Physicochemical Properties of a Protic Ionic Liquid: Ethylammonium Propionate

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ABSTRACT

Ethylammonium Propionate with high polarity and ionic conductivity was synthesized and characterized with ^{1}HNMR and IR. This ionic liquid which is prepared from readily available starting material in high yield shows reasonably high at viscosity and heat stability up to 150 $^{\circ}$C. This Ionic Liquid is able to dissolve most of organic solvents due to the hydrogen interaction between Ionic Liquid and these solvents.

Keywords: Ionic liquids; Ethylammonium propionate; Physicochemical properties

INTRODUCTION

Room Temperature Ionic Liquids (RTILs) have became a hot topic and found great interest in recent years. Due to their unique physicochemical properties, they are showing increasingly promising perspectives in various fields as catalysis, electrochemical devices and separation medium. Physicochemical properties are indispensable for chose and design of RTILs to use them in industry and academic researches [1-3].

Ionic Liquids are expected to be very suitable solvents for the reaction between organo-soluble and water soluble reagents, because of their high polarity and miscibility. RTILs possess a number of interesting properties such as excellent chemical and thermal stability, high ionic conductivity and a wide window of electrochemical potential [4, 5]. They are considered in green chemistry context due to their stability and ease of recovery facilitating recycling.

More interesting is that the properties of Ionic Liquids (ILs) could be tailored by adjusting the structure of cations and anions, which change the features and capability of Ionic Liquids in diverse systems. To design processes involving Ionic Liquids, it is necessary to know many of the fundamental physicochemical properties which are either scarce or absent.

Ethylamine and Propionic acid mixture forms a viscous and clear Ionic Liquid (IL). Although some physical properties of this Ionic Liquid reported previously [1,6,7], but essential physicochemical properties such as electrochemical window, polarity, vapor pressure, solvatochromism, conductivity and viscosity in different temperature and so on are not considered.

EXPERIMENTAL

Materials

2, 6-Diphenyl-4-(2, 4, 6-triphenylpyridinium-1-yl) phenolate (Reichardt's dye 30) was purchased from Aldrich (>99%) and was used without further purification. 4-Nitroaniline and 4-nitroanisole (Merck, 99%)

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were recrystallized multiple times with water/ethanol and water/aceton before use. Ethylamine (Merck) and Propionic acid (Merck) were used without any distillation.

Preparation of Ionic Liquid

Ethylammonium Propionate was prepared by adding excess amount of Ethylamine to Propionic acid drop wise in a two-necked flask under nitrogen atmosphere with vigorous stirring. The flask was mounted in an ice bath. Stirring was continued for 20 h at room temperature. Excess Ethylamine was evaporated under high vacuum at 80 °C. ^{1}H-NMR spectrum (measured on a Bruker 500 MHz spectrometer, using CDCl$_3$ as solvent) δ: 7.2 ppm (s, 1H, H–COO); 1.0 ppm (q, 3H,CH3– C—COO); 6.9–7.3 ppm (broad signal, 3H, –NH3+); 2.8 ppm; (t, 2H, –CH2–N); 2.1 ppm (t, 2H, C—CH2–COO); 1.2 ppm (q, 3H, CH3–C–N);. 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^{-1} range exhibits characteristic ammonium structure. The broad band centered at 1600 cm^{-1} is a combined band of the carbonyl stretching and N–H plane bending vibrations.

Measurements

All indicator stock solutions were prepared in ethanol and stored in dark glass vials at ~4 °C. An appropriate amount of the indicator solution from the stock was transferred to the quartz cuvette, and its solution was evaporated by vacuum. Concentrations of probes were 1×10^{-4} mol dm^{-3}. UV-Vis spectral curves were recorded using GBC UV-Vis Cintra 40 spectrophotometers, and the temperature of the 1 cm quartz cell was controlled. Viscosities were determined by capillary viscometer method using an AMVn Anton viscometer in a thermostated bath. The viscosities were given in terms of centi Poisse (cp), using distilled water as reference. Conductivities were measured by a WTW Multiline P3with TetraCon 325 electrode. Cyclic Voltammetry (CV) traces were obtained by an EG and G Parstat 2263 model potentiostat–galvanostat. Thermo-gravimetric Analysis (TGA) which was performed by a Netzsch model TG 209 F1 at 15 ^{o}C/min (heating rate) under nitrogen flow (20mL/min) shows a sharp decline around 140°C and an inflection at about 180°C.

RESULTS AND DISCUSSION

Ethylammonium Propionate is an organic salt composed of Ethylammonium as cation and Propionate as anion. The reaction of Ethylamine with Propionic acid is highly exothermic, hence cooling is essential though out the reaction. The reaction is an acid-base reaction forming Propionate salt of Ethylamine. To interpret the behavior of solvents in chemical processes, an understanding of the solution interactions with solute is necessary. Solvatochromism is a way to study solute-solvent interactions that show specific and non specific solute-solvent interactions. Solvatochromism is solvent dependence of the electronic spectrum of solutes [8, 9].

Intensity, position, and shape of absorption bands of dissolved chromophores are influenced by the change in solvents, according to their electronic and molecular structure, due to the different stabilization of their electronic ground and excited states [6].

In order to obtain information on structural and physicochemical properties of IL, we have monitored the behavior of selected solvatochromic absorbance probes within this IL. On the basis of these probes' responses, four solvatochromic parameters (i.e., E_T^N, normalized solvent polarity parameter; π*, dipolarity/polarizability; β, hydrogen-bond acceptor (HBA) basicity; α, hydrogenbond donor (HBD) acidity) were determined in Ethylammonium Propionate. Equations 1-4 show the relationship between solvatochromic parameters and experimental values.

$$E_T(30) = hcv_B N_A = 2.8591 v_B \qquad (1)$$

$$\pi^* = \frac{34.12 - v_{ANS}}{2.343} = 0.427(34.12 - v_B) \qquad (2)$$

$$\beta = \frac{31.10 - 3.14\pi^* - v_{ANI}}{2.79} \qquad (3)$$

$$\alpha = 0.186 \,(10.91 - v_A) - 0.72\pi^* \qquad (4)$$

In which v_B, v_{ANI}, and v_{ANS} are the maximum wavenumbers of Betaine dye, 4-nitroaniline, and 4-nitroanisole respectively in kK.

Reichardt's dye (30) exhibits an unusually high solvatochromic absorbance band shift, from λmax~ 810 nm for diphenyl ether to λmax~453 nm for water [10]. Considerable charge transfer from the phenolate to the pyridinium part of the zwitterionic molecule is occurred. Due to the zwitterionic nature of this probe, behavior of Reichardt's dye is strongly affected by HBD acidity of solvent; donating of hydrogen bond stabilize the ground state more than the excited state [10]. Solvatochromic parameters are reported in Tab. 1.

Table1. Solvatochromic parameters of Ethylammonium Propionate and some molecular solvents

	E_T^N	π^*	β	A
IL	0.85	0.79	0.91	1.18
Methanol[a]	0.76	0.58	0.62	0.93
Ethanol[a]	0.65	0.55	0.91	0.97
N-Propanol[a]	0.76	0.5	1.07	0.74

[a]Reference [3, 8]

The π* parameter is derived from the change in solvents maximum absorption energy of the dye induced by the local electric field. The E_T^N parameter is a blend of dipolarity/polarizability and HBD acidity of media [5] and normalized solvent polarity

parameter for Ethylammonium Propionate is significantly higher than this parameter in Imidazolium-based Ionic Liquids with BF4 and PF6 anions [8,9]. It is clear that E_T^N paremeter for IL is higher than that in molecular solvents such as methanol, ethanol and n-Propanol that indicating higher dipolarity/polarizability and/or hydrogen bond donating acidity of Ethylammonium Propionate relative to that of these alcoholic solvents.

The α value is largely determined by the nature of the cation [5]. Ethylammonium cation can act as strong hydrogen bond donor due to the presence of strong acidic N-H group. Also, the positive charge on nitrogen atom increases the capability of this IL for hydrogen bond donating. It can be concluded that cation of IL with the $-NH_3^+$ group enjoys from more acidity than most of molecular solvents. The β value, in contrast to ILs based on Imidazolium and Pyridinium cations, is controlled by both cation and anion [5]. There isn't any hydrogen bond acceptor group in the structure of IL. So β parameter value for Ethylammonium Propionate is close to that in molecular solvent like Ethanol.

Conductivity of IL is reasonably high at room temperature (2.6 mS.cm^{-1}). Ionic conductivity is affected by temperature and increases exponentially as the temperature rises (Figure 1). At high temperature, mobility of ions elevated (Table 1). The corresponding lnK versus 1/T plot is linear at a wide temperature range. Activation energy of the ionic conductivity, E_a is derived from slope of the curve [11].

Table 2. Conductivity and Viscosity of Ionic Liquid in different temperature

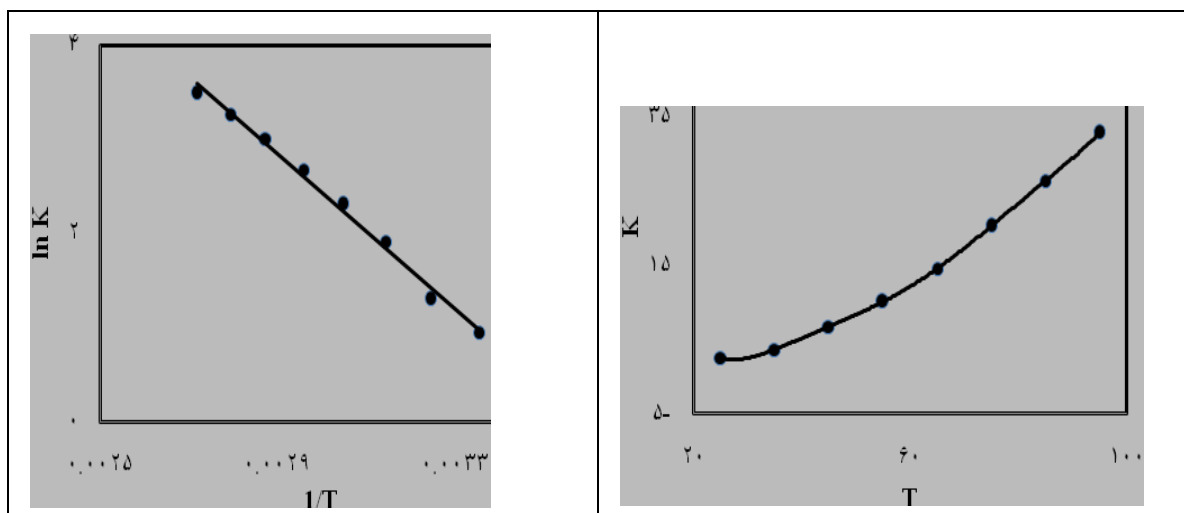| Temperature(^{o}C)	5	15	25	35	45	55	65	75	85	95
Viscosity(cp)	141	136	129	123	117	111	106	101	98	95
Conductivity(mS/cm)			2.6	3.7	6.8	10.1	14.6	20.3	26.4	32.9

Fig. 1. Temperature dependence of conductivity of the Ionic Liquid.

E_a = slope $\times R$ = 8.15 kcal/mol; where R is gas constant

Viscosity of the Ionic Liquid is highly temperature dependent, too. Thus, 129 cP room-temperature viscosities reduce down to 95 cP at 95°C. The $\ln\eta$ versus 1/T plot (Figure 2) is linear from which the activation energy of viscosity can be calculated as 0.93 kcal.mol^{-1}. This amount is comparable with 8.15 kcal.mol^{-1} of the activation energy for the ionic conductivity. This reveals that

molecular mobility is mostly self-diffusive in nature [11].

In redox reactions electrochemical stability of the medium is important. The electrochemical stability was inspected by cyclic voltammetry. Redox stability of the Ionic Liquid must be imposed by the reduction potential of the Ethylammonium cation and oxidation potential of the Propionate anion. The cyclic voltammetry indicates a useful stability range of about 1 V (between 0.1 and +1.1 V).
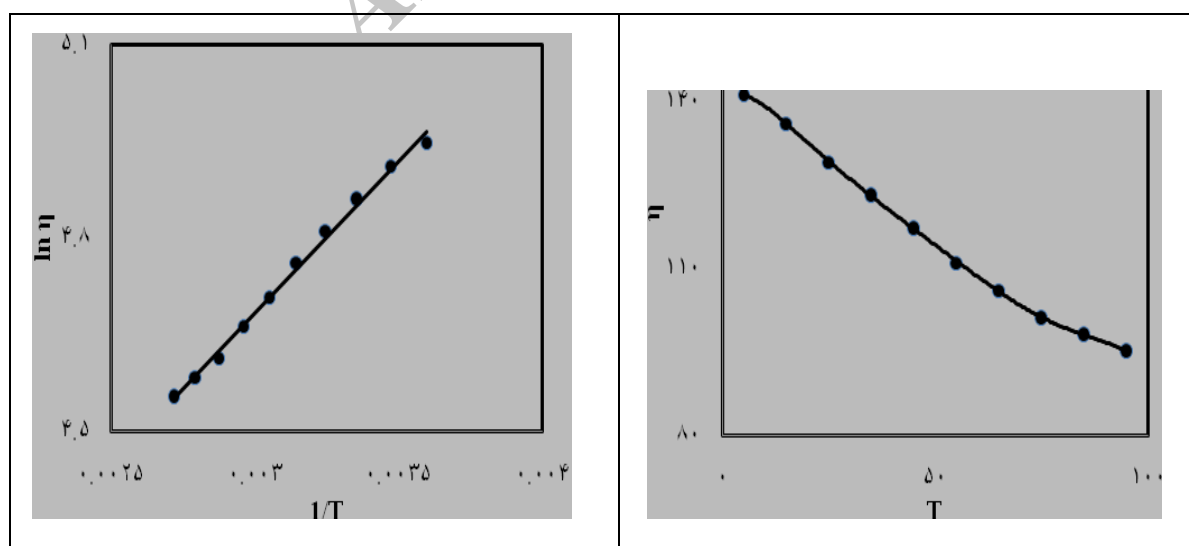

Fig. 2. Temperature dependence of viscosity of the Ionic liquid.

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CONCLUSION

In conclusion, the new Ionic Liquid presented is a promising material due to its high conductivity and powerful solvating ability. Moreover, its high temperature stability makes the Ionic Liquid promising for high 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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