THERMOACOUSTIC, VISCOMETRIC AND OPTICAL STUDY OF MOLECULAR INTERACTION IN BINARY MIXTURES OF TETRAHYDROFURAN WITH PROPANAL-1 AND PROPANOL-2

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ABSTRACT

Mixed solvents rather than single pure liquids are of utmost practical importance in most chemical and industrial processes as they provide a wide range of possibilities for the continuous adjustment of desired properties of the medium. With this view, it appears that THF-Propanol-1/Propanol-2 mixed solvents would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be used for particular processes. Therefore speed of sound, density, viscosity and refractive index of the binary mixtures of THF with Propanol-1 and Propanol-2 have been measured over the entire range of mole fractions at 293K, 303K and 313K. From these data, various excess parameters have been calculated. The changes in these parameters with composition of the mixtures were used to study the nature and the extent of intermolecular interaction between the component molecules present in the binary mixtures. Further, theoretical values of ultrasonic speed and viscosity were evaluated using different empirical relations and theories.

INTRODUCTION

The study of excess thermodynamic properties of mixtures offers a convenient means to understand the inter-relationship between the observed macroscopic properties of the mixtures and the microscopic interactions among like and unlike molecules. The advantage of in-depth and wide study of this inter-relationship is twofold: first, it provides experimental background to develop, test and improve thermodynamical models for calculating and predicting fluid phase equilibria; second, it offers a wide range of possibilities for continuous adjustment of physical properties of a given solvent.

The study of the thermodynamic behaviour of binary mixtures containing cyclic ethers and polyethers have gained importance because of industrial applications and the theoretical interest in studying the structure of such solutions [1-4]. Ottani and coworkers[5] have measured densities, kinematic viscosities and refractive indices for the binary mixture of poly(ethylene glycol) 200 and 400 with four cyclic ethers at T = 303 K and explained the behaviour of excess properties in terms of disruption of hydrogen bonding in polymer .

In order to examine molecular interactions in the mixture of tetrahydrofuran with 1-propanol/2-propanol The present paper reports the excess adiabatic compressibility(β_s^E) , excess molar volume (V^E_m), deviations in viscosity ($\Delta\eta$) and molar refraction (ΔR_m) for the binary mixture of tetrahydrofuran (THF) with 1-propanol (1-P) and 2-propanol (2-P) at T = 293 K, 303 K and 313 K with the aim of analysing the disruption of self association in 1-propanol and 2-propanol and the breaking of dipole-dipole interactions of tetrahydrofuran together with the interaction between oxygen of THF and hydroxyl group of alcohol [6,7].

EXPERIMENTAL DETAILS AND FORMULAE USED

Ultrasonic velocity was measured using the ultrasonic interferometer (Model M-83) provided by Mittal Enterprises, New Delhi. The instrument was calibrated by measuring the velocity in standard liquids, e.g. AR grade benzene and carbon tetrachloride . The density of liquid mixture has been measured using a dilatometer. The dilatometer consists of a long tube graduated in 0.01 ml scale, fitted to a specific gravity bottle of capacity 8 ml with an accuracy of $\pm$ 0.5%. Refractive index was measured using Abbe's refractometer provided by Optics Technologies, Delhi. Refractometer was calibrated by measuring the refractive indices of triply distilled water and benzene at T = 293 K. The viscosity of the mixtures was determined by using Ostwald's viscometer which was kept inside a double wall glass jacket in which water from thermostated water bath was circulated.

By the use of well known equations, the isentropic compressibility, molar volume, viscosity and molar refraction of the mixtures were calculated from measured ultrasonic velocity, density, viscosity and refractive index. The excess function of all these parameters were calculated by the expression :

$$A^E = A_{exp} - (x_1 A_1 + x_2 A_2) ;$$

where A_i represents the different parameters and x_i represents mole fraction for β_s^E, V^E_m, $\Delta\eta$ and volume fraction for ΔR_m.

The theoretical values of ultrasonic velocity were calculated using Nomoto's [8] and Ideal mixing relations [9]. Frenkel [10] and Sutherland-Wassiljewa

[11] empirical relations were used for the prediction of viscosity theoretically.

RESULTS AND DISCUSSION

The results obtained are presented in the figures1a-1d.Excess adiabatic compressibility (β_s^E),excess molar volume (V_m^E),and molar refraction deviation (ΔR_m) have been found to be negative for THF+1-P mixture over the entire composition range at all the temperatures studied here, where as β_s^E ,V_m^E and ΔR_m is found to be positive for THF + 2-P mixture over the entire composition range (Fig. 1a-1d). The values of these excess parameters for these mixtures can be explained as a cumulative manifestation of the various types of intermolecular interactions between the components. It has been reported by earlier workers [1,12-14] that three main types of contributions to excess thermodynamic properties of mixtures are –

(1)   physical: due to non-specific van der Walls type interactions
(2)   chemical: due to hydrogen bonding, and
(3)   structural: due to changes of interstitial accommodation and free volume

It is well known that alkanols are protic and associated through hydrogen-bond in pure state. The mixing of an aprotic liquid THF with alkanols (propanol-1 and pronanol-2) tends to break the associates present in the alkanol molecules and there is possibility of hydrogen-bonding between oxygen atom of THF with its lone pair of electrons and the hydrogen atom of hydroxyl group of alkanols. Thus the observed negative values of β_s^E ,V_m^E and ΔR_m are in the case of THF + 1-P mixture (Fig. 1a-1c) indicates the presence of strong inter-molecular interaction through hydrogen-bonding between unlike molecules. However, in the case of THF + 2P mixture, the positive values of. ΔR_m suggest that the effect due to rupture of hydrogen bonded chain of 2-propanol dominates over that of hydrogen bond formed between the unlike molecules.

Variation of β_s^E is in accordance with the view proposed by Fort and Moore [15] according to which liquids of different molecular size usually mix with decrease in volume yielding negative β_s^E values.

Negative trends in β_s^E have also been reported for binary mixtures of alkanols and alkane Salgado *et al* [16]. The positive deviation in β_s^E for THF+2-P mixture may be attributed to the presence of weak interaction between the component molecules in the mixture, thereby indicating the predominance of long

range dispersive forces. Similar trends in β_s^E were also reported by earlier workers [1,5] for binary mixtures.

Similar results have been reported by Ali *et al.* [1] where values of excess adiabatic compressibility are found to be positive for THF + tert butanol and THF + 1-butanol mixtures at 30°C. However, we have observed negative β_s^E values in the case of THF + 1-P mixtures over the entire composition range and at all the these temperatures. This may be because of the fact that 1-propanol is more acidic than 1-butanol, thus yielding negative contribution to β_s^E values. Results of George *et al.* [17] also corroborate this relative tendency of 1-propanol and 1-butanol towards complex formation.

Fort and Moore [21] suggested that the liquids of almost equal molecular size usually mix with positive excess molar volume. Molar volumes at 293 K are 74.79 cm^3/mol, 76.51 cm^3/mol and 81.09 cm^3/mol for 1-propanol, 2-propanol and THF, respectively. Larger molar volume difference between THF and 1-propanol than that between THF and 2-propanol would allow a more favourable packing of 1-propanol molecule than 2-propanol molecules into the spaces created by THF molecules. This would result in a contraction in volume, hence would give rise to negative values of excess molar volume V_m^E for (THF +1-P) mixture. On contrary, an expansion in volume occurs for the case of (THF +2-P) mixture leading to a positive V_m^E values. It seems that the packing effect as well as formation of hydrogen bond are determining factors for (THF + 1-P) mixture [22-24] whereas the dispersive forces which gives positive contribution to the excess molar volume are predominant over structure making effect in (THF + 2-P) mixture. Similar results have been reported by Ali *et al.* [1] in binary mixture of THF with 1-butanol and tert-butanol.

1-P and 2-P molecules, when mixed with THF molecules, exhibit opposite behaviour towards complex formation, yielding both the negative and positive contribution in β_s^E respectively. This may arise due to two factors :
1. 2-P is less acidic than 1-P due to higher electron releasing tendency of $(CH_3)_2CH-$ than $(C_3H_7) -$
2. Steric hindrance offered by the branched alkyl group attached to the hydroxyl group in 2-P prohibits it to form complex through H-bonding.

Negative and positive values of β_s^E ,V_m^E and ΔR_m have been found to increase with increase in

temperature for both the mixtures (Fig. 4). Increase in negative values β_s^E , V_m^E and ΔR_m for THF+1-P mixture suggest that thermal energy activates the molecules towards complex formation between unlike molecules. Also since self-association in 2-propanol is less stronger, increase in temperature will cause rupture of more and more hydrogen bonded self-association in propanol-2 molecules and steric hindrance will prohibit the formation of new hydrogen bond between unlike molecules in THF + 2-P mixture. This causes more positive deviation as temperature increases for THF + 2-P mixture.

Excess viscosity ($\Delta\eta$) is found to be negative for both the binary mixtures over the entire composition range. The absolute values of $\Delta\eta$ decrease in both the systems as temperature is raised (Fig. 1d).

An increment of temperature diminishes the self association in the pure components and also the hetroassociation between unlikemolecules, because of the increase of the thermal energy. This leads to less negative values of $\Delta\eta$ as temperature is raised as observed in the present study. Similar temperature dependence has been reported by Marigliano *et al.* [20] for formamide + alcohol mixture. It can also be seen from Fig. 1d that $\Delta\eta$ decreases significantly in THF rich region where heteromolecular association acquires predominance. Absolute value of $\Delta\eta$ is less in THF + 1-P mixture as compared to THF + 2P mixture which indicates that dispersive forces are predominant in THF + 2P mixture. Many workers [25,26] have reported similar behaviour where negative values of $\Delta\eta$ indicate dispersive interactions.

Further, theoretical values of ultrasonic velocity and viscosity evaluated using different empirical relations were found to be in good agreement.

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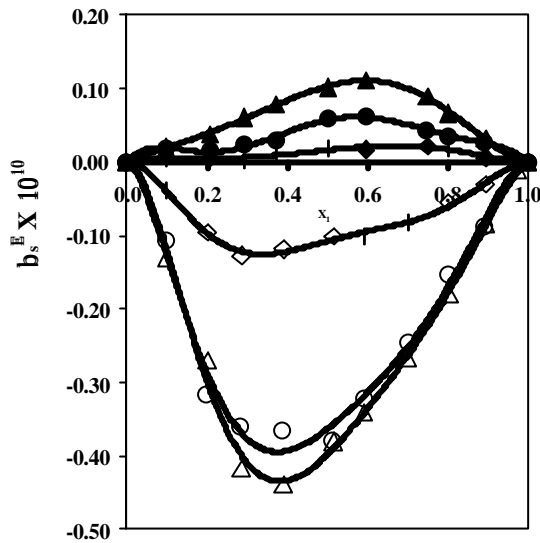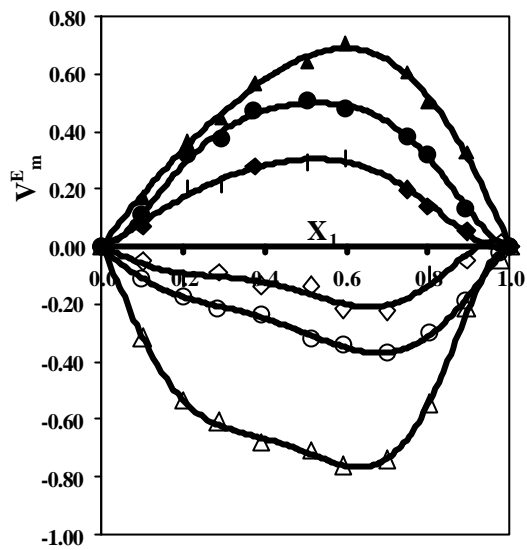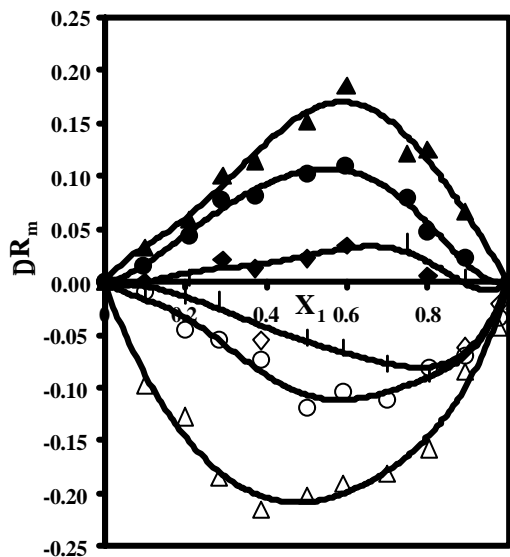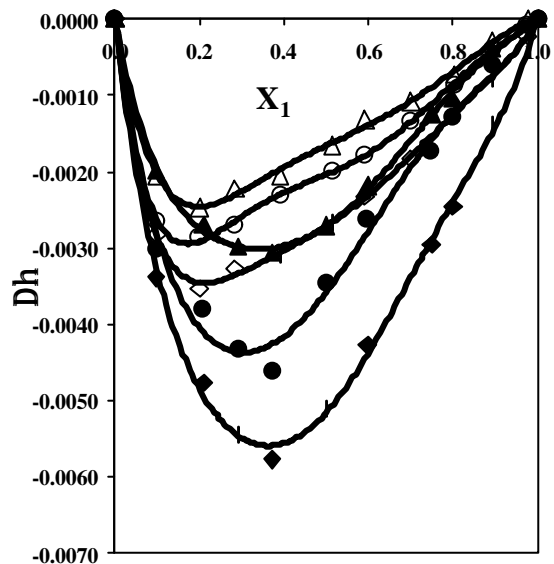[26] J.L. Trenzado, J.S. Matos, R. Alcalde, Fluid Phase Equilib. 200 (2002) 295-315.

Fig.a

Fig.b

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Fig.d

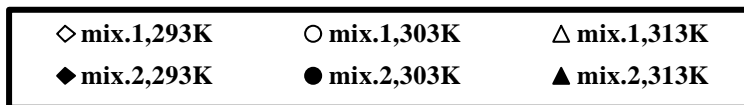| ◇ mix.1,293K | ○ mix.1,303K | △ mix.1,313K |
| ◆ mix.2,293K | ● mix.2,303K | ▲ mix.2,313K |

Figure1:Variation of excess adiabatic compressibility (β_s^E) [Fig.a],excess molar volume (V_m^E) [Fig.b], excess viscosity ($\Delta\eta$) [Fig.c] ,and molar refraction deviation (ΔR_m) against the mole fraction of THF (x_1)for THF+1-P mixture[mix.1] and THF+2-P mixture [mix.2]