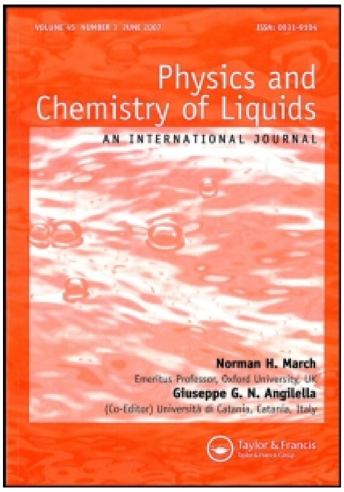

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OPTICAL AND VOLUMETRIC STUDY OF MOLECULAR INTERACTIONS IN BINARY MIXTURES OF TETRAHYDROFURAN WITH 1-PROPANOL AND 2-PROPANOL

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The refractive indices and densities of binary mixtures of tetrahydrofuran (THF) with 1-propanol (1-P) and 2-propanol (2-P) over the entire composition range have been measured at 293, 303 and 313 K. Refractive index and density data have been used to evaluate the molar refraction deviation ΔR_m and excess molar volume V_m^E. The values of ΔR_m and V_m^E are negative for THF + 1-P mixture and are positive for THF + 2-P mixture. This suggests that specific interactions are taking place in THF + 1-P mixture while dispersive forces are responsible for behaviour of THF + 2-P mixture.

Keywords: Refractive index; Density; Molar refraction deviation

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 indepth 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, and second, it offers a wide range of possibilities for continuous adjustment of physical properties of a given solvent.

Properties such as molar volume and refractive index, their deviation from ideality and variation with temperature and composition of binary mixtures are useful for design engineering processes, in chemical and biological industries [1–3], and to test theories of solutions [4].

The study of the thermodynamic behaviour of binary mixtures containing ethers and cycloethers has gained importance because of industrial applications and theoretical interest in studying the structure of such solutions [5–10]. In recent years, Brocos *et al.* [5] have carried out investigation of the thermophysical properties of binary

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liquid mixtures containing cyclic ethers, the second component being either an inert compound or a highly self associated one.

In order to examine molecular interactions in the mixture of tetrahydrofuran (THF) with 1-propanol/2-propanol through excess optical and volumetric properties, we report here the refractive indices (n_m) and densities (ρ_m) of binary mixtures of THF with 1-propanol (1-P) and 2-propanol (2-P) over the entire composition range at $T = 293$, 303 and 313 K. The experimental values of n_m and ρ_m were used to calculate the molar refraction deviation ΔR_m and the excess molar volume V_m^E. These results have been used to discuss the nature of interactions between unlike molecules in terms of hydrogen bonding, dipole–dipole interaction and weak van der Waals type dispersive forces.

EXPERIMENTAL DETAILS

Refractive index was measured using Abbe's refractometer provided by Optics Technologies, Delhi. The refractometer was calibrated by measuring the refractive indices of triply distilled water and benzene at $T = 293$ K. The accuracy in the refractive index measurement was ±0.001 unit. Temperature was controlled by circulating water around the prisms of the refractometer from thermostatically controlled adequately stirred water bath (accuracy ±0.1°C). The sample mixtures were directly injected into the prism assembly of the instrument by means of an air-tight hypodermic syringe. An average of four to five measurements was taken for each sample mixture.

The density of each 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 ±0.5%. A certain mass of the solution is allowed to expand at the desired temperature and the densities were calculated from the fixed mass and the volume at various temperatures.

Mixtures were prepared by weighing the liquids in specially designed ground glass stoppered weighing bottles, taking extreme precautions to minimise preferential evaporation. A Sartorius (BP 121 S) single-pan balance having a stated precision of 0.1 mg was used throughout. The maximum possible error in the mole fraction is estimated to be ±0.0001.

The chemicals used were obtained from Ranbaxy Fine Chemicals Limited. All the chemicals used were purified by standard procedure, discussed by Perrin and Armarego [11]. The purities of all the chemicals were ascertained by the constancy of their boiling points during final distillation, and also by literature comparison [12] of their densities and refractive indices at 293 K (Table I). These values agreed well within the precision of experimental error.

TABLE I Some physical properties of pure components

Component	*Density*		*Refractive index*		*Boiling point*	
	Observed (*at* $T = 293$ K)	*Literature* (*at* $T = 293$ K)	*Observed* (*at* $T = 293$ K)	*Literature* (*at* $T = 293$ K)	*Observed* (°C)	*Literature* (°C)
Tetrahydrofuran	0.8897	0.8892	1.408	1.4050	65	65
1-Propanol	0.8032	0.8035	1.385	1.3850	97	97.2
2-Propanol	0.7872	0.7855	1.378	1.3776	82	82.3

THEORY

The molar refraction deviation ΔR_m and excess molar volume V_m^E were determined using the following equations,

$$\Delta R_m = R_m^{\text{expt}} - R_m^{\text{idl}} \tag{1}$$

where

$$R_m^{\text{expt}} = \left(\frac{n_m^2 - 1}{n_m^2 + 2}\right)\left(\frac{x_1 M_1 + x_2 M_2}{\rho_m}\right) \tag{1a}$$

and

$$R_m^{\text{idl}} = \left[\left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\frac{M_1}{\rho_1}\cdot\phi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\frac{M_2}{\rho_2}\cdot\phi_2\right] \tag{1b}$$

$$V_m^E = \left(\frac{x_1 M_1 + x_2 M_2}{\rho_m}\right) - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \tag{2}$$

In Eqs. (1) and (2), M_i, ρ_i, n_i, ϕ_i and x_i, respectively represent molecular weight, density, refractive index, volume fraction and mole fraction of the ith component ($i = 1$, 2 for binary mixture). ρ_m, n_m and V_m are respectively density, refractive index and molar volume of the mixture.

RESULTS

Refractive indices n_m, deviations in molar refraction ΔR_m, experimental densities ρ_m, and excess molar volume V_m^E are reported for (THF + 1-P) and (THF + 2-P) mixtures in Tables II and III, respectively.

TABLE II Refractive index (n_m), molar refraction deviation (ΔR_m), density (ρ_m) and excess molar volume (V_m^E) for (THF + 1-P) mixture

X_1	$T = 293\,K$				$T = 303\,K$				$T = 313\,K$			
	n_m	ΔR_m	ρ_m	V_m^E	n_m	ΔR_m	ρ_m	V_m^E	n_m	ΔR_m	ρ_m	V_m^E
0.0000	1.385	0.0000	0.8032	0.0000	1.382	0.0000	0.7956	0.0000	1.378	0.0000	0.7862	0.0000
0.0992	1.388	−0.0071	0.8130	−0.0506	1.385	−0.0093	0.8055	−0.1101	1.380	−0.0971	0.7975	−0.3161
0.1999	1.391	−0.0128	0.8228	−0.1108	1.387	−0.0452	0.8149	−0.1745	1.383	−0.1275	0.8079	−0.5374
0.2846	1.393	−0.0170	0.8302	−0.0896	1.389	−0.0541	0.8225	−0.2131	1.384	−0.1853	0.8153	−0.6090
0.3900	1.395	−0.0553	0.8401	−0.1367	1.391	−0.0733	0.8315	−0.2336	1.386	−0.2155	0.8242	−0.6798
0.5146	1.398	−0.0528	0.8509	−0.1366	1.393	−0.1198	0.8426	−0.3206	1.389	−0.2021	0.8339	−0.7100
0.5918	1.400	−0.0624	0.8584	−0.2177	1.395	−0.1039	0.8491	−0.3405	1.391	−0.1911	0.8401	−0.7600
0.7012	1.402	−0.0775	0.8677	−0.2239	1.397	−0.1121	0.8581	−0.3718	1.393	−0.1818	0.8479	−0.7400
0.8028	1.403	−0.0868	0.8748	−0.0954	1.399	−0.0816	0.8652	−0.3007	1.394	−0.1581	0.8531	−0.5463
0.8940	1.405	−0.0616	0.8817	−0.0474	1.400	−0.0708	0.8710	−0.1886	1.395	−0.0843	0.8561	−0.2138
0.9761	1.407	−0.0213	0.8876	0.0151	1.401	−0.0344	0.8754	−0.0195	1.396	−0.0433	0.8600	−0.0446
1.0000	1.408	0.0000	0.8897	0.0000	1.402	0.0000	0.8770	0.0000	1.397	0.0000	0.8612	0.0000

TABLE III Refraction index (n_m), molar refraction deviation (ΔR_m), density (ρ_m) and excess molar volume (V_m^E) for (THF + 2-P) mixture

X_1	$T = 293\,\mathrm{K}$				$T = 303\,\mathrm{K}$				$T = 313\,\mathrm{K}$			
	n_m	ΔR_m	ρ_m	V_m^E	n_m	ΔR_m	ρ_m	V_m^E	n_m	ΔR_m	ρ_m	V_m^E
0.0000	1.378	0.0000	0.7872	0.0000	1.373	0.0000	0.7714	0.0000	1.369	0.0000	0.7620	0.0000
0.0983	1.381	0.0005	0.7970	0.0719	1.376	0.0157	0.7812	0.1090	1.372	0.0321	0.7706	0.1727
0.2085	1.384	0.0035	0.8075	0.2020	1.379	0.0432	0.7912	0.3155	1.375	0.0590	0.7801	0.3652
0.2911	1.387	0.0211	0.8160	0.2150	1.382	0.0770	0.7996	0.3724	1.378	0.1012	0.7877	0.4443
0.3728	1.389	0.0123	0.8239	0.2754	1.384	0.0815	0.8073	0.4700	1.380	0.1143	0.7948	0.5660
0.5014	1.393	0.0220	0.8370	0.2951	1.388	0.1026	0.8206	0.5070	1.384	0.1512	0.8068	0.6418
0.5976	1.396	0.0334	0.8466	0.3075	1.391	0.1088	0.8309	0.4800	1.387	0.1859	0.8156	0.7057
0.7483	1.401	0.0382	0.8629	0.1990	1.395	0.0792	0.8475	0.3800	1.390	0.1208	0.8312	0.6050
0.8001	1.402	0.0049	0.8686	0.1398	1.396	0.0463	0.8535	0.3166	1.392	0.1251	0.8372	0.5000
0.8939	1.405	0.0031	0.8788	0.0528	1.399	0.0221	0.8649	0.1322	1.394	0.0658	0.8479	0.3250
1.0000	1.408	0.0000	0.8897	0.0000	1.402	0.0000	0.8770	0.0000	1.397	0.0000	0.8612	0.0000

Values of ΔR_m and V_m^E for these binary mixtures at $T = 293$, 303 and 313 K respectively are plotted against the mole fraction of THF (x_1) and shown in Figs. 1 and 2 respectively.

DISCUSSION

Molar Refraction Deviation (ΔR_m)

ΔR_m as calculated from Eq. (1) represents the electronic perturbation due to orbital mixing of two components [1,13]. ΔR_m gives the strength of interaction in mixture and is sensitive function of wavelength, temperature and mixture composition.

Figure 1 shows that ΔR_m values are negative for (THF + 1-P) mixture and positive for (THF + 2-P) mixture for all the temperatures studied. ΔR_m values are found to increase with increasing temperature in the negative and positive directions in the two cases of (THF + 1-P) and (THF + 2-P) mixtures respectively.

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 (1-P and 2-P) 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. The observed negative value of ΔR_m is in the case of (THF + 1-P) mixture (Fig. 1) indicates the presence of strong inter-molecular interaction through hydrogen-bonding between unlike molecules. However, in the case of (THF + 2-P) mixture, the positive values of ΔR_m suggest that the effect due to rupture of hydrogen-bonded chain of 2-P dominates over that of hydrogen-bond formed between the unlike molecules.

Positive and negative values of ΔR_m in (THF + 2-P) and (THF + 1-P) mixtures respectively indicate that weaker interaction is taking place between 2-P and THF molecules than that between 1-P and THF molecules. This may be due to the fact that 2-P is less acidic than 1-P due to higher electron releasing tendency of isopropyl group [$(CH_3)_2$ CH−] than *n*-propyl group [(C_3H_7)−] and steric hindrance offered by the branched alkyl group attached to the OH group in 2-P restricts formation of hydrogen bond with THF molecules.

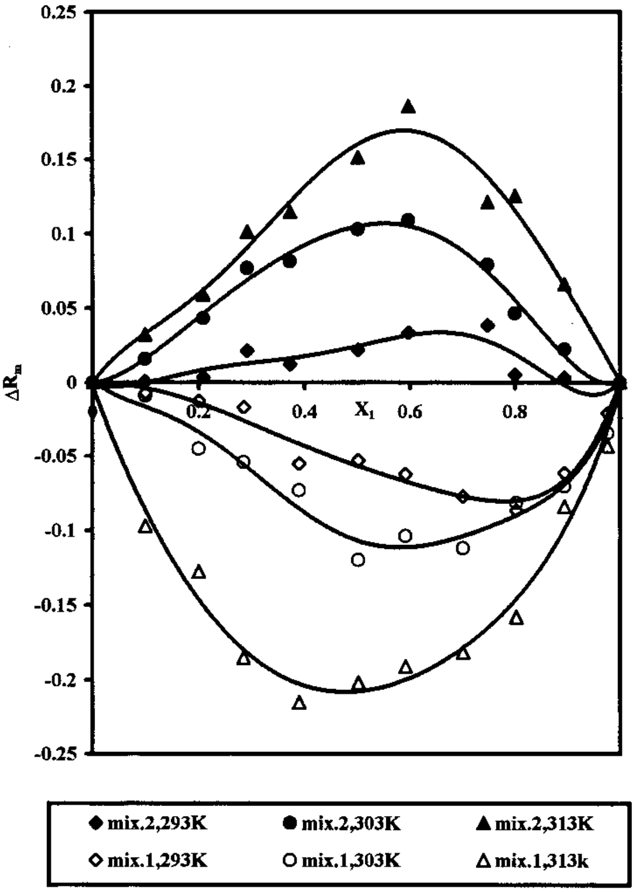

FIGURE 1 Molar refraction deviation (ΔR_m) against mole fraction of THF (x_1) for (THF + 1-P) mixture (mix. 1) and (THF + 2-P) mixture (mix. 2).

Negative and positive values of ΔR_m have been found to increase with increase in temperature for both the mixtures (Fig. 1). Increase in negative ΔR_m value for (THF + 1-P) mixture suggests that thermal energy activates the molecules towards complex formation between unlike molecules. Also since self-association in 2-P is less stronger, increase in temperature will cause rupture of more and more hydrogen bonded self-association in 2-P 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 MOLAR VOLUME

The important effects which are expected to contribute to the value of excess functions in the present work are arbitrarily divided into physical, chemical and structural contributions:

1. Physical contributions comprise non-specific physical interactions.

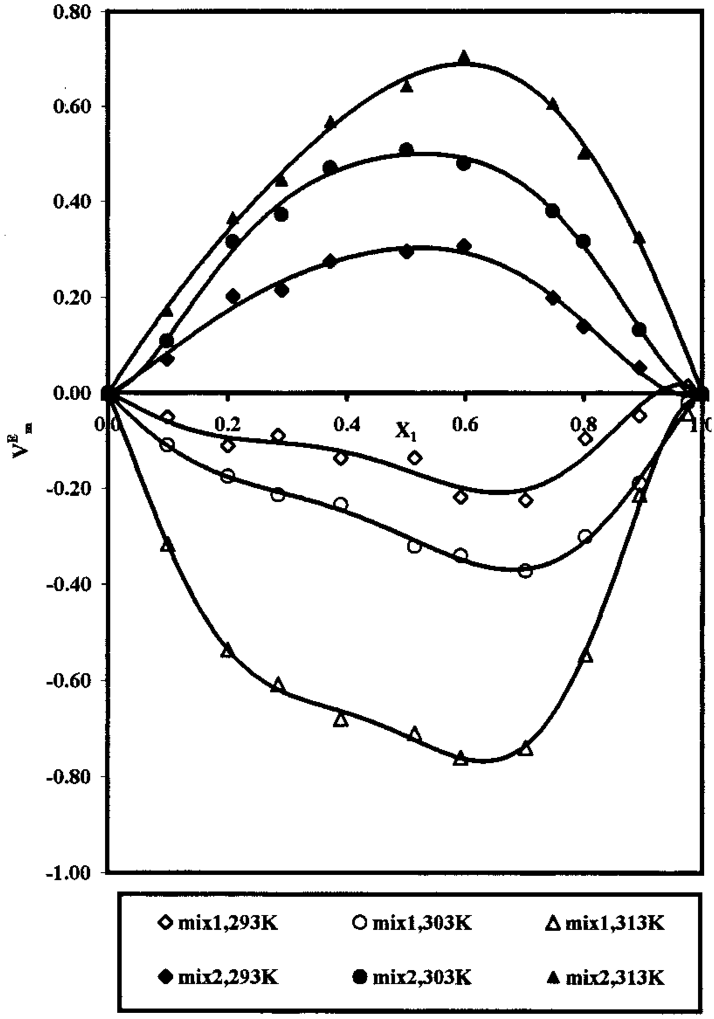

FIGURE 2 Excess molar volume V_m^E against mole fraction of THF (x_1) for (THF + 1-P) mixture (mix. 1) and (THF + 2-P) mixture (mix. 2).

2. Chemical effect occurs due to the breaking up of the liquid order of associated species.
3. Structural effect takes place due to geometrical fitting of THF and 1-P (or 2-P) into the voids created by each other and also due to differences in molar and free volumes of these components.

Each factor makes positive or negative contribution to the resultant value of excess function and the magnitude of the contribution is dependent on mole fraction range [14,15].

Fort and Moore [16] suggested that the liquids of almost equal molecular size usually mix with positive excess molar volume. Molar volumes at 293 K are 74.79, 76.51 and 81.09 cm^3/mol for 1-P, 2-P and THF, respectively. Larger molar volume difference between THF and 1-P than that between THF and 2-P would allow a more favourable packing of 1-P molecule than 2-P 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 [17–19] 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.* [6] in binary mixture of THF with 1-butanol and *tert*-butanol.

Negative and positive values of V_m^E increase with increase in temperature (Fig. 2). This indicates that thermal energy activates unlike molecules towards complex formation through hydrogen-bonding in the case of (THF + 1-P) mixture and breaking of hydrogen-bonding between like molecules in the (THF + 2-P) mixture.

CONCLUSION

(1) Negative values of ΔR_m and V_m^E in (THF + 1-P) mixture can be explained on the basis of hydrogen-bonding between unlike molecules.
(2) Positive values of ΔR_m and V_m^E in (THF + 2-P) mixture are due to predominance of dispersive forces between unlike molecules and steric hindrance offered by 2-P molecules.
(3) Results of ΔR_m and V_m^E support each other.

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