JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Prediction of Partition Coefficients of Organic Compounds in Ionic Liquids Using a Temperature-Dependent Linear Solvation Energy Relationship with Parameters Calculated through a Group Contribution Method

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ABSTRACT: A temperature-dependent linear solvation energy relationship (LSER) is proposed for estimating the gas-to-ionic liquid partition coefficients. The model calculates the LSER parameters using a group contribution method. Large sets of partition coefficients were analyzed using the Abraham solvation parameter model to determine the contributions of 21 groups: 12 groups characterizing the cations and 9 groups for the anions. The derived equations correlate the experimental gas-to-ionic liquid coefficient data to within 0.13 log units. The 21 group parameters are used to predict the partition coefficients of solutes in alkyl or functionalized ionic liquids with good accuracy.

INTRODUCTION

Ionic liquids (IL) have been widely promoted as interesting substitutes for traditional industrial solvents such as volatile organic compounds. Much of the interest in ionic liquids is based on their physicochemical properties: good thermal stability, low vapor pressure, and high ionic conductivity properties. Presently, there are more than 1000 different ILs commercially available, but it has been shown that there are $>10^{14}$ possible combinations.[1] The thermodynamic properties may be adjusted by the choice of the anion and of the R groups grafted in the different cations (see Figure 1). Therefore, the possibility exists to functionalize the IL for a specific application by stepwise tuning the relevant solvent properties.

Nowadays, ILs are emerging as alternative green solvents, that is, as alternative reaction media for synthesis, catalysis, and biocatalysis, but also as electrolytes, lubricants, or modifiers of mobile and stationary phases in the separation sciences.[2−6]

Numerous works have been devoted to a large range of applications of ILs, but the basic understanding of their structure−property relationships has been neglected. Only few studies have examined the relationships between the structures of ILs and their fundamental properties.[7−15] Recently, quantitative structure−property relationship (QSPR) correlations were proposed to estimate the surface tension of ionic liquids using only information on the molecular volumes.[16] The QSPR and quantitative structure−activity relationship (QSAR) approaches were used to predict values of activity coefficients at infinite dilution in different IL solvents.[17,18]

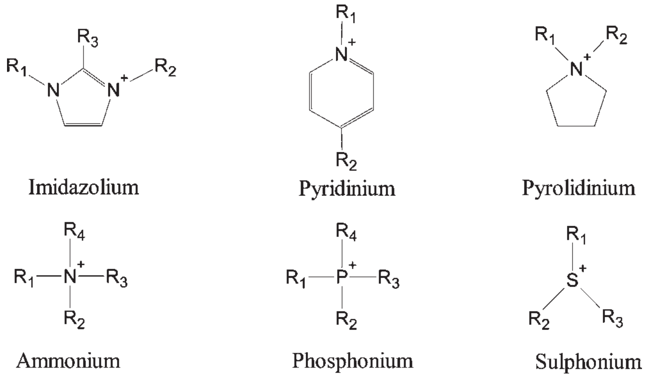
Thermodynamic properties of dialkyl-imidazolium based ILs are relatively well-described in the literature.[19−25] Recently, functionalized ILs such as ether- or cyano-functionalized ILs were studied by gas chromatography.[26,27] A systematic study of interaction between organic compounds and ILs was performed using a solvation model. This study continues our application of the linear solvation energy relationship (LSER) model to describe the interaction between dissolved organic solutes and the IL solvent.

In the early 1990s, Abraham et al.[28−31] developed the LSER model to quantify intermolecular solute-stationary phase interactions for chromatographic processes. This method allows one to correlate the thermodynamic properties governing solute phase transfer processes related to the Gibbs energy such as the chromatographic retention volume and gas-to-liquid partition coefficients. The most recent representation of the LSER model is given by eq 1

$$\log K_L = c + e\cdot E + s\cdot S + a\cdot A + a\cdot B + l\cdot L \qquad (1)$$

The capital letters represent the solute properties and the lower case letters the complementary properties of the ILs. The solute descriptors are the excess molar refraction E, dipolarity/polarizability S, hydrogen bond acidity and basicity, A and B, respectively, and the logarithm of the gas−liquid partition coefficient on n-hexadecane at 298 K, L. Solute descriptors of about 4000 compounds were measured using the experimental procedure or calculated using the group contribution model.[28−34] The coefficients c, e, s, a, b, and l (or v in the case of solute transfer between two condensed phases) are not simply fitting coefficients, but they reflect complementary properties of the solvent phase. The c term is the model constant. The system constants are identified as the opposing contributions of cavity formation and dispersion interactions, l (or v), the contribution from interactions with lone pair electrons, e, the contribution from dipole-type interactions, s, the contribution from the hydrogen-bond basicity of the stationary phase (because a basic phase will interact with an acid solute), a, and b, the contribution from the hydrogen-bond acidity of the stationary phase. Acree and

Received: May 9, 2011
Accepted: July 10, 2011
Published: August 22, 2011



Imidazolium Pyridinium Pyrolidinium

Ammonium Phosphonium Sulphonium

Figure 1. Cation of six families of ionic liquids.

Table 1. List of Ionic Liquids

Imidazolium-Based ILs
1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide
1-methyl-3-hexylimidazolium bis(trifluoromethylsulfonyl)imide
1-methyl-3-octylimidazolium tetrafluoroborate
1-methyl-3-butylimidazolium hexafluorophosphate
1-butyl-3-methylimidazolium tetrafluoroborate
1-methyl-3-ethylimidazolium ethylsulfate
1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide
1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide
1-methyl-3-hexylimidazolium tetrafluoroborate
1-methyl-3-ethylimidazolium tetrafluoroborate
1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide
1-methyl-3-hexylimidazolium hexafluorophosphate
1-butyl-3-methylimidazolium octylsulfate
1,2-dimethyl-3-propylimidazolium tetrafluoroborate
1-methyl-3-ethylimidazolium thiocyanate
1-methyl-3-butylimidazolium trifluoromethylsulfonate
1-methyl-3-ethylimidazolium trifluoromethylsulfonate
1-methyl-3-ethylimidazolium trifluoroacetate
1-methyl-3-hexylimidazolium trifluoromethylsulfonate
1-methyl-3-octylimidazolium hexafluorophosphate
1-ethyl-3-methylimidazolium octylsulfate
1-methyl-3-butylimidazolium trifluoroacetate
1-ethanol-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
1-(methylethylether)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
1,3- dimethoxyimidazolium bis(trifluoromethylsulfonyl)imide
1-methyl-3-ethylimidazolium dicyanamide
1-butyl-3-methylimidazolium thiocyanate
Ammonium-Based ILs
trimethylbutylammonium bis(trifluoromethylsulfonyl)imide
trioctylmethylammonium bis(trifluoromethylsulfonyl)imide
trimethylhexylammonium bis(trifluoromethylsulfonyl)imide
Pyridinium-Based ILs
4-methyl-*N*-butylpyridinium bis(trifluoromethylsulfonyl)imide
N-ethylpyridinium bis(trifluoromethylsulfonyl)imide
4-methyl-*N*-butylpyridinium tetrafluoroborate
Pyrolidinium-Based ILs
1-butyl-3-methylpyrolidinium trifluoromethanesulfonate
1-butyl-3-methylpyrolidinium bis(trifluoromethylsulfonyl)imide
1-hexyl-3-methylpyrolidinium bis(trifluoromethylsulfonyl)imide
1-octyl-3-methylpyrolidinium bis(trifluoromethylsulfonyl)imide
Phosphonium-Based ILs
trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide
Sulphonium-Based ILs
triethylsulphonium bis(trifluoromethylsulfonyl)imide

co-workers reported mathematical correlations based on Abraham's solvation model for the gas-to-IL, K_L, and water-to-IL, P, partition coefficients.[35,36] Sprunger et al.[37−40] modified Abraham's solvation model by rewriting each of the six solvent equation coefficients as a summation of their respective cation and anion contribution:

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

Equation coefficients for 10 cations and 8 anions were determined using a database that contained 976 experimental log K_L and 955 experimental log P values.[40] In Sprunger's approach, the major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that one can make predictions for more ILs. Most of the cations are dialkylimidazolium. The use of this model is somewhat limited since it cannot be extrapolated to dialkylimidazolium ILs not initially defined by the method (e.g., with long alkyl chains).

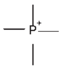
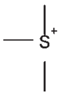
Recently, we proposed to split the cation with its alkyl chains in different contributions: (CH_3, CH_2, N, CH_{cyclic}, etc.). The aim of this work was to develop a group contribution method to estimate the log K_L of organic compounds in ILs at 298 K. Using the LSER model proposed by Abraham, the group contribution method (GC-LSER)[41] which expresses LSER coefficients c_i, e^i, s^i, a_i, b^i, and l^i of eq 3 is given by:

$$\log K_L = \sum_i^{21} n_i \cdot c_i + \sum_i^{21} n_i \cdot e_i \cdot E + \sum_i^{21} n_i \cdot s_i \cdot S + \sum_i^{21} n_i \cdot a_i \cdot A + \sum_i^{21} n_i \cdot b_i \cdot B + \sum_i^{21} n_i \cdot l_i \cdot L \qquad (3)$$

where n_i is the number of groups i present in the IL.

The group contribution model coupled to LSER (GC-LSER) enables one to predict with good accuracy log K_L and log P at 298 K of not only alkyl based ILs but also task-specific ILs. The parameters of the group contribution methods were determined for imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium, and sulphonium based ILs containing several different anions. A comparison between the experimental and calculated values showed that the proposed model describes the available experimental data with a mean absolute error of about 0.15 log units. The predictive power of the GC-LSER was evaluated by the calculation of log K_L of ILs not contained in our database. Results obtained with both short and long alkyl chain dialkylimidazolium-based ILs, such as 1-ethyl-3-methylimidazolium

Table 2. Description of the 21 Groups Used for the Estimation of log K_L

Cation's group		Definition	Anion's group		Definition
Group 1	CH_3-	CH_3 from alkyl chain R_1, R_2,R_3 or R_4	Group 13	$(TF)_2N^-$	bis(trifluoromethylsulfonyl)imide
Group 2	-CH_2-	CH_2 from alkyl chain R_1, R_2,R_3 or R_4	Group 14	PF_6^-	hexafluorophosphate
Group 3	-O-	-O- in alkyl chain R_1, R_2,R_3 or R_4	Group 15	BF_4^-	tettrafluoroborate
Group 4	-O-N_{cyclic}-	Oxygenated atom connected directly to N_{cyclic}	Group 16	$EtSO_4^-$	Ethylsulfate
Group 5	-OH	-OH from alkyl chain R_1, R_2,R_3 or R_4	Group 17	$OcSO_4^-$	Octylsulfate
Group 6	$CH_{2cyclic}$	CH_2 cyclic in pyrolidinium's cation	Group 18	SCN^-	Thiocyanate
Group 7	CH_{cyclic}	CH cyclic in imidazolium or pyridinium's cation	Group 19	$CF_3SO_3^-$	trifluoromethylsulfonate
Group 8	C_{cyclic}	C cyclic in imidazolium or pyridinium's cation	Group 20	ACF_3^-	trifluoroacetate
Group 9	N_{cyclic}	Cyclic nitrogen (imdazolium, pyridinium and pyrrolidinium)	Group 21	$[CH_3OC_2H_4SO_4]^-$	methoxyethyl sulfate
Group 10		Ammonium's cation			
Group 11		Phosphonium's cation			
Group 12		Sulphonium's cation			

trifluoromethylsulfonate[42] and 1-hexadecyl-3-methylimidazolium tetrafluoroborate,[43] as well as task-specific ILs like 1-ethanol-3-methylimidazolium hexafluorophosphate[13] indicated that the GC-LSER is a useful tool to predict the gas-to- IL partition coefficient at 298 K.

In this article, we extend the GC-LSER (eq 3) to enable the model to correlate gas-to-IL partition coefficient data measured at different temperatures by a single correlation equation. This new temperature-dependent GC-LSER (TDGC-LSER) is given by the following expression:

$$\log K_L = -2.84418 + \left(\sum_i^{21} n_i \cdot c_i + \sum_i^{21} n_i \cdot e_i \cdot E + \sum_i^{21} n_i \cdot s_i \cdot S + \sum_i^{21} n_i \cdot a_i \cdot A + \sum_i^{21} n_i \cdot b_i \cdot B + \sum_i^{21} n_i \cdot l_i \cdot L\right)/T \qquad (4)$$

Mintz et al.[44] and Sprunger et al.[45] suggested a slightly different temperature dependence of log K_L for the general Abraham model LSER when describing the partitioning of organic vapors and gases into humic acid and into polyurethane foams. They used the following equation:

$$\log K_L = \frac{c_s}{2.303R} - \frac{c_h}{2.303RT} + \left(\frac{e_s}{2.303R} - \frac{e_h}{2.303RT}\right)E + \left(\frac{s_s}{2.303R} - \frac{s_h}{2.303RT}\right)S + \left(\frac{a_s}{2.303R} - \frac{a_h}{2.303RT}\right)A + \left(\frac{b_s}{2.303R} - \frac{b_h}{2.303RT}\right)B + \left(\frac{l_s}{2.303R} - \frac{l_h}{2.303RT}\right)L \qquad (5)$$

which separates each equation coefficient into a temperature-independent term and a temperature-dependent term. The method proposed here expresses each general equation coefficient in terms of a temperature-dependent term and as a result contains only half the number of curve-fit regression coefficients.

METHODOLOGY

The experimental data used to calculate Abraham's model functional group- and anion-specific equation coefficients were taken from the collection of Sprunger and co-workers[40] and were updated with recent experimental data.[46−54] A total of 6990 gas-to-IL partition coefficients measured in a temperature range from (293 to 396) K was used for the calculation. Solutes were mainly *n*-alkanes, cycloalkanes, alkenes, alkynes, aromatics, alcohols, ethers, aldehydes, ketones, and chloroalkanes. The *E*-scale varies from 0 to 1.5, the *S*-scale from 0 to 1.72, the *A*-scale from 0 to 1.04, the *B*-scale from 0 to 1.28, the *L*-scale from −1.200 to 7.833, and the *V*-scale from 0.109 to 1.799. The list of ILs used for the correlations is given in Table 1. The data set contains 29 imidazolium-, 3 ammonium-, 6 pyridinium-, 4 pyrrolidinium-, 1 sulphonium-, and 1 phosphonium-based ILs.

Partition coefficients K_L are calculated from the experimental activity coefficients at infinite dilution, $\gamma_{1,2}{}^{\infty}$, using the following equation:

$$K_L = \frac{RT}{\gamma_{1,2}^{\infty} P_1^0 V_{\text{solvent}}} \qquad (6)$$

In eq 6, R is the gas constant, T is the system temperature, P_1^0 is the vapor pressure of the solute at T, and V_{solvent} is the molar volume of the solvent.

Table 3. Values of Group's Parameters of the GC-LSER Model for the Calculation of the Gas-to-ILs Using eq 4 (n_g Refers to the Number of Occurrences of Each of the 21 Groups in the log K_L Data Set)

	group	n_g	c_i	e_i	s_i	a_i	b_i	l_i
cation	CH_3-	14290	250.3 (103.8)	318.1 (169.2)	209.2 (233.2)	1353.7 (183.4)	842.7 (233.4)	132.69 (30.09)
	$-CH_2-$	24660	11.471 (1.717)	−29.394 (2.745)	−7.546 (3.416)	−6.836 (3.281)	−20.188 (3.760)	11.188 (0.525)
	$-O-$	208	16.06 (16.13)	−40.73 (20.74)	79.98 (20.92)	−115.45 (27.48)	3.71 (22.87)	−10.971 (4.049)
	$-O-N-$	294	−29.853 (9.060)	−55.23 (12.22)	37.72 (12.31)	−50.87 (15.95)	61.34 (13.26)	5.102 (2.272)
	$-OH$	196	108.3 (104.8)	307.8 (170.4)	276.7 (234.2)	1390.8 (185.8)	1035.4 (234.7)	131.18 (30.28)
	CH_{2cyc}	2602	43.51 (22.04)	0.60 (36.26)	42.20(49.30)	23.30 (38.26)	−122.74 (48.84)	−4.418 (6.327)
	CH_{cyc}	19125	111.056 (8.182)	49.479 (7.517)	71.88 (10.16)	258.921 (9.502)	68.56 (11.47)	18.485 (2.363)
	C_{cyc}	1036	−209.0 (101.2)	−239.7 (167.9)	−94.5 (230.9)	−970.5 (179.7)	−843.8 (229.6)	−103.49 (29.35)
	N^+_{cyc}	11275	−77.62 (99.51)	−167.6 (168.2)	−82.8 (231.7)	−720.9 (182.1)	−686.6 (231.1)	−93.65 (28.87)
	N^+_{am}	90	−387.3 (397.2)	−185.6 (673.1)	−801.4 (928.3)	−3528.1 (727.5)	−2183.8 (928.1)	−535.2 (115.2)
	S^+	250	−177.8 (296.1)	−465.2 (503.1)	88.8 (692.7)	−1923.6 (541.5)	−1990.6 (688.8)	−254.36 (85.89)
	P^+	117	−423.4 (397.1)	−221.3 (672.7)	−424.5 (926.2)	−3377.1 (726.2)	−2480.9 (924.1)	−616.4 (115.1)
anion	$(Tf)_2N^-$	3593	306.61 (53.78)	−304.98 (44.29)	287.04 (61.85)	−1283.12 (56.34)	−322.13 (72.70)	−25.34 (15.75)
	PF_6^-	140	256.49 (56.92)	−148.00 (56.05)	363.34 (75.75)	−1422.73 (67.15)	−379.52 (81.94)	−52.16 (16.84)
	BF_4^-	1253	182.74 (54.22)	−107.31 (45.15)	223.52 (62.69)	−1016.31 (57.73)	−229.52 (73.41)	−50.89 (15.90)
	$EtSO_4^-$	268	186.04 (54.83)	−334.48 (47.76)	388.77 (65.49)	−486.84 (63.79)	−574.88 (78.29)	−30.38 (15.89)
	$OcSO_4^-$	89	346.94 (61.27)	−343.47 (53.24)	−144.67 (68.63)	−599.28 (73.55)	−538.23 (80.72)	5.95 (18.08)
	SCN^-	708	−2.38 (54.27)	−47.73 (47.74)	292.59 (66.52)	−533.27 (57.74)	−233.07 (74.94)	−27.04 (15.88)
	$CF_3SO_3^-$	578	206.82 (55.05)	−184.24 (50.05)	250.22 (69.95)	−868.82 (61.94)	−241.25 (78.98)	−34.51 (16.14)
	AcF_3^-	183	96.29 (55.60)	−77.95 (62.39)	25.56 (84.70)	−382.78 (74.53)	−139.40 (92.83)	−6.03 (16.31)
	$MeSO_4^-$	56	332.50 (67.07)	−584.22 (95.55)	791.3 (142.6)	−440.3 (191.6)	−1046.6 (214.0)	−104.19 (21.86)
	$[CH_3OC_{24}SHO_4]^-$	56	245.22 (71.95)	−312.94 (93.77)	586.0 (147.8)	−1874.6 (755.7)	−727.5 (191.2)	−92.42 (23.87)

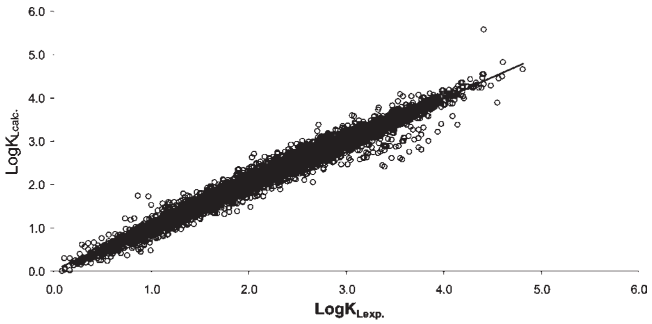


Figure 2. Plot of experimental log K_L data versus calculated values based on eq 4.

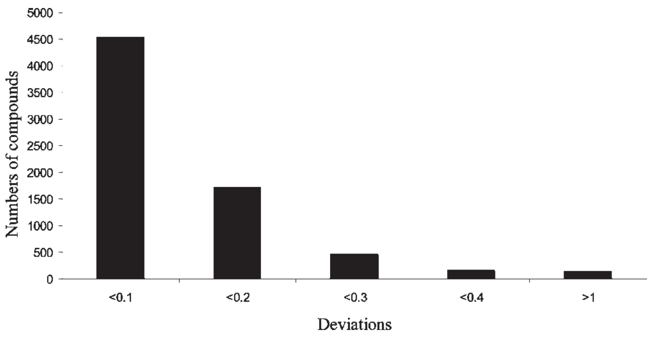


Figure 3. Differences between the experimental log K_L data and the calculated values using the eq 4.

The 21 groups which are defined in this study are listed in Table 2. The decomposition into groups of the ILs is as simple as possible. In Figure 1 are represented all ILs studied in this work. Five groups are defined to describe the chains R_1, R_2, R_3, and R_4 grafted on the cations: CH_3, CH_2, $-O-$, $-O-N_{cycl}$, and $-OH$. These groups allow the calculation of partition coefficients of alkyl-based ILs but also functionalized ILs such as ethers and alcohols. The remaining seven groups are: $CH_{2cyclic}$, CH_{cyclic}, C_{cyclic}, N_{cyclic}, N^+ (ammonium cation), P^+ (phosphonium cation), and S^+ (sulphonium cation).

More precisely, N_{cyclic} represents two structures: $-\underset{|}{N}^{+}=$ and $-\underset{|}{N}-$. Nine groups are used for anions: bis(trifluoromethylsulfonyl)imide: $(TF)_2N^-$, hexafluorophosphate: PF_6^-, tetrafluoroborate: BF_4^-, ethylsulfate: $EtSO_4^-$, octylsulfate: $OcSO_4^-$, thiocyanate: SCN^-, trifluoromethylsulfonate: $CF_3SO_3^-$, trifluoroacetate: ACF_3^-, and $CH_3OC_2H_4SO_4^-$, methoxyethylsulfate. Partition coefficients of dicyanamide, FAP, or cyano-based ILs may be also found in the literature, but these groups were not considered at the present due to a small number of experimental values.

Once the decomposition has been done, the matrices required to determine the LSER parameters of each group are built using the solute descriptors *E*, *S*, *A*, *B*, and *L* weighted by the number of groups present in each IL.

The values are arranged in a 126 column × 6990 row matrix (log K_L). The group parameters have been determined to minimize the deviations between calculated and experimental log K_L data.

RESULTS AND DISCUSSION

TDGC-LSER Correlation. The database contains 42 ILs having imidazolium, pyridinium, ammonium, pyrrolidinium, sulphonium, and phosphonium cations. The ILs are decomposed so that the model may be used as a purely predictive model. The

Table 4. Mean Absolute Error Observed with Ionic Liquids Studied in This Work

ILs	$\Delta\log K_L$	$\Delta\gamma^\infty$ (%)
Imidazolium-Based ILs		
1-methyl-3-methylimidazolium methylsulfate	0.329	31.71
1-ethyl-3-methylimidazolium ethylsulfate	0.259	26.21
	0.091	18.85
1-butyl-3-methylimidazolium octylsulfate	0.149	27.69
	0.072	17.20
1-ethyl-3-methylimidazolium tetrafluoroborate	0.130	38.25
	0.116	32.93
1-butyl-3-methylimidazolium tetrafluoroborate	0.099	26.48
	0.125	23.68
	0.061	14.20
	0.143	31.86
1-hexyl-3-methylimidazolium tetrafluoroborate	0.211	59.47
	0.088	19.59
1-octyl-3-methylimidazolium tetrafluoroborate	0.056	12.93
	0.304	33.61
1-propyl-2,3-dimethylimidazolium tetrafluoroborate	0.252	41.81
	0.160	30.42
1-octyl-3-methylimidazolium tetrafluoroborate	0.310	31.23
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.233	72.70
1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.091	22.50
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.074	18.18
	0.087	19.56
	0.131	38.34
	0.122	30.91
	0.219	16.94
	0.100	27.66
	0.118	32.36
	0.077	19.05
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.327	14.96
	0.074	12.62
	0.065	10.54
	0.045	9.64
1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.096	20.15
	0.101	20.48
1-ethanol-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	0.104	21.16
1-(methylethylether)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	0.209	29.40
1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide	0.076	17.37
1-butyl-3-methylimidazolium hexafluorophosphate	0.110	22.67
1-hexyl-3-methylimidazolium hexafluorophosphate	0.122	25.45
1-ethyl-3-methylimidazolium thiocyanate	0.056	12.72
1-butyl-3-methylimidazolium thiocyanate	0.118	22.18
1-hexyl-3-methylimidazolium thiocyanate	0.114	25.91
1-butyl-3-methylimidazolium trifluoromethanesulfonate	0.067	14.27
1-hexyl-3-methylimidazolium trifluoromethanesulfonate	0.115	22.75
1-ethyl-3-methylimidazolium trifluoroacetate	0.068	13.85
1-methyl-3-methylimidazolium methoxyethylsulfate	0.122	24.29
1-methyl-3-methylimidazolium dimethylphosphate	0.101	22.54
Ammonium-Based ILs		
trimethylbutylammonium bis(trifluoromethylsulfonyl)imide	0.169	31.69
trioctylmethylammonium bis(trifluoromethylsulfonyl)imide	0.170	16.67
Pyrolidinium-Based ILs		
1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate	0.077	14.04
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	0.082	22.4
1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	0.039	9.21
1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	0.061	13.02
Pyridinium-Based ILs		
4-methyl-*N*-butylpyridinium bis(trifluoromethylsulfonyl)-imide	0.107	24.52
ethylpyridinium bis(trifluoromethylsulfonyl)imide	0.124	36.07
N-ethylpyridinium bis(trifluoromethylsulfonyl)imide	0.163	30.09
butylpyridinium bis(trifluoromethylsulfonyl)imide	0.126	26.38
1-butyl-3-methyl-pyridinium trifluoromethanesulfonate	0.123	30.19
4-methyl-*N*-butyl-pyridinium tetrafluoroborate	0.091	21.92
4-methyl-*N*-butylpyridinium tetrafluoroborate	0.087	17.51
4-methyl-*N*-butylpyridinium tetrafluoroborate	0.060	14.91
pentylpyridinium bis(trifluoromethylsulfonyl)imide	0.101	21.29
Piperidinium-Based ILs		
1-propyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide	0.077	15.30
Phosphonium-Based ILs		
trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide	0.113	29.28
Sulphonium-Based ILs		
triethylsulphonium bis(trifluoromethylsulfonyl)imide	0.066	12.07

snalysis of the 6990 experimental log K_L values gave the contribution of each group for the calculation of LSER coefficients c_i, e^i, s^i, a_i, b^i, and l^i needed in eq 4 with a standard deviation SD = 0.130, a squared correlation coefficient R^2 = 0.995, and a Fisher's F statistic F = 2160. The contribution of each group for the calculation of LSER coefficients c_i, e^i, s^i, a^i, b^i, and l^i needed in eq 4 are given in Table 3. Plots of calculated values of log K_L based on eq 4 against the observed values are presented in Figure 2. The standard errors in the coefficients are given in parentheses directly below the respective values. Larger standard

Table 5. Prediction of log K_L at 298.15 K of Organic Compounds in Three ILs Using the TDGC-LSER Model: 1-Ethyl-3-methylimidazolium Trifluoromethylsulfonate, 1-Hexadecyl-3-methylimidazolium Tetrafluoroborate, and 1-Ethanol-3-methylimidazolium Hexafluorophosphate

solute	log $K_{\mathrm{Lpred.}}$	log $K_{\mathrm{Lexp.}}$	$\gamma^{\infty}_{\mathrm{pred.}}$	$\gamma^{\infty}_{\mathrm{exp}}$
1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate, T = 313.15 K				
pentane	0.781	0.658	31.34	41.6
hexane	0.959	0.890	57.20	67
heptane	1.136	1.130	102.56	104
octane	1.314	1.357	183.51	166
hex-1-ene	1.223	1.190	26.91	29
hept-1-ene	1.406	1.417	47.49	46.3
oct-1-ene	1.585	1.629	83.34	75.3
non-1-ene	1.760	1.841	149.29	124
dec-1-ene	1.924	2.114	272.67	176
undec-1-ene	2.095	2.298	507.28	318
pent-1-yne	1.924	1.804	3.02	3.98
hex-1-yne	2.079	2.019	5.53	6.36
hept-1-yne	2.247	2.242	9.60	9.71
oct-1-yne	2.427	2.444	16.54	15.9
non-1-yne	2.598	2.541		
cyclopentane	1.317	1.161	14.73	21.1
cyclohexane	1.520	1.452	28.83	33.7
cycloheptane	1.814	2.025	74.96	46.1
cyclooctane	2.081	2.205	91.12	68.5
methanol	3.557	3.385	0.49	0.73
ethanol	3.453	3.319	0.86	1.17
benzene	2.755	2.723	2.06	2.22
toluene	2.938	2.924	3.46	3.57
ethylbenzene	3.092	3.057	5.73	6.2
1-Methyl-3-octylimidazolium Hexafluorophosphate, T = 313.15 K				
pentane	1.501	1.358	5.97	8.30
hexane	1.759	1.679	9.07	10.90
heptane	2.016	1.995	13.53	14.20
octane	2.273	2.322	20.15	18.00
decane	2.531	2.932	79.82	31.70
undecane	3.045	3.245	66.05	41.70
hex-1-ene	2.017	1.852	4.32	6.31
hept-1-ene	2.271	2.169	6.47	8.20
oct-1-ene	2.530	2.485	9.47	10.50
non-1-ene	2.786	2.794	14.07	13.80
dec-1-ene	3.021	3.142	21.80	16.50
pent-1-yne	2.411	2.171	0.98	1.71
hex-1-yne	2.640	2.462	1.52	2.29
hept-1-yne	2.888	2.772	2.19	2.87
oct-1-yne	3.152	3.061	3.11	3.84
cyclopentane	1.990	1.782	3.12	5.04
cyclohexane	2.252	2.148	5.34	6.78
cycloheptane	2.643	2.779	11.12	8.13
cyclooctane	2.981	3.037	11.49	10.10
methanol	3.422	2.990	0.67	1.81
ethanol	3.528	3.031	0.72	2.27
benzene	3.467	3.083	0.40	0.97
toluene	3.739	3.349	0.55	1.34
ethylbenzene	3.961	3.560	0.77	1.95
1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate, T = 303.15 K				
methanol	3.438	3.436	1.03	1.03
ethanol	3.343	3.223	1.86	2.45
1-propanol	3.520	3.248	2.55	4.76
1-butanol	3.704	3.410	4.34	8.54
2-propanol	3.238	3.015	2.41	4.02
2-methylpropanol	3.560	3.210	3.51	7.86
2-butanol	3.438	3.065	2.91	6.88
acetonitrile	3.329	3.166	0.58	0.85
ethyl acetate	2.666	2.352	3.47	7.16
acetone	2.914	3.173	2.78	1.53
tetrahydrofuran	2.739	2.419	2.09	4.36
1,4-dioxane	3.660	3.482	1.04	1.57
dichloromethane	2.461	2.155	1.35	2.73
trichloromethane	2.585	2.354	2.49	4.24
Trioctylmethylammonium Bis(trifluoromethylsulfonyl)imide, T = 303.15 K				
pentane	2.450	2.415	0.93	1.01
hexane	2.793	2.830	1.23	1.13
heptane	3.134	3.225	1.60	1.3
octane	3.476	3.614	2.09	1.52
nonane	3.817	3.879	2.96	2.57
decane	4.158	4.197	3.49	3.2
pent-1-ene	2.568	2.455	0.60	0.78
hex-1-ene	2.915	2.865	0.79	0.89
hept-1-ene	3.255	3.105	1.03	1.46
oct-1-ene	3.598	3.489	1.32	1.69
non-1-ene	3.938	3.872	1.71	1.99
dec-1-ene	4.250	4.267	2.35	2.26
pent-1-yne	2.922	2.831	0.43	0.53
hex-1-yne	3.228	3.222	0.58	0.59
hept-1-yne	3.556	3.475	0.74	0.89
oct-1-yne	3.906	3.834	0.91	1.07
non-1-yne	4.240	3.834	0.81	1.15
cyclopentane	2.860	2.784	0.60	0.71
cyclohexane	3.213	3.228	0.87	0.84
cycloheptane	3.738	3.723	0.92	0.95
cyclooctane	4.195	4.234	1.18	1.08
methanol	3.368	3.504	1.20	0.88
ethanol	3.612	3.639	1.00	0.94
propan-1-ol	3.976	3.789	0.89	1.37
benzene	3.689	3.741	0.36	0.32
toluene	4.048	3.968	0.42	0.51
acetone	3.384	3.407	0.37	0.35
butan-2-one	3.745	3.748	0.32	0.32
Trimethylhexylammonium Bis(trifluoromethylsulfonyl)imide, T = 322.65 K				
hexane	0.403	0.522	146.68	111.41
3-methylpentane	0.396	0.518	124.10	93.69
heptane	0.444	0.716	342.86	183.33
2,2,4-trimethylpentane	0.456	0.608	286.29	201.73
octane	0.485	0.924	797.15	289.7
nonane	0.526	1.133	2019.46	498.48
decane	0.567	1.352	4264.18	698.76

Table 5. Continued

solute	log $K_{\mathrm{Lpred.}}$	log $K_{\mathrm{Lexp.}}$	$\gamma^{\infty}_{\mathrm{pred.}}$	$\gamma^{\infty}_{\mathrm{exp}}$
undecane	0.607	1.589	9901.95	1033.57
dodecane	0.648	1.844	22108.65	1410.6
tridecane	0.689	2.118	52163.78	1942.69
tetradecane	0.730	2.405	117994.50	2497.08
methylcyclopentane	0.953	0.976	53.07	50.31
cyclohexane	1.115	1.164	51.52	46.01
methylcyclohexane	0.989	1.182	115.32	73.88
cycloheptane	1.264	1.572	259.56	127.53
benzene	2.403	2.504	3.24	2.57
toluene	2.429	2.677	7.47	4.22
ethylbenzene	2.504	2.792	14.42	7.43
m-xylene	2.561	2.850	14.39	7.4
p-xylene	2.542	2.858	14.37	6.93
o-xylene	2.683	3.045	13.49	5.86
1-hexene	0.785	0.870	53.02	43.62
1-hexyne	1.368	1.732	20.09	8.7
1-heptyne	1.396	1.895	45.89	14.54
2-butanone	2.524	2.710	2.44	1.59
2-pentanone	2.499	2.738	5.06	2.92
3-pentanone	2.507	2.863	6.37	2.81
1,4-dioxane	3.246	3.346	1.12	0.89
methanol	3.072	3.426	0.99	0.44
ethanol	2.951	3.297	1.73	0.78
1-propanol	2.976	3.438	3.10	1.07
2-propanol	2.973	3.089	1.57	1.2
2-methyl-1-propanol	2.943	3.424	4.49	1.48
1-butanol	2.998	3.607	6.46	1.59
trifluoroethanol	2.443	4.008	3.68	0.1
diethyl ether	1.717	1.171	2.81	9.88
diisopropyl ether	1.526	1.029	10.23	32.11
chloroform	1.968	2.793	5.08	0.76
dichloromethane	1.910	2.530	2.79	0.67
tetrachloromethane	1.652	2.170	14.79	4.49
acetonitrile	2.469	3.264	4.99	0.8
nitromethane	2.634	3.676	7.26	0.66
1-nitropropane	2.470	3.592	20.00	1.51
triethylamine	2.635	1.902	1.68	9.09
pyridine	3.646	3.935	0.78	0.4
thiophene	2.625	2.826	2.54	1.6
formaldehyde	2.078	2.259	0.49	0.32
propionaldehyde	2.358	2.369	1.44	1.4
butyraldehyde	2.378	2.500	2.96	2.23

errors are observed with groups for which experimental data is limited. Regression analyses were performed using Minitab software. The correlation is statistically very good and describes an experimental log K_L database that covers a 12.6 log unit range to within standard deviations of 0.130 log units. The distribution of the residuals is given in Figure 3. Residuals have been calculated as the difference between the observed and the calculated of the logarithm of the gas-to-IL partition coefficient. It can be seen that about 65 % of the residuals are lower than 0.1 log units, 89 % lower than 0.2 log units, and 96 % lower than 0.3 log units. It is important to note that the model is probably limited in prediction for sulphonium- and phosphonium-based ILs because the data set of log K_L is relatively poor.

Few experimental measurements are not well-represented by the correlations. An examination of the residuals and visual analysis of Table 4 shows few outliers. It may be observed that 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-hexyl-3-methylimidazolium tetrafluoroborate present a larger mean absolute error (about 0.30). Concerning 1-propyl-2.3-dimethylimidazolium tetrafluoroborate, this large deviation seems to indicate that these measurements are spurious. Results obtained from this research group for 1-butyl-3-methylimidazolium tetrafluoroborate were found to be in significant disagreement with experimental literature values reported by other research groups. In Table 4, the average error on the prediction of activity coefficients at infinite dilution, γ^{∞}, is also reported. In most cases, the γ^{∞} values for a series of organic compounds in an IL are estimated with an accuracy of about 10 to 20 %. Low γ^{∞} values are usually well-estimated using the TDGC-LSER model. Important deviations are observed for high activity coefficient values. This is particularly the case of data of apolar compounds in ILs with a short alkyl chain length. For example, the measured activity coefficient at infinite dilution of decane in 1-ethyl-3-methylimidazolium ethylsulfate is equal to 504 at 301 K, while the estimated values by the GC-LSER model is 805.

Results obtained show that the temperature-dependent LSER model coupled to a group contribution method may be applied to represent partition coefficients.

Prediction of Partition Coefficients of Organic Compounds in ILs Not Included in the Database Using the TDGC-LSER Model. To evaluate the predictive power of the TDGC-LSER, 380 partition coefficients of organic compounds in five ILs not included in the regression analysis database were calculated: 1-methyl-3-octylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium trifluoromethylsulfonate, 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, trioctylmethylammonium bis(trifluoromethylsulfonyl)imide, and trimethylhexylmethylammonium bis(trifluoromethylsulfonyl)imide. Experimental data and calculated values at a given temperature for each IL are summarized in Table 5.

For 1-ethyl-3-methylimidazolium trifluoromethylsulfonate, 72 experimental values of log K_L are predicted using the GC-LSER approach with a mean absolute error on log K_L of 0.09. In most cases, estimated values of log K_L are underestimated. A study of results indicated that light hydrocarbons show larger deviations. These log K_L were determined using gas chromatography. In gas chromatography, it is well-known that light hydrocarbons are prime candidates to adsorption, in which case the partition coefficient may be over- or underestimated. For 1-methyl-3-octylimidazolium hexafluorophosphate, 72 experimental values of log K_L are predicted with a mean absolute error on log K_L of 0.18. Results obtained at 313.15 K are listed in Table 5. These data are not particularly well-represented using the TDGC-LSER. In general, partition coefficients are underestimated. The model was also evaluated for functionalized ILs. A total of 110 partition coefficients in 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate was predicted using eq 5 with a deviation of 0.27 log units on log K_L. This large deviation may be explained by the small number of data containing the hydroxyl group.

Data containing 236 log K_L of organic compounds in two ammonium-based ILs were also estimated. Deviations of 0.09 log units were found for trioctylmethylammonium bis(trifluoromethylsulfonyl)imide and 0.20 log units for trimethylhexylmethylammonium bis(trifluoromethylsulfonyl)imide. Results presented in Table 5 indicate that estimated thermodynamic properties are in good agreement with experimental data. In the case of trimethylhexylmethylammonium bis(trifluoromethylsulfonyl)imide, larger deviation are observed with *n*-alkanes, compounds not soluble in this IL. Results obtained on the prediction of log K_L of organic compounds in these ILs show that GC-LSER model may be used with good accuracy.

■ CONCLUSIONS

A temperature-dependent group contribution model coupled to LSER (TDGC-LSER) for estimating the gas-to-ILs partition coefficients was proposed. The TDGC-LSER model allows one to predict with good accuracy log K_L of not only alkyl-based ILs but also functionalized ILs. The parameters of the group contribution method were determined for imidazolium-, pyridinium-, pyrrolidinium-, phosphonium-, ammonium-, and sulphonium-based ILs containing several different anions. A comparison between the experimental and calculated values showed that the proposed model describes the available experimental data to within a mean absolute error of about 0.13 log units. Significantly more experimental data will need to be measured to increase the predictive power of the model.

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