

## Volumetric and Refractive Properties of [Difurylmethane + (2-Propanol or 2-Butanol)] Binary Mixtures at 298.15 K

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Densities ( $\rho$ ) and refractive indices ( $n_D$ ), for [difurylmethane + (2-propanol or 2-butanol)] binary systems have been measured over the entire concentration range at 298.15 K and atmospheric pressure. The  $\rho$ -data were correlated by established literature model in order to check the relationship accounting for the dependence of density on composition. Calculated excess molar volumes ( $V_m^E$ ) and excess molar refraction ( $\Delta R$ ), have been fitted to the Redlich-Kister polynomial to estimate the binary coefficients ( $A_k$ ) and the standard deviations ( $\sigma_{fit}$ ) of the fits. The excess partial molar volumes ( $V_i^E$ ) of the components of each binary system were examined to provide insight into the variation with composition, of the intermolecular interactions present. The results have been discussed in terms of specific intermolecular interactions and structural effects.

**Key Words:** Density, Refractive index, Excess molar volume, Excess molar refraction, Difurylmethane, 2-Propanol, 2-Butanol, Dipole-dipole interactions, Hydrogen bond.

### INTRODUCTION

Studies of volumetric properties of binary mixtures containing difurylmethane (DFM) and (C<sub>1</sub>-C<sub>6</sub>)1-alkanols in temperature range between 288.15 and 308.15 K<sup>1-3</sup> have been reported recently. These investigations revealed deviation from ideal behaviour attributed to chemical, physical, structural and dipole-dipole interaction effects<sup>4</sup>. In the present study and as a further contribution in this area, we report experimental results on density,  $\rho$  and refractive index,  $n_D$ , of [DFM + (2-propanol or 2-butanol)] binary systems over the entire range of composition at 298.15 K and atmospheric pressure. For each of the binary mixtures studied, excess molar volumes ( $V_m^E$ ) and deviation in molar refraction ( $\Delta R$ ) values have been calculated and correlated between the experimentally calculated data and predicted

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quantities. Excess partial molar volumes,  $\bar{V}_i^E$ , of components in each binary system were calculated to probe the variation with composition of the intermolecular interactions and molecular packing efficiencies. We have also used the mixing rules proposed by Lorentz-Lorenz, Gladstone-Dale and Newton equations<sup>5,6</sup>, to estimate refractive indices of binary mixtures from values of refractive indices (nD) values of pure components.

### EXPERIMENTAL

The source and purification procedure of alkanols used in the present study have been reported previously<sup>1,2</sup>. The purity of alcohols was tested by density measurements. The  $\rho$  values were in good agreement with the literature values (Table-1). Benzene (Aldrich Chemicals) was purified as reported elsewhere<sup>7</sup>. Water was first deionized by means of ion exchange resins and then doubly distilled over  $\text{KMnO}_4$  under nitrogen. Its conductivity was always less than  $1.0 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ . DFM was prepared in our laboratory as described elsewhere<sup>8</sup> and its purity confirmed by  $^1\text{H}$  NMR, density measurements and elemental analyses. All purified organic liquids were stored in brown glass bottles.

The [DFM + (2-propanol or 2-butanol)] binary mixtures were prepared by weighing appropriate amounts of the purified DFM and alcohol on a Sartorius Supermicro balance (Fabr.-Nr.,  $\Delta m = \pm 0.000001 \text{ g}$ ) by syringing each component into Teflon stoppered flasks in order to minimize preferential evaporation. Pure components were separately degassed by ultrasound shortly before sample preparations. This procedure eliminated possible changes in mixture composition that could occur during degassing of already prepared binary mixtures. All [DFM + (2-propanol or 2-butanol)] binary mixtures were completely miscible over the entire composition range. The uncertainty in solution composition expressed as mole fraction was found to be less than  $8 \times 10^{-5}$ . A sample volume of not more than 1 mL was needed to fill the densimeter cell and thermal equilibrium was attained quickly at each temperature. The temperature of the sample was controlled electrically by means of a built-in thermostat (a semiconductor Peltier element and a resistance thermometer temperature control system) and was measured with an accuracy of  $\pm 0.01 \text{ K}$ . The densimeter was calibrated after each set of four sample measurements to offset any problem of instrument drift. There was however no noticeable drift in the density of the reference fluid and a linear relation between the density of the fluid and the square of the vibrating period  $\tau$ , ( $\rho = A + B\tau^2$ ), was assumed. Buoyancy corrections to the weight were made by taking into account the air density, the barometric pressure and the relative humidity. Under such conditions quadruplet density measurements of each sample were reproducible to within  $\pm 1 \times 10^{-2} \text{ kg m}^{-3}$ .

Refractive indices of the pure components and liquid mixtures have been measured to an accuracy of  $\pm 10^{-5}$  at 298.15 K using a thermostatic controlled digital refractometer (Atago RX-5000, Tokyo, Japan). The refractive index measurement method relies on an optical detection of the critical angle at the wavelength of the sodium D line (589.6 nm). Temperature was controlled by circulating water into refractometer through thermostatically controlled bath (Labcon CPE), with a digital temperature control unit to maintain the desired temperature within  $\pm 0.05$  K. The refractometer was calibrated using ultra-pure water, in accordance with the instrument manual instructions. Four independent readings were recorded for each liquid and mixture composition and the refractive index was taken as the average of measurements.

## RESULTS AND DISCUSSION

Table-1 presents the measured quantities ( $\rho$  and  $n_D$ ) for pure alkanols and DMF at 298.15 K, together with the literature values. The experimental  $\rho$  and  $n_D$  covering the entire composition range ( $0.00 \leq x_2 \leq 1.00$ ) for {DMF + (2-propanol or 2-butanol)} binary systems at 298.15 K are listed in Table-2.

TABLE-1  
REFERENCE DENSITY VALUES  $\rho$  ( $\text{kg m}^{-3}$ ) FOR  
2-ALKANOLS AND DMF AT 298.15 K

Compd.	$\rho$ ( $\text{kg m}^{-3}$ )		$n_D$	
	Expt.	Reported [Ref.]	Expt.	Reported [Ref.]
2-Propanol	780.81	780.90 [9]	1.37508	1.37520 [7]
2-Butanol	802.69	802.72 [10]	1.39504	1.39503 [11]
DMF	1090.88	1090.88 [1,2]	1.50119	1.50124 [8]

The polynomial equation:

$$\rho / \text{kg m}^{-3} = \sum_{i=0}^{i=n} a_i x_2^i \quad (1)$$

where  $a_i$  are solvent dependent empirical coefficients and  $x_2$  is the mole fraction of DMF, has been isothermally least-squares fitted to the density data of each binary system for the whole composition range at 298.15 K. In each case, the degree of the polynomial was optimized by applying the F-test<sup>12</sup> at the 99.5 % confidence level. Table-3 shows the  $a_i$  coefficients values, along with the relative standard deviations, ( $\sigma_{\text{fit}}$ ), of the fits, for each of the investigated systems.

TABLE-2  
 EXPERIMENTAL DENSITIES  $\rho$  ( $\text{kg m}^{-3}$ ), FOR THE [DFM +  
 (2-PROPANOL OR 2-BUTANOL)] BINARY MIXTURES AT 298.15 K

$x_2$	$\rho$	$n_D$	R	$V_m^E$
DFM + 2-Propanol				
0.000000	780.81	1.37499	17.61921	0.000000
0.022962	793.58	1.38013	18.13786	-0.036690
0.042495	804.01	1.38439	18.58173	-0.062120
0.063265	814.73	1.38871	19.05087	-0.084080
0.083669	824.91	1.39281	19.51139	-0.101260
0.108571	836.89	1.39766	20.07416	-0.117270
0.156665	899.58	1.42845	21.15308	-0.136310
0.256426	876.01	1.41024	23.39655	-0.146420
0.297239	914.76	1.42907	24.31760	-0.144850
0.355818	935.22	1.43736	25.63187	-0.139750
0.410982	953.18	1.44471	26.87136	-0.132260
0.494905	978.33	1.45490	28.74828	-0.114140
0.544968	992.19	1.46060	29.87121	-0.098020
0.617794	1010.99	1.46825	31.49832	-0.066450
0.644788	1017.58	1.47097	32.10322	-0.052540
0.699332	1030.33	1.47624	33.32515	-0.022200
0.754717	1042.58	1.48131	34.56517	0.008579
0.825349	1057.34	1.48744	36.14573	0.039433
0.917997	1075.56	1.49506	38.21757	0.045095
1.000000	1090.88	1.50119	40.02693	0.000000
DFM + 2-Butanol				
0.000000	802.69	1.39504	22.14041	0.000000
0.020759	811.08	1.39825	22.52650	0.014704
0.060961	827.23	1.40401	23.24868	0.044840
0.082562	835.76	1.40708	23.63666	0.049607
0.106085	844.64	1.41032	24.06324	0.080114
0.194808	876.99	1.42206	25.66044	0.135069
0.280329	905.94	1.43261	27.19726	0.181786
0.370412	934.45	1.44311	28.81603	0.209701
0.429668	952.05	1.44958	29.87839	0.234160
0.516392	976.66	1.45861	31.42624	0.236362
0.574980	992.49	1.46446	32.47151	0.226306
0.623259	1004.93	1.46903	33.33120	0.230004
0.731546	1031.53	1.47884	35.25606	0.210904
0.766246	1039.68	1.48191	35.87556	0.199312
0.825952	1053.31	1.48696	36.93451	0.173116
0.862508	1061.53	1.49000	37.58034	0.139865
0.916858	1073.35	1.49447	38.54677	0.095837
1.000000	1090.88	1.50119	40.02693	0.000000

TABLE-3  
 FITTED VALUES AND CORRESPONDING STANDARD DEVIATIONS FOR THE  $a_i$  ( $\text{kg m}^{-3}$ ) COEFFICIENTS OF EQUATION (1) vs.  $x_2$  FOR THE [DFM + 2-ALKANOL] BINARY MIXTURES FROM 298.15 K

Binary mixture	$a_0$	$a_1$	$a_2$	$10^{-2} a_3$	$a_4$	$a_5$	$10^{-2} a_6$	$10^{-2} a_7$	$10^6 \sigma_{\text{fit}}$
DFM + 2-Propanol	780.81	0.56673	-0.51870	57.085	-0.55867	0.30725	-4.1526	-1.5875	4.57
DFM + 2-Butanol	802.49	0.41765	-0.19492	4.7245	0.19659	-0.43090	36.3940	-11.1210	36.70

TABLE-4  
 LEAST SQUARES FITTED  $a_k$  ( $\text{cm}^3 \text{mol}^{-1}$ ) COEFFICIENTS OF THE REDLICH-KISTER EQUATION, CORRESPONDING STANDARD DEVIATIONS OF THE FITS AND  $\sigma(\Delta Y)$  FOR THE [DFM + (2-PROPANOL OR 2-BUTANOL)] BINARY MIXTURES AT 298.15 K

	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	$10^3 \sigma(\Delta Y)$
DFM + 2-Propanol								
$V_m^E$ ( $\text{cm}^3 \text{mol}^{-1}$ )	-0.45089	-0.60270	0.396960	-0.80746	-0.37317	-	-	2.4
$\Delta R$ ( $\text{cm}^3 \text{mol}^{-1}$ )	0.16282	0.08762	0.053819	-0.75122	-0.10230	1.67728	0.44468	1.2
DFM + 2-Butanol								
$V_m^E$ ( $\text{cm}^3 \text{mol}^{-1}$ )	0.94269	-0.10903	0.24417	-0.29754	-0.18321	-	-	4.9
$\Delta R$ ( $\text{cm}^3 \text{mol}^{-1}$ )	0.20072	0.06051	0.00683	0.10263	-0.30657	-0.62936	0.37600	5.7

TABLE-5  
ROOM MEAN SQUARE DEVIATIONS (RMSDS) FOR LORENTZ-LORENZ  
(LL), GLADSTONE-DALE (GD) AND NEWTON (N) EQUATIONS

	LL	G-D	N
DFM + 2-Propanol	0.00194	0.00173	0.00197
DFM + 2-Butanol	0.00028	0.00089	0.00150

Excess molar volumes,  $V_m^E$  were calculated for each composition from experimental density data using eqn. 2:

$$V_m^E = V_m - V_m^{id} = M/\rho - \sum x_i M_i / \rho_i^* \quad (2)$$

where  $M$  is the molar mass of the mixture, which is the mole fraction weighted adduct of the molar masses of the two pure components in each binary mixture,  $V_m^{id}$  is the ideal molar volume,  $V_m$  is the molar volume,  $\rho$  is the density of the binary mixture;  $x_i$ ,  $M_i$  and  $\rho_i^*$  are respectively the mole fraction, the molar mass and the density of the pure liquid component  $i$ .

The deviations in molar refraction data  $\Delta R$ , was calculated from experimental  $n_D$  values using the relationship (eqn. 3):

$$\Delta R = R - x_1 R_1 - x_2 R_2 \quad (3)$$

Values of molar refraction  $R$ , have been calculated from experimental  $n_D$  data using the Lorentz -Lorenz eqn. 4:

$$R = [(n_D^2 - 1)/(n_D^2 + 2)]V_m \quad (4)$$

where  $R$  and  $R_i$  are the corresponding molar refraction of the mixture and the pure component  $i$ , respectively.

The calculated excess molar quantities  $\Delta Y$  ( $V_m^E$  and  $\Delta R$ ), for each binary system were isothermally least-squares fitted to the Redlich-Kister<sup>7</sup> polynomial eqn. 5 in which all points were weighted equally:

$$\Delta Y = x_2(1 - x_2) \sum_{k=0}^n A_k (1 - 2x_2)^k \quad (5)$$

The degree of the polynomial  $n$  and the number of  $A_k$  binary coefficients in eqn. 5 were fixed by testing the statistical significance of including each further term using an F-test at the 99.5 % confidence level<sup>12</sup>. The optimized number ( $n + 1$ ) of regression coefficients  $A_k$ , for each of [DFM + (2-propanol or 2-butanol)] binary systems at 298.15 K are listed in Table-3 along with the corresponding standard deviation  $\sigma(\Delta Y)$  calculated from eqn. 6,

$$\sigma(\Delta Y) = \{\sum[\Delta Y_{\text{expt}} - \Delta Y_{\text{calc}}]^2 / (N - n)\}^{1/2} \quad (6)$$

where  $N$  is the number of data points.

In order to investigate the individual component contribution to the excess molar volumes, excess partial molar volumes of the alcohol ( $\bar{V}_1^E$ )

and DFM ( $\bar{V}_2^E$ ) for each binary system were obtained in accordance with eqns. 7 and 8<sup>13</sup>, respectively,

$$\bar{V}_1^E = V_m^E - x_2(\partial V_m^E / \partial x_2)_{P,T} \quad (7)$$

$$\bar{V}_2^E = V_m^E + (1 - x_2)(\partial V_m^E / \partial x_2)_{P,T} \quad (8)$$

The Redlich-Kister eqn. 5 of an appropriate degree and the corresponding  $A_k$  fitting coefficients (Table-3) for each binary system have been used to obtain values of the derivative  $(\partial V_m^E / \partial x_2)_{P,T}$  for the entire concentration range.

No data have been reported in the literature for the density and refractive index of any of the binary mixtures under investigation. The good agreement, within the experimental uncertainties for the measured and literature data for the pure components (Table-1), confirmed the purity of the chemicals used as well as the accuracy of the equipment and the experimental procedure. The slight differences between the literature and present experimental data on the pure alcohols may be due to differences in purification techniques and error sources arising from different instrumental sensibilities.

The low magnitudes of the relative standard deviations, ( $\sigma_{fit}$ ), of the fitted polynomial to the experimental  $\rho$  values for each binary systems (Table-3) indicate the good quality of fits of the isotherms. For each binary system at 298.15 K, fitted  $a_0$  coefficients of eqn. 1 compare accurately with the experimental density values (Table-1) for the pure components within the standard deviation of those parameters. The regression coefficients in the polynomial eqn. 1 of an appropriate degree, for each binary system, therefore accurately reproduce the experimental  $\rho$  data of both the pure 2-alkanols and the binary mixtures at 298.15 K.

Excess thermodynamic functions such as the  $V_m^E$  values measure the extent of deviation from ideal solution behaviour. These deviations arise from chemical, physical, structural and dipole-dipole interaction effects. The chemical effects involve the break up of the liquid order due to dipole-dipole association and the rupture of the hydrogen-bond structure, both of which contribute positively to  $V_m^E$ . Physical contributions comprise non-specific unfavourable interactions between unlike molecules, which also contribute positively to  $V_m^E$ . Structural effects arise from the restriction of the rotational degrees of freedom due to geometrical interstitial accommodation of liquid components into each other's cavities. These geometrical effects arise from differences in molar masses, shape and free volumes of pure components and they contribute negatively to  $V_m^E$ . Presence of specific dipole-dipole interactions between unlike component molecules also contributes negatively to  $V_m^E$  values.

Fig. 1 displays the experimental  $V_m^E$  vs.  $x_2$  data for [DFM + (2-propanol or 2-butanol)] binary systems at 298.15 K. For each binary system the solid line represents the fitted curves calculated from the smoothing eqn. 5 of an appropriate degree. The  $V_m^E$  curve for [DFM + 2-propanol] binary mixtures present a sigmoidal shaped behaviour, with negative deviation limited respectively to  $0.0 \leq x_2 \leq 0.7$  and positive deviation over the remaining composition range. This behaviour in the  $V_m^E$  data results from several opposing effects<sup>14</sup>. In the  $0.00 \leq x_2 \leq 0.75$  range, negative  $V_m^E$  values can be attributed to predominance of associative dipole-dipole interactions between unlike molecules and geometrical interstitial accommodation of DFM molecules in the 2-propanol hydrogen bonded network. The magnitude of minimum  $V_m^E$  for [DFM + 2-propanol] mixtures ( $-0.15 \text{ cm}^3 \text{ mol}^{-1}$  at  $x_2 = 0.26$ ), was less than one reported for [DFM + 1-propanol] binary system ( $-0.17 \text{ cm}^3 \text{ mol}^{-1}$ , at  $x_2 = 0.31$ )<sup>2</sup> due to stronger intermolecular association resulting from the relatively higher acidity and greater polarity of the  $-\text{OH}$  group in 1-propanol in comparison to 2-butanol. At  $x_2 \geq 0.7$ , positive  $V_m^E$  values indicate an increase in dispersive intermolecular forces, which contribute to disruption of the 2-propanol hydrogen bonded structure leading to the observed volume expansion. Similarly  $V_m^E$  sigmoid behaviour has been reported for [DFM + 1-butanol] mixtures<sup>2,3</sup> whereas the excess molar volumes for the [DFM + 2-butanol] mixtures are positive over the whole composition

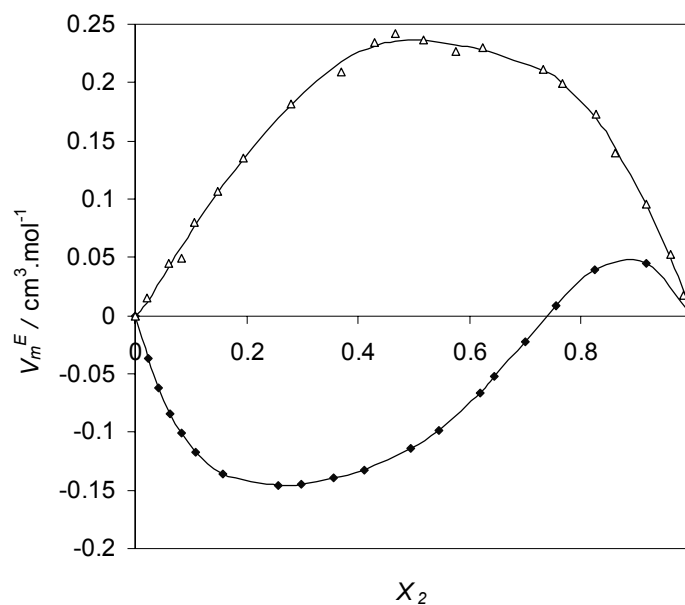


Fig. 1. Excess molar volume  $V_m^E$  vs.  $x_2$  at 298.15 K for mixture of DFM (2) with ( $\blacklozenge$ ) 2-propanol (1) ( $\blacktriangle$ ) 2-butanol (1)



range. The observed positive  $V_m^E$  values are due to the predominance of physical effects such as dispersive intermolecular forces which contribute to the depolymerization of the alcohol hydrogen bond structure and the observed volume expansion. It is also possible that steric hindrance resulting from the branching effects in the secondary alcohols contribute more positively to  $V_m^E$  of [DFM + (2-propanol or 2-butanol)] than [DFM + (1-propanol or 1-butanol)] binary systems.

Differential volumetric properties such as the excess partial molar volumes ( $\bar{V}_i^E$ ) are more sensitive to effects on volume of changes in the aggregation schemes which arise from the mixing process<sup>13</sup>.  $V_i^E$  values of a component in the mixtures describe the rate of change with composition of the excess molar volumes and provide valuable information on individual component response to intermolecular interactions. Fig. 3 presents ( $\bar{V}_i^E$ ) vs.  $x_2$  plots for each of the components in [DFM + (2-propanol or 2-butanol)] binary systems at 298.15 K. The rapid decrease in the  $\bar{V}_2^E$  values for the [DFM + 2-propanol] binary system in the very low  $x_2$  region (Fig. 2a) support the  $V_m^E$  data and suggests a net volume shrinkage when small quantities of DFM are added to 2-propanol. Similar behaviour was observed for the [DFM + 1-propanol] binary mixtures<sup>2,3</sup> and was suggested to arise from the associative dipole-dipole interactions between unlike molecules and the geometrical interstitial accommodation of DFM into the hydrogen bonded alkanol structure. On the other hand the steep rise in the excess partial molar volume of 2-propanol,  $\bar{V}_1^E$ , in the DFM-rich region suggests a volume expansion, as was observed in the  $V_m^E$  trend in the same  $x_2$  range, resulting from the effects of the disruption of the alkanol hydrogen bonded structure. The  $\bar{V}_i^E$  values for both components in the [DFM + 2-butanol] binary mixtures were positive over the entire  $x_2$  range (Fig. 2b). The observed trend in the  $\bar{V}_i^E$  profiles for this binary system, further supports the  $V_m^E$  results and suggests predominance over other effects, the contribution due to dispersive interactions and the breaking of the hydrogen bonded polymeric aggregates in 2-butanol.

The calculated molar refraction values (Table-2) for each of {DFM + (2-propanol or 2-butanol)} binary systems varies linearly with mole fraction (Fig. 3), which is in agreement with the Clausius-Mosotti theory<sup>15</sup> that  $R$  is a measure of the hardcore volume of one mole of molecules. Since the molar refraction is a solution property akin to polarizability  $\alpha_e$ <sup>16</sup> and it is proportional to dispersive interactions<sup>17</sup>, the increase of  $R$  with  $x_2$  suggest strong solute-solvent interactions in each of the two binary systems. The steeper gradient for [DFM + 2-propanol] binary mixtures may be resulting from a greater polarizing effect of the more polar -OH group in 2-propanol on the furan ring on the furan  $\pi$ -electron system of the co-solvent. Fig. 4 represents the experimental  $\Delta R$  vs.  $x_2$  data for [DFM + (2-propanol or

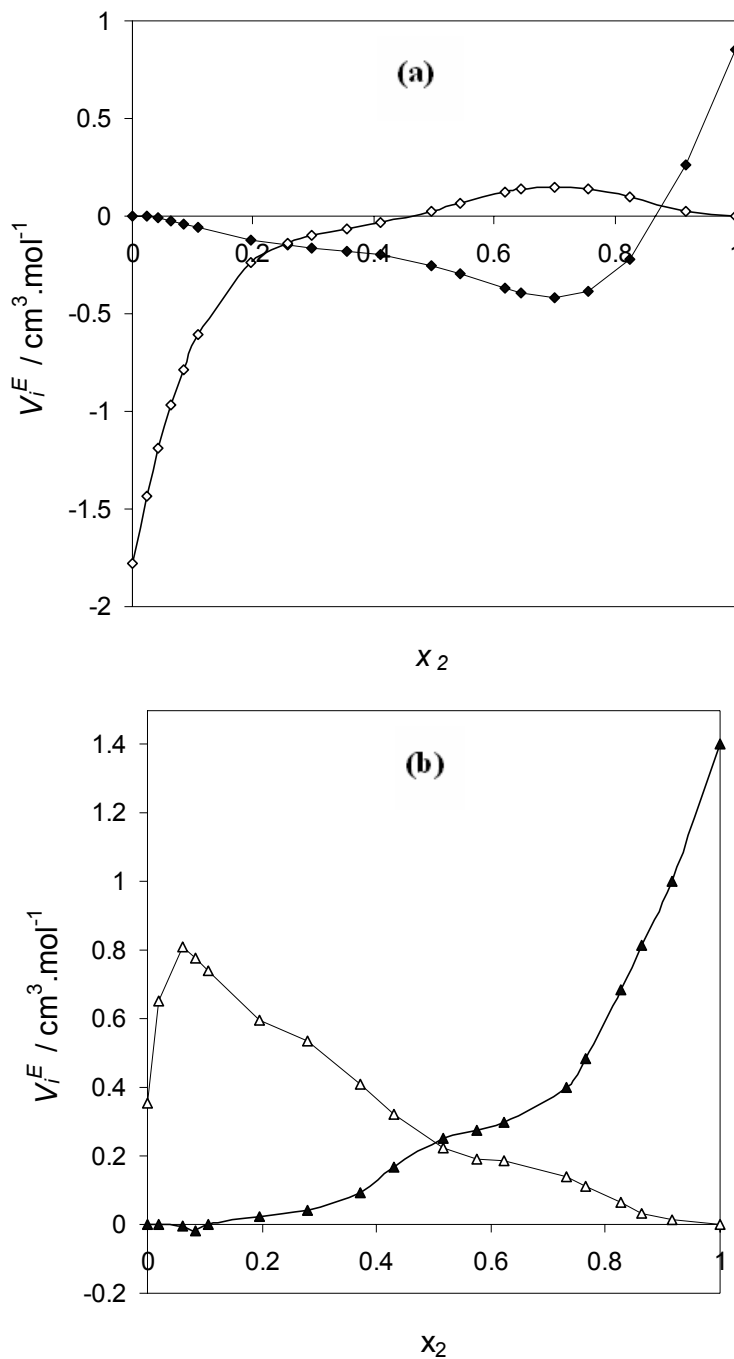


Fig. 2. Excess partial molar volume  $\bar{V}_i^E$  vs.  $x_2$  at 298.15 K for mixture of DFM (2) with 2-propanol or 2-butanol: (a) ( $\blacklozenge$ )  $\bar{V}_1^E$  and ( $\blacktriangle$ )  $\bar{V}_2^E$  in [EFM (2) + 2-propanol (1)]; (b) ( $\blacklozenge$ )  $\bar{V}_1^E$  and ( $\blacktriangle$ )  $\bar{V}_2^E$  in [DFM (2) + 2-butanol (1)]

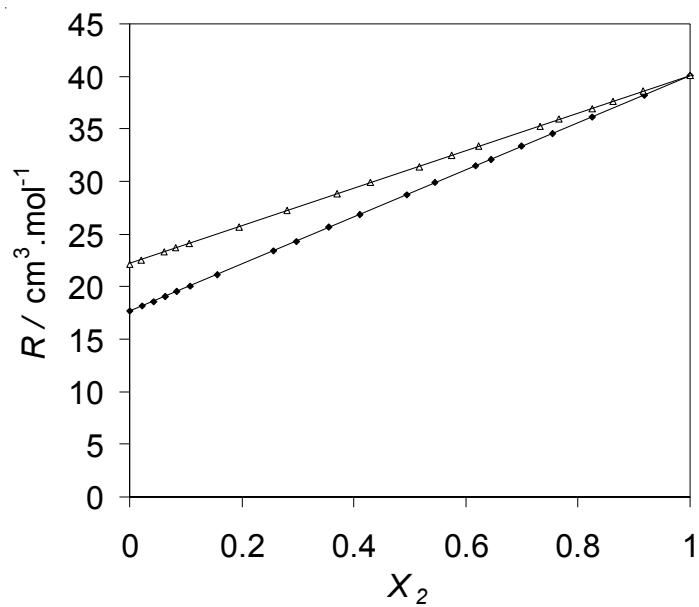


Fig. 3. Molar refraction,  $R$  vs.  $x_2$  at 298.15 K for mixtures of DFM with ( $\blacklozenge$ ) 2-propanol or ( $\triangle$ ) 2-butanol

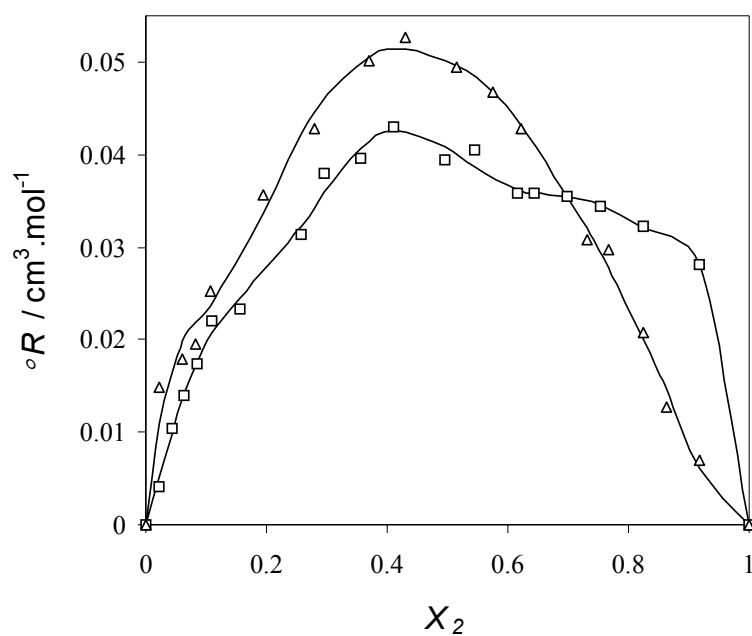


Fig. 4. Deviations in molar refraction,  $\Delta R$  vs.  $x_2$  at 298.15 K for mixtures of DFM with ( $\blacklozenge$ ) 2-propanol or ( $\triangle$ ) 2-butanol

2-butanol)] binary systems at 298.15 K, showing positive deviation over the entire composition range.  $\Delta R$  values measure the change of overall solution  $\alpha_e$  values that results from the disruption of the liquid structure in the pure components and creation of new intermolecular contacts<sup>16</sup>. The positive  $\Delta R$  values suggest that dispersive interactions in the solutions of the two binary systems are greater than the pure components. The  $\Delta R$  profiles also show that the magnitude of these interactions are greater in the [DFM + 2-butanol] than [DFM + 2-propanol] binary mixtures in the concentration range:  $(0.00 < x_2 < 0.7)$ .

The experimental  $n_D$  values of binary mixtures were correlated to three empirical mixing rules. The mixing rules tested in this study were,

$$\text{Lorentz-Lorenz: } (n_D^2 - 1)/(n_D^2 + 2) = \Phi_1(n_{D,1}^2 - 1)/(n_{D,1}^2 + 2) + \Phi_2(n_{D,2}^2 - 1)/(n_{D,2}^2 + 2) \quad (9)$$

$$\text{Gladstone-Dale: } (n_D - 1) = \Phi_1(n_{D,1} - 1) + \Phi_2(n_{D,2} - 1) \quad (10)$$

$$\text{Newton: } (n_{D,2} - 1) = \Phi_1(n_{D,1}^2 - 1) + \Phi_2(n_{D,2}^2 - 1) \quad (11)$$

where  $n_{D,i}$  is refractive index of component  $i$  and volume fraction  $\Phi_i$  as

$$\Phi_i = [x_i M_i / (x_1 M_1 + x_2 M_2)] \sigma / \rho_i^*$$

Table-5 summarizes values of the root mean square deviations, RMSDs, between experimental and calculated  $n_D$  values, the RMSD is defined by:

$$\text{RMSD} = [1/N \sum_i (n_{D,\text{exptl}} - n_{D,\text{calctd}})^2]^{1/2} \quad (12)$$

As RMSD values indicate, the selected mixing rules can be used to predict  $n_D$  values of the binary mixtures with reasonable accuracy. It can also be inferred that Lorentz-Lorenz and Gladstone-Dale equations predicts with greater accuracy the  $n_D$  values for the [DFM + 2-butanol] binary mixtures as can be judged from the low RMSD values.

## Conclusion

Density and refractive index of [DFM + (2-propanol or 2-butanol)] binary systems have been reported for the entire mole fraction range at 298.15 K. From the measured physical data, excess molar volume  $V_m^E$  and excess molar refraction  $\Delta R$  values have been calculated and correlated by the Redlich-Kister polynomial equation to deduce the coefficients and standard deviation of the fit for each binary system. The excess functions were used to account for the intermolecular interactions between components in each binary system investigated. The  $V_m^E$  values for [DFM + 2-propanol] binary system present a sigmoidal shaped behaviour while the data for [DFM + 2-butanol] mixtures displayed positive deviation over the whole  $x_2$  range. The excess molar refraction values for both binary systems were positive for all compositions. Steric hindrance caused by the branching in the alcohol chain probably contribute to the increased dispersive interactions reflected

in the positive  $V_m^E$  and  $\Delta R$  values observed for the two binary systems. The three mixing rules provided reasonable prediction of the refractive indices of the binary systems but Lorentz-Lorenz and Gladstone-Dale equations gave more accuracy the  $n_D$  values for the [DFM + 2-butanol].

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