



On the prediction of the vapor pressure of ionic liquids based on the principle of corresponding states



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ABSTRACT

The complexity, coupled with the high cost of the experimental determination of the vapor pressure of pure ionic liquids (ILs), which at moderate temperatures typically assume values below 0.1 (Pa), make the development of predictive models for this important thermophysical property crucial. Employing 309 experimental data points belonging to 20 ILs of different classes and based on the truncated Pitzer expansion, in the current work a simple analytical expression has been developed for the prediction of the vapor pressure of pure ILs. In doing so, all the required critical properties have been estimated using a well-known group contribution method. Subsequently, utilizing the Clausius-Clapeyron equation, a very simple expression has been derived for the prediction of the enthalpy of vaporization of ILs. Total AARDs of 6.97% in the prediction of the available experimental vapor pressure data, and of 5.89% in the prediction of the molar heat of vaporization of 62 ILs demonstrate the satisfactory accuracy and predictive performance of the model developed in the current study. A thorough comparison has also been made with two previously published generalized expressions based on the zero-pressure liquid fugacity approach, through which the superiority of the proposed model has been established.

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1. Introduction

Room temperature ILs are an interesting new class of organic solvents that exhibit unique properties such as high thermal stability, recyclability, nonflammability, tunable solvating power, wide liquidus range and very low vapor pressures. Considered as environmentally benign solvents, ILs offer an exceptional ability to dissolve a wide variety of organic materials such as carbohydrates, cellulose, and lignin. These features, coupled with the capacity to separate azeotropic mixtures, have contributed to the development of a variety of applications for ILs in several scientific and engineering fields as diverse as biotechnology [1], pharmaceuticals [2,3], supercritical fluids [4], polymer [5] and nuclear sciences [6].

A long-held misconception about these liquid salts was that as they are solely composed of ions, they exert no measurable vapor pressure and as such cannot be distilled without decomposition [7,8]. This presumed involatility and lack of accurate knowledge of the vapor pressure of ILs undermines their potential utilization in several chemical processes [9]. Moreover, development and validation of reliable molecular models and ab initio methods for this important class of organic solvents are highly dependent on the availability of accurate representation of their energy-dependent phase transition data. These molecular

modeling calculations are necessary to understand the nature of interactions in pure ILs and their mixtures, and also for having reliable predictive tools for determining the physicochemical properties of yet to be synthesized ILs [10]. In this regard, knowledge of the temperature dependence of the ILs' vapor pressure data and their associated enthalpy of vaporization is essential for the proposition and testing of new force fields parametrizations used in the molecular dynamics studies; as well as for the development of reliable models for several different thermodynamic properties [11,12].

Despite the importance of developing accurate correlative and predictive models for the vapor pressure of ILs, only a handful of studies have already been undertaken to do so. Recently, the zero-pressure liquid fugacity approach of Wisniak et al. [13] has been adopted by Valderrama and Forero [14] to develop an analytical expression for the vapor pressure of ILs based on the Peng–Robinson equation of state (EOS) [15]. Using the concept of mass connectivity index obtainable from group contribution methods [16], which essentially encodes bond contributions and quantifies the extent of branching in a molecule, they presented generalized predictive expressions for the cohesion factor of the Peng–Robinson EOS. Following their pioneering work and using the same set of 134 experimental vapor pressure data corresponding to ten imidazolium-based ILs available at the time of their study, Joshipura [17] studied three more cohesion factor relations and developed new generalized expressions based on the mass connectivity index and acentric factor. The latter study demonstrated that using

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Table 1
Summary of the available experimental vapor pressure data of ILs used in this study.

IL	IUPAC name	MW (g·mol ⁻¹)	No. of Data	T _{Min} -T _{Max} (K)	P _{Min} -P _{Max} (Pa)	Reference
[C ₂ C ₁ im][NTf ₂]	1-Ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	391.317	34	441.70–538.20	0.0062–1.1190	[10,21,26]
[C ₃ C ₁ im][NTf ₂]	1-Propyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	405.344	21	453.13–492.95	0.0147–0.1669	[26]
[C ₄ C ₁ im][NTf ₂]	1-Butyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	419.371	29	437.84–517.45	0.0036–0.5150	[20,21,26]
[C ₅ C ₁ im][NTf ₂]	1-Pentyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	433.398	19	457.09–492.89	0.0140–0.1482	[26]
[C ₆ C ₁ im][NTf ₂]	1-Hexyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	447.425	22	445.79–493.67	0.0067–0.1716	[21,26]
[C ₇ C ₁ im][NTf ₂]	1-Heptyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	461.452	15	464.95–492.88	0.0174–0.1152	[26]
[C ₈ C ₁ im][NTf ₂]	1-Octyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	475.479	19	455.46–498.19	0.0078–0.1542	[21,26]
[C ₁₀ C ₁ im][NTf ₂]	1-Decyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	503.533	9	479.37–495.38	0.0214–0.0645	[26]
[C ₁₂ C ₁ im][NTf ₂]	1-Dodecyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	531.587	7	480.89–492.81	0.0154–0.0362	[26]
[C ₄ C ₁ im][dca]	1-Butyl-3-methylimidazolium dicyanamide	205.265	5	448.70–479.60	0.1920–2.2060	[10]
[C ₁ C ₁ im][NTf ₂]	1,3-Dimethylimidazolium bis(trifluoromethyl)sulfonylimide	377.290	10	475.62–493.68	0.0415–0.1225	[24]
[C ₂ C ₂ im][NTf ₂]	1,3-Diethylimidazolium bis(trifluoromethyl)sulfonylimide	405.338	13	455.54–479.68	0.0231–0.0989	[22]
[C ₃ C ₃ im][NTf ₂]	1,3-Dipropylimidazolium bis(trifluoromethyl)sulfonylimide	433.391	19	453.52–489.68	0.0285–0.2636	[22]
[C ₄ C ₄ im][NTf ₂]	1,3-Dibutylimidazolium bis(trifluoromethyl)sulfonylimide	461.444	17	455.52–487.65	0.0317–0.2436	[22]
[C ₅ C ₅ im][NTf ₂]	1,3-Dipentylimidazolium bis(trifluoromethyl)sulfonylimide	489.497	17	463.49–495.59	0.0375–0.3006	[22]
[C ₆ C ₆ im][NTf ₂]	1,3-Dihexylimidazolium bis(trifluoromethyl)sulfonylimide	517.550	17	463.53–495.66	0.0205–0.1795	[22]
[C ₂ C ₃ im][NTf ₂]	1-Ethyl-3-propylimidazolium bis(trifluoromethyl)sulfonylimide	419.364	14	463.58–489.62	0.0486–0.2364	[24]
[C ₂ Py][NTf ₂]	1-Ethylpyridinium bis(trifluoromethyl)sulfonylimide	388.313	6	493.55–503.61	0.0319–0.0571	[25]
[C ₃ Py][NTf ₂]	1-Propylpyridinium bis(trifluoromethyl)sulfonylimide	402.334	8	497.47–511.52	0.0333–0.0756	[25]
[C ₄ Py][NTf ₂]	1-Butylpyridinium bis(trifluoromethyl)sulfonylimide	416.367	8	498.07–515.56	0.0519–0.1420	[25]
Overall		205.265–531.587	309	437.84–538.20	0.0036–2.2060	

more appropriate temperature dependent cohesion factor functions, the prediction of the vapor pressure of ILs based on the zero-pressure liquid fugacity approach could be improved to some extent.

Since the publication of these studies, a significant number of new experimental vapor pressure data belonging to both symmetric and asymmetric imidazolium-based and also pyridinium-based ILs have been published. With the objective of expanding the predictive capacity of the vapor pressure models, and also improving their performance in the representation of the experimental vapor pressure data of ILs, this study proposes a new predictive model based on the principle of corresponding states. In doing so, the necessary critical properties and acentric factors are estimated using a modified Lydersen-Joback-Reid group contribution method proposed by Valderrama et al. [18]. Subsequently, the predictive performance of the new model is assessed by determining how well it predicts the enthalpy of vaporization of a large set of ILs, including those not included in the development stage of the model.

2. Literature data

In the case of organic and inorganic compounds, thousands of experimental vapor pressure data have been published over the course of a

century and several predictive and correlative models have been developed so far for their representation [19]. Unlike these compounds and due to the complications involved in measuring the very low vapor pressures of ILs, which are in general below 0.1 (Pa) at moderate temperatures, their experimental determination has been limited. Starting from the work of Paulechka et al. in 2005 [20] who reported the vapor pressure of [C₄C₁im][NTf₂] in the 458–517 (K) temperature range, several research groups have undertaken the task of experimental determination of the vapor pressure of pure ILs. The compounds investigated so far are comprised of both symmetric and asymmetric imidazolium-based, and also pyridinium-based ILs with bis(trifluoromethyl)sulfonylimide ([NTf₂]⁻) and dicyanamide ([dca]⁻) anions. Unlike organic and inorganic compounds, whose experimental vapor pressure data typically span the whole temperature range of triple to the critical points, ILs' data belong to a more limited temperature range; starting from above the triple point and ending below the normal boiling point, where known ILs undergo decomposition. It is also worth noting that the researchers have adopted the transpiration method [10], integral effusion Knudsen method [21], as well as the Knudsen effusion methodology combined with a quartz crystal microbalance [22] in their experimental investigations. The reported uncertainties of the vapor pressure data obtained using these methods are generally below 5% in the temperature ranges covered [23–25]. A summary of the available literature data used in this study alongside their corresponding sources is given in Table 1.

Table 2
Basic properties of the ILs studied in the current study.

IL	T _c (K)	P _c (bar)	ω	λ	Z _c	V _c (cm ³ ·mol ⁻¹)
[C ₂ C ₁ im][NTf ₂]	1249.310	32.653	0.2157	2.379	0.2753	875.910
[C ₃ C ₁ im][NTf ₂]	1259.340	29.959	0.2575	2.522	0.2670	933.020
[C ₄ C ₁ im][NTf ₂]	1269.933	27.646	0.3004	2.664	0.2592	990.130
[C ₅ C ₁ im][NTf ₂]	1281.080	25.641	0.3444	2.807	0.2521	1047.240
[C ₆ C ₁ im][NTf ₂]	1292.779	23.888	0.3893	2.949	0.2454	1104.350
[C ₇ C ₁ im][NTf ₂]	1305.026	22.346	0.4349	3.092	0.2392	1161.460
[C ₈ C ₁ im][NTf ₂]	1317.823	20.978	0.4811	3.235	0.2333	1218.570
[C ₁₀ C ₁ im][NTf ₂]	1279.625	19.669	0.8517	3.520	0.2359	1276.207
[C ₁₂ C ₁ im][NTf ₂]	1306.805	17.697	0.9933	3.805	0.2258	1386.112
[C ₄ C ₁ im][dca]	1035.840	24.401	0.8419	1.802	0.2017	712.010
[C ₁ C ₁ im][NTf ₂]	1239.852	35.823	0.1752	2.236	0.2845	818.800
[C ₂ C ₂ im][NTf ₂]	1259.340	29.959	0.2575	2.522	0.2670	933.020
[C ₃ C ₃ im][NTf ₂]	1281.080	25.640	0.3444	2.807	0.2521	1047.240
[C ₄ C ₄ im][NTf ₂]	1305.026	22.345	0.4349	3.092	0.2392	1161.460
[C ₅ C ₅ im][NTf ₂]	1331.174	19.759	0.5276	3.377	0.2277	1275.680
[C ₆ C ₆ im][NTf ₂]	1293.057	18.633	0.9220	3.662	0.2307	1331.160
[C ₂ C ₃ im][NTf ₂]	1269.933	27.645	0.3004	2.664	0.2592	990.130
[C ₂ Py][NTf ₂]	1207.867	32.748	0.1671	2.406	0.2834	869.030
[C ₃ Py][NTf ₂]	1218.208	30.035	0.2082	2.549	0.2746	926.140
[C ₄ Py][NTf ₂]	1229.064	27.707	0.2505	2.691	0.2666	983.250

3. Zero-pressure fugacity approach

While utilizing various equations of state, the thermodynamically rigorous approach to estimating vapor pressures is through the use of the criterion of the equality of the fugacities of the coexisting phases at equilibrium. However, the numerical complexity of the iterative

Table 3
Estimated parameters of the proposed model.

Parameter	Value
A	3.98736 × 10 ¹
B	1.89490 × 10 ⁴
C	1.12232 × 10 ²
D	9.25559 × 10 ⁻⁴
E	4.88916 × 10 ⁻⁶
F	1.41887 × 10 ⁻¹
G	2.98983 × 10 ⁰
H	7.37863 × 10 ²

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