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Comparative study of molecular interactions in aromatic, cyclic and aliphatic ketones with 1-octanol at 308.15 K: An insight from ultrasonic velocity and density

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ABSTRACT

Ultrasonic velocities, u, densities, ρ, of binary liquid mixtures of 1-octanol with acetophenone (AP), cyclopentanone (CP), and 3-Pentanone (3P), including pure liquids, over the entire composition range have been measured at 308.15 K. Using the experimental results, parameters such as molar volume (V_m), isentropic compressibility (k_s), acoustic impedance (z) and their excess/deviation properties have been calculated. The calculated deviation/excess properties have been fitted to the Redlich–Kister type polynomial equation. Partial molar volumes, excess partial molar volumes and partial molar compressibilities, excess partial molar compressibilities have also been calculated. The observed positive values of V_m^E, Δk_s, and negative values of z^E for all the liquid mixtures indicate the domination of rupture of existing H-bond or reduction in H-bond strength between the carbonyl group (–C═O) of ketones and the hydroxyl group (–OH) of 1-octanol. The strength of weak interactions follows the order: (1-octanol + 3P) > (1-octanol + CP) > (1-octanol + AP). Further, FTIR spectra also support the conclusions drawn from excess/deviation properties. Moreover, theoretical values of sound velocity in the mixtures have been evaluated using various theories and compared with experimental sound velocities to verify the applicability of such theories to the systems studied.

1. Introduction

Ultrasonic velocities, densities and derived thermodynamic, acoustical parameters are of considerable interest in understanding the intermolecular interactions in binary as well as ternary liquid mixtures [1–5]. Ultrasonic studies can also be used to determine the extent of complexation and to calculate the formation constant values of charge transfer complexes [6,7]. It is well known that alcohols are highly associated through hydrogen bonds, thus their structure and properties are determined mainly by quasi-chemical bonds between the molecules which result in the formation of multimers of different sizes and structures [8]. The practical application of mixed solvents rather than single solvent in industrial and biological processes has been recognized all over the world as they provide a wide choice of solutions with appropriate properties [9]. Ketones are organic compounds that contain a carbonyl group (>C^+═O^-) and two aliphatic or aromatic substituents containing the chemical formula RCOR[1]. Here, R and R[1] may be the same or different incorporated into a ring (alkyl, aryl and heterocyclic radicals). The chemical reactivity of the carbonyl group plays a vital role in chemical reactions and is influenced considerably by steric effects. The greater electro negativity of O^-, high dipole moment makes ketones polar. The following resonance structure (structure (a)) illustrates this polarity. Further the presence of oxygen with its nonbonding electron pairs makes them H-bond acceptors. The common solvent chosen here is 1-octanol, a straight chain fatty alcohol with eight carbon atoms (structure (b)). Chemically it is a non-polar liquid. It is used in vinyl resins, plastics, oils, and perfumes, as a defoaming agent and medicinally it is used for controlling essential tremors and other types of

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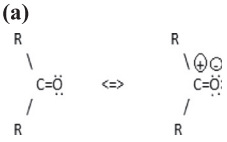
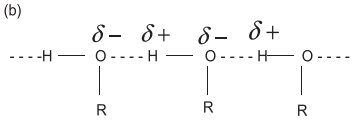
involuntary neurological tremors [10].



Structure (a)



Structure (b)

The present study deals with the ultrasonic and thermodynamic study of mixed solvent system at 308.15 K. The liquids under investigation have been chosen on the basis of their industrial applications. These applications have greatly stimulated the need for extensive information on the thermodynamic, acoustic and transport properties of these solvents and their mixtures. The selected components for the present study are 1-octanol and ketone group liquids acetophenone (AP)/cyclopentanone (CP)/3 pentanone (3P). Literature survey reveals that Sri Lakshmi et al. [11] and Tsierkezos et al. [12] studied the molecular interaction studies in certain alcohol and ketones at different temperatures. Recently, Nayeem et al. [13] studied molecular interactions in cyclohexanone (CH) with Isomers of butanol. Keeping the important aspects of the present liquids, the present study reports the volumetric and ultrasonic properties of the binary system at 308.15 K.

2. Experimental details

High purity analytical grade (AR grade) samples of cyclopentanone (Fluka), 3-pentanone procured from Merck, and acetophenone procured from Sigma Aldrich were used. 1-Octanol (AR grade) obtained from S.d. Fine Chemicals (Bombay) is further purified by standard methods [14,15]. The solutions of binary mixtures of 1-octanol with AP, CP and 3P have been prepared in the specially designed glass bottles with air tight stoppers and adequate precautions have been taken to minimize evaporation losses. Before measurements all the liquids were carefully dried over 0.4 nm molecular sieves and stored in dark bottles. These samples were distilled just before use. The purity of these liquids was ascertained by Gas Chromatography (HP 8610) using a FID detector and the analysis indicated mole percent purities > 99.5%. The weighing of solutions has been made using a METTLER TOLEDO (Switzerland make) ABB5-S/FACT digital balance with an accuracy of ±0.01 mg. The uncertainty in the mole fraction is 10^{-4}.

The ultrasonic velocity of pure liquids and their binary mixtures has been measured by using a multi-frequency ultrasonic interferometer (M-82 Model) supplied by Mittal Enterprise, New Delhi at a fixed frequency of 2 MHz with an accuracy of ±0.2%. The density has been measured using a two stem pyknometer of Parker & Parker type [16–18] having a bulb volume of 5 cm^3. The estimated accuracy in the density measurement is 3 in 10^5 parts. The detailed calculations of ultrasonic velocity and density were described in our previous papers [13,19,20].

The experimentally measured values of ultrasonic velocity (u) and density (ρ) at 308.15 K of all pure liquids have been compared with the literature values [11,21] in Table 1.

3. Results and discussion

The experimentally measured values of u and ρ were used to calculate the values of thermodynamic and acoustical parameters such as molar volume (V_m), isentropic compressibility (k_s), acoustic impedance (z) using standard relations. In order to understand the nature of the molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their concentrations, and this has been interpreted to arise from the presence of strong or weak interactions. The difference between the parameters of the real mixtures (Y_{real}) and those corresponding to an ideal mixture ($Y_{ideal} = \sum x_i Y_i$) values, namely excess parameters (Y^E) such as excess molar volume (V_m^E), acoustic impedance (z^E) are computed by the relation

$$Y^E = Y_{real} - \sum x_i Y_i \quad (1)$$

where $Y^E = V_m^E$ and z^E; x_i is the mole fraction and Y_i is the value of the parameter of the ith component liquid of mixture.

The deviation in isentropic compressibility (Δk_s) has been calculated from the equation

$$\Delta k_s = k_s - (\Phi_1 k_{s1} + \Phi_2 k_{s2}) \quad (2)$$

since k_s is not additive on mole fraction but is additive on volume fraction. Hence, such values are calculated using volume fraction (Φ)

$$\Phi = \frac{x_i V_i}{\sum x_i V_i}. \quad (3)$$

The experimentally measured values of ultrasonic velocity (u), density (ρ) and evaluated values of molar volume (V_m), isentropic compressibility (k_s), acoustic impedance (z) and their excess/deviation in volumetric and acoustic parameters V_m^E, z^E and Δk_s are presented in Table 2 over the entire composition range of 1-octanol. The excess/deviation properties have been fitted to a Redlich–Kister type polynomial equation [22]

$$Y^E = x(1-x)\sum_{i=0}^{j} A_i (1-2x)^i \quad (4)$$

where $Y^E = V_m^E$, z^E and Δk_s; x is the mole fraction of 1-octanol.

The values of Δk_s have been fitted to Redlich–Kister type polynomial with volume fraction ( ) instead of mole fraction (x) in the above polynomial and A_i are the adjustable parameters of the function; and are determined using the least squares method. In the present investigation 'i' values are taken from 0 to 4. The corresponding standard deviations

Table 1
Comparison of experimental values of density, ρ, and ultrasonic velocity, u, of pure liquids with the corresponding literature values at 308.15 K.

Liquid	Temp/(K)	ρ/(kg m^{-3})		u/(m s^{-1})	
		Present work	Literature	Present work	Literature
1-Octanol	308.15	813.20	814.1 [11]	1321.50	1322.4 [11]
Acetophenone	308.15	1013.30	1013.5 [21]	1441.10	1441.2 [21]
Cyclopentanone	308.15	934.60	–	1351.20	–
3-Pentanone	308.15	801.00	–	1218.80	–

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