Ionic Parachor and Its Application II. Ionic Liquid Homologues of 1-Alkyl-3-methylimidazolium Propionate { $[C_n mim][Pro]$ (n = 2-6)}

Jing Tong,* Xue Ma, Yu-Xia Kong, Yan Chen, Wei Guan, and Jia-Zhen Yang

Key Laboratory of Green Synthesis and Preparative Chemistry of Advanced Materials, Liaoning University, Shenyang 110036, China

Supporting Information

ABSTRACT: Five propionic acid ionic liquids (PrAILs) $[C_n \min][Pro]$ (n = 2-6) (1-alkyl-3-methylimidazolium propionate) have been prepared by the neutralization method and characterized by ¹H NMR spectroscopy and differential scanning calorimetry (DSC). Their density, ρ , surface tension, γ , and refractive index, n_D , were measured at (298.15 ± 0.05) K, and the experimental values of parachor for the PrAILs were calculated. Using the parachor values of $[C_n \min]^+$ obtained by Guan et al., the anionic parachor values of $[C_n \min][Pro]$ (n = 2-6), $[C_2 \min][RBF_3]$ ($R = N-C_nH_{2n+1}$ (n = 1-5)), $[C_n \min][Gly]$ (n = 2-6), and $[C_n \min][PF_3(CF_2CF_3)_3]$ (n = 1-6) were determined. Then, the parachor, surface tension, and refractive index of the ILs investigated in this work were estimated. The estimated values correlate quite well with the corresponding experimental values.



1. INTRODUCTION

In the past few decades, interest in ionic liquids (ILs) has increased dramatically,^{1,2} especially because carboxylic acid ionic liquids (CAILs) were successfully synthesized from natural carboxylic acids. CAILs have attracted considerable attention from industry and the academic community as new-generation "greener ionic liquids".^{3–6} CAILs are useful for an enzyme-"friendly" cosolvent for resolution of amino acids,³ ultrasonic irradiation toward synthesis of trisubstituted imidazoles,⁴ assisted transdermal delivery of sparingly soluble drugs,⁵ and some catalytic reactions.⁶ Among CAILs, propionic acid ionic liquids (PrAILs) are the important ones.

In recent years, there has been a developing trend in the literature toward the estimation of the physicochemical properties for ILs by semiempirical methods.⁷⁻⁹ Although these estimated results cannot be regarded as accurate physicochemical data, this approach is recommended because it provides valuable insight into the behavior of materials. Among all of the semiempirical methods, parachor is the simplest.^{7,10–13} The parachor, *P*, is a relatively old concept that is available as a link between the structure, density, and surface tension of the liquids. However, the vast majority of parachor studies have focused on the uncharged compounds.^{14,15} The parachor data obtained from the neutral molecule are difficult to be applied to an IL because there is no consideration of the Coulomb force between ions. Although a number of early studies attempted to determine the parachor values for ions, these studies were hampered by experimental difficulties encountered in determining the surface tensions and densities of high melting salts, and no other related investigations followed.⁹ However, because numerous ILs are fluid at room temperature, they offer a solution to determine the experimental parachor of ionic compounds. Therefore, the ionic parachor has been proposed as a new concept,¹⁶ that is, ions composed of ILs can be seen as independent descriptors of parachor. The ionic parachor, $P_{i\nu}$ can be defined by the following equation

$$P_{\rm i} = \gamma^{1/4} V_{\rm i} \tag{1}$$

where V_i is the molar volume of an ion in an IL. According to the additivity principle, the parachor value of an IL is equal to the sum of ionic parachors of the corresponding cation and anion

$$P = P_+ + P_- \tag{2}$$

where P_+ and P_- are the ionic parachor of the cation and anion, respectively. Now, the key question is how the experimental value of the parachor for an IL can be divided into the corresponding values for the cation and anion. Guan et al.¹⁶ recommended two extrathermodynamic assumptions for the evaluation of an individual ionic parachor. The first of them is the extrapolation method. For example, for the acetic acid ionic liquid homologues of 1-alkyl-3-methylimidazolium acetate ([C_n mim][OAc] (n = 2-6)), according to eq 3

$$P = P_{-} + (M_{+}\gamma^{1/4})/\rho \tag{3}$$

when the molar mass of the cation, M_+ , approaches zero, the ionic parachor of the anion, P_- , could be obtained. The second extrathermodynamic assumption was proposed as eq 4, that is, the volume ratio of the cation and anion the in crystal equals their volume ratio in the IL or their parachor ratio

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$$V_{-}(\text{Crystal})/V_{+}(\text{Crystal}) = V_{m-}(\text{IL})/[V_{m} - V_{m-}(\text{IL})] = P_{-}(\text{IL})/[P - P_{-}(\text{IL})]$$
(4)

where $V_{+}(Crystal)$ and $V_{-}(Crystal)$ are the corresponding cationic and anionic volumes derived from crystal structures and can be obtained from the literature; $V_{\rm m-}({\rm IL})$ is the ionic volume of the corresponding anion in an IL, V_m is the molecular volume of the IL, $P_{-}(IL)$ is the ionic parachor of the corresponding anion, and P is the experimental value of the parachor for the IL. Guan et al. used [OAc]⁻ as the reference ion, the reference value of $P_{-} = 83.9$, which is the average of that obtained from two extrathermodynamic assumptions, and then, the values of the ionic parachor for all corresponding imidazolium cations, $[C_n mim]^+$, were obtained. However, we believe that the second extrathermodynamic assumption is more reliable than the extrapolation. Because the measured range of the molar mass of the cation is about 56 (from about 167.2 to 111.2) and the results are extrapolated to zero (further from 111.2), this extrapolation may have some uncertainty.

In order to use the new experimental data to prove the reliability and authenticity of the second assumption proposed by Guan et al., in this paper, we report that (1) PrAILs $[C_n \min]$ [Pro] (*n* = 2-6) (1-alkyl-3-methylimidazolium propionate) have been prepared by the neutralization method. (2) The density, surface tension, and refractive index for the PrAILs were measured at (298.15 ± 0.05) K. Because the PrAIL molecules can form strong hydrogen bonds with water molecules, which is thus a problematic impurity, the standard addition method (SAM) was applied in these measurements. (3) Using the parachor values of $[C_n \min]^+$ obtained by Guan et al.,¹⁶ the anionic parachor values of $[C_n mim][Pro]$ (n = 2 - 1)6), $[C_2 \min][RBF_3]$ (R = N-C_nH_{2n+1} (n = 1-5)), $[C_n \min]$ -[Gly] (n = 2-6), and $[C_n \text{mim}][PF_3(CF_2CF_3)_3]$ (n = 1-6)were determined. (4) Finally, in terms of the ionic parachor data, the parachor, surface tension, and refractive index $n_{\rm D}$ of the investigated ILs were estimated.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Deionized water was distilled in a quartz still, and its conductance was $(0.8-1.2) \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$. Anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent Co. Ltd. and activated by the regular method before use. Propionic acid was distilled and dried under reduced pressure. *N*-Methylimidazole (AR-grade reagent) was vacuum-distilled prior to use. 1-Bromoethane, 1-bromopropane, 1-bromobutane, 1-bromopentane, and 1-bromohexane (AR-grade reagent) were distilled before use. Ethyl acetate and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles.

2.2. Preparation of the PrAILs. The PrAILs $[C_n mim]$ -[Pro] (n = 2-6) have been prepared by a neutralization method according to Fukumoto et al.¹⁸ Figure 1 is a schematic



Figure 1. Preparation of PrAILs by the neutralization method. 1, $[C_n mim][Br]; 2, [C_n mim][OH]; 3, [C_n mim][Pro].$

of this synthetic route. First, $[C_n \min]$ Br (n = 2-6) were synthesized according to the literature.^{19,20} Then, aqueous 1alkyl-3-methylimidazolium hydroxides ($[C_nmim][OH]$ (n = 2-6)) were prepared from $[C_n \min]$ Br (n = 2-6) by use of an activated anion-exchange resin in a 100 cm column. However, $[C_n \min][OH]$ (*n* = 2–6) are not particularly stable, and they should be used immediately after preparation. These hydroxidecontaining aqueous solutions were added dropwise to a slightly excess of propionic acid in the aqueous solution. The mixture was stirred with cooling for 48 h. Then water was evaporated under reduced pressure at 40-50 °C. To this reaction mixture was added, a mixed solvent of acetonitrile/methanol (volumetric ratio =9/1), and the mixture was stirred vigorously. The mixture was then evaporated under reduced pressure to remove slightly excess propionic acid and solvents. The products of $[C_n \min]$ [Pro] (n = 2-6) were dried in vacuo for 2 days at 80 °C. The structures of the resulting PrAILs were confirmed by ¹H NMR spectroscopy (see the figures in section A in the Supporting Information).

Differential scanning calorimetric (DSC) measurements showed that $[C_n \text{mim}][\text{Pro}]$ (n = 2-6) have no obvious melting point and are given in the figures in section B in the Supporting Information. The water contents (w_2 is the water mass fraction, $w_2 = (8.10 \pm 0.01) \times 10^{-3}$, $(8.30 \pm 0.01) \times 10^{-3}$, $(8.10 \pm 0.01) \times 10^{-3}$, $(8.20 \pm 0.01) \times 10^{-3}$, and $(8.10 \pm 0.01) \times 10^{-3}$ mass fraction, respectively) in the ILs $[C_n \text{mim}][\text{Pro}]$ (n = 2-6) were determined by use of a Karl Fischer moisture titrator (ZSD-2 type).

2.3. Determination of the Density and Surface Tension of the PrAILs. Because the PrAILs can form strong hydrogen bonds with water molecules, small amounts of water in the PrAILs are difficult to remove by conventional methods, and it becomes the most problematic impurity. In order to eliminate the effect of the impurity water, SAM was applied to these measurements. According to the SAM, a series of samples of $[C_n \min][Pro]$ (n = 2-6) with different water contents were prepared.

The density of degassed water was measured on a Westphal balance at (298.15 \pm 0.05) K and was in good agreement with the literature²¹ within an experimental error of \pm 0.0002 g·cm⁻³. Then, the densities of the samples were measured at (298.15 \pm 0.05) K. The sample was placed in a cell with a jacket and was thermostatted with an accuracy of \pm 0.05 K.

By using the tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.), the surface tension of water was measured at (298.15 \pm 0.05) K and was in good agreement with the literature²¹ within an experimental error of \pm 0.1 mJ·m⁻². Then, the values of surface tension of the samples were measured by the same method at (298.15 \pm 0.05) K.

2.4. Determination of the Refractive Index of the **PrAILs**. The refractive index, n_D , of the PrAILs was measured by an Abbe refractometer. First, the refractive index of the degassed water was measured by the instrument at (298.15 ± 0.05) K and was in good agreement with the literature²¹ within an experimental error of ±0.0001. Then, the refractive index of a series of samples, which were prepared by the SAM, was measured at 298.15 K with an accuracy of ±0.05 K.

3. RESULTS AND DISCUSSION

3.1. Values of Density, Surface Tension, and **Refractive Index for the Samples.** The measured values of the density, surface tension, and refractive index for the

Table 1. Values of the Density (ρ /g·cm⁻³), Surface Tension (γ /mJ·m⁻²), and Refractive Index for [C_nmim][Pro] (n = 2-6) Containing Various Amounts of Water at 298.15 K^a

$[C_2 \min][Pro]$										
$10^{3}w_{2}$	8.60	12.1	14.5	16.7	18.6	0	r^2	$s \times 10^5$		
$ ho/\text{g}\cdot\text{cm}^{-3}$	1.1926	1.1937	1.1945	1.1951	1.1957	1.1900	0.999	3.8		
$10^{3}w_{2}$	8.30	10.6	13.2	15.6	18.1	0	r^2	5		
$\gamma/mJ \cdot m^{-2}$	40.7	41.1	41.4	41.7	42.1	39.6	0.99	0.042		
$10^3 w_2$	8.70	11.2	14.2	17.3	19.8	0	r^2	$s \times 10^{5}$		
n _D	1.4882	1.4876	1.4871	1.4866	1.4862	1.4897	0.99	7.42		
[C ₃ mim][Pro]										
$10^3 w_2$	8.80	11.7	14.3	17.1	18.7	0	r^2	$s \times 10^5$		
$\rho/g \cdot cm^{-3}$	1.1575	1.1582	1.1589	1.1595	1.1599	1.1554	0.999	3.7		
$10^{3}w_{2}$	8.40	10.8	13.2	16.1	19.0	0	r^2	5		
$\gamma/mJ \cdot m^{-2}$	39.4	39.6	39.9	40.2	40.6	38.4	0.99	0.042		
$10^3 w_2$	8.80	11.3	14.0	17.0	19.6	0	r^2	$s \times 10^5$		
n _D	1.4871	1.4865	1.4860	1.4855	1.4851	1.4886	0.99	7.85		
				[C ₄ mim][Pro]						
$10^{3}w_{2}$	8.10	11.4	13.6	16.8	19.9	0	r^2	$s \times 10^5$		
$ ho/\text{g}\cdot\text{cm}^{-3}$	1.1300	1.1307	1.1313	1.1321	1.1329	1.1279	0.999	5.1		
$10^3 w_2$	8.90	11.6	14.7	17.4	19.6	0	r^2	5		
$\gamma/mJ \cdot m^{-2}$	38.0	38.3	38.6	38.9	39.2	37.0	0.99	0.030		
$10^3 w_2$	8.80	11.3	14.0	17.0	19.6	0	r^2	$s \times 10^{5}$		
$n_{\rm D}$	1.4847	1.4842	1.4838	1.4833	1.4828	1.4862	0.99	3.88		
				[C ₅ mim][Pro]						
$10^{3}w_{2}$	8.40	11.5	13.4	16.3	19.6	0	r^2	$s \times 10^5$		
$ ho/g\cdot cm^{-3}$	1.1059	1.1066	1.1071	1.1078	1.1087	1.1038	0.999	4.4		
$10^3 w_2$	8.20	10.3	12.6	15.4	17.5	0	r^2	5		
$\gamma/mJ \cdot m^{-2}$	36.9	37.2	37.6	38.0	38.2	35.7	0.99	0.053		
$10^3 w_2$	8.90	11.2	13.9	16.9	19.5	0	r^2	$s \times 10^5$		
n _D	1.4828	1.4824	1.4820	1.4815	1.4812	1.4841	0.99	4.47		
$[C_6 mim][Pro]$										
$10^{3}w_{2}$	8.30	11.1	13.7	16.9	19.7	0	r^2	$s \times 10^5$		
$ ho/g\cdot cm^{-3}$	1.0857	1.0865	1.0872	1.0880	1.0888	1.0835	0.999	3.2		
$10^3 w_2$	8.20	10.7	12.8	15.5	17.9	0	r^2	5		
$\gamma/mJ \cdot m^{-2}$	35.8	36.2	36.5	36.8	37.1	34.8	0.99	0.043		
$10^{3}w_{2}$	8.50	11.2	13.4	15.7	17.5	0	r^2	$s \times 10^5$		
$n_{\rm D}$	1.4816	1.4813	1.4810	1.4807	1.4804	1.4828	0.99	3.66		
w_2^{a} is the water content. r^2 is the correlation coefficient squared, and s is the standard deviation.										

samples of ILs $[C_n mim][Pro]$ (n = 2-6) containing various contents of water are listed in Table 1. Each value in the table is the average of three measurements. According to the SAM, the values of the density or surface tension or refractive index of the samples at a given temperature were plotted against the water content, w_2 (w_2 is the mass percentage), so that a series of good straight lines were obtained. The intercepts of the straight lines are the values of the density or surface tension or refractive index of $[C_n \min][Pro]$ (n = 2-6) without water and can be seen as the experimental values, which are included in the column where $w_2 = 0$ in Table 1. Figures C1–C3 in the Supporting Information are the plots of the density, surface tension, refractive index, respectively, against w_2 at (298.15 \pm 0.05) K. The square of the correlation coefficients, r^2 , of all linear regressions was larger than 0.99, and all values of standard deviation, s, were within the experimental error. These data show that use of the SAM is appropriate in this work.

3.2. Volumetric Properties of ILs $[C_n mim][Pro]$ (n = 2-6). If the liquid state was the reference, from the experimental values of the density, the molecular volumes (the sum of the volumes of the positive and negative ions), V_{m} , of $[C_n mim]$ -[Pro] (n = 2-6), were calculated from the following equation

$$V_{\rm m} = M/(N \cdot \rho) \tag{5}$$

where *M* is the molar mass and *N* is the Avogadro constant, so that $V_{\rm m}(n = 2-6) = 0.2572$, 0.2851, 0.3126, 0.3406, and 0.3685 nm³ for $[C_n \text{mim}][\text{Pro}]$ (n = 2-6) at 298.15 K. The average difference between molecular volumes of $[C_n \text{mim}][\text{Pro}]$ and $[C_{n-1}\text{mim}][\text{Pro}]$ is 0.0278 nm³, which can be seen as the contribution to the molecular volume of one methylene $(-\text{CH}_2-)$ group and was in good agreement with a mean contribution of 0.0272 nm³ per methylene $(-\text{CH}_2-)$ group obtained by Glasser²² from ILs $[C_n\text{mim}][\text{BF}_4]$. The values of the molecular volume, $V_{\rm m}$, are listed in Table 2.

According to Glasser's theory,²² the standard molar entropy for an IL, S^0 , is given by

$$S^{0}(298)/(J \cdot K^{-1} \cdot mol^{-1}) = 1246.5(V_{m}/nm^{3}) + 29.5$$
 (6)

The values of S^0 (J·K⁻¹·mol⁻¹) for [C_nmim][Pro] (n = 2-6) are listed in Table 2. These data imply that the entropy contribution per methylene group to the standard entropy for [C_nmim][Pro] is 34.7 J·K⁻¹·mol⁻¹, and this value is in good agreement with the values of 33.9 J·K⁻¹·mol⁻¹ for [C_nmim]-[BF₄] and 35.1 J·K⁻¹·mol⁻¹ for [C_nmim][NTf₂].²²

Table 2. Values of the Molecular Volume, Standard Molar Entropy, and Lattice Energy of the ILs at 298.15 K

ionic liquid	M/g·mol ⁻¹	$ ho/ m g\cdot cm^{-3}$	$V_{\rm m}/{\rm nm^3}$	$\begin{array}{c} S^0/\\ J{\cdot}K^{-1}{\cdot}mol^{-1} \end{array}$	$U_{ m pot}/kJ\cdot m mol^{-1}$
[C ₂ mim] [Pro]	184.24	1.1900	0.2572	350.1	473
[C ₃ mim] [Pro]	198.27	1.1554	0.2851	384.8	460
[C ₄ mim] [Pro]	212.29	1.1279	0.3126	419.2	450
[C ₅ mim] [Pro]	226.32	1.1038	0.3406	454.0	440
$\begin{bmatrix} C_6 mim \end{bmatrix} \\ \begin{bmatrix} Pro \end{bmatrix}$	240.35	1.0835	0.3685	488.8	431

The lattice energy, U_{pot} , in kJ·mol⁻¹, can be estimated from the following equation²²

$$U_{\rm POT}/\rm kJ \cdot mol^{-1} = 1981.2(\rho/M)^{1/3} + 103.8$$
 (7)

The estimated values of U_{pot} for $[C_n \text{mim}][\text{Pro}]$ are listed in Table 2. Recently, Krossing et al.²³ pointed out that eq 7, which was an old formulation, provides lattice enthalpies of 20–140 kJ·mol⁻¹ that are lower than the ones assessed by the Born– Fajans–Haber (BFH) cycle. Even taking into account this deviation, the lattice energy of ILs, $[C_n \text{mim}][\text{Pro}]$, is less than that of fused salts; for example, $U_{\text{pot}} = 613 \text{ kJ·mol}^{-1}$ for fused CsI,²¹ which is the lowest lattice energy among alkali halides. The lower lattice energy is an essential ingredient for ILs $[C_n \text{mim}][\text{Pro}]$, and the true driver for being liquid at these conditions is the difference between the entropy in the solid state and that in the liquid state.^{24,25} **3.3. Ionic Parachor.** According to the definition of the parachor

$$P = (M\gamma^{1/4})/\rho \tag{8}$$

where γ is the surface tension, *M* is the molar mass, and ρ is the density of a substance, the experimental values, P_{Exp} , of the parachor for the PrAILs are listed in Table 3. In terms of the values of $[C_n \text{mim}]^+$, P_+ , obtained by Guan et al.,¹⁶ the ionic parachor of the anion, P_- , can be determined by eq 2 and are listed in Table 3. From Table 3, the average of the ionic parachor for the anion $[\text{Pro}]^-$ is (109.1 ± 2.0). Similarly, using the parachor values of $[C_n \text{mim}]^+$, the values of P_- for $[C_2 \text{mim}][\text{RBF}_3]$ (R = *N*-C_nH_{2n+1} (*n* = 1–5)), $[C_n \text{mim}][\text{Gly}]$ (*n* = 2–6), and $[C_n \text{mim}][\text{PF}_3(\text{CF}_2\text{CF}_3)_3]$ (*n* = 1–6) were calculated and are listed in Table 3. From Table 3, it can be seen that the relative standard deviations of P_- for $[C_n \text{mim}]$.

For $[C_2\text{mim}][BF_4]$, the ionic volumes of the cation and anion in the crystal²⁷ are $V_+(\text{Crystal}) = 0.156 \text{ nm}^3$ and $V_-(\text{Crystal}) = 0.073 \text{ nm}^3$, respectively, so that according to the second extrathermodynamic assumption, $P_+ = 285.0$ and $P_- =$ 133.3 were obtained. In comparison with $P_+ = 283.1$ and $P_- =$ 135.2 in Table 3, the relative deviation is also less than 2%. These facts show that the second assumption proposed by Guan et al. is more credible.

3.4. Predicting Parachor and Surface Tension. Using parachor values of the above anions and $[C_n \text{mim}]^+$, estimated parachor values of the corresponding ILs, P_{Cab} can be obtained and are listed in Table 3. In Table 3, P_{Exp} is the experimental value. Figure 2 is a comparative plot of the estimated parachor values as a function of the corresponding experimental values

Table 3. Values of Ionic Parachor of the ILs According to the Second Extrathermodynamic Method

	$ ho/{ m g\cdot cm^{-3}}$	$\gamma/mJ \cdot m^{-2}$	$P_{\rm Exp}$	P_{+}^{a}	P_{-}^{b}	$P_{\rm Cal}$
[C ₂ mim] [Pro]	1.1900^{d}	39.6 ^d	388.4	283.1	105.3	392.2
[C ₃ mim] [Pro]	1.1554 ^d	38.4 ^d	427.2	319.0	108.2	428.1
$[C_4 mim]$ [Pro]	1.1279 ^d	37.0 ^d	464.2	355.0	109.2	464.1
[C ₅ mim] [Pro]	^d 1.1038	35.7 ^d	501.1	390.9	110.2	500.0
[C ₆ mim] [Pro]	1.0835 ^d	34.8 ^d	538.6	426.1	112.5	535.2
		P_{-}	of [Pro] ^{-c}		109.1 ± 2.0	
$[C_2 mim][CH_3 BF_3]$	1.1536 ^e	45.2 ^e	436.1	283.1	153.0	
$[C_2 mim][C_2 H_5 BF_3]$	1.1329^{e}	42.5 ^e	468.8	283.1	185.7	
$[C_2 mim][N-C_3H_7BF_3]$	1.1068 ^e	38.0 ^e	498.1	283.1	215.0	
$[C_2 mim][N-C_4H_9BF_3]$	1.0818^{e}	34.2 ^e	527.8	283.1	244.7	
$[C_2 mim][N-C_5H_{11}BF_3]$	1.0645 ^e	33.8 ^e	566.5	283.1	283.4	
$[C_2 mim][CH_2 CHBF_3]$	1.1614 ^e	44.3 ^e	457.6	283.1	174.5	
$[C_2 mim][BF_4]$	1.2853 ^e	54.4 ^e	418.3	283.1	135.2	
$[C_1 mim][PF_3(CF_2CF_3)_3]$	1.75552^{f}	36.3^{f}	758.0	252.6		
$[C_2 mim][PF_3(CF_2CF_3)_3]$	1.70 ^f 926	34.8 ^f	790.3	283.1	507.2	788.5
$[C_3 mim][PF_3(CF_2CF_3)_3]$	1.66756 ^f	34.1 ^{<i>f</i>}	826.3	319.0	507.3	824.4
$[C_4 mim][PF_3(CF_2CF_3)_3]$	1.62962^{f}	33.2^{f}	860.6	355.0	505.6	860.4
$[C_5 mim][PF_3(CF_2CF_3)_3]$	1.59516 ^f	32.4 ^f	894.8	390.9	503.9	896.3
$[C_6 mim][PF_3(CF_2CF_3)_3]$	1.56356 ^f	31.7 ^f	929.2	426.1	503.1	931.5
		505.4 ± 1.9				
$[C_2 mim][Gly]$	1.1589 ^g	48.1 ^g	420.9	283.1	137.8	421.2
$[C_3 mim][Gly]$	1.1358 ^h	45.6 ^h	455.9	319.0	136.9	457.1
$[C_4 mim][Gly]$	1.1109 ^h	43.5 ^h	493.1	355.0	138.1	493.1
[C ₅ mim][Gly]	1.0947 ^{<i>i</i>}	41.9 ^{<i>i</i>}	528.3	390.9	137.4	529.0
$[C_6 mim][Gly]$	1.0755 ^{<i>i</i>}	40.6 ^{<i>i</i>}	566.4	426.1	140.3	564.2
		\overline{P}	of $[Glv]^{-c}$		138.1 + 0.9	

^aReference 14. ^b $P_{-} = P_{Exp} - P_{+}$. $\overline{P_{-}}$ is the average of P_{-} . ^dThis work. ^eReference 27. ^fReference 28. ^gReference 29. ^hReference 30. ⁱReference 12.



Figure 2. Plot of the estimated parachor for the ILs versus their experimental values: \blacksquare [C_n mim][Pro] (n = 2-6); \bullet [C_n mim]][PF_3 (CF_2CF_3)₃] (n = 2-6); \bullet [C_n mim][Gly] (n = 2-6). $P_{Cal} = 0.524 + 0.999P_{Exp}$; s = 1.94; $r^2 = 0.999$.

for the ILs $[C_n \text{mim}][Pro]$, $[C_n \text{mim}][PF_3(CF_2CF_3)_3]$, and $[C_n \text{mim}][Gly]$, and it shows that the estimated parachor and the experimental values are highly correlated (correlation coefficient squared, $r^2 = 0.999$; standard deviation, s = 1.94) and very similar (gradient = 0.999; intercept = 0.524).

In terms of the estimated parachor values of the ILs, P_{Cab} in Table 3, the predicted values of surface tension using eq 8 can be obtained and are listed in Table 4. In Table 4, γ_{Exp} is the corresponding experimental value, and $\Delta \gamma$ is the difference between the experimental value and the corresponding estimated one of the surface tension of the ILs, that is, $\Delta \gamma = \gamma_{Exp} - \gamma_{Cal}$. Figure 3 is a plot of the predicted surface tensions versus their corresponding experimental values, and it shows that the values are highly correlated ($r^2 = 0.99$) and extremely similar (gradient = 1.03; intercept = -0.96), which not only imparts confidence in the application of the ionic parachor but also provides a method to closely predict the former and latter physical properties for ILs using ionic parachor data.

3.5. Predicting Molar Refraction and the Refractive Index. The Lorentz-Lorenz relationship between the refractive index and the mean molecular polarizability, α_{p} , leads to the definition of molar refraction R_m^{31}

$$R_{\rm m} = [(n_{\rm D}^2 - 1)/(n_{\rm D}^2 + 2)] \cdot (M/\rho) = (4\pi N/3) \cdot \alpha_{\rm p}$$
(9)

According to eq 9, values of $R_{\rm m}$ and $\alpha_{\rm p}$ were calculated from $n_{\rm D}$ values of ILs without water and are listed in Table 5.

Because R_m has the property of additivity, its values for the homologues $[C_n mim][Pro]$ (n = 2-6) can be predicted by a semiempirical method. The contribution per methylene ($-CH_2-$) group is 4.65. It is very consistent with 4.60, which was obtained using AAILs $[C_n mim][Ala]$.³² The values



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Figure 3. Plot of the estimated surface tension for the ILs versus their experimental values: \blacksquare [C_n mim][Pro] (n = 2-6); \blacklozenge [C_n mim]-[$PF_3(CF_2CF_3)_3$] (n = 2-6); \blacktriangle [C_n mim][Gly] (n = 2-6). $\gamma_{Cal} = -0.96$ + 1.03 γ_{Exp} ; s = 0.57; $r^2 = 0.99$.

Table 5. Experimental Values of $R_{\rm m}$, $n_{\rm D}$, and $10^{24}\alpha_{\rm p}$ and Predicted Values of $n_{\rm D \ Cal}$ for $[C_n {\rm mim}][{\rm Pro}]$ at 298.15 K

ionic liquid	$R_{ m m}$	n _{D Exp}	$10^{24} \alpha_{\rm p}$	n _{D Cal}	$\Delta n_{\rm D} = n_{\rm D \ Exp} - n_{\rm D \ Cal}$
[C ₂ mim] [Pro]	44.74	1.4897	17.75	1.4896	0.0001
[C ₃ mim] [Pro]	49.50	1.4886	19.64	1.4886	0
[C ₄ mim] [Pro]	54.05	1.4862	21.45	1.4861	0.0001
[C ₅ mim] [Pro]	58.68	1.4841	23.28	1.4841	0
[C ₆ mim] [Pro]	63.33	1.4828	25.13	1.4827	0.0001
[C ₃ mim] [Gly]	52.53	1.5069	20.84	1.5091	-0.0022
$\begin{matrix} [C_4 mim] \\ [Gly] \end{matrix}$	57.28	1.5085	22.73	1.5081	0.0004
[C ₅ mim] [Gly]	61.75	1.5066	24.50	1.5044	0.0022
[C ₆ mim] [Gly]	65.37	1.4944	25.94	1.4193	0.0751
[C ₂ mim] [Ala]	53.22	1.5106	21.12	1.5099	0.0007
[C ₃ mim] [Ala]	57.57	1.5044	22.84	1.5052	-0.0008
[C₄mim] [Ala]	62.14	1.5019	24.65	1.5026	-0.0007
[C ₅ mim] [Ala]	66.72	1.4984	26.47	1.4998	-0.0014
[C₀mim] [Ala]	71.67	1.4970	28.44	1.4991	-0.0021

of R_m of $[C_n mim][Pro]$ calculated from eq 9 are listed in Table 5. In addition, refractive index data of $[C_n mim][Ala]$ and $[C_n mim][Gly]$ from the literature³² are also listed in Table 5.

Table 4. Parachor and Surface Tension of the Investigated ILs

[C _n mim]X	$[C_n \min][Pro]$			$[C_n \text{mim}][PF_3(CF_2CF_3)_3]$			[C _n mim][Gly]		
	$\gamma_{\rm Exp}$	$\gamma_{\rm Cal}$	Δγ	$\gamma_{\rm Exp}$	$\gamma_{\rm Cal}$	Δγ	$\gamma_{\rm Exp}$	$\gamma_{\rm Cal}$	$\Delta \gamma$
[C ₂ mim]X	39.6	41.2	-1.6	34.8	34.5	0.3	48.1	48.2	-0.1
$[C_3 mim]X$	38.4	38.7	-0.3	34.1	33.8	0.3	45.6	46.1	-0.5
[C ₄ mim]X	37.0	37.0	0.0	33.2	33.2	0.0	43.5	43.5	0.0
$[C_5 mim]X$	35.7	35.4	0.3	32.4	32.6	-0.2	41.9	42.1	-0.2
[C ₆ mim]X	34.8	33.9	0.9	31.7	32.0	-0.3	40.6	40.0	0.6

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Tripathi 33 combined eq 9 with the parachor equation, eq 8, to yield an expression

$$\gamma^{1/4} = (P/R_{\rm m})[(n_{\rm D}^2 - 1)/(n_{\rm D}^2 + 2)]$$
(10)

Using eq 10, the refractive index of an IL can be estimated from its surface tension, γ , molar refraction, $R_{\rm m}$, and the predicted parachor, $P_{\rm Cal}$. The values of the predicted refractive index, $n_{\rm D \ Cal}$ for $[C_n {\rm mim}][{\rm Pro}]$, $[C_n {\rm mim}][{\rm Ala}]$, and $[C_n {\rm mim}][{\rm Gly}]$ were calculated from eq 10 and are listed in Table 5. Figure 4 is



Figure 4. Plot of the estimated refractive index for ILs $[C_n \min][Pro]$ versus their experimental values: $\blacksquare [C_n \min][Pro] (n = 2-6); \bullet [C_n \min][Gly] (n = 2-5); \blacktriangle [C_n \min][Ala] (n = 2-6). n_{D Cal} = 0.073 + 0.95 n_{D Exp}; s = 1.6 \times 10^{-3}; r^2 = 0.98.$

a plot of the predicted values of the refractive index for the ILs versus the corresponding experimental values, and it shows that the predicted values of the refractive index and the corresponding experimental values are correlated (correlation coefficient squared, $r^2 = 0.98$) and similar (gradient = 0.95; intercept = 0.073).

ASSOCIATED CONTENT

Supporting Information

¹H NMR, DSC traces, and density, surface tension, and refractive index plots of the various ionic liquids. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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