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Critical Properties, Normal Boiling Temperatures, and Acentric Factors of Fifty Ionic Liquids

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The critical properties, the normal boiling temperatures, and the acentric factors of ionic liquids have been determined using an extended group contribution method based on the well-known concepts of Lydersen and of Joback and Reid. The critical properties of ionic liquids cannot be experimentally determined in many cases since most of these compounds start to decompose as the temperature approaches the normal boiling point. However, for the development of thermodynamic models either for pure components or for mixtures containing ionic liquids, the critical properties and other physical parameters are required. The so-called group contribution methods have been commonly used to estimate the critical properties of many substances for which these properties are not available, but no attempt has been made to estimate the critical properties of ionic liquids, as presented in this study. The method does not require any additional data besides the knowledge of the structure of the molecule and its molecular weight. Since experimental critical properties of ionic liquids are not available, the accuracy of the method is checked by calculating the liquid densities of the ionic liquids considered in the study. The results show that the values determined for the critical properties, for the normal boiling temperatures, and for the acentric factors are accurate enough for engineering calculations, for generalized correlations, and for equation of state methods, among other applications.

Introduction

Ionic liquids have attracted special attention from the scientific community in recent years, and hundreds of studies involving different aspects of properties and applications of ionic liquids have been presented in the literature. Ionic liquids are organic salts with some special characteristics that make them suitable for many applications. Ionic liquids have low melting temperatures, are liquid at room temperature, have thermal stability up to high temperatures, possess high solubility for both polar and nonpolar organic and inorganic substances, exhibit interesting solvation and coordination properties that depend on the nature of the cation and/or anion, and have very low vapor pressures.^{1,2} This special characteristic of almost null vapor pressure has transformed ionic liquids into good alternatives as the green solvents of future potential and of high commercial interest.

Ionic liquids are typically composed of a large organic cation and an inorganic polyatomic anion. There is virtually no limit to the number of possible ionic liquids since there are a large number of cations and anions that can be combined. Among the many applications of ionic liquids that have been reported in the literature are the following: as media for clean liquid–liquid extraction processes;³ as solvents for electrochemical applications;^{4–6} as recyclable alternatives to aprotic solvents or catalysts for organic and organometallic synthesis;⁷ for catalytic cracking of polyethylene,⁸ and for radical polymerization;^{9,10} and as media for analytical and physical chemistry.¹¹ Some ionic liquids possess liquid crystal or lubricant properties,^{12,13} and others can be used as biocatalysts with great advantages compared to conventional organic solvents.^{14,15} Detailed information about the synthesis and application of ionic liquids is available in the literature.^{16,17}

For the development of new processes using ionic liquids or to continue some of the current studies, the knowledge of physical, physicochemical, and transport properties is essential. In particular, the knowledge of the phase equilibrium behavior is required. During the past five years different research groups have started to measure the required pure-component properties and mixture data. Part of the data has been already published.^{18,19}

Studies on physical and chemical properties of ionic liquids, property measurement methodology, high-quality data on reference systems, standards for reporting thermodynamic data, and the creation of a comprehensive database have been promoted by IUPAC and other institutions.²⁰ Another effort has been made by the Dortmund Data Bank that presently contains pure-component data and mixture data for more than 160 ionic liquids.²¹

For a better understanding of several of these applications, the thermodynamic behavior of mixtures containing ionic liquids must be known. Also, the development of acceptable thermodynamic models requires reliable experimental phase equilibrium data and some basic thermophysical data. However, strategies to determine the critical properties of ionic liquids have not received much attention in the literature. One reason for this slow development is that critical properties of ionic liquids cannot be determined since many of these compounds start to decompose as the temperature approaches the normal boiling point (salts that include the nitrate anion are a good example). Therefore, there are not enough data available to test any predicting or correlating method.² To the best of our knowledge, hypothetical critical properties of ionic liquids are unknown until today.

Recently, Rebelo and co-workers² presented a method to estimate the critical temperatures of some ionic liquids based on the temperature dependence of their surface tensions and liquid densities. These authors used the empirical equations proposed by Eotvos and by Guggenheim. They validated their proposal by estimating critical and normal boiling temperatures of 90 compounds with known T_c and/or T_b values. Then, they

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provided estimations of normal boiling temperatures and critical temperatures for 15 ionic liquids. The authors suggest that the method allows the prediction of those properties with accuracy better than 10%.

In this paper, the critical properties (T_c , P_c , V_c), the normal boiling temperatures, and the acentric factors of 50 ionic liquids are determined. The global accuracy and consistency of the estimated values are done by calculating liquid densities of the ionic liquids and bubble pressures of mixtures containing carbon dioxide and ionic liquids.

Group Contribution Methods for Critical Properties

The development of thermodynamic models for both pure components and mixtures requires the knowledge of the critical properties and other physical parameters. As stated above, these properties cannot be measured for ionic liquids but are still needed in modeling and correlating experimental data on ionic liquid properties and mixtures containing ionic liquids. The so-called group contribution methods have been commonly used to estimate the critical properties of many substances for which these properties are not available. No attempts have been made to apply these methods to estimate the critical temperatures, pressures, and volumes of these ionic liquids.

Among the several proposals presented in the literature, the approach developed by Lydersen²² is perhaps the most widely used group contribution method to estimate critical properties. Similar proposals were presented by Ambrose²³ and Klinecicz and Reid.²⁴ Later, Joback and Reid²⁵ developed a method that is frequently mentioned in the literature and used in several applications. In all these methods, the property of a compound is calculated by summing up the contributions of certain defined groups of atoms, considering at the same time the number frequency of each group occurring in the molecule. Although all these methods have been questioned in the literature,²⁶ they have the advantage of quick estimates without requiring sophisticated computational calculations.

Lydersen²² defined 43 structural groups and proposed the following model equations for the critical properties:

$$T_c = \frac{T_b}{A_L + \sum n_i \Delta T_L - (\sum n_i \Delta T_L)^2} \quad (1)$$

$$P_c = \frac{M}{[C_L + \sum n_i \Delta P_L]^2} \quad (2)$$

$$V_c = E_L + \sum n_i \Delta V_L \quad (3)$$

In these equations n_i is the number of times that a group appears in the molecule, T_b is the normal boiling temperature, ΔT_L is the contribution to the critical temperature, ΔP_L is the contribution to the critical pressure, ΔV_L is the contribution to the critical volume, M is the molecular mass, and A_L , C_L , and E_L are constants. The values of these constants are $A_L = 0.567$, $C_L = 0.34$, and $E_L = 40$.

Joback and Reid²⁵ defined 41 structural groups and proposed the following model equations for the critical properties:

$$T_c = \frac{T_b}{A_J + B_J \sum n_i \Delta T_J - (\sum n_i \Delta T_J)^2} \quad (4)$$

$$P_c = \frac{1}{[C_J + D_J N - \sum n_i \Delta P_J]^2} \quad (5)$$

$$V_c = E_J + \sum n_i \Delta V_J \quad (6)$$

In these equations n_i is the number of times that a group appears in the molecule, N is the number of atoms in the molecule, T_b is the normal boiling temperature, ΔT_J is the contribution to the critical temperature, ΔP_J is the contribution to the critical pressure, ΔV_J is the contribution to the critical volume, and A_J , B_J , C_J , D_J , and E_J are constants. The values of these constants are $A_J = 0.584$, $B_J = 0.965$, $C_J = 0.113$, $D_J = 0.0032$, and $E_J = 17.5$.

Constantinou et al.²⁷ proposed a complex estimation technique, which is based on conjugate forms (alternative formal arrangements of valence electrons). This technique provides reasonable estimations of several properties of pure compounds and allows capturing the differences among isomers. However, the generation of conjugate forms is a nontrivial issue and requires a symbolic computing environment. Another somewhat complex method has been proposed by Constantinou and Gani.²⁸ The method considers the molecular structure of the molecule and estimates a given property at two levels. The primary level uses contributions from simple groups that allow describing a wide variety of organic compounds, while the higher level involves polyfunctional and structural groups that provide more information about molecular fragments whose description through first-order groups is not possible. Joback²⁹ has shown that the method of Constantinou and Gani²⁸ gives errors a little higher than the Lydersen method.

Marrero and Pardillo³⁰ proposed another technique that considers the contributions of interactions between bonding groups instead of the contributions of simple groups, a method that allows distinguishing among isomers. Another interesting method based on neural networks that does not need any additional information, besides the molecular structure, can be found on the Internet,³¹ although no details about the method are provided.

Alvarez and Valderrama³² combined the best results of Lydersen's method with the best results of the Joback–Reid method to propose a “modified Lydersen–Joback–Reid” method that proved to give good results for molecules of high molecular weight. The method considers the equations of Lydersen for the critical pressure and critical volume and the equations of Joback–Reid for the normal boiling temperature and the critical temperature. The authors modified the parameters involved in the different equations for the critical properties. The equation for the normal boiling point was kept as in the original method. The modified Lydersen–Joback–Reid method is summarized in the following four equations:

$$T_b = 198.2 + \sum n \Delta T_{bM} \quad (7)$$

$$T_c = \frac{T_b}{A_M + B_M \sum n \Delta T_M - (\sum n \Delta T_M)^2} \quad (8)$$

$$P_c = \frac{M}{[C_M + \sum n \Delta P_M]^2} \quad (9)$$

$$V_c = E_M + \sum n \Delta V_M \quad (10)$$

The parameters that appear in eqs 7–10 were calculated as $A_M = 0.5703$, $B_M = 1.0121$, $C_M = 0.2573$, and $E_M = 6.75$.

To the best of our knowledge the most recent group contribution method proposed in the literature to estimate the critical properties is that of Skander and Chitour.³³ The authors considered the estimation of critical properties, heats of vaporization, refractive index parameters, and molar volumes of hydrocarbons and petroleum fractions. In another development, Kolská³⁴ presented a group contribution method to estimate the enthalpies and entropies of vaporization of pure organic compounds. Stefanis et al.³⁵ have extended the method of Constantinou and Gani²⁸ and applied it to the calculation of the octanol–water partition coefficient, the flash point, and the solubility parameters at 25 °C.

Extension of the Methods to Ionic Liquids

Of the methods explained above, the modified Lydersen–Joback–Reid, developed by one of the authors, has been used to extend its applicability to predict the critical properties of ionic liquids. The extension of the method has been done in a simple way. Three new groups were included: $-B$, $-SO_2$, $-P$. Their contributions to T_b , T_c , P_c , and V_c were determined in a way similar to that explained by Alvarez and Valderrama.³² The values of these groups are summarized in Table 1. The table also shows the values of all groups for this method. Once the values of the three new groups ($-B$, $-SO_2$, $-P$) have been determined, the critical properties, the acentric factors, and the normal boiling temperatures of 50 ionic liquids have been determined.

As a test of the “consistency” of the predicted properties, the liquid densities of the ionic liquids have been estimated using a generalized correlation proposed by one of the authors.³⁶ The generalized correlation is based on the equation of Spencer and Danner³⁷ and needs only the normal boiling temperature, the molecular weight, and the critical properties:

$$\rho_L = \frac{MP_c}{RT_c} \left[\frac{0.3445 P_c V_c^{1.0135}}{RT_c} \right]^\Omega \quad (11)$$

$$\Omega = - \left[\frac{1 + (1 - T_R)^{2/7}}{1 + (1 - T_{bR})^{2/7}} \right]$$

In these equations, ρ_L is the liquid density in grams per cubic centimeter, R is the ideal gas constant, T_R is the reduced temperature ($T_R = T/T_c$), and T_{bR} is the reduced temperature at the normal boiling point ($T_{bR} = T_b/T_c$).

The acentric factors of the ionic liquids, also needed for equation of state applications, were determined using the definition of this property:

$$\omega = -\log \left(\frac{P^s}{P_c} \right)_{(T/T_c)=0.7} - 1.0 \quad (12)$$

The value of the saturation pressure P^s at $T/T_c = 0.7$ was estimated using the values of temperature and pressure at the critical point (P_c , T_c), using the values at the normal boiling point (P_b , T_b), and considering the relation of Rudkin³⁸ for the vapor pressure. In this approach the author considered water as the reference fluid and used the Antoine equation to relate the vapor pressure P^s and the temperature T . Rudkin used the value

Table 1. Groups Considered for the Modified Lydersen–Joback–Reid Method

groups	ΔT_{bM}	ΔT_M	ΔP_M	ΔV_M
Without Rings				
$-CH_3$	23.58	0.0275	0.3031	66.81
$-CH_2-$	22.88	0.0159	0.2165	57.11
$>CH-$	21.74	0.0002	0.1140	45.70
$>C<$	18.18	-0.0206	0.0539	21.78
$=CH_2$	24.96	0.0170	0.2493	60.37
$=CH-$	18.25	0.0182	0.1866	49.92
$=C<$	24.14	-0.0003	0.0832	34.90
$=C=$	26.15	-0.0029	0.0934	33.85
$\equiv CH$		0.0078	0.1429	43.97
$\equiv C-$		0.0078	0.1429	43.97
$-OH$ (alcohol)	92.88	0.0723	0.1343	30.40
$-O-$	22.42	0.0051	0.1300	15.61
$>C=O$	94.97	0.0247	0.2341	69.76
$-CHO$	72.24	0.0294	0.3128	77.46
$-COOH$	169.06	0.0853	0.4537	88.60
$-COO-$	81.10	0.0377	0.4139	84.76
$HCOO-$		0.0360	0.4752	97.77
$=O$ (others)	-10.50	0.0273	0.2042	44.03
$-NH_2$	73.23	0.0364	0.1692	49.10
$>NH$	50.17	0.0119	0.0322	78.96
$>N-$	11.74	-0.0028	0.0304	26.70
$-N=$	74.60	0.0172	0.1541	45.54
$-CN$	125.66	0.0506	0.3697	89.32
$-NO_2$	152.54	0.0448	0.4529	123.62
$-F$	-0.03	0.0228	0.2912	31.47
$-Cl$	38.13	0.0188	0.3738	62.08
$-Br$	66.86	0.0124	0.5799	76.60
$-I$	93.84	0.0148	0.9174	100.79
With Rings				
$-CH_2-$	27.15	0.0116	0.1982	51.64
$>CH-$	21.78	0.0081	0.1773	30.56
$=CH-$	26.73	0.0114	0.1693	42.55
$>C<$	21.32	-0.0180	0.0139	17.62
$=C<$	31.01	0.0051	0.0955	31.28
$-O-$	31.22	0.0138	0.1371	17.41
$-OH$ (phenol)	76.34	0.0291	0.0493	-17.44
$>C=O$	94.97	0.0343	0.2751	59.32
$>NH$	52.82	0.0244	0.0724	27.61
$>N-$		0.0063	0.0538	25.17
$-N=$	57.55	-0.0011	0.0559	42.15
New Groups				
$-B$	-24.56	0.0352	0.0348	22.45
$-P$	34.86	-0.0084	0.1776	67.01
$-SO_2$	147.24	-0.0563	-0.0606	112.19

$C = 43$ (with T in Kelvin), a value corresponding to water, the reference fluid. The equation is

$$\log P^s = A - \frac{B}{T - 43} \quad (13)$$

Replacing the above equations, the acentric factor is calculated as

$$\omega = \frac{(T_b - 43)(T_c - 43)}{(T_c - T_b)(0.7T_c - 43)} \log \left[\frac{P_c}{P_b} \right] - \frac{(T_c - 43)}{(T_c - T_b)} \log \left[\frac{P_c}{P_b} \right] + \log \left[\frac{P_c}{P_b} \right] - 1 \quad (14)$$

The calculated critical properties, the normal boiling temperatures (T_b for $P_b = 1$ atm), and the acentric factors are presented in Table 2. The molecular weight is also included in Table 3, a value that is needed in density calculations (eq 11).

Results and Discussion

The estimated critical properties are listed in Table 2 for 50 ionic liquids. Table 3 presents the estimated densities of the

Table 2. Critical Properties of Ionic Liquids, Calculated by Group Contribution

no.	ionic liquid	global formula	IUPAC name	T_b (K)	T_c (K)	P_c (bar)	V_c (cm ³ /mol)	ω	T_b/T_c
1	[bmim][BF ₄]	C ₈ H ₁₅ N ₃ BF ₄	1-butyl-3-methylimidazolium tetrafluoroborate	484.6	632.3	20.4	672.0	0.8489	0.766
2	[emim][BF ₄]	C ₈ H ₁₁ N ₃ BF ₄	1-ethyl-3-methylimidazolium tetrafluoroborate	438.9	585.3	23.6	557.8	0.7685	0.750
3	[hmim][BF ₄]	C ₁₀ H ₁₉ N ₃ BF ₄	1-hexyl-3-methylimidazolium tetrafluoroborate	530.4	679.1	17.9	786.2	0.9258	0.781
4	[mbupyl][BF ₄]	C ₁₀ H ₁₆ NBF ₄	4-methyl- <i>n</i> -butylpyridinium tetrafluoroborate	484.8	625.8	18.9	703.7	0.8923	0.775
5	[<i>N</i> -bupyl][BF ₄]	C ₉ H ₁₄ NBF ₄	<i>N</i> -butylpyridinium tetrafluoroborate	456.9	597.6	20.3	648.1	0.8307	0.765
6	[omim][BF ₄]	C ₁₂ H ₂₃ N ₃ BF ₄	1- <i>n</i> -octyl-3-methylimidazolium tetrafluoroborate	576.1	726.1	16.0	900.4	0.9954	0.793
7	[phoedma][Br]	C ₈ H ₂₀ NBrO	butyl-(2-hydroxyethyl)-dimethylammonium bromide	554.8	732.3	25.2	626.4	0.8841	0.758
8	[phoedma][Br]	C ₈ H ₁₆ NBrO	ethyl-(2-hydroxyethyl)-dimethylammonium bromide	509.1	687.9	30.2	512.2	0.8078	0.740
9	[phoedma][Br]	C ₁₀ H ₂₄ NBrO	hexyl-(2-hydroxyethyl)-dimethylammonium bromide	600.6	776.6	21.7	740.7	0.9601	0.773
10	[hoedmpa][Br]	C ₇ H ₁₈ NBrO	(2-hydroxyethyl)-dimethylpropylammonium bromide	531.9	710.1	27.5	569.3	0.8455	0.749
11	[beim][bti]	C ₁₁ H ₁₇ N ₃ F ₆ S ₂ O ₄	1-butyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide	874.7	1275.9	25.6	1064.2	0.3093	0.686
12	[bmim][bti]	C ₁₀ H ₁₅ N ₃ F ₆ S ₂ O ₄	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	851.8	1265.0	27.6	1007.1	0.2656	0.673
13	[bmpryl][bti]	C ₁₀ H ₁₇ N ₃ F ₆ S ₂ O ₄	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	741.6	1110.1	27.9	960.1	0.2383	0.668
14	[deim][bti]	C ₉ H ₁₃ N ₃ F ₆ S ₂ O ₄	1,3-diethylimidazolium bis(trifluoromethylsulfonyl)imide	829.0	1254.7	29.9	950.0	0.2231	0.661
15	[dmeim][bti]	C ₉ H ₁₆ N ₃ F ₆ S ₂ O ₄	dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide	833.9	1254.1	29.7	948.4	0.2447	0.665
16	[dmim][bti]	C ₇ H ₉ N ₃ F ₆ S ₂ O ₄	1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	833.2	1235.7	35.8	835.8	0.1418	0.634
17	[ednim][bti]	C ₈ H ₁₃ N ₃ F ₆ S ₂ O ₄	1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	833.9	1254.1	29.7	948.4	0.2447	0.665
18	[eDnim][bti]	C ₈ H ₁₃ N ₃ F ₆ S ₂ O ₄	1-ethyl-1,3,5-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	833.9	1254.1	29.7	948.4	0.2447	0.665
19	[emim][bti]	C ₈ H ₁₁ N ₃ F ₆ S ₂ O ₄	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	806.1	1244.9	32.6	892.9	0.1818	0.647
20	[hmim][bti]	C ₁₂ H ₁₉ N ₃ F ₆ S ₂ O ₄	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	897.6	1287.3	23.9	1121.3	0.3539	0.697
21	[ibmim][bti]	C ₁₀ H ₁₅ N ₃ F ₆ S ₂ O ₄	1-isobutyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	851.4	1270.4	27.8	1005.4	0.2501	0.670
22	[mdemim][bti]	C ₁₀ H ₁₅ N ₃ F ₆ S ₂ O ₄	5-methyl-1,3-diethylimidazolium bis(trifluoromethylsulfonyl)imide	856.8	1264.7	27.4	1005.4	0.2875	0.678
23	[meim][bti]	C ₈ H ₁₁ N ₃ F ₆ S ₂ O ₄	1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide	806.1	1244.9	32.6	892.9	0.1818	0.647
24	[moemim][bti]	C ₉ H ₁₃ N ₃ F ₆ S ₂ O ₄	1-methoxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	851.4	1280.6	27.9	965.6	0.2208	0.665
25	[omim][bti]	C ₁₂ H ₂₃ N ₃ F ₆ S ₂ O ₄	1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	943.4	1311.9	21.0	1235.6	0.4453	0.719
26	[tfemim][bti]	C ₈ H ₈ N ₃ F ₆ S ₂ O ₄	1-trifluoroethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	800.7	1205.3	26.6	942.3	0.2604	0.664
27	[fomim][Cl]	C ₁₂ H ₂₃ N ₂ Cl	1-octyl-3-methylimidazolium chloride	638.9	860.1	20.3	814.2	0.6190	0.743
28	[emim][EtSO ₄]	C ₈ H ₁₆ N ₂ S ₂ O ₄	1-ethyl-3-methylimidazolium ethyl sulfate	702.1	1061.1	40.4	676.8	0.3368	0.662
29	[OHea][f]	C ₃ H ₉ NO ₃	2-hydroxyethylammonium formate	491.2	683.2	54.0	285.2	0.8979	0.719
30	[bmim][hb]	C ₁₂ H ₁₅ N ₂ F ₇ O ₂	1-butyl-3-methylimidazolium heptafluorobutanoate	644.9	836.7	15.6	894.0	0.7249	0.771
31	[emim][hb]	C ₁₀ H ₁₁ N ₂ F ₇ O ₂	1-ethyl-3-methylimidazolium heptafluorobutanoate	599.2	793.9	17.4	779.8	0.6393	0.755
32	[beim][MsO]	C ₁₀ H ₂₀ N ₂ S ₂ O ₃	1-butyl-3-methylimidazolium methylsulfonate	725.4	1062.7	33.5	775.4	0.3986	0.683
33	[emim][MsO]	C ₇ H ₁₄ N ₂ S ₂ O ₃	1-ethyl-3-methylimidazolium methylsulfonate	656.8	1019.5	48.0	604.0	0.2930	0.644
34	[beim][NFO]	C ₁₃ H ₁₇ N ₂ F ₇ SO ₃	1-butyl-3-ethylimidazolium nonafluorobutanesulfonate	774.6	1038.5	16.4	1078.9	0.5256	0.746
35	[emim][NFO]	C ₁₂ H ₁₅ N ₂ F ₇ SO ₃	1-butyl-3-methylimidazolium nonafluorobutanesulfonate	752.4	1012.1	16.7	1031.5	0.5159	0.743
36	[bmim][NO ₃]	C ₈ H ₁₅ N ₃ O ₂	1- <i>n</i> -butyl-3-methylimidazolium nitrate	684.3	946.3	27.3	662.9	0.6039	0.723
37	[bmim][PF ₆]	C ₈ H ₁₅ N ₃ PF ₆	1- <i>n</i> -butyl-3-methylimidazolium hexafluorophosphate	544.0	708.9	17.3	779.5	0.7553	0.767
38	[emim][PF ₆]	C ₈ H ₁₁ N ₃ PF ₆	1-ethyl-3-methylimidazolium hexafluorophosphate	498.2	663.5	19.5	663.3	0.6708	0.751
39	[hmim][PF ₆]	C ₁₀ H ₁₉ N ₃ PF ₆	1-hexyl-3-methylimidazolium hexafluorophosphate	589.7	754.3	15.5	893.7	0.8352	0.782
40	[omim][PF ₆]	C ₁₂ H ₂₃ N ₃ PF ₆	1- <i>n</i> -octyl-3-methylimidazolium hexafluorophosphate	635.5	800.1	14.0	1007.9	0.9069	0.794
41	[beim][ta]	C ₁₁ H ₁₇ N ₂ F ₃ O ₂	1-butyl-3-ethylimidazolium trifluoroacetate	631.4	838.0	19.6	781.7	0.6936	0.754
42	[bmim][ta]	C ₁₀ H ₁₅ N ₂ F ₃ O ₂	1-butyl-3-methylimidazolium trifluoroacetate	608.6	817.2	20.9	724.6	0.6509	0.745
43	[deim][ta]	C ₈ H ₁₃ N ₂ F ₃ O ₂	1,3-diethylimidazolium trifluoroacetate	585.7	796.5	22.4	667.5	0.6085	0.735
44	[emim][ta]	C ₈ H ₁₅ N ₂ F ₃ O ₂	1-ethyl-3-methylimidazolium trifluoroacetate	562.8	775.7	24.2	610.4	0.5664	0.725
45	[beim][TFO]	C ₁₀ H ₁₇ N ₂ F ₃ SO ₃	1-butyl-3-ethylimidazolium trifluoromethanesulfonate	720.0	1032.1	27.0	824.8	0.4091	0.698
46	[bmim][TFO]	C ₈ H ₁₅ N ₂ F ₃ SO ₃	1-butyl-3-methylimidazolium trifluoromethanesulfonate	697.1	1016.3	29.4	767.6	0.3677	0.686
47	[deim][TFO]	C ₈ H ₁₃ N ₂ F ₃ SO ₃	1,3-diethylimidazolium trifluoromethanesulfonate	674.2	1000.7	32.3	710.5	0.3276	0.674
48	[doemim][TFO]	C ₁₈ H ₃₁ N ₂ F ₃ SO ₃	1-dodecyl-3-ethylimidazolium trifluoromethanesulfonate	903.0	1168.6	16.0	1281.6	0.7552	0.773
49	[ednimim][TFO]	C ₈ H ₁₃ N ₂ F ₃ SO ₃	1-ethyl-3,5-dimethylimidazolium trifluoromethanesulfonate	679.2	1001.9	32.0	709.0	0.3499	0.678
50	[emim][TFO]	C ₇ H ₁₁ N ₂ F ₃ SO ₃	1-ethyl-3-methylimidazolium trifluoromethanesulfonate	651.4	985.2	35.8	653.4	0.2891	0.661

Table 3. Densities Calculated with the Generalized Correlation (Equation 11) and Comparison with Literature Values^a

no.	formula	<i>M</i>	<i>T</i>	ρ^{lit}	ρ^{calc}	% $\Delta\rho^{\text{calc}}$
1	[bmim][BF ₄]	226.0	298.15	1.2080 ⁴¹	1.1398	-5.6
2	[emim][BF ₄]	198.0	295.15	1.2400 ⁴¹	1.1541	-6.9
3	[hmim][BF ₄]	254.0	298.15	1.1484 ⁴²	1.1415	-0.6
4	[mbupy][BF ₄]	237.0	298.15	1.1842 ⁴³	1.1514	-2.8
5	[<i>N</i> -bupy][BF ₄]	223.0	313.15	1.2030 ¹⁹	1.1229	-6.7
6	[omim][BF ₄]	282.1	313.15	1.0800 ¹⁹	1.1362	5.2
7	[bhoedma][Br]	226.2	298.15	1.0670 ⁴⁴	1.2602	18.1
8	[ehoedma][Br]	198.1	298.15	1.1018 ⁴⁴	1.3002	18.0
9	[hhoedma][Br]	254.3	298.15	1.0412 ⁴⁴	1.2425	19.3
10	[hoedmpa][Br]	212.1	298.15	1.0827 ⁴⁴	1.2762	17.9
11	[beim][bti]	433.3	295.15	1.4040 ⁴¹	1.4284	1.7
12	[bmim][bti]	419.2	295.15	1.4290 ⁴¹	1.4381	0.6
13	[bmpyr][bti]	407.3	313.15	1.3860 ⁴⁵	1.4125	1.9
14	[deim][bti]	405.2	295.15	1.4520 ⁴¹	1.4515	-0.03
15	[dmeim][bti]	405.2	298.15	1.4802 ⁴⁶	1.4593	-1.4
16	[dmim][bti]	377.2	298.15	1.5590 ⁴¹	1.4910	-4.4
17	[edmim][bti]	405.2	295.15	1.4950 ⁴¹	1.4609	-2.3
18	[eDmim][bti]	405.2	295.15	1.4700 ⁴¹	1.4609	-0.6
19	[emim][bti]	391.2	295.15	1.5200 ⁴¹	1.4689	-3.4
20	[hmim][bti]	447.3	313.15	1.3560 ⁴⁵	1.4118	4.1
21	[ibmim][bti]	419.2	295.15	1.4280 ⁴¹	1.4365	0.6
22	[mdeim][bti]	419.2	295.15	1.4320 ⁴¹	1.4473	1.1
23	[meim][bti]	391.2	298.15	1.5252 ⁴⁶	1.4673	-3.8
24	[moemim][bti]	405.2	295.15	1.4960 ⁴¹	1.4482	-3.2
25	[omim][bti]	475.4	313.15	1.3110 ⁴⁵	1.4049	7.2
26	[tfemim][bti]	445.2	295.15	1.6560 ⁴¹	1.6212	-2.1
27	[omim][Cl]	230.8	298.15	1.0070 ⁴⁷	1.0158	0.9
28	[emim][EtSO ₄]	236.3	313.15	1.2250 ¹⁹	1.1476	-6.3
29	[OHea][f]	107.1	298.15	1.2040 ⁴⁸	1.2420	3.2
30	[bmim][hb]	352.3	295.15	1.1330 ⁴¹	1.4850	11.4
31	[emim][hb]	324.2	295.15	1.4500 ⁴¹	1.5130	4.3
32	[beim][MsO]	248.3	298.15	1.1400 ⁴¹	1.0830	-5.0
33	[emim][MsO]	206.2	298.15	1.2400 ⁴¹	1.0990	-11.3
34	[beim][NfO]	452.3	295.15	1.4270 ⁴¹	1.5796	10.7
35	[emim][NfO]	438.3	295.15	1.4430 ⁴¹	1.5905	8.0
36	[bmim][NO ₃]	201.2	313.15	1.1490 ¹⁹	1.0758	-6.4
37	[bmim][PF ₆]	284.2	313.15	1.3460 ¹⁹	1.2760	-5.2
38	[emim][PF ₆]	256.2	298.15	1.4133 ^b	1.3122	7.2
39	[hmim][PF ₆]	312.2	298.15	1.2781 ⁴²	1.2871	0.7
40	[omim][PF ₆]	340.3	313.15	1.2110 ¹⁹	1.2744	5.2
41	[beim][ta]	266.3	295.15	1.1830 ⁴¹	1.2422	5.0
42	[bmim][ta]	252.2	295.15	1.2090 ⁴¹	1.2474	3.2
43	[deim][ta]	238.2	295.15	1.2500 ⁴¹	1.2568	0.5
44	[emim][ta]	224.2	295.15	1.2850 ⁴¹	1.2710	-1.1
45	[beim][TfO]	302.2	295.15	1.2700 ⁴¹	1.2690	-0.1
46	[bmim][TfO]	288.2	298.15	1.2980 ⁵⁰	1.2795	-1.4
47	[deim][TfO]	274.2	295.15	1.3300 ⁴¹	1.2963	-2.5
48	[doeim][TfO]	412.5	295.15	1.1000 ⁴¹	1.2698	15.4
49	[edmim][TfO]	274.2	295.15	1.3340 ⁴¹	1.3061	-2.1
50	[emim][TfO]	260.2	298.15	1.3900 ⁴¹	1.3168	-5.3

^a The reference corresponds to the source from where the literature value was obtained. ^b Extrapolated value.

substances determined using the generalized correlation given by eq 11. As explained above, this calculation of density is done as a global test of the consistency of the estimated critical properties presented in Table 3. In fact, the 50 ionic liquids considered in this study are those for which density values are available in the literature, so that the test could be performed.

As explained in the Introduction, Rebelo and co-workers² presented some values for the critical temperature of selected ionic liquids using the empirical equations proposed by Eotvos and by Guggenheim. However, the calculation method deserves at least some comments. They determined first the normal boiling temperature using the methods of Eotvos and of Guggenheim. Then they assumed that the ratio T_b/T_c was equal to 0.6 and estimated the critical temperatures as $T_c = 0.6T_b$. Riddick et al.³⁹ gives the average value of this ratio for groups of compounds and shows that for all of them the ratio is higher than 0.6: it is 0.686 for alcohols, 0.676 for acids, 0.677 for esters, 0.658 for amines, and 0.621 for halides. If one takes all the substances for which T_b and T_c are available in the database of Poling et al.,²⁶ the average ratio T_b/T_c is 0.71; if one takes

the 29 substances with molecular weight higher than 200 (as the majority of the ionic liquids considered in this study), the average ratio T_b/T_c is 0.71. The conclusion one can obtain from these values is that considering the ratio $T_b/T_c = 0.6$ for ionic liquids is not sustained by the tendency of hundreds of other substances. The results presented in Table 2 give values of T_b/T_c in the range 0.64–0.79, the average being 0.72.

As observed in Table 3, the predicted densities, using exclusively the calculated critical properties and the calculated normal boiling temperatures, are within acceptable margins of errors for the purpose of the checking. The maximum deviation is 19.3% for [hhoedma][Br], the average deviation is 1.6%, and the average absolute deviation is 5.2%.

It should be finally mentioned that the generalized correlation used to estimate the densities of ionic liquids (eq 11), was derived totally independent of the group contribution method used to estimate the critical properties of ionic liquids (eqs 7–10) and has been successfully applied to estimate the densities of complex substances.^{36,40} Therefore, density calculation is a reliable independent test to show that the values of the critical

properties of ionic liquids are acceptable and can be used in other applications where these properties are needed.

Conclusions

A consistent group contribution method has been extended to evaluate the critical properties of 50 ionic liquids. Additionally, estimated values for the normal boiling temperatures and the acentric factors of these substances were determined. The consistency of the method has been checked using literature values of ionic liquid densities and comparing them with calculated values using a generalized correlation that makes use of those estimated critical properties. The values provided for the critical properties, for the normal boiling temperature, and for the acentric factors are believed to be accurate enough for engineering calculations, for generalized correlations, and for equation of state calculations, among other applications.

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Notation

A, B, C = constants of the Antoine equation
 A_L, C_L, E_L = coefficients in the Lydersen method
 A_J, B_J, C_J, D_J, E_J = coefficients in the Joback–Reid method
 A_M, B_M, C_M, D_M, E_M = coefficients in the modified Lydersen–Joback–Reid method
 M = molecular mass
 N = number of atoms in the molecule
 n_i = number of times that a group appears in a molecule
 P_b = boiling pressure
 P_c = critical pressure
 P^s = vapor pressure
 P^{calc} = calculated pressure
 P^{exp} = experimental pressure
 T = temperature
 T_b = normal boiling temperature
 T_{bR} = reduced temperature at the normal boiling point
 T_c = critical temperature
 T_R = reduced temperature
 V_c = critical volume

Abbreviations

eq = equation
 log = base 10 logarithm

Greek Symbols

ρ_L = liquid density
 ρ^{lit} = ionic liquid density from the literature
 ρ^{calc} = liquid density calculated with the proposed method
 $\%\Delta\rho^{\text{calc}}$ = percent relative deviation between calculated and literature values for the liquid density
 ω = acentric factor
 ΔT_{bJ} = contribution to the normal boiling temperature in the Joback–Reid method (eq 7)
 $\Delta T_L, \Delta P_L, \Delta V_L$ = contribution to the critical properties in the Lydersen method (eqs 1–3)
 $\Delta T_J, \Delta P_J, \Delta V_J$ = contribution to the critical properties in the Joback–Reid method (eqs 4–6)

$\Delta T_M, \Delta P_M, \Delta V_M$ = contribution to the critical properties in the modified Lydersen–Joback–Reid method (eqs 7–10)

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