Evaluation of molecular interactions by volumetric and acoustic studies in binary mixtures of the ionic liquid [EMIM][MeSO$_4$] with ethanoic and propanoic acid at different temperatures

P. Bhanuprakash [a], C. Narasimha Rao [b], K. Sivakumar [c],*

[a] Department of Chemistry, P.V.K.N. Govt. College, Chittoor-517 002, India
[b] Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, India
[c] Department of Chemistry, S.V. Arts UG & PG College, Tirupati-517 502, India

ABSTRACT

In the present work, molecular interactions in the binary mixtures of 1-Ethyl-3-methylimidazolium methylsulphate [EMIM][MeSO$_4$] with ethanoic acid (EA) and propanoic acid (PA) have been evaluated using the measured densities (ρ) and speeds of sound (u) over the entire range of composition at temperatures of 298.15, 303.15, 308.15 and 313.15 K. The excess volumes (V^E) for the said binary mixtures have been computed from the experimental density data. Further, excess isentropic compressibilities (κ_s^E) have been calculated from density and speed of sound data for the binary mixtures. The V^E and κ_s^E values for the binary mixtures were found to be negative over the whole range of composition at all the specified temperatures which suggest the existence of specific interactions between component molecules. Furthermore, Redlich–Kister equation was used to fit the derived excess functions V^E and κ_s^E in order to determine the fitting parameters and the root mean square deviations.

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1. Introduction

Ionic liquids (ILs) are a promising class of new materials which are environmentally more benign and potential enough to replace volatile, flammable, toxic and hazardous organic compounds used in many industrial processes. Ionic liquids are salt like materials in the liquid phase, whose melting points are lower than 100 °C in their pure state. They consist of larger organic cations and smaller organic and inorganic anions which are responsible for their high ionic conductivity. The low melting point of ILs is attributed to the asymmetrical structure of the larger cation, which do not pack well with small anions. In addition, they have attractive physical properties compared to molecular solvents, such as very low vapour pressure, broad liquid range, wide range of miscibility with compounds of varying polarity and non-inflammability. Further, they are highly polar, non-volatile, easily recyclable and thermally stable with a large electrochemical window [1–3]. The added advantage of ILs is that their physico-chemical properties can be tuned for a specific application by the selection of different combinations of anions and cations. Hence they are often termed as designer solvents [4].

The peculiar properties of ILs make them more than just green solvents and have drawn the attention of scientific community and

industry to explore their new applications. It includes their usage as novel solvents and catalysts in organic and organometallic synthesis [4], bio-catalysis [5] and in synthesis of nano materials [6].They are useful as the working fluid in a variety of electrochemical applications like batteries [7], capacitors [8], solar cells [9], fuel cell [10], transistors [11] and chemical sensors [12].In addition they find applications in separation and extraction technologies [13,14], as liquid crystals [2], as thermal fluids [15], as lubricants and fuel additives [16], as matrices in mass spectrometry, in preparation of polymer–gel catalytic membranes and in generation of high conductivity materials [17].

The majority of research works related to ILs have focussed on synthesis and study of chemical reactions in ILs. But, the systematic investigations of thermophysical properties of pure and mixtures containing ILs in wide range of temperature and pressure are scarce. The lack of thermodynamic data of mixtures of ILs with other molecular solvents restricts their use as process chemicals and processing aids. Therefore, there is a need to investigate and obtain reliable thermophysical properties of ILs and their mixtures. The study on the thermodynamic properties of ILs is the need of the hour in order to design the desirable ILs and make them available for theoretical research. In particular, the knowledge on density and speed of sound measurements of binary mixtures is significant not only to design physical and chemical processes on an industrial scale but also to predict the properties and characteristics of ILs from the theoretical point of view [18–22]. The thermophysical properties of mixtures containing ILs bear a practical interest in

theoretical, modelling and technological applications [23].The measurement of excess thermodynamic properties of binary mixtures has been found to be an excellent qualitative and quantitative way to obtain and understand information on the intermolecular interactions between the component molecules with different sizes, shapes and chemical nature [22,24]. Further, the study of excess thermodynamic properties is desirable to develop reliable correlations and to test solution theories [25].

The alkyl sulphate based imidazolium ILs containing anions like $MeSO_4^-$ or $EtSO_4^-$ represent halogen-free and relatively hydrolysis-stable compounds than other imidazolium based ILs [26]. Besides, they contain an anion with low toxicity when compared to ILs with anions such as BF_4^- or PF_6^- which emit toxic gases like HF and POF_3 upon hydrolysis. Hence they could be an interesting alternative for industrial application [1].

The carboxylic acids are highly polar protic solvents. In pure form they self-associate strongly through hydrogen bonding and mainly exists as a chain structure [27] as shown in Scheme 1. The carbonyl (>CO) and hydroxyl groups (—O—H) of carboxylic acid acts as hydrogen-bond acceptors and donors respectively to other molecules in the chain structure.

Most of the natural products are the derivatives of carboxylic acids. They are the remarkable class of chemicals with wide variety of industrial applications such as cleaning agents, in separation processes and manufacture of pharmaceutical products [28,29].They are extensively used as buffers, food preservatives, flavoring agents, fungicides, insecticides catalysts and as raw material for the production of biodegradable plastics [28–30]. Moreover, they are used as catalysts in the synthesis of biodiesel [31] and as natural colorants for food and Nutraceutical [32]. Ethanoic acid (EA) and propanoic acid (PA) are well-known in the feed industry as an effective and affordable tool to control mold growth. PA is also used as an intermediate in the synthesis of herbicides, cellulose acetate–propionate plastics and pharmaceuticals.

These favourable properties have drawn a great interest and motivated us to investigate the interactions of [EMIM][MeSO₄] with EA and PA and solvation behavior through thermo physical property measurements. These measurements aid as potential tools to understand and analyze the solvation behavior of solutes in aqueous and non-aqueous solutions [33]. In addition, the present work aims to contribute to the data bank of thermodynamic properties of mixtures containing ILs. Further, it aims to investigate the relationship between densities, speeds of sound and the ionic structures of ILs in mixtures and also to institute principles for the molecular design of suitable ILs for industrial processes.

The thermophysical properties of [EMIM][EtSO₄] with water, alcohols (C_1 to C_{12}) [34–36], acetone, propylene carbonate, dichloromethane [37], acetonitrile [37,38], acetic acid and propionic acid [39] have been studied at several temperatures. A survey of literature has shown that excess properties for the mixtures of [EMIM][MeSO₄] with alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 1-pentanol) [1,26] were reported. However, no literature data were available on the systematic investigations on densities (ρ), speeds of sound (u), excess volumes (V^E) and excess isentropic compressibilities (κ_s^E) for the binary

systems containing [EMIM][MeSO₄] with EA and PA at temperatures of 298.15, 303.15, 308.15 and 313.15 K.

In the present work, we report new experimental data on ρ and u and the derived data on V^E and κ_s^E for the liquid mixtures of [EMIM][MeSO₄] with EA and PA at temperatures of 298.15, 303.15, 308.15 and 313.15 K over the complete range of composition. The derived excess functions V^E and κ_s^E were fitted with Redlich–Kister equation and have been discussed based on the molecular interactions between component molecules of the binary mixtures.

2. Experimental

2.1. Materials

1-Ethyl-3-methylimidazolium methylsulfate was procured from Sigma-Aldrich, India with mass fraction purity greater than 0.980. To reduce the water content, the IL was dried under vacuum for 48 h at a temperature of about 343 K prior to its use. The Karl Fischer titrations of dried IL revealed very low levels of water content of 0.05% by mass. Ethanoic and propanoic acids were obtained from Sigma-Aldrich, India with mass fraction purities greater than 0.998 and 0.995 respectively and were used without further purification. The purity of the chemicals were checked by GC analysis and showed no significant impurities. The purity of the compounds were also assessed by comparing the measured density and speed of sound values at different temperatures which were in good agreement with the reported values [1,39–44] and these were listed in Table 1.

2.2. Methods

2.2.1. Sample preparation

The homogeneous binary mixtures of [EMIM][MeSO₄] with EA and PA were prepared by syringing known masses of pure liquids into air tight glass bottles to minimize the absorption of atmospheric moisture. The mass measurements were performed on digital electronic balance (Acculab, ALC-210-4, India) with an uncertainty of $\pm 1 \times 10^{-4}$ g. The resulting uncertainty in mole fraction was found to be less than $\pm 2 \times 10^{-4}$.

2.2.2. Density measurements

Densities (ρ) of the pure solvents and their mixtures were measured by using Rudolph Research Analytical Digital Densimeter (DDM-2911 model). The instrument has a built-in solid-state thermostat and a resident program with accuracy in temperature of ± 0.02 K. The densities were automatically measured at the specified temperature by transferring the homogeneous and bubble free sample into the U-tube of the densimeter with the help of medical syringe [22]. The calibration of the instrument was done on each day with air, double-distilled and de-ionized water as standards. Typically the density values were accurate to $\pm 5 \times 10^{-5}$ g cm^{-3}.
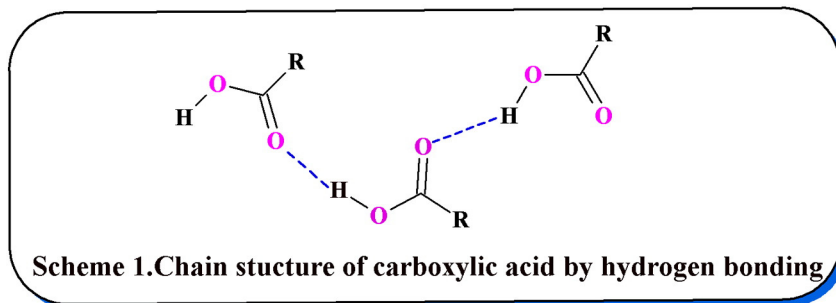
Scheme 1. Chain structure of carboxylic acid by hydrogen bonding.