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Synthesis, characterization, physical and thermodynamic properties of diazobicyclo undecene based dicyanamide ionic liquids

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ABSTRACT

Synthesis of new ionic liquids (ILs) based on diazobicyclo undacane (DBU) cation containing various alkyl groups such as ethyl, butyl, hexyl, octyl, decyl and tetradecyl group with dicyanamide anion were performed. The characterization of the ILs was carried out using NMR (^{1}H and ^{13}C) spectroscopy and elemental analysis. The water content, halide content and the thermal decomposition temperature of the synthesized ILs were determined. The density and viscosity of the ILs were measured in a large temperature range. The effect of temperature and alkyl spacer length on the physical properties such as density, viscosity and surface tension of the DBU based ILs were presented. The thermodynamic properties such as surface enthalpy and entropy, critical temperature and the total surface energy of the ILs were derived from their experimental surface tension and density data.

1. Introduction

The area of ILs expanded exponentially during the past decades because of their wide acceptability in scientific and industrial applications. ILs can be considered as solvents composed entirely of ions with the ability to remain liquid in a wide temperature range [38,39]. The wide acceptability of ILs related to their special properties such as intrinsic conductivity, very low vapor pressure, high thermal stability, wide electrochemical window etc. Because of the availability of a large number of cations and anions, properties of the ILs can be tailored according to the applications by the careful selection of the constituent ions. Due to this designer nature, ILs found a place in chemical industry application such as electro deposition of metals [1,7], liquid–liquid extraction [11,24], electrolytes in solar cells [13,37] and lithium batteries [10,30], solvents in organic synthesis [8,48], catalysis [25,35] etc. In order to exploit the complete potential of ILs in industrial process and design of new products, good understanding about their physical and thermodynamic properties is required. Although a large number of ILs are commercialized, a comprehensive thermophysical characterization is still in the preliminary stage [17–19,23,26,29,36,40,41]. The applications of protic ILs based on 1,8-diazobicyclo [5.4.0]undec-7-ene (DBU) were reported in organic synthesis [3,5,42,44], however, a systematic study of their physical and thermodynamic properties with varying alkyl chain length is limited [18]. In this work, the synthesis, characterization, physical and thermodynamic properties of DBU based dicyanamide ILs were studied, which is a continuation of our recent work on DBU derived ionic liquids [18]. The DBU derived dicyanamide ILs were developed for the deacidification of naphthenic acid from crude oil and the extraction studies are in progress in our laboratory.

2. Experimental

The starting materials and reagents were purchased from Acros Organics. All the starting materials were used without further purification. The purities of the materials are as follows: diazobicyclo[5.4.0]eundec7-ene (98%), 1-Bromoethane (98%), 1-Bromobutane (95%), 1-Bromohexane (98%), 1-Bromooctane (98%), 1-Bromodecane (98%),1-Bromotetradecane (98%), sodiumdicyanamide (98%), and dichloromethane (HPLC grade). An elemental analyzer (EA-1110) was used to measure carbon, hydrogen and nitrogen content of the ionic liquids. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer. Coulometric Karl Fischer titrator (Mettler Toledo, model DL39) was used to analyze the water content in the ionic liquids. Density and viscosity measurements were performed on an Anton Paar viscometer (model SVM3000) and Anton Paar densitimeter (DMA5000) respectively. The surface tension was measured using surface tensiometer (model OCA 20). The thermal decomposition temperature was measured using a thermal gravimetric analyzer (Perkin-Elmer, Pyris V-3.81). The samples were heated in an inert atmosphere from 50 °C to 750 °C at a heating rate of 10 °C·min^{-1}. The uncertainty of the measurement is ±1 °C. Ion chromatogram (Metrohm model

Abbreviations: DBU, diazobicycloundecene.

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761 Compact IC) was used to measure the chloride and bromide content in the ionic liquids.

3. Results and discussion

An overview of the studied ILs is given in Fig. 1.

The synthesis of the halide salt of the DBU cation was performed according to the previously reported procedure and the dicyanamide anion was introduced by the anion exchange reaction of the corresponding halide salt with sodium dicyanamide [18]. Thermal decomposition temperature, water content and halide content of the synthesized ILs were given in Table 1 in supporting information. The TGA profiles of all the dicyanamide salts are given Fig. 2 and they showed a good thermal stability (>300 °C). DBU based thiocyanate ILs also showed similar thermal behavior [18]. DBU based dicyanamide salts are thermally more stable than imidazolium, pyrrazolium, pyrrolidinium and thiazolium cations [21,34,46]. For instance, thermal decomposition temperature of 1-butyl-3-methylimidazolium dicyanamide is 220 °C, which is 103 °C lower than DBU cation with analogous alkyl group.

3.1. Effect of temperature on density and viscosity

The density and viscosity of the synthesized ILs were measured at different temperatures (293.15 K to 373.15 K) and the results are given in Tables 1 and 2 and in Figs. 3, 4 and 5.

Density and viscosity of ILs are correlated with temperature using the following equations:

$$\ln\rho/\left(\mathrm{kgm}^{-3}\right) = A_0 - A_1(T - 298.15), \quad (1)$$

where $A_1 = \frac{a}{K^{-1}} = -\left(\frac{\partial \ln\rho}{\partial(T-298.15)}\right)_p$

$$\log\eta/(\mathrm{mPa}\cdot\mathrm{s}) = A_4 + (A_5/T). \quad (2)$$

The values of the fitting parameter for density and viscosity are given in Table 2 in the supporting information. As speculated, density and viscosity decrease with an increase in temperature. Among the ILs studied, lowest density was observed for DBU cation containing tetradecyl as the alkyl side chain. The bulkiness of the longer alkyl chains prevents the effective close packing leading to a decrease in density. The density of the DBU derived ILs decreases with an increase in alkyl spacer length and follows the order [DBU-Et] $[N(CN)_2]$ > [DBU-But] $[N(CN)_2]$ > [DBU-Hex] $[N(CN)_2]$ > [DBU-Oct] $[N(CN)_2]$ > [DBU-Dec] $[N(CN)_2]$ > [DBU-Tet Dec] $[N(CN)_2]$. The dicyanamide anion based DBU ILs have comparable density values with their thiocyanate analogs [18]. The DBU-thiocyanate ILs with shorter (2 and 4 carbon atoms) and very long alkyl groups (14 carbon atoms) were solids at room temperature. Pyrazolium, morpholinium, imidazolium and pyridinium dicyanamide ILs have similar density values as those of their DBU analogs [2,6,20,21,26,28,45,46]. The viscosity of the ILs showed significant decrease at higher temperatures. The viscosity of all the ILs under study was below 15 mPa·s at 373.15 K, except [DBU-But]$[N(CN)_2]$. From Table 3

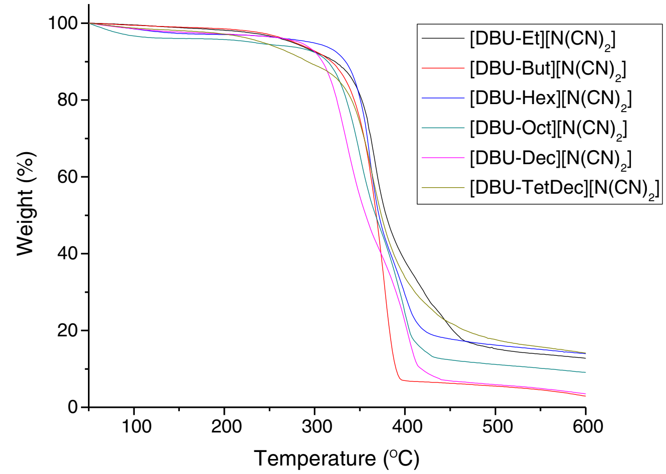

Fig. 2. TGA Profile for ionic liquids: [DBU-But] $[N(CN)_2]$, [DBU-Et] $[N(CN)_2]$, [DBU-Dec] $[N(CN)_2]$, [DBU-Oct] $[N(CN)_2]$, [DBU-Hex] $[N(CN)_2]$, and [DBU-TetDec] $[N(CN)_2]$.

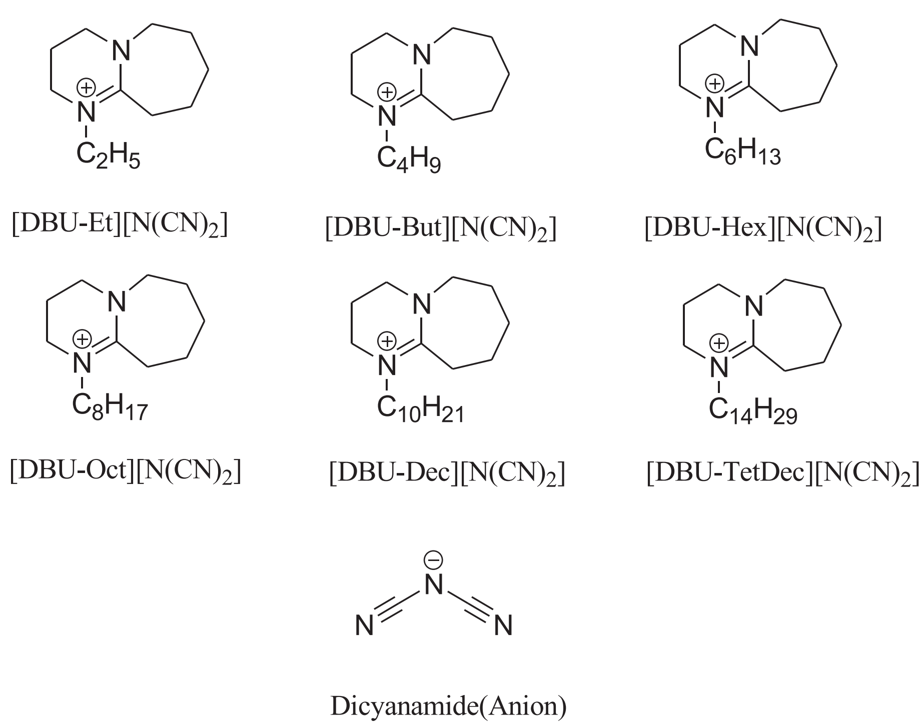

Fig. 1. Overview of the chemical structures and abbreviation of ionic liquids used in this study.