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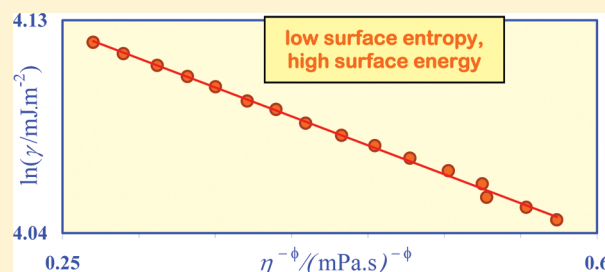
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# A Functionalized High-Surface-Energy Ammonium-Based Ionic Liquid: Experimental Measurement of Viscosity, Density, and Surface Tension of (2-Hydroxyethyl)ammonium Formate

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**ABSTRACT:** The ammonium-based ionic liquid (2-hydroxyethyl)ammonium formate has been known for ease of synthesis and great solvation properties. In this work, this ionic liquid was synthesized, and its temperature-dependent density, surface tension, and viscosity were measured. Surface tension was measured by the capillary rise method using a homemade capillary apparatus in which the liquid and vapor can be brought into equilibrium. Measurements of viscosity and surface tension were performed under a water-vapor-free atmosphere. The viscosity was measured using a capillary viscometer and found to fit the Vogel–Fulcher–Tammann (VFT) equation, indicative of a non-Arrhenius ionic liquid. Also, the viscosity of the ionic liquid was fitted quite accurately using the relation we developed recently with the characteristic exponent  $\phi = 0.166893$ . This ionic liquid has a rather high surface energy and low surface entropy, which can be attributed to the role of the  $-\text{OH}$  group involved. The determined surface thermodynamic properties could in part account for the good solvation properties shown by this ionic liquid.



## INTRODUCTION

(2-Hydroxyethyl)ammonium formate (2-HEAF) is a newly developed ionic liquid (IL) that has been shown to have special properties in synthesis as a solvent. 2-HEAF has a good gas solubility capacity, although it is the lowest among those of hydroxylammonium IL counterparts.<sup>1</sup> With an efficient recovery in gas adsorption–desorption cycles, it also has the highest electrical conductivity, lowest shear viscosity, and lowest melting point among the counterpart ILs.<sup>1</sup> 2-HEAF is able to dissolve many inorganic salts.<sup>2</sup> Also, many insoluble polymers such as polyaniline and polypyrrole are highly soluble in this ionic liquid.<sup>2</sup>

With such interesting features for potential applications in industry, much work has been done to address the demand for data on the thermophysical properties of the ionic liquid. Cota et al.<sup>3</sup> have studied the temperature dependence of the density, ultrasonic velocity, and ionic conductivity of 2-HEAF over the temperature range  $T = (278 \text{ to } 338) \text{ K}$ . Pinkert et al.<sup>4</sup> have measured the density, viscosity, and electrical conductivity of a series of protic alkanolammonium ionic liquids, including 2-HEAF, over the range  $T = (278 \text{ to } 358) \text{ K}$ . Kurnia et al.<sup>5</sup> have reported the densities, dynamic viscosities, and coefficients of thermal expansion [over the range  $T = (293 \text{ to } 363) \text{ K}$ ], the refractive indexes [over the range  $T = (293 \text{ to } 348) \text{ K}$ ], and thermal decomposition temperatures of several ammonium-based ionic liquids. Yuan et al.<sup>1</sup> have measured the viscosity, density, and electrical conductivity of 2-HEAF at 298 K as well as the melting point, glass transition temperature, and decomposition temperature. Also, experimental measurements have been conducted to measure the capacities for solubility of the gases  $\text{SO}_2$ <sup>1</sup> and  $\text{CO}_2$ .<sup>6</sup> Ionic liquids with this type of polarity

have been used for versatile ceramic synthesis.<sup>7,8</sup> The viscosity, surface tension, density, and refractive index of the ionic liquid at room temperature have been measured by Greaves et al.<sup>9</sup> Very recently, the interaction of this IL with polar solvents has been studied<sup>10</sup> by the determination of solvatochromic parameters, which revealed the role of the OH group in the solvation properties. It was also found that zein, an industrially important natural protein polymer, can be dissolved in the ionic liquid very easily.<sup>11</sup>

The surface tension of this ionic liquid ( $65.0 \text{ mJ}\cdot\text{m}^{-2}$ , measured at 300 K by Greaves et al.<sup>9</sup>) indicates rather high tension among counterpart ionic liquids and polar liquids. This can be used to account for its high solvation capacity, because it is known that the solubility is not only ordered by the free energy of solvation but also governed by the interfacial tension of the solute and solvent.

The temperature dependence of the surface tension is also important for practical applications and modeling of the liquid state. Basically, accurate experimental measurements of surface tension as a function of temperature would provide the possibility of accurate determination of surface thermodynamic functions (e.g., surface energy and surface entropy). The temperature-dependent surface tension of this ionic liquid has not been reported in the literature.

The demanding temperature-dependent viscosity of this ionic liquid has not been investigated widely. A plot of viscosity versus temperature has been reported in ref 2, but it is

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contradictory with the single measurement at room temperature reported in the same article (see Table 1 of ref 2). Theoretically, the temperature-dependent viscosity can provide valuable information on the dynamic properties of the ionic liquid at the molecular level, including information on the glass formation properties.

In this paper, we report measurements of the density, viscosity, and surface tension of 2-HEAF over the temperature range  $T = (298 \text{ to } 353) \text{ K}$ . Surface tension was measured by the capillary rise method using a special capillary apparatus. The system was sealed under vacuum to provide a water-vapor-free atmosphere during the measurement. Also, the viscosity measurement was performed under a water-vapor-free atmosphere. The temperature-dependent density and surface tension are presented here, and the temperature-dependent viscosity and the relation between the surface tension and the viscosity over the temperature range  $T = (298 \text{ to } 353) \text{ K}$  were studied using the most commonly used equations and the relation we have developed recently.

## EXPERIMENTAL PROCEDURES

**Materials.** All of the chemicals were analytical grade. Formic acid (Merck) and 2-aminoethanol (BDH) were distilled before use.

**Synthesis of 2-HEAF.** The synthesis closely followed the literature procedure.<sup>2</sup> 2-Aminoethanol (0.2 mol) was placed in a two-necked flask equipped with a reflux condenser and a dropping funnel. While the flask was mounted in an ice bath, formic acid (0.2 mol) was added to the flask dropwise under vigorous stirring with a magnetic stirrer for about 1 h. Stirring was continued for 24 h at room temperature to obtain a viscous clear liquid. The product was dried under vacuum at 323 K for 48 h. All vacuum drying was performed under a pressure of 1.2 Pa and all freeze-drying at a pressure of 1.2 Pa and liquid nitrogen temperature. The IL was produced as a clear liquid.

The product's chemical formula is  $[\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+][^- \text{OOCH}]$ . Elemental analysis gave the following percent composition: C, 33.42 %; H, 8.51 %; N, 13.15 %. The calculated values for 2-HEAF ( $\text{C}_3\text{H}_9\text{NO}_3$ ) are C, 33.64 %; H, 8.47 %; N, 13.08 %. The reaction took place in one step without possible side reactions. Since the amounts of the starting materials used were based on the mole ratio and no starting material was detected at the NMR detection limit, the high purity of the IL is substantial.

<sup>1</sup>H NMR spectra in DMSO- $d_6$  with tetramethylsilane as an internal standard were measured on a Bruker 250 MHz NMR spectrometer. For the freshly synthesized ionic liquid, spectra were measured at three successive stages: (1) after vacuum drying for 24 h at room temperature [ $\delta$  8.35 ppm (s, 1H, H-COO<sup>-</sup>), (6.9 to 7.0) ppm (broad, 4H, -NH<sub>3</sub>+OH), 3.4 ppm (t, 2H, -CH<sub>2</sub>-N), 2.8 ppm (t, 2H, -O-CH<sub>2</sub>-)]; (2) after freeze-drying for 2 h [ $\delta$  (8.05 to 8.1) ppm (s, 1H, HCOO<sup>-</sup>), 5.86 ppm (broad, 4H, NH<sub>3</sub>+OH), (3.25 to 3.29) ppm (t, 2H, CH<sub>2</sub>N), (2.52 to 2.56) ppm (t, 2H, OCH<sub>2</sub>)]; and (3) after heating to 353 K [ $\delta$  8.09 ppm (s, 1H, HCOO<sup>-</sup>), 7.72 ppm (s, 1H, NOCH), 6.16 ppm (broad, 6H, NH<sub>3</sub>+OH+HONH), (3.28 to 3.33) ppm (t, 2H, CH<sub>2</sub>N), (3.1 to 3.19) ppm (t, 2H, CH<sub>2</sub>NOC), 2.89 ppm (t, 2H, CH<sub>2</sub>CNOC), (2.56 to 2.61) ppm (t, 2H, OCH<sub>2</sub>)].

**Surface Tension Measurements.** The surface tension of the ionic liquid was measured by the capillary rise method. To eliminate water content as much as possible and to provide a water-vapor-free atmosphere during the surface tension

measurements, the experiment was performed in a homemade capillary apparatus invented in our earlier work,<sup>12</sup> as detailed in the following. Favorably, the capillary apparatus can be sealed under vacuum, so the surface tension measurement can be regarded as being performed at the interface of liquid and vapor at equilibrium. To calibrate the capillary, it was partially filled with some mercury, and from measurements of the length (by micrometer,  $\pm 0.01 \text{ mm}$ ) of the mercury column at different positions along the capillary as well as its weight, the inner radius was determined using the density of mercury at the laboratory temperature. The calibration along the capillary was carefully repeated, and any nonuniform capillary was rejected. The inner radius of the used capillary was  $0.34 \pm 0.01 \text{ mm}$ . While the capillary apparatus was loaded with the vacuum-dried ionic liquid sample, the system was freeze-dried (at liquid nitrogen temperature) under vacuum several times, and finally, it was kept at room temperature under vacuum until effervescence (due to dissolved water and atmospheric gases) completely ceased. This process was done with great care to ensure that water and dissolved gases were removed as much as possible. The capillary apparatus was sealed under vacuum (1.2 Pa) and then transferred to an thermostatted oil bath for the surface tension measurement. Therefore, the surface tension of the ionic liquid was determined in the absence of water vapor and air (i.e., at an equilibrated liquid-vapor interface). The temperature of the thermostatted oil bath was measured within  $\pm 0.5 \text{ K}$ . Measurement of surface tension was performed over the range  $T = (298 \text{ to } 353) \text{ K}$  at intervals of 5 K. When the temperature of the oil bath was increased to next desired temperature, thermal equilibration was considered to be achieved when the height of liquid sample completely stopped moving in the capillary (within 45 min). After sufficient time for the thermal equilibration, the digital camera in the cathometer was focused horizontally on the middle of the column of the ionic liquid raised in the capillary. The camera was interfaced with a personal computer, and the absolute heights were determined within  $\pm 0.03 \text{ mm}$ .

**Density Measurements.** To measure the density, a standard 5.00 mL pycnometer (Marienfeld) was calibrated using deionized water at 298 K ( $997.0 \text{ kg}\cdot\text{m}^{-3}$ ).<sup>13</sup> The pycnometer was filled with freeze-dried and degassed ionic liquid sample and thermostatted as in the surface tension measurements. The density of the ionic liquid was measured over the range  $T = (298 \text{ to } 353) \text{ K}$  at intervals of 5 K.

**Viscosity Measurements.** A Cannon-Fenske capillary viscometer (size 300) was used for the viscosity measurements. This viscometer provides a practical vacuum line set up to furnish elimination of water content of the sample and providing a water-vapor-free atmosphere during the measurements. The vacuum-dried ionic liquid sample was initially loaded in the viscometer and freeze-dried several times under vacuum (1.2 Pa) for about 2 h, until the effervescence stopped. At low temperatures, extensive effervescence occurred over a relatively long time, while at the high temperatures the effervescence process ceased quickly. At this point, it was expected that most of the water content and dissolved gases had been removed. During the viscosity measurements, however, the vacuum was removed, and dried air was let in. The water content after drying in a vacuum oven and subsequent freeze-drying by vacuum line was measured by Karl Fischer titration (870 KF Titrino Plus, Metrohm). An oil bath with a glass thermometer was used to control the temperature within  $\pm 0.5 \text{ K}$ . The system was allowed to

equilibrate for at least 45 min at each temperature. The time for the ionic liquid sample to pass through the capillary viscometer was measured over the temperature range  $T = (298 \text{ to } 353) \text{ K}$  using a digital stopwatch ( $\pm 0.01 \text{ s}$ ). The absolute value of the viscosity was then calculated from the measured time ( $t$ ) and the experimental density of the ionic liquid sample ( $\rho_{\text{IL}}$ ) using eq 1:

$$\eta_{\text{IL}} = \eta_{\text{ref}} \cdot \left( \frac{\rho_{\text{IL}} \cdot t_{\text{IL}}}{\rho_{\text{ref}} \cdot t_{\text{ref}}} \right) \quad (1)$$

The viscometer was calibrated using diisodecyl phthalate (Merck, synthesis grade, lot no. S5148332, batch 914, nominal mass-fraction purity of 0.99), for which the published viscosity is  $\eta_{\text{ref}} = 87.62 \text{ mPa}\cdot\text{s}$  at  $298.15 \text{ K}$ .<sup>14</sup>

## RESULTS AND DISCUSSION

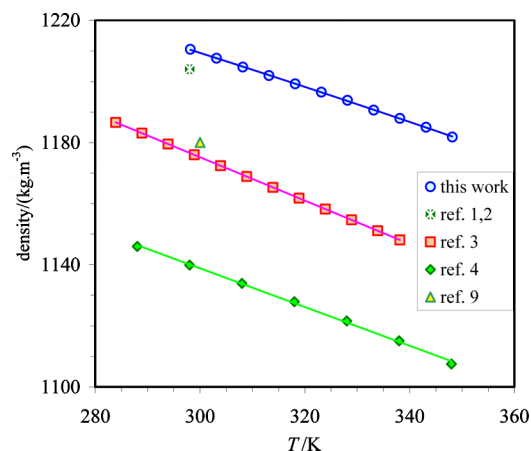
Polar ionic liquids are of special interest in that they can serve as media with suitable polarity required for some types of synthesis, such as that of high-thermally-stable ceramics. Polar ionic liquids have been used for the synthesis of sodium-based fluorophosphate cathode materials of ceramics at rather low temperatures. One of the main factors responsible for such a property is the high surface tension, which additionally can lead to the production of certain lattice types with particular exposed crystal surface planes. This can be attributed to the fact that the solubility is not only ordered by the free energy of solvation but also governed by the interfacial tension of the solute and solvent. Therefore, the use of polar ionic liquids not only benefits from a good solvation property for the solutes but also involves a solvation mechanism suitable for controlling the production of the chemical product with exposed crystal facets of interest.

**Synthesis and Characterization of 2-HEAF.** The  $^1\text{H}$  NMR spectra of the synthesized ionic liquid were in close agreement with those reported by Yuan et al.<sup>1</sup> and Bicak.<sup>2</sup> The results of elemental analysis also confirmed accurate product formation. No water content was detected at the detection limit of NMR spectroscopy. A sample of freshly synthesized ionic liquid contained a 0.00560 mass fraction of water after vacuum drying. After freeze-drying, the water mass fraction was 0.00234, and after measurement up to  $353 \text{ K}$ , the water content was updated to a mass fraction of 0.00788. The water content was determined by the Karl Fischer method. Under ordinary conditions, the ionic liquid undergoes degradation spontaneously to produce water.<sup>15</sup> In another test, we found that the vacuum-dried ionic liquid with a water mass fraction of 0.00586 underwent degradation to produce an overall water mass fraction of 0.0685 after 12 weeks, which is consistent with the literature.<sup>15</sup>

As indicated by the  $^1\text{H}$  NMR spectra, freeze-drying did not change the ionic liquid chemically, except for some chemical shifting and line broadening. However, consistent with the literature, it was found that the ionic liquid undergoes degradation over time as well as upon heating but is resistant to mild vacuum drying and freeze-drying. We detected  $T \approx 353 \text{ K}$  as the temperature at the onset of decomposition, as indicated by the NMR spectra and the test for the increase in water content (see Experimental Procedures and the preceding paragraph). The decomposition of the ionic liquid has been studied, and different decomposition temperatures ( $T_d$ ) have been reported in the literature:  $T_d = 339 \text{ K}$  at a low heating rate and  $T_d = 384 \text{ K}$  at a high heating rate;<sup>4</sup>  $T_d = 444.5 \text{ K}$  as

determined by differential scanning calorimetry;<sup>1</sup> and  $T_d = 423 \text{ K}$  determined by thermogravimetric analysis.<sup>16,17</sup> Indeed, a vast variety of  $T_d$  values have been reported for this ionic liquid. It is negotiable whether  $T_d$  is a function of the initial water content, as water is one of the products of the decomposition process.

**Temperature-Dependent Density.** The density of the ionic liquid was measured over the range  $T = (298 \text{ to } 353) \text{ K}$ . A plot of the density of the ionic liquid versus temperature is shown in Figure 1. As can be seen from figure, the density



**Figure 1.** Plot of the experimental density of 2-HEAF vs temperature (blue ●). The line is a quadratic fit to the experimental density. Data from the literature are shown for comparison.

decreases linearly with temperature. In Table 1, the experimental values of the density are compared with values obtained from a fit to the following quadratic expression:

$$\rho / (\text{kg}\cdot\text{m}^{-3}) = -4.4289 \times 10^{-4} T^2 / \text{K}^2 - 2.8158 \times 10^{-1} T / \text{K} + 1333.7 \quad (2)$$

where  $T$  is the absolute temperature. The uncertainty in the calculated densities was estimated to be  $0.1 \text{ kg}\cdot\text{m}^{-3}$  (see Table 1). To our knowledge, a limited number of experimental densities of the ionic liquid have been reported in the literature. Single measurements of the density at  $298 \text{ K}$  have been reported by Yuan et al.<sup>1</sup> and Bicak<sup>2</sup> ( $1204 \text{ kg}\cdot\text{m}^{-3}$ ). Our measured density at  $298 \text{ K}$  is in agreement with these measurements within  $0.537 \%$ . Also a value of  $1180 \text{ kg}\cdot\text{m}^{-3}$  was reported for the density of the ionic liquid at  $300 \text{ K}$ .<sup>9</sup> These data points are included in Figure 1 for comparison. Cota et al.<sup>3</sup> reported the experimental density of the ionic liquid over the range  $T = (278.15 \text{ to } 338.15) \text{ K}$  but did not report the water content. The density of this ionic liquid was also reported by Pinkert et al.<sup>4</sup> These data are also shown in Figure 1. As can be seen, the density measured in this work is higher than the set of literature data at all temperatures.

**Temperature-Dependent Surface Tension.** The capillary rise method has been known as the most accurate method of measuring the surface tension of ordinary liquids. The experimental error substantially can be reduced to a minimum if good temperature control, sufficient thermal equilibration, a high-purity IL, and ultraclean glassware are used. The water content of the ionic liquid is the major source of error in the measurement of surface tension. Another difficulty is the extensive adsorption of atmospheric water vapor during the surface tension measurement, the effect of which has been



**Table 1.** Experimentally Measured Thermophysical Properties of 2-HEAF and Deviations of the Density and Surface Tension with Respect to the Corresponding Fitting Values (For Viscosity Deviations, See Table 2)

<i>T</i>	density		surface tension		viscosity
	$\rho_{\text{exp}}^a$	dev <sup>b,c</sup>	$\gamma_{\text{exp}}^a$	dev <sup>b,d</sup>	$\eta_{\text{exp}}^a$
K	kg·m <sup>-3</sup>	%	mJ·m <sup>-2</sup>	%	mPa·s
298.15	1210.5 (0.1)	0.010	70.3 (2.1)	−0.014	252.5 (5.0)
303.15	1207.6 (0.1)	−0.003	69.9 (2.1)	−0.044	190.5 (3.8)
308.15	1204.7 (0.1)	−0.015	69.6 (2.1)	0.013	143.3 (2.9)
313.15	1201.9 (0.1)	−0.016	69.2 (2.1)	0.010	110.3 (2.2)
318.15	1199.2 (0.1)	−0.007	68.8 (2.1)	0.002	86.98 (1.8)
323.15	1196.5 (0.1)	0.004	68.5 (2.1)	−0.032	69.54 (1.4)
328.15	1193.8 (0.1)	0.016	68.1 (2.1)	−0.004	56.89 (1.2)
333.15	1190.6 (0.1)	−0.012	67.8 (2.0)	0.035	46.22 (0.9)
338.15	1187.9 (0.1)	0.005	67.4 (2.0)	0.002	37.88 (0.9)
343.15	1185.0 (0.1)	0.006	67.0 (2.0)	0.003	30.30 (0.6)
348.15	1181.8 (0.1)	−0.016	66.7 (1.9)	−0.022	25.09 (0.5)
353.15	1178.3 (0.1)	−0.061	66.3 (1.9)	−0.040	20.20 (0.5)

<sup>a</sup>Uncertainties are given in parentheses. <sup>b</sup>Deviations (dev) were calculated as dev = 100 % × (exp − fit)/exp. Average absolute deviations (AAD) were calculated as AAD = (1/*n*)∑<sub>*i*=1</sub><sup>*n*</sup>|dev<sub>*i*</sub>|, where *n* is the number of data points. <sup>c</sup>AAD = 0.014 %. <sup>d</sup>AAD = 0.018 %.

discussed elsewhere.<sup>12,15</sup> This effect can be observed easily by monitoring the height of the ionic liquid column during the surface tension measurement when the capillary apparatus is left open to air.<sup>18</sup> When the capillary apparatus is used, the measured surface tension may represent the true surface character at the equilibrated liquid–vapor interface. Water vapor and atmospheric gases could deteriorate the microscopic liquid surface structure, which may not correspond precisely to the nature of the bulk liquid. Such precautions are particularly important if the surface tension is to be used for the calculation of the surface entropy to assess the liquid surface microstructure.

The surface tension ( $\gamma$ ) of the ionic liquid was calculated using eq 3:

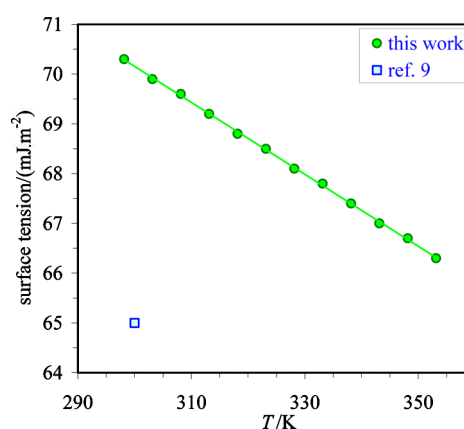
$$2\gamma \cos \theta = g\rho r(h + r/3) \quad (3)$$

where  $\theta$  is the contact angle, *h* is the height of the liquid in the capillary, *g* is the acceleration due to gravity,  $\rho$  is the liquid density (neglecting the vapor density), and *r* is the inner radius of the capillary. The second term inside the parentheses is the correction for the height of the liquid above the meniscus. Since the ionic liquid wets the inside surface of the glass capillary to a high extent,  $\theta \approx 0$ .

The values of the surface tension determined for the ionic liquid over the range *T* = (298 to 353) K are shown in Table 1 and plotted in Figure 2. The surface tension values were fitted to the equation<sup>19</sup>

$$\gamma = E^s - TS^s \quad (4)$$

where  $E^s$  is the surface energy and  $S^s$  is the surface entropy. As can be seen from Figure 2, surface tension decreases quite linearly with increasing temperature. The deviation from linear behavior is quite small (Table 1), which can be attributed to the precautions taken in the surface tension measurements. In previous work, our tests showed that surface tension measurements on imidazolium-based ionic liquids using this capillary apparatus under atmosphere produce surface tension values with some scattering around linear behavior.<sup>12</sup> No temperature-dependent surface tension of 2-HEAF has been reported in the literature to date. Greaves et al.<sup>9</sup> measured the surface tension at the liquid–air interface by the ring method and reported a

**Figure 2.** Plot of surface tension measured for 2-HEAF vs temperature. The line is a linear fit to the equation  $\gamma = E^s - TS^s$ .

single value of 65.0 mJ·m<sup>-2</sup> at 300 K (Figure 2). Their measured surface tension at this temperature is lower than ours (70.1 mJ·m<sup>-2</sup>) by 7.28 %. This difference can be attributed to the difference in the methods of measurement and to the levels of water content (as mass fraction) in this work (0.00234) and their work (0.0043).<sup>9</sup>

The value of  $E^s$  is almost constant at low temperatures. On the other hand, the surface entropy, which is a measure of the temperature dependence of the surface tension [i.e.,  $S^s = -(\partial\gamma/\partial T)$ ], is also constant. At low temperatures far from the critical temperature,  $S^s$  is a constant characteristic of the liquid. Indeed, by measurement of the temperature-dependent surface tension, information can be gained about the microscopic molecular ordering at the interface. It turns out that the surface tension and its temperature dependence are important for practical validation of experiments and modeling of the liquid surface. Fitting the measured surface tensions of 2-HEAF using eq 4 gave the expression  $\gamma/\text{mJ}\cdot\text{m}^{-2} = 91.8 - 0.0723\cdot T/\text{K}$ . The uncertainty in the calculated surface tensions was estimated to be less than 2.1 mJ·m<sup>-2</sup> (see Table 1). Quite interestingly, the value of  $S^s$  for 2-HEAF is about equal to the average value for most nonfunctionalized imidazolium-based ionic liquids, but the surface energy is much higher.<sup>12</sup>

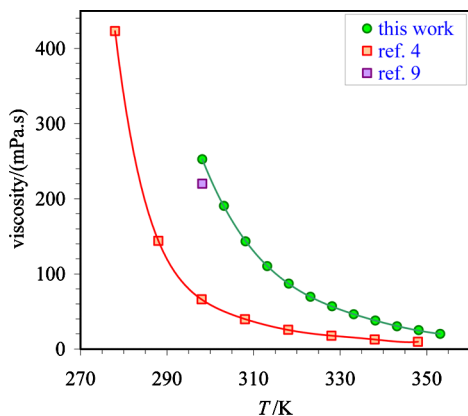
Recently, some  $-OH$ -functionalized ionic liquids based on alkylammonium, quaternary ammonium,<sup>20</sup> and imidazolium<sup>21–23</sup> cations with different anions have been synthesized and characterized, and their thermophysical properties have been measured. However, temperature-dependent surface tension data for 2-HEAF have not been reported to date.

The role of the  $-OH$  group in the surface properties of 2-HEAF can be clarified by comparison with the ionic liquid ethylammonium formate (EAF). For EAF, the experimental value of the surface tension has been reported only at one point,  $\gamma = 38.5 \text{ mJ}\cdot\text{m}^{-2}$  at  $T = 300 \text{ K}$ .<sup>9</sup> Comparison with the value  $\gamma = 70.1 \text{ mJ}\cdot\text{m}^{-2}$  at  $T = 300 \text{ K}$  for 2-HEAF shows that the role of  $-OH$  in the surface tension is substantial. The lack of temperature-dependent surface tension data for EAF prevents comparisons of  $E^s$  and  $S^s$ .

To our knowledge, the only  $-OH$ -functionalized ionic liquid for which temperature-dependent surface tension data have been measured is 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate,  $[\text{C}_2\text{OHmim}]\text{BF}_4$ .<sup>24</sup> The value of  $E^s$  for  $[\text{C}_2\text{OHmim}]\text{BF}_4$  is  $84.3 \text{ mJ}\cdot\text{m}^{-2}$ , and its  $S^s$  value is  $0.0648 \text{ mJ}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ . Its high surface energy in comparison with similar but non- $-OH$ -functionalized ionic liquids has been discussed and attributed to the role of  $-OH$ . 2-HEAF, for which  $E^s = 91.8 \text{ mJ}\cdot\text{m}^{-2}$  and  $S^s = 0.0723 \text{ mJ}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$  as measured in this work, shows surface thermodynamic properties comparable with those of  $[\text{C}_2\text{OHmim}]\text{BF}_4$ . Therefore, it can be concluded that functionalization with a  $-OH$  group can enhance the surface properties of the corresponding ionic liquid.

**Temperature-Dependent Viscosity.** The viscosity of the ionic liquid was measured over the range  $T = (298 \text{ to } 353) \text{ K}$ . In the measurements of viscosity, the viscometer was loaded with a vacuum-dried ionic liquid sample and freeze-dried by the same procedure as in the surface tension measurements. The viscometer was then connected to a vacuum line to evacuate the system, absorbing as much of the water content as possible and providing a water-vapor-free atmosphere during the viscosity measurement (see Experimental Procedures). The calibration of the viscometer is sensitive to the choice of reference liquid. Care was taken to provide reliable viscosity by calibrating the viscometer with a suitable reference liquid<sup>13</sup> having a viscosity close to that of the ionic liquid.

The measured viscosity values are shown in Table 1 and plotted versus temperature in Figure 3. The uncertainty in the measured viscosities was estimated to be less than  $5.0 \text{ mPa}\cdot\text{s}$ . As



**Figure 3.** Plot of the experimental viscosity of 2-HEAF vs temperature. Data from refs 4 and 9 are shown for comparison, and the lines are trend lines.

for other viscous liquids, the viscosity increases rather rapidly at low temperatures and decreases asymptotically to a small value at high temperatures. The electrostatic interaction between the (2-hydroxyethyl)ammonium cation and the formate anion play the main role in the rather high viscosity of this ionic liquid.

The experimental density and viscosity values measured by Pinkert et al.<sup>4</sup> over the range  $T = (278 \text{ to } 348) \text{ K}$  are lower than those obtained in the present work, as shown in Figures 1 and 3. They have measured the viscosity under a  $\text{N}_2$  atmosphere, and the reported water content after the measurement (0.0082 mass fraction) was larger than that before the measurement (0.0043). It is well-known that increasing the water content lowers the viscosity (and the density as well), and therefore, the lower values reported by Pinkert et al. could be due to water uptake under the measurement conditions.<sup>25</sup> Bicak<sup>2</sup> also presented a plot of the measured viscosity of 2-HEAF versus temperature. No trustworthy comparison can be made here because their water content level was not reported.

The equations most commonly used to fit the temperature-dependent viscosities of ionic liquids accurately are empirical equations obtained by extension of the Arrhenius equation. These non-Arrhenius models that have been used widely to model various ionic liquids are the Litovitz and Vogel–Fulcher–Tammann (VFT) equations (see eqs 5 to 7). The fitting results (Table 2) show that the deviations from both the

**Table 2.** Results of Fits of the Viscosity of 2-HEAF to Different Model Equations<sup>a</sup>

Arrhenius	
$\eta_\infty/\text{mPa}\cdot\text{s}$	$1.7\cdot 10^{-5} \pm 6.1\cdot 10^{-6}$
$(E_a/R)/\text{K}$	$4920 \pm 7$
$R^2$	0.9992
AAD/%	3.3
Litovitz	
$A/\text{mPa}\cdot\text{s}$	$0.5892 \pm 0.0215$
$10^{-8}\cdot(B/R)/\text{K}$	$1.607 \pm 0.014$
$R^2$	0.9997
AAD/%	2.48
VFT	
$A'/\text{mPa}\cdot\text{s}$	$0.00091 \pm 0.0002$
$k/\text{K}$	$2785 \pm 661$
$T_0/\text{K}$	$76 \pm 29$
$R^2$	0.9995
AAD/%	1.5
Our Recent Work	
$a$	$-0.7123 \pm 0.017$
$b$	$0.0037 \pm 0.0000$
$\phi$	$0.166893 \pm 0.020200$
$R^2$	0.9995
AAD/%	1.7

<sup>a</sup>It should be noted that the result for the range of accuracy in some cases is irrelevant.

Arrhenius and Litovitz model equations are rather high. However, the fits to the VFT equation and our recently developed equation (eq 8)<sup>26</sup> show appreciably low deviations. The feature of our equation is that it considers the fluidity ( $1/\eta$ ) raised to a characteristic power ( $\phi$ ) to be a linear function of temperature.

$$\text{Arrhenius equation: } \eta = \eta_\infty \exp(-E_a/RT) \quad (5)$$

$$\text{Litovitz equation: } \eta = A \exp(B/RT^3) \quad (6)$$

$$\text{VFT equation: } \eta = A' \exp[k/(T - T_0)] \quad (7)$$

$$\text{Recent work:}^{26} \left(\frac{1}{\eta}\right)^\phi = a + bT \quad (8)$$

The quality of the fits can be determined by examining the values of the absolute average deviation (AAD), which are in the order Litovitz > Arrhenius > VFT (See Table 2). The trend in the quality of the fits to these model equations for this ionic liquid is the same as those found for other ionic liquids.<sup>15,27–33</sup> Viscosities of ionic liquids in most instances have been found to be non-Arrhenius, with the VFT equation being applied with high accuracy.

The fitted values of the parameters in eq 8 are also shown in Table 2. The  $\phi$  value of 0.166893<sup>34,35</sup> calculated for 2-HEAF is rather close to the value we determined and proposed for other counterpart ionic liquids [e.g., (2-hydroxyethyl)ammonium acetate,  $\phi = 0.193800$ ]. In a very recent work,<sup>36</sup> we further studied eq 8 to unravel the physical meaning of its parameters  $a$  and  $b$ .<sup>26</sup> Quite importantly, we showed that eq 8 has the privilege of the linear behavior, which can be used suitably in extrapolations to predict viscosities at low temperatures down to the fragile-to-strong crossover temperature ( $T_x$ ), where the viscosity of glassy materials increases sharply. Among other findings, there was an emphasis on the value of  $\phi$  with six significant digits, which was essential for achieving accurate predictions of the viscosity at all temperatures.

**Relation between Surface Tension and Viscosity.** On the basis of the relation tried by Pelofsky,<sup>37</sup> we previously proposed a relation between the logarithm of the surface tension and the fluidity based on eq 8:<sup>26</sup>

$$\ln \gamma = \ln C + D \left(\frac{1}{\eta}\right)^\phi \quad (9)$$

where  $C$  and  $D$  are constant characteristics of the liquid. The above equation has been applied to several ionic liquids accurately. Value of  $\ln C$  has been shown to be related to the alkyl chain length of imidazolium-based ionic liquids.<sup>26</sup> The fitting parameters of eq 9 applied to 2-HEAF using the surface tensions and viscosities measured in this work are shown in Table 3, and the fit is plotted in Figure 4. It can be seen that the

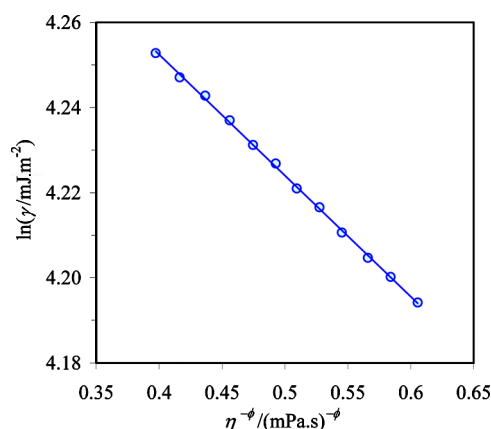
**Table 3. Results of the Fitting to Equation 9 for 2-HEAF**

$\ln(C/\text{mJ}\cdot\text{m}^{-2})$	$4.36 \pm 0.00$
$D/(\text{mPa}\cdot\text{s})^\phi$	$-0.242 \pm 0.006$
$R^2$	0.9993
AAD/%	0.04

experimental surface tension and viscosity data follow eq 9 rather accurately. Therefore, the exponent  $\phi$  is also applicable to 2-HEAF with a characteristic value close to those suggested for other ionic liquids.<sup>26</sup> The fit of the experimental values to eq 9 gave the expression  $\ln(\gamma/\text{mJ}\cdot\text{m}^{-2}) = 4.37 - 0.284[1/(\eta/\text{mPa}\cdot\text{s})^\phi]$ .

## CONCLUSIONS

The ionic liquid 2-HEAF has been synthesized, and its temperature-dependent density, surface tension, and viscosity have been measured experimentally. Care was taken to make



**Figure 4.** Values of  $\ln \gamma$  versus  $1/\eta^\phi$  measured for 2-HEAF. The line is the fit to eq 9.

surface tension and viscosity measurements on the dried ionic liquid under a water-vapor-free atmosphere using a capillary apparatus and the vacuum line. The synthesized 2-HEAF ionic liquid shows a rather high viscosity.  $E^s$  for this ionic liquid (which is  $-\text{OH}$ -functionalized) is much higher than the surface energies of similar but non- $\text{OH}$ -functionalized ionic liquids, which substantiates the role of the  $-\text{OH}$  group in the surface properties. On the other hand, its  $E^s$  is comparable to those of imidazolium-based ionic liquids containing the  $-\text{OH}$  group. Since the surface entropy is rather low, all of these surface thermodynamic functions can be used in part to account for the capability of the ionic liquid to dissolve many substances.

We propose that the surface thermodynamic functions calculated in this work could be helpful to provide insight into the appreciable solvation ability that has been claimed for this ionic liquid in the literature, allowing it to dissolve substances spanning a wide range of chemical natures. From a physical point of view, a substance, either ionic or molecular, could have appreciable solubility in the ionic liquid if, *in part*, the solvation process does not disturb much the rather highly ordered molecular microstructure of the ionic liquid at the interface of the solute and the solvent. From another point of view, the ionic liquid favors high solubility energy-wise (because of the high surface energy of the pure ionic liquid) and entropy-wise (because of the low surface entropy of the pure ionic liquid) in the case of substances not having small molecular sizes. This can be deduced generally from the solubility data for different substances (see Table 2 in ref 2) ranging from small inorganic salts with different ionic sizes to large polymeric substances.

The measured temperature-dependent viscosity follows two model equations with high accuracy: the VFT equation and our recently developed equation containing a characteristic exponent. The value of the exponent for 2-HEAF is close to those reported for other ionic liquids.

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