The molar surface Gibbs energy and prediction of surface tension of [C$_n$py][DCA] (n = 3,4,5)

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ABSTRACT

Three pyridinium-based ionic liquids of [C$_n$py][DCA] (n = 3,4,5) (*N*-alkyl-pyridinium dicyanamide) were prepared and characterized by ^{1}H NMR (^{1}H nuclear magnetic resonance) spectroscopy, ^{13}C NMR (^{13}C nuclear magnetic resonance) spectroscopy. Their densities, surface tensions and refractive indices were measured at different temperatures. The molar surface Gibbs energy, g_s, critical temperature, T_c and Eötvös empirical parameter related to polarity, k_E, were also calculated. In terms of the concept of molar surface Gibbs energy, g_s, a new Eötvös equation was obtained. It is found that the slope of the new Eötvös equation is the molar surface entropy of the ILs and the intercept is the molar surface enthalpy which is a temperature-independent constant. By using the refractive index and the molar surface Gibbs energy, an equation to predict surface tension of the ILs was derived and the predicted values of the surface tension of [C$_n$py][DCA] (n = 3,4,5) are all most the same with the corresponding experimental values.

1. Introduction

From the nineties of last century, ionic liquids (ILs) have attracted more and more attention from industry and academic community. That is because ionic liquids have some peculiar physicochemical properties including negligible vapor pressure, high heat capacity, high thermal conductivity and a wide temperature range [1]. Due to these practical properties, they have been applied in pharmaceuticals [2], therapeutics [3], biotechnology [4], physical and chemical fields [5,6]. In addition, pyridinium-based ionic liquids can capture large amounts of SO$_2$ by simple physical absorption [7]. They have a promising prospect in solvents for many organic reactions [8,9] and as a recyclable catalyst for acid-catalyzed transesterification [10]. The ILs with N(CN)$_2$ anions have been used as absorbents to capture CO$_2$ [11,12], novel hypergolic materials, propellants [13,14] and electrolytes for dye-sensitized solar cells [15–18]. Hence, the knowledge of physicochemical properties of pyridinium-based ionic liquids is indispensable for its theoretical research and practical application. Therefore, as our continual investigation [19–23], the followings were reported in this work: (1) The ILs [C$_n$py][DCA] (n = 3,4,5) were prepared; (2) Their densities, surface tensions and refractive indices were measured from *T* = (303.15 to 338.15) K with an interval of 5 K; (3) The molar surface Gibbs energy, g_s, critical temperature, T_c, and Eötvös empirical parameter, k_E, were also discussed. (4) On the basis of the concept of the molar surface Gibbs energy, a new Eötvös equation was gained. (5) By using the refractive index and the molar surface Gibbs energy, an equation to predict surface tension of the ILs was derived.

2. Experimental

2.1. Chemicals

The source and purity of the materials are listed in table S1 of Supporting Information.

2.2. Preparation of ILs [C$_n$py][DCA] (n = 3,4,5)

[C$_n$py][Br] (n = 3,4,5) was synthesized and the purification accomplished using standard procedure [24,25]. Then [C$_n$py][DCA] (n = 3,4,5) was prepared [19]. Figure S1 shows a schematic of this synthetic route. Structures of the [C$_n$py][DCA] (n = 3,4,5) were confirmed by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy. Chromatographic analysis was performed on a unitary C18 column (150 · 4.60 mm, 5 μm) (A China Chromatography Co., Ltd, Zhejiang, China). Samples of [C$_n$py][DCA] (n = 3,4,5) are the same as in

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reference [19] were used in our previous work. The mass fraction purity of [C$_n$py][DCA] (n = 3,4,5) is >0.98, >0.99 and >0.99 determined by high performance liquid chromatography (HPLC). The mass fractions of water in ILs [C$_n$py][DCA] (n = 3,4,5) determined by a Karl Fischer moisture titrator (ZSD-2 type) were 0.00121, 0.00123 and 0.00124, respectively.

2.3. Measurement of densities, surface tensions, and refractive indices of ILs [C$_n$py][DCA] (n = 3,4,5)

Because [C$_n$py][DCA] (n = 3,4,5) strongly form hydrogen bonds [26] with water, any water in them is difficult to eliminate by ordinary methods. Actually even a trace amount of water becomes the most effective element of impurity, so the standard addition method (SAM) [22,23] was applied in order to eradicate the effect of water in measurements of density, surface tension and refractive index. According to the need of SAM, a series of samples of [C$_n$py][DCA] (n = 3,4,5) with various water contents were prepared.

By using an Anton Paar DMA 4500 oscillating U-tube densitometer, the density of the samples was measured. The temperature in the cell was adjusted to T = ±0.03 K with a solid state thermostat. Before the measurement, the apparatus was calibrated once each day with dry air and double-distilled freshly degassed water. First, the density of degassed water was measured at T = {(298.15 to 338.15) ± 0.03} K, which was in good agreement with the literature values [27], within an experimental error of ±0.00002 g · cm^{-3}. Then, the density of the samples with different water content was measured by the instrument from T = (303.15 to 338.15) K, respectively.

The tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.) was used to measure the surface tension of the samples. First, surface tension of degassed water was measured at T = {(298.15 to 338.15) ± 0.01} K, which was in good agreement with the literature values [27], within an experimental error of ±0.1 mJ · m^{-2}. Then, the surface tension of the samples was measured by the instrument from T = (303.15 to 338.15) K, respectively.

By using an Abbe refractometer, the refractive index, n_D, of the samples was measured. First, refractive index of degassed water was measured at T = {(298.15 to 338.15) ± 0.01} K, which was in agreement with the literature values [27], within an experimental error of ±0.0001. Then, the refractive index of the samples was measured by the instrument from T = (303.15 to 338.15) K, respectively.

In the process of the experiments, the density, surface tension and refractive index of ILs [C$_n$py][DCA] (n = 3,4,5) were measured in the glove-box which is full of argon with volume fraction purity 0.9999. Before and after the experiments, the water contents of the samples were exactly the same.

3. Results and discussion

3.1. The values of density, surface tension and refractive index of ILs [C$_n$py][DCA] (n = 3,4,5)

The values of density, surface tension and refractive index of [C$_n$py][DCA] (n = 3,4,5) with various water content were measured three times and then an average value determined, which are listed in tables S2–S4. At constant temperature, plotting the values of, ρ, γ, n_D, against, w_2, a series of straight lines were obtained from T = (303.15 to 338.15) K (see figures S2–S4). According to SAM, the values of density, surface tension and refractive index without water are the intercepts obtained from the linear regression. Their expanded combined uncertainty at 0.95 confidence level is also included in table 1. The values of correlation coefficients, r, are

TABLE 1

The values of density, ρ/g · cm^{-3}, surface tension, γ/mJ · m^{-2}, and refractive index, n_D, of ILs [C$_n$py][DCA] (n = 3,4,5) at T = (298.15 to 338.15) K,[a] p[b] = 0.1 MPa.

T/K	ρ/g · cm^{-3}	γ/mJ · m^{-2}	n_D
	[C$_3$py][DCA][c]		
298.15	1.09006 ± 0.00010[d]	57.9 ± 0.3[d]	1.5407 ± 0.0003[d]
303.15	1.08692	57.7	1.5390
308.15	1.08379	57.4	1.5374
313.15	1.08069	57.0	1.5356
318.15	1.07760	56.7	1.5342
323.15	1.07452	56.4	1.5329
328.15	1.07146	56.1	1.5312
333.15	1.06842	55.7	1.5293
338.15	1.06540	55.4	1.5276
	[C$_4$py][DCA][c]		
298.15	1.06883 ± 0.00007[d]	55.7 ± 0.3[d]	1.5345 ± 0.0003[d]
303.15	1.06576	55.5	1.5325
308.15	1.06270	55.2	1.5309
313.15	1.05966	54.9	1.5285
318.15	1.05664	54.5	1.5270
323.15	1.05363	54.2	1.5253
328.15	1.05063	53.9	1.5237
333.15	1.04766	53.6	1.5217
338.15	1.04469	53.4	1.5202
	[C$_5$py][DCA][c]		
298.15	1.05307 ± 0.00007[d]	53.4 ± 0.3[d]	1.5300 ± 0.0003[d]
303.15	1.05005	53.0	1.5287
308.15	1.04703	52.7	1.5272
313.15	1.04403	52.4	1.5258
318.15	1.04104	52.1	1.5243
323.15	1.03807	51.7	1.5230
328.15	1.03511	51.4	1.5212
333.15	1.03217	51.2	1.5194
338.15	1.02924	51.0	1.5179

The standard uncertainty (0.68 level of confidence).
[a] $u(T)$ = 0.03 K for density, $u(T)$ = 0.01 K for surface tension and refractive index.
[b] $u(p)$ = ± 0.002 MPa.
[c] The expanded uncertainties U_c (0.95 level of confidence): $U_c(\rho)$ = 0.004 g · cm^{-3}, $U_c(\gamma)$ = 0.4 mJ · m^{-2}, $U_c(n_D)$ = 0.006 for [C$_3$py][DCA]; $U_c(\rho)$ = 0.002 g · cm^{-3}, $U_c(\gamma)$ = 0.3 mJ · m^{-2}, $U_c(n_D)$ = 0.003 for [C$_4$py][DCA]; $U_c(\rho)$ = 0.002 g · cm^{-3}, $U_c(\gamma)$ = 0.3 mJ · m^{-2}, $U_c(n_D)$ = 0.003 for [C$_5$py][DCA].
[d] Reference [19].

greater than 0.997 and values of standard deviation, sd, were within experimental error. This fact shows that the SAM is appropriate for this work. In addition, the molar volume, V, for the ILs [C$_n$py][DCA] (n = 3,4,5) from T = (298.15 to 338.15) K were calculated and are listed in table 2. From the results, it can be seen that the values of V increase with the increase of temperature.

3.2. A new Eötvös equation

For most of the liquids, the surface tension decreases with an increase in the temperature, and it is usually expressed as the Eötvös equation [28]:

$$\gamma V^{2/3} = k_E(T_c - T), \tag{1}$$

where V is molar volume, γ is surface tension; k_E is the Eötvös empirical parameter and k_E is related to polarity. For organic solvents that have weak polarity, $k_E \approx 2.2 \cdot 10^{-7}$ J · mol$^{-2/3}$ · K^{-1} and for NaCl molten salt with high polarity, $k_E \approx 0.4 \cdot 10^{-7}$ J · mol$^{-2/3}$ · K^{-1}. Plotting $\gamma V^{2/3}$ vs T, a set of straight lines is obtained (see figure 1). The values of k_E obtained from the slope of the curve are k_E = 1.32 · 10^{-7} J · mol$^{-2/3}$ · K^{-1} for [C$_3$py][DCA], k_E = 1.33 · 10^{-7} J · mol$^{-2/3}$ · K^{-1} for [C$_4$py][DCA] and k_E = 1.45 · 10^{-7} J · mol$^{-2/3}$ · K^{-1} for IL [C$_5$py][DCA]. It can be seen that values of k_E of [C$_n$py][DCA] (n = 3,4,5) are between (2.2 and 0.4) · 10^{-7} J · mol$^{-2/3}$ · K^{-1}, so this fact means that the polarity of [C$_n$py][DCA] (n = 3,4,5) is smaller than NaCl molten salt but higher than organic solvents. In addition, the values of k_E increase as the methylene number increases, that is,