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Comparative studies of intermolecular interaction of aromatic amines with ethyl lactate at different temperatures

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In this work, the study of interactions between ethyl lactate and aromatic amine mixtures are examined through insight from density and speed of sound measurements. The density (ρ) and sound velocity (u) of ethyl lactate and aromatic amines such as aniline, N-methyl aniline and N-ethyl aniline and their binary systems are measured at (303.15, 308.15, 313.15 and 318.15) K and at 0.1 MPa. The derived properties such as excess molar volume (V_m^E), excess partial molar volume ($\bar{V}_{m,1}^E$, $\bar{V}_{m,2}^E$) excess partial molar volume at infinite dilution $(V_1^E)^\infty$, $(V_2^E)^\infty$ and excess isentropic compressibility (κ_s^E) are computed. The Redlich–Kister polynomial equation is used to fit the excess properties. The experimental results are discussed in terms of intermolecular interactions between component molecules. FT-IR studies support the findings.

1. Introduction

Solvents are chemicals that have highly improved modern day living in and around the world. They are exploited in an array of applications including, personal care products, pharmaceuticals, pesticides, paints and coatings household and industrial cleaners, and so on. Solvents provide solutions for many challenges for our increasing demand for innovative materials in modern life. Ethyl lactate (EL) is gaining attention as a bio-based solvent as it is derived from carbohydrate feed stock. Experts suggest that ethyl lactate could replace the traditional solvents in more than 80% of their applications [1]. The unique properties like, 100% biodegradability, reduced eco-toxicity [2], non-carcinogenic, non-corrosive solvent, non-ozone depleting, high solvency power for resins and polymers makes it a promising solvent. Ethyl lactate (EL) has been used in a wide variety of applications, effective paint strippers, graffiti ink remover [3], in pharmaceutical industry as a dissolving/dispersing excipient, cleaning agent, effective in the removal of copper from contaminated soils [4], magnetic tape coating [5]. Despite numerous properties, less work has been dedicated to this eco-friendly chemical. Hence the authors are interested to know the thermodynamic behavior of this potentially useful chemical with other industrial solvents.

Mixtures containing anilines exhibit very interesting properties [6]. The treatment of a component with primary or secondary amines allows the study of the size and steric effects produced by the alkyl groups attached to the amine group. Three aromatic amines, aniline (AN), N-methyl aniline (NMA) and N-ethyl aniline (NEA) are selected for the study with ethyl lactate. Aniline is predominantly used as a parent substance in the manufacture of several chemical products and intermediates [7]. It is also used in the production of synthetic dyes and pigments, hydroquinone, drugs and agriculture chemicals, and as an accelerator in vulcanization of rubber. Aniline polymers are widely studied due to their high stability and wide range of electrical conductivity. They are used in transistors, solar cells or light emitting diodes [8]. N-substituted polymers provide better solubility and process ability, which is of importance in printable electronics. Poly (N-methyl aniline) has been studied as cathode active material in aqueous rechargeable batteries [9]. Secondary amines N-methyl aniline and N-ethyl aniline are also used as a latent and coupling solvent molecule. The binary systems of ethyl lactate and amines are particularly seemed to be interesting due to their complexity, consequences after the interaction of self-associated ethyl lactate molecules with the active molecules of amines.

In continuation of our work on thermodynamic properties of binary liquid mixtures [10–13] we present densities and speeds of sound for binary mixtures of ethyl lactate and aromatic amines at four different temperatures T = (303.15, 308.15, 313.15 and

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318.15) K and 0.1 MPa. Experimental data are used to calculate excess molar volumes (V_m^E) partial molar volume ($\bar{V}_{m,1}^E$), excess partial molar volume at infinite dilution $(V_1^E)^{\infty}$ and isentropic compressibility (κ_s^E) and thereafter correlated with the Redlich–Kister equation [14]. Additionally, the molecular interactions between the components are examined and interpreted based on FT-IR spectra.

A review of literature reveals that so far no systematic study on thermodynamic and thermo acoustic properties of ethyl lactate with aromatic anilines had been reported. However certain other binary mixtures of ethyl lactate were studied and reported. Zivkovic et al. [15] conducted studies on volumetric and viscometric behavior of the binary systems of ethyl lactate with diols and ethers and analyzed results in terms of specific molecular interaction. Lomba et al. [16] reported a comparison of the thermophysical behavior of methyl, ethyl and butyl lactate in terms of intermolecular interactions. Aparicio et al. [17–19] did a thorough study on characterization of ethyl lactate using thermodynamic, spectroscopic and molecular dynamics simulations studies. Pereira et al. [20] reported the main properties and applications of ethyl lactate, as well as its synthesis and production processes. Chen et al. [21] measured densities and viscosities of binary mixture of ethyl lactate with acrylates. Lomba et al. [22] reported isobaric expansibility and isothermal compressibility of ethyl lactate from the measured densities, and the results were interpreted in terms of molecular interactions and structure. Thermodynamic properties were carried out for binary mixtures of ethyl lactate with acetates and alcohols by Resa et al. [23,24]. Experimental measurements and modelling of volumetric properties of binary systems of ethyl lactate with methyl ethyl ketone, toluene and n-methyl-2-pirrolidone were carried out by Divna et al. [25]. Most of the reported data were focused on phase equilibrium studies of ethyl lactate and its liquid mixtures [26–30].

2. Experimental section

2.1. Materials

For the investigation, the racemic mixture of ethyl lactate is procured from Sigma –Aldrich. The mass fraction purity is 0.98 and is used without further purification. Aniline, N-methyl aniline and N-ethyl aniline are purchased from SD-fine chemicals and are of analytical grade. The claimed mass fraction purity is >0.99. The above liquids are kept in dark bottles in an inert atmosphere and are subjected to distillation and dried over 4 Å molecular sieves and partially degassed by sonication followed by keeping them in a reduced pressure of 65.2 kPa prior to use. A specific assembly was set-up consisting of two vertical columns, the first column filled with 4 Å molecular sieves mounted by a vigreux column to reduce the impurity and moisture content from the chemicals. The purity of these experimental liquids is examined by gas chromatography and the results are presented in Table 1 along with the specifications of the chemicals. The water content in the amines is determined by the Karl Fischer method and it was 400 ppm. The purity is also tested by comparing the measured density and speed of sound values of the pure chemicals at various temperatures with those reported in the literature [31–43]. The values are found to be in good agreement with the literature values and are presented in Table 2. We have taken density and speed of sound of ethyl lactate from our previous studies [10]. The maximum absolute average deviations in density for ethyl lactate, aniline, methyl aniline and ethyl aniline are observed to be 0.021% at T = 303.15 K [31], 0.015% at T = 313.15 K [39], 0.047% at T = 318.15 K [40] and 0.066% at T = 318.15 K [39] respectively. Similarly maximum average absolute deviations in speed of sound are 0.063% at T = 318.15 K for ethyl lactate [31], 0.168% at T = 303.15 K for aniline [33], 0.042% at T = 303.15 K for methyl aniline [41] and 0.311% at T = 313.15 K for ethyl aniline [44]. Ethyl aniline speeds of sound of values were found to be different from those reported by Master et al. [44] and were not satisfactory with our present work. The deviations in our opinion could be due to the purity of ethyl aniline used for the measurements as well as the measuring methods.

2.2. Method

Speed of sounds are determined using a single crystal variable path ultrasonic interferometer operating at 2 MHz frequency provided by Mittal Enterprises, India, Model F-81, at T = (303.15–318.15) K at an interval of 5 K at a pressure of 0.1 MPa, calibrated with bi distilled water, methanol and benzene at T = 298.15 K. For all the measurements, temperatures are controlled by circulating water through an ultra thermostat (supplied by Mittal enterprises) keeping fluctuations within ±0.02 K. Binary mixtures are prepared using an electronic balance (Shimadzu Analytical Balance, Japan. Model AUW-120D) with accuracy ±1.10$^{-4.}$ Airtight stoppered bottles are used for the preparation of the mixtures. The weight of the dry bottle is first determined. The less volatile component of the binary mixtures is introduced first into the bottle followed by second component, and the weight at each step is taken. The density of pure liquids and mixtures are also determined at four different temperatures 303.15–318.15 K using a vibrating-tube densimeter Rudolph Research Analytical DDM 2911, with an accuracy of 5.10^{-5} g.cm^{-3} with an automatic viscosity correction. Proper care has taken to ensure that there was no bubble formation during the measurement since the cell should be air-free. The temperature of the samples is automatically maintained constant to an accuracy of ±0.02 K with a solid state thermostat (Peltier-type) and before each series of measurements it is calibrated at the atmospheric pressure. Ambient air and bi-distilled ultrapure water with a pH 6.8 and conductivity 1.2 μS is used for the calibration. The instrument is inbuilt with a moisture adsorbent. Each experimental density value is the average of at least three measurements.

3. Theory

The experimental value of densities and speed of sound for mixture of ethyl lactate with aniline, N-methyl aniline, N-ethyl aniline over the whole composition range at different temperatures are

Table 1
Materials description.

Component	Source	Purification method	GC Analysis	Mass fraction purity by supplier	Water content mass fraction
EL (racemic mixture)	Sigma-Aldrich	None	0.980	0.980	0.0004
AN	SD-Fine	Distillation	0.996	>0.99	0.0004
NMA	SD-Fine	Distillation	0.997	>0.99	0.0004
NEA	SD-Fine	Distillation	0.996	>0.99	0.0004

Dried over molecular sieves.