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Prediction of the Physicochemical Properties of Valine Ionic Liquids [$C_n$mim][Val] (n = 2,3,4,5,6) by Semiempirical Methods

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ABSTRACT: An amino acid ionic liquid (AAIL), [C_2mim][Val] (1-ethyl-3-methy-limidazolium valine), was synthesized and characterized by ^{1}H NMR. To avoid the influence of trace water in the IL, in terms of the standard addition method (SAM), the density, surface tension, and refractive index for [C_2mim][Val] were measured in different temperature ranges. On the basis of parachor and molar volume for [C_2mim][Val], the molecular volume, V_m, surface tension, γ, molar enthalpy of vaporization, $\Delta_l^g H_m°$, refractive index, n_D, the thermal expansion coefficients, α, the standard molar entropy, $S°$, and the molar polarization, R_m, for the homologue of [$C_n$mim][Val] (n = 2, 3, 4, 5, 6) were estimated using semiempirical methods. The estimated results were consistent with the experimental data in the order of magnitude.

1. INTRODUCTION

Ionic liquids (ILs), which have been widely considered as greener alternatives to volatile organic solvents used in many process, have now become an interdisciplinary cutting-edge research area;[1−7] in particular, amino acid ionic liquids (AAILs) have attracted more attention from both the academic and the industrial communities as new function materials.[8,9] In recent years, there has been a developing trend in the literature toward estimation of the physicochemical properties for compounds by semiempirical methods,[10−17] in particular, for ILs. Although the estimated results cannot be regarded as accurate physicochemical data, it is to be commended because it provides valuable insight into the origins of the behavior of materials. Among all the semiempirical methods, parachor is the simplest. The parachor is defined as the following equation[15]

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

where M is the molar mass, γ is the surface tension, and ρ is the density. As a first approximation, parachor amounts to the sum of the contributions of the various components of the molecule. Although the estimated results cannot be regarded as accurate data, it is helpful in the synthesis of ionic liquids with special properties.

In this paper, an AAIL, [C_2mim][Val] (1-ethyl-3-methylimidazolium valine), was synthesized and characterized. To avoid the influence of trace water in the IL, in terms of the standard addition method (SAM), the density, surface tension, and refractive index for [C_2mim][Val] were measured in the temperature range from 303.15 to 333.15 ± 0.05, 303.15 to 338.15 ± 0.05, and 308.15 to 328.15 ± 0.05 K, respectively. On the basis of parachor and molar volume for [C_2mim][Val], the molecular volume, V_m, surface tension, γ, molar enthalpy of vaporization, $\Delta_l^g H_m°$, refractive index, n_D, thermal expansion coefficients, α, standard molar entropy, $S°$, and molar polarization, R_m, for the homologue of [$C_n$mim][Val] (n = 2, 3, 4, 5, 6) were estimated using semiempirical methods.

2. EXPERIMENTAL SECTION AND RESULTS

2.1. Chemicals and Instruments. Deionized water was distilled, and its conductance was 0.8−1.2 × 10^{-4} S·m^{-1}. *N*-Methylimidazole (AR-grade reagent), 1-bromoethane (AR-grade reagent), ethyl acetate, and acetonitrile were distilled prior to use. Valine was purchased from Hefeibomei Biotechnology Co. Ltd. with 99% purity. Anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent Co. Ltd. and activated by regular method before use.

The densities were measured by a DMA 4500 Density Meter (Anton Paar Co.). The surface tension was measured by a tensionmeter of the forced bubble method (DPAW type produced by Sang Li Electronic Co.). The refractive indices were measured by a WZS-1 Abbe refractometer (Shanghai Optics Instrument Co.). All instruments were calibrated by standard methods before measurements.

2.2. Synthesis of an AAIL [C_2mim][Val]. [C_2mim]Br (1-ethyl-3-methyl-imidazolium bromide) was synthesized according to the literature.[18,19] Then the sample was characterized by ^{1}H NMR, and the the content of water was also determined by a Karl Fischer moisture titrator (ZSD-2 type). The ^{1}H NMR spectrum confirmed the structure of [C_2mim][Val].

2.3. Determination of density of [C_2mim][Val]. Since the AAIL [C_2mim][Val] has a strong hydrogen-bonding ability, the small amount of water in the IL is difficult to be removed by common methods; so, trace water becomes the most problematic impurity. In order to eliminate the effect of the water impurity, the SAM was applied to the measurements. According to SAM, a series of samples of water-containing [C_2mim][Val] were prepared.

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Table 1. Values of the Density, ρ/g·cm^{-3} of IL [C_2mim][Val] Containing Various Known Amounts of Water in the Temperature Range from 303.15 to 333.15 K ($10^3 w_2$)[a]

T/K	7.80	9.97	11.01	12.98	15.49	0	r	$s \times 10^4$
298.15						1.11259*		
303.15	1.11368	1.11471	1.11515	1.11611	1.11751	1.10976	0.997	0.81
308.15	1.11041	1.11145	1.11186	1.11296	1.11423	1.10647	0.998	0.69
313.15	1.10702	1.10804	1.10849	1.10953	1.11091	1.10300	0.997	0.78
318.15	1.10399	1.10497	1.10543	1.10630	1.10769	1.10021	0.996	0.88
323.15	1.10094	1.10193	1.10239	1.10325	1.10464	1.09717	0.996	0.86
328.15	1.09791	1.09889	1.09936	1.10018	1.10149	1.09429	0.998	0.66
333.15	1.09486	1.09584	1.09634	1.09710	1.09843	1.09127	0.997	0.79

[a] w_2 is the water content, r are correlation coefficients, and s are standard deviations. The asterisk (*) indicates an estimated value.

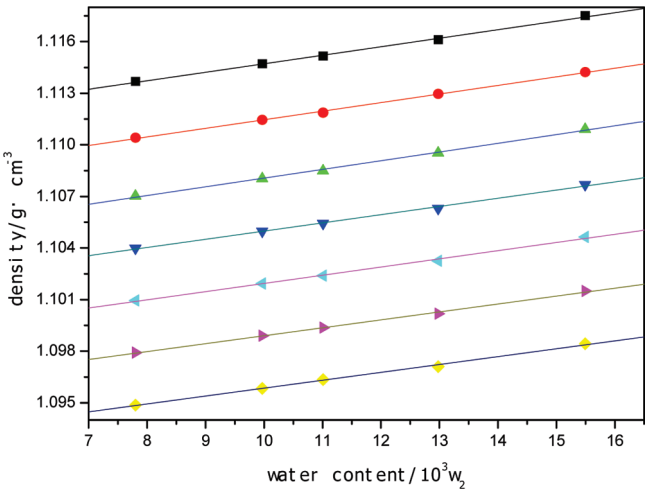

Figure 1. Plot of density vs the amount of water in [C_2mim][Val] in the temperature range from 303.15 to 333.15 K. (Black squares) 303.15 K: $\rho = 1.10976 - 4.95211 \times 10^{-4} w_2$, $s = 0.81 \times 10^{-4}$, $r = 0.997$. (Red circles) 308.15 K: $\rho = 1.10647 - 4.99203 \times 10^{-4} w_2$, $s = 0.69 \times 10^{-4}$, $r = 0.998$. (Green triangles pointing up) 313.15 K: $\rho = 1.10300 - 5.06256 \times 10^{-4} w_2$, $s = 0.78 \times 10^{-4}$, $r = 0.997$. (Blue triangles pointing down) 318.15 K: $\rho = 1.10021 - 4.77125 \times 10^{-4} w_2$, $s = 0.88 \times 10^{-4}$, $r = 0.996$. (Light blue triangles pointing left) 323.15 K: $\rho = 1.09717 - 4.76566 \times 10^{-4} w_2$, $s = 0.86 \times 10^{-4}$, $r = 0.996$. (purple triangles pointing left) 328.15 K: $\rho = 1.09429 - 4.61110 \times 10^{-4} w_2$, $s = 0.66 \times 10^{-4}$, $r = 0.998$. (Yellow triangles pointing right) 333.15 K: $\rho = 1.09127 - 4.58215 \times 10^{-4} w_2$, $s = 0.79 \times 10^{-4}$, $r = 0.997$.

The densities for a series of samples were measured in the temperature range from 303.15 to 333.15 K. The results are listed in Table 1. Each value of the density in Table 1 was the average of three measurements. A good straight line was obtained (see Figure 1) through plotting the values of the densities against the water content in the IL. It is clear that SAM has good applicability. From the intercepts of these straight lines, the values of the densities for IL [C_2mim][Val] without water were obtained at different temperatures and are listed in Table 1. The values of the standard deviation and correlation coefficient for the fitting are also shown in Table 1.

2.4. Determination of the Surface Tension of [C_2mim][Val]. In the temperature range from 303.15 to 338.15 K, the values of the surface tension for the samples were measured and are listed in Table 2. Each value in Table 2 was the average of three measurements. A good straight line was obtained (see Figure 2) through plotting values of the surface tension against

Table 2. Values of the Surface Tension, γ/mJ·m^2, of IL [C_2mim][Val] Containing Various Known Amounts of Water in the Temperature Range from 303.15 to 338.15 K ($10^3 w_2$)[a]

T/K	7.80	9.70	11.10	12.50	14.00	0	r	$s \times 10^2$
298.15						39.1*		
303.15	42.9	44.0	44.7	45.4	46.2	38.8	0.99	4.3
308.15	42.6	43.5	44.2	45.0	45.8	38.5	0.99	5.4
313.15	42.2	43.2	43.8	44.6	45.5	38.1	0.99	8.0
318.15	41.8	42.8	43.5	44.2	45.0	37.8	0.99	1.6
328.15	41.2	42.2	42.9	43.6	44.4	37.2	0.99	1.6
333.15	40.8	41.8	42.5	43.2	44.0	36.8	0.99	1.6
338.15	40.5	41.5	42.2	42.9	43.7	36.5	0.99	1.6

[a] w_2 is the water content, r are correlation coefficients, and s are standard deviations. The asterisk (*) indicates an estimated value.

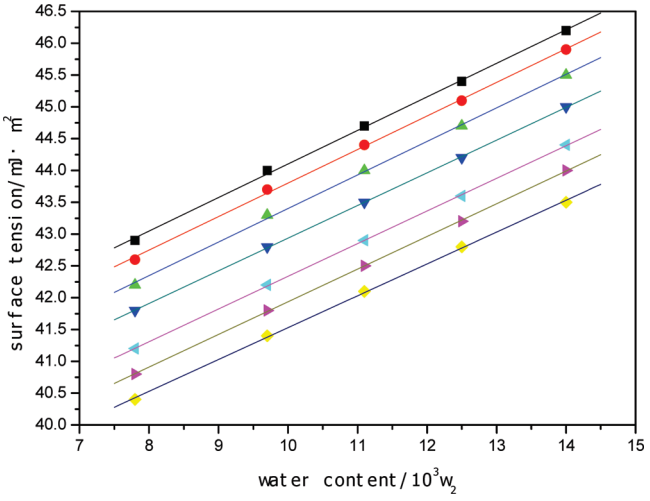

Figure 2. Plot of the surface tension vs the amount of water in [C_2mim][Val] in the temperature range from 303.15 to 338.15 K. (Black squares) 303.15 K: $\gamma = 38.8 - 5.2726 \times 10^{-4} w_2$, $s = 0.043$, $r = 0.99$. (Red circles) 308.15 K: $\gamma = 38.5 - 5.1872 \times 10^{-4} w_2$, $s = 0.054$, $r = 0.99$. (Green triangles pointing up) 313.15 K: $\gamma = 38.1 - 5.2588 \times 10^{-4} w_2$, $s = 0.080$, $r = 0.99$. (Blue triangles pointing down) 318.15 K: $\gamma = 37.8 - 5.1337 \times 10^{-4} w_2$, $s = 0.016$, $r = 0.99$. (Light blue triangles pointing left) 328.15 K: $\gamma = 37.2 - 5.1337 \times 10^{-4} w_2$, $s = 0.016$, $r = 0.99$. (Purple triangles pointing right) 333.15 K: $\gamma = 36.8 - 5.1337 \times 10^{-4} w_2$, $s = 0.016$, $r = 0.99$. (Yellow triangles pointing right) 338.15 K: $\gamma = 36.5 - 5.1337 \times 10^{-4} w_2$, $s = 0.016$, $r = 0.99$.

the water content. It is clear that SAM has good applicability. From the intercepts of these straight lines, the values of the

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Table 3. Values of the Refractive Index of IL [C_2mim][Val] Containing Various Amounts of Water in the Temperature Range from 308.15 to 328.15 K ($10^3 w_2$)[a]

T/K	7.60	9.20	11.8	13.6	15.4	0	r	$s \times 10^5$	R_m
298.15						1.4940*			59.49*
308.15	1.4920	1.4921	1.4923	1.4925	1.4926	1.4913	0.99	2.7	59.54
313.15	1.4909	1.4911	1.4913	1.4915	1.4917	1.4901	0.99	2.6	59.57
318.15	1.4897	1.4898	1.4901	1.4903	1.4905	1.4888	0.99	3.4	59.60
323.15	1.4883	1.4885	1.4887	1.4889	1.4891	1.4875	0.99	2.6	59.63
328.15	1.4869	1.4871	1.4873	1.4875	1.4877	1.4861	0.99	2.6	59.65

[a] w_2 is the water content, r are correlation coefficients, and s are standard deviations. The asterisk (*) indicates an estimated value.

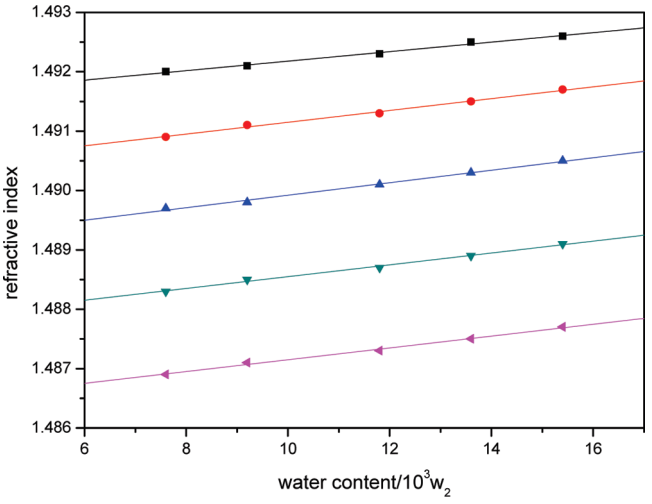

Figure 3. Plot of the refractive index vs the amount of water in [C_2mim][Val] in the temperature range from 308.15 to 328.15 K. (Black squares) 308.15 K: $n_D = 1.4913 + 8.00836 \times 10^{-5} w_2$, $s = 2.7 \times 10^{-5}$, $r = 0.99$. (Red circles) 313.15 K: $n_D = 1.4901 + 9.94827 \times 10^{-5} w_2$, $s = 2.6 \times 10^{-5}$, $r = 0.99$. (Blue triangles pointing up) 318.15 K: $n_D = 1.4888 + 1.05253 \times 10^{-4} w_2$, $s = 3.4 \times 10^{-5}$, $r = 0.99$. (Green triangles pointing down) 323.15 K: $n_D = 1.4875 + 9.94827 \times 10^{-5} w_2$, $s = 2.6 \times 10^{-5}$, $r = 0.99$. (Purple triangles pointing left) 333.15 K: $n_D = 1.4861 + 9.94827 \times 10^{-5} w_2$, $s = 2.6 \times 10^{-5}$, $r = 0.99$.

surface tension for [C_2mim][Val] without water were obtained and are listed in Table 2. The values of the standard deviation and correlation coefficient for the fitting are also listed in Table 2.

2.5. Determination of the Refractive Index of [C_2mim][Val]. The values of the refractive index of samples for [C_2mim][Val] with known different water contents were determined in the temperature range from 308.15 to 328.15 ± 0.05 K (see Table 3). A good straight line was obtained (see Figure 3) through plotting the values of the refractive index against the water content, and it is clear that the standard addition method has good applicability. The values of the refractive index for [C_2mim][Val] without water were obtained from the intercepts of these straight lines, and the results are listed in Table 3. The values of the correlation coefficient and standard deviation for the fitting are shown in Table 3.

3. DISCUSSION

3.1. Estimation of the Volumetric Properties of [$C_n$mim][Val]. First, the experimental values of ln ρ of IL [C_2mim][Val] without water against $T - 298.15$ were fitted,

Table 4. Predicted Volumetric Properties of the Homologous Series [$C_n$mim][Val] (n = 2, 3, 4, 5, 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][Val][a]	1.11254	0.3393	452.4	204.3265	440.2
[C_3mim][Val]	1.09167	0.3671	487.1	221.0676	431.5
[C_4mim][Val]	1.07380	0.3949	521.7	237.8088	423.6
[C_5mim][Val]	1.05828	0.4227	556.4	254.5499	416.4
[C_6mim][Val]	1.04467	0.4505	591.0	271.2911	409.8

[a] Experimental value.

and an empirical equation was obtained

$$\ln \rho = 0.1067 - 5.56 \times 10^{-4}(T - 298.15) \quad (2)$$

The correlation coefficient of the fitting is 0.998. The values of the densities for IL [C_2mim][Val] at 298.15 K can be obtained from the intercepts of the empirical equation. According to the definition of the thermal expansion coefficients, $\alpha = -(\partial \ln \rho / \partial T)_p$, where V is the molar volume and ρ is the density, the negative slope of the empirical equation is the coefficient of thermal expansion, that is, $\alpha = 5.6 \times 10^{-4}$ K^{-1} for [C_2mim][Val].

The molecular volume, V_m, of [C_2mim][Val] was calculated using following equation[20]

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

where M is the molar mass, N is the Avogadro constant, and V_m = 0.3393 nm^3 for [C_2mim][Val].

According to our previous research on alanine IL homologue [$C_n$mim][Ala],[21] the contribution per methylene ($-CH_2-$) to the volume may be a constant, so we can use the mean value, 0.0278 nm^3, to predict the molecular volume and density of other ILs of the homologue of [$C_n$mim][Val] (n = 2, 3, 4, 5, 6). The predicted results are listed in Table 4.

According to Glasser's theory,[20,22] the lattice energy, U_{POT}, and the standard molar entropy, $S°$, for IL may be estimated using the following equations

$$U_{POT}/\text{kJ·mol}^{-1} = 1981.2(\rho/M)^{1/3} + 103.8 \quad (4)$$

and

$$S^0(298)/\text{J·K}^{-1}\text{·mol}^{-1} = 1246.5(V_m/\text{nm}^3) + 29.5 \quad (5)$$

The predicted results for [$C_n$mim][Val] (n = 2, 3, 4, 5, 6) are also shown in Table 4. From Table 4, the biggest value of U_{POT} for [C_2mim][Val], U_{POT} = 440.2 kJ·mol^{-1}, is much less than that of CsI[23] (U_{POT} = 613 kJ·mol^{-1}), which is the lowest lattice energy

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Table 5. Predicted Values of the Surface Tension, γ, Parachor, P, Molar Enthalpy of Vaporization, $\Delta_l^g H_m^\circ$(298.15 K), Refractive Index, n_D, and Thermal Expansion Coefficient, α, of the Homologous Series [$C_n$mim][Val] (n = 2, 3, 4, 5, 6)

ionic lquid	P	P'(1%)	ΔP	$\gamma/10^3$ N·m^{-1}	$\Delta_l^g H_m^0$/kJ·mol^{-1}	10^4 α/K^{-1}(cald)	n_D	R_m	$10^{24}\alpha_p$
[C_2mim][Val][a]	510.9	535.54	−24.64	39.1	130.8	6.05	1.4941	59.49	23.60
[C_3mim][Val]	548.4	575.44	−27.04	37.8	133.2	5.90	1.4916	64.09	25.42
[C_4mim][Val]	585.9	615.34	−29.44	36.9	136.5	5.71	1.4895	68.69	27.24
[C_5mim][Val]	623.4	651.24	−27.84	36.0	139.3	5.56	1.4876	73.29	29.07
[C_6mim][Val]	660.9	695.14	−34.24	35.2	142.0	5.41	1.4860	77.89	30.89

[a] Experimental value.

among the alkali halides. The low lattice energy is a major reason for forming an ionic liquid at room temperature.

3.2. Estimation of the Parachors and Surface Tension of [$C_n$mim][Val]. According to the surface tension (γ) and density (ρ), the experimental parachor [C_2mim][Val] was obtained, P = 510.9, from eq 1, which is a remarkably useful tool to predict the physicochemical properties of ILs.[15]

We found that the contribution of per methylene to parachor is 37.5 obtained in our previous paper.[21] As a first approximation, parachor is the sum of the contribution of the various components of molecule. Considering that each methylene (−CH_2−) group has almost the same chemical environment in the alkyl chains of the imidazolum-based ionic liquids, we proposed a semiempirical method of predicting P of the IL homologue[21] that is the sum of an experimental value of [C_2mim][Val] and contributions of methylene (−CH_2−). The values of parachor for the homologue of ILs [$C_n$mim][Val] (n = 2, 3, 4, 5, 6) can be estimated from (510.9 + 37.5n), where n is the number of methylenes (−CH_2−). Meanwhile, we predicted parachor P'(1%) using the neutral contribution to parachor, where (1%) means that the allowable error of the training set is set at <1%. All predicted values for the homologue are listed in Table 5. In Table 5, $\Delta P = P - P'(1\%) = -24.64$ for [C_2mim][Val], meaning that comparing the experimental parachor value with that predicted using neutral parachor contribution values, the relative deviation, E%, is larger than 4.8% (E% = [experimental value − neutral calculated value]/experimental value). The larger error implies that the Coulombic interaction cannot be ignored when calculating parachors using neutral contribution data.

3.3. Estimation of the Vaporization Enthalpies and Vapor Pressure of [$C_n$mim][Val]. Rebelo et al.[24] thought that the molar enthalpy of vaporization for the ILs could be estimated by the hypothetical normal boiling point (NBP) of ionic liquids, T_b, and the Trouton constant (~90 J·mol^{-1}·K^{-1}). The relationship between T_b and T_c is $T_b \approx 0.6T_c$ for ionic liquids. The critical temperature of the ILs, T_c, was estimated using the Eötvös equation[25]

$$\gamma V^{2/3} = k(T_c - T) \quad (6)$$

where k is an empirical constant and V is the molar volume. Plotting $\gamma V^{2/3}$ against the absolute temperature T, the values of k and T_c were obtained. From T_c = 893 K, the NBP of ionic liquid [C_2mim][Val] was obtained, T_b = 536 K. Then the predicted value of $\Delta_l^g H_m^\circ$ (T_b) was also calculated, $\Delta_l^g H_m^\circ$ = 48.2 kJ·mol^{-1}.

According Kabo's empirical equation,[26] the molar enthalpy of vaporization, $\Delta_l^g H_m^\circ$ (298 K), of ionic liquids can be estimated as

$$\Delta_l^g H_m^0(298\ \mathrm{K}) = 0.01121(\gamma V^{2/3} N^{1/3}) + 2.4\ \mathrm{kJ\cdot mol^{-1}} \quad (7)$$

Table 6. Predicted Values of $\Delta_l^g H_m^\circ$ and p of Ionic Liquids [C_2mim][Val] at Various Temperatures

T/K	500	450	400	350	300
$\Delta_l^g H_m^\circ$/kJ·mol^{-1}	60.7	78.1	95.4	112.8	130.2
p/ kPa	82.60	28.08	2.77	4.58×10^{-2}	5.26×10^{-5}

where γ is the surface tension, V is the molar volume, and N is Avogadro's constant. The values of the molar enthalpy of vaporization, $\Delta_l^g H_m^\circ$ (298 K), for [$C_n$mim][Val] were calculated by the estimated values of V and γ from eq 7 and are listed in Table 5.

From Table 5, $\Delta_l^g H_m^\circ$ (298 K) estimated by Kabo is very different from $\Delta_l^g H_m^\circ$ (T_b) estimated by Rebelo. This is because the heat capacity is different between the liquid and the gas phases at different temperatures. We assume a linear change of $\Delta_l^g H_m^\circ$ with temperature in the range from 298 K to T_b; the vapor pressure, p, of the ILs at various temperatures can be estimated using the Clapeyron−Clausius equation

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

where R is the gas constant.

The estimated values of $\Delta_l^g H_m^\circ$ and p of [C_2mim][Val] at various temperatures are shown in Table 6. Figure 4 shows the plot of $\Delta_l^g H_m^\circ$ and p of the IL against temperature, T. It shows that the vapor pressure is very small, which is only 10^{-5} Pa at 298 K. This is consistent with our experience on ILs.

3.4. Estimation of the Thermal Expansion Coefficient of [$C_n$mim][Val]. The thermal expansion coefficient of ILs [$C_n$mim][Val] can be predicted using estimated values of the density and surface tension. An expression for calculation of thw interstice volume, v, was obtained according to the interstice model[27,28] by classical statistical mechanics

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

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

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

If the inherent volume of ILs is constant while interstices expand when temperature increases, then calculation of the thermal expansion coefficients, α, was derived from the interstice model

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

The values of α(cald) for ILs [$C_n$mim][Val] were calculated using eq 11 and are listed in Table 5. As seen from the table, the corresponding experimental value, α(exp) = 5.6×10^{-4} K^{-1}, for [C_2mim][Val] is in good agreement with the calculated value,

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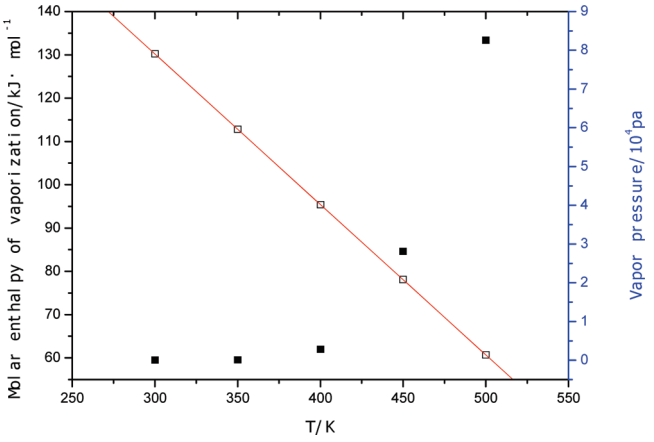

Figure 4. Plot of the vapor pressure, p, and $\Delta_l^g H_m^\circ$ of the IL [C_2mim]-[Val] vs temperature T: (■) vapor pressure, (□) molar enthalpy of vaporization, $\Delta_l^g H_m^\circ$.

α(cald) = 6.05 × 10^{-4} K^{-1}. The results show the rationality of estimation of the thermal expansion coefficient.

3.5. Estimation of the Molar Polarization and Refractive Index of [C$_n$mim][Val]. According to the Lorentz−Lorenz equation, the molar polarization, R_m, of ILs was defined by the following equation[29]

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

where n_D is the refractive index and α_p is the polarization coefficient. According to eq 12, values of the molar polarization were obtained and are shown in Table 3.

Fitting the R_m of [C_2mim][Val] without water against T − 298.15, an empirical equation, R_m = 59.49 + 0.0056(T − 298.15), was obtained with a correlation coefficient of 0.993 and standard deviation of 0.0037. The intercept of the empirical equation is the molar polarization at 298.15 K, R_m = 59.49. Also, α_p=23.60 × 10^{-24} for [C_2mim][Val] was obtained.

Considering that each methylene (−CH_2−) group in the alkyl chains of the imidazolum-based ionic liquids has almost the same chemical environment, we put forward a semiempirical method of predicting R_m of the ILs homologue [C$_n$mim]-[Val]. The contribution of each methylene to the molar polarization is 4.60, as obtained in our previous paper.[30] The polarization coefficient was also estimated. All results are listed in Table 5.

Substitution of eq 1 into eq 12 and rearrangement yields[15]

$$\gamma^{1/4} = (P/R_m)[(n_D^2 - 1)/(n_D^2 + 2)] \quad (13)$$

In terms of eq 13, the refractive index of IL homologue [C$_n$mim][Val] (n = 2, 3, 4, 5, 6) could be predicted using the values of the above estimated surface tension, parachor, and molar polarization. The estimated values of n_D are also shown in Table 5. When comparing the predicted values of the refractive index for [C_2mim][Val], n_D =1.4941, with the experimental one, 1.4940, obtained by extrapolation, the values were close. The result indicates that our semiempirical method is reasonable.

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GLOSSARY

^{1}H NMR = nuclear magnetic resonance
$\Delta_l^g H_m^\circ$ = molar enthalpy of vaporization
k = empirical constant in the Eötvös equation
k_b = Boltzmann constant
M = molar mass
N = Avogadro constant
n_D = refractive index
P = parachor
R_m = molar polarization
S^0 = standard molar entropy
SAM = standard addition method
T = absolute temperature
T_c = critical temperature
T_b = hypothetical temperature
T_g = glass transition temperature
U_{POT} = lattice energy
V = interstice volume
v_i = inherent volume
V_m = molecular volume

GREEK LETTERS

α = thermal expansion coefficients
α_p = polarization coefficient
γ = surface tension
ρ = density

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