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A Case Study on Excess Thermodynamic properties and Molecular Interactions in Binary liquid Mixture

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Abstract:

Experimentally measured data for viscosity and refractive index of binary mixture are reported in this research paper for various compositions for three different temperatures at atmospheric pressure. Modified Ubbelholde viscometer and Abbe-3L Refractometer were used for experimental measurements. Deviation in molar refraction (ΔR) and deviation in viscosity (Δη) w.r.t composition have been calculated from the experimental data. 'Grunberg and Nissan' equation and Herric's Correlation were used to correlate the viscosity data. Excess thermodynamic properties were fitted to Redlich-Kister equation. Coefficients and standard deviations, hence obtained are reported. Variation in Excess Thermodynamic properties for the mixture have been discussed in terms of intermolecular interactions.

Keyword:Excess molecularvolume, Intermolecular free-length, Viscosity, isentropic compressibility, Molar refraction.

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I. INTRODUCTION

Propiophenone is a generally used component in some perfumes. Propiophenone is used in the synthesis of ketoamphetamines such as cathinone and methcathinone. Propiophenone can also be converted to synthetic aryl alkenes such as cinnamic acids. Properties such as density, viscosity of pure chemicals and of their binary mixtures over the whole composition range at a particular temperature or several temperatures, are useful for a complete understanding of their thermodynamic properties and for practical chemical engineering purposes. Physico chemical and thermodynamic investigations play an important role to understand the nature and extent of the aggregation of molecules that exists inthe binary liquid mixtures and their sensitivities to the variations in composition and the molecular structure of the pure components [1, 2]. In the recent years there has been considerable interest in theoretical and experimental investigations of the excess thermodynamic properties of binary mixtures. Density and ultrasonic velocity properties of binary liquid mixtures are essential in process simulation, equipment design, solution theory, important parameter in calculations of the thermodynamic properties of matter and molecular dynamics. The ultrasonic velocity measurement is an excellent tool to investigate inter and intra molecular interactions between liquid mixtures of non-electrolytes. Acoustic properties are useful in understanding the molecular interactions. The present research paperpresents the data on densities, viscosity and ultrasonic velocity of binary liquid mixtures of Propiophenone(PPH) with 2-Alkoxy Ethanols 2-Methoxy Ethanol (2-MOE), 2-Ethoxy Ethanol (2-EOE), 2-Butoxy Ethanol (2-BOE)] at temperatures 303.15K,308.15K, 313.K, and 318.15K.By using this data, various acoustical parameters like Acoustic impedance (Z), Isentropic compressibility (Ks), Inter molecular free-length (Lf) and also various excess properties like excess ultrasonic velocity (VE), excess acoustic impedance (ZE), excess isentropic compressibility (KSE) and excess inter molecular free-length (LfE) were calculated and fitted to the Redlich Kister equation to estimate the standard deviations.Above results are used to explain the nature of intermolecular interactions between mixing components. This work provides a test of various empirical equations to correlate viscosity and acoustic data of binary mixtures in terms of pure component properties.

II. Material and Methods :

Propiophenone, 2-Alkoxy Ethanols [2-Methoxy Ethanol (2-MOE), 2-Ethoxy Ethanol (2-EOE), 2-Butoxy Ethanol (2-BOE)], these chemicals purchased from S.D. Fine chemicals Ltd, India and used in the present investigation, details as shown in Table.

TABLE : PROVENANCE AND PURITY OF THE MATERIALS USED

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CHEMICALS	CAS number	Source	Water content (%)	Mass fraction purity(final)
Propiophenone	92-54-0	S.D fine Chemicals, India	0.00059	> 98%
2-Methoxy ethanol	100-86-4	S.D fine Chemicals, India	0.00045	0.983
2-Ethoxy ethanol	120-80-5	S.D fine Chemicals, India	0.0004 1	0.978
2-Butoxy ethanol	131-76-2	S.D fine Chemicals, India	0.0004	0.985

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0.00059	> 98%
0.00045	0.983
0.0004 1	0.978
0.0004	0.985

Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of closed system by using Mettler Toledo (ME204)balance with the precision of ± 0.1 mg. Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles. The purities of the liquids were checked by comparing the values of densities and ultrasonic velocities with literature data and are given and proper care was taken to avoid any evaporation loss while doing the experiment. The densities of liquids and their mixtures were measured using bi-capillary pycnometer having a capillary diameter of 0.85 mm, which was calibrated using double distilled water. The necessary buoyancy corrections were applied. The density (ρ) values were reproducible within ± 0.2 Kg m-3. The ultrasonic velocity (u) measurements were made by a single frequency (2 MHz) variable path interferometer with an error of ± 0.0001%ultrasonic interferometer model F-05(s.no.1415342) Mittal Enterprises, New Delhi. Formulae used are:

$V^E = x^1M^1+x^2M^2\rho^m - x^1M^1\rho^1 + x^2M^2\rho^2$ …… (1)

$K_s = \cup^{-2}\rho^{-1}$ …… (2)

$K_S{}^E = K_S - K_S{}^{iD}$ …….. (3)

$K_S{}^{iD} = \phi_i K_s i + TV_i\alpha_i{}^2Cp_i - Tx_iV_i{}^2 + \phi_i\alpha_i{}^2 + x_iCpi^2$ ….. (4)

$\Delta u = u - x_1u_1 + x_2u_2$ …… (5)

$\Delta\eta = \eta - x_1\eta_1 + x_2\eta_2$ …….. (6)

In the above equations:M_i , $K_s{}^E$, η_i ,u_i and ρ_i represent the molecular weight, isentropic compressibility,viscosity, ultrasonic velocity and density of component.

Results and Discussions: The experimental values of Ultrasonic velocity, density and viscosity of three binary mixtures at temperatures 303.15, 308.15, 313.15 and 318.15 K are presented in Table-02. From these values, it is observed that, in all the systems, ultrasonic speed (u) and density (ρ) increased non-linearly with mole fraction of PPH and the viscosity is decreased at 303.15k for all three binary mixtures, where as in the case of other temperatures, the viscosity is increased for the binary mixtures of PPH+2-MOE & PPH+2-EOE, but in the case of PPH+2-BOE, viscosity is decreased at all temperatures.

Excess molar volume ($\boldsymbol{VmE}$) : The excess molar volumes for all the three binary systems over the whole composition range are Positive and the value decreases with increase in temperatures at 303.15k, 308.15K, 313.15k, 318.15K.The maximum deviation in excess molar volume is obtained at 0.4730, 0.4239 and 0.4989 mole fractions of PPh for (PPh+2-MOE),PPh+2-EOE) and (PPh+2-BOE)

respectively. The Excess molar volume (VmE) values depends upon three factors mainly physical, chemical and structural properties. The sign and magnitude of the excess properties depend on the following factors [7]: (i) The disruption of dipolar molecules in the like associated molecules is due to the addition of second component molecule. (ii) Chemical association between unlike molecules through the formation of hydrogen bond, which is a strong specific interaction, (iii) Association through weaker physical forces like dipole-dipole interaction and (iv) Accommodation of molecules of one component in to the interstitial positions of the structural network of molecules of other component. The first factor contributes to the positive excess molar volume (VmE) due to the expansion in volume and the other three contributes negative excess molar volume. In our present binary systems shows positive excess molar volumes. The addition of propiophenone to alkoxy ethanols, first breaks the intra molecular hydrogen bond within alkoxy ethanols, and then forms a new hydrogen bond between hetero molecules leading to a complex formation. It is assumed that in the present case there is a intermolecular hydrogen bonding is expected than that of intramolecular hydrogen bonding because of polarized C=O…..H bond it causing the breakage of self-association. This is evident from the IR graphs which are discussed in separate section of this paper. The observed higher values of PPh+2-BOE indicate the dominance of molecular dissociation over association. In addition to this the interstitial accommodation of MOE, EOE and BOE molecules into the voids of PPH, the molar volume of PPH (133.5789 cm3mol−1) is greater than the two alkoxy-ethanols under study at 303.15 K.(Vm=79.8950 cm3mol−1 for MOE, 97.8321 cm3mol−1 for EOE and 132.4226 cm3mol−1for BOE) is expected, but alkoxy ethanol molecules being expected to exist in rings of 5/6/7members, it is expected that the molar volume remains positive even though there is possibility of hydrogen bond formation between the C=O group of Propiophenone and the -OH group of alkoxyethanol, the same is observed in the research analysis of anisaldehyde with alkoxyethanol done by Zereena [9] and indicating a very possible reason for the positive values of VmE. Same is observed in the research analysis of anisaldehyde with cresols by Narendra et al. [16]. In alkoxyalchohols, the hydrogen atom of alcohols forms hydrogen bond with C =O of the Propiophenone. The newly formed inter-molecular hydrogen bond has more effect than the intramolecular Hydrogen bonding causing the breakage of self-associates. The observed higher positive values of (VmE) over the entire range of mole fraction in PPH+BOE system may be attributed to the dominance of molecular dissociation over association. In all systems the VmE values decreased with a rise in temperature from 303.15 to 318.15 K. This may be attributed to the rise in kinetic energy of interactingmolecules and breakage of intermolecular association followed by new hydrogen bond formations.

Excess intermolecular free length ($\boldsymbol{Lf}$) : Ultrasound waves are high frequency mechanical waves. Their velocities in a medium depend inversely on the density and compressibility of the medium. The variation of ultrasonic velocity in a mixture depends upon the increase or decrease of intermolecular free length (Lf), after mixing the components computed excess intermolecular free lengthLf $E$and is graphically represented as

$L_f{}^E = L_f - (x_1 L_f{}^1 + x_2 L_f{}^2)$

Deviation in Viscosity ($\Delta\boldsymbol{\eta}$) : The deviation in Viscosity is calculated as below for the experimental data of viscosity (η) of the binary mixtures.

$\Delta\eta = \eta - (x_i\eta_i)$

where η and ηi are viscosities of the mixture and the pure compounds respectively.

The nature of intermolecular forces' attraction between the molecules of the binary liquid mixtures can be analyzed by using the viscosity measurements. The values of $\Delta\eta$ are negative for all the binary mixturesof PPH+2MOE, PPH+2EOE, and PPH+2BOE at the temperatures 303.15 to

318.15. In Table-03a to 3d, the viscosity deviation may be generally explained by considering the following factors [24]. (i) The difference in size and shape of the component molecules and the loss of dipolar association in pure component may contribute to a decrease in viscosity and (ii) Specific interactions between unlike components such as hydrogen bond formation and charge transfer complexes may cause increase in viscosity in mixtures compared to pure components. The former effect produces negative deviation in viscosity and latter effect produces positive viscosity deviation.

Conclusion : In this paper, the densities, excess molar volume, viscosities and speed of sound at temperatures 303.15K, 308.15K, 313.5K and 318.15K over the entire range of composition of Propiophenone with alkoxyethanols have been measured. From these measured physical property data, excess molar volumes, deviation in viscosity, excess ultrasonic velocity and excess isentropic compressibility have been calculated and correlated by a Redlich–Kister type polynomial equation to derive the coefficients and standard deviation. The intermolecular interactions of the components are interpreted and found the results as positive and negative for excess molar volume and viscosity respectively. It is observed that aninter and intramolecular association is formed between Propiophenone and 2- alkoxyethanols. FT IR data indicates the strength of inter and intra molecular association between carbonyl group of Propiophenone with OH group of 2-Alkoxy alkanols.

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