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Critical Properties and Vapor Pressure of Twenty Imidazolium based Ionic Liquids used in Extraction Bioprocesses

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Abstract

The critical properties and the vapor pressure of twenty of the most common imidazolium based ionic liquids (ILs) are determined using a group contribution method proposed by the authors. This special type of ionic liquids have been widely tested in several bioprocesses but the critical properties and the vapor pressure are not available. This is mainly due to the fact that ILs start to decompose at low temperature and in many cases at temperatures approaching the normal boiling point. For the development of new bioprocesses using ionic liquids or to continue some of the studies currently investigated, the knowledge of physical, physicochemical and transport properties of these substances are required. In particular if some advances are to be done on applications of standard correlations, equations of state calculations, phase equilibrium correlation, and thermodynamic consistency, the critical properties are needed. An extended group contribution method based on the wellknown concepts of Lydersen and of Joback and Reid developed by the authors has been employed to determine the critical properties and the normal boiling temperature of IL`s. From these calculated values the vapor pressure curve is estimated. Since there are not experimental data to compare the predicted critical properties, density calculations correlations are done to test the consistency of the estimated group contribution values. Overall average deviations are lower than 1.2% and overall absolute deviations are lower than 5.4%. The values provided for the critical properties and for the vapor pressures are believed to be accurate enough for engineering calculations, for generalized correlations and for equation of state methods, among other uses.

Introduction

Ionic liquids have received increasing attention as potential substitutes for classic organic solvents in many different applications, especially as reaction media and separation agents. Organic solvents are volatile substances, which contribute to environmental pollution and lead to important operating costs due to losses by evaporation (Roger and Seddon, 2002). 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; posses high solubility for both polar and non-polar 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 pressure [Roger and Seddon, 2002; Wasserscheid and Welton, 2002]. This special characteristic of almost null vapor pressure has transformed ionic liquids into good alternatives as the green solvents of potential commercial interest.

Bioproceses such as recovery of amino acids, processing of lignocellulosic materials, extration of essential oils, extraction of organic acids, separation of polyphenolic compounds extracted from plant matrices, extraction and recovery of azo dyes, separation of bioactive flavonoids, solvents for multiphase bioprocess operations, analysis of amino acids, peptides and proteins in ionic liquids, among others have been discussed in the literature. Zhao (2006) has reviewed some of the most important advances of ILs as versatile "green" engineering liquids in a variety of industrial applications including heat transfer fluids, azeotrope-breaking liquids, lubricants, electrolytes, liquid crystals, supported IL membranes, and plasticizers, among others. The Table 1 presents some recent advances on which we call here bioproceses and the ionic liquids commonly involved in these applications. As seen in Table 1, the imidazolium based ionic liquids have been widely tested in several bioproces.

For the development of new processes using ionic liquids or to continue some of the studies currently investigated, the knowledge of physical, physicochemical and transport properties of ionic liquids are required. In particular if some advances are to be done on applications of standard correlations, equations of state calculations, phase equilibrium correlation and prediction, the critical properties are needed.

Theoretical studies have been developed to calculate some physical and transport properties and to explain the fundamentally different behavior of ionic liquids from that of molecular liquids.1,2 One could think then that to correlate and to develop predictive methods to estimate

properties of ionic liquids one would require a completely new formalism that could explain such a different behavior. However it has been already proved that some methods developed for molecular liquids can be extended to accurately predict the properties of ionic liquids. 3,5,6 On this same line, this work proposes to use classical group contribution methods as the thermodynamic tool and artificial neural networks (ANN) as the mathematical tool to relate the properties and the molecular structure. An extension of classical group contribution methods to estimate the normal boiling temperature (Tb), critical temperature (Tc), critical pressure (Pc), critical volume (Vc), and acentric factor (□) of ionic liquids have been presented in the literature.5,6 The method followed the classical scheme of determining the values of the contributions and applying model equations for each property of interest and did not consider the use of artificial neural networks (ANN) as proposed in this work.

Table 1: Selected applications of ionic liquids to bioproceses

IL	Applications	Reference
$[C_4mim][PF_6]$, $[C_6mim][PF_6]$, $[C_6mim][BF_4]$ and $[C_8mim][BF_4]$	Recovery of amino acids by imidazolium based ionic liquids from aqueous media	Wang et al (2005)
$[BF_4]$ anion	Selective Extraction of Bioproducts by Ionic Liquids	Wang et al. (2005)
imidazolium-based ionic liquids	Extraction of organic acids using imidazolium-based ionic liquids	Matsumoto et al. (2004)
1-alkyl-3-methyl-imidazolium-based ionic liquids	Separation of bioactive flavonoids by capillary zone electrophoresis	Yue and Shi (2005)
$[bmim][PF_6]$	Ionic liquids solvents in multiphase bioprocess operations	Cull et al. (2000)
$[hmim][CF_3SO_3]$, $[mmim][MeSO_4]$ $[bmim][MeSO_4]$.	Ionic Liquid as a Green Solvent for Lignin	Pu et al. (2007)
1-butyl-3-methylimidazolium chloride	Properties of starch of four botanical sources dispersed in the ionic liquid	Stevenson et al. (2007)
1-n-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$).	Processing of lignocellulosic materials	Fort et al. (2007)
1-ethyl-3-methylimidazolium methanesulfonate	Citrus essential oil deterpenation	Arce et al. (2007)

Property estimation

The basis of the estimation method is the concept of group contribution for the critical properties and the Antoine equation for the vapor pressure. Both type of calculations are generalizations derived for molecular fluids and have not been applied to ionic liquids.

i) crtitical properties

Among the several proposals presented in the literature, the approach developed by Lydersen (1957) is perhaps the most widely used group contribution method to estimate critical properties. Later, Joback and Reid (1987) 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 (Reid et al., 1987), they have the advantage of quick estimates without requiring sophisticated computational calculations.

Alvarez and Valderrama (2004) combined the best results of Lydersen`s method with the best results of Joback-Reid method to proposed 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. Valderrama and Robles (2007, 2007a) have recently presented a procedure to estimate the critical properties of ionic liquids using the "*Modified Lydersen-Joback-Reid*". The method have been extended and applied to another 200 ionic liquids by Valderrama and Sanga (2008).

Since there are not experimental critical properties to evaluate the accuracy of the estimates, these values were tested for accuracy and consistency by determining the density of the ionic liquids, for which experimental data are available, using an independent equation, not employed in determining the critical properties. The deviations found between experimental and calculated densities are within experimental errors as shown by the authors. Since experimental data do not exist and there is no reasonable and generally accepted theory yet available to estimate these properties for ionic liquids, the extension of standard methods such as Group Contribution seems to be reasonable. Also, the independent test of using the estimated critical properties to calculate the density of ionic liquids gives indication of the consistency of the estimated values. Details of the group contribution method has been given by Valderrama and Robles (2007) so it is only summarized in Tables 1 and 2. Table 1 shows the main equations for the normal boiling temperature and the critical properties while Table 2 lists the groups used in estimating the properties of the selected ionic liquids.

Table 2: Groups considered in the Modified Lydersen-Joback-Reid method and equations describing the model

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< [>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
-O- [-O]$^-$	22.42	0.0051	0.1300	15.61
>C=O	94.97	0.0247	0.2341	69.76
-COO-	81.10	0.0377	0.4139	84.76
>N- [>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
-F [F^-]	-0.03	0.0228	0.2912	31.47
-Cl [Cl^-]	38.13	0.0188	0.3738	62.08
-I [I^-]	93.84	0.0148	0.9174	100.79
with rings				
$-CH_2-$	27.15	0.0116	0.1982	51.64
=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
>N- [>N<]$^+$	68.16	0.0063	0.0538	25.17
-N= [>N=]$^+$	57.55	-0.0011	0.0559	42.15
New groups				
-B	-24.56	-0.0264	0.0348	22.45
-P	34.86	0.0067	0.1776	67.01
-S- [>S-]$^+$	117.52	-0.0004	0.6901	184.67
$-SO_2-$	147.24	-0.0563	-0.0606	112.19
Model equations				Constants
$T_b = 198.2 + \sum n\Delta T_{bM}$ $T_c = \frac{T_b}{\left[A_M + B_M \sum n\Delta T_M - \left(\sum n\Delta T_M\right)^2\right]}$		$P_c = \frac{M}{\left[C_M + \sum n\Delta P_M\right]^2}$ $V_c = E_M + \sum n\Delta V_M$		$A_M = 0.5703$ $B_M = 1.0121$ $C_M = 0.2573$ $E_M = 6.75$

As a test of the "consistency" of the predicted properties, the liquid density of the ionic liquids has been estimated using a generalized correlation. In this work a more flexible correlation proposed by one of the authors have been used (Valderrama and Abu-Shark, 1989). This correlation has shown to give accurate predictions for many fluids and is based on the equation of Shah and Yaws (1976). It needs only the normal boiling temperature, the molecular weight and the critical properties:

$$\rho_L = (0.01256 + 0.9533M / V_C)\left[(0.0039 / M + 0.2987 / V_C)V_C^{1.033}\right]^{\Psi} \qquad (1)$$

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

In these equations, ρ_L is the liquid density in (gr/cc), 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).

Vapor Pressure

Rudkin (1961), considered water as reference fluid and used the Antoine equation (Log P^s=A-B/[T+C] to relate the vapor pressure P^s of any fluid with the temperature T. Rudkin used a value C=43 (with T in Kelvin), value corresponding to water, the reference fluid. The equation is:

$$\mathrm{Log}P^s = A - \frac{B}{T - 43} \qquad (13)$$

The constants A and B were estimated for the 20 ionic liquids considereded in this paper.

$$A = \mathrm{Log}(P_c) * (T_c - 43)/(T_c - T_b) \qquad (3)$$

$$B = \mathrm{Log}(P_c) * (T_c - 43) * (T_b - 43)/(T_c - T_b)$$

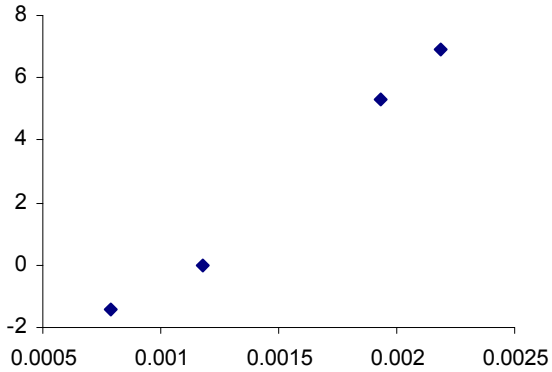
Results and Discussion

The calculated critical properties, the normal boiling temperature (T_b for P_b=1 atm), the vapor pressure constants and the estimated densities at room temperature are presented in Table 3. The molecular weight is also included in the Table 3, value that is needed in density calculations (eqn. 1).

As explained above, the calculation of the density is done as a global test of the consistency of the estimated critical properties. For the 20 ionic liquids considered in this study density values are available in the literature, so that the test could be performed. Deviations between predicted densities and the xperimental values are 1.7% in the average, being a little higher than 10% for only 2 cases. The predictions are within the deviations presented by reported experimental data found in the literature for ionic liquids. For insdtance, for [omim][PF6] differences up to 17.6% are found between density data at 298K reported by Wu et al. (2001) and Branco et al. (2002). The calculated values are for now very aproximates estimations but that show the expected tendency. Proof of this is figure 1 in which the estimated vapor pressure of xxxx are plotted in a logP-vs-(1/T) graph. Also some experimental data avilable in the literature for this ionic liquids is ploted. The figure correponds to bti ionic liquids since no data waere found for imidazolium pf6 or bf4 ionic liquids were found. We expect similar behaviuor for other ionic liquids when vapor pressure data are available.

Table 3: Critical properties of ionic liquids calculated by group contribution and constant A and B in the Antoine equation for the vapor pressure.

Nº	Ionic Liquid	M	T_b (K)	T_c (K)	Pc (bar)	V_c (cc/mol)	A	B	ω	T	ρlit	ρ^{calc}	%Δρ
1	[dmim][BF4]	310	632.5	784.6	14.5	997.7	5.663	3338.1	1.082	298	1.040	1.144	10.0
2	[prmim][BF4]	212	472.3	619.7	21.8	597.9	5.237	2248.1	0.848	298	1.240	1.164	-6.1
3	[bdmim][BF4]	240	523.1	671.0	18.9	710.5	5.420	2602.1	0.948	300	1.094	1.157	5.8
4	[mommim][BF4]	214	471.9	623.7	23.3	556.4	5.231	2243.5	0.829	298	1.330	1.260	-5.3
5	[moemim][BF4]	228	494.8	647.0	21.7	613.5	5.304	2396.2	0.869	298	1.260	1.240	-1.6
6	[moeoemim][BF4]	272	562.9	720.2	18.8	743.3	5.485	2851.9	0.964	298	1.220	1.282	5.1
7	[N-epy][BF4]	195	411.2	549.9	23.5	533.9	5.011	1845.0	0.750	293	1.302	1.141	-12.4
8	[C15guan][BF4]	343	620.3	755.9	12.2	1146.7	5.711	3297.2	1.145	298	1.050	1.116	6.3
9	[C27guan][BF4]	512	894.8	1100.3	8.2	1832.0	4.702	4004.8	0.708	298	0.970	1.075	10.8
10	[hpmim][PF6]	326	623.2	787.8	14.7	933.8	5.282	3064.6	0.906	298	1.262	1.258	-0.3
11	[nmim][PF6]	354	669.0	834.1	13.4	1048.1	5.401	3380.8	0.968	298	1.212	1.250	3.1
12	[oprim][PF6]	368	691.9	857.6	12.8	1105.2	5.443	3532.1	0.994	298	1.821	1.247	11.5
13	[bdmim][PF6]	298	582.4	746.3	16.2	818.0	5.190	2799.5	0.853	296	1.242	1.283	3.4
14	[mpim][PF6]	298	577.5	742.1	16.3	819.6	5.148	2751.9	0.832	294	1.333	1.276	-4.3
15	[mommim][PF6]	272	531.2	701.2	19.3	663.9	4.977	2430.0	0.727	298	1.480	1.382	-6.7
16	[eommim][PF6]	286	554.1	723.7	18.2	721.0	5.057	2584.8	0.769	298	1.400	1.360	-2.9
17	[moeemim][PF6]	330	622.3	795.3	16.1	850.8	5.248	3040.1	0.868	298	1.320	1.387	5.1
18	[N-bupy][PF6]	281	516.3	674.4	17.3	755.6	4.944	2340.2	0.738	298	1.214	1.249	2.8
19	[bdmim][BF4]	240	523.1	671.0	18.9	710.5	5.420	2602.1	0.948	300	1.094	1.157	5.8
20	[bdmim][PF6]	298	582.4	746.3	16.2	818.0	5.190	2799.5	0.853	296	1.242	1.283	3.4



Conclusions

A consistent group contribution method has been developed to evaluate the critical properties of ionic liquids. Additionally, estimated values for the normal boiling temperatures and the vapor pressure constants in a vapor pressure eqution 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 make use of those estimated critical properties. The values provided for the critical properties, for the normal boiling temperature and for vapor pressure constants are believed to be accurate enough for engineering calculations, for generalized correlations and for equation of state methods, among other uses.

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