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Solvation of ionic liquids based on *N*-alkyl-*N*-methylmorpholinium cations in *N*,*N*-dimethylformamide and dimethyl sulfoxide – A volumetric and acoustic study

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ABSTRACT

Apparent molar volumes and molar isentropic compressibilities for *N*-ethyl-*N*-methylmorpholinium and *N*-decyl-*N*-methylmorpholinium tetrafluoroborates in *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) have been determined from density and speed of sound measurements over the temperature range $T = (298.15,\ 303.15,\ 308.15,\ 313.15,\ 318.15 \text{ and } 328.15)$ K at experimental pressure $p = 0.1$ MPa. This data has been used to calculate partial molar volumes and partial molar isentropic compressibilities at infinite dilution. The partial molar expansion coefficients and their secondary derivative have been estimated as well. The obtained results indicate that dimethyl sulfoxide interacts more effectively with ionic liquids studied than *N*,*N*-dimetylformamide and ion–ion interaction are stronger for *N*,*N*-dimetylformamide solutions than corresponding in dimethyl sulfoxide. Moreover the temperature dependence of the limiting apparent molar volumes and compressibilities is a result of temperature influence on the electrostriction effect, the ordering of a bulk solvent and number solvent molecules in the nearest presence of the salt.

1. Introduction

In recent years, ionic liquids (ILs) becomes a promising group of compounds that are considered as attractive alternative for volatile organic solvents. Generally, ionic liquids are organic salts in liquid state (built entirely of organic and/or inorganic ions) below some arbitrary temperature, such as 100 °C. Exclusively ionic structure of ILs cause that they possess set of unique physicochemical properties, such as negligible vapor pressure, high thermal stability and large range of temperatures where they are liquid [1–3].

Selective utilization of ionic liquids require accurate knowledge of physicochemical properties of both pure ionic liquids as well as their solutions. Detailed understanding of how ionic liquids behave in the solution has great relevance in theoretical and practical exploration of the subject. The thermodynamic studies of ILs solutions allow to evaluation the intermolecular interactions and geometrical effects in the systems. Measurements of properties such as density, sound velocity and related thermodynamic parameters such as apparent molar volume and apparent molar isentropic compressibility have been applied as a way to study ion–ion and ion–solvent interactions by many researchers [4–7]. The vast majority of papers describes the results of studies for binary mixtures containing typical ionic liquids (with imidazolium and ammonium cations and various anions) with such solvents as water [8,9], dimethyl sulfoxide (DMSO) [10,11], *N*,*N*-dimethylformamide (DMF) [11,12], acetonitrile (MeCN) [13] and alcohols [9,14].

The aim of the present work was to study the solvation of the *N*-alkyl-*N*-methylmorpholinium ions in *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solutions. DMF and DMSO are polar aprotic solvents with a high boiling point which have useful properties for industrial usage. *N*,*N*-Dimethylformamide (DMF) is a solvent with great potential as the separation agent and as a catalyst [15,16] dimethyl sulfoxide (DMSO) has been widely used as a solvent in wide range of fields such as chemistry, biotechnology and pharmaceutical industry, enzyme-catalyzed reactions, dermatology, experimental immunology and microbiology [17,18].

This work is a continuation of our investigation on solvation of ionic liquids in organic solvents [19,20], and presents the densities and sound velocities of DMF and DMSO solutions of *N*-ethyl-*N*-

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methylmorpholinium and N-decyl-N-methylmorpholinium tetrafluoroborates obtained at T = (298.15, 303.15, 308.15, 313.15, 318.15 and 328.15) K. The experimental data determines the partial molar volumes, partial molar compressibilities as well as expansibilities which are fully discussed in terms of ion–solvent interactions and coordination number.

2. Experimental

2.1. Materials

N,N-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), both Fluka, *puriss*, absolute, mass fraction of water, w (H_2O) < $1{\cdot}10^{-4}$, were dried with 0.4 nm molecular sieves. Silver tetrafluoroborate was synthesized by previously reported method [21]. 1-bromoethane (ReagentPlus, >99%), 1-bromodecane (ReagentPlus, >99%), 4-methylmorpholine (>99,5%) and sodium tetrafluoroborate (>99,9% trace metals basis) was purchased from Sigma-Aldrich and used without any further purification.

2.2. Synthesis of N-alkyl-N-methylmorpholinium tetrafluoroborate ionic liquids

Fig. 1 presents the molecular structures of N-ethyl-N-methylmorpholinium and *N*-decyl-*N*-methylmorpholinium tetrafluoroborate that were synthesized by pre-modified previously published method [22]. The sequence of reactions lead to the formation of the required ionic liquid shown in Scheme 1. 1.1 mmol of 1-bromoalkane was added dropwise to stirring solution of 10 mmol *N*-methylmorpholine in 75 ml of acetonitrile. Reaction was carried out in 65 °C for 48 h in inert gas atmosphere, after that corresponding bromide salt was filtered and washed with acetone. Bromide salt was converted into the tetrafluoroborate salt (1 mmol) by metathesis reaction with sodium tetrafluoroborate (1.2 mmol) in acetonitrile. After removing inorganic salt and evaporating solvent *N*-alkyl-*N*-methylmorpholinium tetrafluoroborate was dissolved in dry acetone and remained bromide residues were precipitated by addition of silver tetrafluoroborate (0.1 mmol). Precipitate was filtered off and after evaporation of solvent obtained ionic liquids were dried in vacuum to give colorless liquid or solid in 95–98% yield. All ionic liquids were characterized by ^{1}H NMR, ^{13}C NMR and bromide content was measured (see supplementary material).

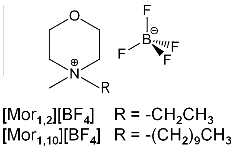


Fig. 1. Molecular structures of the studied ionic liquids.

2.2.1. N-Ethyl-N-methylmorpholinium tetrafluoroborate [$Mor_{1,2}$][BF_4]

^{1}H NMR (400 MHz, D_2O) δ 3.92 (s, 4H, 2 × OCH_2), 3,42 (q, J = 7,5 Hz, 2H, NCH_2), 3.34 (m, 4H, 2 × NCH_2), 3.03 (s, 3H, NCH_3), 1.25 (t, J = 6.3 Hz, 3H, CH_3).

^{13}C NMR (125 MHz, D_2O) δ 60.76, 30.33, 58.99, 45.92, 6.41.

Br^- concentration 0,001%.

2.2.2. N-Decyl-N-methylmorpholinium tetrafluoroborate [$Mor_{1,10}$][BF_4]

^{1}H NMR (400 MHz, DMSO-d_6) δ 3.91 (s, 4H, 2 × OCH_2), 3.39 (m, 6H, 3 × NCH_2), 3.11 (s, 3H, NCH_3), 1.68 (m, 2H, CH_2), 1.27 (m, 14H, 7 × CH_2), 0.87 (t, J = 6.8 Hz, 3H, CH_3).

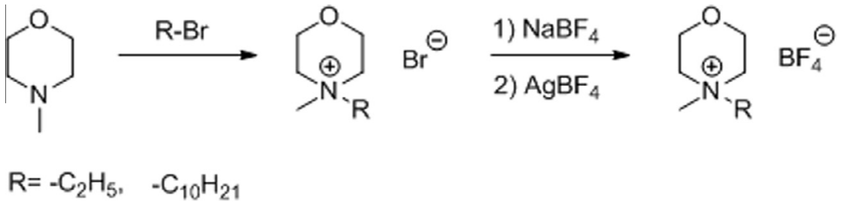
^{13}C NMR (125 MHz, DMSO-d_6) δ 64.22, 60.26, 59.37, 46.41, 31.76, 29.37, 29.28, 29.14, 28.98, 26.22, 22.58, 21.16, 14.43.

Br^- concentration 0,003%.

Before measurements, the ionic liquids were dried by purging them with a neutral gas (N_2) at 323 K for more than 72 h. The average water content in the ILs was measured by the Karl Fischer titration method (831 KF Coulometer apparatus from Metrohm). A summary of the provenance of the chemicals used in studies is listed in Table 1.

2.3. Density and speed of sound measurements

Stock solutions of the ionic liquids were prepared by mass and then diluted by *N,N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), to get the test samples. All the preparations and manipulations involving anhydrous materials were performed in a dry box. The samples were stored in air tight bottles and measurements were performed immediately after preparation of the solutions. The density and sound velocity of the mixtures were measured at different temperatures with a digital vibration-tube analyzer (Anton Paar DSA 5000, Austria) with proportional temperature control that kept the samples at working temperature with an accuracy of 0.01 K. Experimental frequency for the measurements of the ultrasonic speed was equal to 3 MHz. The apparatus was calibrated with double distilled, deionized and degassed water and with dry air at atmospheric pressure accordingly with the apparatus manual. The experimental uncertainty of density and ultrasonic velocity measurements was better than 0.15 $kg{\cdot}m^{-3}$ and 0.5 $m{\cdot}s^{-1}$, respectively. Before each measurement series, the accuracy of the density and sound velocity measurements and solvent purity were verified by measuring the density and sound velocity of pure DMF and DMSO at T = 298.15 K. The density values of 943.952 $kg{\cdot}m^{-3}$ for DMF and 1095.247 $kg{\cdot}m^{-3}$ for DMSO were found in the present study while literature values vary from 942.92 to 944.60 $kg{\cdot}m^{-3}$ and 1095.174 $kg{\cdot}m^{-3}$ to 1095.74 $kg{\cdot}m^{-3}$, respectively [5,23–34]. The speed of sound obtained for DMF was 1456.99 $m{\cdot}s^{-1}$ while the corresponding literature values range from 1448.55 to 1469.5 $m{\cdot}s^{-1}$ [24,27–29,35]. The sound velocity in DMSO was found to be 1484.82 $m{\cdot}s^{-1}$ while the literature values are in the range from 1484.00 to 1494.0 $m{\cdot}s^{-1}$ [5,29,31,32]. From Table 2, the experimental values of density and speed of sound of pure DMF and DMSO are in agreement with literature data in whole temperature range T = (298.15–318.15) K [36].



Scheme 1. The sequence of reactions leading to the formation of studied ionic liquids.