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Influence of temperature on thermo physical properties of binary mixtures of ethyl acrylate and alkyl amines: An experimental and theoretical approach

A. Shakila [a], S. Ravikumar [a], V. Pandiyan [a], Rekha Gaba [b],*

[a] Department of Physics, Nehru Memorial College, Puthanampatti, 621 007, Tamil Nadu, India
[b] Department of Chemistry, DAV University, Jalandhar, 144 012, Punjab, India

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ABSTRACT

Densities (ρ) and speed of sound (u) values have been measured for the binary mixtures of ethyl acrylate with propylamine, dipropylamine, diisopropylamine and tripropylamine at four temperatures (T = 303.15, 308.15, 313.15 and 318.15 K) and at atmospheric pressure over the entire composition range. Further, the measured data has been utilized to compute excess molar volume (V_m^E) and excess isentropic compressibility (κ_S^E) for all the systems under the same experimental conditions. Expansion of our study has been done by calculating other thermodynamic parameters such as excess intermolecular free length (L_f^E) and excess speed of sound (u^E). These calculated excess parameters have been correlated by Redlich-Kister equation. The experimental results have also been analysed by using Prigogine–Flory–Patterson (PFP) theory, intermolecular free length theory and collision frequency theory. To elucidate the presence of intermolecular interactions and structural effects the work has been augmented by FTIR studies also.

1. Introduction

Now a days, research on thermodynamic properties of binary liquid mixtures are capturing a frequent recognition owing to their direct execution in certain chemical and biochemical industriels as well as in understanding the nature and extent of intermolecular interactions present between the different components of liquid mixtures [1–4]. Accurate knowledge of requisite thermodynamic properties of non-aqueous liquid mixtures also play a significant role in testing and developing certain theories and models related to solvent media [5].

It has already been verified that measurements of density play a vital role in many chemical engineering estimations such as in designing industrial equipment, condensers and storage deposits, dimensions of boilers etc. [6, 7]. In addition, the high quality data of these volume and thermodynamic properties is also very crucial in various industrial process like heat transfer, mass transfer, separation and purification as well as in fluid flow [8–12]. Speed of sound studies in liquid-liquid mixtures can be utilized to verify complexation behaviour by knowing the effect of structure of donor molecules along with polarity of medium on the stability of complexes [13]. Measurement of ultrasonic velocities of liquid mixtures further acts as an excellent tool to determine the presence of intermolecular as well intra-molecular interactions between the like and unlike molecules [3]. Further, enlightenment of the dependence of density/ultrasonic velocity on the temperature, composition and pressure is obligatory in perceiving the phase behaviour and intermolecular attractions. In continuation of our progressing research focussed on experimental and theoretical studies of non-aqueous binary liquid mixtures [14–17], we present the results of our new study on binary mixtures of ethyl acrylate with propyl amine, di propyl amine, diisopropylamine and tripropylamine at different temperatures. Acrylic esters are very inserting and important industrial chemicals which are widely used as precursors in the fabrication of technically important special type polymers due to the presence of a double bond as well as carbonyl group [18]. They are also used to enhance color stability, low temperature flexibility, heat resistance, wear & tear resistance as well as clarity of polymers. Glass transition temperature of these chemicals decides the hardness, softness and flexibilities of polymeric films. Ethyl acrylate can be used as a flavouring agent in certain food industries. It is also one of the main volatile component identified in organic passion fruit pulp. Due to theses sensational properties and wide applicability, studies of binary mixtures containing acrylic esters as one of the component are of much significance. On the other hand aliphatic amines also have wide industrial applications

* Corresponding author.
E-mail address: rekhagaba@gmail.com (R. Gaba).

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due to their self-association through intermolecular hydrogen bonding. Amines are also very important intermediates due to their interesting structural features in the preparation of cosmetics, fine chemicals, agro chemicals (like herbicides, pesticides), solvents, and azo dyes [19]. An amide-based agrochemical is often used which gets metabolised to an amine [19]. Primary, secondary and tertiary amine differ strongly by their static environment of their nucleophilic centre. Recently, a lot of researchers have published their work on thermodynamic properties of binary liquid mixtures containing acrylates with alcohol, ketones, nitrile, thiols, benzene, cyclic ethers, cyclic amines [20–24]. But still there exist a gap in these reported studies. To fulfil this existing gap and to reveal the structural influence of aliphatic amines, the present research work has been carried out by measurement of thermodynamic, physic-chemical as well as spectral studies of binary mixtures containing ethyl acrylate and amines (propylamine, dipropylamine, diisopropylamine and tripropylamine) over the entire range of mole fraction at temperatures $T = (303.15–318.15\ \text{K})$ with an interval of 5 K and at atmospheric pressure. The experimental data on density and ultrasonic velocity has been further utilized to calculate excess molar volume (V_m^E), excess isentropic compressibility (κ_S^E), excess speed of sound (u^E) and excess inter molecular free lengths (L_f^E). The calculated excess parameters have been correlated with the help of Redlich – Kister polynomial equation to obtain the binary coefficient and estimate the standard deviation between experimental and calculated result. The strength of specific and non-specific interactions between components of the binary mixtures has also been explored in terms of structural differences between the two components. Further, the relative merit of various theoretical models has also been discussed in the proposed in the present study to verify the reported results. The combined study of thermophysical properties, FT-IR (spectroscopic) and theoretical analysis will help us to grasp how specific interactions occur between components of mixtures and identification of active sites of molecules involving in specific interactions. It will also provide information about the type, strength, type and behavior of specific interactions at different concentration regions of solute and solvent molecules at different temperatures.

2. Experimental

2.1. Materials and methods

The chemicals used in the present study has been checked with their mass fraction were >0.995, specified by the manufacturer and the chemicals suppliers of these compounds. The details of mass fraction purity, purification method along with structures are summarized in Table 1. These liquids are dried over a molecular sieves 4 Å. The purity of the experimental liquids was thoroughly checked by comparing with the densities and speeds of sound with those reported in the literature [24–43] and these were presented in Table 2. The preparations of the mixtures for this study are used by airtight stoppered bottles to avoid evaporation of the liquids. The weights of the empty dried bottles have been determined before starting the mixing preparation procedure.

2.2. Apparatus and procedures

In the present study, the densities of pure liquids and the binary mixtures were measured by calibrated single stem capillary pycnometer having its volume ≈ 14 ml. The speeds of sound data of pure liquids and their mixtures were measured using single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, Model: M-82) operating at 2 MHz. During the experiment, all the measurements and temperatures were controlled by circulating the water through an ultra-thermostat JULABO F-25 (made in Germany) keeping temperature accuracy within ±0.02 K. The details of the experimental procedure have been described elsewhere [17]. The binary mixtures were prepared by mixing known masses of pure liquids in air tight stoppered bottles by taking utmost care and precautions to minimize evaporation losses. All the mass measurements were performed on an electronic balance (Mettler-AE 240, Switzerland) with precision up to ±0.05 mg. Samples have been analysed immediately, after the preparation. The uncertainty in densities and speeds of sound measurements was within $0.1\ \text{kg}\cdot\text{m}^{-3}$ and $1\ \text{m}\cdot\text{s}^{-1}$.

2.3. I R measurements

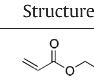
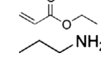
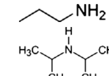
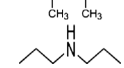
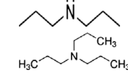
The I.R. spectra of the pure components and their equimolar mixtures were measured using a Fourier Transform Infrared Spectrometer (Spectrum RX I; Perkin Elmer, Inc., USA), based on double beam performance having a resolution of $2\ \text{cm}^{-1}$ provided with a sample space $150\ \text{mm}^2$. The spectrum was recorded at a temperature of 303.15 K using quartz crystal in the region $4000\ \text{cm}^{-1}$ to $400\ \text{cm}^{-1}$.

3. Results and discussion

The experimental values of density (ρ) and ultrasonic velocity (u) for the binary mixtures of ethyl acrylate with propylamine, dipropylamine, diisopropylamine and tripropylamine, over the whole composition range, expressed as mole fraction x_1, of ethyl acrylate at different temperatures are listed in Table 3 and graphically represented in Figs. 1 and 2 respectively. For all investigated systems, ρ values and u values decrease with an increase of temperature. The measured values of densities, ρ and ultrasonic velocity, u were fitted to a polynomial expression given by equation

$$F(x) = \sum_{i=1}^{k} A_i x_1^{i-1} \tag{1}$$

Table 1
The specifications of pure components used in the present study.

Components	Source	CAS number	Purity in mass fraction (as received from supplier) (%)	Analysis method	Structure
Ethyl acrylate	S.D. fine-chemicals, India	140-88-5	>0.993	GC#	
Propylamine	S.D. fine-chemicals, India	107-10-8	>0.995	GC#	
Di-isopropylamine	S.D. fine-chemicals, India	108-18-9	>0.995	GC#	
Di-propylamine	S.D. fine-chemicals, India	142-84-7	≥0.995	GC#	
Tri-propylamine	S.D. fine-chemicals, India	102-69-2	>0.995	GC#	

GC = Gas chromatography.