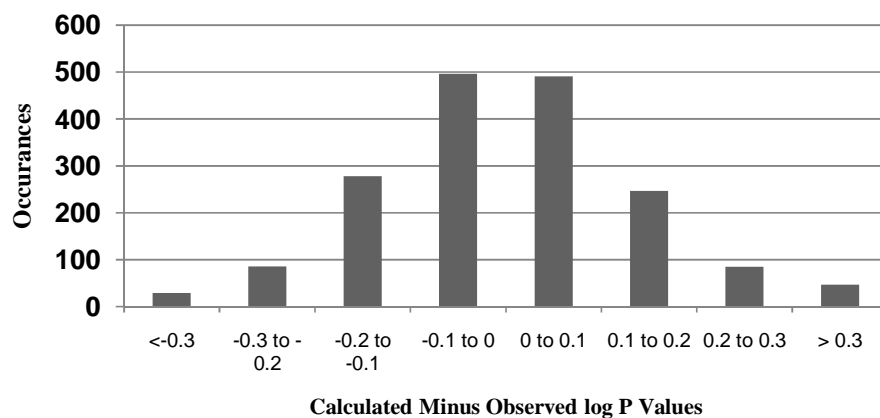


Figure 4. Differences between the experimental log P data and backcalculated values based on Eqn. 12.

equation coefficients. Predicted activity coefficients can be converted to infinite dilution activity coefficients, $\gamma_{\text{solute}}^{\infty}$, through Eqns. 5 – 7.

Revelli and coworkers [3] have extended the predictive applicability of the Abraham by further splitting the cation-specific equation coefficients into functional group values. Functional group values do allow one to make predictions for cations not listed in Tables 5 and 6. The contributions of Revelli and coworkers represent a significant advance in extending the basic Abraham model to IL solvents. The increased predictive applicability does come at the cost of perhaps slightly larger deviations. Revelli and coworkers noted in their statistical analysis of 1450 log K values that 12 residuals were in the 0.5 to 1.0 log unit range. One residual exceeded 1.0 log units. The authors needed equation coefficients for 21 groups - 12 functional groups characterizing the cations and 9 individual anions – to perform the 1450 log K predictions. In comparison, the ion-specific correlations that we developed for a much larger

database had only 4 residuals in the 0.5 to 1.0 log unit range, with the largest residual being 0.55 log units.

Figure 5 compares the mean absolute errors (MAE) of experimental versus calculated log K values based on our ion-specific equation coefficient model (Eqn. 11, dark blue) and the corresponding MAE values for the group contribution method of Revelli *et al.* (Eqn. 3, light blue) for 29 different ILs. The ion-specific equation coefficient model provides a slightly better mathematical description of the log K data as expected. The equation coefficients of Eqn. 11 are based on gas-to-liquid partition coefficient data for ILs containing the cation and anion in the given IL, rather than group values averaged across all cations. We suggest that when selecting a predictive model that the first choice by the IL-specific Abraham LSER if available, followed by the ion-specific Abraham LSER model, and then the Abraham group contribution-LSER

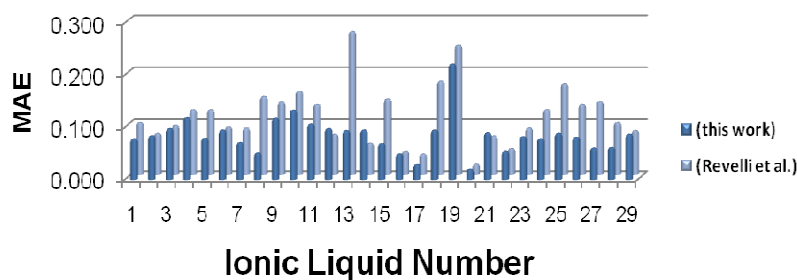


Figure 5. Summarized comparison of the mean absolute errors (MAE) for the experimental versus calculated log K values based on the ion-specific equation coefficient model (front dark blue) and on the group contribution method of Revelli *et al.* (back light blue). The ionic liquids are as follows: (1) is ([MBIm]⁺[(Tf)₂N]⁻); (2) is ([MHIm]⁺[(Tf)₂N]⁻); (3) is ([MOIm]⁺[BF₄]⁻); (4) is ([MBIm]⁺[PF₆]⁻); (5) is ([MBIm]⁺[BF₄]⁻); (6) is ([MEIm]⁺[EtSO₄]⁻); (7) is ([MEIm]⁺[(Tf)₂N]⁻); (8) is ([M₂EIm]⁺[(Tf)₂N]⁻); (9) is ([MHIm]⁺[BF₄]⁻); (10) is ([MEIm]⁺[BF₄]⁻); (11) is ([MHIm]⁺[PF₆]⁻); (12) is ([MBIm]⁺[OtSO₄]⁻); (13) is ([PM₂Im]⁺[BF₄]⁻); (14) is ([MEIm]⁺[SCN]⁻); (15) is ([MEIm]⁺[Trif]⁻); (16) is ([MEIm]⁺[F₃Ac]⁻); (17) is ([MHIm]⁺[Trif]⁻); (18) is ([MOIm]⁺[PF₆]⁻); (19) is ([MEIm]⁺[OtSO₄]⁻); (20) is ([MBIm]⁺[F₃Ac]⁻); (21) is ([EtOHMIm]⁺[(Tf)₂N]⁻); (22) is ([MeoeMIm]⁺[(Tf)₂N]⁻); (23) is ([MEIm]⁺[C(CN)₂]⁻); (24) is ([M₃BAm]⁺[(Tf)₂N]⁻); (25) is ([HexM₃Am]⁺[(Tf)₂N]⁻); (26) is ([BMPy]⁺[(Tf)₂N]⁻); (27) is ([NEPy]⁺[(Tf)₂N]⁻); (28) is ([BMPy]⁺[BF₄]⁻); and (29) is ([H₃TdP]⁺[(Tf)₂N]⁻).

Table 5. Cation-specific and anion-specific equation coefficients for the Abraham model gas-to-RTIL correlation (Eqn.11).

Ion ^a	c _{ion}	e _{ion}	s _{ion}	a _{ion}	b _{ion}	l _{ion}
CATIONS						
[MEIm] ⁺ (N=347) ^b	-0.505 (0.026)	0.090 (0.076)	2.409 (0.090)	2.327 (0.117)	0.903 (0.102)	0.644 (0.009)
[BmIm] ⁺ (N=402)	-0.414 (0.023)	0.063 (0.053)	2.076 (0.062)	2.284 (0.078)	0.764 (0.078)	0.701 (0.007)
[MHIm] ⁺ (N=154)	-0.339 (0.028)	-0.169 (0.081)	2.046 (0.095)	2.038 (0.113)	0.479 (0.102)	0.762 (0.009)
[MOIm] ⁺ (N=114)	-0.233 (0.033)	-0.245 (0.091)	1.293 (0.115)	1.811 (0.109)	1.148 (0.128)	0.837 (0.010)
[M ₃ BAm] ⁺ (N=58)	-0.457 (0.045)	-0.005 (0.124)	2.188 (0.142)	2.375 (0.188)	0.663 (0.187)	0.668 (0.012)
[M ₂ EIm] ⁺ (N=39)	-0.611 (0.073)	0.188 (0.136)	2.380 (0.143)	2.101 (0.177)	0.899 (0.139)	0.667 (0.022)
[BMPy] ⁺ (N=76)	-0.480 (0.055)	0.142 (0.116)	2.292 (0.134)	2.365 (0.139)	0.673 (0.122)	0.713 (0.017)
[NEP] ⁺ (N=31)	-0.668 (0.077)	0.246 (0.194)	2.399 (0.182)	2.403 (0.211)	0.936 (0.152)	0.672 (0.029)
[PM ₂ Im] ⁺ (N=34)	-0.827 (0.121)	0.781 (0.171)	2.358 (0.198)	3.435 (0.230)	0.929 (0.209)	0.526 (0.036)
[HexM ₃ Am] ⁺ (N=50)	-0.459 (0.084)	-0.039 (0.103)	2.096 (0.096)	2.021 (0.139)	0.624 (0.102)	0.684 (0.020)
[HexdMIm] ⁺ (N=31)	0.014 (0.143)	-0.451 (0.159)	0.822 (0.167)	1.813 (0.248)	0.526 (0.189)	0.998 (0.044)
[HxomMIm] ⁺ (N=34)	-0.463 (0.110)	-0.394 (0.214)	2.478 (0.269)	2.428 (0.210)	0.337 (0.225)	0.786 (0.031)
[(Hxom) ₂ Im] ⁺ (N=34)	-0.314 (0.110)	-0.479 (0.215)	2.076 (0.275)	2.376 (0.207)	0.287 (0.219)	0.835 (0.033)
[(Meo) ₂ Im] ⁺ (N=48)	-0.762 (0.084)	-0.013 (0.105)	2.557 (0.097)	2.427 (0.142)	1.154 (0.103)	0.584 (0.020)
[EtOHMIm] ⁺ (N=151)	-0.845 (0.040)	0.097 (0.060)	2.438 (0.063)	2.685 (0.074)	1.403 (0.074)	0.578 (0.010)
[H ₃ TdP] ⁺ (N=59)	-0.406 (0.058)	-0.576 (0.125)	1.602 (0.127)	2.338 (0.158)	-0.009 (0.149)	0.959 (0.019)
[MeoeMIm] ⁺ (N=52)	-0.507 (0.079)	-0.015 (0.101)	2.644 (0.095)	2.378 (0.136)	0.413 (0.101)	0.602 (0.019)

[BMPyrr] ⁺	-0.609	-0.074	2.689	2.386	0.590	0.720
(N=31)	(0.110)	(0.215)	(0.275)	(0.207)	(0.219)	(0.033)
[CNPrMIm] ⁺	-1.106	0.147	2.665	2.444	1.167	0.693
(N=45)	(0.111)	(0.158)	(0.161)	(0.220)	(0.179)	(0.029)
ANIONS						
[(Tf) ₂ N] ⁻	0.000	0.000	0.000	0.000	0.000	0.000
(N=797)						
[BF ₄] ⁻	-0.198	0.216	0.369	1.090	-0.411	-0.068
(N=306)	(0.027)	(0.067)	(0.074)	(0.092)	(0.086)	(0.009)
[PF ₆] ⁻	-0.027	-0.181	0.645	0.003	-0.362	-0.087
(N=169)	(0.029)	(0.068)	(0.075)	(0.091)	(0.093)	(0.010)
[EtSO ₄] ⁻	-0.172	-0.074	0.135	2.987	-0.890	-0.057
(N=53)	(0.063)	(0.145)	(0.164)	(0.209)	(0.191)	(0.017)
[Trif] ⁻	-0.295	0.026	0.327	1.689	-0.324	0.011
(N=127)	(0.046)	(0.115)	(0.134)	(0.150)	(0.130)	(0.015)
[F ₃ Ac] ⁻	-0.295	-0.224	0.500	3.189	-0.353	0.023
(N=32)	(0.056)	(0.236)	(0.347)	(0.691)	(0.733)	(0.019)
[OtSO ₄] ⁻	0.275	-0.241	-0.153	2.409	-1.023	0.123
(N=58)	(0.073)	(0.100)	(0.118)	(0.177)	(0.158)	(0.019)
[SCN] ⁻	-0.718	0.282	0.787	2.601	-0.299	-0.008
(N=91)	(0.070)	(0.154)	(0.204)	(0.155)	(0.169)	(0.020)
[C(CN) ₂] ⁻	-0.383	0.271	0.424	2.363	-0.539	-0.049
(N=119)	(0.064)	(0.115)	(0.120)	(0.160)	(0.129)	(0.018)
[E ₂ PO ₄] ⁻	0.092	0.106	-0.172	5.125	-0.994	0.070
(N=38)	(0.106)	(0.177)	(0.184)	(0.242)	(0.187)	(0.035)

^a Cation and anion abbreviations are given in Table 1.

^b Number of experimental data points associated with the specified ion.

Table 6. Cation-specific and anion-specific equation coefficients for the Abraham Model water-to-RTIL correlation (Eqn.12).

Ion ^a	c _{ion}	e _{ion}	S _{ion}	a _{ion}	b _{ion}	V _{ion}
CATIONS						
[MEIm] ⁺ (N=342) ^b	-0.032 (0.044)	0.208 (0.092)	0.519 (0.113)	-1.388 (0.145)	-3.957 (0.125)	3.120 (0.046)
[BmIm] ⁺ (N=392)	-0.037 (0.036)	0.449 (0.065)	0.182 (0.078)	-1.394 (0.098)	-4.154 (0.097)	3.338 (0.034)
[MHIm] ⁺ (N=152)	-0.038 (0.046)	0.197 (0.100)	0.198 (0.116)	-1.303 (0.139)	-4.427 (0.124)	3.603 (0.041)
[MOIm] ⁺ (N=112)	-0.016 (0.055)	0.013 (0.110)	-0.152 (0.141)	-1.640 (0.135)	-3.975 (0.157)	3.875 (0.051)
[M ₃ BAm] ⁺ (N=57)	0.047 (0.070)	-0.051 (0.153)	0.356 (0.178)	-1.262 (0.233)	-4.400 (0.228)	3.209 (0.057)
[M ₂ EIm] ⁺ (N=39)	-0.095 (0.115)	0.292 (0.156)	0.443 (0.187)	-1.681 (0.224)	-4.024 (0.172)	3.174 (0.103)
[BMPy] ⁺ (N=76)	-0.129 (0.085)	0.210 (0.131)	0.588 (0.167)	-1.349 (0.173)	-4.278 (0.149)	3.434 (0.078)
[NEP] ⁺ (N=31)	-0.322 (0.130)	0.323 (0.219)	0.552 (0.228)	-1.234 (0.269)	-3.951 (0.186)	3.370 (0.138)
[PM ₂ Im] ⁺ (N=34)	-0.505 (0.171)	0.690 (0.190)	0.566 (0.253)	-0.238 (0.280)	-3.999 (0.254)	2.910 (0.149)
[HexM ₃ Am] ⁺ (N=48)	-0.278 (0.139)	0.013 (0.127)	0.401 (0.129)	-1.476 (0.176)	-4.315 (0.123)	3.512 (0.111)
[HexdMIm] ⁺ (N=31)	0.161 (0.209)	-0.214 (0.179)	-0.449 (0.223)	-1.884 (0.306)	-4.589 (0.231)	4.463 (0.187)
[HxomMIm] ⁺ (N=34)	-0.039 (0.163)	-0.645 (0.250)	1.184 (0.332)	-1.374 (0.251)	-4.779 (0.272)	3.609 (0.140)
[(Hxom) ₂ Im] ⁺ (N=34)	0.107 (0.161)	-0.628 (0.252)	0.747 (0.331)	-1.441 (0.252)	-4.808 (0.272)	3.750 (0.140)
[(Meo) ₂ Im] ⁺ (N=34)	-0.412 (0.140)	-0.104 (0.129)	0.761 (0.130)	-1.124 (0.180)	-3.776 (0.124)	3.055 (0.112)
[EtOHMIm] ⁺ (N=148)	-0.407 (0.061)	0.229 (0.070)	0.517 (0.080)	-1.029 (0.092)	-3.491 (0.091)	2.933 (0.052)
[H ₃ TdP] ⁺ (N=59)	-0.155 (0.093)	-0.164 (0.148)	-0.055 (0.154)	-1.317 (0.189)	-4.985 (0.168)	4.250 (0.086)
[MeoeMIm] ⁺	-0.166	0.014	0.658	-1.282	-4.262	3.125

(N=50)	(0.129)	(0.026)	(0.126)	(0.171)	(0.122)	(0.102)
[BMPyrr] ⁺	-0.198	-0.748	2.179	-1.424	-5.021	3.431
(N=31)	(0.183)	(0.369)	(0.481)	(0.351)	(0.358)	(0.162)
[CNPrMIm] ⁺	-0.591	0.228	0.688	-1.463	-3.454	3.253
(N=44)	(0.177)	(0.192)	(0.208)	(0.275)	(0.218)	(0.147)
ANIONS						
[(Tf) ₂ N] ⁻	0.000	0.000	0.000	0.000	0.000	0.000
(N=780)						
[BF ₄] ⁻	-0.078	0.124	0.241	1.107	-0.409	-0.298
(N=304)	(0.044)	(0.079)	(0.093)	(0.114)	(0.106)	(0.043)
[PF ₆] ⁻	0.010	-0.299	0.542	0.085	-0.323	-0.272
(N=164)	(0.048)	(0.082)	(0.095)	(0.115)	(0.114)	(0.048)
[EtSO ₄] ⁻	-0.047	-0.230	0.035	2.879	-0.987	-0.225
(N=53)	(0.095)	(0.174)	(0.205)	(0.258)	(0.234)	(0.078)
[Trif] ⁻	-0.190	-0.343	0.512	1.503	-0.303	-0.045
(N=126)	(0.074)	(0.134)	(0.166)	(0.186)	(0.159)	(0.070)
[F ₃ Ac] ⁻	-0.287	-0.824	0.915	2.206	0.292	0.075
(N=32)	(0.093)	(0.266)	(0.420)	(0.843)	(0.892)	(0.096)
[OtSO ₄] ⁻	0.000	-0.261	0.000	2.531	-1.008	0.672
(N=56)		(0.121)		(0.249)	(0.201)	(0.109)
[SCN] ⁻	-0.557	-0.761	1.880	2.381	-0.851	-0.124
(N=91)	(0.104)	(0.188)	(0.247)	(0.191)	(0.209)	(0.189)
[C(CN) ₂] ⁻	-0.291	0.122	0.386	2.316	-0.579	-0.224
(N=116)	(0.105)	(0.139)	(0.155)	(0.201)	(0.158)	(0.093)
[E ₂ PO ₄] ⁻	0.054	0.080	-0.085	5.183	-1.084	0.227
(N=38)	(0.162)	(0.192)	(0.239)	(0.300)	(0.229)	(0.154)

^a Cation and anion abbreviations are given in Table 1.

^b Number of experimental data points associated with the specified ion.

(GC-LSER) model. For many ILs the GC-LSER model will be the only option available at the present time.

While we have determined 174 ion-specific equation coefficients, each calculation uses only the values for the cation and anion in the given RTIL. For example, the correlation equations used to calculate the log K values for 1-methyl-3-butylimidazolium hexafluorophosphate ([MBIm]⁺[PF₆]⁻) ionic liquid would be

$$\text{Log K} = -0.441 - 0.118 \text{ E} + 2.721 \text{ S} + 2.287 \text{ A} + 0.402 \text{ B} + 0.614 \text{ L} \quad (13)$$

constructed from the [MBIm]⁺-specific and [PF₆]⁻-specific equation coefficients given in Table 5. The resulting correlations are in good agreement with the benchmark RTIL-specific correlation equation

$$\text{Log K} = -0.460 - 0.191 \text{ E} + 2.747 \text{ S} + 2.228 \text{ A} + 0.363 \text{ B} + 0.663 \text{ L} \quad (14)$$

that was determined by regression analysis of the

log K data for solutes dissolved in just ([MBIm]⁺[PF₆]⁻). Both correlations have nearly identical standard deviations, SD = 0.154 for Eqn. 13 versus SD = 0.161 for Eqn. 14. Solute in the ([MBIm]⁺[PF₆]⁻) data set cover approximately the same area of chemical space as the entire RTIL database that was used in determining the ion-specific equation coefficients. Similar results were noted for the other seven “benchmark” ionic liquid correlations reported in Tables 5 and 6. Very little (if any) descriptive ability was lost by splitting the Abraham model equation coefficients into cation-specific and anion-specific values.

In order to assess the predictive ability of Eqns. 11 and 12 we divided the data points into a training set and a test set by selecting every other data point in each of the two large databases. This selection method insured that

Table 7. Experimental gas-to-IL (log K) and water-to-IL (log P) partition coefficients for solutes dissolved in 1-methyl-3-ethylimidazolium *tris*(pentafluoroethyl)trifluorophosphate, ([MEIm]⁺[FAP]⁻) at 298.15 K.

Solute	log K	log P
Pentane	1.238	2.938
Hexane	1.397	3.217
Heptane	1.633	3.593
Octane	1.931	4.041
Nonane	2.297	4.447
Cyclohexane	1.643	2.543
Methylcyclohexane	1.819	3.069
1-Hexene	1.528	2.688
1-Octene	2.129	3.539
1-Decene	2.873	4.513
1-Pentyne	1.636	1.646
1-Hexyne	1.919	2.129
1-Heptyne	2.357	2.797
1-Octyne	2.606	3.126
Benzene	2.778	2.148
Toluene	3.142	2.492
Ethylbenzene	3.418	2.838
o-Xylene	3.631	2.971
m-Xylene	3.500	2.890
p-Xylene	3.465	2.875
Methanol	2.110	-1.630
Ethanol	2.345	-1.325
1-Propanol	2.665	-0.895

Table 8. Experimental gas-to-IL (log K) and water-to-IL (log P) partition coefficients for solutes dissolved in 1-methyl-3-ethylimidazolium tetracyanoborate, ([MEIm]⁺[B(CN)₄]⁻) at 298.15 K.

Solute	Log K	Log P
Pentane	1.254	2.954
Hexane	1.465	3.285
Heptane	1.739	3.699
Octane	2.060	4.170
Nonane	2.414	4.564
Cyclohexane	1.850	2.750
Methylcyclohexane	2.002	3.252
1-Hexene	1.655	2.815
1-Octene	2.216	3.626
1-Decene	2.979	4.619
1-Pentyne	1.928	1.938
1-Hexyne	2.248	2.458
1-Heptyne	2.689	3.129
1-Octyne	2.922	3.442
Benzene	2.925	2.295
Toluene	3.289	2.639
Ethylbenzene	3.560	2.980
o-Xylene	3.802	3.142
m-Xylene	3.631	3.021
p-Xylene	3.634	3.044
Methanol	2.839	-0.901
Ethanol	3.004	-0.666
1-Propanol	3.340	-0.220

each cation and anion were equally represented in both the training set and test set. The selected data points became the training sets and the remaining compounds that were left served as the test sets. The experimental data in the log K and log P training sets were analyzed in accordance with the ion-specific version of the Abraham general solvation model. The derived training set equations were then used to predict the respective partition coefficients for the compounds in the test sets. To conserve journal space only the test set calculations are presented. For the predicted and experimental values, we found SD = 0.131 (Eqn. 11) and SD = 0.168 (Eqn. 12), AAE (average absolute error) = 0.094 (Eqn. 11) and AAE = 0.126 (Eqn. 12), and AE (average error) = -0.006 (Eqn. 11) and AE = 0.001 (Eqn. 12). There is therefore very little bias in using Eqns. 11 and 12 with AE equal to -0.006 and 0.001 log units. The training and test set analyses were performed two more times with similar results by

SPSS software to randomly select half of the experimental data points.

The list of ion-specific equation coefficients that we have calculated in the present study can be easily increased to include more cations/anions as additional experimental data for solutes dissolved in ILs becomes available. As noted above there are limited activity coefficient data for 23 organic solutes dissolved in 1-methyl-3-ethylimidazolium *tris*(pentafluoroethyl) trifluoro-phosphate, ([MEIm]⁺[FAP]⁻) [23]. Normally this is not a sufficient number of experimental data points to develop a meaningful IL-specific Abraham LSER model. The number is sufficient, however, for us to illustrate a simple computation methodology for calculating equation coefficients for new cations/anions that does not significantly change the values that have already been calculated. It is not feasible to reanalyze the large log K and log P databases every time that one wishes to add one more cation/anion to the list. The experimental $\gamma_{\text{solute}}^{\infty}$

values measured by Yan and coworkers have been converted to log K and log P values through Eqns. 5 – 7. The resulting numerical values (see Table 7) were then regressed to yield

$$\text{Log K} = -0.271(0.084) - 0.605(0.250) \text{ E} + 3.031(0.325) \text{ S} + 0.161(0.450) \text{ A} + 1.082(0.416) \text{ B} + 0.616(0.025) \text{ L} \quad (15)$$

(N = 23, SD = 0.056, R² = 0.994, F = 568.8) and

$$\text{Log P} = 0.376(0.198) - 1.294(0.475) \text{ E} + 2.048(0.595) \text{ S} - 3.649(0.803) \text{ A} - 4.428(0.753) \text{ B} + 2.918(0.176) \text{ V} \quad (16)$$

(N = 23, SD = 0.099, R² = 0.996, F = 846.6)

The predictive ability of Eqns. 15 and 16 was assessed with the “leave-one-out” method. One solute was left out of the regression analysis and its log K (or log P) value predicted with the derived correlation. The solute was then returned to the dataset, another solute removed and a new regression performed. The method was repeated until every solute had been eliminated once. The 23 residuals, one from each of the 23 regression equations, were then averaged to give an average deviation of AD = 0.070 log units (Eqn. 15) and AD = 0.145 log units (Eqn. 16), which we believe is the best indication of the predictive ability of each equation given the limited number of experimental data points. The ion-specific equation coefficients for the [FAP]⁻ anion is obtained by subtracting the cation-specific values for [MEIm]⁺ in Tables 5 and 6 from their respective IL-specific counterpart. For the log K correlation, the anion-specific values for [FAP]⁻ are: c_{FAP} = -0.776; e_{FAP} = -0.695; s_{FAP} = 0.622; a_{FAP} = -2.166; b_{FAP} = 0.179; and l_{FAP} = -0.028. For the log P correlation, the anion-specific values for [FAP]⁻ are: c_{FAP} = 0.408; e_{FAP} = -1.502; s_{FAP} = 1.529; a_{FAP} = -2.261; b_{FAP} = -0.471; and v_{FAP} = -0.202.

Infinite dilution activity coefficient data were also found for 23 solutes in 1-methyl-3-ethylimidazolium tetracyanoborate ([MEIm]⁺[B(CN)₄]⁻) [24]. The gas-to-IL and water-to-IL partition coefficients calculated from the published $\gamma_{\text{solute}}^{\infty}$ values are compiled in Table 8. Analysis of the log K and log P data

$$\text{Log K} = -0.258(0.066) - 0.297(0.198) \text{ E} + 2.866(0.257) \text{ S} + 2.300(0.356) \text{ A} + 0.650(0.329) \text{ B} + 0.646(0.020) \text{ L} \quad (17)$$

(N = 23, SD = 0.045, R² = 0.998, F = 995.4) and

$$\text{Log P} = 0.309(0.150) - 0.859(0.395) \text{ E} + 1.749(0.489) \text{ S} - 1.526(0.673) \text{ A} - 4.687(0.609) \text{ B} + 3.080(0.129) \text{ V} \quad (18)$$

(N = 23, SD = 0.083, R² = 0.997, F = 1034.7)

The derived correlations were validated using the “leave-one-out” method. The calculated average deviations were SD = 0.058 (Eqn. 17) and SD = 0.121 (Eqn. 18). The ion-specific equation coefficients for the [B(CN)₄]⁻ anion is obtained by subtracting the cation-specific values for [MEIm]⁺ in Tables 5 and 6 from their respective IL-specific counterpart. For the log K correlation, the anion-specific values for [B(CN)₄]⁻ are: c_{B(CN)₄} = 0.247; e_{B(CN)₄} = -0.387; s_{B(CN)₄} = 0.457; a_{B(CN)₄} = -0.027; b_{B(CN)₄} = -0.253; and l_{B(CN)₄} = 0.002. For the log P correlation, the anion-specific values for [B(CN)₄]⁻ are: c_{B(CN)₄} = 0.341; e_{B(CN)₄} = -1.067; s_{B(CN)₄} = 1.230; a_{B(CN)₄} = -0.138; b_{B(CN)₄} = -0.730; and v_{B(CN)₄} = -0.040. The preliminary values for these latter two anions, [FAP]⁻ and [B(CN)₄]⁻, will be refined when more experimental activity coefficient and gas solubility data becomes available.

4. Conclusions

The specific-ion equation coefficient version of the Abraham model has been shown to provide a reasonably accurate mathematical description of the thermodynamic properties for solute transfer into ILs from both water and the gas phase. The 19 cation-specific and 12 anion-specific equation coefficients that have been reported in the present study will allow one to predict infinite dilution activity coefficients and gas solubilities at 298 K in the 228 different ILs comprised of these cation-anion combinations. Ion-specific equation coefficients [25] have been computed for several cations and anions that permit one to project estimated log K and log P values to temperatures not too far removed from 298 K. The popularity of ILs as solvent media for chemical separations continues to grow. New ionic liquids continue to be synthesized in response to the growing industrial demand for these rather novel liquid organic compounds. The ion-specific equation coefficient of the Abraham model discussed here, as well as the recently proposed group contribution extension of the model proposed by Revelli and coworkers [3] for ILs and Sprunger *et al.* [14] for alcohol solvents, provides a convenient method for estimating solute properties in the newly synthesized ILs.

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