

# A new ionic liquid: 2-hydroxy ethylammonium formate

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## Abstract

A new ionic liquid (2-hydroxyethylammonium formate), with extremely low melting temperature ( $-82\text{ }^{\circ}\text{C}$ ), is presented. This ionic liquid of equimolar mixture of formic acid and 2-hydroxyethylamine shows reasonably high at ionic conductivity ( $3.3\text{ mS cm}^{-1}$ ) room temperature and heat stability up to  $150\text{ }^{\circ}\text{C}$ . Both  $^1\text{H-NMR}$  and FT-IR spectra establish its simple salt structure. Due to its high polarity, the ionic liquid is able to dissolve many inorganic salts. Also some insoluble polymers such as polyaniline and polypyrrole are highly soluble in the ionic liquid.

In the study, the physical characteristics of the ionic liquid, such as conductivity, viscosity and solvation abilities have been investigated.

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## 1. Introduction

Ionic liquids are salts consisting of ions, which exist in the liquid state at ambient temperatures [1].

They show reasonably high ionic conductivities. Although the first ionic liquid, ethylammonium nitrate (mp  $12\text{ }^{\circ}\text{C}$ ) was reported as early as 1914 [2], ionic liquids have found great interest only recently. More than 500 papers have been published in 2001–2002. Being ion conducting, viscous, non-volatile and non-flammable, they are now finding applications in various fields as catalysis, separation medium and elements of electrochemical devices [3]. Due to their high polarities, the ionic liquids are expected to be very suitable solvents for the reactions between organo-soluble and water soluble reagents.

Utility of the ionic liquids as solvents for various organic reactions [4,5] and polymerization reactions [6–8] have been studied. The most common ionic liquid, 2-butyl imidazolium salt has proved to be very useful in preparing fast switching electrochromic devices [9–11], when used as solvent for  $\Pi$ -conjugated polymers.

The ionic liquids, reported so far, are almost confined to salts of organic amines such as 1 and 3 substituted imidazolines [12,13], alkyl pyridiniums [14] and trialkylamines [15]. The counter ions are mostly weak nucleophilic inorganic anions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{SbF}_6^-$  [16]. Also sulfonate anions, especially alkyl sulfonates such as propanesulfonate [17] have been used together with trialkyl amines.

During research in our laboratory, accidentally it was discovered that formic acid–ethanol amine mixture forms a highly conducting ionic liquid. It was observed that the liquid does not freeze at temperatures around  $0\text{ }^{\circ}\text{C}$  and dissolves appreciable amounts of inorganic salts. This report deals with investigation of physical properties of the new ionic liquid.

## 2. Experimental

### 2.1. Materials

Formic acid (E. Merck), 2-aminoethanol (Fluka), aniline (Aldric) were distilled before use. All the other chemicals were analytical grade commercial products; NaCl, KBr,

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LiClO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>Cl which were powdered (<100 μm) before use.

## 2.2. Preparation of the ionic liquid (2-hydroxy ethyl ammonium formate)

2-Amino ethanol (119.8 g, 0.2 mol) was placed in a two-necked flask equipped with a reflux condenser and a dropping funnel. The flask was mounted in an ice bath. Under vigorous stirring with a magnetic stirring bar, 76 ml (0.2 mol) formic acid was added dropwise to the flask in about 45 min. Stirring was continued for 24 h at room temperature, to obtain a viscous clear liquid. No crystallization or solidification was observed when the liquid sample was stored at 20 °C for over 1 month. Freezing point of the liquid was found to be –82 °C. This was measured simply by determination of melting temperature of the sample frozen in liquid nitrogen.

<sup>1</sup>H-NMR spectrum (measured on a Bruker 250 MHz spectrometer, using DMSO-d<sub>6</sub> as solvent with TMS as internal standard) δ: 8.4 ppm (s, 1H, H–COO<sup>–</sup>); 6.9–7.7 ppm (broad signal, 4H, –NH<sub>3</sub><sup>+</sup>+OH); 3.6 ppm; (t, 2H, –CH<sub>2</sub>–N); 2.8 ppm (t, 2H, –O–CH<sub>2</sub>–).

FT-IR spectrum was taken by a Jasco FT/IR-3300 model IR spectrometer, using a NaCl disk. The broad band in the 3500–2400 cm<sup>–1</sup> range exhibits characteristic ammonium structure. The OH stretching vibration is embedded in this band. The broad band centered at 1600 cm<sup>–1</sup> is a combined band of the carbonyl stretching and N–H plane bending vibrations.

## 2.3. Measurements

Vapor pressure was determined by the simplest variation of air-saturation method, [17] which can be employed satisfactorily for measurement of extremely low vapor pressures as follows: A stream of air (dried by CaCl<sub>2</sub> tube) was passed through the liquid sample (6.3104 g) in a small bottle equipped with an air-inlet tube dipped into the liquid and an outlet tube. The bottle was mounted in an oil bath at 25 °C. The air flow was adjusted to 3 mL/min by a Gilmont flowmeter which was connected between the CaCl<sub>2</sub> tube and the bottle. 1.5 mg of mass loss was determined after passing 11.84 L of air. Based on these data, vapor pressure of the ionic liquid was estimated simply by the ideal gas equation. This result corresponds to a vapor pressure of (2.2±0.14)·10<sup>–2</sup> Torr at 25 °C.

Viscosities were determined by capillary viscometer method using a Canon-Fenske viscometer in a thermostated bath. The viscosities were given in terms of centi Poise (cp), using distilled water as reference.

Conductivities were measured by a WTW Multiline P3 with TetraCon 325 electrode.

Cyclic Voltammetry (CV) traces were obtained by a EG and G Parstat 2263 model potentiostat–galvanostat.

Thermo-gravimetric Analysis (TGA) (which was performed by a Shimadzu TG-50 at 10 °C/min. heating rate, under nitrogen flow, 23 mL/min) curve shows a sharp decline around 150 °C and an inflection at about 190 °C. Hundred percent mass losses occur at 277 °C.

## 3. Results and discussion

Dropwise addition of formic acid to 2-hydroxyethylamine (ethanol amine), under continuous stirring at 0 °C, gives a viscous clear liquid which remains non-frozen when stored in a deep-freeze compartment of a refrigerator (–20 °C) for over 1 month. The liquid freezes at –82 °C. The reaction is a simple acid–base reaction forming formate salt of ethanolamine (Scheme 1).

Both <sup>1</sup>H-NMR and FT-IR spectra indicate simple salt structure of the liquid. Thus, in IR spectrum the broad band 3500–2400 cm<sup>–1</sup> ranges imply typical ammonium structure.

The carbonyl stretching and N–H plane bonding vibrations are observed as a combined band centered around 1600 cm<sup>–1</sup>. In its <sup>1</sup>H-NMR spectra, proton of the formyl group exhibits a sharp singlet at 8.4 ppm. Integral of the broad singlet in the 6.9–7.0 ppm range represents four protons and it must be the sum of ammonium and OH protons. Signals of the methylene protons adjacent to the nitrogen atom and OH groups are observed at 3.6 and 2.8 ppm, respectively.

Since the reaction of ethanolamine with formic acid is highly exothermic, an efficient cooling is essential throughout the reaction. Otherwise vigorous heat evolution may result in following dehydration of the salt to give the corresponding formamide as in the case for Nylon salts (salts of diamines with dicarboxy acids).

Dehydration of the liquid salt commences around 150 °C, as it has been deduced from the TGA curve. Pure 2-hydroxyethyl formamide can be isolated by distillation at 168–170 °C (10 mm) as it has been evidenced by a separate experiment. The TGA shows a hundred percent of mass loss at 277 °C. This implies that evaporation of the dehydration product, 2-hydroxyethyl formamide or its decomposition products occurs under this temperature.

### 3.1. Conductivity

Conductivity of the liquid, at room temperature is 3.3 mS cm<sup>–1</sup> which is reasonably high. The ionic conductivity, σ, depends largely on temperature and rises exponentially as



Scheme 1. Formation of the ionic liquid.

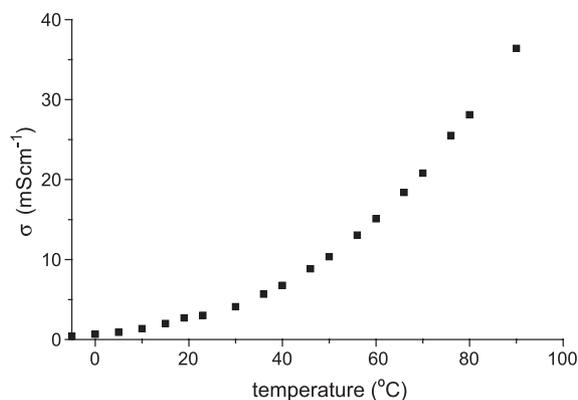


Fig. 1. Temperature dependence of conductivity of the ionic liquid.

the temperature increases and reaches  $40 \text{ mS cm}^{-1}$  at  $92^\circ\text{C}$  (Fig. 1). This can be ascribed to fast ion mobilities at elevated temperatures.

The corresponding  $\ln \sigma$  versus  $1/T$  plot is almost linear in a wide temperature range ( $-5$  to  $92^\circ\text{C}$ ). From the slope of the curve activation energy of the ionic conductivity,  $E_a$  is estimated as,

$$E_a = \text{slope} \times R = 9.2 \pm 1 \text{ kcal/mol, where } R \text{ is gas constant.}$$

On the other hand, the ac conductivity–frequency plot of the ionic liquid (Fig. 2) represents a sharp increase in the 0.1–10 Hz range. There appears a plateau between 10 Hz

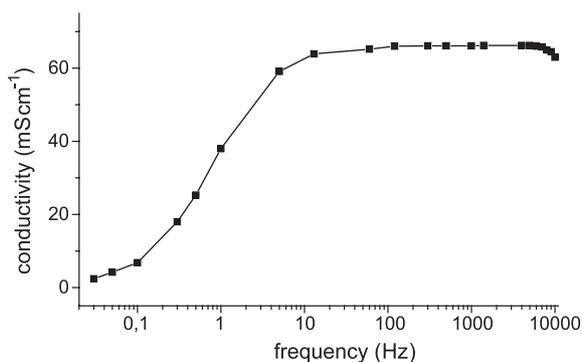


Fig. 2. ac conductivity versus frequency plots of the ionic liquid.

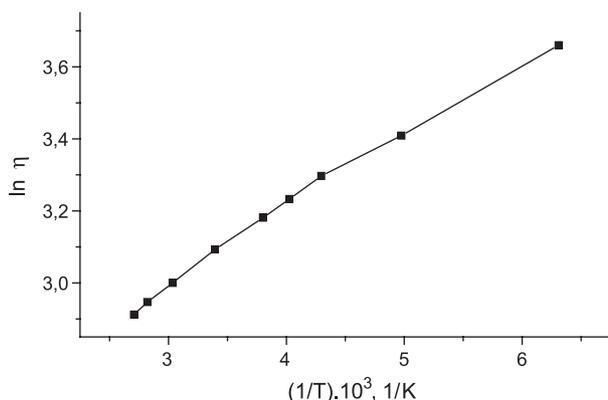


Fig. 3.  $\ln \eta$  versus reciprocal temperature plot of the ionic liquid.

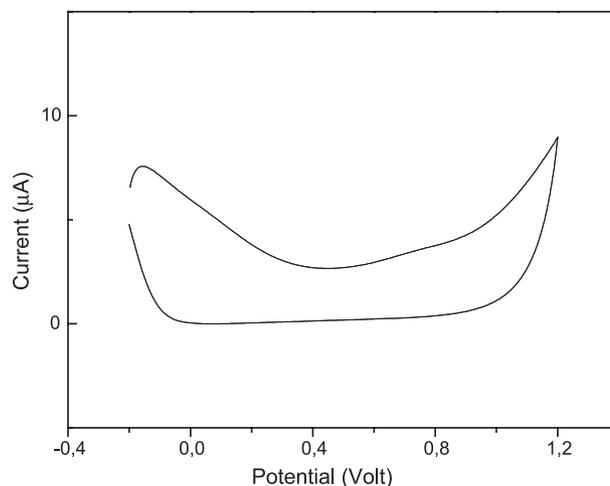


Fig. 4. Cyclic voltammogram of the ionic liquid.

and 10 MHz in which conductivity is around  $68 \text{ mS cm}^{-1}$  at room temperature.

Also viscosity of the ionic liquid is highly temperature dependent. Thus, 105 cP room-temperature viscosity reduces down to 15 cP at  $70^\circ\text{C}$ . The  $\ln \eta$  versus  $1/T$  plot (Fig. 3) is linear from which the activation energy of viscosity can be calculated as  $7.8 \text{ Kcal mol}^{-1}$ . This amount is comparable with  $9.2 \text{ Kcal mol}^{-1}$  of the activation energy for the ionic conductivity. This reveals that molecular mobility is mostly self-diffusive in nature.

Electrochemical stability of the ionic liquid is important when redox reactions are performed in such a medium. The electrochemical stability was inspected by cyclic voltammetry. Redox stability of the ionic liquid must be imposed by the reduction potential of the ammonium cation and oxidation potential of the formate anion. The cyclic voltammetry (Fig. 4) indicates a useful stability range of about 1.1 V (between  $-0.1$  and  $+1.1$  V). Those limits practically do not change after 20 times of oxidation–reduction cycle. Some common physical characteristics of the liquid have been tabulated in Table 1.

### 3.2. Solvating properties of the ionic liquid

Despite its high ionic conductivity, the liquid shows also high solvating ability for some inorganic salts and polymers. The solubilities were estimated by gradual addition of

Table 1  
Some physical characteristics of the ionic liquid

Appearance	Viscous clear liquid
Density	$1.204 \text{ g cm}^{-3}$
Refractive index	$n_D=1.4772$ (at $25^\circ\text{C}$ )
Viscosity	$\eta=105 \text{ cP}$ (at $25^\circ\text{C}$ )
Conductivity	$\sigma=3.3 \text{ mS cm}^{-1}$ (at $25^\circ\text{C}$ )
Decomposition Temperature	Approx. $150^\circ\text{C}$ (by TGA)
Vapor pressure	$2.2 \times 10^{-2}$ Torr (air-saturation method)
Melting point	Mp (freezing point): $-82^\circ\text{C}$

Table 2  
Conductivities of various salts in the ionic liquid

Substance	Solubility (g/100 mL)	Ionic conductivity (mS cm <sup>-1</sup> )
–	–	3.30
Na <sub>2</sub> SO <sub>4</sub>	26	3.06
NaCl	8.4	3.10
KCl	10.2	3.09
KBr	11.1	3.12
NH <sub>4</sub> Cl	28.3	7.20
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N.HCl	12.3	5.90
Polyaniline (neutral)	17	3.03

Error limits of the solubilities:  $\pm 0.5$  g per 100 mL.

anhydrous salts. Anhydrous salts were chosen deliberately to avoid disturbing effects of trace water. The alkaline metal salts studied are highly soluble in the ionic liquid (Table 2). Surprisingly, NaCl, KBr, KCl and Na<sub>2</sub>SO<sub>4</sub> when dissolved in the liquid do not impart any rise in the conductivity. This implies that those salts do not dissociate in the liquid phase. By contrast, ammonium chloride and triethylammonium chloride induce reasonable enhancement in the conductivity. In other words, salts of weak bases are dissociable in the liquid, whereas the salts derived from strong acids and strong bases do not undergo ionic dissociation.

The reason for this unusual behavior is unclear. However, one can conclude that this is due to large differences in the electronegativities of anions and cations associated. For instance, in the case for Na<sub>2</sub>SO<sub>4</sub>, electronegativity difference between sodium and sulfate ions is higher than between 2-hydroxyethylammonium and formate ions. Consequently ion exchange between the two species is not thermodynamically favored and dissociation of Na<sub>2</sub>SO<sub>4</sub> in the ionic liquid does not take place.

More important is that polyaniline and polypyrrole are very soluble in the ionic liquid. Solubility of polyaniline (prepared by oxidation with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in water) is 17 g per 100 ml of the liquid at room temperature.

Moreover, cellulose powder shows also dissolving tendency in the liquid. Dispersions up to 30% of cellulose content can be prepared but no clear solutions are obtained even when stirred for 24 h. Presumably the ionic liquid

serves as a somewhat plasticizing effect for cellulose. Obviously solvation effects of this ionic liquid deserve a detailed investigation. However, due to its high polarity, the ionic liquid is a powerful solvent and expected to be useful in many reactions.

In conclusion, the new ionic liquid presented is a promising material due to its high conductivity and powerful solvating ability. Moreover, its low melting temperature ( $-82$  °C) makes the ionic liquid promising for low temperature reactions.

Although it shows a relatively narrow range of redox stability (0.1–1.1V), being obtainable from commercially available low-cost chemicals, this ionic liquid is expected to be useful as solvent for various reactions.

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