PHYSICO-CHEMICAL PROPERTIES OF MAGNESIUM IONIC LIQUID ANALOGOUS

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ABSTRACT

In this paper, the solubility of Choline chloride (ChCl) in ethylene glycol (EG) was measured by isothermal method in the temperature range between 0°C and 120°C. The solubility of MgCl₂ in saturated ChCl-EG mixture was measured by isothermal method at 20°C, 50°C and 70°C, respectively. Ionic liquid analogous containing MgCl₂ was prepared based on the measured solubility data. The structure of the ionic liquid analogous is preliminarily investigated by Fourier transform infrared spectroscopy. The physical and electrochemical properties of the ionic liquid such as viscosity, conductivity, molar conductivity and density were measured as function of temperature and compositions. It was found that magnesium ionic liquid analogous was highly conducting and low viscosity. The ChCl and MgCl₂ had a great effect on the studied properties.

Keywords: ionic liquid; magnesium ionic liquid analogous; physical properties; electrochemical properties;

INTRODUCTION

The main applications of magnesium salts are to produce magnesium and its alloys. Some researchers were making effort to develop electrolyte solutions in which Mg(ClO₄)₂, Mg(CF₃SO₃)₂, Mg((CF₃SO₂)₂N)₂ and Grignard reagent were used as magnesium source to synthesize a variety of imidazolium ionic liquids¹⁻⁴. A magnesium-based ionic liquid with wide electrochemistry window was reported². The highly reversible magnesium deposition and dissolution processes on silver substrate in the ionic liquid were described. Moreover, investigation has been developed to deposit magnesium from room temperature⁵⁻⁶. But deep eutectic solvent has recently been considered as alternatives to classical ionic liquids⁷. Room temperature molten salts have been formed by mixing quaternary ammonium salts with metal salts⁸. Since Deep eutectic solvent (DES) possess the same chemical and physical properties with ionic liquids, such as large liquid temperature ranges, high ionic conductivities, and wide electrochemical window⁹⁻¹¹, it seems appropriate to classify them as ionic liquids analogous. Works in this area focused on ChCl/ZnCl₂^{7,12,13}, ChCl/urea⁹, ChCl/CrCl₃•6H₂O¹⁴ ionic liquid analogous. Abbott has recently developed a range of ionic compounds which are fluid at room temperature. These ionic liquids are based on simple precursors such as ChCl (vitamin B4) which is cheap. Using these liquids, a number of applications are now under development such as electrodeposition of metals, synthesis of cadmium and zinc semiconductor compounds and so on. The electrodeposition of chromium in a mixture of ChCl and chromium (III) chloride hexahydrate has been reported recently¹⁴. These studies suggest that choline cations can substitute for synthetic cations. Ionic liquids based on ChCl has the additional advantage to be easy to prepare, to be water and air stable, which enable their use in large scale applications. Choline is a naturally occurring biocompatible compound if it was released back to nature. These will provide evidence for the change in properties of ionic liquid. But many physical properties such as viscosity, conductivity, molar conductivity and density of magnesium ionic liquid analogous are few reported.

In this paper, we reported a method of synthesis and characterization of novel air and moisture stable ionic liquids made from magnesium chloride choline chloride and EG. These offer the potential to tailor the physical properties such as melting point, viscosity and conductivity. The advantages of these new ionic liquids over presently available magnesium-containing ionic liquids are moisture stable and much cheaper than imidazolium-based liquids.

EXPERIMENTAL SECTION

ChCl [HOC₂H₄N(CH₃)₃⁺Cl⁻] (Aldrich, 99%, Sinopharm chemical Reagent Co., Ltd, China) was, when necessary, recrystallised from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) (Aldrich 99+%, Tianjin Baishi Chemical Co., Ltd, China), was used as received. Magnesium chloride (MgCl₂) (Aldrich 99+%, Tianjin Baishi Chemical Co., Ltd, China) was used as received.

The ChCl were gradually added in EG in a round bottom flask with three necks until ChCl was not dissolved in the temperature range between 0°C and 120°C. The variation of the temperature was done by using a water-bath with temperature control and mechanical stirrer.

ChCl and EG in a molar ratio of 2:5; 7:10; 1:1(saturated) were combined and heated at 20°C, 50°C and 70°C, respectively by Collector-type magnetic heating stirrer. Follow above steps, the MgCl₂ was gradually added in liquid until MgCl₂ was not dissolved and a homogeneous liquid was formed. All synthesis procedures were done at atmospheric pressure. The viscosity, conductivity, density and Cyclic Voltammetry curves (CV) were measured by different instrument when MgCl₂ was added in ChCl-EG each time.

Fourier transform infrared spectroscopy (FTIR) analysis was carried out by a Nicolet Nexus 670 FTIR Spectrophotometer (Thermo Nicolet Corporation, Madison, USA) in liquid films using KBr salt tablets.

The viscosity of magnesium ionic liquid analogous was determined using a rotary (NDJ-1 shanghai yueping scientific instrument Co.,Ltd, China) viscometer. The variation of the temperature was done by using a water-bath with temperature control.

The conductivity and its temperature dependence was measured using shanghai scientific instrument Co., Ltd conductivity meter with temperature and conductivity probes. The variation of the temperature was done by using a water-bath with temperature control.

Cyclic voltammetry were obtained using CS310 electrochemical workstation (WuHan CorrTest Instrument Co.Ltd.). A three-electrode electrochemical cell was used for the electrochemical experiments system consisting of an Ag wire; a platinum wire counter electrode and a platinum wire reference electrode were used. The working electrode was polished with sandpaper, rinsed and dried prior to all measurements. Electrochemical measurements were performed at 20°C, 50°C, 70°C and a scan rate of 20mVs⁻¹ was used in voltammetric experiments.

RESULTS AND DISCUSSION

1. The solubility of ChCl in EG

Figure 1 The solubility of ChCl in EG as a function of temperature.

Figure 1 shows the solubility of ChCl in EG as a function of temperature. It is noticeable that the solubility of ChCl in EG is considerably high. The solubility of the medium is increasing as the increasing temperature.

Table 1 The solubility of MgCl_2 in ChCl-EG saturated mixture at 20°C, 50°C, 70°C, respectively.

T/°C	$m_{\text{MgCl}_2}/\text{g}$
20	2.024
50	3.669
70	4.755

Table 1 shows the solubility of MgCl_2 in ChCl-EG saturated mixture at 20°C, 50°C, 70°C, respectively. It is noticeable that the solubility of MgCl_2 in ChCl-EG saturated mixture considerably decrease compared to MgCl_2 in EG (table 2), which can attribute to salting out effect of MgCl_2 and ChCl.

Table 2 The solubility of MgCl_2 in EG saturated at 20°C, 50°C, 70°C, respectively.

T/°C	$m_{\text{MgCl}_2}/\text{g}$
20	8.492
50	15.344
70	17.833

2. FTIR

Fourier transform infrared spectroscopy (FTIR) is used to study the interaction between different groups, analyze and identify structures. Frequency shifts, band widths and absorbance values of the same bond in different systems are used to interpret the structure of the ionic liquid.

Figure 2. The FTIR spectra of ChCl-EG- MgCl_2 ionic liquid analogous

Figure 2 is the FTIR spectroscopy of ionic liquids analogous ChCl-EG- MgCl_2 . The broad peak between 3500 and 3000 cm^{-1} in figure 2 shows the hydrogen bond forming in ionic liquids analogous. The hydrogen bonds formed in system ChCl-EG- MgCl_2 is the $\text{H-O}\cdots\text{H}$. The weak peak between 2875 and 2940 cm^{-1} in the figure 2 also shows the hydrogen bonds $\text{H-O}\cdots\text{H}$ exist. In the ionic liquid analogous systems, it can be noted the $\nu_{\text{C-Cl}}$ at 955.31 cm^{-1} , 955.06 cm^{-1} , 958.98 cm^{-1} associated to ChCl. Compared with ChCl (The FTIR spectra of ChCl is not listed), the frequency of $\nu_{\text{C-Cl}}$ is not changed which indicates the structure of Ch^+ is not destroyed.

3. Viscosity

Viscosity is an important property of ionic liquids used as electrolyte solutions and low viscosity of ionic liquid is expected. The viscosity of ionic liquids is determined by Vander Waals forces and hydrogen bonding. Electrostatic forced may also play an important role.

Figure 3 The viscosities of ChCl-EG- MgCl_2 mixtures as a function of temperature and compositions.

Figure 3 shows the viscosity of ChCl-EG- MgCl_2 mixtures as a function of temperature and compositions. It is noticeable that the viscosity of ChCl-EG- MgCl_2 covers the range 10 to 60 cp. The minimum viscosity is not observed at the eutectic composition. The viscosity of ChCl-EG- MgCl_2 mixtures decreases with the increasing temperature and increases as the increasing mole fraction of MgCl_2 , which can attribute to the high temperature leads the Van Der Waals Force between different groups change to weak. Halide salts can also form complexes with hydrogen bond honors.¹⁵ When more MgCl_2 are added, the numbers of molecules in per unit volume increase which leads to the Van Der Waals Force between different groups become stronger. It also can be concluded that maybe MgCl_2 play the role of bridge that connect the other ionic groups. As more MgCl_2 are added, more bridges are built. Then the network between different groups is formed. Since the formation of network structure, viscosity increases.

It also shows that the viscosity of these ionic liquids is considerably lower than ionic liquid analogous based on ChCl reported previously¹⁴ and are similar to those for most imidazolium based ionic liquids reported previously^{1,15,16}, suggesting that the H-bonds played a significant role in magnesium ionic liquid analogous.

Figure 4 The viscosities of ChCl-EG- MgCl_2 mixtures as a function of ChCl.

Figure 4 shows the viscosity of ChCl-EG- MgCl_2 mixtures as a function of ChCl. It is noted that the viscosity increased as the salt is added in the mixture. This is because the diols form linear aggregates of hydrogen-bonded molecules. The change in viscosity (η) with temperature is given by Equation (1):

$$\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \quad (1)$$

In which η_0 is a constant, E_η is the energy for activation of viscous Flow¹⁶ and R is the gas constant. Table 3 shows that all the data in figure 3 fit well to Equation (1). The values obtained for E_η helps with the design of low viscosity ionic liquids.

Table 3 Activation energies for viscous flow (E_η) and conductivity (E_Λ) as a function of liquid composition. Coefficients of correlation (r) for the fits to Equations (1) and (2) are also given.

ChCl/EG/ MgCl ₂	E_η [kJ·mol ⁻¹]	r	E_Λ [kJ·mol ⁻¹]	$-r$
2:5:0	292.1	0.933	473.2	-0.998
2:5:0.035	244.0	0.969	295.0	-0.958
2:5:0.06	238.7	0.972	284.9	-0.957

4. Conductivity

The conductivity of ionic liquids is inversely linked to their viscosity. Hence, ionic liquids of higher viscosity exhibit lower conductivity. Deep eutectic solvents are highly conducting (ca. 8.74 mS·cm⁻¹ at 20°C)¹⁵, confirming that the ionic species are dissociated in the liquid and can move independently. The viscosity and conductivity are strongly affected by quaternary ammonium salt and hence the fluid properties could be tailored for specific applications.

Figure 5 Conductivity of ChCl-EG-MgCl₂ mixtures as a function of temperature and compositions.

Figure 5 shows the conductivity of ChCl-EG-MgCl₂ mixtures as a function of temperature and compositions. It is noticeable that the conductivity of MgCl₂-EG-ChCl covers the range 5.99 to 22.7 mS·cm⁻¹. The conductivity inconsiderably decreases with the increasing MgCl₂. For ionic liquids the conductivity is generally governed by the mobility of the charge carrier. Charge carrier decreases with the increasing MgCl₂, which is probably the formation of complex between MgCl₂ and EG when MgCl₂ is added in the liquid. The large constituent ions of ionic liquids reduced the ion mobility which, in turn, leads to lower conductivities. Furthermore, ion pair formation and/or ion aggregation lead to reduced conductivity. Values are similar to those for most imidazolium based ionic liquids and two orders of magnitude larger than for the choline chloride-zinc chloride system previously studied¹³. This is probably related to the viscosity of the ionic liquid, since the viscosity of MgCl₂-EG-ChCl shown in figure 3 is similar to that of imidazolium ionic liquid and smaller than ChCl-urea⁹. Comparison between figure 3 and figure 5, it can be noted that the conductivity decreases with the increase of viscosity in the same compositions. This may be result from the high viscosity prevents the movement of ions. Abbott and co-worker reported the highest conductivity of ChCl-EG ionic liquid analogous at the molar ratio of 1:4¹⁸.

Figure 6 The conductivity of ChCl-EG-MgCl₂ as a function of ChCl.

Figure 6 shows the conductivity of ChCl-EG-MgCl₂ as a function of ChCl. It is noticeable that the conductivity of ChCl-EG-MgCl₂ is the highest at the mole ratio 2:8:0.06. Analogous to the viscosity data, conductivity (σ) of ionic liquids has been fitted to Equation (2)¹⁶

$$\ln \sigma = \ln \sigma_0 - \frac{E_\Lambda}{RT} \quad (2)$$

The activation energy for conduction (E_Λ) is listed in Table 3 as a function of composition. As for the E_Λ values, they are significantly larger than choline chloride/CrCl₂·6H₂O ionic liquid analogous (values from 37.8 to 50.5)¹⁴

The molar conductivity was calculated by (3)¹⁹

$$\Lambda = \kappa M / \rho \quad (3)$$

Where κ is the conductivity, ρ is the density, and M is the molar mass which is taken as being the molar mass of the three components multiplied by their mole fraction in the mixtures. It is noted that mole conductivity firstly increases, then decreases with the increasing ChCl and decreases as the increasing MgCl₂. This is consistent with the trend of conductivity. At low concentrations, most of the ions exist as ion pairs, and the molar conductivity is relatively low. The molar conductivity increases as the concentration of triple ion increases according to occur in non-aqueous solutions¹⁸.

The molar conductivity is inversely proportional to the viscosity of ionic liquid and this correlation is virtually independent of the cation and anion. This has been used as a method of defining the properties of an ionic liquid¹⁸.

Figure 7 Conductivity as a function of 1/viscosity for the data in Figures 3 and 5.

Figure 7 shows a strong linear correlation between conductivity and the reciprocal of viscosity, which shows that the ionic mobility is controlling the conductivity of the liquid. It also shows that since the slope is approximately constant at all compositions, the charge-carrying species is dominated by one species¹⁸.

The relatively high conductivities of magnesium ionic liquid analogous make them good candidates for electrochemical applications, such as electrodeposition, electrofinishing.

5. Cyclic Voltammetry curves

The clear application of ionic liquid analogous containing magnesium is for the study of magnesium electrodeposition. And reduction potential of the electrolyte solution is one of the important properties. The reduction potential is governed not only by the chemical structure of the materials used but also by the electrode materials, sweep rate of the potential, temperature, solvent, impurity and so on.

Figure 8 The CV curves as a function of temperature and compositions. X (MgCl₂): a 0.3, b 0.8, at 20°C, c 1.1 at 50°C, d 0.8 at 70°C.

Figure 8 shows the CV curves as a function of temperature and compositions on an Ag wire at a sweep rate of 20 mV×s⁻¹. As can be seen from the figure 8, a the peak reduction potentials for magnesium is about -1.8V. Figure 8, b, c, d show the peak reduction potentials for magnesium are very similar in different components MgCl₂ based liquids in the same temperature (50°C, 70°C) (-0.315 V and -0.474 V, respectively). But The peak reduction potentials for magnesium is great changing from -0.88V to -1.66V at 20°C. The large reduction peak at -1.66 V at 20°C is probably due to reduction of the magnesium cation. It is clear that the reduction process does not produce an entirely adherent deposit, because the charge of the anodic process is much less than that of the cathodic process.

6. Density

The variation ratio of magnesium ionic liquid analogous density with temperature is shown in figure 9.

$$\rho / g \cdot cm^{-3} = a(t / ^\circ C) + b \quad (5)$$

Where ρ is the density, t is the temperature, a and b are a constant that depends on the type of magnesium ionic liquid analogous. The values of a and b for the tested magnesium ionic liquid analogous are shown in Table 4.

Table 4 Values of Parameters a and b Used in Equation 5.

ChCl/EG/MgCl ₂	a	b
2:5:0	$-5.25 \cdot 10^{-4}$	1.1322
2:5:0.035	$-5.57 \cdot 10^{-4}$	1.1385
2:5:0.06	$-5.23 \cdot 10^{-4}$	1.1396

Figure 9 Densities of magnesium ionic liquid analogous as a function of temperature.

The behavior here is linear as expected. The results for these magnesium ionic liquid analogous are fitted by a linear relationship as follows¹⁹:

CONCLUSION

Solubility of choline chloride was first surveyed in ethylene glycol (EG) and the solubility of MgCl₂ was acquired in saturated ChCl-EG. Magnesium ionic liquid analogous has been synthesized by mixing choline chloride with magnesium chloride and Ethylene glycol. Physico-chemical properties were experimentally measured for this novel magnesium ionic liquid analogous.

Fourier transform infrared spectroscopy shows that the hydrogen bond forming in ionic liquids analogous. It was found that the type of ionic liquid was low viscosity, high ionic conductivity. The effect of temperature and compositions on the measured physical properties was discussed in detail. The viscosity of ChCl-EG-MgCl₂ decreased with the increasing temperature and increased as the increasing mole fraction of MgCl₂. The conductivity of MgCl₂-EG-ChCl inconsiderably decreased with the increasing MgCl₂. The conductivity was the highest at the mole ratio 2:8:0.06 at the same temperature. A straight line equation was used to fit the density while Arrhenius equation was used to fit both viscosity and conductivity profiles. Cyclic voltammetry showed that the peak reduction potentials for magnesium is lower than standard reduction potentials of magnesium (-2.37V).

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REFERENCES

- [1] G. P. Pandey, S. A. Hashmi, *J. Power Sources*, **187**, 627, (2009)
- [2] Y.N. NuLi, J. Yang, R.Wu, *Electrochem. Commun.* **7**, 1105, (2005)
- [3] G.T. Cheek, W.E. O'Grady, A.S.Z. bedin, E.M. Moustafa, F. Endres, *J. Electrochem. Soc.* **155**, D91, (2008)
- [4] N. Amir, Y. Vestfrid, O. Chusid, Y. Gofer, D. Aurbach, *J. Power Sources*, **174**, 1234, (2007)
- [5] N. Yoshimoto, Y. Tomonaga, M. Ishikawa, M. Morita, *Electrochimica Acta*, **46**, 1195, (2001)
- [6] M. Moritaa, T. Shirai, N. Yoshimotoa, I.M. shikawa, *J. Power Sources*, **139**, 351, (2005)
- [7] A.P. Abbott, G. Capper, D.L. Davies, H.L. Munro, R.K. Rasheed, V. Tambyrajah, *Chem. Commun.* 2010, (2001)
- [8] A.P. Abbott, K.J. McKenzie, *Phys. Chem. Chem. Phys.* **8**, 4265, (2006)
- [9] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, *Chem. Commun.* 70, (2003)
- [10] Frank E. Abedin S, *Phys. Chem. Chem. Phys.* **8**, 2101, (2006)
- [11] S.J. Zhang, X.M. Liu, X.Q. Yao, H.F. Dong, X.P. Zhang, *SCIENCE CHINA, B*, **39** (10), 1134, (2009)

- [12] A.P. Abbott, G. Capper, K.J. McKenzie, K.S. Ryder, *J. Electroanal. Chem.* **599**, 288, (2007)
- [13] Y. Zou, H.J. Xu, G.Z. Wu, Z. Jiang, S.M. Chen, Y.Y. Huang, W. Huang, X.J. Wei, *J. Phys. Chem. B* **113**, 2066(2009)
- [14] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, *Chem. Eur. J.* **10**, 37, 69, (2004)
- [15] A.P. Abbott, *Chem. Phys. Chem.* **5**, 1242, (2004)
- [16] J.O'M. Bockris, A.K.N. Reddy, *Modern Electrochemistry* Vol. 1, Plenum, New York Chapter 6 1970
- [17] G. J. Janz, *Molten Salt Handbook*, Academic Press, New York 1967
- [18] A.P. Abbott, R.C. Harris, K.S. Ryder, *J. Phys. Chem. B.* **111**, 4910, (2007)
- [19] M.A. Kareem, F.S. Mjalli, M.A. Hashim, I.M. AlNashe, *J. Chem. Eng. Data.*, **Vol. 55(11)**, 4632, (2010)