# Ionic Parachor and Its Application in Acetic Acid Ionic Liquid Homologue 1-Alkyl-3-methylimidazolium Acetate $\{[C_n\text{mim}][\text{OAc}](n = 2,3,4,5,6)\}$

Wei Guan, Xiao-Xue Ma, Long Li, Jing Tong, Da-Wei Fang, and Jia-Zhen Yang*

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

S *Supporting Information*

ABSTRACT: Five acetic acid ionic liquids (AcAILs) $[C_n\text{mim}][\text{OAc}](n = 2,3,4,5,6)$ (1-alkyl-3-methylimidazolium acetate) were prepared by the neutralization method and characterized by ^{1}HNMR spectroscopy and differential scanning calorimetry (DSC). The values of their density and surface tension were measured at 298.15 ± 0.05 K. Since the AcAILs can strongly form hydrogen bonds with water, the small amounts of water are difficult to remove from the AcAILs by common methods. In order to eliminate the effect of the trace water, the standard addition method (SAM) was applied to these measurements. As a new concept, ionic parachor was put forward. $[\text{OAc}]^-$ was seen as a reference ion, and its individual value of ionic parachor was determined in terms of two extrathermodynamic assumptions. Then, the values of ionic parachors of a number of anions, $[\text{NTf}_2]^-$, $[\text{Ala}]^-$, $[\text{AlCl}_4]^-$, and $[\text{GaCl}_4]^-$, were obtained by using the value of the ionic parachor of the reference ion; the parachor and surface tension of the investigated ionic liquids in literature were estimated. In comparison, the estimated values correlate quite well with their matching experimental values.
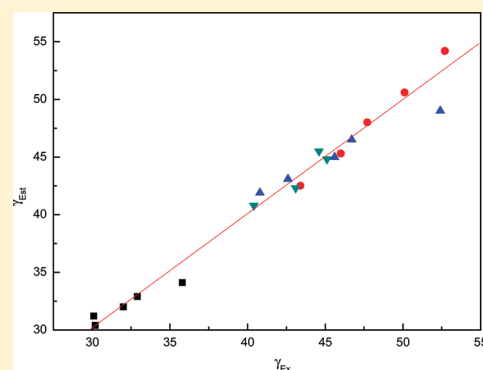
1. INTRODUCTION

Ionic liquids (ILs) have several unique properties including minuscule vapor pressure, nonflammability, and dual natural polarity, making them greatly applicable in many physical and chemical fields.[1] Acetic acid ionic liquids (AcAILs) have attracted considerable attention from industry and the academic community as a new-generation greener ionic liquid. The AcAILs have strong solubility and good catalytic properties, which are useful for an enzyme-friendly cosolvent for the resolution of amino acids,[2] ultrasonic irradiation toward synthesis of trisubstituted imidazoles,[3] assisted transdermal delivery of sparingly soluble drugs,[4] and some catalytic reactions.[5] Thus, AcAILs have been expected to be applied in various fields, such as industrial chemistry and pharmaceutical chemistry.

In recent years, there has been a developing trend in the literature toward the estimation of the physicochemical properties for compounds by semiempirical methods, in particular, for ILs.[6–8] Although the estimated result cannot be regarded as accurate physicochemical data, it is to be commended because it provides valuable insight into the origins of the behavior of the materials. Among all the empirical methods, parachor is the simplest.[9–11] As a continuation of our previous investigation,[12,13] this article reports the following: (1) five acetic acid ionic liquids $[C_n\text{mim}][\text{OAc}]$ (n = 2,3,4,5,6) (1-alkyl-3-methylimidazolium acetate) were prepared by the neutralization method; (2) the values of the density and surface tension for $[C_n\text{mim}][\text{OAc}]$ (n = 2,3,4,5,6) were measured at 298.15 ± 0.05 K. Since AcAILs can

strongly form hydrogen bonds with water, which is problematic as an impurity, the standard addition method (SAM) was applied in these measurements;[14] (3) as a new concept, the ionic parachor was put forward and was applied to the AcAILs. $[\text{OAc}]^-$ was seen as a reference ion, and its particular value of ionic parachor was determined in terms of two extrathermodynamic assumptions, then values of ionic parachor for the corresponding cations, $[C_n\text{mim}]^+$, in the AcAILs were calculated from the reference value of $[\text{OAc}]^-$; (4) finally, in terms of the estimation of the parachor and surface tension of the investigated ionic liquids in literature using the ionic parachors for $[\text{OAc}]^-$ and $[C_n\text{mim}]^+$, the credibility of the new concept, ionic parachor, was tested and verified.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Deionized water was distilled in a quartz still, and its conductance was $0.8-1.2 \times 10^{-4}\,\text{S}\cdot\text{m}^{-1}$. Acetic 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
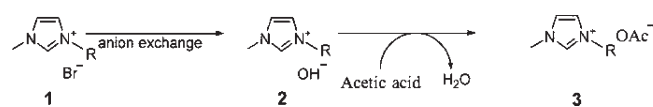
Figure 1. Preparation of AcAILs by the neutralization method. 1, $[C_n\text{mim}][Br]$; 2, $[C_n\text{mim}][OH]$; and 3, $[C_n\text{mim}][OAc]$.

over molecular sieves in tightly sealed glass bottles. Anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent Co. Ltd. and activated by the regular method before use.

2.2. Preparation of the AcAILs. The AcAILs $[C_n\text{mim}][OAc]$ (n = 2,3,4,5,6) were prepared by a neutralization method according to Fukumoto et al.[15] Figure 1 is a schematic of this synthetic route. First, $[C_n\text{mim}]Br$ (n = 2,3,4,5,6) was synthesized according to the literature.[16,17] Then, aqueous 1-alkyl-3- methylimidazolium hydroxide ($[C_n\text{mim}][OH]$) (n = 2,3,4,5,6) was prepared from $[C_n\text{mim}]Br$ (n = 2,3,4,5,6) by use of the activated anion-exchange resin over a 100 cm column. However, $[C_n\text{mim}][OH]$ (n = 2,3,4,5,6) is not particularly stable and should be used immediately after preparation. The onium hydroxide aqueous solution was added dropwise to a slight excess of acetic acid aqueous solution. The mixture was stirred under cooling for 24 h. Then, water was evaporated under reduced pressure at 40−50 °C. To this reaction mixture was added the mixed solvent acetonitrile/methanol (volumetric ratio = 9/1), and it was stirred vigorously. The mixture was then filtered to remove the slight excess of acetic acid. The filtrate was evaporated to remove the solvents. The product of $[C_n\text{mim}][OAc]$ (n = 2,3,4,5,6) was dried in vacuo for 2 days at 85 °C. Structures of the resulting acetic acid ionic liquids were confirmed by ^{1}HNMR spectroscopy (see Figure A of the Supporting Information).

Differential scanning calorimetric (DSC) measurements showed that ILs $[C_n\text{mim}][OAc]$ (n = 2,3,4,5,6) had no obvious melting point, but their glass transition temperatures $T_{g(n=2,3,4,5,6)}$ = −75.5 °C, −73.4 °C, −70.5 °C, −68.5 °C, and −63.2 °C, respectively. All traces of DSC are listed in Figure B of the Supporting Information. The water content, w_2 (in mass fraction), in the AcAILs was determined by the use of a Karl Fischer moisture titrator (ZSD-2 type).

2.3. Determination of Density and Surface Tension of the AcAILs. Since the AcAILs can strongly form hydrogen bonds with water, the small amount of water in the AcAILs is difficult to remove by common methods so that trace water becomes the most problematic impurity. In order to eliminate the effect of the impurity of water, the standard addition method (SAM) was applied to these measurements. According to SAM, a series of samples of $[C_n\text{mim}][OAc]$ (n = 2,3,4,5,6) with different water contents were prepared.

The density of degassed water was measured on a Westphal balance at 293.15 ± 0.05 K and was in good agreement with the literature[18] within the experimental error of ±0.0002 g·cm^{-3}. Then, the densities of the samples were measured at 298.15 ± 0.05 K. The sample was placed in a cell with a jacket and was thermostatted with an accuracy of ±0.05 K.

By use of the tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.), the surface tension of the water was measured at 298.15 ± 0.05 K and was in good agreement with the literature[18] within the experimental error of ±0.1 mJ·m^{-2}. Then, the values of surface tension of the samples were measured by the same method at 298.15 ± 0.05 K.

Table 1. Density Values of Ionic Liquids Containing Various Amounts of Water at 298.15 K ($\rho/\text{g}\cdot\text{cm}^{-3}$)^a

density ρ for $[C_n\text{mim}][OAc]$ (n = 2,3,4,5,6)							
$[C_2\text{mim}][OAc]$							
$10^3 w_2$	6.79	8.03	9.58	10.34	11.87	0	r^2	$s \times 10^5$
ρ (g·cm^{-3})	1.1471	1.1478	1.1485	1.149	1.1497	1.1437	0.99	5.5
$[C_3\text{mim}][OAc]$							
$10^3 w_2$	6.31	7.84	9.51	10.31	11.87	0	r^2	$s \times 10^5$
ρ (g·cm^{-3})	1.1219	1.1226	1.1232	1.1238	1.1244	1.1190	0.99	9.9
$[C_4\text{mim}][OAc]$							
$10^3 w_2$	5.88	7.18	8.43	9.72	11.06	0	r^2	$s \times 10^5$
ρ (g·cm^{-3})	1.0995	1.1001	1.1006	1.1012	1.1019	1.0968	0.99	4.8
$[C_5\text{mim}][OAc]$							
$10^3 w_2$	6.13	7.35	8.69	9.95	11.23	0	r^2	$s \times 10^5$
ρ (g·cm^{-3})	1.0803	1.0809	1.0814	1.0821	1.0828	1.0773	0.99	7.9
$[C_6\text{mim}][OAc]$							
$10^3 w_2$	5.74	7.02	8.28	9.52	10.74	0	r^2	$s \times 10^5$
ρ (g·cm^{-3})	1.0633	1.0638	1.0643	1.0649	1.0656	1.0606	0.99	8.9

^{a} w_2 is the water content; r^2 is the squared correlation coefficient; and s is the standard deviation.

Table 2. Surface Tension Values of Ionic Liquids Containing Various Amounts of Water at 298.15 K ($\gamma/\text{mJ}\cdot\text{m}^{-2}$)^a

surface tension γ for $[C_n\text{mim}][OAc]$ (n = 2,3,4,5,6)							
$[C_2\text{mim}][OAc]$							
$10^3 w_2$	6.65	8.05	9.71	11.15	12.74	0	r^2	s
γ (mJ·m^{-2})	39.6	39.9	40.3	40.6	41.0	38.1	0.99	0.018
$[C_3\text{mim}][OAc]$							
$10^3 w_2$	5.66	7.37	9.13	10.97	12.84	0	r^2	s
γ (mJ·m^{-2})	38.2	38.7	39.1	39.6	40.0	36.8	0.99	0.041
$[C_4\text{mim}][OAc]$							
$10^3 w_2$	7.00	8.26	9.88	11.97	14.72	0	r^2	s
γ (mJ·m^{-2})	37.4	37.7	38.2	38.9	39.4	35.2	0.99	0.106
$[C_5\text{mim}][OAc]$							
$10^3 w_2$	6.43	8.10	9.81	11.39	12.95	0	r^2	s
γ (mJ·m^{-2})	35.8	36.2	36.5	37.0	37.6	34.1	0.99	0.119
$[C_6\text{mim}][OAc]$							
$10^3 w_2$	6.25	7.91	9.58	11.18	12.83	0	r^2	s
γ (mJ·m^{-2})	34.6	34.8	35.3	35.8	36.1	33.0	0.99	0.099

^{a} w_2 is the water content; r^2 is the squared correlation coefficient; and s is the standard deviation.

3. RESULTS AND DISCUSSION

3.1. Values of Density and Surface Tension for the Samples. The values of density and surface tension for the samples of ILs $[C_n\text{mim}][OAc]$ (n = 2,3,4,5,6) containing various contents of water are listed in Tables 1 and 2, respectively. Each value in the tables is the average of triplicate measurements. According to SAM, the values of the density or surface tension of the samples at a given temperature were plotted against the water content,
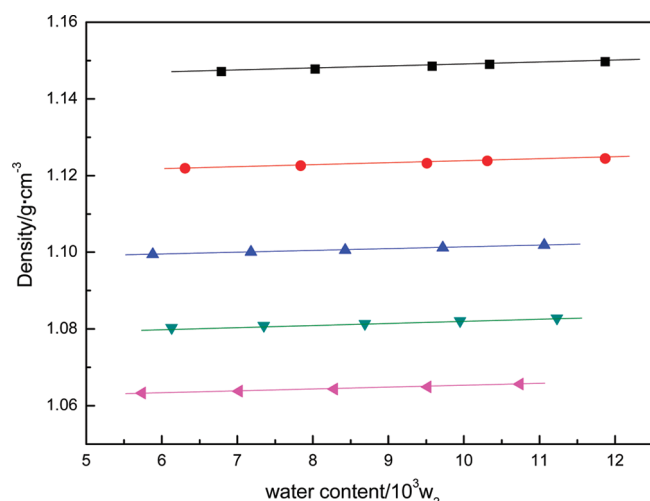
Figure 2. Plot of density vs amount of water in $[C_n mim][OAc]$ (n = 2,3,4,5,6). (black square) $[C_2 mim][OAc]$ ρ = 1.1437 + 5.1136 × $10^{-4} w_2$, s = 5.5 × 10^{-5}, r^2 = 0.99; (red circle) $[C_3 mim][OAc]$ ρ = 1.1190 + 4.5245 × $10^{-4} w_2$, s = 9.9 × 10^{-5}, r^2 = 0.99; (blue upward facing triangle) $[C_4 mim][OAc]$ ρ = 1.0968 + 4.5759 × $10^{-4} w_2$, s = 4.8 × 10^{-5}, r^2 = 0.99; (green downward facing triangle) $[C_5 mim][OAc]$ ρ = 1.0773 + 4.8418 × $10^{-4} w_2$, s = 7.9 × 10^{-5}, r^2 = 0.99; (pink left facing triangle) $[C_6 mim][OAc]$ ρ = 1.0606 + 4.5564 × $10^{-4} w_2$, s = 8.9 × 10^{-5}, r^2 = 0.99.

w_2 (w_2 is the mass percentage) so that a series of good straight lines were obtained. The intercepts of the straight lines were the values of the density or surface tension of $[C_n mim][OAc]$ (n = 2,3,4,5,6) without water and were seen as experimental values, which are included in the column of w_2 = 0 in Tables 1and 2, respectively. Figures 2 and 3 are plots of the density and surface tension, respectively, against w_2 at 298.15 ± 0.05 K. The squared correlation coefficients, r^2, of all linear regressions were larger than 0.99, and all values of the standard deviation, s, were within experimental error. These facts show that the standard addition method is suitable in this work.

3.2. Volumetric Properties of [$C_n$mim][OAc] (n = 2,3,4,5,6). From the experimental values of density, the molecular volume (sum of the positive and negative ion volumes), V_m, of $[C_n mim]-[OAc]$ (n = 2,3,4,5,6) was calculated from the following equation:

$$V_m = M/(N\rho) \tag{1}$$

where M is molar mass, and N is Avogadro's constant so that $V_{m(n=2,3,4,5,6)}$ = 0.2471 nm^3, 0.2734 nm^3, 0.3002 nm^3, 0.3272 nm^3, and 0.3543 nm^3 for $[C_n mim][OAc]$ (n = 2,3,4,5,6), respectively, at 298.15 K. The average difference between the molecular volumes of $[C_n mim][OAc]$ and $[C_{n-1} mim][OAc]$ is 0.0268 nm^3, which can be seen as the contribution to the molecular volume of one methylene $(-CH_2-)$ group, and was in good agreement with a mean contribution of 0.0272 nm^3 per methylene $(-CH_2-)$ group obtained by Glasser[19] from ionic liquids $[C_n mim][BF_4]$. The values of molecular volume, V_m, are listed in Table 3.

According to Glasser's theory,[19] the standard molar entropy for IL, S^0, is given by the following equation, and the values of S^0 (J·K^{-1}·mol^{-1}) for $[C_n mim][OAc]$ (n = 2,3,4,5,6) are listed in Table 3.

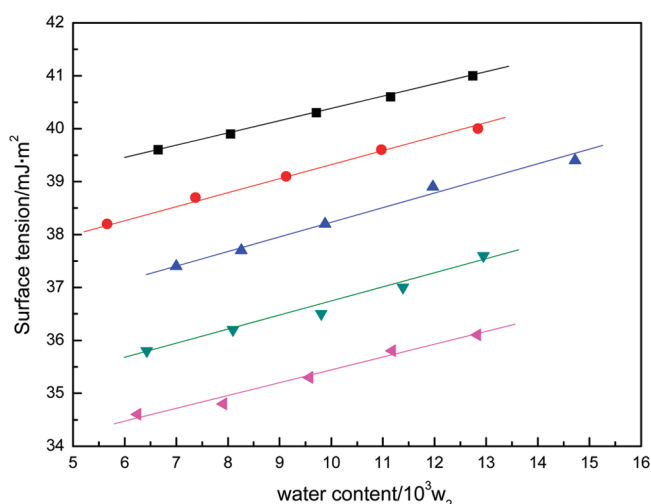$$S^0(298)/(\text{J·K}^{-1}\text{·mol}^{-1}) = 1246.5(V_m/\text{nm}^3) + 29.5 \tag{2}$$

Figure 3. Plot of surface tension vs amount of water in $[C_n mim][OAc]$ (n = 2,3,4,5,6). (black square) $[C_2 mim][OAc]$ γ = 38.1 + 0.223w_2, s = 0.018, r^2 = 0.99; (red circle) $[C_3 mim][OAc]$ γ = 36.8 + 0.250w_2, s = 0.041, r^2 = 0.99; (blue upward facing triangle) $[C_4 mim][OAc]$ γ = 35.5 + 0.269w_2, s = 0.106, r^2 = 0.99; (green downward facing triangle) $[C_5 mim][OAc]$ γ = 34.1 + 0.269w_2, s = 0.119, r^2 = 0.99; (pink left facing triangle) $[C_6 mim][OAc]$ γ = 33.0 + 0.243w_2, s = 0.099, r^2 = 0.99.

Table 3. Values of Molecular Volume, Standard Molar Entropy, and Lattice Energy of Ionic Liquids at 298.15 K

ionic liquid	M (g·mol^{-1})	ρ (g·cm^{-3})	V_m (nm^3)	S^0 (J·K^{-1}·mol^{-1})	U_{pot} (kJ·mol^{-1})
$[C_2 mim][OAc]$	170.21	1.1437	0.2471	337.5	478
$[C_3 mim][OAc]$	184.24	1.1190	0.2734	370.3	465
$[C_4 mim][OAc]$	198.26	1.0968	0.3002	403.7	454
$[C_5 mim][OAc]$	212.29	1.0773	0.3272	437.4	444
$[C_6 mim][OAc]$	226.32	1.0606	0.3543	471.1	435

According to eq 2, the mean methylene volume is 0.0268 nm^3, and the fitted slope of eq 2 is 1246.5, so the mean entropy contribution per methylene group is 33.4 J·K^{-1}·mol^{-1}, and this value is in good agreement with the values of 33.9 J·K^{-1}·mol^{-1} for $[C_n mim][BF_4]$ and 35.1 J·K^{-1}·mol^{-1} for $[C_n mim][NTf_2]$.[19]

The lattice energy, U_{pot} (kJ·mol^{-1}), may be estimated from the following equation:[19]

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

The estimated values of U_{pot} for $[C_n mim][OAc]$ are listed in Table 3. The largest value, U_{pot} = 478 kJ·mol^{-1} for $[C_n mim]-[OAc]$, is much less than that of fused salts; for example, U_{pot} = 613 kJ·mol^{-1} for fused CsI,[18] which is the lowest lattice energy among alkali halides. The lower lattice energy is the underlying reason for forming an ionic liquid at room temperature.

3.3. Ionic Parachor. The parachor, P, is a relatively old concept that is available as a link between the structure, density, and surface tension of liquids.[9,10] The parachor as a tool to predict physical properties of substances was developed in 1924 by Sugden[11] and was defined using the following equation:

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

where γ is the surface tension, M is the molar mass, and ρ is the density of the substance. However, the vast majority of parachor
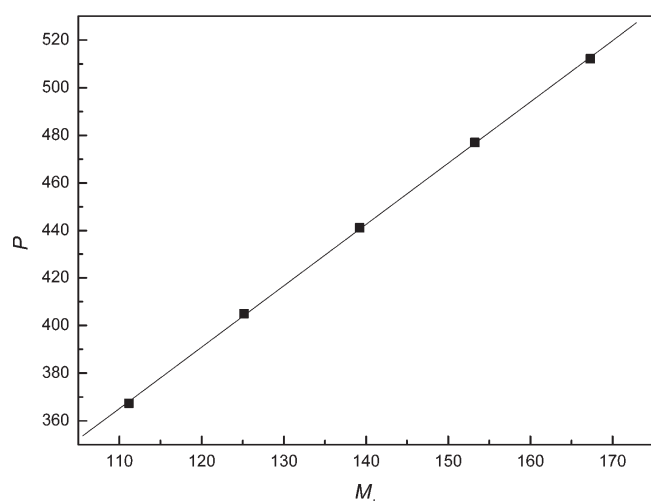
Figure 4. Plot of parachor P vs M_+. Fitting equation: $P = 81.66 + 2.577 M_+$.

Table 4. Values of the Ionic Parachor for the ILs According to the Second Extrathermodynamic Assumption

ionic liquid	M_+ (g·mol^{-1})	P (exp)	V_+ (crystal) (nm^3)[20]	V_- (crystal) (nm^3)[21]	P_+	P_-
[C$_2$mim][OAc]	111.168	369.1	0.156	0.048	283.1	86.0
[C$_3$mim][OAc]	125.194	405.0	0.178	0.048	319.0	86.0
[C$_4$mim][OAc]	139.220	441.1	0.196	0.048	355.0	86.1
[C$_5$mim][OAc]	153.246	476.9	0.219	0.048	390.9	86.0
[C$_6$mim][OAc]	167.272	512.1	0.242	0.048	426.1	86.0

Table 5. Values of Ionic Parachor of ILs at 298.15 K

	[C$_2$mim]$^+$	[C$_3$mim]$^+$	[C$_4$mim]$^+$	[C$_5$mim]$^+$	[C$_6$mim]$^+$
cation parachor	285.2	321.1	357.2	393.0	428.2
	[NTf$_2$]$^-$ [22]	[Ala]$^-$ [12]	[AlCl$_4$]$^-$ [23]	[GaCl$_4$]$^-$ [24]	
anion parachor	335.9	197.1	287.1	283.1	

studies have focused on uncharged compounds. The data of the individual group contribution of parachor determined by Rowley and co-workers[10] are from the neutral molecule and difficult to use in the application of an ionic liquid because there is no consideration of the Coulomb force between the ions. Although a number of early studies attempted to determine parachor for ions, 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. However, since numerous ionic liquids are fluid at room temperature, they offer a solution to determining experimental parachor of ionic compounds. Therefore, ionic parachor was proposed as a new concept, that is, ions composed of ionic liquids can be seen as independent descriptors of parachor. Ionic parachor, P_i, can be defined by the following equation:

$$P_i = \gamma^{1/4} V_i \tag{5}$$

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

$$P = P_+ + P_- \tag{6}$$

where P_+ and P_- are the ionic parachors of the cation and anion, respectively. Now, the key question is how the experimental value of parachor for an ionic liquid was divided into ionic parachors of the corresponding cation and anion. Two extrathermodynamic assumptions were recommended for the evaluation of the individual ionic parachor. The first of them is the extrapolation method. For the acetic acid ionic liquid homologue 1-alkyl-3-methylimidazolium acetate ([C$_n$mim][OAc] ($n = 2,3,4,5,6$)), according to eq 7, when the molar mass of the cation, M_+, approaches zero, the ionic parachor of the anion, P_-, could be obtained.

$$P = P_- + (M + \gamma^{1/4})/\rho \tag{7}$$

The second extrathermodynamic assumption was proposed as eq 8

$$V_-(\text{crystal})/V_+(\text{crystal}) = V_{m-}(\text{IL})/[V_m - V_{m-}(\text{IL})]$$
$$= P_-(\text{IL})/[P - P_-(\text{IL})] \tag{8}$$

where V_+(crystal) and V_-(crystal) are the corresponding cationic and anionic volumes derived from crystal structures, respectively; V_{m-} (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. If the values of V_+(crystal) and V_-(crystal) may be obtained, the ionic parachor of the cation and anion can be determined with eq 8.

According to the first extrathermodynamic assumption, plotting the experimental values of P against the molar mass of the cations, M_+, of ILs [C$_n$mim][OAc], we obtained a good straight line (see Figure 4). The regression eq is $P = 81.66 + 2.577 M_+$ with a correlation coefficient of $r = 0.999$ and standard deviation of $s = 0.85$. The value of the intercept 81.66 means a contribution of the anion to P; that is $P_- = 81.7$, ionic parachor of [OAc]$^-$.

The values of V_+(crystal) and V_-(crystal) for [C$_n$mim][OAc] obtained from the literature[20,21] are listed in Table 4. According to the second extrathermodynamic assumption, the values of ionic parachor of the cation and anion for the ILs can be calculated by eq 8 and are also listed in Table 4. From Table 4, the average of the ionic parachor, P_-, can be seen, and for anion [OAc]$^-$, it is 86.0.

If [OAc]$^-$ was used as the reference ion, the reference value of $P_- = 83.9$, which is the average of that obtained from two extrathermodynamic assumptions, values of the ionic parachor for all corresponding imidazolium cations, [C$_n$mim]$^+$, were obtained and are listed in Table 5. Then, using data in the literature and P_+ of [C$_n$mim]$^+$, the ionic parachors of [NTf$_2$]$^-$, [Ala]$^-$, [AlCl$_4$]$^-$, and [GaCl$_4$]$^-$ were obtained and are also listed in Table 5.

3.4. Predicting Parachor and Surface Tension. In order to verify the reliability of the ionic parachors for [C$_n$mim]$^+$ and the anions in Table 5, the parachors for the ILs ([C$_n$mim][NTf$_2$], [C$_n$mim][Ala], [C$_n$mim][AlCl$_4$], and [C$_n$mim][GaCl$_4$]) were estimated. The estimated values, P_{Est}, and the experimental values, P_{Ex}, determined by eq 4 are listed in Table 6, where ΔP means the difference between the experimental value and corresponding estimated value of the parachor for the ILs, that is, $\Delta P = P_{Ex} - P_{Est}$. As can be seen from Table 6, only ΔP for [C$_2$mim]-[AlCl$_4$] is relatively large (relative deviation is close to 2%). This may be due to the use of a different author's data in the calculation of the experimental parachor for [C$_n$mim][AlCl$_4$].[10] For the remaining

Table 6. Parachors and Surface Tensions of the Investigated Ionic Liquids

[C$_n$mim]X	[C$_n$mim][NTf$_2$]						[C$_n$mim][Ala]					
	P_{Ex}	P_{Est}	ΔP	γ_{Ex}	γ_{Est}	$\Delta\gamma$	P_{Ex}	P_{Est}	ΔP	γ_{Ex}	γ_{Est}	$\Delta\gamma$
[C$_2$mim]X	628.8	621.1	7.7	35.8	34.1	1.7	479.0	482.3	−3.3	52.7	54.2	−1.5
[C$_3$mim]X	657.0	657.0	0.0	32.9	32.9	0.0	516.9	518.2	−1.3	50.1	50.6	−0.5
[C$_4$mim]X	692.9	693.1	−0.2	32.0	32.0	0.0	553.4	554.3	−0.9	47.7	48.0	−0.3
[C$_5$mim]X	722.5	728.9	−6.4	30.1	31.2	−1.1	592.4	590.1	2.3	46.0	45.3	0.7
[C$_6$mim]X	762.8	764.1	−1.3	30.2	30.4	−0.2	628.6	625.3	3.3	43.4	42.5	0.9

[C$_n$mim]X	[C$_n$mim][AlCl$_4$]						[C$_n$mim][GaCl$_4$]					
	P_{Ex}	P_{Est}	ΔP	γ_{Ex}	γ_{Est}	$\Delta\gamma$	P_{Ex}	P_{Est}	ΔP	γ_{Ex}	γ_{Est}	$\Delta\gamma$
[C$_2$mim]X	581.8	572.3	9.5	52.4	49.0	3.4	565.6	568.3	−2.7	44.6	45.5	−0.9
[C$_3$mim]X	608.8	608.3	0.5	46.7	46.5	−0.2						
[C$_4$mim]X	646.5	644.3	2.2	45.6	45.0	0.6	641.3	640.3	1.0	45.1	44.8	0.3
[C$_5$mim]X	678.1	680.1	−2.0	42.6	43.1	−0.5	679.5	676.1	3.4	43.1	42.3	0.8
[C$_6$mim]X	705.4	715.3	−9.9	40.8	41.9	−1.1	709.7	711.3	−1.6	40.4	40.8	−0.4
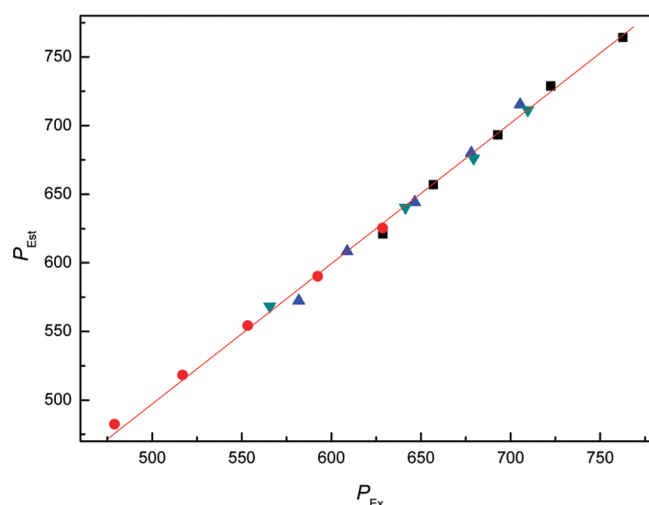
Figure 5. Plot of the estimated parachor for ILs [C$_n$mim]([NTf$_2$], [Ala], [AlCl$_4$], and [GaCl$_4$]) vs their experimental values. P_{Est} = −7.907 + 1.012P_{Ex}, s = 4.45, r^2 = 0.99. (black square) [C$_n$mim][NTf$_2$] (n = 2−6); (red circle) [C$_n$mim][Ala] (n = 2−6); (blue upward facing triangle) [C$_n$mim][AlCl$_4$] (n = 2−6); (green downward facing triangle) [C$_n$mim][GaCl$_4$] (n = 2, 4−6).

Figure 6. Plot of the estimated surface tension for ILs [C$_n$mim]-([NTf$_2$], [AlCl$_4$], [GaCl$_4$], and [Ala]) vs their experimental values. γ_{Est} = 1.127 + 0.971γ_{Ex}, s = 1.14, r^2 = 0.99. (black square) [C$_n$mim][NTf$_2$] (n = 2−6); (red circle) [C$_n$mim][Ala] (n = 2−6); (blue upward facing triangle) [C$_n$mim][AlCl$_4$] (n = 2−6); (green downward facing triangle) [C$_n$mim][GaCl$_4$] (n = 2, 4−6).

ILs, ΔP values are very small, that is, the experimental values of the parachor are in accordance with the estimated one. This implies that the data of the ionic parachors for [C$_n$mim]$^+$ and the anions are reliable. Figure 5 is a comparative plot of estimated parachor values as a function of corresponding experimental values for the investigated ionic liquids and shows that the estimated parachor and the experimental values are highly correlated (squared correlation coefficient r^2 = 0.99; standard deviation s = 4.45) and extremely similar (gradient = 1.01; intercept = −7.91).

In terms of the ionic parachor values in Table 5, the predicted values of the surface tension for the ILs using eq 1 and their corresponding experimental values are listed in Table 6. In Table 6, $\Delta\gamma$ means the difference between the experimentally determined and corresponding estimated surface tensions for the ILs, that is, $\Delta\gamma = \gamma_{Ex} - \gamma_{Est}$. As can be seen from Table 6, only the values of $\Delta\gamma$ for [C$_2$mim][AlCl$_4$] are relatively large

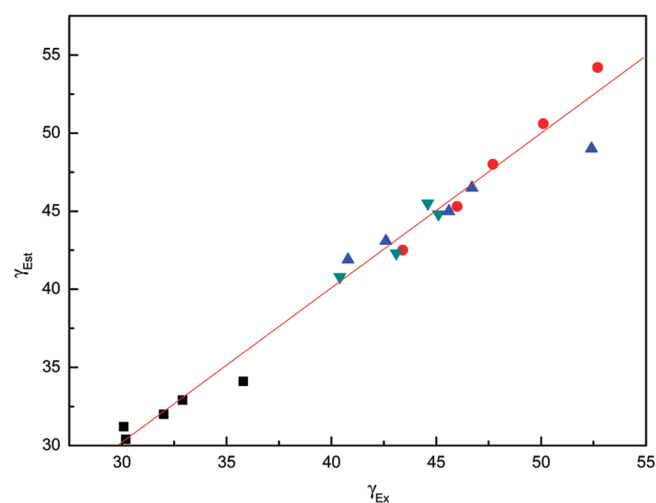(relative deviation is close to 7%). As illustrated by Figure 6, the predicted surface tensions of the ILs correlate quite well with their matching experimental values (squared correlation coefficient r^2 = 0.99; standard deviation s = 1.14).

■ ASSOCIATED CONTENT

ⓢ Supporting Information. ^{1}HNMR spectra and DSC traces of the five studied acetic acid ionic liquids. This material is available free of charge via the Internet at http://pubs.acs.org.

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