Refractive index, molar refraction deviation and excess molar volume of binary mixtures of 1,4-dioxane with carboxylic acids

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The refractive indices and densities of three carboxylic acids viz formic acid (FA), acetic acid (AA) and propionic acid (PA) in 1,4-dioxane (D) 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 for all the three binary mixtures have been found to be negative. However, a smaller positive trend in V_m^E has been observed for the 1,4-D + PA mixture in the D rich region. Values of ΔR_m and V_m^E are more negative in the case of 1,4-D + FA, suggesting that intermolecular interaction is strongest between unlike molecules as compared to the other two binary mixtures. Further, various theoretical mixing rules for the prediction of refractive index of liquid mixtures have been applied to predict the refractive index of these binary mixtures. A critical analysis of these rules from the point of view of their applicability at different temperatures has been carried out.

Keywords: refractive index; molar refraction deviation; excess molar volume; 1,4-dioxane; carboxylic acid

1. Introduction

The study of molecular interaction in binary liquid mixtures has been an important area of research for more than a century. Properties such as refractive indices or densities and their variation with temperature and composition of the binary mixture are useful to design engineering processes and in chemical and biological industries [1–3]. Excess properties of liquid systems, such as deviation in molar refraction ΔR_m and excess molar volume V_m^E are needed for the design of separation equipment and to test theories of solutions [4]. In addition, excess properties provide information about the molecular interactions and macroscopic behaviour of fluid mixtures, and can be used to test and improve thermodynamical models for calculating and predicting fluid phase equilibria. The knowledge of excess molar volume helps in understanding the molecular orientation and to study the extent of intermolecular interaction between component molecules of the liquid mixtures. In recent years, there has been considerable upsurge in the theoretical and experimental investigation of the excess thermodynamic properties of binary liquid mixtures [5–7].

Simultaneous presence of a carbonyl group and a proton donating hydroxyl group in carboxylic acids governs their physico-chemical behaviour. Also, the easy reducibility of the long straight-chain carboxylic acids, which are amply available from fats, into corresponding alcohols offers these acids as a raw material for the production of alcohols, from which a host of other compounds can be prepared. The study of the thermodynamic behaviour of binary mixtures containing cyclic ethers and polyethers has been carried out extensively because of its industrial applications and the theoretical interest in studying the structure of such solutions [8,9]. Earlier, ultrasonic studies of the solution of the carboxylic acids with dioxane [10] have yielded valuable information regarding the association between the monomers of carboxylic acid and free oxygen of dioxane (D) through hydrogen bonding.

Prediction of refractive index of multicomponent liquid mixtures is essential for many physico-chemical calculations involving multiphase systems. Many workers [11–13] have studied various empirical and semi-empirical rules for the refractive index of liquid mixtures, and scrutinised their validity at different temperatures.

In order to examine molecular interactions in the mixture of dioxane with carboxylic acid through excess optical and volumetric properties, we report here the refractive indices (n_m) and densities (ρ_m) of binary mixtures of D with formic acid (FA), acetic acid (AA) and propionic acid (PA) 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 molar refraction deviation ΔR_m and excess molar volume V_m^E. These results have been used to discuss the nature of interaction between unlike molecules in terms of hydrogen bonding, dipole–dipole interaction, and weak van der Waals types dispersive forces. Further, eight theoretical mixing rules for refractive index proposed by Gladstone–Dale (G–D), Arago–Biot (A–B), Weiner (W), Heller (H), Lorentz–Lorentz (L–L), Eykmen (Eyk), Oster (Os) and Newton (Nn) for the prediction of refractive index of liquid mixtures have been applied to these binary mixtures. A comparative study has been made between the experimental and theoretically calculated values of refractive indices at 293, 303 and 313 K.

2. Experimental

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 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 a sample mixture.

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 10 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 a specially designed ground glass stoppered weighing bottles, taking extreme precautions to minimise

Table 1. Some physical properties of pure components.

| Component | Density (g cm^{-3}) | | 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)
1,4-dioxane	1.034	1.0337	1.422	1.4224	102.0	101.5
Formic acid	1.221	1.220	1.371	1.3714	99.0	101.0
Acetic acid	1.0492	1.0492	1.372	1.372	118.0	117.9
Propionic acid	0.995	0.993	1.381	1.3809	141.0	141.1

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 [14]. The purities of all the chemicals were ascertained by the constancy of their boiling points during final distillation, and also by literature comparison [15] of their densities and refractive indices at $T = 293$ K (Table 1). These agreed well within the precision of experimental error.

3. Theory

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

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

where

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

and

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

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

Various mixing rules for the prediction of refractive index of liquid mixtures are as follows [12,13,16]:

Gladstone–Dale (G–D) relation:

$$(n_m - 1) = \phi_1(n_1 - 1) + \phi_2(n_2 - 1), \tag{3}$$

Arago–Biot (A–B) relation:

$$n_m = n_1\phi_1 + n_2\phi_2, \tag{4}$$

Heller's (H) relation:

$$\left(\frac{n_m - n_1}{n_1}\right) = \frac{3}{2}\phi_2\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 1}\right], \tag{5}$$

Wiener's (W) relation:

$$\left[\frac{n_m^2 - n_1^2}{n_m^2 + 2n_1^2}\right] = \phi_2\left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right], \tag{6}$$

Lorentz–Lorentz (L–L) relation:

$$\left[\frac{n_m^2 - 1}{n_m^2 + 2}\right]\frac{1}{\rho_m} = \left[\frac{n_1^2 - 1}{n_1^2 + 2}\right]\frac{w_1}{\rho_1} + \left[\frac{n_2^2 - 1}{n_2^2 + 2}\right]\frac{w_2}{\rho_2}, \tag{7}$$

Eykmen's (Eyk) relation:

$$\left[\frac{n_m^2 - 1}{n_m + 0.4}\right]V_m = \left[\frac{n_1^2 - 1}{n_1 + 0.4}\right]\frac{M_1 x_1}{\rho_1} + \left[\frac{n_2^2 - 1}{n_2 + 0.4}\right]\frac{M_2 x_2}{\rho_2}, \tag{8}$$

Oster's (Os) relation:

$$\left[\frac{(n_m^2 - 1)(2n_m^2 + 1)}{n_m^2}\right]V_m = \frac{(n_1^2 - 1)(2n_1^2 + 1)}{n_1^2}\frac{M_1 x_1}{\rho_1} + \frac{(n_2^2 - 1)(2n_2^2 + 1)}{n_2^2}\frac{M_2 x_2}{\rho_2}, \tag{9}$$

Newton's (Nn) relation:

$$(n_m^2 - 1) = (n_1^2 - 1)\phi_1 + (n_2^2 - 1)\phi_2. \tag{10}$$

In Equations (1)–(10), M_i, ρ_i, n_i, ϕ_i, w_i and x_i, represent molecular weight, density, refractive index, volume fraction, weight 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.

4. 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 D + FA, D + AA and D + PA in Tables 2–4, respectively. The values of average percentage deviation (APD) for these binary mixtures are given in Table 5.

Values of ΔR_m and V_m^E for these binary mixtures at $T = 293$ K are plotted against the mole fraction of dioxane (x_1) and shown in Figures 1 and 2, respectively. Also, the variation of ΔR_m and V_m^E with x_1 for D + PA mixture for all the three temperatures are shown graphically in Figures 3 and 4, respectively.

5. Discussion

5.1. *Molar refraction deviation (ΔR_m)*

ΔR_m as calculated from Equation (1) represents the electronic perturbation due to orbital mixing of two components [1,17]. ΔR_m gives the strength of interaction

Table 2. Refractive index n_m, molar refraction deviation ΔR_m, density ρ_m and excess molar volume V_m^E of (1,4-D + FA) at the mole fraction x_1 of 1,4-D and temperature T.

	$T = 293\,K$				$T = 303\,K$				$T = 313\,K$			
x_1	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})
0.0000	1.3710	0.0000	1.221	0.0000	1.3690	0.0000	1.2161	0.0000	1.3680	0.0000	1.2129	0.0000
0.0435	1.3750	−0.7598	1.2180	−0.4705	1.3730	−0.6268	1.2135	−0.4800	1.3700	−0.6676	1.2100	−0.4713
0.1304	1.3810	−1.8437	1.2053	−1.1520	1.3780	−1.6915	1.1930	−0.8723	1.3760	−1.7059	1.1918	−0.9454
0.2391	1.3870	−2.5727	1.1763	−1.3707	1.3850	−2.5311	1.1730	−1.4084	1.3820	−2.5534	1.165	−1.2108
0.3478	1.3960	−2.8663	1.1502	−1.4788	1.3930	−2.8860	1.1469	−1.5064	1.3920	−2.8720	1.1452	−1.5706
0.4348	1.4040	−2.8401	1.1304	−1.4505	1.4020	−2.8042	1.1258	−1.4000	1.4000	−2.8240	1.1247	−1.5010
0.5217	1.4080	−2.8103	1.1135	−1.4289	1.4060	−2.6774	1.1073	−1.2800	1.4050	−2.5722	1.0970	−0.8712
0.6087	1.4100	−2.5667	1.0974	−1.3318	1.4080	−2.4720	1.0915	−1.1800	1.4070	−2.3946	1.085	−0.9627
0.6739	1.4120	−2.3277	1.0868	−1.2671	1.4100	−2.2018	1.0796	−1.0159	1.4080	−2.1797	1.075	−0.9077
0.7391	1.4140	−1.9594	1.0759	−1.1227	1.4120	−1.8812	1.0695	−0.9032	1.4100	−1.9025	1.068	−0.9967
0.7826	1.4160	−1.6419	1.0672	−0.8897	1.4140	−1.5924	1.0621	−0.7475	1.4120	−1.6298	1.0616	−0.9100
0.8370	1.4170	−1.3128	1.0590	−0.7419	1.4150	−1.3024	1.0560	−0.7389	1.4130	−1.3340	1.0550	−0.8733
0.8696	1.4180	−1.0535	1.0528	−0.5365	1.4160	−1.0883	1.0520	−0.6940	1.4140	−1.1030	1.0500	−0.7560
0.9022	1.4190	−0.8279	1.0490	−0.4936	1.4170	−0.8419	1.0470	−0.5604	1.4150	−0.8173	1.0429	−0.4600
0.9348	1.4200	−0.5461	1.0430	−0.2672	1.4180	−0.5808	1.0420	−0.4107	1.4150	−0.6006	1.0380	−0.3152
0.9674	1.4210	−0.2705	1.0380	−0.1007	1.4190	−0.2689	1.0352	−0.0994	1.4170	−0.2702	1.0325	−0.1046
1.0000	1.4220	0.0000	1.0340	0.0000	1.4200	0.0000	1.0313	0.0000	1.4180	0.0000	1.0285	0.0000

Table 3. Refractive index n_m, molar refraction deviation ΔR_m, density ρ_m and excess molar volume V_m^E of (1,4-D + AA) at the mole fraction x_1 of 1,4-D and temperature T.

x_1	$T = 293$ K				$T = 303$ K				$T = 313$ K			
	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})
0.0000	1.3720	0.0000	1.0492	0.0000	1.3700	0.0000	1.0450	0.0000	1.3680	0.0000	1.0422	0.0000
0.0468	1.3770	−0.1344	1.0490	−0.0466	1.3750	−0.1334	1.0448	−0.0413	1.3730	−0.1331	1.0420	−0.0413
0.1138	1.3810	−0.3757	1.0480	−0.0714	1.3790	−0.3752	1.0446	−0.1041	1.3770	−0.3745	1.0417	−0.1018
0.1709	1.3840	−0.5484	1.0470	−0.0810	1.3820	−0.5521	1.0443	−0.1506	1.3800	−0.5525	1.0416	−0.1576
0.2275	1.3870	−0.6861	1.0462	−0.1001	1.3850	−0.6926	1.0442	−0.2068	1.3830	−0.6921	1.0414	−0.2070
0.3417	1.3900	−0.9785	1.0456	−0.1906	1.3870	−1.0231	1.0439	−0.3135	1.3850	−1.0231	1.0411	−0.3138
0.3988	1.3930	−1.0337	1.0453	−0.2409	1.3900	−1.0712	1.0435	−0.3499	1.3880	−1.0734	1.0409	−0.3632
0.4559	1.3970	−0.9880	1.0439	−0.2088	1.3930	−1.0701	1.0414	−0.2725	1.3910	−1.0688	1.0385	−0.2654
0.6592	1.4050	−0.8916	1.0390	−0.0787	1.4040	−0.8750	1.0376	−0.2068	1.4020	−0.8784	1.0351	−0.2232
0.7271	1.4090	−0.7453	1.0378	−0.0552	1.4080	−0.7209	1.0360	−0.1507	1.4050	−0.7637	1.0334	−0.1575
0.7958	1.4120	−0.6112	1.0368	−0.0442	1.4100	−0.6103	1.0340	−0.0559	1.4080	−0.6276	1.0322	−0.1305
0.8638	1.4150	−0.4498	1.0359	−0.0348	1.4130	−0.4469	1.0330	−0.0340	1.4110	−0.4657	1.0312	−0.1122
0.9316	1.4180	−0.2602	1.0349	−0.0182	1.4160	−0.2599	1.0322	−0.0221	1.4140	−0.2695	1.0299	−0.0605
0.9658	1.4200	−0.1350	1.0345	−0.0119	1.4180	−0.1339	1.0317	−0.0135	1.4160	−0.1407	1.0293	−0.0407
1.0000	1.4220	0.0000	1.0340	0.0000	1.4200	0.0000	1.0313	0.0000	1.4180	0.0000	1.0285	0.0000

Table 4. Refractive index n_m, molar refraction deviation ΔR_m, density ρ_m and excess molar volume V_m^E of (1,4-D + PA) at the mole fraction x_1 of 1,4-D and temperature T.

x_1	$T = 293\,K$				$T = 303\,K$				$T = 313\,K$			
	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})	n_m	ΔR_m	ρ_m (g cm^{-3})	V_m^E (cm^3 mol^{-1})
0.0000	1.3810	0.0000	0.9950	0.0000	1.3790	0.0000	0.9903	0.0000	1.3780	0.0000	0.9877	0.0000
0.0446	1.3830	−0.0307	0.9971	−0.0111	1.3810	−0.0458	0.9937	−0.1005	1.3790	−0.0869	0.9913	−0.1145
0.1209	1.3860	−0.0893	1.0005	−0.0153	1.3840	−0.1045	0.9973	−0.1076	1.3820	−0.1501	0.9954	−0.1635
0.1719	1.3890	−0.0839	1.0029	−0.0291	1.3870	−0.1093	1.0005	−0.1775	1.3850	−0.1476	0.9982	−0.2058
0.2475	1.3920	−0.1271	1.0063	−0.0506	1.3900	−0.1531	1.0041	−0.2000	1.3880	−0.1919	1.0020	−0.2470
0.3898	1.3980	−0.1727	1.0129	−0.1136	1.3960	−0.1905	1.0104	−0.2190	1.3940	−0.2363	1.0091	−0.3260
0.4777	1.4010	−0.2092	1.0166	−0.1273	1.3990	−0.2423	1.0150	−0.3002	1.3970	−0.2708	1.0128	−0.3400
0.5819	1.4050	−0.2030	1.0199	−0.0750	1.4030	−0.2370	1.0185	−0.2447	1.4000	−0.2622	1.0139	−0.0912
0.6590	1.4090	−0.1490	1.0227	−0.0662	1.4060	−0.1832	1.0190	−0.0416	1.4030	−0.2343	1.0160	−0.0168
0.7308	1.4120	−0.1215	1.0252	−0.0576	1.4110	−0.0558	1.0210	0.0212	1.4090	−0.0623	1.0181	0.0360
0.7949	1.4150	−0.0696	1.0271	−0.0224	1.4130	−0.0575	1.0235	0.0165	1.4110	−0.0613	1.0206	0.0320
0.8701	1.4170	−0.0715	1.0295	0.0037	1.4150	−0.0644	1.0262	0.0254	1.4130	−0.0590	1.0230	0.0675
0.9327	1.4190	−0.0537	1.0314	0.0200	1.4170	−0.0390	1.0279	0.0754	1.4150	−0.0456	1.0254	0.0597
0.9679	1.4200	−0.0510	1.0327	0.0129	1.4180	−0.0375	1.0293	0.0655	1.4160	−0.0444	1.0268	0.0434
1.0000	1.4220	0.0000	1.0340	0.0000	1.4200	0.0000	1.0313	0.0000	1.4180	0.0000	1.0285	0.0000

Table 5. APD for the binary mixtures at different temperatures using different mixing rules.

| Mixture	T (K)	APD(G-D)	APD(A-B)	APD(H)	APD(W)	APD(L-L)	APD(Eyk)	APD(Os)	APD(Nn)
1,4-Dioxane + Formic acid	293	-0.1013	-0.2198	-0.0448	-0.0490	-0.5214	-0.4957	-0.4578	-0.1023
	303	-0.0607	-0.0607	-0.0542	-0.0584	-0.4974	-0.4741	-0.4396	-0.0683
	313	-0.0798	-0.0798	-0.0735	-0.0776	-0.4986	-0.4754	-0.4436	-0.0871
1,4-Dioxane + Acetic acid	293	-0.1055	-0.1116	-0.0941	-0.1003	-0.1340	-0.1372	-0.1409	-0.1135
	303	-0.1108	-0.1108	-0.0998	-0.1083	-0.1659	-0.1677	-0.1693	-0.1192
	313	-0.1156	-0.1156	-0.1068	-0.1130	-0.1773	-0.1787	-0.1797	-0.1240
1,4-Dioxane + Propionic acid	293	-0.0198	-0.0198	-0.0140	-0.0181	-0.0288	-0.0315	-0.0347	0.0420
	303	-0.0189	-0.0189	-0.0128	-0.0172	-0.0479	-0.0497	-0.0516	-0.0246
	313	-0.0523	-0.0523	-0.0468	-0.0507	-0.0550	-0.0581	-0.0621	-0.0573
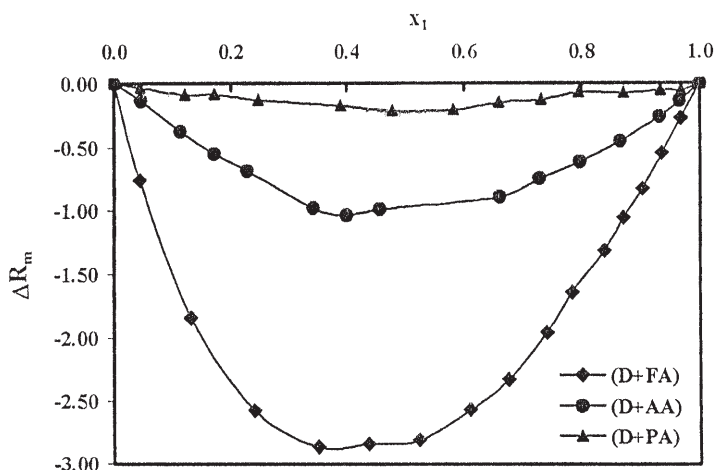
Figure 1. Molar refraction deviation ΔR_m of (D + FA), (D + AA), (D + PA) at $T = 293$ K against the mole fraction of 1,4-D (x_1).
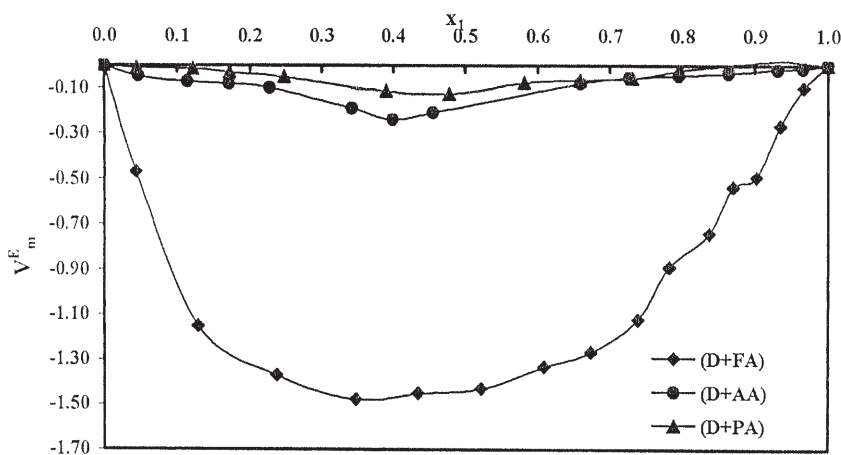

Figure 2. Excess molar volume V_m^E of (D + FA), (D + AA), (D + PA) at $T = 293$ K against the mole fraction of 1,4-D (x_1).

in mixture and is sensitive function of wavelength, temperature and mixture composition. Figure 1 shows that ΔR_m values are negative for all the binary mixtures studied here, indicating the presence of strong intermolecular interaction. The order of negative magnitude of ΔR_m values is (D + FA) > (D + AA) > (D + PA). The highest negative value of ΔR_m for D + FA mixture suggests that interaction between D and FA is strongest as compared to that between D and AA or PA.

It is also seen from Figure 1 that in all the three binary mixtures ΔR_m decreases as a function of mole fraction of D, attains a minimum and then increases. The minimum of ΔR_m *versus* x_1 curve shifts towards higher x_1 values (i.e. towards D-rich region), as the chain length of the carboxylic acid is increased. This may arise due
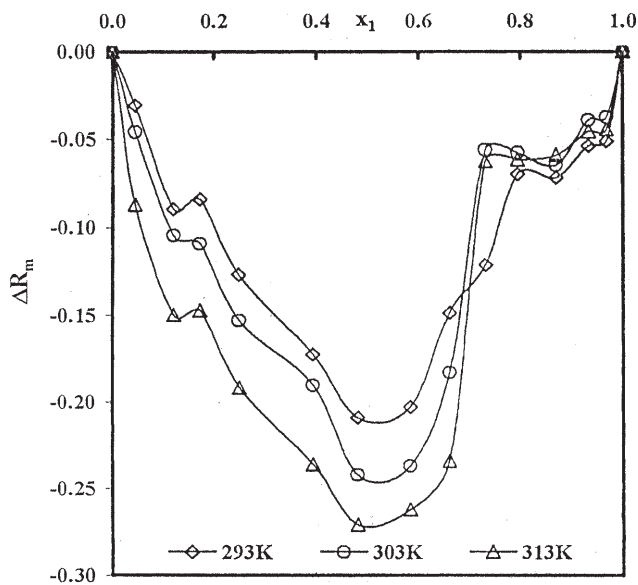
Figure 3. Molar refraction deviation ΔR_m of (D + PA) at $T = 293$, 303, 313 K against the mole fraction of 1,4-D (x_1).
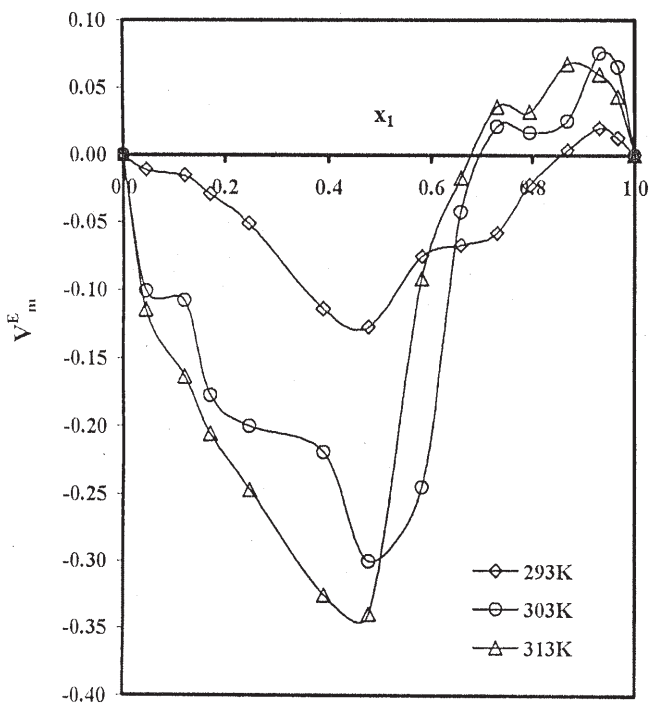

Figure 4. Excess molar volume V_m^E for (D + PA) at $T = 293$, 303, 313 K against the mole fraction of 1,4-D (x_1).

to the fact that FA is more acidic in nature than the other two acids, as is also evident from pK_a values of these acids ($pK_a = 3.75$, 4.75, 4.86 for FA, AA and PA, respectively) [15]. Higher acidity of FA implies that the complexation between acidic H-atom of FA with the O-atom of D through hydrogen bonding will become maximum at a smaller concentration of D than that in D + AA or D + PA mixture.

Tables 2–4 show that ΔR_m values are all negative and its magnitude increases with an increase in temperature. However, the effect of temperature on ΔR_m for D + FA mixture is not considerable as is clear from Table 2, and hence variation is not displayed graphically. It is found that position of minima is not affected by increase in temperature. The variation of ΔR_m with temperature is most significant for D + PA mixture as is seen from Table 4 and Figure 3. Similar results for the binary mixture of ethyl chloroacetate with aromatic liquids have been reported by Nayak *et al.* [18].

5.2. Excess molar volume (V_m^E)

V_m^E is influenced by:

(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.

The first effect leads to expansion in volume, hence positive contribution of V_m^E values, while the other two effects lead to contraction in volume, resulting in a negative contribution to V_m^E values. Higher negative V_m^E values for D + FA mixture (Table 2) are attributed to the presence of strong specific interaction (hydrogen bonding between D and FA) and also due to filling of smaller molecules (molar volume of FA $= 37.6740\,cm^3\,mol^{-1}$) into the voids created by bigger molecules of D (molar volume $= 85.1064\,cm^3\,mol^{-1}$). The negative deviation of V_m^E confirms the presence of strong molecular association in the system [19]. However, V_m^E values for D + PA mixture are slightly negative turning to small positive values in D-rich regions for all the temperatures considered (Figure 4). This suggests that the molecular association through hydrogen bonding between unlike molecules becomes weak in D-rich regions. The negative values of V_m^E follow the sequence D + FA > D + AA > D + PA, and the position of the minimum of V_m^E *versus* x_1 plot tends to shift towards the D-rich region.

For all the systems, excess molar volume curves show the minima at or near those mole fraction of dioxane where values of ΔR_m also attain minima. This further supports the molecular association through hydrogen bonding between unlike molecules, as suggested earlier by several other workers [18,20].

As can be seen from the Table 2, the change in V_m^E values for D + FA mixture with temperature is not considerable. However, for D + AA and D + PA mixtures, the change in V_m^E values is quite significant, when the temperature is raised from $T = 293$ to $303\,K$. However, the change in V_m^E values is again insignificant when T changes from 303 to 313 K. Herráez *et al.* [1] have also reported some inconsistency in temperature dependence of V_m^E.

5.3. *Validity of mixing rules*

A close perusal of the Table 5 reveals, that for all the binary mixtures, these mixing rules show a good agreement. APD is minimum for H relation for all the mixtures for the given temperatures. Also, it is remarkable that although the L–L relation has a sound theoretical foundation [15], APD is maximum for this relation for the D + FA mixture for all three temperatures. APD is maximum for the Os relation for the other two binary mixtures. For any given mixing rule, APD is minimum for D + PA among all the binary mixtures considered.

6. Conclusion

The deviation in molar refraction ΔR_m, and excess molar volume V_m^E results suggest that specific interaction between dioxane (D) and carboxylic acids increases as the carbon chain length decreases.

All the mixing rules for the prediction of refractive index of the mixture are based on ideal molar or volume additivity and do not take care of the definite contraction in the volume, as is indicated by V_m^E values. It may be anticipated that these mixing rules can be modified to give better results, if the concept of V_m^E is incorporated in these relations, as proposed by Aminabhavi [21] and Pandey *et al.* [12].

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