



# A new theoretical model – The ionic molar surface Gibbs free energy and its application



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## ABSTRACT

Three novel ether-functionalized ionic liquids (ILs) 1-ethyl-3-(2-methoxyethyl)-imidazolium acetate, [C<sub>2</sub>2O1IM][OAc], 1-ethyl-3-(2-methoxyethyl)-imidazolium thiocyanate, [C<sub>2</sub>2O1IM][SCN], 1-ethyl-3-(2-methoxyethyl)-imidazolium trifluoromethanesulfonate, [C<sub>2</sub>2O1IM][TfO], and two ILs 1-ethyl-3-(2-methoxyethyl)-imidazolium dicyanamide, [C<sub>2</sub>2O1IM][DCA], 1-ethyl-3-(2-methoxyethyl)-imidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>2</sub>2O1IM][NTF<sub>2</sub>] were prepared and characterized. Their density and surface tension were measured at  $T = (298.15–338.15)$  K. As a new theoretical model, the ionic molar surface Gibbs free energy,  $g_i$ , was put forward. The ionic molar surface Gibbs free energy,  $g_{-}$ , for [BF<sub>4</sub>]<sup>-</sup>, which was as reference ion, was obtained in terms of the extrathermodynamic assumptions so that the ionic molar surface Gibbs free energy,  $g_{+}$ , of the corresponding cations, [C<sub>n</sub>mim]<sup>+</sup> ( $n = 2–6$ ), were determined. In terms of the  $g_{+}$  values of [C<sub>n</sub>mim]<sup>+</sup> ( $n = 2–6$ ), the  $g_{-}$  values of 12 kinds of anions were determined and then the average  $g_{+}$  value of [C<sub>2</sub>2O1IM]<sup>+</sup> ( $9.52 \pm 0.21$  kJ·mol<sup>-1</sup>) was gotten. By using the values of these  $g_i$ , the predicted values of molar surface Gibbs free energy,  $g_{est}$ , and surface tension,  $\gamma_{est}$ , for [C<sub>2</sub>2O1IM][X] ( $X = OAc, SCN, DCA, TfO, NTF_2$ ) and other 45 ionic liquids were estimated. In comparison, the predicted values correlated quite well with their matching experimental values.

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## 1. Introduction

Ionic liquids have been envisaged as promising materials for several technological applications, including their use as solvent and/or catalyst in organic synthesis [1,2], gases and/or green house gas absorbers [3–8], and electrolytes for batteries and/or supercapacitors [9–13]. In most cases, the required viscosity of ILs should be as low as possible [14–16]. Incorporating an ether group with electron-donating effect can decrease melting point and viscosity of ILs [17]. So, the data of physicochemical properties of ether-functionalized ionic liquids is indispensable for their research and application. Five ILs [C<sub>2</sub>2O1IM][X] ( $X = OAc, SCN, DCA, TfO, NTF_2$ ) (hereinafter called these five ILs) with low viscosity are designed and synthesized, three of which [the ILs [C<sub>2</sub>2O1IM][X] ( $X = OAc, TfO, SCN$ )] are synthesized for the first time. The physicochemical properties of these five ILs are investigated.

Recently, it can be found in literature that a trend toward the estimation of the physicochemical properties of compounds by

semi-empirical methods, in particular, for ILs. Fu et al. [18] and Zhang et al. [19] have successfully proposed a model, which correctly captures the effects of temperature, mass fraction of ILs on the surface tension for aqueous solutions of IL and the calculated results agree well with the experimental ones. The estimated result is commended because it provides valuable insight into the origins of the behavior of the materials. Among all the semi-empirical methods, molar surfaces Gibbs free energy is the best one. Although the majority of molar surfaces Gibbs free energy studies have focused on uncharged compounds [20,21], our group has applied the molar surfaces Gibbs free energy to ILs [22,23] and proposed a new theoretical model—ionic molar surfaces Gibbs free energy,  $g_i$ , which is regarded as an independent descriptor obtained by the extrathermodynamic assumption. With the data of ionic molar surfaces Gibbs free energy,  $g_i$ , the molar surfaces Gibbs free energy and relevant properties of ionic liquids can be predicted without synthesis.

In order to illustrate the model of ionic molar surfaces Gibbs free energy and its application, this paper reports the new results as follows: (1) Three novel ether-functionalized ionic liquid(IL) [C<sub>2</sub>2O1IM][X] ( $X = OAc, TfO, SCN$ ) and two IL [C<sub>2</sub>2O1IM][X] ( $X = DCA, NTF_2$ ) are prepared and proved by <sup>1</sup>H-NMR spectrum,

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$^{13}\text{C}$ -NMR spectrum, element analysis and ESI mass spectra; (2) The determination of densities,  $\rho$ , and surface tensions,  $\gamma$ , of these five ILs at  $T = (298.15\text{--}338.15)$  K. Since  $[\text{C}_2\text{2O1IM}][\text{X}]$  ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}$ ) are hydrophilic ionic liquid, they can form strong hydrogen bonds with water and small amounts of water as the main impurity are difficult to be removed by conventional methods. In order to eliminate the effect of the impurity of water, the standard addition method (SAM) is applied to these measurements; (3) The volume properties of these five ILs are discussed and the molar surface Gibbs free energy,  $g$ , are calculated; (4) As a new theoretical model, ionic molar surface Gibbs free energy,  $g_i$ , is put forward. The values of molar surfaces Gibbs free energy,  $g$ , are divided into ionic molar surfaces Gibbs free energy,  $g_i$ , using the extrathermodynamic assumption. (5) With the new theoretical model, the values of molar surfaces Gibbs free energy,  $g_{\text{est}}$ , for 50 ionic liquids are estimated so that the values of surface tension of these ILs are predicted by  $g_{\text{est}}$ .

## 2. Experimental

### 2.1. Preparation of IL $[\text{C}_2\text{2O1IM}][\text{X}]$ ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}, \text{NTF}_2$ )

The scheme shows the synthetic route (Scheme 1).

The synthesis and characterizations of ILs  $[\text{C}_2\text{2O1IM}][\text{X}]$  ( $\text{X} = \text{OAC}, \text{TfO}, \text{SCN}, \text{DCA}, \text{NTF}_2$ ) are in Supporting information. The purity of these five IL is more than 0.99.

### 2.2. Measurement of densities, $\rho$ , and surface tensions, $\gamma$ , of $[\text{C}_2\text{2O1IM}][\text{X}]$ ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}, \text{NTF}_2$ )

It is scarcely possible to remove any water in  $[\text{C}_2\text{2O1IM}][\text{X}]$  ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}$ ) because the existence of strong hydrogen bonds [24]. So the SAM [25,26] is applied in order to eradicate the effect of water in measurements. According to SAM, a series of samples of  $[\text{C}_2\text{2O1IM}][\text{X}]$  ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}$ ) with various mass fraction of water are prepared.

For all the quantities measured in this paper, the complete analysis of the experimental uncertainties is carried out with the consideration of sources of uncertainties which include: standard uncertainty of multiple measurements,  $u(\text{sd})$ , standard uncertainty of the maximum error of the instrument,  $u(\text{MPE})$ , standard uncertainty of the fitting parameters (intercept),  $u(\text{fit})$ , standard uncertainty of sample purity,  $u(\text{r})$  so that the standard combined uncertainties,  $u(\text{c})$ , and the expanded uncertainties,  $U(95)$ , are calculated and the values of  $U(95)$  are listed in the footnotes of Table 1 and Tables S2–10 in Supporting information.

An Anton Paar DMA 4500 oscillating U-tube densitometer is used to measure the density of the samples. The temperature in the cell is regulated to  $\pm 0.02$  K with solid state thermostat. Before measurement, the apparatus was calibrated once a day with dry

air and double-distilled freshly degassed water. Using the calibrated densitometer, the densities of the degassing water are measured at  $T = 298.15 \pm 0.02$  K with an expanded uncertainty ( $k = 2$ )  $\pm 0.0023 \text{ g}\cdot\text{cm}^{-3}$ . Then the densities of all samples are measured by the densitometer in the same temperature range.

Using the tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.), the surface tension,  $\gamma$ , of water is measured at  $T = 298.15 \pm 0.02$  K with an expanded uncertainty ( $k = 2$ )  $\pm 0.3 \text{ mJ}\cdot\text{m}^{-2}$ . Then the values of surface tension of the samples are measured by using the same method in the same temperature range.

## 3. Results and discussion

### 3.1. The values of density, $\rho$ , and surface tensions, $\gamma$ , of ILs $[\text{C}_2\text{2O1IM}][\text{X}]$ ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}, \text{NTF}_2$ )

The measured values of density,  $\rho$ , and surface tension,  $\gamma$ , of  $[\text{C}_2\text{2O1IM}][\text{X}]$  ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}$ ) containing various mass fraction of water (water content in the ionic liquid is accounted for upon solution preparation) at  $T = (298.15\text{--}338.15)$  K are listed in Tables S2–10 in Supporting information. Each value in these tables is the average of three measurements. According to the SAM, the values of density or surface tension of the samples are plotted against the mass fraction of water respectively, so that a series of fine straight lines are obtained (see Figs. S23–30) in Supporting information. The values of correlation coefficient,  $r$ , for all linear regressions are larger than 0.99 and all values of standard deviation,  $sd$ , are within standard uncertainty of the measurement. These data show that the SAM is appropriate in this study. The intercepts of the straight lines are the values of density or surface tension of  $[\text{C}_2\text{2O1IM}][\text{X}]$  ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}$ ) without water and can be viewed as experimental values. For  $T = 298.15 \pm 0.02$  K as an example, the measured values of density,  $\rho$  and surface tension,  $\gamma$ , of  $[\text{C}_2\text{2O1IM}][\text{X}]$  ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}, \text{NTF}_2$ ) are listed in Table 1. Figs. 1 and 2 are the plots of density and surface tension against  $w_2$ , respectively.

### 3.2. Volumetric properties of $[\text{C}_2\text{2O1IM}][\text{X}]$ ( $\text{X} = \text{OAC}, \text{SCN}, \text{DCA}, \text{TfO}, \text{NTF}_2$ )

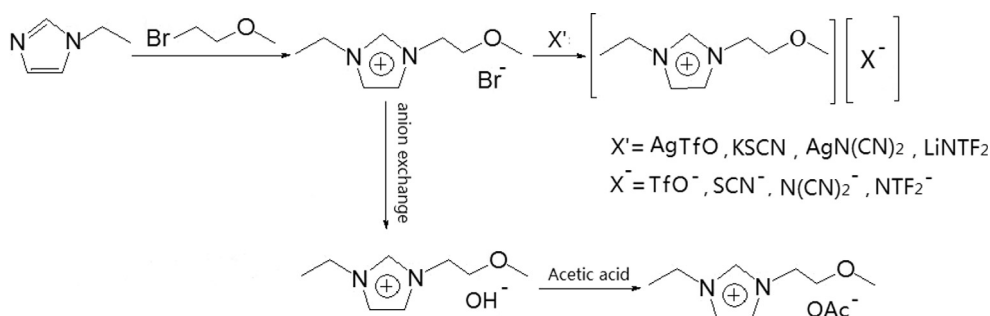
Plotting  $\ln \rho$  against  $T$ , five good straight line are gotten (see Fig. 3). According to definition of thermal expansion coefficient,  $\alpha$ :

$$\alpha \equiv (1/V)(\partial V/\partial T)_p = -(\partial \ln \rho/\partial T)_p \quad (1)$$

where  $V$  is molar volume. The negative value of the straight line slope is the thermal expansion coefficient, which listed in Table 2, can be seen as experimental value of thermal expansion coefficient.

The molar volume,  $V$ , is defined as follows:

$$V = M/\rho \quad (2)$$



Scheme 1. Synthesis of ether-functionalized ILs  $[\text{C}_2\text{2O1IM}][\text{X}]$  ( $\text{X} = \text{OAC}, \text{TfO}, \text{SCN}, \text{DCA}, \text{NTF}_2$ ).

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