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# Thermophysical properties for the mixed solvents of N-methyl-2-pyrrolidone with some of the imidazolium-based ionic liquids

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ABSTRACT

This work presents the thermophysical properties and structure of N-methyl-2-pyrrolidone (NMP) in the binary mixtures with 1-alkyl-3-methyl imidazolium cation $[amim]^+$ with different anions (chloride, methyl sulfate and tetrafluoroborate) of ionic liquids (ILs). A comprehensive set of properties such as densities ($\rho$), ultrasonic sound velocities ($u$) and viscosities ($\eta$) have been measured at the temperature range from 298.15 to 313.15 K over the whole concentration range of ILs under atmospheric pressure. The ILs used for the present study included 1-ethyl-3-methylimidazolium methylsulfate [Emim][$MeSO_4$], 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][$BF_4$], 1-ethyl-3-methyl imidazolium chloride [Emim][Cl] and 1-butyl-3-methylimidazolium chloride [Bmim][Cl] from imidazolium family of ILs. From these experimental data, the excess molar volume ($V^E$), the deviation in isentropic compressibility ($\Delta\kappa_s$) and deviation in viscosity ($\Delta\eta$) were calculated and adequately correlated by using the Redlich–Kister polynomial equation. The measured and calculated data were interpreted on the basis of intermolecular interactions and structural effects between like and unlike molecules upon mixing.


## 1. Introduction

Knowledge of thermophysical properties of mixed solvents is a subject of intensive research in these days due to their wide areas of applications [1,2]. These properties provide information about the nature of interactions that are dependent on the charge distribution and molecular geometry of the solvents [3,4]. Knowledge of structure and properties of ionic liquids (ILs) is essential for the understanding of their molecular interactions in the binary mixtures, which is essentially required for the scientific community. In recent years, ILs have attracted worldwide scientific interest in both academia and industry, due to their tunable and unique physical and chemical properties [5–15]. Moreover, ILs appear as suitable alternative and complementary solvents for volatile organic solvents in synthesis and separation processes [1,5,13–16].

One of the most popular and widely used polar solvents in industries and academics is N-methyl-2-pyrrolidone (NMP). It is a useful solvent in all scientific fields mainly due to its advantages in stability at ambient temperature, low volatility, low flammability, and its industrial scale usage in polymerization, petrochemical processing, surface coating and the plastics industry [17]. NMP is used as an extractive agent for paraffin and aromatic separations [17,18]. Moreover, NMP is a strong polar liquid and has the potential for use in the solvent extraction process for separating polar substances from non-polar substances [4, 18–21], as it has a large dipole moment ($\mu = 4.09$ D) and a high dielectric constant ($\varepsilon = 32.2$ at T = 298.15 K) [2].

The knowledge of thermophysical properties of mixed solvents of ILs with organic molecular liquid are paramount for the design of many technological processes and required for many practical applications. However, the thermophysical properties of ILs particularly in molecular solvents have not been explored in a systematic way. In this context, our aim is to explore thermophysical properties such as density ($\rho$), ultrasonic sound velocity ($u$) and viscosity ($\eta$) for the mixed solvents of ILs and polar solvent for expand basic needs for scientific research. To gain advantage of their novel applications in basic research, a detailed and systematic analysis of the thermophysical properties of liquid mixtures containing ILs is essentially required. The properties of liquid mixtures of ILs and polar solvent bear a practical interest in theoretical, modeling and technological applications. A detailed survey of recent literature reveals the scarce number of systematic studies on molecular interactions between ILs and polar solvents. The present work is a part of our comprehensive investigation on the thermophysical properties of ILs with polar solvents [21–31]. Here, we uncover the characterization of the structural variation of ions of imidazolium-based IL as well as molecular interactions with a molecular solvent, NMP, through temperature variable properties.

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**Table 1**
Solvent molecular weight (MW), purity, density ($\rho$), ultrasonic sound velocity ($u$) and viscosity ($\eta$) for the solvents such as NMP and ILs at 298.15 K.

| Solvent | MW (g $mol^{-1}$) | Mass fraction purity | $\rho$/(g $cm^{-3}$) | | $u$/(m $s^{-1}$) | | $\eta$/(mPa s) | |
|---|---|---|---|---|---|---|---|---|
| | | | Expt. | Lit. | Exp. | Lit. | Exp. | Lit. |
| NMP | 99.13 | 0.99 | 1.02590 | 1.02590 [19] | 1552[a] | 1552 [36][a] | 1.66 | 1.66 [19] |
| | | | | 1.025590 [32] | | 1527 [18][a] | | 1.68 [38] |
| | | | 1.02374[a] | 1.02395 [18][a] | | | 1.49[a] | 1.55 [18] |
| | | | | 1.02370 [19][a] | | | | |
| | | | | 1.02342 [34][a] | | | | |
| | | | | 1.02347 [35][a] | | | | |
| | | | | 1.02340 [36][a] | | | | |
| | | | | 1.02376 [37][a] | | | | |
| [Emim][$MeSO_4$] | 222.26 | 0.99 | 1.27984 | 1.28730 [39][b] | 1730 | – | 84.30 | 83.885 [39] |
| | | | | 1.26290 [40] | | | | |
| [Bmim][$BF_4$] | 226.13 | 0.99 | 1.20107 | 1.20150 [41] | 1566 | – | 101.00 | 103.4 [42] |
| | | | | 1.201129 [42] | | | | 103.8 [48] |
| | | | | 1.20057 [43] | | | 80.66[a] | 81.40 [46][a] |
| | | | | 1.20110 [44] | | | | 80.60 [48][a] |
| | | | | 1.20100 [45] | | | | |
| | | | | 1.20089 [46] | | | | |
| | | | | 1.20030 [47] | | | | |
| [Emim][Cl] | 146.06 | 0.99 | – | – | – | – | – | – |
| [Bmim][Cl] | 174.67 | 0.99 | – | – | – | – | – | – |

[a] At 303.15 K.
[b] At 0.0023 mol fraction of IL.

To understand impact of change in the structure of ILs on their mixtures with NMP, in the present study, we explore the measurements of three thermophysical properties such as $\rho$, $u$, and $\eta$ of binary mixtures involving NMP with 1-ethyl-3-methyl imidazolium methylsulfate [Emim][$MeSO_4$], 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][$BF_4$], 1-ethyl-3-methylimidazolium chloride [Emim][Cl]

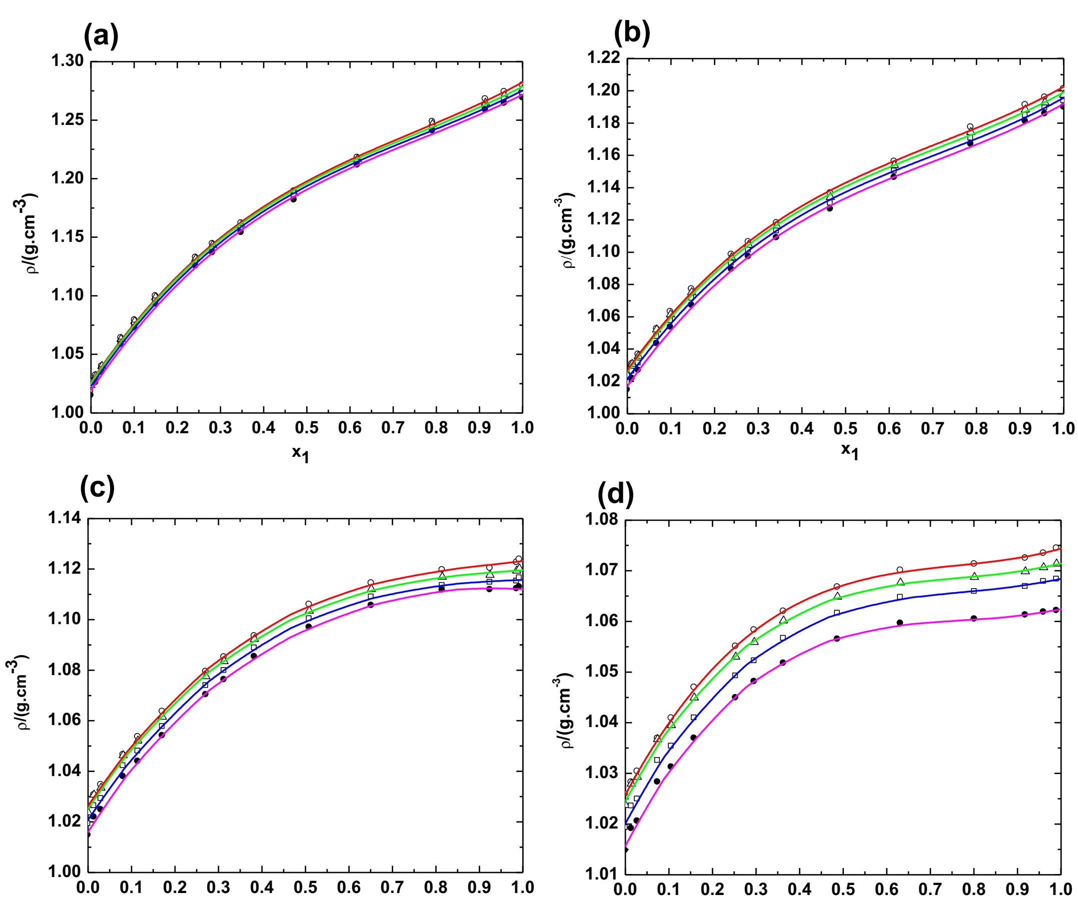


**Fig. 1.** Densities ($\rho$) for the mixtures of ILs + NMP as a function of the composition expressed in the mole fraction ($x_1$) of IL for (a) [Emim][$MeSO_4$] (1) + NMP (2); (b) [Bmim][$BF_4$] (1) + NMP (2); (c) [Emim][Cl] (1) + NMP (2); and (d) [Bmim][Cl] (1) + NMP (2) at (○) 298.15, (△) 303.15, (□) 308.15, and (●) 313.15 K at atmospheric pressure. The solid line represents the smoothness of these data.