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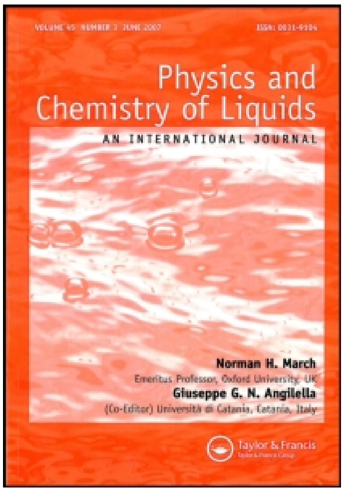

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Partition coefficient correlations for transfer of solutes from gas phase and water to room temperature ionic liquids

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Gas-to-room temperature ionic liquid (RTIL) and water-to-RTIL partition coefficients have been calculated for a series of solutes from published experimental infinite dilution activity coefficient data. The calculated partition coefficients are correlated with the Abraham solvation parameter model. The derived correlations are able to describe the gas-to-RTIL partitioning behavior and infinite dilution activity coefficients of organic and gaseous solutes in 1-methyl-3-ethylimidazolium ethylsulfate and 1-butyl-3-methylimidazolium tetrafluoroborate to better than 0.11 log units.

Keywords: Activity coefficient; Room temperature ionic liquids; Partition coefficient

1. Introduction

Room temperature ionic liquids (RTILs) are ionic organic compounds that are liquid at ambient room temperature. The majority of RTILs reported thus far can be classified as combinations of weak Lewis-acidic organic cations and weak Lewis-basic anions. Anions may be either inorganic (i.e. PF_6^-, BF_4^-) or organic (i.e. $(Tf)_2N^-$, $CH_3CH_2SO_4^-$) negatively charged ions. Synthetic procedures are known for preparing more than 200 RTILs. Novel analytical and synthetic applications involving RTILs are rapidly emerging. Ionic liquids have been employed as gas chromatographic stationary phases in numerous chemical separations [1–3], and most (if not all) of the named synthetic methods have been performed in RTILs [4–6].

The thermodynamic and solubilizing properties of RTILs depend on the polarity and dispersive forces, and the hydrogen-bonding and ionic character of both the large cation (alkylimidazolium, alkylpyridinium, alkylphosphonium, quaternary ammonium) and ionic anion bearing the negative charge. The ionic nature in the liquid state contributes to the ionic salt's relatively low vapor pressure at ambient room temperature.

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Numerous spectroscopic studies have been published probing solute and solvent interactions in neat RTILs and binary RTIL mixtures. Spectroscopic studies employ a probe molecule whose fluorescence and/or absorption spectrum depends on the properties of the surrounding solvent media. While probe studies have provided some information regarding probe interactions with the different RTILs, our understanding has not reached the point where a solute molecule's activity coefficient in a given RTIL can be predicted from measured spectroscopic probe data. Activity coefficients represent a quantitative measure of solute solubilizations.

Several recent articles have reported equations for correlating and predicting infinite dilution activity coefficients of solutes dissolved in RTILs. For example, Tämm and Burk [7] correlated activity coefficients of 38 solutes in 4-butyl-N-methylpyridinium tetrafluoroborate ($[\mathrm{BMPy}]^+[\mathrm{BF}_4]^-$), 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide ($[\mathrm{MEIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$) and 1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide ($[\mathrm{M}_2\mathrm{EIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$) with molecular descriptors obtained using CODESSA PRO software. The authors' three-parameter correlations described the experimental data to within standard errors ranging from SE = 0.30 to 0.35 log units. Training and test set validation analyses on the 38 experimental data points indicated an average predicting quality of SE = 0.365. Lee [8] analyzed solvation in ionic liquids using various linear free energy relationships. One of the models considered was the Abraham solvation parameter equation. The equation Lee [8] reported for ($[\mathrm{MEIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$) is:

$$\Delta G\,(\mathrm{kJ\,mol^{-1}}) = RT\ln\gamma^{\infty}_{\mathrm{solute}} = 1.48 - 2.42\mathbf{E} - 6.45\mathbf{S} + 6.69\mathbf{A} - 6.11\mathbf{B} + 6.94\mathbf{V}$$
$$N = 38,\ R = 0.9765 \text{ and } \mathrm{SD} = 0.766 \qquad (1)$$

The dependent variable in equation (1) is what Lee called the free energy of transfer, ΔG. The independent variables, or descriptors, are solute properties as follows: **E** and **S** refer to the excess molar refraction and dipolarity/polarity descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and hydrogen-bond basicity, and **V** is the McGowan volume of the solute. While the statistics of equation (1) are quite good (correlation coefficient of $R = 0.9765$ and a standard deviation of $\mathrm{SD} = 0.766\,\mathrm{kJ\,mol^{-1}}$ for 38 data points), Lee noted that the negative basicity contribution for an ionic liquid is unrealistic. Acree and Abraham [9] subsequently showed Lee's application of the Abraham model to be incorrect. When correctly applied the Abraham model did give realistic values for all equation coefficients.

As an informational note, the infinite dilution activity coefficient data for ($[\mathrm{MEIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$) and ($[\mathrm{M}_2\mathrm{EIm}]^+[(\mathrm{Tf})_2\mathrm{N}]^-$) used by both Tämm and Burk [7] and Lee [8] came from the same cited reference. Tämm and Burk correlated the experimental data at 313 and 343 K; whereas Lee used the values at 298 K obtained through thermodynamic extrapolation of the data measured at the slightly higher temperatures. Expressed in terms of infinite dilution activity coefficients, the standard deviation of equation (1) is SD = 0.154 log units, which is better than the predictive ability of the CODESSA PRO descriptor correlations reported by Tämm and Burk. Correct application of the Abraham model gave even a better predictive expression, which was capable of describing the 298 K infinite dilution activity coefficient data to a standard deviation of SD = 0.068 [9].

To date we have derived mathematical correlations based on the Abraham model for the gas-to-solvent, *K*, and water-to-solvent partition coefficients, *P*, for eight different anhydrous RTILs [9,10] and for two practical water-to-RTIL partitioning systems [11]. The eight anhydrous water-to-RTIL correlations describe "hypothetical" partitions, and the partition coefficient is calculated as a molar solubility ratio. Hypothetical partitions differ from "practical" partitions in that both the organic and aqueous phases do not contain the second solvent. Practical partitions, on the other hand, describe the equilibrium distribution of the solute between the water-saturated organic phase and an aqueous phase that is saturated with the organic solvent. In the present communication, we extend our earlier studies on RTILs to include 1-methyl-3-ethylimidazolium ethylsulfate ($[\mathrm{MEIm}]^+[\mathrm{EtSO_4}]^-$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($[\mathrm{BMIm}]^+[\mathrm{BF_4}]^-$). Abraham model correlations have been derived for the two aforementioned RTILs based on published infinite dilution activity coefficient and solubility data for dissolved organic and gaseous solutes.

2. Experimental method

The Abraham model method [12–19] of correlation relies on two linear free energy relationships, one for processes within condensed phases

$$\mathrm{SP} = c + e\cdot\mathbf{E} + s\cdot\mathbf{S} + a\cdot\mathbf{A} + b\cdot\mathbf{B} + v\cdot\mathbf{V} \tag{2}$$

and one for the processes involving gas to condensed phase transfer.

$$\mathrm{SP} = c + e\cdot\mathbf{E} + s\cdot\mathbf{S} + a\cdot\mathbf{A} + b\cdot\mathbf{B} + l\cdot\mathbf{L} \tag{3}$$

The dependent variable, SP, is some property of a series of solutes in a fixed phase. The independent variables or descriptors, are solute properties that remain constant unchanged irrespective of what process is being described. Molecular descriptors for all of the compounds considered in the present study are tabulated in table 1. The tabulated values of a few compounds may differ slightly from values found in much earlier publications. The numerical values are periodically updated as additional experimental data becomes available. Our solute descriptor database contains values for more than 4000 different organic and organometallic compounds. The descriptor values were calculated in accordance with our published computational methodology [20–25]. The characteristic McGowan volume, **V**, is calculated from the individual atomic sizes and numbers of bonds in the molecule [20]. For liquid solutes, the excess refraction descriptor, **E**, is calculated from the liquid refractive index [21]. In the case of solid solutes, one either estimates a hypothetical liquid refractive index using any of several available methods, or one can calculate **E** directly through addition of fragments or substructures. Numerical values of the three remaining descriptors, **S**, **A** and **B**, are determined through regression analysis using available organic solvent/water partition coefficients, chromatographic retention data, solubilities and infinite dilution activity coefficients as described elsewhere [22–25].

Most of the experimental data that we were able to retrieve from the published literature [26–30] pertained to the infinite dilution activity coefficient, $\gamma^{\infty}_{\mathrm{solute}}$, for solutes dissolved in RTILs. In order to apply Abraham model the infinite dilution activity

Table 1. Molecular solute descriptors of the compounds considered in the present study.

Solute	**E**	**S**	**A**	**B**	**V**	**L**
Argon	0.000	0.000	0.000	0.000	0.191	−0.688
Hydrogen	0.000	0.000	0.000	0.000	0.109	−1.200
Nitrogen	0.000	0.000	0.000	0.000	0.222	−0.978
Oxygen	0.000	0.000	0.000	0.000	0.183	−0.723
Carbon monoxide	0.000	0.000	0.000	0.040	0.222	−0.836
Carbon dioxide	0.000	0.280	0.050	0.100	0.281	0.058
Methane	0.000	0.000	0.000	0.000	0.250	−0.323
Ethane	0.000	0.000	0.000	0.000	0.390	0.492
Pentane	0.000	0.000	0.000	0.000	0.813	2.162
Hexane	0.000	0.000	0.000	0.000	0.954	2.668
Heptane	0.000	0.000	0.000	0.000	1.095	3.173
Octane	0.000	0.000	0.000	0.000	1.236	3.677
Nonane	0.000	0.000	0.000	0.000	1.377	4.182
Decane	0.000	0.000	0.000	0.000	1.518	4.686
Undecane	0.000	0.000	0.000	0.000	1.659	5.191
Dodecane	0.000	0.000	0.000	0.000	1.799	5.696
Cyclopentane	0.263	0.100	0.000	0.000	0.705	2.477
Cyclohexane	0.305	0.100	0.000	0.000	0.845	2.964
Methylcyclohexane	0.244	0.060	0.000	0.000	0.986	3.319
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	1.236	3.106
Cyclopentene	0.335	0.200	0.000	0.100	0.661	2.401
Cyclohexene	0.395	0.200	0.000	0.100	0.802	3.021
1-Hexene	0.078	0.080	0.000	0.070	0.911	2.572
1-Heptene	0.092	0.080	0.000	0.070	1.052	3.063
1-Octene	0.094	0.080	0.000	0.070	1.193	3.568
1-Nonene	0.090	0.080	0.000	0.070	1.334	4.073
1-Decene	0.090	0.080	0.000	0.070	1.475	4.533
1-Undecene	0.090	0.080	0.000	0.070	1.616	5.023
1-Dodecene	0.089	0.080	0.000	0.070	1.757	5.515
Cyclopentene	0.335	0.200	0.000	0.100	0.661	2.402
Cyclohexene	0.395	0.200	0.000	0.100	0.802	3.021
Styrene	0.849	0.650	0.000	0.160	0.955	3.908
Benzene	0.610	0.520	0.000	0.140	0.716	2.786
Toluene	0.601	0.520	0.000	0.140	0.857	3.325
Ethylbenzene	0.613	0.510	0.000	0.150	0.998	3.788
o-Xylene	0.663	0.560	0.000	0.160	0.998	3.939
p-Xylene	0.613	0.520	0.000	0.160	0.998	3.839
m-Xylene	0.623	0.520	0.000	0.160	0.998	3.839
Propylbenzene	0.604	0.500	0.000	0.150	1.139	4.230
Butylbenzene	0.600	0.510	0.000	0.150	1.280	4.730
Pentylbenzene	0.594	0.510	0.000	0.150	1.421	5.230
Methanol	0.278	0.440	0.430	0.470	0.308	0.970
Ethanol	0.246	0.420	0.370	0.480	0.449	1.485
1-Propanol	0.236	0.420	0.370	0.480	0.590	2.031
1-Butanol	0.224	0.420	0.370	0.480	0.731	2.601
1-Pentanol	0.219	0.420	0.370	0.480	0.872	3.106
1-Hexanol	0.210	0.420	0.370	0.480	1.013	3.610
2-Propanol	0.212	0.360	0.330	0.560	0.590	1.764
2-Methyl-1-propanol	0.217	0.390	0.370	0.480	0.731	2.413
tert-Butanol	0.180	0.300	0.310	0.600	0.731	1.963
2-Butanol	0.217	0.360	0.330	0.560	0.731	2.338
2-Methyl-2-butanol	0.194	0.300	0.310	0.600	0.872	2.630
3-Methyl-1-butanol	0.192	0.390	0.370	0.480	0.872	3.011
Propanal	0.196	0.650	0.000	0.450	0.547	1.815
Butanal	0.187	0.650	0.000	0.450	0.688	2.270
Pentanal	0.163	0.650	0.000	0.450	0.829	2.770
Hexanal	0.146	0.650	0.000	0.450	0.970	3.370
Heptanal	0.140	0.650	0.000	0.450	1.111	3.860

(*Continued*)

Table 1. Continued.

Solute	**E**	**S**	**A**	**B**	**V**	**L**
Octanal	0.160	0.650	0.000	0.450	1.252	4.380
Methyl propanoate	0.128	0.600	0.000	0.450	0.747	2.431
Methyl butanoate	0.106	0.600	0.000	0.450	0.888	2.943
Methyl pentanoate	0.108	0.600	0.000	0.450	1.028	3.442
Methyl hexanoate	0.080	0.600	0.000	0.450	1.169	3.984
Acetonitrile	0.237	0.900	0.070	0.320	0.404	1.739
Acetone	0.179	0.700	0.040	0.490	0.547	1.696
Ethyl acetate	0.106	0.620	0.000	0.450	0.747	2.314
1,4-Dioxane	0.329	0.750	0.000	0.640	0.681	2.892
Dichloromethane	0.387	0.570	0.100	0.050	0.494	2.019
Trichloromethane	0.425	0.490	0.150	0.020	0.617	2.480
Tetrachloromethane	0.458	0.380	0.000	0.000	0.739	2.823
α-Methylstyrene	0.851	0.640	0.000	0.190	1.096	4.290
Cyclohexanone	0.403	0.860	0.000	0.560	0.861	3.792

coefficients need to be converted to $\log K$ values for gas to ionic liquid partition through equation (4)

$$\log K = \log\left(\frac{RT}{\gamma^{\infty}_{\text{solute}} P^{0}_{\text{solute}} V_{\text{solvent}}}\right) \tag{4}$$

or to $\log P$ values for partition from water to the ionic liquid through equation (5)

$$\log P = \log K - \log K_{\text{w}} \tag{5}$$

Here R is the universal gas constant, T is the system temperature, P^{0}_{solute} is the vapor pressure of the solute at T, and V_{solvent} is the molar volume of the solvent. The calculation of $\log P$ requires knowledge of the solute's gas phase partition coefficient into water, K_{w}. Table 2 lists the respective $\log K$ and $\log P$ values for the values organic and gaseous solutes dissolved in ($[\text{MEIm}]^{+}[\text{EtSO}_4]^{-}$) and ($[\text{BMIm}]^{+}[\text{BF}_4]^{-}$) at 298 K. Note that the water-to-RTILs are "hypothetical partitions" between water and pure RTIL. Even so, the values are quite useful. Values of the hypothetical partition coefficients can be used to calculate infinite dilution activity coefficients and solubilities for solutes dissolved in pure RTILs.

3. Results and discussion

We have assembled in table 2 values of $\log P$ and $\log K$ for 42 solutes dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIm}]^{+}[\text{BF}_4]^{-}$) covering a reasonably wide range of compound type and descriptor values. Analysis of the experimental data yielded for partition from water to ($[\text{BMIm}]^{+}[\text{BF}_4]^{-}$) and from the gas phase to ($[\text{BMIm}]^{+}[\text{BF}_4]^{-}$) equations (6) and (7)

$$\begin{aligned}\log P = {} & -0.012(0.064) + 0.540(0.174)\mathbf{E} + 0.287(0.208)\mathbf{S} - 0.443(0.253)\mathbf{A} \\ & - 4.346(0.249)\mathbf{B} + 2.911(0.075)\mathbf{V} \\ & (N = 42,\ \text{SD} = 0.142,\ R^2 = 0.991,\ R^2_{\text{adj}} = 0.989 \text{ and } F = 760.7)\end{aligned} \tag{6}$$

Table 2. log P and log K partitioning data for solutes in ($[\mathrm{BMIm}]^+[\mathrm{BF}_4]^-$) and ($[\mathrm{MEIm}]^+[\mathrm{EtSO}_4]^-$) ionic liquids.

	($[\mathrm{BMIm}]^+[\mathrm{BF}_4]^-$)			($[\mathrm{MIm}]^+[\mathrm{EtSO}_4]^-$)	
Solute	log K_w	log P	log K	log P	log K
Argon	−1.47	0.427	−1.043		
Hydrogen	−1.72	0.533	−1.187		
Nitrogen	−1.80	0.688	−1.112		
Oxygen	−1.51	0.431	−1.079		
Carbon monoxide	−1.62	0.585	−1.035		
Carbon dioxide	−0.082	0.454	0.372		
Methane	−1.46	0.630	−0.829		
Ethane	−1.34	0.981	−0.359		
Pentane	−1.70	2.366	0.666		
Hexane	−1.82	2.826	1.006	2.565	0.745
Heptane	−1.96	3.316	1.356	2.893	0.933
Octane	−2.11	3.792	1.682	3.567	1.457
Nonane	−2.15	4.123	1.973	3.906	1.756
Decane	−2.26	4.500	2.244	4.384	2.124
Undecane	−2.38			4.903	2.523
Dodecane	−2.53			5.448	2.918
Cyclopentane	−0.88			1.872	0.992
Cyclohexane	−0.90	2.375	1.475	2.242	1.342
Methylcyclohexane	−1.25	2.878	1.628		
2,2,4-Trimethylpentane	−2.12	3.439	1.319		
1-Hexene	−1.16			2.049	0.889
1-Heptene	−1.22			2.432	1.212
1-Octene	−1.41			2.963	1.553
1-Nonene	−1.51			3.411	1.901
1-Decene					2.210
1-Undecene	−1.85			4.454	2.604
1-Dodecene	−1.91			4.828	2.908
Cyclopentene	−0.41			1.684	1.274
Cyclohexene	−0.27	2.153	1.883	1.969	1.699
Styrene	0.95	2.940	3.890		
Benzene	0.63	2.152	2.782	1.890	2.520
Toluene	0.65	2.429	3.079	2.091	2.741
Ethylbenzene	0.58	2.681	3.261	2.296	2.876
o-Xylene	0.66	2.889	3.549		
p-Xylene	0.59	2.769	3.359		
m-Xylene	0.61	2.471	3.351		
Propylbenzene	0.39			2.688	3.078
Butylbenzene	0.29			3.035	3.325
Pentylbenzene	0.17			3.436	3.606
Methanol	3.74	−0.781	2.959	−0.486	3.254
Ethanol	3.67	−0.669	3.001	−0.405	3.265
1-Propanol	3.56	−0.378	3.182	−0.072	3.488
1-Butanol	3.46	0.066	3.526	0.401	3.861
1-Pentanol	3.35	0.375	3.725	0.724	4.074
1-Hexanol	3.23			1.138	4.368
2-Propanol	3.48	−0.588	2.892	−0.325	3.155
2-Methyl-1-propanol	3.30	0.034	3.334	0.389	3.689
tert-Butanol	3.28			−0.238	3.042
2-Butanol	3.39	−0.264	3.126	0.018	3.408
2-Methyl-2-butanol	3.25			0.101	3.351
3-Methyl-1-butanol	3.24	0.447	3.687		
Propanal	2.52			−0.377	2.143
Butanal	2.33			0.052	2.382
Pentanal	2.22			0.445	2.665
Hexanal	2.06			0.881	2.941

(*Continued*)

Table 2. Continued.

	$([\mathrm{BMIm}]^+[\mathrm{BF}_4]^-)$			$([\mathrm{MIm}]^+[\mathrm{EtSO}_4]^-)$	
Solute	$\log K_\mathrm{w}$	$\log P$	$\log K$	$\log P$	$\log K$
Heptanal	1.96			1.288	3.248
Octanal	1.68			1.776	3.456
Methyl propanoate	2.15			0.151	2.301
Methyl butanoate	2.08			0.409	2.489
Methyl pentanoate	1.88			0.858	2.738
Methyl hexanoate	1.83			1.251	3.081
Acetonitrile	2.85	0.323	3.173	0.260	3.110
Acetone	2.79	−0.189	2.571	−0.395	2.395
1,4-Dioxane	3.71	−0.479	3.231	−0.626	3.084
Ethyl acetate	2.16	0.349	2.509		
Dichloromethane	0.96	1.360	2.320		
Trichloromethane	0.79	1.878	2.668	2.262	3.052
Tetrachloromethane	−0.06	2.241	2.181		
α-Methylstyrene	0.96				
Cyclohexanone	3.60	0.346	3.946		

and

$$\log K = -0.576(0.027) + 0.605(0.108)\mathbf{E} + 2.278(0.121)\mathbf{S} + 3.427(0.149)\mathbf{A} + 0.471(0.148)\mathbf{B} + 0.590(0.011)\mathbf{L}$$
$$(N = 42,\ \mathrm{SD} = 0.085,\ R^2 = 0.997,\ R^2_\mathrm{adj} = 0.997 \text{ and } F = 2537.2) \tag{7}$$

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 Fischer's F statistic. The errors in the coefficients are shown in parentheses.

Also in table 2 are the values of $\log P$ and $\log K$ for 48 and 49 solutes, respectively, in 1-methyl-3-ethylimidazolium ethylsulfate ($[\mathrm{MEIm}]^+[\mathrm{EtSO}_4]^-$). The regression equations for partition from water and from the gas phase into ($[\mathrm{MEIm}]^+[\mathrm{EtSO}_4]^-$)

$$\log P = -0.059(0.112) - 0.013(0.166)\mathbf{E} + 0.609(0.196)\mathbf{S} + 1.526(0.244)\mathbf{A} - 5.054(0.240)\mathbf{B} + 2.894(0.080)\mathbf{V}$$
$$(N = 48,\ \mathrm{SD} = 0.138,\ R^2 = 0.993,\ R^2_\mathrm{adj} = 0.992 \text{ and } F = 1186.3) \tag{8}$$

and

$$\log K = -0.709(0.077) + 0.137(0.125)\mathbf{E} + 2.544(0.145)\mathbf{S} + 5.262(0.182)\mathbf{A} + 0.042(0.181)\mathbf{B} + 0.592(0.018)\mathbf{L}$$
$$(N = 49,\ \mathrm{SD} = 0.104,\ R^2 = 0.986,\ R^2_\mathrm{adj} = 0.985 \text{ and } F = 615.0) \tag{9}$$

The regression statistics for equations (6)–(9) are all quite good. While there is insufficient data to construct separate training and test sets to fully assess the predictive capability of the derived correlations, based on our past experience using regression equations based on the Abraham model we expect that these equations would be able to estimate $\log P$ and $\log K$ values of additional compounds within the covered solute descriptor range to close to the obtained SD values. Infinite dilution activity coefficients are related to water-to-solvent and gas-to-solvent partition coefficients through equations (4) and (5), and our derived correlations should be able to estimate $\gamma_{\mathrm{solute}}^{\infty}$ values for solutes dissolved in both ($[\mathrm{MEIm}]^{+}[\mathrm{EtSO}_4]^{-}$) and ($[\mathrm{BMIm}]^{+}[\mathrm{BF}_4]^{-}$) to close to the obtained SD values as well.

No previous studies pertaining to the prediction of activity coefficients in ($[\mathrm{MEIm}]^{+}[\mathrm{EtSO}_4]^{-}$) and ($[\mathrm{BMIm}]^{+}[\mathrm{BF}_4]^{-}$) were found during our search of the published chemical and engineering literature. We did find predictive expressions though for other RTILs that have been studied using the Abraham model. As noted earlier Tämm and Burk [7] correlated activity coefficients of 38 solutes in 4-butyl-*N*-methylpyridinium tetrafluoroborate ($[\mathrm{BMPy}]^{+}[\mathrm{BF}_4]^{-}$), 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide ($[\mathrm{MEIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$) and 1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide ($[\mathrm{M}_2\mathrm{EIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$) with molecular descriptors obtained using CODESSA PRO software. The authors' three-parameter correlations described the experimental data to within standard errors ranging from $\mathrm{SE} = 0.30$ to 0.35 log units. Equation (3) of the Abraham model applied to these three RTILs had much smaller standard deviations of $\mathrm{SD} = 0.062$ ($[\mathrm{BMPy}]^{+}[\mathrm{BF}_4]^{-}$) [10], $\mathrm{SD} = 0.079$ ($[\mathrm{MEIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$) [9] and $\mathrm{SD} = 0.071$ ($[\mathrm{M}_2\mathrm{EIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$) [9]. The Abraham correlation for ($[\mathrm{MEIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$) was derived from a slightly larger data base that included not only the organic solutes used by Tämm and Burk, but several gaseous solutes (CO_2, propane, propene, ethane and ethene) as well. Eike *et al.* [31] also proposed quantitative structure–property relationship correlations for estimating infinite dilution activity coefficients in ($[\mathrm{BMPy}]^{+}[\mathrm{BF}_4]^{-}$), ($[\mathrm{MEIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$) and ($[\mathrm{M}_2\mathrm{EIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$) at 298 K that had squared correlation coefficients ranging from $R^2 = 0.952$ to 0.975. The corresponding R^2 values for the Abraham model were greater than $R^2 = 0.99$ [9,10]. Kato and Gmehling [32] measured infinite dilution activity coefficients of several nonpolar and polar solutes in ($[\mathrm{MEIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\mathrm{HMIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$) and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\mathrm{OMIm}]^{+}[(\mathrm{Tf})_2\mathrm{N}]^{-}$). The experimental data was combined with published literature values to calculate group interaction parameters for the original UNIFAC and modified UNIFAC (Dortmund) group contribution models. Statistical information was not reported for the individual RTILs; however, the authors did give the mean relative percent deviation of the predicted and experimental $\gamma_{\mathrm{solute}}^{\infty}$ values of imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids as a whole, which were 14.1% for UNIFAC and 11.6% for UNIFAC (Dortmund) models. Expressed on a logarithmic scale, the deviations would correspond to 0.05–0.06 log units. Deviations for the Abraham model are slightly higher and fall in the 0.06–0.10 log unit range, which is sufficient for most design and engineering applications. Group contribution methods employ more curve-fit parameters than the Abraham solvation parameter model. Predictive ability will generally improve as more curve-fit parameters are introduced.

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