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Optical and Volumetric Study of Molecular Interactions in Binary Mixtures of 1-Propanol (1-PrOH) and Fluorobenzene (FB)

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Abstract: The refractive index (n) and density (ρ) of pure 1-Propanol (1-PrOH), fluorobenzene (FB) and their binary mixtures have been measured over the whole composition range at temperature 303.15 K. Using the experimental data, deviations in refractive index (Δn), molar refraction (ΔR_m), reduced free volume $\Delta(V_m/R_m)$ and internal pressure (ΔP_{int}) have been estimated and fitted in polynomials. Parameters of polynomial equations, which represent the composition dependence of physical and derived properties, are gathered. The results are discussed in terms of molecular interactions between the constituent molecules. Furthermore, a comparative study of refractive index mixing rules–Lorentz-Lorenz (L-L), Weiner (W), Heller (H), Gladstone-Dale (G-D), Arago-Biot (A-B), Eykman (Eyk), Newton (Nw), Eyring-John (E-J) and Oster (Os) relations–for determining the refractive index of a liquid has been carried out to test their validity for the binary system over the entire mole fraction range. Moreover, molar volume (V_m), molar refraction (R_m), atomic polarization (P_A), polarizability (α), molecular radii (r), and average molecular radii (r_{ave}) of the liquids and their mixtures have been calculated.

Keywords: Alcohol, Atomic polarization, Binary mixtures, Density, Internal pressure, Molecular interaction, Refractive index.

1. Introduction

In the past few years physicochemical properties of pure and binary mixtures are of considerable interest in the fundamental understanding of the nature of interactions between the unlike molecules. In recent years, the theoretical and experimental investigations of excess and deviation functions are taken as interaction parameters to improve the results[1-3]. These data has great significance in applied areas of research. They are needful for design processes in chemical, pharmaceutical, petrochemical and to develop models. Among them alcohols are undoubtedly the center of interest. Because of its outstanding role in chemistry and biology, hydrogen bonding in liquid systems has been intensively studied for long and it is still subject to a lively scientific debate. 1-PrOH is associative polar molecule used principally as a solvent in printing inks, paint, cosmetics, pesticides and insecticides[4]. Fluorobenzene is a polar molecule used as an intermediate for pharmaceuticals, pesticides and other organic compounds. In view of their industrial importance, the present study reports the experimental values of refractive index (n) and density (ρ) of pure 1-Propanol (1-PrOH), Fluorobenzene (FB) and their binary mixtures over the entire concentration range at 303.15 K. The above experimental data are used to evaluate molar volumes (V_m), molar refraction (R_m), atomic polarization (P_A), polarizability (α) and molecular radii (r) and average molecular radii (r_m), internal pressure (P_{int}), excess molar volume $(V_m)^E$, deviation in refractive index (Δn), molar refraction deviation (ΔR_m), deviation in reduced free volume $\Delta(V_m/R_m)$ and deviation in internal pressure ΔP_{int} at each temperature. All of these excess and deviation quantities have been fitted to Redlich-Kister polynomial equation[5].

To the best of our knowledge, no such study on 1-Propanol with fluorobenzene mixture over a very wide concentration (0-1) range are available in literature. This prompted us to carry out the experimental measurement of values of the refractive index and density of 1-Propanol with fluorobenzene system over the entire concentration range.

2. Experimental

1-Propanol (1-PrOH) of AR grade is supplied by Ranbaxy Laboratories Ltd, SAS Nagar(India). GR grade fluorobenzene (FB) is supplied by Spectrochem (India). Both the chemicals are used without further purification. Binary mixtures are prepared at different volume percentage and converted in to mole fraction[6].

The refractive index of the binary mixtures are measured at a wavelength of 589 nm using an Abbe Refractometer. The refractometer is initially calibrated by HPLC grade Chemicals (acetone and methanol) and then used to perform refractive index measurement at temperatures 303.15 K. The temperature of the refractometer is controlled by circulation of water and measured with a thermometer located near the sample holder assembly. Refractive index data are accurate to 0.0001 units. Density of pure liquids and their binary mixtures are measured by using pycnometer having bulb volume of 10 cm^3 and capillary with the internal diameter 1 mm. The experimental values of refractive index and density of individual compound namely 1-PrOH and FB along with their literature values are presented in Table 1.

3. Results and Discussion

The molar volume of binary mixtures are determine by

$$V_m = \frac{(x_A M_A + x_B M_B)}{\rho}, \tag{3.1}$$

where M_A and M_B are the molecular weights of the molecular species (FB and 1-PrOH) and ρ is the density of the solution.
The molar refraction (R_m) is also calculated using the equation,

$$R_m = \left(\frac{n^2 - 1}{n^2 - 1} \right) V_m . \tag{3.2}$$

The atomic polarization (P_A) is determined using the relation

$$P_A = 1.05 n^2 . \tag{3.3}$$

Polarizability is related to the refractive index of molecule by the Lorentz-Lorentz formula as

$$\left(\frac{n^2 - 1}{n^2 - 1} \right) = \left(\frac{4}{3} \right) \pi n' \alpha, \tag{3.4}$$

where n' = (N/V_m), N is Avogadro's constant and V_m is the molar volume. Besides these parameters the molecular radii is one of the important parameter of pure liquids and liquid mixtures, which reflects their structural features. Liquids in their mixtures behave differently than they behave individually. Relative strength of hetero-molecular interaction is different in different mixtures. In recent years, several attempts have been made to predict theoretically the values of molecular radii of liquid and liquid mixtures. Ernst and Glinski used several empirical relations based on acoustic methods to calculate the molecular radii of pure liquids[7]. In the present paper, we have calculated molecular radii (r) and average molecular radii (r_{ave}) of pure liquids and their binary mixtures using refractive index data[8].

$$r = \left[\left\{ \left(\frac{3}{4\pi N} \right) \left(\frac{n^2 - 1}{n^2 + 2} \right) \right\} V_m \right]^{\frac{1}{3}}, \tag{3.5}$$

$$r_{ave} = \left(r_1 x_1 + r_2 x_2 \right). \tag{3.6}$$

The internal pressure P_{int} can be obtained by using the Buchler-Hirschfelder Curties equation of state[9], by applying the following relation

$$P_{int} = \frac{2^{1/6} R T}{2^{1/6} V_m - 2 r N^{1/3} V_m^{2/3}}. \tag{3.7}$$

Molar volume (V_m), molar refraction (R_m), atomic polarization (P_A), polarizability (α) , molecular radii (r), average molecular radii (r_{ave}) and internal pressure (P_{int}) have been determined from the experimentally measured values of refractive index (n) and density (ρ) of pure components and their binary mixtures are presented in Table 2. From the Table 1 it is clear that the experimental values of refractive index (n) and density (ρ) of individual component namely 1-PrOH and FB found in the present investigation are in good agreement with the literature values.

Table 1. Comparison of experimental and literature values of pure compounds

Compound	mol. wt.	n_{expt}	n_{lit}	ρ_{expt}	ρ_{lit}
1-PrOH	60.11	1.3788	1.3841[a]	0.7937	0.7955[a]
FB	96.12	1.4584	1.4629[b]	1.0075	1.0188[b]

*(a) –Ref 14 (303.15 K), (b)- Ref 15 (298.15 K)

Table 2. Values of refractive index (n), density (ρ) gm/cm^3, molar volume (V_m) cm^3/mol, molar refraction (R_m) cm^3/mol, atomic polarization (P_A), polarizability (α), molecular radii (r) Å, average molecular radii (r_{avg}) Å and internal pressure (P_{int}) MPa for the binary liquid mixtures of FB with 1-PrOH at 303.15 K.

x	**n**	ρ	V_m	R_m	P_A	α	r	r_{ave}	P_{int}
0.0000	1.3788	0.7937	75.72	17.49	2.00	0.69	1.91	1.91	103.48
0.0811	1.3856	0.8098	77.82	18.26	2.02	0.72	1.93	1.93	101.83
0.1656	1.3930	0.8245	80.12	19.12	2.04	0.76	1.96	1.95	100.10
0.2538	1.4030	0.8359	82.84	20.21	2.07	0.80	2.00	1.98	98.42
0.3461	1.4110	0.8595	84.42	20.96	2.09	0.83	2.03	2.00	97.84
0.4425	1.4188	0.8841	85.99	21.71	2.11	0.86	2.05	2.03	97.27
0.5435	1.4267	0.8978	88.73	22.77	2.13	0.90	2.08	2.05	95.49
0.6494	1.4349	0.9330	89.47	23.34	2.16	0.93	2.10	2.08	95.95
0.7605	1.4424	0.9573	91.38	24.20	2.18	0.96	2.13	2.11	95.08
0.8772	1.4509	0.9809	93.46	25.16	2.21	1.00	2.15	2.14	94.23
1.0000	1.4584	1.0075	95.39	26.05	2.23	1.03	2.18	2.18	93.45

A close perusal of Table 2 indicate that refractive index (n) and density (ρ) of each binary mixtures increases as the concentration of FB increases, because refractive index (n) and density (ρ) of FB is higher than that of 1-PrOH. Molar refraction is a measure of volume occupied with an atom or molecule and depends on the refractive index. It is noticed that the molar refraction (R_m) of the studied binary mixtures increases as the molar volume and refractive index. These reflect in increase in atomic polarization (P_A), polarizability (α), molecular radii (r), average molecular radii (r_{ave}) and internal pressure (P_{int}) of binary mixtures as the concentration of FB increases in the mixtures. The internal pressure (P_{int}), is defined as the energy required to vaporize a unit volume of a substance. Many researchers have suggested that molecules with similar internal pressures would interact with each other[9-11]. Comparison of the values for the pure components reveals that the internal pressure (P_{int}) of 1-PrOH (103.48 MPa) is very close to the internal pressure (P_{int}) of FB (93.45 MPa) suggests hetero interaction is possible in the molecular species.

The deviation in refractive index, molar refraction, reduced free volume, internal pressure, excess molar volume and excess molecular radii of the binary mixtures are evaluated.

$$\Delta n = n - (n_A x_A + n_B x_B), \tag{3.8}$$

$$\Delta R_m = R_m - (R_{mA} x_A + R_{mB} x_B), \tag{3.9}$$

$$\Delta(V_m/R_m)=(V_m/R_m)-((V_{mA}/R_{mA})x_A+(V_{mB}/R_{mB})x_B), \quad (3.10)$$

$$\Delta P_{int} = P_{intm} - (P_{intA}x_A + P_{intB}x_B), \quad (3.11)$$

$$(V_m)^E=\frac{(x_AM_A+x_BM_B)}{\rho}-\left(\frac{x_AM_A}{\rho_A}+\frac{x_BM_B}{\rho_B}\right), \quad (3.12)$$

$$(r)^E = r - (r_A x_A + r_B x_B), \quad (3.13)$$

where x, ρ, n, V_m, R_m, (V_m/R_m), r and P_{int} are the mole fraction, density, refractive index, molar volume molar refraction, reduced free volume, molecular radii and internal pressure respectively. The subscripts m, A and B denote mixture, molecular species FB and 1-PrOH respectively.

The evaluated values of Δn, ΔR_m, $\Delta(V_m/R_m)$, ΔP_{int}, $(V_m)^E$ and $(r)^E$ were fitted to Redlich–Kister polynomial[5].

$$A^E = (x_A x_B)\sum_i a_i (x_A - x_B)^i . \quad (3.14)$$

The values of coefficients, a_i evaluated by the method of least-squares, with all points weighted equally, together with the corresponding standard deviation, σ calculated by using the relation.

$$\sigma = \left[\frac{\sum (A^E_{exp} - A^E_{cal})^2}{m\text{-}k}\right]^{\frac{1}{2}}, \quad (3.15)$$

where, m is the number of experimental data points and k is the number of a_i coefficients considered. The values of coefficients, a_i and corresponding standard deviation (σ) against deviation functions are presented in Table 3.

The variation of deviation and excess functions against mole fraction of first component (FB) are shown in Figure 1. The curves shown in the Fig. 1 are the calculated values, and the points represent the experimental values of deviation/excess functions. It is clear from Figures1(a-f) that Δn, $(V_m)^E$ ΔR_m, and $(r)^E$ values are positive, while $\Delta(V_m/R_m)$ and ΔP_{int} values show reverse trend over the whole composition range. According to Brocos et al., deviation in refractive index (Δn) on a volume fraction basis can be interpreted as a measure of intermolecular interactions[12]. ΔR_m represents the electronic perturbation due to orbital mixing of two components and gives

information regarding the strength of interaction in mixture and is sensitive function of wavelength, temperature and mixture composition[2] .$(V_m)^E$ is mainly influenced by three effects (1) physical interactions mainly due to dispersive forces (2) the dipole–dipole and donor–acceptor interaction between unlike molecules and (3) the filling of smaller molecules into the voids created by bigger molecules.

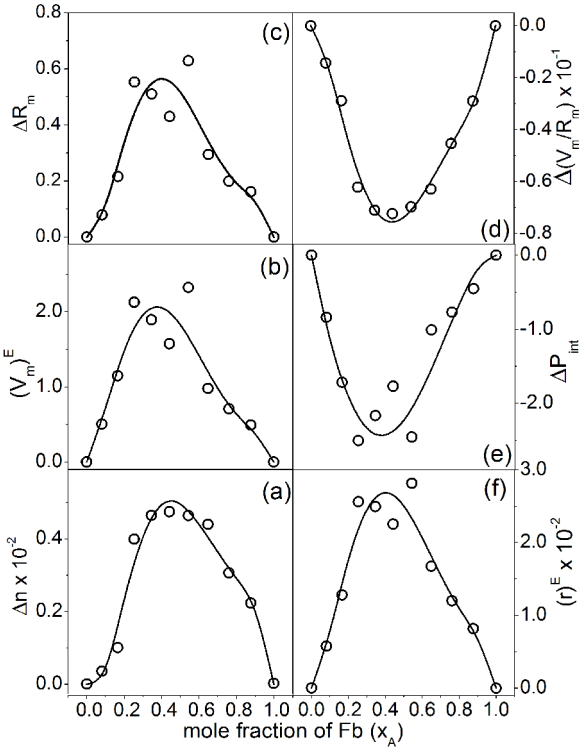

Fig. 1. Variation of Δn, $(V_m)^E$, ΔR_m, $\Delta(V_m/R_m)$, ΔP_{int} and $(r)^E$ against mole fraction of FB. (o) and solid line shows experimental points Redlich- Kister fitting respectively.

The two effect leads to expansion in volume, hence positive contribution of $(V_m)^E$ values, while the third effect lead to contraction in volume, resulting in a negative contribution to $(V_m)^E$ values. Figure 1(b) shows positive deviation of $(V_m)^E$ with variation in mole fraction of FB. It is known that 1-PrOH is protic and associated through hydrogen-bond in pure state. The mixing of an aprotic liquid FB with 1-PrOH tends to break the associates present in the 1-PrOH molecules and there is possibility of hydrogen-bonding between fluorine atom of FB with its lone pair of electron and the hydrogen atom of hydroxyl group of 1-PrOH. The positive deviation of Δn, $(V_m)^E$ ΔR_m, and $(r)^E$ indicate the breaking of hydrogen-bonded chain of 1-PrOH dominates over that of hydrogen-bond formed

between the unlike molecules. This results in weak intermolecular interaction between the molecular constituents. The negative deviation in ΔP_{int} (Fig.1(e)) indicates that the repulsive forces are greater than those of the attractive forces. Similar results have also been reported by Aminabhavi et for the binary system of styrene with n-alkanes[13].

Table. 3 Values of coefficients of Redlich-Kister polynomial (a_i) with standard deviation (σ) and fitness coefficient (δ)

a_o	a_1	a_2	a_3	σ	δ
Δn	0.01981	-0.00667	-0.00959 0.98444	0.02706	0.00041
$(V_m)^E$	7.42510	-6.72976	-2.30102 0.93720	6.59397	0.34138
ΔR_m	2.06208	-1.78555	-1.10488 0.93736	2.83924	0.09247
$\Delta(V_m/R_m)$	-0.29548	0.10683	0.08863 0.99404	-0.25768	0.00368
ΔP_{int}	-8.08671	7.87296	0.02316 0.94415	-3.24252	0.36926
$(r)^E$	0.10014	-0.06844	-0.03039 0.97045	0.09377	0.00293

Table 3 shows the Redlich-Kister parameters along with standard deviations and fitness coefficients **(δ)** for the Δn, $(V_m)^E$ ΔR_m, ΔP_{int}, $\Delta(V_m/R_m)$ and $(r)^E$. The fitness coefficient for above functions is very close to one: this is indicative of a quite good agreement of data with Δn, $(V_m)^E$ ΔR_m, ΔP_{int}, $\Delta(V_m/R_m)$ and $(r)^E$.

Since the mixtures are composed of constituents belonging to different classes of compounds, various molecular interactions are present. In that sense, the applicability of the most important mixing rules suitable for predicting refractive index in various physical situations to the binary mixtures under consideration has been tested. The experimental values of refractive index were compared with the estimated ones by means of the various mixing rules. The applicability of various mixing rules for predicting the refractive index of binary mixtures has been studied. The following mixing rules have been analyzed.

Lorentz- lorentz (L-L)

$$\left(\frac{n^2-1}{n^2+2}\right)=\left(\frac{n_A^2-1}{n_A^2+2}\right)\Phi_A+\left(\frac{n_B^2-1}{n_B^2+2}\right)\Phi_B. \qquad (3.16)$$

Heller (H)

$$\frac{(n - n_A)}{n_A} = \frac{3}{2}\left(\frac{(n_B/n_A)^2 - 1}{(n_B/n_A)^2 + 2}\right)\Phi_B. \quad (3.17)$$

Arago- Biot (A-B)

$$n = n_A\Phi_A + n_B\Phi_B. \quad (3.18)$$

Eyring – John (E-J)

$$n = n_A\Phi_A^2 + n_B\Phi_B^2 + 2(n_A n_B)^{\frac{1}{2}}\Phi_A\Phi_B. \quad (3.19)$$

Gladstone – Dale (G-D)

$$n - 1 = (n_A - 1)\Phi_A + (n_B - 1)\Phi_B. \quad (3.20)$$

Newton (Nw)

$$n^2 - 1 = (n_A^2 - 1)\Phi_A + (n_B^2 - 1)\Phi_B. \quad (3.21)$$

Weiner (W)

$$\left(\frac{n^2 - n_A^2}{n^2 + 2n_A^2}\right) = \left(\frac{n_B^2 - n_A^2}{n_B^2 - 2n_A^2}\right)\Phi_B. \quad (3.22)$$

Eykman (Eyk)

$$\left(\frac{n^2 - 1}{n + 0.4}\right) = \left(\frac{n_A^2 - 1}{n_A + 0.4}\right)\Phi_A + \left(\frac{n_B^2 - 1}{n_B + 0.4}\right)\Phi_B. \quad (3.23)$$

Oster (Os)

$$\frac{(n^2 - 1)(2n^2 + 2)}{n^2} = \frac{(n_A^2 - 1)(2n_A^2 + 2)}{n_A^2}\Phi_A + \frac{(n_B^2 - 1)(2n_B^2 + 2)}{n_B^2}\Phi_B. \quad (3.24)$$

In Eqs. (3.16) to (3.24) n, n_A, n_B, Φ_A and Φ_B represent refractive index of mixture, FB, 1-PrOH, volume fraction of FB and volume fraction 1-PrOH respectively.

$$R.M.S.D = \left[\frac{1}{m} \sum \left(n_{expt} - n_{cal} \right)^2 \right]^{\frac{1}{2}}. \quad (3.25)$$

Table 4. Values of R.M.S.D. against Various mixing rules.

Mixing rule	R.M.S.D
L-L	0.006788
W	0.006304
H	0.006071
G-D	0.006399
Eyk	0.006566
Nw	0.006023
E-J	0.006443
Os	0.006192
A-B	0.006399

The Root Mean Square Deviation (R.M.S.D) values for the Lorentz–Lorenz (L-L), Gladstone–Dale (G-D), Arago–Biot (A-B), Wiener (W), H (Heller), Newton (Nw), Oster (Os), Erying-Johns (E-J) and Eykman (Eyk) relations are presented in Table 4. As R.M.S.D values indicate, refractive index for mixtures are predicted with high accuracy for all the mixtures under consideration. A close similarity is observed between the A-B and G-D relations. The R.M.S.D values for G-D and A-B relations are found to be identical when volume additivity is assumed. The best predictions are observed for the Nw and H relations while the R.M.S.D values predicted by A-B, G-D, W, Eyk, Os, E-J and L-L relations are relatively higher. Since the liquid mixtures of different nature and significantly different molecular sizes are considered, a particular relation provides good agreement at one place and deviates at others. This study indicates that all the theoretical mixing rules are interrelated in a simple quantitative manner and perform well within the limits of experimental error. The applicability of these semi-empirical relations for predicting refractive indices has also been emphasized by others[11-13]. The deviations between the theoretically calculated and the experimentally observed values for all the systems might be reduced further if volume changes during mixing are taken into consideration in various mixing rules.

4. Conclusion

It is realized that this binary data will have some relevance in industries because the both compounds (1-PrOH and FB) are directly or indirectly

associated with various applications in biochemistry and materials science. In this paper density and refractive index are measured over the entire range of mixture composition of 1-PrOH with FB at 303.15 K. A good agreement has been found between the experimental and the literature values of refractive index and density of 1-PrOH and FB. Out of these measured data molar volume (V_m), molar refraction (R_m), atomic polarization (P_A), polarizability (α) , molecular radii (r), average molecular radii (r_{ave}) and internal pressure (P_{int}) have been determined. Δn, $(V_m)^E$ ΔR_m, $(r)^E$, $\Delta(V_m/R_m)$ and ΔP_{int} values have been computed and the results of deviation/excess functions have been fitted to the Redlich–Kister equation. Δn, $(V_m)^E$ ΔR_m, and $(r)^E$ values are positive, while $\Delta(V_m/R_m)$ and ΔP_{int} values show reverse trend over the whole composition range confirm that weak physical intermolecular interactions or the structure breaking effect of 1-PrOH on the addition of FB dominate over the H-bond interactions of the type F·····H–O between 1-PrOH and FB molecules. The refractive index of binary mixtures are correlated theoretically from pure component data by using the various empirical and semi empirical relations.

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