

A Group Contribution Method for Heat Capacity Estimation of Ionic Liquids

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Based on experimental liquid heat capacity (C_{pL}) data collected from the literature, a second-order group additivity method has been developed for the estimation of the liquid heat capacity of imidazolium-, pyridinium-, and pyrrolidinium-based ionic liquids (ILs) containing hexafluorophosphate (PF_6), tetrafluoroborate (BF_4), bis(trifluoromethanesulfonyl) amide (Tf_2N), bromide (Br), ethyl sulfate (EtSO_4), or trifluoromethane sulfonate (CF_3SO_3) as anions, covering wide ranges of temperature (196.36–663.10 K) and liquid heat capacity (264.8–825.0 $\text{J mol}^{-1} \text{K}^{-1}$). It is shown that a good description of the literature data is obtained with the proposed method. For ca. 2400 data points from 19 ILs that have been studied, a mean percent deviation (MPD) of 0.36% with a maximum deviation of <2.5% was observed. From the total data points of estimated heat capacities, 90.2% present deviations of <1% from the experimental values, whereas only 0.9% have deviations of >2%. A correlation of heat capacities with molar volumes of the ILs was also developed for the estimation of heat capacity at 298.15 K. Therefore, the group contribution method developed here can be used to evaluate the liquid heat capacity of new ILs and, as data for new groups of cations and anions become available, can be extended to a larger range of ionic liquids.

1. Introduction

Ionic liquids (ILs) consist of bulky and asymmetric organic cations, such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, *N*-methyl-*N*-alkylpyrrolidinium, ammonium ions, and a wide range of anions, from simple halides, to inorganic anions such as tetrafluoroborate, hexafluorophosphate, to large organic anions such as bistriflimide, triflate, or tosylate. The wide range of combinations of cation and anion for ILs allow a great variety of tunable interactions and applications. The research areas on ILs are growing very rapidly and the potential application of ILs are numerous, because of their unique properties, such as negligible volatility, wide liquidus range, nonflammability, high thermal conductivity, chemical and physical stability, and high potential for recycling.

The development of ILs for specific tasks is currently being pursued by many researchers as the large number of cation/anion combinations makes it possible to produce ionic liquids with a set of desired properties. With the increasing availability of experimental data and their quality, the development of predictive methods for IL properties and computer-aided molecular design (CAMD) of ILs becomes possible.

The heat capacity of a compound is defined as the enthalpy dependency with temperature. Heat capacity is one of the basic thermophysical and thermodynamic properties that characterizes a compound. The influence of temperature on phase and reaction equilibria may be evaluated through the knowledge of heat capacity. Variations in heat capacities provide information of phase transitions and are important for understanding changes in the structure of compound. Heat capacity is connected with temperature derivatives of basic thermodynamic functions and, therefore, it is central for the calculation of differences in these functions between different temperatures. This information is necessary in most engineering calculations, for example, in thermodynamics for obtaining entropy and enthalpy data, and in thermochemistry for calculating changes in reaction enthalpies with temperature, and so forth.

Generally, there are three types of liquid capacities in use: (i) the change in enthalpy with temperature at constant pressure (C_{pL}), (ii) the variation in enthalpy of a saturated liquid with temperature (C_{oL}), and (iii) the energy required to affect a temperature change while maintaining the liquid in a saturated state (C_{sat}). These three heat capacities are related to each other and, except at high reduced temperature, they are in close numerical agreement. The present study is concerned with the first form of liquid heat capacity, i.e., C_{pL} .

Heat capacities and derived thermodynamic properties of ILs are important to understand why the melting points of ILs composed only of ions are lower than room temperature. It is known that the heat capacities of ILs vary widely, depending on the type of cation and anion. Experimental data for heat capacity of ionic liquids are still scarce and limited to a few classes of well-studied ILs. More heat capacity data and a better understanding of this property are required to develop ILs for specific purposes, and if experimentally measured heat capacity data are not available, theoretical or empirical methods must be used to establish if the heat capacities are within acceptable limiting values defined in the design specifications. For this purpose, prediction methods for heat capacity of ILs are required.

While much work has been devoted to the wide range of applications of ILs, the basic understanding and study of their structure–property relationships is equally important but has lagged behind. More specifically, studies on how the structure of the ions in the IL influences their physical properties are rare. Systematic study of the qualitative and/or quantitative relationships between the structures of ILs and their fundamental properties, such as melting point, viscosity, density, surface tension, heat capacity, thermal and electrochemical stability, and solvent properties are important for assessing the suitability of ILs for specific applications, as well as the design of new ILs. At present, however, data for many other physicochemical properties of ILs are in short supply, or too unreliable to allow similar structure–property relationship studies.

Since last year, our research group has presented several contributions to this field through the measurement of new experimental data and the development and evaluation of

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Table 1. Prediction of Liquid Heat Capacity (C_{pL}) of Imidazolium-, Pyridinium-, and Pyrrolidinium-Based Ionic Liquids

ionic liquid	temperature range (K)	data points	percent deviation (range) (%)	mean percent deviation (%)	reference
[C4mim][PF ₆]	300.05–524.87	1528	–1.12 to 0.44	0.23	16
	283.15–323.15	9	–0.96 to 0.55	0.39	17
[C2mim][BF ₄]	283.15–358.15	16	–2.41 to –1.42	1.70	18
[C4mim][BF ₄]	278.15–333.15	12	–0.31 to 0.54	0.31	19
	283.15–358.15	16	–0.01 to 0.86	0.61	18
[C2mim][Tf ₂ N]	283.15–358.15	16	–0.83 to 0.74	0.50	18
	256.91–370	16	–1.33 to 1.41	0.91	20
[C4mim][Tf ₂ N]	283.15–328.15	20	0.03 to 1.68	1.07	17
[C6mim][Tf ₂ N]	280.00–425.15	54	–2.43 to 2.39	1.22	21
[C1mpim][Tf ₂ N]	323.1–663.1	35	–0.06 to 0.03	0.02	22
[C2mim][Br]	347.66–370.00	16	–0.60 to 0.58	0.27	23
[C4mim][Br]	298.1–323.1	2	–1.71 to –0.50	1.11	24
	225.62–370.00	22	–0.25 to 1.64	0.52	23
[C2mim][EtSO ₄]	196.36–389.95	170	–0.14 to 0.35	0.05	25
[C2mim][CF ₃ SO ₃]	313.13–425.15	64	–1.25 to 1.98	0.63	21
[C4mim][CF ₃ SO ₃]	313.16–425.15	46	–0.86 to 2.22	0.86	21
[C6mim][CF ₃ SO ₃]	313.14–425.15	64	–1.92 to 2.14	1.03	21
[C8mim][CF ₃ SO ₃]	313.17–423.14	41	–1.05 to 1.53	0.69	21
[C4py][Tf ₂ N]	323.18–425.15	60	–2.12 to 1.61	0.80	21
[C2(dmN)py][Tf ₂ N]	313.12–425.15	46	–0.89 to 2.00	0.52	21
[C4(dmN)py][Tf ₂ N]	313.13–425.15	64	–1.48 to 1.48	0.52	21
[C6(dmN)py][Tf ₂ N]	313.15–425.15	63	–1.61 to 2.02	1.03	21
[C3mpyr][Tf ₂ N]	283.15–358.15	16	–0.09 to 0.12	0.06	18
total	196.36–663.10	2396	–2.43 to 2.39	0.36	

predictive models of thermophysical and thermodynamic properties of ILs.^{1–11} We have succeeded in developing rapid predictive methods for density¹² in wide ranges of temperature and pressure, surface tension,¹³ viscosity,¹⁴ and speed of sound¹⁵ of ILs in a wide temperature range and at atmospheric pressure. In continuation of our studies on the development of predictive methods for physical properties of ILs, a second-order group additivity method has been developed for the estimation of the liquid heat capacities (C_{pL}) of ILs, and it will be shown that it allows a good description of the experimental liquid heat capacities available for wide temperature range (196–663 K).

The objectives of the present study were as follows: (i) to provide an extensive survey of the literature for heat capacities of pure ILs, (ii) to correlate experimental data and provide recommended values for the heat capacities of liquid compounds as a function of temperature (the recommended data are presented in terms of parameters of correlating equation), (iii) to evaluate the effect of cation and anion on the heat capacity of ionic liquid, and (iv) to understand the relation between molar volume and heat capacity of ionic liquids.

2. Results and Discussion

A database of experimental liquid heat capacities (C_{pL}) of ILs available in the open literature was collected and is reported in Table 1. A global number of 2396 data points for 19 ILs based on imidazolium cations with hexafluorophosphate (PF₆), tetrafluoroborate (BF₄), bis(trifluoromethanesulfonyl) amide (Tf₂N), bromide (Br), ethyl sulfate (EtSO₄), or trifluoromethane sulfonate (CF₃SO₃) as anions and pyridinium and pyrrolidinium cations with bis(trifluoromethanesulfonyl) amide (Tf₂N) as the anion, covering wide ranges of temperature (196.36–663.10 K) and liquid heat capacity (264.8–825.0 J mol^{–1} K^{–1}),^{16–25} were used in this study.

Many estimation methods, including empirical, semiempirical, correlation, and group contribution methods, for the heat capacity of pure components are available in literature reviews and books.^{26–39} Ruzicka and Domalski^{33,34} described an estimation method for the heat capacity of pure organic liquids as a function of temperature, based on the second-order group additivity scheme proposed by Benson and co-workers for ideal

gases^{40,41} and for liquid hydrocarbons.⁴² Ruzicka and Domalski^{33,34} were concerned with revision of the existing group contributions and structural corrections developed by Benson and co-workers^{41,42} and with the extension of the method to cover a broader range of organic liquids that contained elemental carbon, hydrogen, oxygen, nitrogen, sulfur, and halogens.

Here, we have adopted the approach proposed by Ruzicka and Domalski,^{33,34} and we use a second-order group additivity method for the estimation of the liquid heat capacity (C_{pL}) of ionic liquids. It applies a group contribution technique to estimate the parameters A , B , and D in eq 1:

$$C_{pL} = R \left[A + B \left(\frac{T}{100} \right) + D \left(\frac{T}{100} \right)^2 \right] \quad (1)$$

where R is the gas constant ($R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (in Kelvin). The group contributions used to calculate parameters A , B , and D are obtained from the following relations:

$$A = \sum_{i=1}^k n_i a_i \quad (2a)$$

$$B = \sum_{i=1}^k n_i b_i \quad (2b)$$

$$D = \sum_{i=1}^k n_i d_i \quad (2c)$$

where n_i is the number of groups of type i , k is the total number of different types of groups, and the parameters a_i , b_i , and d_i here (estimated for ILs) are given in Table 2.

The method proposed here permits the estimation of heat capacities of ILs as a function of temperature over wide ranges of temperature (196.36–663.10 K), which covers the temperature range required in most chemical engineering calculations. The present method can be extrapolated to temperatures outside the temperature range recommended. However, the predictive accuracy remarkably decreases with the increase of an extent of the temperature extrapolation and the user must also be aware of the possible degradation of the ILs at high temperatures. Because of the temperature range to which the method is

Table 2. Group Contributions for Parameters A, B, and D in eq 1

Species	a_i	b_i (K)	d_i (K ²)
Cations			
1,3-dimethylimidazolium (+)	11.930	8.794	-1.584
1-methylpyridinium (+)	54.063	-13.390	1.280
1,1-dimethylpyrrolidinium (+)	42.446	-9.419	1.000
Anions			
PF ₆ ⁻	4.674	-0.379	1.110
BF ₄ ⁻	3.017	-1.061	0.968
Tf ₂ N ⁻	14.161	5.316	0.357
Br ⁻	28.638	-20.704	3.928
EtSO ₄ ⁻	22.335	-6.164	1.522
CF ₃ SO ₃ ⁻	29.551	-11.280	2.453
Groups			
CH ₂	-1.133	2.443	-0.259
CH ₃	6.218	-9.318	1.328
dimethyl ammonium	28.980	-10.669	1.555

applicable, no distinction is made between the isobaric heat capacity and the saturation heat capacity.

The experimental heat capacities were correlated by minimizing the objective function (OF) to estimate parameters a_i , b_i , and d_i of eqs 2a–2c:

$$OF = \frac{100 \times \sum_{i=1}^{N_p} \left| \left\{ R \left[A + B \left(\frac{T}{100} \right) + D \left(\frac{T}{100} \right)^2 \right] - C_{pL}^{\text{exp}} \right\} / C_{pL}^{\text{exp}} \right|_i}{N_p} \quad (3)$$

where C_{pL}^{exp} is the experimental heat capacity and N_p is the number of data points.

After collection of all the data available in the open literature for ILs, a critical analysis of the data was conducted before using it for parameter estimation. Because of the availability of a good amount of experimental data for most ILs studied, the rejection of doubtful experimental data was possible in the estimation of the proposed group contribution parameters. We discarded any IL that was obtained from one or more sources for which a total of less than three experimental points were available. Parameters for any species were obtained using at least two different ILs. A single available ionic liquid with a new cation and/or anion was discarded in this study, with the exception of the cation with three methyl groups attached to the imidazolium ring that was used to estimate the CH₃ group. For some ILs, more than one data set is available in the same

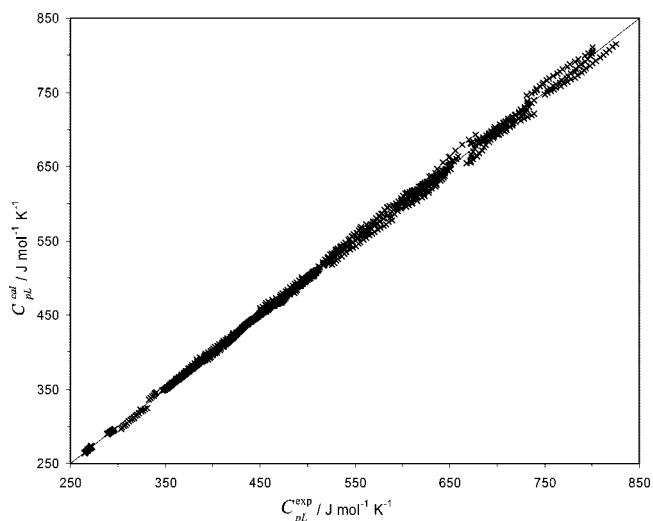


Figure 1. Linear relationship between experimental and calculated heat capacity using eq 1 for all ionic liquids (ILs) in the current study.

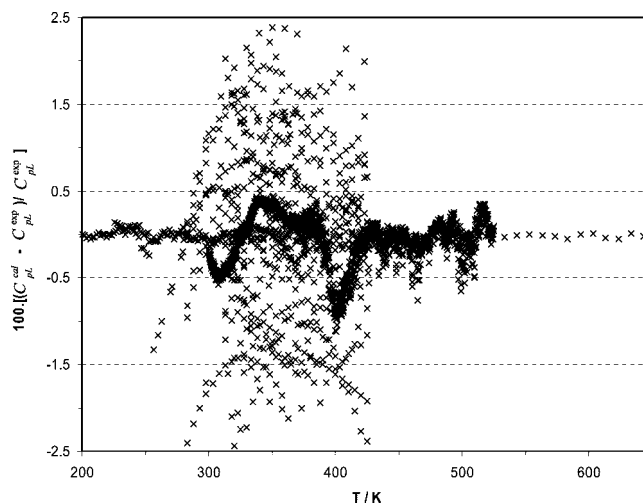


Figure 2. Relative deviations between the calculated and experimental heat capacity data as a function of temperature for all ILs in the current study.

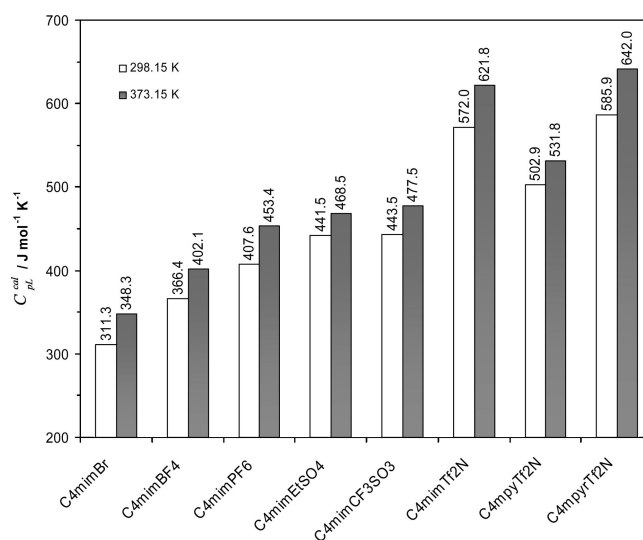


Figure 3. Calculated heat capacities of imidazolium-, pyridinium-, and pyrrolidinium-based ILs with butyl chain length and different anions at 298.15 and 373.15 K.

source; in such cases, one or more datasets that show large deviations among them are discarded. ILs from any sources exhibiting large systematic deviations with other sources also were rejected.

During the development of parameters, it was observed that insufficient accuracy of the experimental heat capacity data and the narrow temperature range that was available for some ILs restricted the use of a more-extensive functional form for the dependence of parameters with temperature. Finally, the group contribution parameters were estimated using 2396 heat capacity data points for 19 ILs studied, by minimizing the objective function (OF) described in eq 3, to obtain the optimum values of the group parameters reported in Table 2.

The mean percent deviation (MPD) is defined as

$$MPD (\%) = \frac{100 \times \sum_{i=1}^{N_p} |(C_{pL}^{\text{cal}} - C_{pL}^{\text{exp}}) / C_{pL}^{\text{exp}}|_i}{N_p} \quad (4)$$

where C_{pL}^{cal} and C_{pL}^{exp} are calculated and experimental heat capacity respectively, and N_p represents the number of data

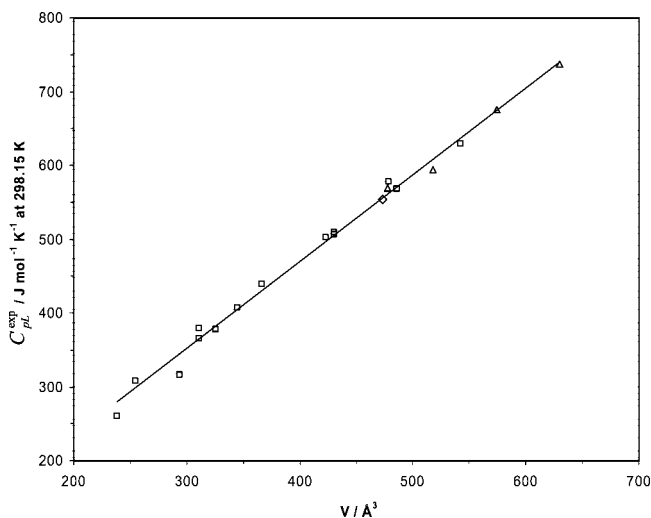


Figure 4. Linear relationship between experimental heat capacity and molecular volume at 298.15 K for ILs with (□) imidazolium-, (Δ) pyridinium-, and (◇) pyrrolidinium-based cations.

points that were estimated for each system and are reported in Table 1.

The experimental heat capacity data can be described with success, as shown in Figure 1, using a group contribution approach for parameters A , B , and D for imidazolium-, pyridinium-, and pyrrolidinium-based ILs that contain PF_6 , BF_4 , Tf_2N , Br , EtSO_4 , and CF_3SO_3 anions. The calculated heat capacity (C_{pL}^{cal}) of the ILs studied displays a very good agreement with the corresponding experimental heat capacity (C_{pL}^{exp}), where $C_{pL}^{\text{cal}} = 0.9994 \pm 0.0002 C_{pL}^{\text{exp}}$ (correlation coefficient: $R^2 = 0.9988$ at a 95% level of confidence). The relative deviations between the calculated and experimental heat capacity data, as a function of temperature for all data points used in the current study, are shown in Figure 2. For 2396 data points of 19 ILs available in the literature,^{16–25} the overall MPD is 0.36%, with a maximum deviation of <2.5%. From these values, 51.4% of the estimated heat capacities were within an absolute deviation

of 0.00%–0.20%, 27.1% were within 0.201%–0.50%, 11.6% were within 0.501%–1.00%, 8.9% were within 1.001%–2.00%, and only 0.9% of the estimated heat capacities had a deviation larger than 2.00%. The deviations above 1% can probably be assigned to the uncertainty of the experimental data, as is the case with the maximum absolute deviation of 2.43% for $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) at 320.15 K from Diedrichs and Gmehling,²¹ which is well below the experimental uncertainty assigned (~5%) by the authors.²¹ In almost all cases where the experimental uncertainty is provided in the original reference, the deviations in predicted heat capacities are inferior to the assigned experimental uncertainties. The proposed method for the estimation of the heat capacities of the ILs is not only a powerful and accurate tool for the estimation of heat capacities when no experimental information is available, but also to evaluate the quality of the available or new data, because it can check the coherence between the data from various datasets for different ILs.

3. Heat Capacity Dependency on the Structure and Molar Volume of the Ionic Liquid

Small changes in the structure of the ILs can produce considerable differences in heat capacity. To observe the influence of the IL anion and temperature on the heat capacity, estimations using eq 1, for the series of $[\text{C}_4\text{mim}]^+$ (1-butyl-3-methylimidazolium cation) with different anions, and $[\text{C}_4\text{mpy}]^+$ (1-butyl-3-methylpyridinium cation) and $[\text{C}_4\text{mpyr}]^+$ (1-butyl-1-methylpyrrolidinium cation) with $[\text{Tf}_2\text{N}]$ anion at 298.15 and 373.15 K are presented in Figure 3. The results show that the heat capacity of ILs increases with temperature. For ILs that have the imidazolium cation, the heat capacity increases with the anion mass in the following order: $\text{Br} < \text{BF}_4 < \text{PF}_6 < \text{EtSO}_4 \approx \text{CF}_3\text{SO}_3 < \text{Tf}_2\text{N}$. This trend is consistent with the results from different sources.^{16–19,21,23,24} For ILs that have a common anion and a similar alkyl chain length on the cation, it is observed that the heat capacity increases with the cation in the following order: $[\text{py}] < [\text{Im}] < [\text{pyr}]$, as shown in Figure 3.

Table 3. Molecular Weight (M), Molecular Volume (V), Experimental Heat Capacity (C_{pL}^{exp}), and Calculated Heat Capacity (C_{pL}^{cal}), Using eqs 1 and 2, and Using eq 5, for Studied Ionic Liquids at 298.15 K

ionic liquid	M (g/mol)	V (\AA^3)	C_{pL}^{exp}		C_{pL}^{cal} ($\text{J mol}^{-1} \text{K}^{-1}$)	
			value ($\text{J mol}^{-1} \text{K}^{-1}$) ^a	reference source	using eqs 1 and 2	using eq 5
[C ₄ mim][PF ₆]	284.18	345	407.6	16	407.6	405.0
			407.66	17		
[C ₂ mim][BF ₄]	197.97	255	308.1	18	302.4	299.3
[C ₄ mim][BF ₄]	226.03	311	364.71	19	366.4	365.1
			364.8	18		
[C ₂ mim][Tf ₂ N]	391.32	430	505.7	20	508.0	504.7
			509.2	18		
[C ₄ mim][Tf ₂ N]	419.37	486	567.33	17	572.0	570.5
[C ₆ mim][Tf ₂ N]	447.42	542	629.2	21	636.0	636.2
[C ₂ mim][EtSO ₄]	236.29	326	378	25	377.5	382.7
[C ₂ mim][CF ₃ SO ₃]	260.24	311	379.2	21	379.5	365.1
[C ₄ mim][CF ₃ SO ₃]	288.29	367	439.7	21	443.5	430.8
[C ₆ mim][CF ₃ SO ₃]	316.34	423	502.3	21	507.5	498.0
[C ₈ mim][CF ₃ SO ₃]	345.41	479	577.7	21	571.5	562.3
[C ₄ py][Tf ₂ N]	416.37	478	569.0	21	584.5	561.1
[C ₂ (dmN)py][Tf ₂ N]	431.38	518	594.3	21	611.5	608.0
[C ₄ (dmN)py][Tf ₂ N]	459.43	574	676.0	21	675.5	673.8
[C ₆ (dmN)py][Tf ₂ N]	487.49	630	737.3	21	739.5	739.5
[C ₃ mpyr][Tf ₂ N]	408.39	473	554	18	553.9	555.2
[C ₂ mim][Br]	191.07	238	260.1	23	247.3	279.4
[C ₄ mim][Br]	219.12	294	311.5	23	311.3	345.1
			316.7	24		
[C ₁ mpim][Tf ₂ N]	419.37	493	458.81	22	458.9	578.7

^a In cases where data were unavailable, data were obtained using second-order polynomial extrapolations with temperature.

The additivity of the heat capacities is similar to that observed previously for the densities,¹² suggesting that a relation between the two properties could be easily established. A plot of total 21 data points of experimental heat capacity from different sources versus molecular volumes of imidazolium-based ILs that contain PF₆, BF₄, Br, EtSO₄, CF₃SO₃, and Tf₂N as anions, and pyridinium- and pyrrolidinium-based ILs that contain Tf₂N as an anion at 298.15 K is shown in Figure 4. For the studied ILs, the experimental heat capacities (C_{pL}^{exp}) at 298.15 K shows a good linear relationship with molecular and molar volume (V), as described by eqs 5 and 6, respectively.

$$C_{pL}^{\text{exp}} (\text{J mol}^{-1} \text{K}^{-1}) = (1.1738 \pm 0.0054) V / \text{\AA}^3 \quad (R^2 = 0.9935, \text{ at a 95\% level of confidence}) \quad (5)$$

$$C_{pL}^{\text{exp}} (\text{J mol}^{-1} \text{K}^{-1}) = (1.9516 \pm 0.0090) V / \text{cm}^3 \text{ mol}^{-1} \quad (R^2 = 0.9935, \text{ at a 95\% level of confidence}) \quad (6)$$

The [C₁mpim][Tf₂N] was not included in Figure 4 nor in the development of eqs 5 and 6, because it presented an unexpectedly large deviation that may be related to deviations on the experimental heat capacity data that a lack of other trisubstituted imidazolium cations prevented the evaluation. Using eq 5, the MPD observed is of 1.85% for 21 heat capacity data points available in the literature at 298.15 K for a total of 18 ILs. The large deviations observed for imidazolium ILs that have Br as an anion ([C₂mim][Br] and [C₄mim][Br]) are 7.5% and 9.0%, respectively, which are most probably due to corrections required in the molecular volume of the Br anion, because, excluding these two data points, the MPD decreases remarkably to 1.15%, with the largest deviation being less than 3.5% for the remaining 19 heat capacity data points. Experimental densities or molar volumes are not available for most of the studied ILs; therefore, for the development of eq 6, the densities of ILs at 298.15 K and 0.1 MPa are calculated using our previously proposed estimation method,¹² using eq 7.

$$\rho = \frac{M}{NV(e + fT + gP)} \quad (7)$$

where ρ is the density (expressed in units of g/cm³), M the molecular weight (in units of g/mol), N Avogadro's constant, V the molecular volume (in units of \AA³), T the temperature (in Kelvin), and P the pressure (in units of MPa). The coefficients e , f , and g were estimated by fitting eq 7 to our previously published experimental data.^{1,3} A total amount of ca. 800 density data points were used. The values of coefficients e , f , and g obtained are 0.8005 ± 0.0002 , $(6.652 \pm 0.007) \times 10^{-4} \text{ K}^{-1}$, and $(-5.919 \pm 0.024) \times 10^{-4} \text{ MPa}^{-1}$, respectively, at the 95% confidence level. The MPD of the calculated densities from the experimental densities is 0.29%.

The heat capacities for all ILs studied at 298.15 K were estimated using eqs 1, 2, and 5, and these were compared with the experimental data given in Table 3. The molecular volumes (V) of ions and groups used were either directly taken from Ye and Shreeve⁴³ or calculated following the Jenkins' procedure.⁴⁴ The molecular volumes of ILs used are shown in Table 3.

4. Conclusions

Here, we have shown that the Ruzicka and Domalski approach^{33,34} was successfully applied to the development of a second-order group additivity method for the estimation of the liquid heat capacity of ionic liquids (ILs). Parameters for a group contribution method, including three cations and six anions, are determined, which enables the user to obtain the heat capacity of at least 200 ILs, as a function of temperature. For a database

of 2396 data points for 19 ILs,^{16–25} imidazolium-based ILs that contained PF₆, BF₄, Tf₂N, Br, EtSO₄, and CF₃SO₃ anions and pyridinium- and pyrrolidinium-based ILs that contained the Tf₂N anion, in wide ranges of temperature (196.36–663.10 K) and liquid heat capacity (264.8–825.0 J mol⁻¹ K⁻¹), the mean percent deviation (MPD) observed was 0.36%, with a maximum deviation of <2.5%. Calculated heat capacities are in very good agreement with experimental literature data. In most of the cases the deviations in predicted heat capacities are inferior to the assigned experimental uncertainties.

A new correlation is here proposed for the estimation of the heat capacity of ILs at 298.15 K, using only information on the molecular volume or molar volume. Using this correlation, the MPD observed is 1.85%, with a maximum deviation of <9.0% for 21 heat-capacity data points available in the literature at 298.15 K for a total of 18 ILs.

Both of the proposed methods should be able to predict the heat capacity of new ionic liquids with good accuracy and could be extended to a larger range of ionic liquids as data for these become available, and it may also be useful to evaluate the quality of the available or new data, because it can check the coherence between the data from various datasets for different ILs.

Appendix

Nomenclature

List of Abbreviations

- IL = ionic liquid
 CAMD = computer-aided molecular design
 OF = objective function
 MPD = mean percentage deviation
 [C₄mim][PF₆] = 1-butyl-3-methylimidazolium hexafluorophosphate
 [C₂mim][BF₄] = 1-ethyl-3-methylimidazolium tetrafluoroborate
 [C₄mim][BF₄] = 1-butyl-3-methylimidazolium tetrafluoroborate
 [C₂mim][Tf₂N] = 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
 [C₄mim][Tf₂N] = 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
 [C₆mim][Tf₂N] = 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
 [C₁mpim][Tf₂N] = 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide
 [C₂mim][Br] = 1-ethyl-3-methylimidazolium bromide
 [C₄mim][Br] = 1-butyl-3-methylimidazolium bromide
 [C₂mim][EtSO₄] = 1-ethyl-3-methylimidazolium ethyl sulfate
 [C₂mim][CF₃SO₃] = 1-ethyl-3-methylimidazolium trifluoromethane sulfonate
 [C₄mim][CF₃SO₃] = 1-butyl-3-methylimidazolium trifluoromethane sulfonate
 [C₆mim][CF₃SO₃] = 1-hexyl-3-methylimidazolium trifluoromethane sulfonate
 [C₈mim][CF₃SO₃] = 1-methyl-3-octylimidazolium trifluoromethane sulfonate
 [C₄py][Tf₂N] = 1-butylpyridinium bis(trifluoromethylsulfonyl)imide
 [C₂(dmN)py] [Tf₂N] = *n*-ethyl-4-(*N,N'*-dimethylammonium)pyridinium bis(trifluoromethylsulfonyl)imide
 [C₄(dmN)py] [Tf₂N] = *n*-butyl-4-(*N,N'*-dimethylammonium)pyridinium bis(trifluoromethylsulfonyl)imide
 [C₆(dmN)py] [Tf₂N] = *n*-hexyl-4-(*N,N'*-dimethylammonium)pyridinium bis(trifluoromethylsulfonyl)imide
 [C₃mpyr][Tf₂N] = 1-propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

List of Symbols

C_{pL} = liquid heat capacity

R = gas constant

T = temperature

A, B, D = parameters in eq 1

a_i, b_i, d_i = parameters in eqs 2a–2c for groups of type i

n_i = number of groups of type i

N_p = number of data points

C_{pL}^{exp} = experimental heat capacity

C_{pL}^{cal} = calculated heat capacity

V = molecular or molar volume

M = molecular weight

P = pressure

N = Avogadro's constant

e, f, g = coefficients of density correlation described by eq 7

Greek Letters

ρ = density

Superscripts

exp = experimental property

cal = calculated property

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