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Prediction of the thermodynamic properties of 1-alkyl-3-methylimidazolium lactate ionic liquids [C$_n$mim][Lact] (n = 2, 3, 4, 5, and 6) by parachor

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An ionic liquid (IL) based on lactate, 1-butyl-3-methylimidazolium lactate ([C$_4$mim][Lact]), has been prepared and characterized by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and differential scanning calorimetry (DSC). Since the IL can form strong hydrogen bonds with water, trace water is a problematic impurity in the IL. Using the standard addition method (SAM), the density, refractive index and surface tension of [C$_4$mim][Lact] were measured in the temperature range (308.15 to 343.15 ± 0.05) K. On the basis of the experimental data, the parachor and molar volume for [C$_4$mim][Lact], and the molecular volume V_m, surface tension γ, molar enthalpy of vaporization $\Delta_l^g H_m^0$, refractive index n_D, and the thermal expansion coefficients α, for the homologues [C$_n$mim][Lact] (n = 2, 3, 4, 5, and 6) were estimated using semi-empirical methods. The estimated values are in good agreement with the experimental data.

parachor, lactate, ionic liquid, density, surface tension, refractive index

1 Introduction

In recent years, there has been a developing trend in the literature towards estimation of physicochemical properties for compounds by semi-empirical methods, in particular, for ionic liquids [1–5]. Although the estimated results cannot be regarded as accurate physicochemical data, they do provide valuable insight into the origins of the behavior of materials. Among all the semi-empirical methods, the parachor is the simplest. The parachor is defined as:

$$P = \left(M\gamma^{1/4}\right)\Big/\rho \quad (1)$$

where M is the molar mass, γ is the surface tension, and ρ is the density. In 1924, Sugden [6] surveyed the existing data for surface tensions and densities and calculated the parachors of 167 nonpolar compounds, and then applied them to estimate thermophysical properties. So far, such studies have mainly focused on organic compounds, because the role of Coulombic forces must be considered in studying the parachors of electrolytes [7]. Although a number of early studies attempted to determine parachor values for ions, unfortunately these studies were hampered by the experimental difficulties encountered in determining the surface tensions and densities of high melting salts and no related investigations followed [4]. Since numerous ionic liquids are fluid at room temperature, they offer a solution to the handling difficulties previously encountered when performing physical property measurements on conventional salts.

Ionic liquids have now become one of the most rapidly growing areas in chemistry [8–14]. In particular, amino acid-based ionic liquids have attracted increasing attention from both academic and industrial communities as greener

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alternatives to volatile organic solvents and new functional materials [15–18]. Lactic acid is a naturally occurring organic acid which plays important roles in the human body. It is a chiral compound and has strong hydrogen bonding ability. In this paper, an ionic liquid based on lactate, 1-butyl-3-methylimidazolium lactate ([C_4mim][Lact]), has been synthesized and characterized. The values of density, refractive index and surface tension for [C_4mim][Lact] were measured in the temperature range (308.15 to 343.15 ± 0.05) K. Since the lactate-based ionic liquid can form strong hydrogen bonds with water, trace water is a problematic impurity in the IL, so that the standard addition method (SAM) was employed in these measurements [19]. Based on the experimental parachors and molar volume for [C_4mim][Lact], the volumetric properties, parachors, surface tension, molar enthalpies of vaporization, coefficient of thermal expansion, and refractive index for the IL homologues, [$C_n$mim][Lact] (n = 2, 3, 4, 5, and 6), have been predicted by semi-empirical methods and the values compared with experiment.

2 Experimental procedures and results

2.1 Chemicals and instrumentation

Deionized water was distilled in a quartz still, and its conductance was $0.8\times10^{-4}-1.2\times10^{-4}$ S m^{-1}. *N*-methylimidazole (AR grade reagent) was vacuum distilled prior to use. Bromobutane (AR grade reagent) was distilled before use. Ethyl acetate and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles. Sodium lactate (99% purity) was purchased from Shanghai Reagent Co. Ltd.

Densities were measured using a PZ-D-5 Westphal balance (Shanghai Liangping Balance Co.). The surface tension was measured by a tensiometer of the forced bubble type (DPAW type produced by Sang Li Electronic Co.). The refractive indices were measured by a WZS-1 Abbe refraction instrument (Shanghai optics instrument Co.). All instruments were calibrated before use by standard methods.

2.2 Synthesis of the ionic liquid [C_4mim][Lact]

1-Butyl-3-methylimidazolium chloride ([C_4mim]Cl) was synthesized according to the literature [20, 21]. The structure of [C_4mim]Cl was confirmed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy (Varian XL-300) and the ^{1}H NMR spectrum is shown in the supporting information.

Synthesis of IL [C_4mim][Lact] was carried out in acetone as shown in the following equation [22]:

$$\mathrm{Na[Lact]+[C_4mim]Cl\rightarrow NaCl\downarrow+[C_4mim][Lact]}$$

The solubilities of Na[Lact] and [C_4mim]Cl in acetone are small, but NaCl is insoluble. As a result, NaCl is continually precipitated during the reaction, so the reaction is driven towards the right. Equimolar amounts of [C_4mim]Cl and Na[Lact] were added to acetone, stirred for 72 h, and the solution was then filtered to remove the insoluble NaCl. After removing the acetone by vacuum distillation, a yellow liquid, [C_4mim][Lact], was obtained. It was dried in a vacuum desiccator at 80 °C under reduced pressure for 24 h and stored in a desiccator prior to use. It was characterized by ^{1}H NMR spectroscopy and differential scanning calorimetry (DSC) (Mettler-Toledo Co., Switzerland), and the water content was determined by a Karl Fischer moisture titrator (ZSD-2 type). The ^{1}H NMR spectrum (see the supporting information) confirmed the structure of [C_4mim][Lact] and confirmed the absence of impurities in the sample. The DSC trace of the product showed that the IL has no melting point but has a glass transition temperature (T_g = −55.45 °C) (see the Supporting Information).

2.3 Determination of the density of [C_4mim][Lact]

According to the SAM, a series of samples of [C_4mim][Lact] with different known water contents were prepared. The densities of the samples were measured in the temperature range 308.15 to 343.15 K. The sample was placed in a cell with a jacket and was thermostated at each temperature with an accuracy ± 0.05 K. The results are listed in Table 1. A plot of density against water content gave a good straight

Table 1 Values of density, ρ (g·cm^{-3}), of the ionic liquid [C_4mim][Lact] containing various known amounts of water in the temperature range 308.15–343.15 K

T (K)	10^3w_2						r	$s\times10^4$
	6.50	7.20	8.30	9.90	10.3	0		
298.15						1.1282*		
308.15	1.0982	1.0962	1.0917	1.0862	1.0839	1.1227	0.99	4.2
313.15	1.0950	1.0930	1.0888	1.0830	1.0807	1.1196	0.99	4.3
318.15	1.0925	1.0905	1.0868	1.0805	1.0782	1.1173	0.99	5.6
323.15	1.0900	1.0880	1.0826	1.0780	1.0757	1.1143	0.99	6.5
328.15	1.0867	1.0847	1.0801	1.0747	1.0724	1.1112	0.99	4.2
333.15	1.0835	1.0816	1.0770	1.0715	1.0692	1.1082	0.99	4.4
338.15	1.0815	1.0799	1.0749	1.0695	1.0672	1.1065	0.99	5.6
343.15	1.0793	1.0765	1.0730	1.0673	1.0650	1.1030	0.99	4.0

w_2 is the water content; r is the correlation coefficient; s is the standard deviation; * is an estimated value.

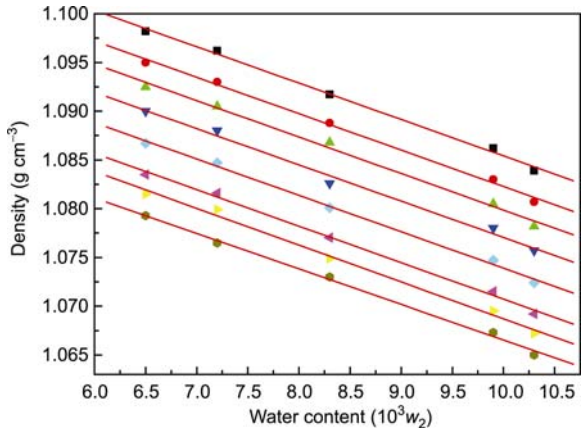

Figure 1 Plots of density vs. the amount of water in [C_4mim][Lact] in the temperature range 308.15 – 343.15 K. ■308.15 K: $\rho = 1.1227 - 0.00373w_2$, $s = 4.2 \times 10^{-4}$, $r = 0.99$; ●313.15 K: $\rho = 1.1196 - 0.00374w_2$, $s = 4.3 \times 10^{-4}$, $r = 0.99$; ▲318.15 K: $\rho = 1.1173 - 0.00374w_2$, $s = 5.6 \times 10^{-4}$, $r = 0.99$; ▼323.15 K: $\rho = 1.1143 - 0.00372w_2$, $s = 6.5 \times 10^{-4}$, $r = 0.99$; ◆328.15 K: $\rho = 1.1112 - 0.00373w_2$, $s = 4.2 \times 10^{-4}$, $r = 0.99$; ◀333.15 K: $\rho = 1.1082 - 0.00374w_2$, $s = 4.4 \times 10^{-4}$, $r = 0.99$; ▶338.15 K: $\rho = 1.1065 - 0.00378w_2$, $s = 5.6 \times 10^{-4}$, $r = 0.99$; ⬢343.15 K: $\rho = 1.1030 - 0.00364w_2$, $s = 4.0 \times 10^{-4}$, $r = 0.99$.

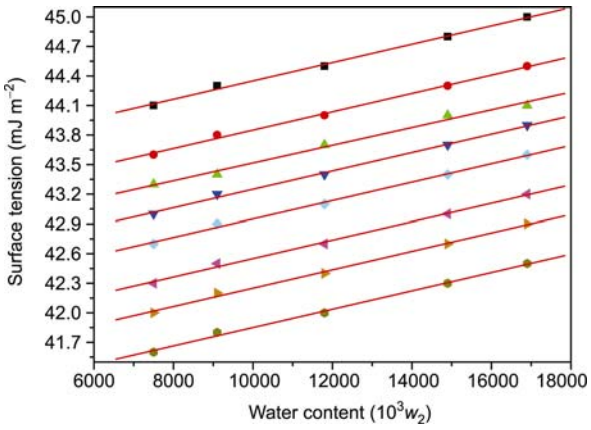

Figure 2 Plots of surface tension vs. the amount of water in [C_4mim][Lact] in the temperature range 308.15–343.15 K. ■308.15 K: $\gamma = 43.4 - 9.314 \times 10^{-5}\ w_2$, $s = 0.025$, $r = 0.99$; ●313.15 K: $\gamma = 42.9 - 9.314 \times 10^{-5}\ w_2$, $s = 0.025$, $r = 0.99$; ▲318.15 K: $\gamma = 42.6 - 9.000 \times 10^{-5}\ w_2$, $s = 0.041$, $r = 0.99$; ▼323.15 K: $\gamma = 42.3 - 9.314 \times 10^{-5}\ w_2$, $s = 0.025$, $r = 0.99$; ◆328.15 K: $\gamma = 42.0 - 9.314 \times 10^{-5}\ w_2$, $s = 0.025$, $r = 0.99$; ◀333.15 K: $\gamma = 41.6 - 9.314 \times 10^{-5}\ w_2$, $s = 0.025$, $r = 0.99$; ▶338.15 K: $\gamma = 41.3 - 9.314 \times 10^{-5}\ w_2$, $s = 0.025$, $r = 0.99$; ⬢343.15 K: $\gamma = 40.9 - 9.314 \times 10^{-5}\ w_2$, $s = 0.025$, $r = 0.99$.

line at each temperature (see Figure 1) showing that the SAM is an appropriate technique in this case. From the intercepts of these straight lines, the values of the densities for the pure ionic liquid [C_4mim][Lact] without any water were obtained and are listed in Table 1. The values of correlation coefficient and standard deviation for the fitting are also shown in Table 1.

2.4 Determination of the surface tension of [C_4mim][Lact]

The values of surface tension for the samples were measured by a calibrated tensiometer in the temperature range 308.15 to 343.15 K and are listed in Table 2. Each value in Table 2 is the average of three measurements. By plotting values of surface tension against water content, a set of good straight line was obtained (see Figure 2) showing that the SAM has good applicability. From the intercepts of these straight lines, the values of surface tension for the pure ionic liquid [C_4mim][Lact] without any water were obtained and are listed in Table 2. The values of correlation coefficient and standard deviation for the fitting are also shown in Table 2.

2.5 Determination of the refractive index of [C_4mim][Lact]

The values of the refractive index of samples of [C_4mim][Lact] with known different water contents were determined in the temperature range 308.15 to 343.15 K, and are listed in Table 3. By plotting values of the refractive index against water content, a set of good straight lines was obtained (see Figure 3), showing that the SAM has good applicability. From the intercepts of these straight lines, the values of the refractive index for pure [C_4mim][Lact] without any water

Table 2 Values of surface tension, γ (mJ m^2), of the ionic liquid [C_4mim][Lact] containing various known amounts of water in the temperature range 308.15–343.15 K

T (K)	10^3w_2						r	$s \times 10^2$
	7.50	8.90	11.8	14.9	16.9	0		
298.15						44.0*		
308.15	44.1	44.3	44.5	44.8	45.0	43.4	0.99	2.5
313.15	43.6	43.8	44.0	44.3	44.5	42.9	0.99	2.5
318.15	43.3	43.4	43.7	44.0	44.1	42.6	0.99	4.1
323.15	43.0	43.2	43.4	43.7	43.9	42.3	0.99	2.5
328.15	42.7	42.9	43.1	43.4	43.6	42.0	0.99	2.5
333.15	42.3	42.5	42.7	43.0	43.2	41.6	0.99	2.5
338.15	42.0	42.2	42.4	42.7	42.9	41.3	0.99	2.5
343.15	41.6	41.8	42.0	42.3	42.5	40.9	0.99	2.5

w_2 is the water content; r is the correlation coefficient; s is the standard deviations; * is an estimated value.

Table 3 Values of the refractive index of the ionic liquid [C4mim][Lact] containing various amounts of water in the temperature range 308.15–343.15 K

T (K)	$10^3 w_2$						r	$s\times10^5$	R_m
	7.60	9.20	11.8	13.6	15.4	0			
298.15						1.4927*			58.87*
308.15	1.4920	1.4921	1.4923	1.4925	1.4926	1.4913	0.99	2.7	58.91
313.15	1.4906	1.4908	1.4910	1.4912	1.4913	1.4899	0.99	3.4	58.93
318.15	1.4897	1.4898	1.4900	1.4902	1.4904	1.4889	0.99	3.8	58.95
323.15	1.4883	1.4885	1.4887	1.4889	1.4891	1.4875	0.99	2.6	58.96
328.15	1.4868	1.4870	1.4872	1.4874	1.4876	1.4860	0.99	2.6	58.97
333.15	1.4854	1.4856	1.4858	1.4860	1.4862	1.4846	0.99	2.6	58.98
338.15	1.4847	1.4849	1.4851	1.4853	1.4855	1.4839	0.99	2.6	59.00
343.15	1.4831	1.4832	1.4835	1.4837	1.4839	1.4823	0.99	2.9	59.02

w_2 is the water content; r is the correlation coefficient; s is the standard deviations; * is an estimated value.

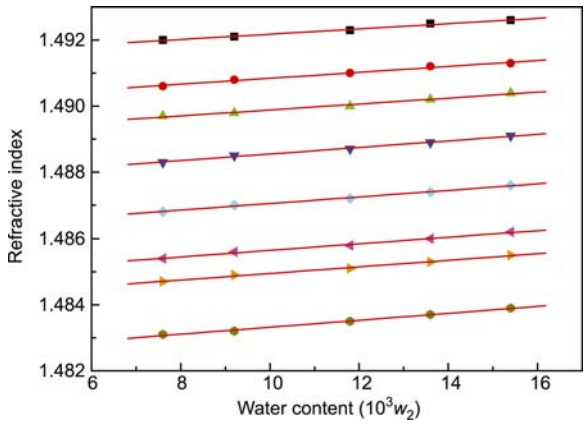

Figure 3 Plots of refractive index vs. the amount of water in [C4mim][Lact] in the temperature range 308.15–343.15 K. ■308.15 K: n_D = 1.4913 + 8.00836 × 10^{-5} w_2, s = 2.7 × 10^{-5}, r = 0.99; ●313.15 K: n_D = 1.4899 + 8.98329 × 10^{-5} w_2, s = 3.4 × 10^{-5}, r = 0.99; ▲318.15 K: n_D = 1.4889 +8.97334 × 10^{-5} w_2, s = 3.8 × 10^{-5}, r = 0.99; ▼323.15 K: n_D = 1.4875 + 9.94827 × 10^{-5} w_2, s = 2.6 × 10^{-5}, r = 0.99; ◆328.15 K: n_D = 1.4860 + 9.94827 × 10^{-5} w_2, s = 2.6 × 10^{-5}, r = 0.99; ◀333.15 K: n_D = 1.4846 + 9.94827 × 10^{-5} w_2, s = 2.6 × 10^{-5}, r = 0.99; ▶338.15 K: n_D = 1.4839 + 9.94827 × 10^{-5} w_2, s = 2.6 × 10^{-5}, r = 0.99; ⬬343.15 K: n_D = 1.4823 + 10.5253 × 10^{-5} w_2, s = 2.9 × 10^{-5}, r = 0.99.

were obtained and are listed in Table 3. The values of correlation coefficient and standard deviation for the fitting are also listed in Table 3.

3 Discussion

3.1 Estimation of the volumetric properties of [C$_n$mim][Lact]

Plots of the experimental values of ln ρ of the ionic liquid [C4mim][Lact] without water against $(T-298.15)$ were fitted by the method of least-squares and an empirical equation was obtained.

$$\ln\rho = 0.1207 - 5.00\times10^{-4}\left(T-298.15\right) \quad (2)$$

The correlation coefficient of the fitting is 0.999. From the intercepts of the empirical equation, the value of the density of the ionic liquid [C4mim][Lact] at 298.15 K can be obtained. According to the definition, $\alpha\equiv(1/V)(\partial V/\partial T)_p = -(\partial\ln\rho/\partial T)_p$, where V is the molar volume, the negative slope of the empirical equation is equal to the coefficient of thermal expansion, that is $\alpha = 5.00\times10^{-4}$ K^{-1} for [C4mim][Lact].

From the value of the density, the molecular volume, V_m, of [C4mim][Lact] was calculated using the following equation [23]:

$$V_m = M/\left(N\rho\right) \quad (3)$$

where M is the molar mass, N is the Avogadro constant and V_m = 0.3359 nm^3 for [C4mim][Lact].

In our previous research on alanine-based ionic liquid homologues [C$_n$mim][Ala] [24], the contribution to molecular volume per methylene (–CH$_2$–) group was found to be 0.0278 nm^3, which is in good agreement with a mean contribution of 0.0275 nm^3 per methylene group obtained by Glasser [23] using the ionic liquids [C$_n$mim][BF$_4$] and [C$_n$mim][NTf$_2$]. This suggests that the contribution of per methylene group to the volume may be treated as a constant so that we can use the mean value, 0.0278 nm^3, to predict the volumetric properties of other ILs which are homologues of [C$_n$mim][Lact] (n = 2, 3, 5, and 6). The predicted results are listed in Table 4.

According to Glasser's theory [23, 25], the standard molar entropy, S^0, and the crystal energy, U_{POT}, for an IL may be estimated using following equation:

$$S^0\left(298\right)/\left(\text{J K}^{-1}\text{mol}^{-1}\right) = 1246.5\left(V_m/\text{nm}^3\right)+29.5 \quad (4)$$

and

$$U_{POT}/\text{kJ mol}^{-1} = 1981.2\left(\rho/M\right)^{1/3}+103.8 \quad (5)$$

The predicted results for [C$_n$mim][Lact] (n = 2, 3, 4, 5, and 6) are also listed in Table 4. From Table 4, the largest value, U_{POT} = 462 kJ mol^{-1} for [C2mim][Lact], is much less than that of fused salts, for example, U_{POT} = 613 kJ mol^{-1} for

Table 4 The predicted volumetric properties of the homologous series [$C_n$mim][Lact] (n = 2, 3, 4, 5, and 6) at 298.15 K

Ionic liquid	ρ (g cm^{-3})	V_m (nm^3)	S^0 (J K^{-1} mol^{-1})	V (cm^3 mol^{-1})	U_{POT} (kJ mol^{-1})
[C_2mim][Lact]	1.1860	0.2803	379	168.8	462
[C_3mim][Lact]	1.1545	0.3081	414	185.6	451
[C_4mim][Lact]a)	1.1282	0.3359	448	202.3	441
[C_5mim][Lact]	1.1059	0.3637	483	219.0	432
[C_6mim][Lact]	1.0869	0.3915	517	235.8	424

a) Experimental value.

fused CsI [26] which has the lowest lattice energy among the alkali halides. The low lattice energy is the underlying reason for forming ionic liquid at room temperature.

3.2 Estimation of parachors and surface tension of [$C_n$mim][Lact]

Although the parachor, P, is a relatively old concept that relates the surface tension (γ) and density (ρ) of a substance using eq. (1), Deetlefs *et al*. [4] pointed out that it is a remarkably useful a tool to predict physicochemical properties of ILs. Therefore the experimental parachor for [C_4mim][Lact] was obtained from eq. (1), which gives a value of P = 521.0.

Considering that each methylene group in the alkyl chains of imidazolium-based ionic liquids has almost the same chemical environment, we have put forward a semi-empirical method for predicting P of IL homologues [24], using the sum of the experimental value for [C_4mim][Lact] and contributions from the methylene groups. In this way, the values of the parachor for the homologues of ILs [$C_n$mim][Lact] (n = 2, 3, 4, 5 , and 6) can be predicted from the formula (521.0 + 37.5 n), where n is the number of methylene groups; the contribution per methylene to the parachor of 37.5 was obtained in our previous paper [24]. The predicted values for the homologues are listed in Table 5. In Table 5, P'(1%) are the parachor values predicted using a neutral contribution to the parachor, where (1%) means that the allowable error of the training set is set at <1% [27]. From Table 5, $\Delta P = P - P'(1\%) = 39.65$ for [C_4mim][Lact]; this means that comparing the parachor value predicted using neutral parachor contribution values with the experimental one, the relative deviation, E%, is larger than 7.6% (E% = (experimental value − neutral calculated value)/ experimental value). The larger error implies that the parachors calculated using neutral contribution data do not account for Coulombic interactions in the ILs.

3.3 Estimation of vaporization enthalpies and vapor pressures of [$C_n$mim][Lact]

The molar enthalpy of vaporization, $\Delta_l^g H_m^0$ (298 K), of ionic liquids can be estimated according Kabo's empirical equation [28]:

$$\Delta_l^g H_m^0\left(298\ \mathrm{K}\right) = 0.01121\left(\gamma V^{2/3} N^{1/3}\right) + 2.4\ \mathrm{kJ\ mol^{-1}} \quad (6)$$

In eq. (6), V is the molar volume, γ is the surface tension, and N is Avogadro's constant. Using the estimated values of V and γ, the values of the molar enthalpy of vaporization, $\Delta_l^g H_m^0$ (298 K), for the homologous series [$C_n$mim][Lact] were calculated from eq. (6) and are listed in Table 5.

Rebelo *et al*. [29] put forward a method of estimating the hypothetical temperature of the normal boiling point (NBP) of ionic liquids, T_b, in terms of the critical temperature, T_c. They suggested that the relationship between T_b and T_c is $T_b \approx 0.6T_c$ for ionic liquids. The molar enthalpy of vaporization for the ILs at NBP, $\Delta_l^g H_m^0$ (T_b), can be estimated using the Trouton constant (≈ 90 J mol^{-1} K^{-1}). The critical temperature, T_c, of the ILs was estimated using the Eötvös equation [30]:

$$\gamma V^{2/3} = k\left(T_c - T\right) \quad (7)$$

Table 5 Predicted values of the surface tension, γ, the parachor, P, the molar enthalpy of vaporization, $\Delta_l^g H_m^0$(298.15 K), refractive index, n_D, and the thermal expansion coefficient, α, of the homologous series [$C_n$mim][Lact] (n = 2, 3, 4, 5, and 6)

Ionic liquid	P	P' (1%)	ΔP	γ (mJ m^{-2})	$\Delta_l^g H_m^0$ (kJ mol^{-1})	$10^4\alpha$ (K^{-1}) (Cal.)	n_D	R_m	$10^{24}\ \alpha_p$
[C_2mim][Lact]	446.0	401.55	44.45	48.7	143.3	5.98	1.5004	49.67	19.70
[C_3mim][Lact]	483.5	441.45	42.05	46.1	144.4	5.91	1.4968	54.27	21.53
[C_4mim][Lact]a)	521.0	481.35	39.65	44.0	146.0	5.82	1.4939	58.88	23.35
[C_5mim][Lact]	558.5	521.25	37.25	42.3	147.8	5.70	1.4914	63.47	25.17
[C_6mim][Lact]	596.0	561.15	34.85	40.8	149.9	5.58	1.4892	68.07	27.00

a) Experimental value.

where k is an empirical constant. The linear regressions of the product of γ and $V^{2/3}$ for [C_4mim][Lact] against absolute temperature T were made and straight lines were obtained. From the slopes and the intercepts of the straight lines, the values of k and T_c, respectively, were obtained. From T_c = 1098 K, the NBP of the ionic liquid [C_4mim][Lact] was obtained, T_b = 659 K. According to Rebelo's method, the predicted value of $\Delta_l^g H_m^0$ (T_b) was also calculated, $\Delta_l^g H_m^0$ = 59.3 kJ mol^{-1}. The difference between $\Delta_l^g H_m^0$ (T_b) estimated by Rebelo's method and $\Delta_l^g H_m^0$ (298 K) estimated by Kabo's method is very large. This is because of the heat capacity difference between the liquid and gas phases at different temperatures. Assuming a linear change of $\Delta_l^g H_m^0$ with temperature in the range between 298 K and T_b, the vapor pressure, p, of the ILs at various temperatures may be estimated using the Clausius–Clapeyron equation.

$$\ln(p_2/p_1) = \left(\Delta_l^g H_m^0/\mathrm{R}\right)\left(1/T_1 - 1/T_2\right) \quad (8)$$

The estimated values of $\Delta_l^g H_m^0$ and p of IL [C_4mim][Lact] at various temperatures are listed in Table 6. Figure 4 shows plots of the vapor pressure, p, and $\Delta_l^g H_m^0$ of the IL against temperature, T. It shows that the vapor pressure is very small, being only 10^{-6} Pa at 298 K. This is consistent with experimental observation of ILs.

3.4 Estimation of the thermal expansion coefficient of [C$_n$mim][Lact]

Using the estimated values of density and surface tension, the thermal expansion coefficient of ionic liquids [$C_n$mim][Lact] can be predicted in terms of the interstice model.

According to the interstice model [31, 32], an expression for calculating the interstice volume, v, can be obtained by classical statistical mechanics:

$$v = 0.6791\left(k_b T/\gamma\right)^{3/2} \quad (9)$$

where k_b is the Boltzmann constant. The molar volume of an ionic liquid, V, consists of the inherent volume, V_i, and total volume of the all interstices, that is:

$$V = V_i + 2Nv \quad (10)$$

If the expansion of the IL volume only results from the expansion of the interstices when the temperature increases, then the thermal expansion coefficients, α, given by the interstice model is:

$$\alpha = \left(1/V\right)\left(\partial V/\partial T\right)_p = 3Nv/VT \quad (11)$$

The values of α (cal.) were calculated using eq. (11) for ILs [$C_n$mim][Lact] and are listed in Table 5. The Table shows that the experimental value, α (exp.) = 5.00×10^{-4} K^{-1}, for [C_4mim][Lact] is in good agreement with the calculated value, α (cal.) = 5.82×10^{-4} K^{-1}. This confirms the interstice model is a suitable way to estimate the thermal expansion coefficient.

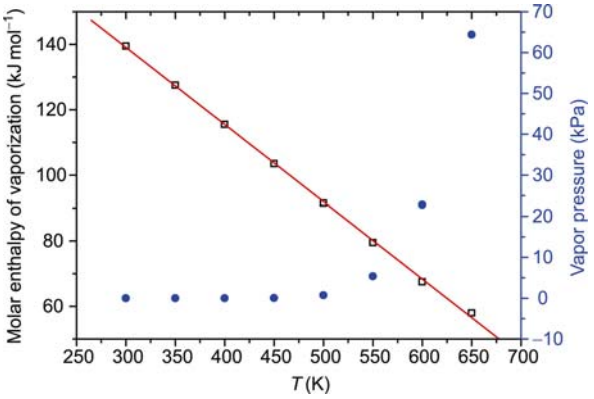

Figure 4 Plots of vapor pressure, p, and $\Delta_l^g H_m^0$ of the IL [C_4mim][Lact] against temperature T.

3.5 Estimation of molar polarization and refractive index of [C$_n$mim][Lact]

According to the Lorentz-Lorenz equation, the molar polarization, R_m, is defined as [33]:

$$R_m = \left[\left(n_D^2 - 1\right)/\left(n_D^2 + 2\right)\right]\cdot\left(M/\rho\right) = \left(4\pi N/3\right)\alpha_p \quad (12)$$

where n_D is the refractive index, and α_p is the polarization coefficient. Values of the molar polarization were obtained according to eq. (12) and are listed in Table 3.

Fitting the values of R_m of [C_4mim][Lact] without water against (T − 298.15), an empirical equation, $R_m = b + c(T - 298.15)$, was obtained with a correlation coefficient of 0.992 and standard deviation of 0.005. The intercept of the empirical equation gives the molar polarization at 298.15 K, R_m = 58.88. In addition, a value of α_p = 23.35 × 10^{-24} for [C_4mim][Lact] was obtained.

In our previous investigation of 1-alkyl-3-methylimidazolium alanine ionic liquids [34], the contribution of per methylene group to the molar polarization was found to be 4.60. Considering that each methylene group in the alkyl chains of the imidazolium-based ionic liquids has almost the same chemical environment, we have proposed a semi- empirical method for predicting the value of R_m of the IL homologues [$C_n$mim][Lact], and hence estimated the

Table 6 Predicted values of $\Delta_l^g H_m^0$ and p of ionic liquids [C_4mim][Lact] at various temperatures

T (K)	650	600	550	500	450	400	350	300
$\Delta_l^g H_m^0$ (J mol^{-1})	58.0	67.5	79.5	91.5	104	116	128	140
p (kPa)	64.4	22.8	53.5	7.24×10^{-1}	4.55×10^{-2}	9.60×10^{-4}	4.01×10^{-6}	1.36×10^{-9}

polarization coefficient. The results are listed in Table 5.

Substitution of eq. (1) into eq. (12) and rearrangement yields [4]:

$$\gamma^{1/4} = \left(P/R_{\mathrm{m}}\right)\left[\left(n_{\mathrm{D}}^2 - 1\right)/\left(n_{\mathrm{D}}^2 + 2\right)\right] \quad (13)$$

Then, in terms of eq. (13), the refractive index of the IL homologues [$C_n$mim][Lact] (n = 2, 3, 4, 5, and 6) can be predicted using the above values of the estimated surface tension, molar polarization and parachor. The estimated values of n_{D} are also listed in Table 5. The predicted value of the refractive index of [C_4mim][Lact], n_{D} = 1.4939, is in good agreement with the experimental value, 1.4927, obtained by extrapolation. This suggests that our semi-empirical method is a reasonable approach to study ILs.

4 Conclusion

An ionic liquid based on lactate, [C_4mim][Lact] has been prepared and characterized. Using the standard addition method, the density, surface tension and refractive index of the IL were measured in the temperature range (308.15 to 343.15 ± 0.05) K. On the basis of the experimental parachor and molar volume for [C_4mim][Lact], the molar volume, surface tension, molar enthalpy of vaporization, refractive index and thermal expansion coefficient of the IL homologues [$C_n$mim][Lact] (n = 2, 3, 5, and 6) were predicted using semi-empirical methods. The estimated values are in good agreement with the experimental data.

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