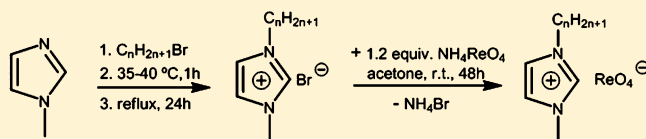


# Physicochemical Properties of Air and Water Stable Rhenium Ionic Liquids

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**ABSTRACT:** Air and water stable ionic liquids (ILs) based on catalytic functional metal rhenium,  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ) (1-alkyl-3-methylimidazolium perrhenate), are designed and synthesized. Their density and surface tension are measured in the temperature range of  $293.15\text{--}343.15 \pm 0.05$  K. Some physical-chemical properties of the ILs have been calculated or estimated by the empirical methods. The ion parachor is put forward and calculated by two extrathermodynamic assumptions. According to the interstice model, the thermal expansion coefficient of ILs  $[C_n\text{mim}][\text{ReO}_4]$ ,  $\alpha$ , are calculated and in comparison with experimental values, their magnitude order is in good agreement.



## 1. INTRODUCTION

First-generation ionic liquids (ILs), such as  $[C_n\text{mim}][\text{AlCl}_4]$ , are based on metal, which has good catalysis in some reactions, and wider and variable Lewis acidity, so they have been studied in depth.<sup>1–4</sup> However, they are reactive with water and difficult to handle so their application has been restricted.<sup>5</sup> Since Wilkes et al. synthesized the air and water stable IL  $[C_2\text{mim}][\text{BF}_4]$  (1-ethyl-3-methylimidazolium tetrafluoroborate) in 1992,<sup>6</sup> a new epoch has been initiated for research and application of ILs. ILs are being explored vigorously as recent publications hint at their use in many typical chemical reactions.<sup>7–9</sup> However, all these new ILs were organic salts without metals. So in this paper, we advance the idea of designing and synthesizing new kinds of ILs with catalytic functional metal and good solubility for inorganic and organic compounds, which are also stable in air and moisture.

As a continuation of our previous work, and to expand our knowledge of IL chemistry,<sup>10–13</sup> we synthesize a new series of ILs  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ) (1-alkyl-3-methylimidazolium perrhenate), which are all air and water stable. We have also measured the density and the surface tension of the ILs  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ) in the temperature range of  $293.15\text{--}343.15$  K. As a new concept, the ion parachor is put forward and applied to the ILs. Values of the IL's parachor are determined in terms of experimental data, and then the concept of ion parachor is calculated by two extrathermodynamic assumptions; values of ionic parachor for the corresponding cations  $[C_n\text{mim}]^+$  are calculated from the reference value of  $[\text{ReO}_4]^-$ . The ionic volume and surface properties of the ILs are estimated by extrapolation. In terms of Glasser's theory,<sup>14</sup> the lattice energy and standard entropy of the ILs were estimated. Using Kabo's method,<sup>15</sup> the molar enthalpy of vaporization,  $\Delta_f^\circ H_m^0$  (298 K), at 298 K is estimated. The interstice model is applied to calculate the thermal expansion coefficient of ILs  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ),  $\alpha$ , and the magnitude order of its calculated value is the same as the experimental one. With the interstice model, we have

deduced the enthalpy of vaporization equation, which is similar to Kabo's method, and calculated the enthalpy of vaporization and vapor pressure of ILs  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ) by the equation.

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.**  $\text{NH}_4\text{ReO}_4$  (99.5%) (From Jiangxi Copper Co. Ltd.) was refined by recrystallization and dried under reduced pressure. Ethyl acetate, acetone and acetonitrile (from Shanghai Reagent Co. Ltd.) were distilled and then stored over vacuum distilled prior to use. 1-Bromoethane, 1-bromobutane, 1-bromopentane, and 1-bromohexane (all from Shanghai Reagent Co. Ltd.) were refined by distillation and stored over molecular sieves before use.

**2.2. Preparation of ILs.** According to ref 16, 1-alkyl-3-methylimidazolium bromides ( $[C_n\text{mim}]\text{Br}$ ,  $n = 2,4,5,6$ ) were synthesized. The products were slightly yellow liquid. The yields were approximately 80%.

In our laboratories, a series of imidazolium perrhenates of  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ) have been synthesized (see Figure 1), where  $[C_2\text{mim}][\text{ReO}_4]$  is 1-ethyl-3-methylimidazolium perrhenate,  $[C_4\text{mim}][\text{ReO}_4]$  is 1-butyl-3-methylimidazolium perrhenate,  $[C_5\text{mim}][\text{ReO}_4]$  is 1-pentyl-3-methylimidazolium perrhenate, and  $[C_6\text{mim}][\text{ReO}_4]$  is 1-hexyl-3-methylimidazolium perrhenate, respectively. General preparation of ILs: The 1-alkyl-3-methylimidazolium bromide  $[C_n\text{mim}]\text{Br}$  and 1.2 equiv of  $\text{NH}_4\text{ReO}_4$  were mixed in acetone under argon and stirred at room temperature for 48 h. The slurry was then filtrated by a Gooch funnel to remove  $\text{NH}_4\text{Br}$  and residual  $\text{NH}_4\text{ReO}_4$ . Then ILs were obtained by removal of acetone, washed three times with *n*-hexane, and dried under oil pump vacuum.

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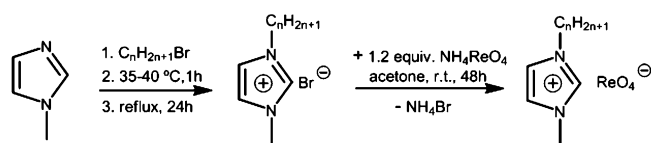


Figure 1. Synthesis of ILs  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ).

The ILs are characterized by Fourier transform infrared (FT-IR),  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis (see the Supporting Information). Raman spectra of the ILs were measured on a Microscopic Confocal Raman Spectrometer (RM2000) by Renishaw. The water content was determined by a Karl Fischer moisture titrator (ZSD-2 type), which all showed under 500 ppm. The content of  $\text{Br}^-$  was determined by dripping the silver nitrate solution, that is, taking 0.5 mL of the product to dissolve in water, and then dripping aqueous silver nitrate; no yellow deposit appeared. All of the details are in the Supporting Information, which confirm the structure of synthesized ILs.

### 2.3. Measurement of Density and Surface Tension.

The density of degassed water is measured by a Westphal balance at  $(293.15 \pm 0.05)$  K and is in good agreement with the literature<sup>17</sup> within experimental error  $\pm 0.0002 \text{ g}\cdot\text{cm}^{-3}$ . Then, the densities of the samples are measured in the temperature range of  $(293.15$  to  $343.15)$  K. The sample is placed in a cell with a jacket and is thermostatted at each temperature with an accuracy  $\pm 0.05$  K.

Using the tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.), the surface tension of water is measured at  $(293.15$  to  $343.15)$  K and is in good agreement with the literature<sup>17</sup> within experimental error  $\pm 0.1 \text{ mJ}\cdot\text{m}^{-2}$ . Then the values of surface tension of the samples are measured by the same method in the same temperature range of  $(293.15$  to  $343.15)$  K.

## 3. RESULTS AND DISCUSSION

The values of density and surface tension for the samples of  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ) are listed in Tables 1 and 2, respectively. Each value in the tables is the average of triple measurements.

Table 1. The Values of Density ( $\rho/\text{g}\cdot\text{cm}^{-3}$ ) of Pure ILs  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ) at  $293.15\text{--}343.15 \pm 0.05$  K

T/K	$[C_2\text{mim}][\text{ReO}_4]$	$[C_4\text{mim}][\text{ReO}_4]$	$[C_5\text{mim}][\text{ReO}_4]$	$[C_6\text{mim}][\text{ReO}_4]$
293.15	2.1633	1.9689	1.8563	1.7991
298.15	2.1570	1.9633	1.8508	1.7938
303.15	2.1513	1.9576	1.8453	1.7885
308.15	2.1460	1.9520	1.8399	1.7831
313.15	2.1420	1.9464	1.8344	1.7778
318.15	2.1349	1.9407	1.8289	1.7724
323.15	2.1278	1.9351	1.8235	1.7671
328.15	2.1227	1.9295	1.8180	1.7618
333.15	2.1170	1.9239	1.8125	1.7564
338.15	2.1115	1.9182	1.8070	1.7511
343.15	2.1050	1.9126	1.8016	1.7457

**3.1. The Estimation of Volumetric Properties for the ILs.** Plotting of values of  $\ln \rho$  against  $T$ , a straight line is obtained (see Figure 2) for a given IL, and its empirical linear equation is

$$\ln \rho = b - \alpha T \quad (1)$$

Table 2. The Values of Surface Tension ( $\gamma/\text{mJ}\cdot\text{m}^{-2}$ ) of pure ILs  $[C_n\text{mim}][\text{ReO}_4]$  ( $n = 2,4,5,6$ ) at  $293.15\text{--}343.15 \pm 0.05$  K

T/K	$[C_2\text{mim}][\text{ReO}_4]$	$[C_4\text{mim}][\text{ReO}_4]$	$[C_5\text{mim}][\text{ReO}_4]$	$[C_6\text{mim}][\text{ReO}_4]$
293.15	49.3	45.0	43.0	41.6
298.15	49.1	44.8	42.7	41.4
303.15	48.8	44.6	42.5	41.0
308.15	48.5	44.3	42.2	40.8
313.15	48.2	44.0	41.9	40.4
318.15	47.9	43.7	41.6	40.1
323.15	47.5	43.3	41.3	39.8
328.15	47.2	42.9	40.8	39.4
333.15	46.9	42.7	40.6	39.2
338.15	46.6	42.4	40.3	38.9
343.15	46.2	42.0	40.0	38.7

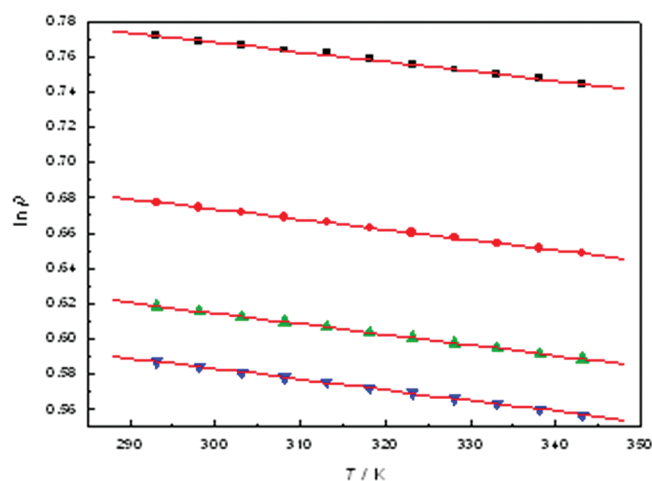


Figure 2. The plot of  $\ln \rho$  versus  $T$  for ILs  $[C_n\text{mim}][\text{ReO}_4]$ . ■  $[C_2\text{mim}][\text{ReO}_4]$ :  $\ln \rho = 0.93084 - 5.427 \times 10^{-4} T$ ,  $r = 0.999$ ,  $s = 3.63 \times 10^{-4}$ . ●  $[C_4\text{mim}][\text{ReO}_4]$ :  $\ln \rho = 0.84762 - 5.802 \times 10^{-4} T$ ,  $r = 0.999$ ,  $s = 0.41 \times 10^{-4}$ . ▲  $[C_5\text{mim}][\text{ReO}_4]$ :  $\ln \rho = 0.7940 - 5.982 \times 10^{-4} T$ ,  $r = 0.999$ ,  $s = 0.44 \times 10^{-4}$ . ▼  $[C_6\text{mim}][\text{ReO}_4]$ :  $\ln \rho = 0.76402 - 6.026 \times 10^{-4} T$ ,  $r = 0.999$ ,  $s = 0.44 \times 10^{-4}$ .

where  $b$  is an empirical constant, the negative value of slope,  $\alpha = -(\partial \ln \rho / \partial T)_p$ , is the thermal expansion coefficient of the IL  $[C_n\text{mim}][\text{ReO}_4]$ , and values of  $\alpha$  are listed in Table 8 as the experimental ones (Exp.). Correlation coefficients of all linear fitting of  $\ln \rho$  versus  $T$  are larger than 0.99, and standard deviations of the fitted lines are within experimental error.

The molecular volume,  $V_m$ , of ILs  $[C_n\text{mim}][\text{ReO}_4]$  is the sum of the cation volume and anion volume. The value of  $V_m$  is calculated using the following equation:

$$V_m = M / (N \cdot \rho) \quad (2)$$

where  $M$  is molar mass of ILs, and  $N$  is the Avogadro constant. The values of  $V_m$  calculated using eq 2 are listed in Table 3. Plotting  $V_m$  against the number ( $n$ ) of carbons in alkyl chain of ILs  $[C_n\text{mim}][\text{ReO}_4]$ , a good straight line is obtained ( $V_m = 0.2219 + 0.0273n$ , with the standard deviation of the fitted line  $s = 2.7 \times 10^{-3}$  and the correlation coefficient  $r = 0.99$ ) and its slope,  $0.0273 \text{ nm}^3$ , is a mean contribution of per methylene ( $-\text{CH}_2-$ ) to the molecular volume and is in good agreement with  $0.0275 \text{ nm}^3$  from the ILs  $[C_n\text{-mim}][\text{BF}_4]$  and  $[C_n\text{-mim}][\text{NTf}_2]$ .<sup>14</sup>

According to Glasser's theory,<sup>14</sup> the estimated values of the standard entropy,  $S^0(298)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , for ILs using eq 3 are listed in Table 3.

**Table 3. The Values of Volume Properties and Surface Properties of ILs  $[\text{C}_n\text{mim}][\text{ReO}_4]$  ( $n = 2, 4, 5, 6$ ) at 298.15 K<sup>a</sup>**

IL	$V_m/\text{nm}^3$	$S^0/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$10^3 S_a/\text{mJ}\cdot\text{K}^{-1}\cdot\text{m}^{-2}$	$E_a/\text{mJ}\cdot\text{m}^{-2}$	$U_{\text{POT}}/\text{kJ}\cdot\text{mol}^{-1}$
$[\text{C}_2\text{mim}][\text{ReO}_4]$	0.2772	376.0	62.7	67.8	463
$[\text{C}_4\text{mim}][\text{ReO}_4]$	0.3282	439.7	61.5	63.1	444
$[\text{C}_5\text{mim}][\text{ReO}_4]$	0.3606	480.3	61.3	61.0	433
$[\text{C}_6\text{mim}][\text{ReO}_4]$	0.3850	510.8	60.5	59.5	426

<sup>a</sup> $S_a$  is the surface excess entropy, and  $E_a$  is the surface excess energy, which will be mentioned in section 3.3.

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

Also, the contribution of the per methylene group to the standard entropy  $S^0(298)$  of the ILs can be calculated directly by eq 3 as  $0.0273 \times 1246.5 = 34.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . This value is in agreement with the value of  $33.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  from  $[\text{C}_n\text{mim}][\text{BF}_4]$ .<sup>14</sup>

The crystal energy,  $U_{\text{POT}}$ , of ILs may be estimated in terms of Glasser's empirical equation:<sup>14</sup>

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

The values of  $U_{\text{POT}}$  are obtained and listed in Table 3. From Table 3, it is shown that crystal energies of  $[\text{C}_n\text{mim}][\text{ReO}_4]$  are much less than that of inorganic fused salts; for example,  $U_{\text{POT}} = 613 \text{ kJ}\cdot\text{mol}^{-1}$  for fused CsI,<sup>17</sup> which has the least crystal energy among alkali halides. The low crystal energy is the underlying reason for forming ILs at room temperature.

**3.2. Ion Parachor of ILs.** According to the definition of parachor,  $P$ ,

$$P = (M\gamma^{1/4})/\rho \quad (5)$$

where  $\gamma$  is surface tension,  $M$  is molar mass, and  $\rho$  is density of a substance. The experimental values,  $P_{\text{ex}}$ , of the IL  $[\text{C}_n\text{mim}][\text{ReO}_4]$  parachor calculated by eq 5 are listed in Table 4.

**Table 4. The Values of of Ionic Parachor for  $[\text{C}_n\text{mim}]^+$  and the Anions**

	$M_+/g\cdot\text{mol}^{-1}$	$P_{\text{Ex}}$	$P_-$ of $[\text{ReO}_4]^-$	$P_+$ of $[\text{C}_n\text{mim}]^+$
$[\text{C}_2\text{mim}][\text{ReO}_4]$	111.2	443.2	157.5	291.2
$[\text{C}_4\text{mim}][\text{ReO}_4]$	139.2	512.8	156.4	360.8
$[\text{C}_5\text{mim}][\text{ReO}_4]$	153.2	556.8	157.0	404.8
$[\text{C}_6\text{mim}][\text{ReO}_4]$	167.2	589.9	154.7	437.9
$[\text{ReO}_4]^-$	250.2	147.6	$156.4 \pm 1.2$	-

In the absence of sufficient data of parachor contribution values for ions, Deetlefs et al.<sup>18</sup> considered that the parachor of ILs may be calculated using neutral parachor contribution values<sup>19</sup> so that parachor may become as a tool to predict the physical properties of ILs. However, the parachors calculated using neutral contribution data do not account for Coulombic interaction in the ILs, which were not accurate. Therefore, ionic parachor was proposed as a new concept, that is, ions composed of ILs can be seen as independent descriptors of

parachor. Ionic parachor,  $P_i$ , can be defined with the following equation:

$$P_i = (M_i\gamma^{1/4})/\rho = \gamma^{1/4}V_i \quad (6)$$

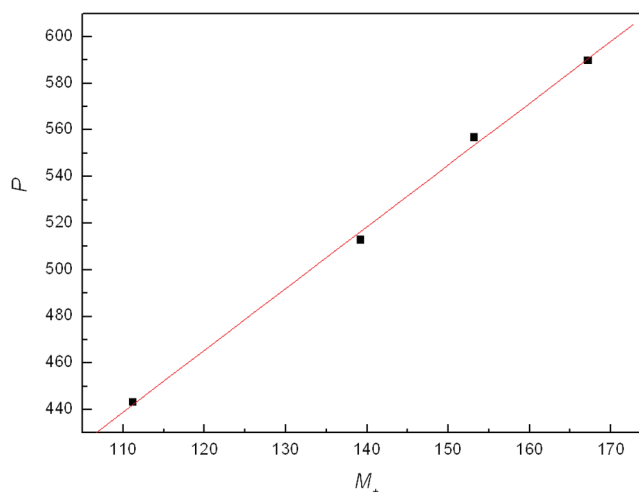
where  $M_i$  is the molar mass of an ion, and  $V_i$  is the molar volume of an ion in the IL. According to the additivity, the parachor value of an IL is equal to the sum of the corresponding cationic and anionic parachor:

$$P = P_+ + P_- \quad (7)$$

where  $P_+$  and  $P_-$  are the ionic parachors of cations and anions, respectively. Now, the key question is how the experimental values of parachor for an IL are divided into the corresponding values of individual positive and negative ions. Therefore, two extrathermodynamic assumptions were recommended. One of them is the extrapolation method, applied to the IL homologue.<sup>20</sup> This is application of eq 8:

$$P = P_- + (M_+\gamma^{1/4})/\rho \quad (8)$$

$M_+$  is the molar mass of the cation, and values of  $M_+$  for  $[\text{C}_n\text{mim}]^+$  are listed in Table 4. According to eq 8, the values of IL  $P$  were plotted against  $M_+$  so that a good straight line was obtained (Figure 3) with the correlation coefficients,  $r = 0.999$ ,



**Figure 3.** Plot of the parachor vs  $M_+$  of ILs  $[\text{C}_n\text{mim}][\text{ReO}_4]$  ( $P = 147.6 + 2.6492M_+$ , with  $s = 3.56$  and  $r = 0.999$ ).

and the standard deviation of the fitted lines,  $s = 3.56$ . The intercept,  $P_- = 147.6$ , of the straight line was the value of the ionic parachor of the anion  $[\text{ReO}_4]^-$ , which is consistent with the result of the other recommended extrathermodynamic assumption. This assumption is proposed as eq 9:

$$\begin{aligned} V_-(\text{Crystal})/V_+(\text{Crystal}) &= V_-(\text{IL})/[V(\text{IL}) - V_-(\text{IL})] \\ &= P_-(\text{IL})/[P(\text{IL}) - P_-(\text{IL})] \end{aligned} \quad (9)$$

where  $V_+(\text{Crystal})$  and  $V_-(\text{Crystal})$  are the corresponding cationic and anionic volumes derived from crystal structures, respectively;  $V_-(\text{IL})$  is the molar volume of the corresponding anion in IL,  $V(\text{IL})$  is the molar volume of the IL,  $P_-(\text{IL})$  is the parachor of the corresponding anion, and  $P(\text{IL})$  is the experimental value of the parachor for the IL. If the values of  $V_+(\text{Crystal})$  and  $V_-(\text{Crystal})$  may be obtained, the ionic parachor of cation and anion can be determined with eq 7. For ease of use, the

values of ionic volume<sup>23</sup> derived from crystal structures for the involved ions in this work are listed in Table 5. In terms of eq 7

**Table 5. Ionic Volumes Derived from Crystal Structures for Ions (nm<sup>3</sup>)**

cation	$V_+/nm^3$	anion	$V_-/nm^3$
[C <sub>2</sub> mim] <sup>+</sup>	0.156 ± 0.018	Ala <sup>-</sup>	0.094 ± 0.018
[C <sub>3</sub> mim] <sup>+</sup>	0.178 ± 0.028	BF <sub>4</sub> <sup>-</sup>	0.073 ± 0.028
[C <sub>4</sub> mim] <sup>+</sup>	0.196 ± 0.021	Gly <sup>-</sup>	0.125 ± 0.021
[C <sub>5</sub> mim] <sup>+</sup>	0.219 ± 0.015	AlCl <sub>4</sub> <sup>-</sup>	0.203 ± 0.015
[C <sub>6</sub> mim] <sup>+</sup>	0.242 ± 0.015	ReO <sub>4</sub> <sup>-</sup>	0.086 ± 0.013

and the experimental parachor for [C<sub>*n*</sub>mim][ReO<sub>4</sub>], the values of ionic parachor for [ReO<sub>4</sub>]<sup>-</sup> can be calculated using the values of [C<sub>*n*</sub>mim]<sup>+</sup>  $V_+$ (Crystal) and the average of [ReO<sub>4</sub>]<sup>-</sup> is obtained,  $P_- = 156.4 \pm 1.2$ , which are listed at the bottom of column  $P_-$  of [ReO<sub>4</sub>]<sup>-</sup> in Table 4.

In order to obtain the reference value of the ionic parachor of [ReO<sub>4</sub>]<sup>-</sup>,  $P_- = 152.0$  is the mean from the two assumptions. Using the reference value of [ReO<sub>4</sub>]<sup>-</sup>  $P_-$ , the ionic parachor of cations [C<sub>*n*</sub>mim]<sup>+</sup> were calculated and are listed in the column  $P_+$  of [C<sub>*n*</sub>mim]<sup>+</sup> in Table 4. Fitting ionic parachors of [C<sub>*n*</sub>mim]<sup>+</sup> in Table 4 versus  $n$  ( $n$  is number of carbons in the alkyl chains of the [C<sub>*n*</sub>mim]<sup>+</sup>), a good linear empirical equation,  $P_+ = 216.0 + 37.1n$ , was obtained with correlation coefficient,  $r = 0.999$ , and standard deviation of the fitted lines,  $s = 3.56$ . The slope, 37.1, is a mean contribution of per methylene (-CH<sub>2</sub>-) and in good agreement with 37.5 obtained by Fang<sup>20</sup> within experimental error. In addition, the values of [C<sub>*n*</sub>mim]<sup>+</sup> can be used to predict values of the parachors of other anion. For example,  $\gamma$  (mJ m<sup>-2</sup>) = 39.6,<sup>21</sup>  $\rho = 1.12749$  g cm<sup>-3</sup>,<sup>22</sup>  $P = 536.4$  for IL [C<sub>5</sub>mim][BF<sub>4</sub>], and using  $P_+ = 404.8$  of [C<sub>5</sub>mim]<sup>+</sup> the ionic parachor of anion [BF<sub>4</sub>]<sup>-</sup> was obtained, that is,  $P_- = 131.6$ . If the extrathermodynamic assumption was used directly, that is, eq 7, the ionic parachor of anion [BF<sub>4</sub>]<sup>-</sup> was 134.1, and  $P_+ = 402.3$  for [C<sub>5</sub>mim]<sup>+</sup>. In view of the above fact, the value of the ionic parachor has certain rationality.

In terms of the ionic parachor values of [ReO<sub>4</sub>]<sup>-</sup>, the predicted values of parachor and surface tension for the ILs are listed in Table 6. In Table 6,  $\Delta P$  means the difference between the experimentally determined and corresponding estimated parachor for the ILs, that is,  $\Delta P = P_{Ex} - P_{Est}$ . As can be seen from Figure 4, all the values are fitted well.

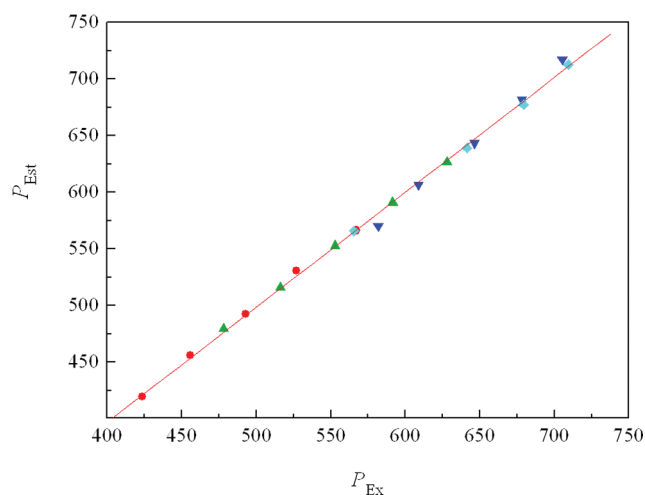
### 3.3. The Estimation of Surface Properties for the ILs.

The experimental values of  $\gamma$  for given [C<sub>*n*</sub>mim][ReO<sub>4</sub>] have been fitted against  $T$  by the least-squares method to a linear equation and several good straight lines were obtained with all correlation coefficients of the fitting being larger than 0.99 and the standard deviations of the fitted lines being within experimental error. (See Figure 5).

From the slopes of fitting lines, values of the surface excess entropy,  $S_a$ , are obtained and are listed in Table 3. In addition, the values of the surface excess energy  $E_a$  likewise may be obtained from the surface tension:  $E_a = \gamma - T(\partial\gamma/\partial T)_p$  at 298.15 K and are also listed in Table 3. In comparison with fused salts, for example,  $E_a = 146$  mJ·m<sup>-2</sup> for fused NaNO<sub>3</sub>, the values of  $E_a$  for [C<sub>*n*</sub>mim][ReO<sub>4</sub>] are much lower and are close to that of organic liquids, for example, 67 mJ·m<sup>-2</sup> for benzene and 51.1 mJ·m<sup>-2</sup> for *n*-octane.<sup>17</sup> This fact shows that interaction energy between ions in the ILs [C<sub>*n*</sub>mim][ReO<sub>4</sub>] is much less than that in inorganic fused salts because the surface excess energy is dependent on the interaction energy between ions,

**Table 6. Parachors and Surface Tensions of the Investigated ILs**

[C <sub><i>n</i></sub> mim]X	[C <sub><i>n</i></sub> mim][ReO <sub>4</sub> ]					
	$P_{Ex}$	$P_{Est}$	$\Delta P$	$\gamma_{Ex}$	$\gamma_{Est}$	$\Delta\gamma$
[C <sub>2</sub> mim]X	443.2	446.6	-3.4	49.1	50.6	-1.5
[C <sub>3</sub> mim]X						
[C <sub>4</sub> mim]X	512.8	517.2	-4.4	44.8	46.4	-1.8
[C <sub>5</sub> mim]X	556.8	557.9	-1.1	42.7	43.0	-0.3
[C <sub>6</sub> mim]X	589.9	595.0	-5.1	41.4	42.8	-1.4
[C <sub><i>n</i></sub> mim]X	[C <sub><i>n</i></sub> mim][NTf <sub>2</sub> ]					
	$P_{Ex}$	$P_{Est}$	$\Delta P$	$\gamma_{Ex}$	$\gamma_{Est}$	$\Delta\gamma$
[C <sub>2</sub> mim]X	628.8	621.1	7.7	35.8	34.1	1.7
[C <sub>3</sub> mim]X	657.0	657.0	0.0	32.9	32.9	0.0
[C <sub>4</sub> mim]X	692.9	693.1	-0.2	32.0	32.0	0.0
[C <sub>5</sub> mim]X	722.5	728.9	-6.4	30.1	31.2	-1.1
[C <sub>6</sub> mim]X	762.8	764.1	-1.3	30.2	30.4	-0.2
[C <sub><i>n</i></sub> mim]X	[C <sub><i>n</i></sub> mim][Ala]					
	$P_{Ex}$	$P_{Est}$	$\Delta P$	$\gamma_{Ex}$	$\gamma_{Est}$	$\Delta\gamma$
[C <sub>2</sub> mim]X	479.0	482.3	-3.3	52.7	54.2	-1.5
[C <sub>3</sub> mim]X	516.9	518.2	-1.3	50.1	50.6	-0.5
[C <sub>4</sub> mim]X	553.4	554.3	-0.9	47.7	48.0	-0.3
[C <sub>5</sub> mim]X	592.4	590.1	2.3	46.0	45.3	0.7
[C <sub>6</sub> mim]X	628.6	625.3	3.3	43.4	42.5	0.9
[C <sub><i>n</i></sub> mim]X	[C <sub><i>n</i></sub> mim][GaCl <sub>4</sub> ]					
	$P_{Ex}$	$P_{Est}$	$\Delta P$	$\gamma_{Ex}$	$\gamma_{Est}$	$\Delta\gamma$
[C <sub>2</sub> mim]X	565.6	568.3	-2.7	44.6	45.5	-0.9
[C <sub>3</sub> mim]X						
[C <sub>4</sub> mim]X	641.3	640.3	1.0	45.1	44.8	0.3
[C <sub>5</sub> mim]X	679.5	676.1	3.4	43.1	42.3	0.8
[C <sub>6</sub> mim]X	709.7	711.3	-1.6	40.4	40.8	-0.4



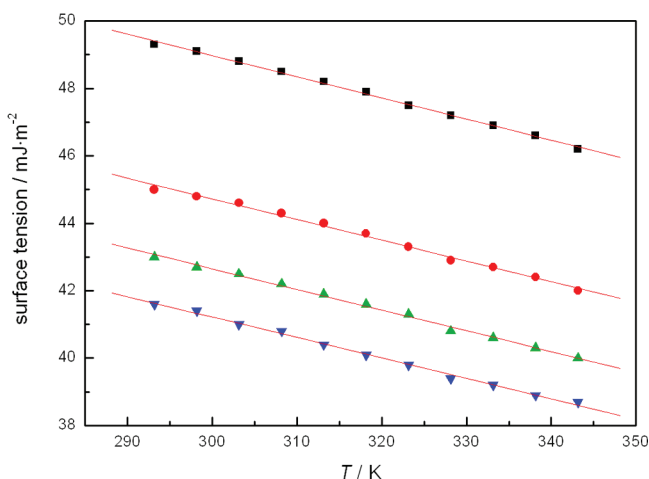
**Figure 4.** Plot of the estimated parachor for ILs [C<sub>*n*</sub>mim]([ReO<sub>4</sub>], [Ala], [NTf<sub>2</sub>], [GaCl<sub>4</sub>]) versus their experimental values.  $P_{Est} = 6.16659 + 0.991P_{Ex}$ ,  $s = 3.5$ ,  $r = 0.99$ . ● [C<sub>*n*</sub>mim][ReO<sub>4</sub>] ( $n = 2, 4-6$ ); ▲ [C<sub>*n*</sub>mim][Ala] ( $n = 2-6$ ); ▼ [C<sub>*n*</sub>mim][NTf<sub>2</sub>] ( $n = 2-6$ ); ◆ [C<sub>*n*</sub>mim][GaCl<sub>4</sub>] ( $n = 2, 4-6$ ).

that is, the crystal energy of ILs [C<sub>*n*</sub>mim][ReO<sub>4</sub>] is much less than that of inorganic fused salts.

In general, surface tension,  $\gamma$ , of many liquid almost linearly decreases while temperature elevates, and the relationship is expressed in the Eötvös equation:<sup>23</sup>

$$\gamma V^{2/3} = k(T_c - T) \quad (10)$$





**Figure 5.** Plot of surface tension versus  $T$  for ILs  $[C_n\text{mim}][\text{ReO}_4]$ . ■  $[C_2\text{mim}][\text{ReO}_4]$ :  $\gamma=67.79-0.06273T$ ,  $r=0.99$ ,  $s=0.0527$ ; ●  $[C_4\text{mim}][\text{ReO}_4]$ :  $\gamma=63.16-0.06145T$ ,  $r=0.99$ ,  $s=0.0839$ ; ▲  $[C_3\text{mim}][\text{ReO}_4]$ :  $\gamma=61.03-0.06127T$ ,  $r=0.99$ ,  $s=0.0675$ ; ▼  $[C_6\text{mim}][\text{ReO}_4]$ :  $\gamma=59.38-0.06055T$ ,  $r=0.99$ ,  $s=0.0629$ .

where  $V$  is the molar volume of the liquid,  $T_c$  is the critical temperature, and  $k$  is an empirical constant. The linear regression of the product of  $\gamma$  and  $V^{2/3}$  obtained from this experiment against absolute temperature  $T$  was made, and a good straight line was obtained. The correlation coefficients of the linear regression were all over 0.99. From the slope of the straight line, the values of  $k$  obtained from 1.390 to 1.694 and from the intercept  $T_c$  (critical temperature) were obtained, respectively. For the majority of organic liquids,  $k$  is about  $2.1 \times 10^{-7} \text{ J}\cdot\text{K}^{-1}$ , but for fused salts with large polarity, it is rather small, for example,  $k = 0.4 \times 10^{-7} \text{ J}\cdot\text{K}^{-1}$  for fused  $\text{NaCl}$ ;<sup>23</sup> therefore, the magnitude of  $k$  can represent the polarity of the IL. The value of  $k$  implies that  $[C_n\text{mim}][\text{ReO}_4]$  has medium polarity between organic liquid and fused salt.

**3.4. The Interstice Model for the ILs.** For pure IL, a new theoretic model,<sup>4</sup> the expression of calculation of interstice volume,  $\nu$ , was obtained on the classical statistical mechanics:

$$\nu = 0.6791(k_b T / \gamma)^{3/2} \quad (11)$$

where  $k_b$  is the Boltzmann constant,  $T$  is the thermodynamic temperature, and  $\gamma$  is the surface tension of IL. According to eq 11, the values of the average volume of the interstices of ILs at different temperatures are obtained, which were listed in Table 8.

The molar volume of the interstice,  $\sum \nu = 2N\nu$ , and the volume fractions of interstice,  $\sum \nu / V$ , are between 11.02% and 11.85%. This is in good agreement with that of the majority of materials that exhibit 10–15% volume expansion in the process from the solid to liquid state. This result means that the interstice model is reasonable.

The volume of ILs,  $V$ , consists of the inherent volume,  $V_i$ , and total volume of all the interstices, that is,

$$V = V_i + 2N\nu \quad (12)$$

If the expansion of IL volume only results from the expansion of the interstices when temperature increases, then the calculation expression of thermal expansion coefficients,  $\alpha$ , was derived from the interstice model:

$$\alpha = (1/V)(\partial V / \partial T)_p = 3N\nu / VT \quad (13)$$

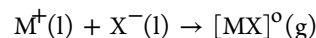
**Table 7.** The Molar Enthalpy of Vaporization,  $\Delta_1^g H_m^0$  (298 K), and  $\Delta_1^g H_m^0(T_b)$  for ILs  $[C_n\text{mim}][\text{ReO}_4]$

IL	$10^7 k / \text{J}\cdot\text{K}^{-1}$	$T_c / \text{K}$	$T_b / \text{K}$	$\Delta_1^g H_m^0(T_b) / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_1^g H_m^0(298 \text{ K}) / \text{kJ}\cdot\text{mol}^{-1}$	parachor
$[C_2\text{mim}][\text{ReO}_4]$	1.390	1371	823	74.0	143.6	443.2
$[C_4\text{mim}][\text{ReO}_4]$	1.528	1296	777	70.0	146.6	512.8
$[C_3\text{mim}][\text{ReO}_4]$	1.632	1247	748	67.3	148.7	556.8
$[C_6\text{mim}][\text{ReO}_4]$	1.694	1221	733	65.9	150.6	589.9

The values of  $\alpha$  (calculated) calculated using eq 13 and of corresponding experimental values,  $\alpha$  (experimental), for ILs  $[C_n\text{mim}][\text{ReO}_4]$  at 298.15 K are listed in Table 6. From Table 6, we can use “Comparison of  $\alpha$ /%” (which defines as:  $[\alpha(\text{experimental}) - \alpha(\text{calculated})] / \alpha(\text{experimental}) \times 100\%$ ) showing the difference of the two values, the magnitude order of  $\alpha$  (calculated) are in good agreement with  $\alpha$  (experimental), so that this result means that the interstice model is reasonable.

**3.5. Estimating Enthalpy of Vaporization by Interstice Model.** According to the interstice model, because of the large size and the asymmetric shape, the ions may not be closely packed, and lots of interstices of ions come into existence. In order to calculate the volume easily, the interstice is regarded as a bubble. There are  $2N$  interstices for 1 mol of 1:1 IL, where  $N$  is the Avogadro number. The interstice in ILs can move about like an ion or other particles; in the movement the interstice does not vanish, but can be compressed and expanded, which has an extra feature of motion of an interstice called the breathing motion.

When the IL (cation:anion = 1:1)  $\text{MX}(l)$  evaporates to gas, cation, and anion form ion-pair  $[\text{MX}]^o(g)$ :



If we consider that the ion-pair  $[\text{MX}]^o(g)$  is caused by interstice partly expanding from liquid IL  $\text{MX}(l)$ , then the interstice potential energy is almost zero at infinity volume by  $E_q = (P_i - P_0)(4/3)\pi r^3 + 4\pi r^2 \gamma$ . The enthalpy of vaporization of IL,  $\Delta_1^g H_m^0$ , is

$$\Delta_1^g H_m^0 = \varepsilon N E_q = 4\pi r^2 \gamma \varepsilon N + (P_i - P_0)(4/3)\pi r^3 \varepsilon N \quad (14)$$

where  $\varepsilon$  is the cracking interstice coefficient. When the interstice in IL is very small ( $r < 10^{-5} \text{ cm}$ ),  $4\pi r^2 \gamma N \gg (P_i - P_0)(4/3)\pi r^3 N$ , so the constant  $B = (P_i - P_0)(4/3)\pi r^3 \varepsilon N$ .

$$4\pi r^2 \gamma \varepsilon N = (36\pi)^{1/3} \nu^{2/3} \gamma \varepsilon N \quad (15)$$

$l$  is the interspace ratio of the IL to 1:1-type IL:

$$l = 2N\nu / V \quad (16)$$

where  $V$  is the molar volume of the IL,

$$\nu = lV / 2N \quad (17)$$

then

$$\begin{aligned} 4\pi r^2 \gamma \varepsilon N &= (36\pi)^{1/3} (lV / 2N)^{2/3} \gamma \varepsilon N \\ &= (36\pi)^{1/3} \varepsilon (l/2)^{2/3} (\gamma V^{2/3} N^{1/3}) \end{aligned} \quad (18)$$

So we obtain

$$\begin{aligned} \Delta_1^g H_m^0(298 \text{ K}) &= (36\pi)^{1/3} \varepsilon (l/2)^{2/3} (\gamma V^{2/3} N^{1/3}) \\ &\quad + (P_i - P_0)(4/3)\pi r^3 \varepsilon N \end{aligned} \quad (19)$$

Table 8. The Parameters of the Interstice Model for ILs, [C<sub>n</sub>mim][ReO<sub>4</sub>], at 298.15 K

IL	10 <sup>-24</sup> v/cm <sup>3</sup>	∑v/cm <sup>3</sup>	V/cm <sup>3</sup> .mol <sup>-1</sup>	10 <sup>2</sup> ∑v/V	10 <sup>4</sup> α/K <sup>-1</sup> (Cal)	10 <sup>4</sup> α/K <sup>-1</sup> (Ex)	comparison of α/%
[C <sub>2</sub> mim][ReO <sub>4</sub> ]	16.48	19.85	167.4	11.85	5.97	5.43	-9.95
[C <sub>4</sub> mim][ReO <sub>4</sub> ]	18.91	22.77	198.2	11.49	5.78	5.80	0.34
[C <sub>5</sub> mim][ReO <sub>4</sub> ]	20.33	24.47	217.8	11.23	5.65	5.98	5.47
[C <sub>6</sub> mim][ReO <sub>4</sub> ]	21.29	25.64	232.6	11.02	5.55	6.03	7.93

Kabo put forward a method of estimating vaporization heat  $\Delta_f^s H_m^0$  (298 K) and interspace in ILs:

$$\Delta_f^s H_m^0(298\text{K}) = A(\gamma V^{2/3} N^{1/3}) + B \quad (20)$$

In comparison, we can obtain

$$A = (36\pi)^{1/3} \epsilon(1/2)^{2/3} \quad (21)$$

$$B = (P_i - P_0)(4/3)\epsilon\pi r^3 N \quad (22)$$

where  $N$  is Avogadro's constant, and  $A$  and  $B$  are empirical constants,  $A = 0.01121$  and  $B = 2.4 \text{ kJ}\cdot\text{mol}^{-1}$ .

The molar enthalpies of vaporization for IL [C<sub>n</sub>mim]-[ReO<sub>4</sub>] calculated from eq 20 are listed in Table 7.

This table implies that the estimated enthalpy of vaporization of ILs decreases with the length of aliphatic chains in the 1-alkyl-3-methylimidazolium cation and it can be interpreted considering that longer side chains decrease the relative importance of Coulomb forces leading to smaller values of  $\Delta_f^s H_m^0$ .

Rebello et al.<sup>24</sup> put forward a method of estimating the hypothetical temperature of normal boiling point (NBP) of ILs,  $T_b$ , in terms of critical temperature,  $T_c$ . They thought that the relationship between  $T_b$  and  $T_c$  was  $T_b \approx 0.6T_c$  for ILs. The molar enthalpy of vaporization for the ILs at NBP,  $\Delta_f^s H_m^0(T_b)$ , can be estimated by the Trouton constant ( $\approx 90 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ). According to Rebello's method, the predicted values of  $\Delta_f^s H_m^0(T_b)$  of the ILs [C<sub>n</sub>mim][ReO<sub>4</sub>] are also listed in Table 4. From Table 7, the difference between  $\Delta_f^s H_m^0(T_b)$  estimated using Rebello's method and  $\Delta_f^s H_m^0(298 \text{ K})$  estimated using Kabo's method is very large. This is because of the heat capacity difference between the liquid and gas phases at different temperatures.<sup>22-25</sup>

#### 4. CONCLUSION

In summary, a series of 1-alkyl-3-methylimidazolium perchlorate ILs showing similar properties to conventional ILs are synthesized and characterized. In terms of Glasser's theory, the standard molar entropy and lattice energy of the ILs are calculated, respectively. Using Kabo's method, the molar enthalpy of vaporization of the IL,  $\Delta_f^s H_m^0(298 \text{ K})$ , at 298 K is estimated. As a new concept, the ion parachor is put forward and applied to the ILs. The ionic volume and surface properties of the ILs are estimated by extrapolation. The interstice model is applied to calculate the thermal expansion coefficient of ILs [C<sub>n</sub>mim][ReO<sub>4</sub>] ( $n = 2,4,5,6$ ),  $\alpha$ , and the magnitude order of its value calculated is the same as the experimental one. With the interstice model, we have deduced the enthalpy of vaporization equation, which is similar to Kabo's method, and calculated the enthalpy of vaporization and vapor pressure of ILs [C<sub>n</sub>mim][ReO<sub>4</sub>] ( $n = 2,4,5,6$ ) by the equation.

#### ASSOCIATED CONTENT

##### Supporting Information

Additional details as described in the text. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Notes

The authors declare no competing financial interest.

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