# Heat Capacities of Ionic Liquids as a Function of Temperature at 0.1 MPa. Measurement and Prediction

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Heat capacities of nine ionic liquids were measured from (293 to 358) K by using a heat flux differential scanning calorimeter. The impact of impurities (water and chloride content) in the ionic liquid was analyzed to estimate the overall uncertainty. The Joback method for predicting ideal gas heat capacities has been extended to ionic liquids by the generation of contribution parameters for three new groups. The principle of corresponding states has been employed to enable the subsequent calculation of liquid heat capacities for ionic liquids, based on critical properties predicted using the modified Lydersen−Joback−Reid method, as a function of the temperature from (256 to 470) K. A relative absolute deviation of 2.9 % was observed when testing the model against 961 data points from 53 different ionic liquids reported previously and measured within this study.

## Introduction

In recent years, there has been a dramatic increase in research into the use of ionic liquids as potential replacements for organic solvents in chemical processes.[1−4] Their negligibly low vapor pressures[5] allow volatile organics to be easily removed by distillation without significant loss of the ionic liquid. This low volatility provides ionic liquids with an environmental advantage over volatile organic compounds (VOCs) as industrial solvents, which can easily escape into the atmosphere. Ionic liquids also tend to have much greater liquidus temperature ranges[6] at atmospheric pressure than molecular solvents, allowing greater flexibility in processing conditions. Consisting solely of ions, the properties of ionic liquids can be designed for purpose by careful selection of the cation−anion combination. This ability to vary the combination of cations and anions leads to the potential to create an almost limitless amount of different ionic liquids. However, to enable ionic liquids to become truly "designer" materials, adequate models to predict their physical and chemical properties are required. Group contribution models (GCMs) are commonly used as predictive tools by engineers in process design, and many have become an integral part of process simulation software, due to their wide applicability, ease of use, and relative accuracy. The basic assumptions of GCMs are that the physical properties of a component are dependent on the functional groups which make up its structure, and each functional group provides a fixed contribution toward the physical properties, irrespective of the species involved.[7] Although the number of studies is limited, group contribution models have been used to predict the properties of ionic liquids. For example, Kim et al.[8,9] used GCMs for the calculation of the density and $CO_2$ gas solubility for 1-alkyl-3-methylimidazolium-based ionic liquids as a function of the temperature and the $CO_2$ gas pressure. These studies have been extended further with a number of modified GCMs used for the prediction of ionic liquid densities.[10−14] Recently, Strechan et al.[15] reported a predictive method for determining heat capacities of ionic liquids by correlating this property with intramolecular vibrational contribution, $C_{vib}$, with a reported relative deviation for $C_p$ of 0.9 %. However, the model was only tested against data for six different ionic liquids, and significant computational effort is required to determine the $C_{vib}$ value from quantum-chemical calculations for each ionic liquid and at each temperature before the heat capacity can be estimated. Therefore, there is a need to develop a model which is easy to use and can be applied to a wide variety of ionic liquids, without the need for quantum calculations on each individual ionic liquid. To date, prediction of heat capacity by group contribution has not been reported for ionic liquids although there are a number of methods for predicting ideal gas heat capacity for molecular solvents such as the Joback[16] and Benson[17] group contribution methods, both of which are used in process simulation packages. This paper describes the extension of the Joback group contribution model to predict the liquid heat capacities of ionic liquids using a large amount of experimental data taken from both reported values as well as new measurements performed in our laboratory. Herein, heat capacities of nine ionic liquids were measured from (293 to 358) K by using a heat flux differential scanning calorimeter as described by Diedrichs and Gmehling.[18]

Knowledge of this property is essential in determining the heat transfer properties of ionic liquids and for enthalpy calculations in process simulation.

## Experimental

All ionic liquids were prepared in-house, except for 1-butyl-1-methylpyrrolidinium trispentafluoroethyltrifluorophosphate ([$C_4$mPyrr][FAP]) which was obtained from Merck (≥ 98 %). 1-Alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([$C_n$mim][$NTf_2$]) ionic liquids were prepared by metathesis reaction of the appropriate chloride salt with lithium bis{(trifluoromethyl)sulfonyl}imide according to previously reported procedures.[19] An analogous procedure was used to prepare trihexyltetradecylphosphonium bis{(trifluoromethyl)sulfonyl}imide ([$P_{66614}$][$NTf_2$]) and 1-butyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}imide ([$C_4$mPyrr][$NTf_2$]) from [$P_{66614}$]Cl and [$C_4$mPyrr]Cl, respectively. 1-Butyl-3-methylimidazolium

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**Table 1. Molar Mass ($M^{\mathrm{IL}}$), Water Mass Fraction Content ($w_{\mathrm{w}}$), Chloride Mass Fraction Content ($w_{\mathrm{Cl^-}}$), and Lithium Mass Fraction Content ($w_{\mathrm{Li^+}}$), of ILs Measured in This Study**

| ionic liquid | $M^{\mathrm{IL}}$/g·mol$^{-1}$ | source | $w_{\mathrm{w}}\cdot 10^6$ | $w_{\mathrm{Cl^-}}\cdot 10^6$ | $w_{\mathrm{Li^+}}\cdot 10^6$ |
|---|---|---|---|---|---|
| [$P_{66614}$][$NTf_2$] | 764.01 | QUILL | 95 | < 5 | < 1 |
| [$C_2$mim][$NTf_2$] | 391.31 | | 100 | < 5 | 2.35 |
| [$C_4$mim][$NTf_2$] | 419.37 | | 96 | < 5 | < 1 |
| [$C_6$mim][$NTf_2$] | 447.42 | | 23 | < 5 | < 1 |
| [$C_8$mim][$NTf_2$] | 475.47 | | 38 | < 5 | < 1 |
| [$C_2$mim][$EtSO_4$] | 236.29 | | 279 | –[a] | – |
| [$C_4$mim][OTf] | 288.29 | | 681 | < 11 | 4.24 |
| [$C_4$mPyrr][$NTf_2$] | 422.41 | | 20 | < 5 | < 1 |
| [$C_4$mPyrr][FAP] | 587.27 | Merck | 132 | < 100 | –[b] |

[a] Halide-free sample. [b] Lithium-free sample.

trifluoromethanesulfonate ([$C_4$mim][OTf]) was prepared via a metathesis reaction between [$C_4$mim]Cl and lithium trifluoromethanesulfonate.[20] 1-Ethyl-3-methylimidazolium ethyl sulfate ([$C_2$mim][$EtSO_4$]) was prepared by direct alkylation of 1-methylimidazole using diethyl sulfate according to previously reported procedures.[21] Samples were washed 6 times using distilled water to ensure removal of any remaining lithium chloride byproduct or starting materials and dried overnight at 343 K under high vacuum (0.1 Pa) prior to use. All ionic liquids were analyzed for water content using Karl Fischer titration and chloride content using ion chromatography (IC)[22] prior to the measurements. The source, molar mass, and halide and water content of the ionic liquids measured in this study, after drying, are summarized in Table 1. In this paper, the name, chemical structures, molar mass, and abbreviated notations (AN) of ions used in the present work are described in the Supporting Information.

Heat capacities were performed using a "heat flux" differential scanning calorimeter by TA Instruments (model DSC Q100), based on the method described by Diedrichs and Gmehling.[18] An accurately known mass of sample [(5 to 10) mg] was placed in an aluminum sample pan. The sample pan and a blank (empty pan) were placed on separate raised platforms within the furnace chamber, and a temperature program was performed, consisting of an isothermal period of 15 min at 273 K, followed by a constant heating rate of 20 K·min$^{-1}$ to 363 K at which point the temperature was held for 15 min. The same procedure was performed on a pan containing a sapphire standard and again using an empty pan. The heat capacity of the sample, $C_{p,\mathrm{sample}}$, was then calculated as a function of temperature from the resulting heat flows using eq1

$$C_{p,\mathrm{sample}} = \left(\frac{Q_{\mathrm{sample}} - Q_{\mathrm{empty}}}{Q_{\mathrm{ref}} - Q_{\mathrm{empty}}}\right)\cdot\left(\frac{n_{\mathrm{ref}}}{n_{\mathrm{sample}}}\right)\cdot C_{p,\mathrm{ref}} \tag{1}$$

where $Q_{\mathrm{sample}}$, $Q_{\mathrm{ref}}$, and $Q_{\mathrm{empty}}$ are the heat flow measurements for the sample, the reference standard, and the empty pan, respectively; $n_{\mathrm{sample}}$ and $n_{\mathrm{ref}}$ are the quantities of the sample and the reference standard in moles; and $C_{p,\mathrm{ref}}$ is the known heat capacity of the reference standard at the given temperature. At least three independent values were obtained at each temperature. The repeatability of these measurements was 3 %. The results have an uncertainty, estimated by the manufacturer of the instrument, of 5 % which has been verified in this study by the measurement of the heat capacity of the pure water.

## Methodology

The Joback group contribution method,[16,17] widely used to predict the ideal gas heat capacities of molecular compounds, was chosen for investigation as a potential predictive tool for ionic liquids. Ideal gas heat capacities are calculated as a function of temperature, based on the summation of contribution parameters for the functional groups present in the molecular structure of the component, using the following eq 2

$$C_p^{\mathrm{o}}(T) = \left[\sum_k n_k A_{Cpk} - 37.93\right] + \left[\sum_k n_k B_{Cpk} + 0.210\right]T + \left[\sum_k n_k C_{Cpk} - 3.91\cdot 10^{-4}\right]T^2 + \left[\sum_k n_k D_{Cpk} + 2.06\cdot 10^{-7}\right]T^3 \tag{2}$$

where $A_{Cpk}$, $B_{Cpk}$, $C_{Cpk}$, and $D_{Cpk}$ are group contribution parameters; $n_k$ is the number of groups of type $k$ in the molecule; and $T$ is the temperature in K. While ideal gas heat capacities are important thermodynamic properties in their own right, for ionic liquids, it is much more useful to consider liquid heat capacities at typical processing temperatures. By applying the principle of corresponding states,[17] it is possible to use the ideal gas heat capacity, along with other thermodynamic properties of the component, to estimate the liquid heat capacity, using the following eq 3

$$\frac{C_p^{\mathrm{r}}}{R} = \frac{C_p - C_p^{\mathrm{o}}}{R} = 1.586 + \frac{0.49}{1 - T_{\mathrm{r}}} + \omega\left[4.2775 + \frac{6.3(1 - T_{\mathrm{r}})^{1/3}}{T_{\mathrm{r}}} + \frac{0.4355}{1 - T_{\mathrm{r}}}\right] \tag{3}$$

Therefore, to enable the estimation of ionic liquid heat capacities, it is necessary to know, or be able to estimate, the boiling points and critical properties of ionic liquids. Recently, Valderrama and Robles developed and applied the modified Lydersen–Joback–Reid group contribution model for the determination of normal boiling points, acentric factors, and critical properties of ionic liquids[23] (see example in the Supporting Information). Although they were unable to validate this directly, due to the lack of experimental data on ionic liquid boiling points or critical properties, they used the values obtained in a model for the prediction of densities, obtaining a relative absolute deviation of 5.2 % when tested against 50 ionic liquids. The modified Lydersen–Joback–Reid method is summarized in the following eqs 4 to 7

$$T_{\mathrm{b}} = 198.2 + \sum_k n_k \Delta T_{\mathrm{b}Mk} \tag{4}$$

$$T_{\mathrm{c}} = \frac{T_{\mathrm{b}}}{A_M + B_M \sum_k n_k \Delta T_{Mk} - (\sum_k n_k \Delta T_{Mk})^2} \tag{5}$$

$$P_{\mathrm{c}} = \frac{M}{\left[C_M + \sum_k n_k \Delta P_{Mk}\right]^2} \tag{6}$$

$$\omega = \frac{(T_{\mathrm{b}} - 43)(T_{\mathrm{c}} - 43)}{(T_{\mathrm{c}} - T_{\mathrm{b}})(0.7T_{\mathrm{c}} - 43)}\log\left[\frac{P_{\mathrm{c}}}{P_{\mathrm{b}}}\right] - \frac{(T_{\mathrm{c}} - 43)}{(T_{\mathrm{c}} - T_{\mathrm{b}})}\log\left[\frac{P_{\mathrm{c}}}{P_{\mathrm{b}}}\right] + \log\left[\frac{P_{\mathrm{c}}}{P_{\mathrm{b}}}\right] - 1 \tag{7}$$

where $T_{\mathrm{b}}$ is the normal boiling point; $T_{\mathrm{c}}$ and $P_{\mathrm{c}}$ are the critical temperature and critical pressure, respectively; $\omega$ is the acentric factor; $\Delta T_{\mathrm{b}Mk}$, $\Delta T_{Mk}$, and $\Delta P_{Mk}$ are group contribution parameters for group type $k$; and $A_M$, $B_M$, and $C_M$ are coefficients (see Supporting Information).

In this work, heat capacities of ionic liquids were calculated using the original parameters developed by Joback.[16] It should be noted that since this model was developed for molecular

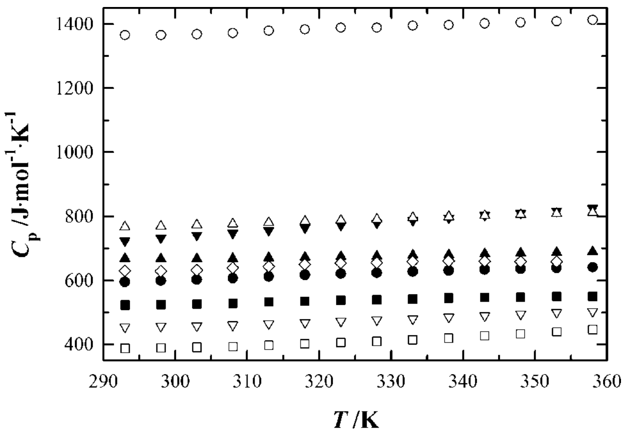

**Figure 1.** Experimentally determined heat capacities of ionic liquids as a function of temperature. ■, [$C_2$mim][$NTf_2$]; ●, [$C_4$mim][$NTf_2$]; ▲, [$C_6$mim][$NTf_2$]; ▼, [$C_8$mim][$NTf_2$]; ○, [$P_{66614}$][$NTf_2$]; ◇, [$C_4$mPyrr][$NTf_2$]; △, [$C_4$mPyrr][FAP]; ▽, [$C_4$mim][OTf]; □, [$C_2$mim][$EtSO_4$].

**Table 2. Experimental Heat Capacities, $C_p$, of Ionic Liquids As a Function of Temperature at Atmospheric Pressure**

| | $C_p$/J·mol$^{-1}$·K$^{-1}$ | | | | |
|---|---|---|---|---|---|
| $T$/K | [$C_2$mim] [$NTf_2$] | [$C_4$mim] [$NTf_2$] | [$C_6$mim] [$NTf_2$] | [$C_8$mim] [$NTf_2$] | [$P_{66614}$] [$NTf_2$] |
| 293 | 523 | 595 | 669 | 724 | 1366 |
| 298 | 525 | 599 | 667 | 733 | 1366 |
| 303 | 527 | 603 | 667 | 741 | 1368 |
| 308 | 529 | 607 | 668 | 748 | 1372 |
| 313 | 533 | 612 | 671 | 756 | 1379 |
| 318 | 535 | 617 | 673 | 765 | 1384 |
| 323 | 538 | 621 | 675 | 773 | 1389 |
| 328 | 539 | 624 | 676 | 779 | 1389 |
| 333 | 542 | 628 | 679 | 788 | 1395 |
| 338 | 545 | 631 | 680 | 795 | 1397 |
| 343 | 547 | 634 | 683 | 803 | 1402 |
| 348 | 548 | 636 | 685 | 810 | 1405 |
| 353 | 550 | 639 | 687 | 817 | 1409 |
| 358 | 551 | 641 | 689 | 825 | 1413 |

| | $C_p$/J·mol$^{-1}$·K$^{-1}$ | | | |
|---|---|---|---|---|
| $T$/K | [$C_4$mPyrr] [$NTf_2$] | [$C_4$mPyrr] [FAP] | [$C_4$mim] [OTf] | [$C_2$mim] [$EtSO_4$] |
| 293 | 630 | 767 | 455 | 388 |
| 298 | 629 | 769 | 457 | 389 |
| 303 | 632 | 773 | 459 | 391 |
| 308 | 639 | 776 | 461 | 394 |
| 313 | 644 | 781 | 465 | 398 |
| 318 | 650 | 785 | 469 | 402 |
| 323 | 654 | 788 | 473 | 406 |
| 328 | 656 | 791 | 477 | 410 |
| 333 | 659 | 796 | 481 | 415 |
| 338 | 661 | 799 | 486 | 420 |
| 343 | 660 | 803 | 490 | 427 |
| 348 | 659 | 806 | 495 | 433 |
| 353 | 658 | 809 | 500 | 440 |
| 358 | - | 812 | 504 | 447 |

species no consideration is given to any effect the ionic charges present in ionic liquids may have on their heat capacities. In applying this model, it is assumed here that such effects can be considered negligible in comparison to the cumulative effects of the various functional groups present in the ionic liquid. In developing group contribution parameters for the three new groups, "B", "P", and "−SO−", the model was first tested against small data sets for ionic liquids containing those groups. Least squares linear regression was used to generate best fit group contribution parameters based on these initial data sets. In all three cases, the use of two parameters for each group was found to be sufficient to adequately model their contribution. The uncertainties of the group contribution model were determined by calculating the relative deviation (RD) and relative absolute deviation (RAD), as defined by eqs 8 and 9

$$\mathrm{RD} = \frac{1}{N}\sum\left(\frac{C_{p,\mathrm{calcd}} - C_{p,\mathrm{exptl}}}{C_{p,\mathrm{exptl}}}\right) \tag{8}$$

$$\mathrm{RAD} = \frac{1}{N}\sum\left|\frac{C_{p,\mathrm{calcd}} - C_{p,\mathrm{exptl}}}{C_{p,\mathrm{exptl}}}\right| \tag{9}$$

where $N$ is the total number of data used; $C_{p,\mathrm{calcd}}$ is the heat capacity value calculated using the model for a given ionic liquid at a given temperature; and $C_{p,\mathrm{exptl}}$ is the corresponding heat capacity value obtained from experimental work reported herein or from data reported previously. Once the model was validated against the complete data set, further optimization of the parameters for these three groups was performed by using the Solver function in Microsoft Excel, which is based on the generalized reduced gradient (GRG) method, to minimize the RAD.

## Results and Discussion

***Heat Capacity Measurements.*** The heat capacity for the nine ionic liquids [$C_2$mim][$NTf_2$], [$C_4$mim][$NTf_2$], [$C_6$mim][$NTf_2$], [$C_8$mim][$NTf_2$], [$C_2$mim][$EtSO_4$], [$C_4$mim][OTf], [$P_{66614}$][$NTf_2$], [$C_4$mpyrr][$NTf_2$], and [$C_4$mpyrr][FAP] was measured using DSC over the temperature range from (293 to 358) K. The experimental data obtained are reported in Table 2 and in Figure 1 for all the pure ILs studied. In all cases, the relationship between heat capacity and temperature was found to be approximately linear, with only around 10 % increase observed over the temperature range used. The impact of increasing the chain length of [$C_n$mim][$NTf_2$] ionic liquids is clearly demonstrated, with each additional $-CH_2-$ group increasing the heat capacity by approximately 35 J·mol$^{-1}$·K$^{-1}$ at 298 K, for example. Similar observations were made by Holbrey et al.,[24] Archer et al.,[25] and Paulechka et al.,[26] who reported incremental increases in $C_p$ of 40 J·mol$^{-1}$·K$^{-1}$, 30 J·mol$^{-1}$·K$^{-1}$, and 31 J·mol$^{-1}$·K$^{-1}$ respectively, for each additional $-CH_2-$ group. This suggests that the use of a group contribution method is a reliable way to model the heat capacities of ionic liquids, since each additional group has a unitwise effect on the overall value. The heat capacity of [$P_{66614}$][$NTf_2$] is much greater than any of the other ionic liquids, with a value of 1366 J·mol$^{-1}$·K$^{-1}$, compared with 525 J·mol$^{-1}$·K$^{-1}$ for [$C_2$mim][$NTf_2$] as shown in Table 2 at 298 K, for example. Again, this demonstrates the cumulative effect of increasing the length of hydrocarbon chains on the cation. Significant changes in the heat capacity as a function of the anion are also observed, for example, [$C_4$mim][OTf] < [$C_4$mim][$NTf_2$] and [$C_4$mpyrr][$NTf_2$] < [$C_4$mpyrr][FAP], demonstrating that the heat capacity increases with the size of the anion. As found for other properties, such as density[12] and viscosity,[27] the anion type has a greater impact than the cation on the heat capacity. Compared with traditional organic solvents, the heat capacities of ionic liquids are generally higher; for example, at 298 K, the heat capacities of water, ethanol, nitromethane, and benzene are between (75 and 292) J·mol$^{-1}$·K$^{-1}$.[28,29]

The data reported herein are found to be close to those reported previously over a range of ionic liquids. For example, the heat capacity measured for [$C_6$mim][$NTf_2$] corresponds well with that of Diedrichs and Gmehling[18] (higher by < 1.7 %), Blokhin et al.[30] (lower by < 1.7 %), and Archer[31] (lower by < 1.9 %), while the heat capacities obtained by Crosthwaite et

**Table 3. Experimental Heat Capacities, $C_p$, at 298 K of $[C_4mim][OTf]$ and $[C_4mim][NTf_2]$ as a Function of the Mole Fraction of Water ($x_w$) and Chloride ($x_{Cl^-}$), Respectively**

| | $C_p/J\cdot mol^{-1}\cdot K^{-1}$ | | $C_p/J\cdot mol^{-1}\cdot K^{-1}$ |
|---|---|---|---|
| $x_w$ | ($[C_4mim][OTf]$ + water) | $x_{Cl^-}$ | ($[C_4mim][NTf_2]$ + chloride) |
| [a]0.0108 | 448 | 0 | 582 |
| 0.1370 | 401 | 0.0919 | 549 |
| 0.3379 | 325 | 0.2394 | 515 |
| 0.5215 | 257 | 0.4129 | 468 |
| [b]0 | 451.6 | 0.5832 | 420 |
| 1 | 75.3 | [c]1 | 366 |

[a] Corresponding to the dried IL. [b] Estimation for IL with $x_w = 0$. [c] Corresponding to $[C_4mim]Cl$.

**Table 4. Group Contribution Parameters for the Joback Method[16,17] Relevant to the Ionic Liquids Studied[a]**

| groups | $A_{Cpk}$ $J\cdot mol^{-1}\cdot K^{-1}$ | $10^3\cdot B_{Cpk}$ $J\cdot mol^{-1}\cdot K^{-2}$ | $10^6\cdot C_{Cpk}$ $J\cdot mol^{-1}\cdot K^{-3}$ | $10^8\cdot D_{Cpk}$ $J\cdot mol^{-1}\cdot K^{-4}$ |
|---|---|---|---|---|
| | | Without Rings | | |
| $-CH_3$ | 19.5 | −8.08 | 153 | −9.67 |
| $-CH_2-$ | −0.909 | 95.0 | −54.4 | 1.19 |
| >C< | −66.2 | 427 | −64.1 | 30.1 |
| −O− | 25.5 | −63.2 | 111 | −5.48 |
| >N− | −31.1 | 227 | −320 | 14.6 |
| −CN | 36.5 | −73.3 | 184 | −10.3 |
| −F | 26.5 | −91.3 | 191 | −10.3 |
| −Cl | 33.3 | −96.3 | 187 | −9.96 |
| −Br | 28.6 | −64.9 | 136 | −7.45 |
| | | With Rings | | |
| $-CH_2-$ | −6.03 | 85.4 | −8.00 | −1.80 |
| =CH− | −2.14 | 57.4 | −1.64 | −1.59 |
| =C> | −8.25 | 101 | −142 | 6.78 |
| <N− | −31.1 | 227 | −320 | 14.6 |
| −N= | 8.83 | −3.84 | 43.5 | −2.60 |

[a] '-' denotes a single bond, '=' denotes a double bond. '−X', '−X−', '>X−', and '>X<' denote functional group or atom X bonded to 1, 2, 3, and 4 other groups, respectively.

**Table 5. Initial and Optimized Group Contribution Parameters Developed in This Work for the Groups $-SO_2-$, B, and P, which are Common to Ionic Liquids**

| | initial | | optimized | |
|---|---|---|---|---|
| groups | $A_{Cpk}$ $J\cdot mol^{-1}\cdot K^{-1}$ | $10^3\cdot B_{Cpk}$ $J\cdot mol^{-1}\cdot K^{-2}$ | $A_{Cpk}$ $J\cdot mol^{-1}\cdot K^{-1}$ | $10^3\cdot B_{Cpk}$ $J\cdot mol^{-1}\cdot K^{-2}$ |
| $-SO_2-$ | 89.96 | 49.9 | 90.184 | 7.53 |
| B | −62.65 | 193 | −71.235 | 211 |
| P | −87.56 | 332 | −72.867 | 287 |

al.[32] are lower by > 10 %. For $[C_2mim][NTf_2]$, there is no significant difference between the values measured within this study and those of Fredlake et al.[6] with the values reported by Waliszewski et al.[33] being < 5 % lower. The data for $[C_4mim][OTf]$ are higher than those of Diedrichs and Gmehling[18] by ≈ 5 % and higher than those of Fredlake et al.[6] by ≈ 10 %.

Due to the small number of heat capacity data points reported to date, many of which do not specify the impurity content of water and halide, for example, the influence of impurities on the heat capacity is difficult to quantify accurately. For example, the heat capacity for $[C_2mim][BF_4]$ was reported by Waliszewski et al.[33] and by Van Valkenburg et al.[34] to be (306.5 and 250.0) $J\cdot mol^{-1}\cdot K^{-1}$, respectively, at 293 K. The ≈ 20 % deviation observed could not be explained by the uncertainty of each apparatus used only but is more likely to be associated with the sum of different factors including the equipment uncertainty and the influence of the impurities present in each ionic liquid sample. Waliszewski et al.[33] reported the mass fraction of water of $400\cdot 10^{-6}$ but did not quote the halide content. Van Valkenburg et al.[34] reported the mass fraction of water of $600\cdot 10^{-6}$ and the mass fraction of chloride of $1130\cdot 10^{-6}$. Similar conclusions can be made from data reported for $[C_4mim][NTf_2]$, $[C_2mim][EtSO_4]$, and $[C_4mim][BF_4]$.[33−37] Holbrey et al.[24] reported a mass fraction of water of $9000\cdot 10^{-6}$ for $[C_6mim][PF_6]$ and up to $2000\cdot 10^{-6}$ for $[C_2mim][PF_6]$, $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, and $[C_4mim][NTf_2]$, while the halide content was not reported. While their data for $[C_4mim]Cl$ compare well with the reported data herein and elsewhere,[6,35] the data for the other ionic liquids, $[C_2mim][PF_6]$, $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, and $[C_4mim][NTf_2]$, are, on average, 22 % lower than those reported in other studies. This discrepancy may be due to the presence of impurities in these ionic liquids impacting the observed heat capacities (see the Supporting Information). To quantify this effect in detail, $[C_4mim][OTf]$ and $[C_4mim][NTf_2]$ were doped with water and chloride and their heat capacities measured at 298.15 K (Table 3). With increasing water or chloride content, the heat capacity was found to be lowered compared with dried and/or halide-free samples. Furthermore, the variation of heat capacity with mole fraction chloride and water content could be fitted using a linear trendline. For small chloride mass fraction content, up to $1000\cdot 10^{-6}$, a decrease in the heat capacity of ≈ 0.15 % on average when compared with the halide-free IL was observed. This observation supports the report of Tronsoco et al.,[37] which noted that an increase of the mass fraction of chloride from (20 to 130)$\cdot 10^{-6}$ in $[C_4mim][NTf_2]$ had little influence on $C_p$. For small water mass fractions, up to $1000\cdot 10^{-6}$, a decrease of ≈ 1.3 % on $C_p$ was observed when compared with the dried IL. Since the dried $[C_4mim][OTf]$ used in this study had a mole fraction content up to 0.0108 from the linear regression, it is also possible to estimate the heat capacity for water-free $[C_4mim][OTf]$ to be 451.6 $J\cdot mol^{-1}\cdot K^{-1}$. This observation is in agreement with the recent report of García-Miaja et al.[28] on the heat capacity measurement for the binary mixture of (1-butyl-3-methylpyridinium tetrafluoroborate + water). From this study, it appears clearly that the presence of water has a more important effect on the heat capacity than the presence of halide in the ionic liquid. Due to the clear and significant discrepancies between the data reported by Holbrey et al.,[24] Van Valkenburg et al.,[34] and Fernandez et al.[36] compared with all other available data, it was decided not to include these data in fitting the model, since the accuracy of a GCM depends directly on the accuracy of the data used in its development. Despite some scatter of the other data reported to date, there exist sufficient data over a range of ionic liquids to serve as a basis for the development and testing of a predictive group contribution method.

***Heat Capacity Prediction.*** In its original form, the Joback group contribution method cannot be applied to the vast majority of ionic liquids due to the lack of group contribution parameters for the $-SO_2-$, P, and B groups which are commonly found in ionic liquids. However, sufficient group parameters exist to make predictions for the heat capacities of many halide-based ionic liquids and are shown in Table 4. Such predictions were found to have an RD of −0.27 % and an RAD of 5.9 % when tested against 15 data for six bromide- and chloride-based ionic liquids. Importantly, this result suggests that these group contribution parameters, which were originally developed by Joback for molecular liquids, are equally applicable to ionic liquids. Furthermore, it provides additional validation of the modified Lydersen−Joback−Reid method used to determine the critical properties.

**Table 6. Relative Absolute Deviation (RAD) for the Extended Joback Model When Tested against Different Datasets Using the Initial and Optimized Group Contribution Parameters**

| dataset | | | | initial | optimized |
|---|---|---|---|---|---|
| description | ref | no. of points | no. of unique ionic liquids | 100·RAD | 100·RAD |
| all data | [a]6, 15, 18, 26, 28, 30−33, 37−47 | 961 | 53 | 4.42 | 2.91 |
| halide-based ionic liquids | 6, 32, 41 | 15 | 6 | 5.86 | 5.86 |
| $[C_n\text{mim}][\text{OTf}]$-based ionic liquids | 6, 18 | 147 | 4 | 2.19 | 1.64 |
| $[C_n\text{mim}][\text{NTf}_2]$-based ionic liquids | [a]6, 18, 30−33, 37, 46, 47 | 345 | 4 | 3.26 | 2.74 |
| ionic liquids containing $-SO_2-$ | [a]6, 18, 26, 30−33, 37, 38, 44−47 | 777 | 35 | 4.44 | 2.85 |
| ionic liquids containing B | 6, 26, 28, 32, 33, 39, 42, 43 | 100 | 6 | 6.12 | 2.72 |
| ionic liquids containing P | [a]6, 37, 40 | 64 | 4 | 3.09 | 1.20 |

[a] This work.

However, to extend this method to $[\text{NTf}_2]^-$ and $[\text{OTf}]^-$ based ionic liquids, it is necessary to generate the parameters for the $-SO_2-$ group. Experimental data from Diedrichs and Gmehling[18] for $[C_n\text{mim}][\text{OTf}]$ ionic liquids ($n = 2, 4, 6, 8$) were initially used to generate parameters for $-SO_2-$. By calculating the total contributions from each of the other groups and using least-squares linear regression to minimize the difference between experimental and correlated values, the parameter values were optimized. The resulting correlations yielded an RAD of 2.2 %. This low uncertainty was obtained using four different ionic liquids and 147 data[6,18] to generate the parameters and was also used to test the model. When these parameters were then used to predict, this time, heat capacities for a more extensive range of $[C_n\text{mim}][\text{NTf}_2]$ ionic liquids ($n = 2, 4, 6, 8$), an RAD of 3.3 % for 345 data points[6,18,30−33,37,46,47] and an overall RAD of 4.4 % for a total of 35 different ionic liquids containing the $-SO_2-$ group, using 777 data points from 14 different sources, were obtained.[6,18,26,30−33,37,38,44−47] Using a similar procedure, parameters were generated for the B and P groups from data for $[C_4\text{mim}][\text{BF}_4]$[33] and $[C_4\text{mim}][\text{PF}_6]$,[37] respectively, and subsequently used to predict heat capacities of other ionic liquids containing these groups. An RAD of 6.1 % was obtained for six $[\text{BF}_4]^-$ based ionic liquids with 100 data points from eight sources,[6,26,28,32,33,39,42,43] while the application of the P parameters in predicting the heat capacities of four different ionic liquids, including the data for $[P_{66614}][\text{NTf}_2]$ and $[C_4\text{mpyrr}][\text{FAP}]$ reported herein, resulted in an RAD of 3.1 % for 64 data points from four sources.[6,37,40] For the complete data set of 961 points for 53 different ionic liquids,[6,15,18,26,28,30−33,37−47] from 21 different sources over a temperature range from (256 to 470) K, the RAD is 4.4 %. This clearly illustrates the widespread applicability and validity of the model since only a small subset of data were used to generate the group contribution parameters, but the model was successfully tested against a much larger set of data using many different ionic liquids. The parameters which were initially fitted are shown in Table 5, with the RAD values for different data sets, shown in Table 6.

To minimize this overall RAD, the fitted parameters for the B, P, and $-SO_2-$ groups were then further optimized, by regressing these parameters against the full data set and reparameterizing. The resultant model gave an overall RAD of 2.9 % (see the Supporting Information). The optimized parameters are shown in Table 5, and the RAD values for different data sets, calculated using both parameter sets, are shown in Table 6. The parity plot, shown in Figure 2, shows the excellent agreement between experimental and predicted values and demonstrates the accuracy of the model over a wide range of heat capacities. As discussed previously, this model takes no account of any effect the ionic charges may have on the heat capacity of ionic liquids, which were assumed negligible. The low RAD value obtained shows that such effects must be relatively small, thus validating this assumption. With additional experimental heat capacity data, it should be possible to improve the accuracy of the model further by consolidating functional groups into larger groups, such as the imidazolium ring, commonly found in ionic liquids, and reparameterizing the model accordingly. This method would allow the effects of ionic charge to be accounted for. However, even with the limited data sets available, the extended Joback model provides an effective and relatively simple method of predicting heat capacities for a wide range of ionic liquids as a function of temperature.

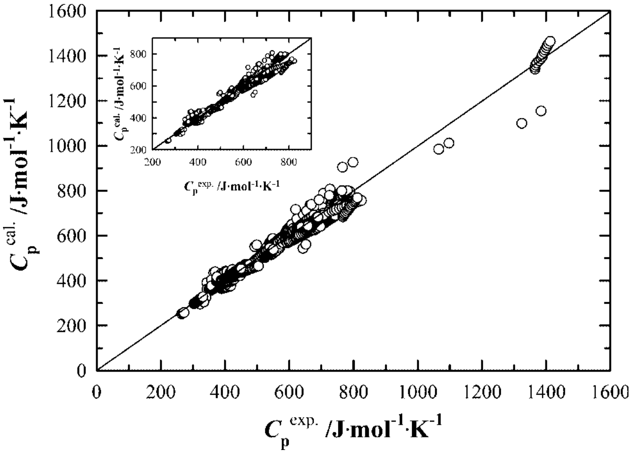

**Figure 2.** Parity plot comparing experimentally determined heat capacity results, both from this work and the literature, with those predicted by applying the principle of corresponding states to the extended Joback group contribution method for heat capacity.

## Conclusions

The extended Joback model has been used to predict the heat capacities as a function of the temperature from (256 to 470) K of a range of ionic liquids at 0.1 MPa via a group contribution method. New parameters have been determined for P, B, and $-SO_2-$ groups leading to an overall RAD of 2.9 % for 961 data points from 53 ionic liquids. The effect of halide and water on the heat capacity has also been determined and shows that water content is more influential than that of chloride, for example.

### Supporting Information Available:

Additional Supporting Information spreadsheets of the IL heat capacity database, chemical structures, molar mass, and abbreviated notations (AN) of ions used in the present work and one example of the methodology used in the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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