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Physical–chemical properties of nickel analogs ionic liquid based on choline chloride

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Abstract In this paper, a homogeneous, green analogs ionic liquid containing choline chloride and nickel chloride hexahydrate is formed. The structure of the analogs ionic liquid is preliminary investigated by Fourier transform infrared spectroscopy. It is shown that the nickel chloride hexahydrate bond via hydrogen bonds with choline chloride and urea. The physico-chemical properties of the analogs ionic liquid such as viscosity, conductivity, density, and thermal stability are measured as a function of temperature and composition. The thermal expansion coefficients (r), the molar Gibbs energy of activation (ΔG^*) for viscous flow, the molar enthalpy of activation (ΔH^*), and the molar entropy of activation (ΔS^*) for viscous flow have been calculated. A straight-line equation is used to fit the density data while the Arrhenius equation is used to fit both viscosity and conductivity. Thermal stability of analogs ionic liquid was carried out from room temperature to 973.15 K. It indicates that analogs ionic liquid is stable from room temperature to 488.2 K.

Keywords Analogs ionic liquid · Structure analysis · Viscosity · Conductivity · Density · Thermal stability

Introduction

Eutectic mixtures of salts have been utilized for a long time to decrease the temperature for molten salt applications. In recent years, ionic liquids analogs formed based on deep eutectic solvents (DESs) have been seen as an alternative to traditional solvents and ionic liquids [1–6]. The ionic liquids analogs exhibit some properties similar to ionic liquids such as a wide electrochemical window, a low viscosity, a high conductivity, etc. The ionic liquids analogs of choline chloride and urea, glycerol, and ethylene glycol were first developed by Abbott et al. [7, 8]. This principle can be applied to a lot of other hydrogen-bond donors such as phosphonium and acids [2, 4, 9, 10]. These liquids possess unique solvent properties that are strongly influenced by hydrogen bonding. DESs have been used for a variety of applications such as metal deposition, solvent systems [11–16]. Electrodeposition of metals [17–19] and alloys [20–22] from DES have recently been reported. A wide variety of hydrated salt mixtures with choline chloride have been found to form these ionic liquids, including $CaCl_2 \cdot 6H_2O$, $LaCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$ [23], and $MgCl_2 \cdot 6H_2O$ [24]. But many physical properties of nickel analogs ionic liquid are reported. Good physical properties of nickel analogs ionic liquid help for its applications, such as nickel electrodeposition.

The current work reports the system formed from choline chloride and nickel chloride hexahydrate. The structure analysis and physico-chemical properties of ionic liquids analogs are obtained. The r, ΔG^*, ΔH^*, and ΔS^* for viscous flow have been calculated. Thermal stability of analogs ionic liquid was carried out.

Experimental section

Chemicals

Choline chloride (ChCl) (Aldrich, 99 %, Sinopharm Chemical Reagent Co., Ltd., China) was recrystallized

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from absolute ethanol, filtered and dried at 353.15 K under vacuum. The nickel chloride hexahydrate (Aldrich 99+%, Tianjin Baishi Chemical Co., Ltd., China) was used as received. Urea (Aldrich 99+%, Tianjin Baishi Chemical Co., Ltd., China) was recrystallised from absolute ethanol, filtered, and dried in a vacuum. The analogs ionic liquid was prepared by stirring the three components at 338.15 K until a homogeneous, green liquid was formed.

FTIR measurement

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

Physico-chemical properties

The viscosity of analogs ionic liquid was determined using a rotary viscometer (Brookfield Engineering Laboratories, Inc. USA). The variation of the temperature was done by using low temperature thermostat bath.

The conductivity and its temperature dependence was measured using shanghai scientific instrument Co., Ltd. conductivity meter (DDSJ-318) with temperature and conductivity probes. The variation of the temperature was done by using an oil-bath.

The density was measured by densimeter (MH-124S, Matsuhaku, Taiwan) at the temperature ranged from 298.15 to 238.15 K.

Thermal analysis experiment

Thermal analysis is determined by a thermal analysis instrument (STA 449F3, NETZSCH, Germany). The heating rate of 5 K min^{-1} were maintained while recording the mass loss as a function of time and temperature ranging from ambient to 973.15 K under the protection of nitrogen atmosphere.

Results and discussion

FTIR

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 1 is the FTIR spectroscopy of the mixture of ChCl–urea–$NiCl_2{\cdot}6H_2O$, Fig. 2 shows the FTIR spectra of $NiCl_2{\cdot}6H_2O$. The spectra of Fig. 1 show some changes different from Fig. 2, especially the peaks in high-wave number. The strong peak of $\nu_{O\text{–}H}$ between 3,200 and 3,413.07 cm^{-1} in Fig. 1 becomes broader than that of in Fig. 2 because of the hydrogen bond formed between the coordinated water and ChCl, such as the H–O···H and O–H···Cl. Simultaneously the hydrogen bonds N–H···N and N–H···O in system of ChCl–urea–$NiCl_2{\cdot}6H_2O$ are formed. The hydrogen bond in the ionic liquid is very important for the ionic liquids analogs of ChCl and $NiCl_2{\cdot}6H_2O$, because the hydrogen bond may reduce the lattice energy of ChCl and decrease the freeing point of ionic liquid. The absorption band at 1,662.80 and 1,621.46 cm^{-1} is because of stretching vibration peak of C=O and O–H. The absorption band at 1,474.36 cm^{-1} appears due to the existence CH_3 of ChCl. It may cover the band at 1,456 cm^{-1}, so the δCH_2 at 1,456 cm^{-1} disappears. In ChCl–urea–$NiCl_2{\cdot}6H_2O$, it can be noted the $\nu_{C\text{–}C}$ at 954.63 cm^{-1} of ChCl. Compared with ChCl, the frequency of $\nu_{C\text{–}C}$ is not changed which indicates the structure of Ch^+ is not destroyed.

Viscosity

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

Figure 3 shows the viscosity of ChCl–urea–$NiCl_2{\cdot}6H_2O$ mixtures as a function of temperature and composition. The viscosity of these ionic liquids analogs is considerably lower than that of ChCl/urea [7] analogs ionic liquid reported previously, suggesting that the waters of hydration play a significant role in analogs ionic liquid. The viscosity

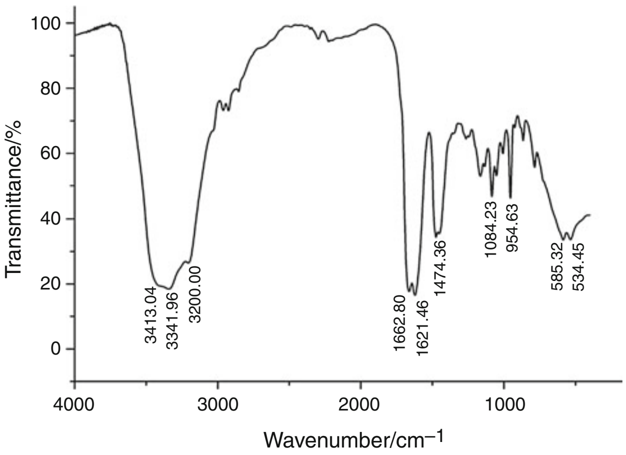


Fig. 1 The FTIR spectra of ChCl–urea–$NiCl_2{\cdot}6H_2O$ analogs ionic liquid

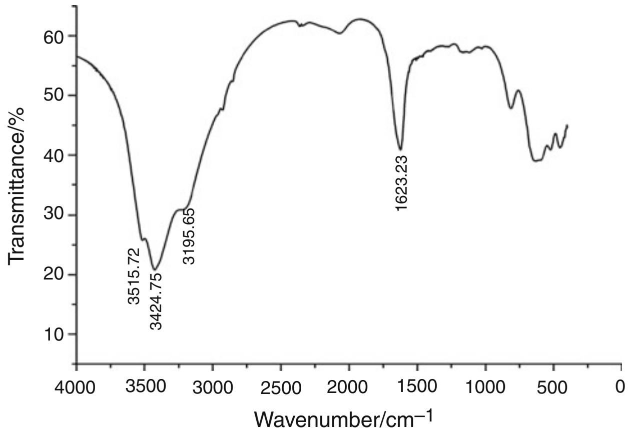


Fig. 2 The FTIR spectra of $NiCl_2 \cdot 6H_2O$

increases with the increasing mole fraction of $NiCl_2 \cdot 6H_2O$. This is because a large number of hydrogen bonds are formed between ChCl and $NiCl_2 \cdot 6H_2O$, leading to the viscosity of the analogs ionic liquid increasing. As a group, ionic liquids are more viscous than the most common molecular classical solvents. The viscosity of these ionic liquids analogs is higher compared to ChCl–urea/EG/Gl–$MgCl_2$ system [25–27].

The change in viscosity (η) with temperature is given by Eq. (1) [28]

$$\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \tag{1}$$

in which η_0 is a constant, E_η is the energy for activation of viscous flow and R is the gas constant.

Figure 4 is the relationship of lnη and T^{-1}. We can obtain E_η and correlation coefficient (r) according to the scope and intercept of Fig. 4. Table 1 shows all the data in Fig. 3 fit well to Eq. (1). It is noted that the viscosity of ChCl–urea–$NiCl_2 \cdot 6H_2O$ mixtures is inversely linked to their E_η. The values obtained for E_η help with the design of low viscosity ionic fluids.

The viscosity of ionic liquids analogs is strongly dependent upon temperature and exhibits classical Arrhenius behavior in the studied temperature range. For a better understanding of the viscous flow, the thermodynamic functions of activation were calculated from the dynamic viscosity values according to Eyring's transition state theory. The absolute rate approach of Eyring provides the following expression for the dynamic viscosity of a liquid mixture [29, 30]:

$$\eta = \frac{hN_A}{V} \exp\left(\frac{\Delta G^*}{RT}\right), \tag{2}$$

where h is the Planck's constant, N_A Avogadro's number, V the molar volume of the eutectic mixture (calculated as the ratio of average molar mass and density of the mixture), ΔG^* the molar Gibbs energy of activation for the viscous flow process. Combining with

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{3}$$

yields the equation

$$\ln\left(\frac{\eta V}{hN_A}\right) = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R}. \tag{4}$$

From the experimental density and viscosity data, ln($\eta V/hN_A$) as a function of $1/T$ has been calculated.

Figure 5 is the relationship of ln($\eta V/hN_A$) and T^{-1}. The enthalpy (ΔH^*) and entropy (ΔS^*) of activation of viscous flow were obtained according to the slope and intercept of Fig. 5. The ΔH^* values are constant in the studied temperature range. The obtained values of thermodynamic functions of activation at 363 K are presented in Table 2, together with the coefficients of correlation for the fits to Eq. (4).

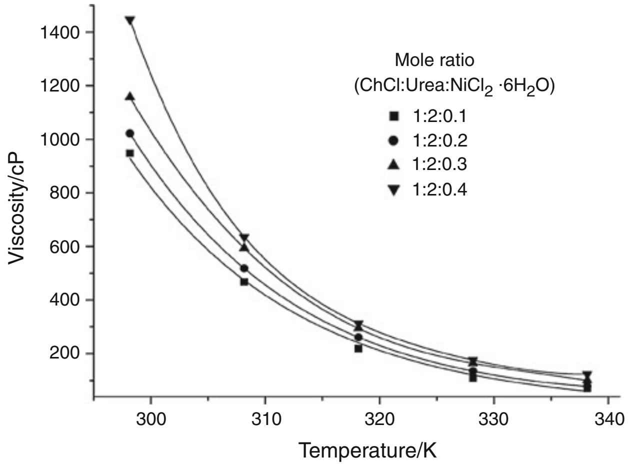


Fig. 3 The viscosities of ChCl–urea–$NiCl_2 \cdot 6H_2O$ analogs ionic liquid as a function of temperature and composition

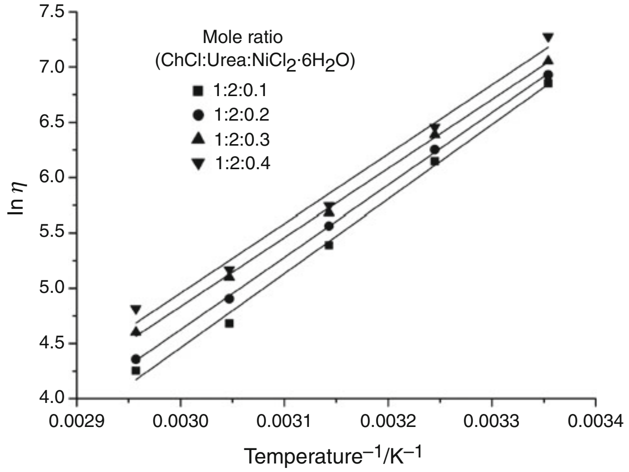


Fig. 4 The relationship of ln η and T^{-1}

Table 1 Activation energies for viscous flow (E_η) and conductivity (E_Λ) as a function of liquid composition

ChCl:urea:NiCl$_2$·6H$_2$O	E_η/kJ mol^{-1}	r	E_Λ/kJ mol^{-1}	$-r$
1:2:0.1	55.973	0.995	4.378	0.998
1:2:0.2	54.426	0.999	3.998	0.994
1:2:0.3	51.926	0.998	4.093	0.987
1:2:0.4	52.231	0.984	4.095	0.999

Coefficients of correlation (r) for the fits to Eqs. (1) and (5) are also given

Table 2 The thermodynamic functions of activation of viscous flow, ΔH^*, ΔS^*, ΔG^*, and coefficients of correlation (r) for the fits to Eq. (4)

ChCl:urea:NiCl$_2$·6H$_2$O	ΔH^*/ kJ mol^{-1}	$T\Delta S^*$/ kJ mol^{-1}	ΔG^*/ kJ mol^{-1}	r
1:2:0.1	56.432	24.777	81.209	0.9948
1:2:0.2	54.981	26.431	81.412	0.9887
1:2:0.3	51.988	29.653	81.641	0.9981

Table 2 reveals that the magnitude of molar enthalpy of activation for viscous flow is higher than $T\Delta S^*$ values. Therefore, the molar enthalpy of activation for viscous flow is more important than the entropic contribution to the molar Gibbs energy of activation for viscous flow values. It seems that for the viscous flow process the interactional factor is predominant over structure for all investigated systems.

Conductivity

The conductivity is an important characteristic of ionic liquids for application in the electrochemistry. The conductivity of ionic liquids analogs is inversely linked to their viscosity. Thereby, ionic liquids analogs with higher viscosity possess lower conductivity. In general, ionic liquids analogs are highly conducting [7, 8, 22]. It can be confirmed that the ionic species are dissociated in the liquid and can move independently. The viscosity and conductivity are strongly affected by quaternary ammonium salt. As a result, ionic liquids analogs properties could be designed for specific applications.

Figure 6 shows the conductivity of ChCl–urea–NiCl$_2$·6H$_2$O as a function of temperature and composition. It proposed that the conductivity of ChCl–urea–NiCl$_2$·6H$_2$O increases with the increasing of mole fraction of NiCl$_2$·6H$_2$O and temperature. For the investigated systems, the conductivity values cover the range from 0.031 to 14.40 mS cm^{-1} over the studied temperature. It is noticeable that the conductivity of these ionic liquids is familiar to ChCl/urea [8] and larger than ChCl/glycerol [7], ChCl/chromium chloride hexahydrate [1], and phosphonium-based ionic liquids analogs [9]. It is smaller than the

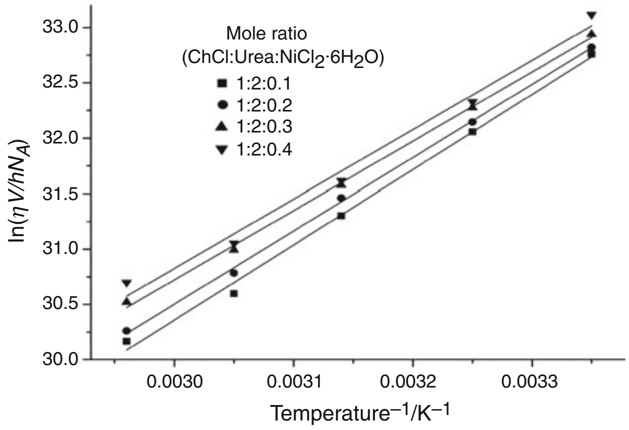


Fig. 5 The relationship of ln($\eta V/hN_A$) and T^{-1}

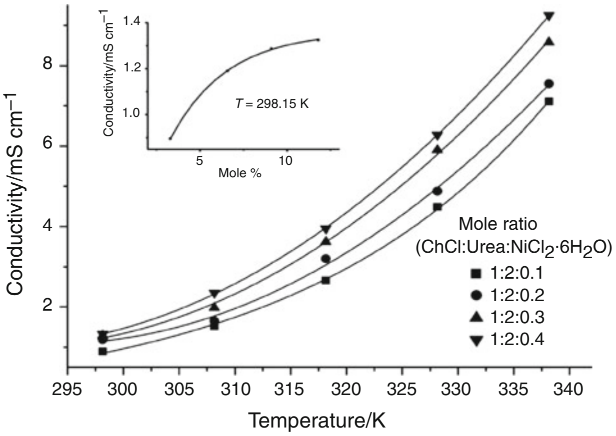


Fig. 6 The conductivity of ChCl–urea–NiCl$_2$·6H$_2$O analogs ionic liquid as a function of temperature and composition

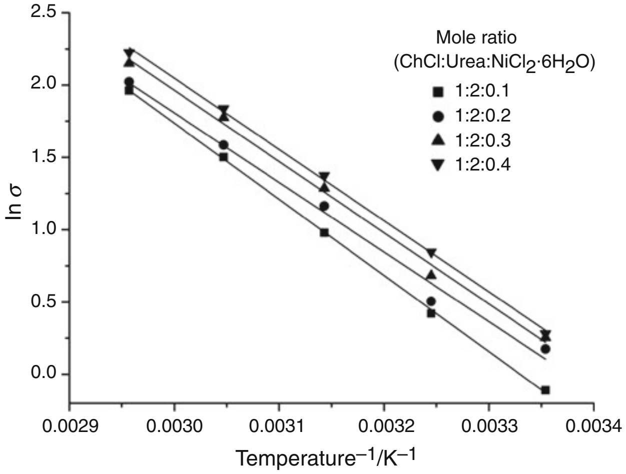


Fig. 7 The relationship of lnσ and T^{-1}

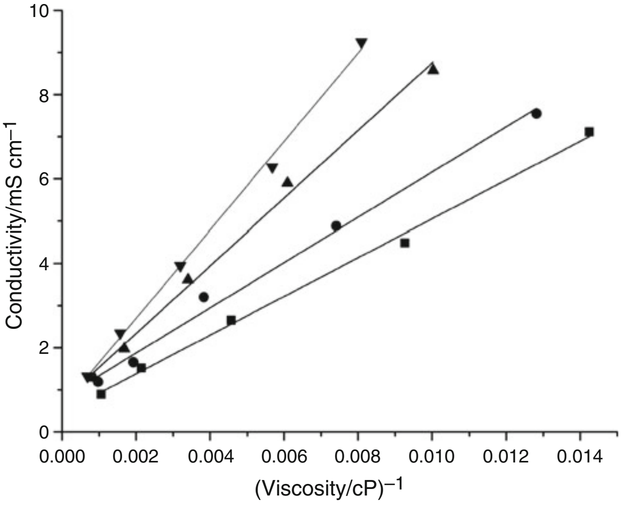


Fig. 8 Conductivity as a function of 1/viscosity for the data in Figs. 3 and 6

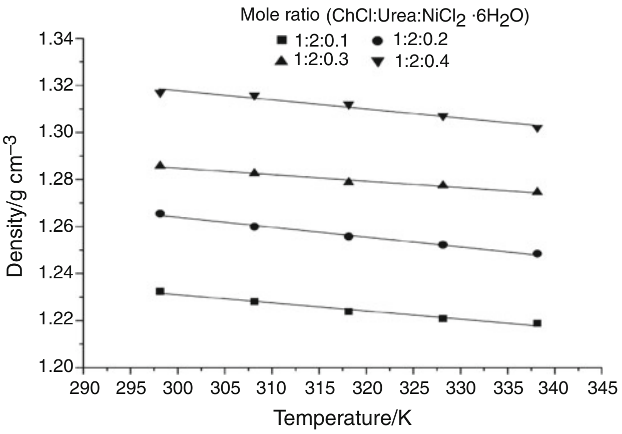


Fig. 9 The density of ChCl–urea–$NiCl_2{\cdot}6H_2O$ analogs ionic liquid as a function of temperature and composition

Mg-based analogs ionic liquid [25–27]. It also can be seen from Fig. 6 that the conductivity of ChCl–urea–$NiCl_2{\cdot}6H_2O$ considerably increases with the increasing temperature. Analogs to the viscosity data, conductivity of ionic liquids has been fitted to Eq. (5) [29]

$$\ln \sigma = \ln \sigma_0 - \frac{E_\Lambda}{RT}. \tag{5}$$

The activation energy for conduction (E_Λ), which is obtained according to Fig. 7 and Eq. 5, is listed in Table 1. As for the E_η values, they are significantly smaller than choline chloride/$MgCl_2{\cdot}6H_2O$ [24] and similar to choline chloride/$CrCl_3{\cdot}6H_2O$ analogs ionic liquid (values from 3.998 to 4.378 kJ mol^{-1}) [1].

Figure 8 shows a strong linear correlation between conductivity and the reciprocal of viscosity, which indicates that the ionic mobility is controlling the conductivity of the liquid.

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

Density

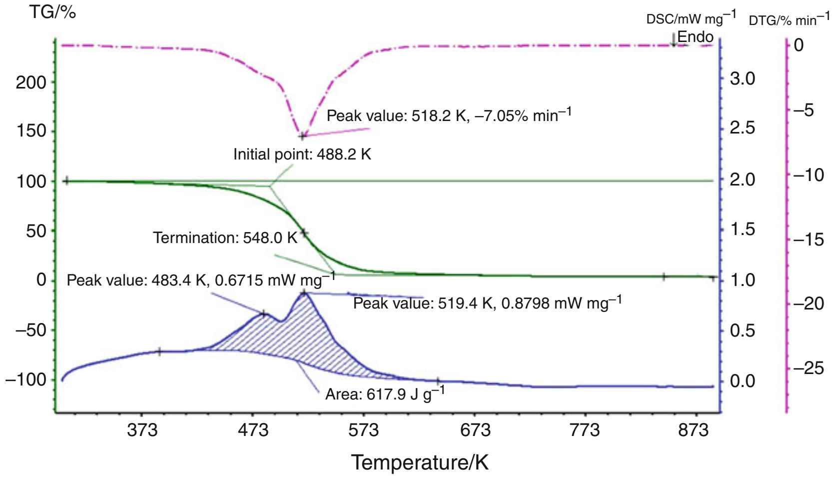
The variation ratio of analogs ionic liquid density with temperature and composition is shown in Fig. 9.

The relationship between density and temperature here is linear as expected. The results for these analogs ionic liquid are fitted by a linear relationship as follows [9]:

$$\rho/\mathrm{g\,cm^{-3}} = a(t/^\circ\mathrm{C}) + b, \tag{6}$$

where ρ is the density, t is the temperature, a and b are a constant that depends on the type of nickel analogs ionic liquid. Also Fig. 9 shows the density of ChCl–urea–$NiCl_2{\cdot}6H_2O$ as a function of composition. It is concluded that the density of ChCl–urea–$NiCl_2{\cdot}6H_2O$ is bigger than analogs ionic liquid ChCl–urea and ChCl–urea/EG/–$MgCl_2$

Fig. 10 Thermal stability analysis of ChCl–urea–$NiCl_2{\cdot}6H_2O$ analogs ionic liquid



system [25, 27]. For the studied systems, the density values vary typically from 1.2188 to 1.3170 g cm^{-3} at 298.15–338.15 K. The density of analogs ionic liquid does not expand appreciably in the studied temperature range, as was indicated in literature for other ionic liquids analogs [6].

Thermal stability analysis

The most important merits of ionic liquids analog are low melting points and greatly wide liquids range. The thermal stability analysis of ChCl–urea–$NiCl_2 \cdot 6H_2O$ is illustrated in Fig. 10. It is noted that there is almost no mass loss below 488.2 K, which indicates the ionic liquid analog is stable from room temperature to 488.2 K. At the same temperature range, the liquid range of the system is larger than EG–ChCl [25] and $MgCl_2$–EG–ChCl [26].

Conclusions

It has been shown that ionic liquids analogous can be prepared based on choline chloride-containing nickel chloride hexahydrate and urea. It is shown that hydrogen bonds of ChCl–urea–$NiCl_2 \cdot 6H_2O$ analogous ionic liquid are H–O···H, O–H···Cl, N–H···N, and N–H···O. The viscosity of the studied ionic liquids exhibits classical Arrhenius behavior, being determined by the strength of the interactions in the mixture: van der Waals forces and hydrogen bonds. The absolute rate approach of Eyring concerning the viscosity flow indicates that the interactional factor is predominant over structural, for all investigated ionic liquids analogous. It is found that nickel analogous ionic liquid is highly conducting and low viscosity. The density of analogous ionic liquid does not expand appreciably in the studied temperature range. Thermal stability analysis shows that stable temperature of nickel analogous ionic liquid range from room temperature to 488.2 K.

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