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Thermodynamic interactions in binary mixtures of anisole with ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, and 3-methylbutan-1-ol at $T = (298.15, 303.15, \text{and } 308.15)$ K ☆

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Abstract

In this paper, excess thermodynamic functions have been computed from the measured values of density, viscosity, and refractive index at $T = (298.15, 303.15, \text{and } 308.15)$ K, ultrasonic velocity at $T = 298.15$ K over the entire mixture composition range of (anisole with ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, or 3-methyl butan-1-ol). Excess molar volume, V^E has been calculated from densities, whereas deviations in viscosity, $\Delta\eta$, were computed from the measured viscosities. From ultrasonic velocities, isentropic compressibilities were calculated, from which deviations in isentropic compressibility, Δk_s have been computed. Lorenz–Lorentz mixture rule was used to compute molar refractivity, R from refractivity index data and from these data, deviations in molar refractivity, ΔR have been computed. Computed thermodynamic quantities have been fitted to Redlich and Kister polynomial equation to derive the coefficients and standard errors between experimental and predicted quantities. Intermolecular interactions between anisole and alkanols have been studied based on the computed excess thermodynamic quantities.

Keywords: Density; Viscosity; Refractive index; Speed of sound; Anisole; Alkanols

1. Introduction

Accurate measurement of experimental data on physical properties of organic binary liquid mixtures is of great interest to understand their thermodynamic interactions in terms of excess quantities. In particular, (anisole + alkanol) mixtures are of interest in chemical/pharmaceutical industries and therefore, understanding of their mixing behaviour is important. In addition, such data are important for thermodynamic model development and engineering applications. In our previous studies [1–4], thermodynamic and transport properties of binary liquid mixtures containing alkanols have been investigated. Alkanols exist in associated forms due to intermolecular hydrogen bonding interactions. When these are mixed with a less polar liquid such as anisole could produce varying interactions with increasing alkyl groups or carbon–carbon chain lengths in higher alkanols as well as due to differences in polarity of the hydroxyl (–OH) group. Anisole (methoxy benzene) in which $-OCH_3$ group is attached to the benzene ring has a dipole moment value of 1.38 D, which will interact systematically with decreasing polarity of higher alkanols starting from ethanol and hence, exhibit varying thermodynamic interactions as the length and branching in the carbon chain of alkanols change. In order to study such effects, we felt it essential to investigate thermodynamic properties of binary mixtures of anisole with linear and branched chain alkanols.

A search of the literature indicated only a handful of data on studies related to binary mixtures of anisole with

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alkanols [5–7]. For instance, Weng *et al.* [5] studied excess molar volume, V^E and deviations in viscosity, $\Delta\eta$ for mixtures of anisole with six pentyl alcohols, for which V^E values are positive, whereas the results of $\Delta\eta$ are negative. In another study, Weng [6] showed that when anisole was mixed with butan-2-ol and two other isomers of propan-2-ol, the negative values of V^E and $\Delta\eta$ have been observed over the entire range of compositions studied. Weng [7] in another paper, reported the values of V^E and $\Delta\eta$ for mixtures of anisole with *n*-alkanols viz., (anisole + butan-1-ol, +pentan-1-ol, +hexan-1-ol, +heptan-1-ol, and +octan-1-ol), wherein positive V^E and negative $\Delta\eta$ values were observed. In continuation of these studies and as a further contribution in this area, we report here the experimental results on density, ρ, viscosity, η, and refractive index, n_D, of (anisole + ethanol, +propan-1-ol, +propan-2-ol, +butan-1-ol, +pentan-1-ol, or +3-methylbutan-1-ol) mixtures at temperatures ranging from (298.15 to 308.15) K, but ultrasonic velocity, u are measured at $T = 298.15$ K.

From the density results, V^E has been calculated, whereas viscosity data have been used to calculate $\Delta\eta$. From refractive index data, we have computed deviations in Lorenz–Lorentz molar refractivity, ΔR of the mixtures. Deviations in isentropic compressibility, Δk_s, were calculated using the ultrasonic velocity data. All the computed quantities viz. V^E, $\Delta\eta$, ΔR and Δk_s have been fitted to Redlich and Kister polynomial Equation (8) to derive the binary coefficients and estimate standard errors between the experimentally calculated quantities and the predicted results. These data are displayed graphically to discuss the nature and type of intermolecular interactions between the mixing components. These interactions could be due to H-bonding, dipole–dipole or dispersion-type interactions as indicated by the shapes of thermodynamic quantities.

2. Experimental

2.1. Materials

Anisole (Sisco Research Laboratories, Mumbai, India, mass fraction purity 0.995), ethanol (Changshu Yang Yuan Chemicals-China, mass fraction purity 0.999), propan-1-ol (0.995), butan-1-ol (0.99) (both were purchased from Ranbaxy Chemicals, Mumbai, India), pentan-1-ol (0.99), propan-2-ol (0.995), and 3-methylbutan-1-ol (0.99) (all procured from s.d. fine chemicals, Mumbai, India). Mass fraction purities of these liquids as determined by GC (HP 6890) using FID detector were > 0.98. Experimental densities and refractive indices at $T = 298.15$ K presented in table 1 compared with the literature data [9–14] are agreeable within the limits of experimental errors (i.e., <3%).

2.2. Methods

Mixtures were prepared on the basis of mass (accurate to ±0.01 mg) by mixing calculated volumes of liquid components in a specially designed glass-stoppered bottle [15] on a digital electronic balance (Mettler, Model AE 240, Switzerland). In total, nine mixture compositions ranging from (0.1 to 0.9) mole fractions in steps of 0.1 were prepared for each binary mixture. All the physical properties of the mixtures were prepared and measured on the same day to avoid preferential evaporation losses. The uncertainty in mole fraction of the binary mixture was within $\pm 10^{-4}$ in all cases.

2.3. Density

Densities, ρ, of pure liquids and their binary mixtures for all compositions were measured at $T = (298.15$ to $308.15)$ K by the Anton Paar oscillating U-tube density meter (Model DMA 4500, K.G. Austria) within a precision of $\pm\ 5 \cdot 10^{-2}\,\mathrm{kg \cdot m^{-3}}$. The oscillation period, τ, in the vibrating U-tube of the densitymeter was converted to density, ρ, using the equation:

$$\rho = A\tau^2 - B, \tag{1}$$

where A and B are instrument constants determined by using density of dry air and ultrapure water (produced in the laboratory itself using Permeonics ultrafiltration membrane module). A unique reference oscillator, in addition to U-tube oscillator, provides an extraordinary long-term stability and adjustments at higher temperatures. By measuring the damping of U-tube's oscillation caused by viscosity of the filled-in sample, the instrument automatically corrects for viscosity related errors. Two integrated platinum

TABLE 1
Comparison of experimental densities (ρ) and refractive indices (n_D) of liquids with literature values at $T = 298.15$ K

Liquid	Mol. % purity	$\rho/(\mathrm{kg \cdot m^{-3}})$		n_D	
		Experimental	Literature	Experimental	Literatute
Ethanol	99.9	785.91	785.46 [9]	1.3591	1.3593 [10]
Propan-1-ol	99.5	799.96	799.62 [10]	1.3826	1.3830 [10]
Propan-2-ol	99.5	781.36	781.40 [12]	1.3745	1.3752 [11]
Butan-1-ol	99.0	806.12	806.00 [11]	1.3968	1.3973 [11]
Pentan-1-ol	99.0	810.92	810.83 [10]	1.4073	1.4080 [10]
3-Methylbutan-1-ol	99.0	807.20	807.10 [13]	1.4050	1.4052 [13]
Anisole	98.5	989.15	989.20 [14]	1.5137	1.5143 [14]