

Internal pressure and optical properties of binary mixture of formamide with dimethylaminoethanol and diethylaminoethanol at different temperatures

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The density (ρ) and refractive indices (n_D) of binary mixtures of formamide (FA) with dimethylethanolamine (DMEA) and diethylethanolamine (DEEA) have been recorded at different temperatures for the whole composition ranges. The experimental values of density data and refractive index are used to estimate the molar refraction (R_m), reduced molar free volume (V_m/R_m), molecular radii (r) and internal pressure (P_{int}). The deviations of refractive index (Δn_D), molar refractions (ΔR_m), reduced molar free volumes $\Delta (V_m/R_m)$ and internal pressures (ΔP_{int}) have been also calculated. The variations of these parameters with composition and temperature of the mixtures are discussed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules. The applicability of different refractive index mixing rules is tested against the experimentally measured values and good agreement has been obtained.

Keywords: DMAE, Refractive index, Molar refractions, Internal pressures, Formamide

1 Introduction

In chemical and engineering processes, physicochemical properties of pure amino alcohols and their mixtures with formamide are needed different operations for the design process. Amino alcohols are used as agricultural products, surfactants and additives in detergents. It is used for removal of sour gases from natural gas and petroleum streams. This paper is a continuation of our earlier work related to the study of thermodynamic properties of binary mixtures¹⁻⁷. Mass and heat transfer processes and flow operations are evident examples of the importance of the knowledge for these properties^{8,9}. Experimental thermo-physical properties are used to obtain information about the molecular level structures of liquid mixtures, as well as about the intermolecular interactions and structural features leading to the behavior and macroscopic properties of fluids¹⁰. Intermolecular interactions are a very complex subject, and thus, experimental results and theoretical models have to be combined to elucidate the fluid structure¹¹. Prediction of n_D of liquid mixtures is essential for many physicochemical calculations, which include correlation of n_D with density¹² excess molar volume^{13,14} and surface tension¹⁴. Literature survey¹⁵⁻²¹ indicates that

refractive index and related properties have been used to study the solute-solvent interactions in the liquid mixtures. FA molecules are highly polar and are strongly self-associated through extensive three-dimensional network of hydrogen bonds, through its three hydrogen bond donors (3 H-atoms) and three acceptors (two lone pairs of electrons at oxygen and one at nitrogen atom). FA is the simplest molecule containing a peptide linkage ($-\text{NH}-\text{CO}-$) and a study of their hydrogen bonding yields into the nature of protein structure. The binary systems of FA with DMEA and DEEA are of considerable interest for investigating the intra- and inter-molecular behavior of amino-alcoholic solvent systems. To the best of our knowledge, there has been no temperature-dependent study on these systems from the view point of their refractive index behavior. This fact allows us to plan some extensive studies in this research field in order to investigate the closest interactions between the unlike molecules by examining the optical and thermodynamic parameters.

In this study, we have reported a detailed investigation on the refractive indices (n_D) of binary mixtures of FA with DMEA and DEEA at 303.15, 313.15 and 323.15 K covering the entire miscibility range ($0 \leq x \leq 1$). The experimental values of density and refractive index are used to calculate the molar refractions (R_m), reduced molar free volumes

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(V_m/R_m), molecular radii (r) and internal pressure (P_{int}). The deviations of refractive index (Δn_D), molar refractions (ΔR_m), reduced molar free volumes ($\Delta(V_m/R_m)$) and internal pressures (ΔP_{int}) have been also calculated. The applicability of nine different refractive index mixing rules is tested against the experimentally measured values. The deviations in molar refractions and internal pressures have been fitted to Redlich-Kister polynomial equation.

2 Experimental Details

The chemical used were of analytical grade, formamide (FA), dimethylethanolamine (DMEA), diethylethanolamine (DEEA) and their mixtures were stored in glass stoppered flasks to avoid contamination and evaporation. All mixtures were prepared by mass using sartorius electronic balance, model-CPA225D with a precision of ± 0.01 mg. Density measurements were made using a single-capillary pycnometer made of Borosil glass having a bulb capacity of 13.5 cm^3 . The precision of density measurement was $\pm 0.00001 \text{ g cm}^{-3}$. The measurements were replicated at least three times for each measurement, and the results reported are the average values. The refractive indices of pure liquids and their binary mixtures were measured using a thermostated Abbe's refractometer. The refractometer was calibrated by measuring refractive indices of triply distilled water and toluene at known temperatures. The refractive index values were obtained using sodium D-line accurate to ± 0.0001 units. The sample mixtures were directly injected into the prism assembly of the instrument by means of an air-tight hypodermic syringe. The refractometer containing the sample to be tested was allowed to stand for around 30 min in a thermostatic water bath so as to minimize any possible thermal fluctuations in

the refractometer. A minimum of three independent readings were taken for each composition. The temperature was maintained by an electronically controlled thermostated water bath supplied by orbit. The purity of solvents and reliability of experimental measurements of density and refractive index data was ascertained by comparing the data of pure liquids with the corresponding values, which were available in the literature^{1, 22-28} at 303.15, 313.15 and 323.15 K.

3 Results and Discussion

The values of density and refractive index of pure components are listed in Table 1. The experimentally measured values of refractive indices (n_D) of both the binary mixtures of FA + DMEA and FA + DEEA at different temperatures are shown in Tables 2 and 3, respectively. The deviations in refractive index (Δn_D) also known as synergy of refractive index has been calculated using the following relation:

$$\Delta n_D = n_{D(\text{mix})} - (\phi_1 n_{D1} + \phi_2 n_{D2}) \quad \dots (1)$$

Where, ϕ_1 , ϕ_2 , n_{D1} and n_{D2} represent the volume fractions and refractive indices of components 1 and 2, respectively.

The molar refraction (R_m) gives information about the presence of specific intermolecular interactions in the binary liquid mixture. The experimental molar refractions (R_m) are obtained by the relation given as:

$$R_m = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \left(\frac{M_1 x_1 + M_2 x_2}{\rho_m} \right) \quad \dots (2)$$

Where, ρ_m is the density of the mixture, x_1 and x_2 are mole fractions and M_1 and M_2 are the molecular weights of component 1 and 2, respectively. Deviations in molar refractions have been calculated using the relation²⁹ as:

Table 1 – Experimental values of density (ρ) and refractive index (n_D) of pure liquids along with the corresponding values available in the literature at various temperatures.

Liquid	T/K	ρ ($\text{g} \cdot \text{m}^{-3}$)		n_D	
		Expt.	Lit.	Expt.	Lit.
Formamide	303.15	1.1254	1.1250 [28]	1.444	1.444 [22]
	313.15	1.1167	1.1164 [29]	1.440	1.440 [22]
	323.15	1.1070	1.1078 [29]	1.436	1.436 [23]
2-Dimethylethanolamine	303.15	0.8791	0.8792 [32]	1.425	1.420 [24]
	313.15	0.8707	0.8707 [32]	1.420	1.419 [24]
	323.15	0.8621	0.8614 [33]	1.415	1.415 [24]
2-Diethylethanolamine	303.15	0.8788	0.8761 [34]	1.433	1.428 [24]
	313.15	0.8691	0.8668 [34]	1.426	1.419 [24]
	323.15	0.8570	0.8573 [34]	1.418	1.401 [24]

Table 2 – Refractive indices (n_D), molar refractions (R_m), reduced molar free volumes (V_m/R_m), molecular radii (r), internal pressure (P_{int}), dielectric constant (ϵ) and polarizability (α) for FA (1) + DMEA (2).

x_1	ϕ_1	n_D	R_m ($\text{cm}^3 \text{mol}^{-1}$)	V_m/R_m	r (\AA)	P_{int} (MPa)
303.15 K						
0.0000	0.0000	1.4252	25.94	3.9092	2.1749	83.38
0.1006	0.0423	1.4264	24.38	3.9000	2.1304	87.94
0.1960	0.0877	1.4276	22.90	3.8904	2.0865	93.01
0.2957	0.1421	1.4290	21.37	3.8790	2.0388	99.25
0.3999	0.2082	1.4306	19.77	3.8661	1.9866	107.05
0.4915	0.2761	1.4321	18.36	3.8547	1.9383	115.32
0.5959	0.3678	1.4337	16.76	3.8423	1.8803	126.83
0.6973	0.4762	1.4354	15.21	3.8290	1.8203	140.98
0.8067	0.6222	1.4377	13.54	3.8117	1.7513	160.98
0.9044	0.7887	1.4404	12.06	3.7914	1.6851	185.10
1.0000	1.0000	1.4442	10.64	3.7632	1.6158	217.73
313.15 K						
0.0000	0.0000	1.4203	25.92	3.9491	2.1745	84.73
0.1006	0.0422	1.4214	24.36	3.9399	2.1299	89.40
0.1960	0.0875	1.4226	22.88	3.9300	2.0859	94.58
0.2957	0.1417	1.4241	21.35	3.9180	2.0382	100.96
0.3999	0.2076	1.4258	19.75	3.9043	1.9860	108.94
0.4915	0.2754	1.4274	18.34	3.8920	1.9377	117.39
0.5959	0.3671	1.4290	16.74	3.8788	1.8797	129.14
0.6973	0.4754	1.4308	15.19	3.8646	1.8197	143.59
0.8067	0.6214	1.4333	13.53	3.8456	1.7508	164.00
0.9044	0.7882	1.4362	12.06	3.8232	1.6848	188.59
1.0000	1.0000	1.4403	10.64	3.7921	1.6158	221.78
323.15 K						
0.0000	0.0000	1.4155	25.92	3.9891	2.1744	85.91
0.1006	0.0421	1.4166	24.35	3.9799	2.1296	90.70
0.1960	0.0874	1.4178	22.87	3.9698	2.0855	96.00
0.2957	0.1416	1.4193	21.33	3.9574	2.0378	102.50
0.3999	0.2074	1.4211	19.74	3.9425	1.9857	110.63
0.4915	0.2752	1.4227	18.34	3.9295	1.9376	119.23
0.5959	0.3668	1.4244	16.74	3.9157	1.8794	131.22
0.6973	0.4750	1.4263	15.19	3.9004	1.8195	145.96
0.8067	0.6211	1.4289	13.53	3.8798	1.7506	166.79
0.9044	0.7879	1.4321	12.06	3.8551	1.6850	191.81
1.0000	1.0000	1.4364	10.65	3.8216	1.6163	225.47

$$\Delta R_m = R_m - (x_1 R_{m1} + x_2 R_{m2}) \quad \dots (3)$$

Where, R_{m1} and R_{m2} are the molar refractions of pure components 1 and 2, respectively.

The deviations of reduced molar free volumes have been calculated using the relation²⁹:

$$\Delta \left(\frac{V_m}{R_m} \right) = \left(\frac{n_D^2 + 2}{n_D^2 - 1} \right) - \left(\frac{x_1 V_1 + x_2 V_2}{x_1 R_{m1} + x_2 R_{m2}} \right) \quad \dots (4)$$

The theoretical estimation of molecular radii of pure liquids can be successfully done by using the values of refractive index as:

$$r = \left[\left\{ \left(\frac{3}{4\pi N_A} \right) \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \right\} V_m \right]^{1/3} \quad \dots (5)$$

Internal pressures of binary liquid mixture can be evaluated using the well-known Buchler–Hirschfelder–Curtiss equation³⁰ of state given as:

Table 3 – Refractive indices (n_D), molar refractions (R_m), reduced molar free volumes (V_m/R_m), molecular radii (r), internal pressure (P_{int}), dielectric constant (ϵ) and polarizability (α) for FA (1) + DEEA (2).

x_1	ϕ_1	n_D	R_m ($\text{cm}^3 \text{mol}^{-1}$)	V_m/R_m	r (Å^0)	P_{int} (M Pa)
303.15 K						
0.0000	0.0000	1.4335	34.69	3.8438	2.3963	64.24
0.1022	0.0330	1.4342	32.19	3.8384	2.3373	67.95
0.1962	0.0683	1.4352	29.92	3.8306	2.2810	72.05
0.2949	0.1115	1.4364	27.55	3.8219	2.2191	77.28
0.4000	0.1667	1.4374	25.02	3.8142	2.1490	84.16
0.4939	0.2265	1.4382	22.76	3.8083	2.0823	91.91
0.5990	0.3096	1.4389	20.23	3.8023	2.0021	103.14
0.7003	0.4122	1.4398	17.80	3.7962	1.9184	117.78
0.8012	0.5473	1.4407	15.38	3.7891	1.8273	138.27
0.9034	0.7372	1.4421	12.94	3.7790	1.7248	169.53
1.0000	1.0000	1.4442	10.64	3.7632	1.6158	217.73
313.15 K						
0.0000	0.0000	1.4261	34.55	3.9020	2.3931	64.85
0.1022	0.0329	1.4269	32.06	3.8960	2.3341	68.67
0.1962	0.0681	1.4280	29.80	3.8873	2.2779	72.88
0.2949	0.1112	1.4292	27.44	3.8775	2.2161	78.22
0.4000	0.1663	1.4304	24.93	3.8679	2.1463	85.25
0.4939	0.2259	1.4314	22.68	3.8599	2.0799	93.17
0.5990	0.3089	1.4325	20.17	3.8515	2.0000	104.65
0.7003	0.4114	1.4337	17.75	3.8425	1.9166	119.62
0.8012	0.5465	1.4351	15.35	3.8315	1.8259	140.59
0.9034	0.7366	1.4372	12.92	3.8158	1.7240	172.55
1.0000	1.0000	1.4403	10.64	3.7921	1.6158	221.78
323.15 K						
0.0000	0.0000	1.4185	34.36	3.9640	2.3886	65.44
0.1022	0.0329	1.4193	31.87	3.9574	2.3294	69.39
0.1962	0.0680	1.4205	29.62	3.9478	2.2734	73.70
0.2949	0.1111	1.4218	27.29	3.9365	2.2120	79.15
0.4000	0.1661	1.4233	24.80	3.9248	2.1427	86.32
0.4939	0.2257	1.4245	22.58	3.9146	2.0767	94.41
0.5990	0.3086	1.4260	20.09	3.9032	1.9972	106.14
0.7003	0.4111	1.4275	17.69	3.8910	1.9143	121.43
0.8012	0.5462	1.4294	15.30	3.8756	1.8242	142.84
0.9034	0.7363	1.4322	12.90	3.8537	1.7232	175.44
1.0000	1.0000	1.4364	10.65	3.8216	1.6163	225.47

$$P_{int} = \frac{2^{1/6}RT}{2^{1/6}V_m - 2rN_A^{1/3}V_m^{2/3}} \quad \dots (6)$$

Where, r is the molecular radius and V_m the molar volume of the mixture. N_A is the Avogadro's number, T is absolute temperature in Kelvin and R is the universal gas constant. Deviations of internal pressures of binary liquid mixture have been obtained by the relation as:

$$\Delta P_{int} = P_{int} - (x_1 P_{int,1} + x_2 P_{int,2}) \quad \dots (7)$$

Where, P_{int} , $P_{int,1}$ and $P_{int,2}$ are the internal pressures of binary mixture and pure components 1 and 2, respectively.

The values of Eykman's constant (C_m), deviation of Eykman's constant (ΔC_m) and relative synergies of refractive index of both the binary mixtures are

shown in Tables 1 and 2, respectively. The values of molar refraction (R_m), reduced molar free volumes (V_m/R_m), molecular radii (r_m), internal pressure (P_{int}), deviations of reduced molar free volumes $\{\Delta(V_m/R_m)\}$, molecular radii (Δr_m) and internal pressures (ΔP_{int}) of both the binary mixtures of FA + DMEA and FA + DEEA, at different temperatures, are presented in Tables 3 and 4, respectively.

The deviations of internal pressure (ΔP_{int}) and molar refraction (ΔR_m) have been fitted to the Redlich-Kister³¹ polynomial equation of the type:

$$\Delta Y = x_1 \cdot x_2 \sum_{i=1}^k A_i (x_1 - x_2)^{i-1} \quad \dots (8)$$

Where, k is the number of estimated parameters and A_i is the coefficients of the polynomial obtained by fitting the equation to the experimental results by least square regression method. The values of the coefficients (A_i) are listed in Table 4.

The standard deviations (σ) were calculated using the relation³² and are given in the Table 4:

$$\sigma(Y) = \left[\frac{(Y_{exp} - Y_{cal})^2}{N - n} \right]^{1/2} \quad \dots (9)$$

Where, N is the number of data points and n is the number of coefficients.

3.1 Mixing rules for refractive index

Various mixing rules are used to predict the refractive index of binary mixtures from density of the mixtures together with refractive indices of the

pure components. In the present study, we have applied nine different mixing rules^{33,34}, viz. Arago-Biot, Newton, Heller, Gladstone-Dale, Eyring-John³⁴, Eykman, Lorentz-Lorentz, Weiner and Oster to test their validities for the present systems. The details of these 'mixing rules' equations are discussed below: Arago-Biot (A-B) relation:

$$n_D = \phi_1 \cdot n_{D1} + \phi_2 \cdot n_{D2} \quad \dots (10)$$

Newton (Nw) relation:

$$(n_D^2 - 1) = \phi_1 \cdot (n_{D1}^2 - 1) + \phi_2 \cdot (n_{D2}^2 - 1) \quad \dots (11)$$

Heller (H) relation:

$$\left(\frac{n_D - n_{D1}}{n_{D1}} \right) = \frac{3}{2} \phi_2 \left(\frac{m^2 - 1}{m^2 + 2} \right) \quad \dots (12)$$

Where, $m = n_{D2}/n_{D1}$

Gladstone-Dale (G-D) relation:

$$(n_D - 1) = \phi_1 \cdot (n_{D1} - 1) + \phi_2 \cdot (n_{D2} - 1) \quad \dots (13)$$

Eyring-John (E-J) relation:

$$n_D = \phi_1^2 \cdot (n_{D1}) + \phi_2^2 \cdot (n_{D2}) + (2 \cdot n_{D1} \cdot n_{D2})^{1/2} \cdot (\phi_1 \cdot \phi_2) \dots (14)$$

Eykman (Eyk) has the following form:

$$\left(\frac{n_D^2 - 1}{n_D + 0.4} \right) \cdot V = \left[(x_1 \cdot V_1) \left(\frac{n_{D1}^2 - 1}{n_{D1} + 0.4} \right) \right] + \left[(x_2 \cdot V_2) \left(\frac{n_{D2}^2 - 1}{n_{D2} + 0.4} \right) \right] \quad \dots (15)$$

Lorentz-Lorentz (L-L) relation is given as:

$$\left(\frac{n_D^2 - 1}{n_D + 2} \right) = \left[\phi_1 \cdot \left(\frac{n_{D1}^2 - 1}{n_{D1} + 2} \right) \right] + \left[\phi_2 \cdot \left(\frac{n_{D2}^2 - 1}{n_{D2} + 2} \right) \right] \quad \dots (16)$$

Table 4 – Values of average percentage deviations (APD) in experimentally and theoretically calculated refractive indices using various mixing rules at different temperatures.

T (K)	A-B	G-D	Nw	H	E-J	Eyk	L-L	W	Os
FA (1) + DMEA(2)									
303.15	0.0561	0.0561	0.0549	0.0579	0.0567	0.0565	0.0573	0.0417	0.0554
313.15	0.0497	0.0497	0.0484	0.0518	0.0504	0.0502	0.0511	0.0337	0.0490
323.15	0.0438	0.0438	0.0424	0.0460	0.0445	0.0443	0.0453	0.0262	0.0430
FA (1) + DEEA(2)									
303.15	0.0839	0.0839	0.0836	0.0845	0.0841	0.0840	0.0843	0.0791	0.0837
313.15	0.0782	0.0782	0.0776	0.0793	0.0785	0.0784	0.0789	0.0697	0.0779
323.15	0.0724	0.0724	0.0714	0.0742	0.0729	0.0727	0.0734	0.0587	0.0719

Weiner (W) relation is applicable to spherically shaped isotropic bodies and is given by the relation as:

$$\left(\frac{n_D^2 - n_{D1}^2}{n_D^2 + 2n_{D1}^2} \right) = \phi_2 \cdot \left(\frac{n_{D2}^2 - n_{D1}^2}{n_{D2}^2 + 2n_{D1}^2} \right) \quad \dots (17)$$

Oster (Os) equation is of the form:

$$\frac{(n_D^2 - 1) - (2n_D^2 + 1)}{n_D^2} = \phi_1 \cdot \left[\frac{(n_{D1}^2 - 1) - (2n_{D1}^2 + 1)}{n_{D1}^2} \right] + \phi_2 \cdot \left[\frac{(n_{D2}^2 - 1) - (2n_{D2}^2 + 1)}{n_{D2}^2} \right] \quad \dots (18)$$

The values of molar refraction (R_m), reduced molar free volumes (V_m/R_m), molecular radii (r) and internal pressure (P_{int}) of both the binary mixtures of FA +

DMEA and FA + DEEA at different temperatures are presented in Tables 2 and 3, respectively. The deviations of refractive index (Δn_D), molar refractions (ΔR_m), reduced molar free volumes ($\Delta(V_m/R_m)$) and internal pressures (ΔP_{int}) are shown in Figs 1-4 (a and b), respectively.

The predicted refractive indices of the binary mixtures at each temperature studied were compared with the experimentally measured values. The effectiveness of these rules is tested in terms of the average percentage deviations (APD) values, which are presented in Table 3. It is observed from Tables 1 and 2 that the experimental refractive index of FA + DMEA and FA + DEEA systems increases linearly with an increase in mole fractions of FA.

Figure 1(a and b) exhibit that Δn_D values are positive and non-linear over the entire composition range at all temperatures for both the systems. The

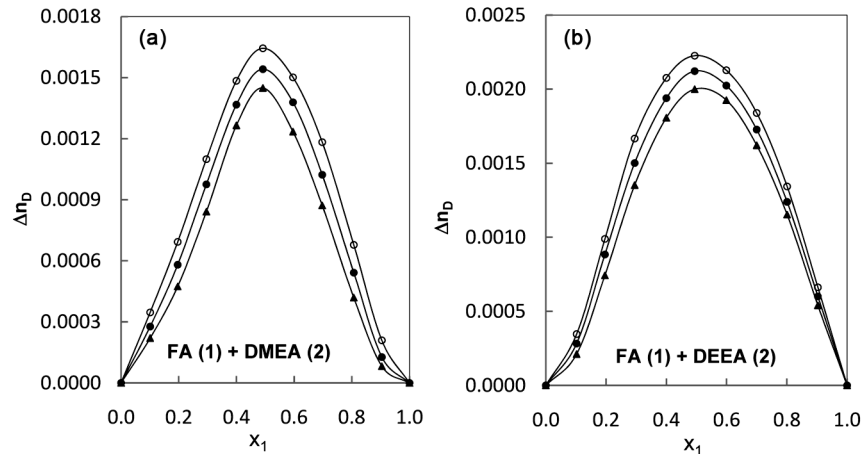


Fig. 1 – (a and b) Plot of Δn_D as a function of mole fraction of FA (x_1) at (o) 303.15 K, (●) 313.15 K, (▲) 323.15 K.

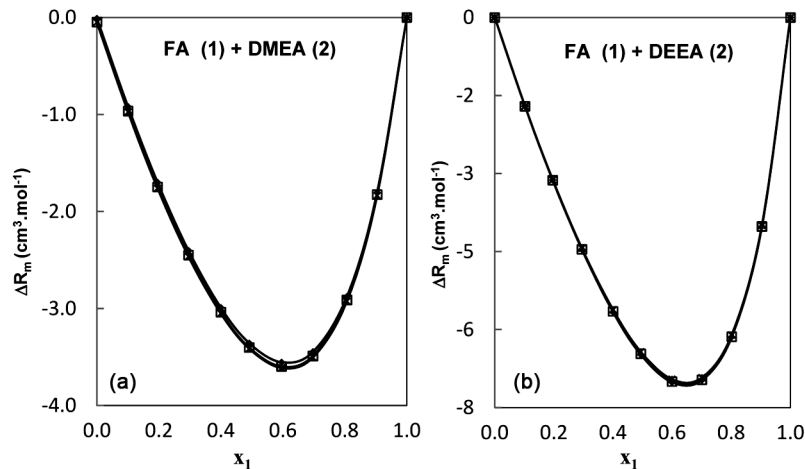


Fig. 2 – (a and b) Plot of ΔR_m as a function of mole fraction of FA (x_1) at (o) 303.15 K, (●) 313.15 K, (▲) 323.15 K.

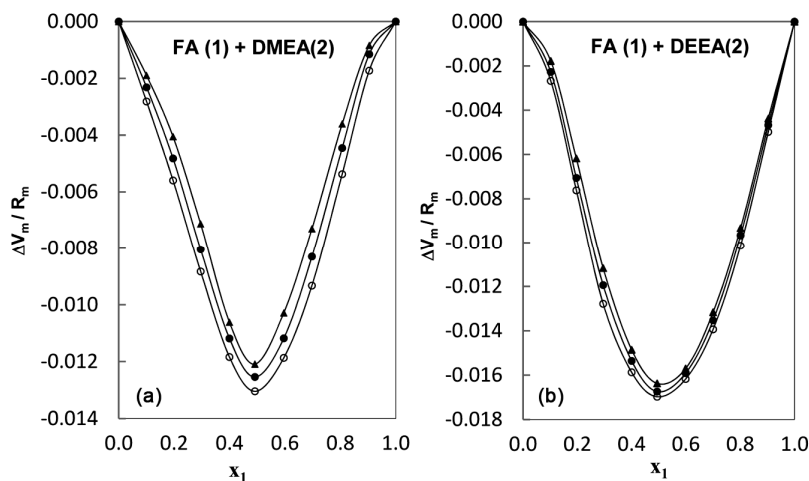


Fig. 3 – (a and b) Plot of $\Delta(V_m/R_m)$ as a function of mole fraction of FA (x_1) at (o) 303.15 K, (●) 313.15 K, (▲) 323.15 K.

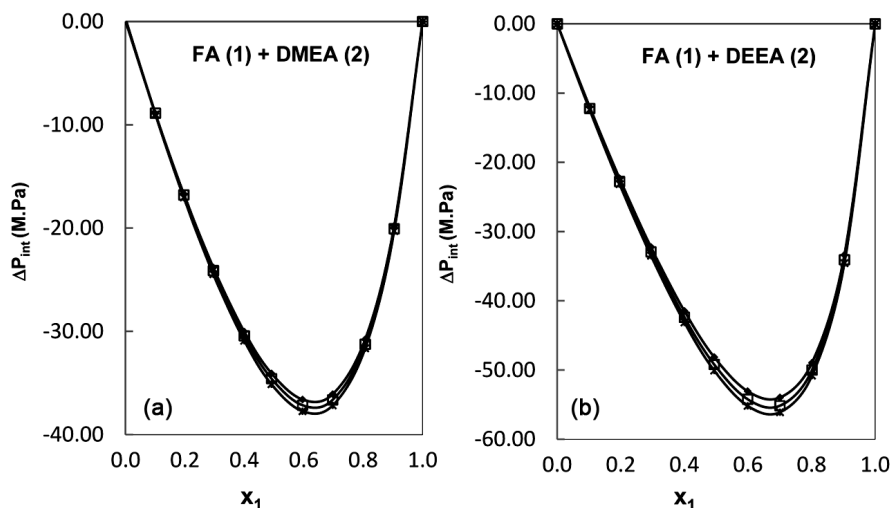


Fig. 4 – (a and b) Plot of ΔP_{int} as a function of mole fraction of FA (x_1) at (o) 303.15 K, (●) 313.15 K, (▲) 323.15 K.

Δn_D value shows maximum at $x_1 \sim 0.5726$ for (FA + DMEA) and $x_1 \sim 0.5054$ for (FA + DEEA) binary system. It is well known that the refractive index deviation depend on several energetic and structural effects^{35,36}. The positive deviations Δn_D (on volume fraction dependence basis) is considered due to the presence of significant interactions in the mixtures, whereas negative deviations Δn_D indicates weak interactions between the contributing components of the mixtures^{20,29,37}. The observed variations of Δn_D values indicate the presence of significant interactions in these mixtures. The extent of the positive deviations Δn_D from linear dependence on composition is in order: FA + DEEA > FA + DMEA. Both, FA and dialkylethanolamines molecules are polar and strongly self-associated liquids having inter- and intra-molecular hydrogen bonding.

The availability of three donors and three acceptors sites in FA molecules, which promotes the self-association and also the hetero-molecular association with different polar molecules. The presence of intra-molecular hydrogen bonding in pure state of FA and DMEA/DEEA molecules may reduce the possibility of intermolecular interaction with the unlike molecules, which occur only via weak dipolar interactions. In a reliable abstraction, a negative contribution to the Δn_D values should be expected. But contrary to our expectation, the positive trends are observed in Δn_D values for FA + DMEA/DEEA mixtures. It is possible to identify favorable interactions, such as strong hydrogen bonds, between the hydroxyl group (–OH) of DMEA/DEEA and amidic group (–O–C–N=) of FA acting as hydrogen acceptor. On this basis, a positive contribution to Δn_D

should be expected on mixing the liquids when favorable interactions between groups occur. For FA+DMEA and FA+DEEA systems, the positive Δn_D values suggest that the dialkylethanolamines-FA interaction pre-dominates those between dialkylethanolamines molecules. It is suggested that mixing of FA with dialkylethanolamines would induce mutual dissociation of the hydrogen-bonded structures present in pure liquids with subsequent formation of (new) hydrogen bonds (C=O \cdots H-O) between proton acceptor oxygen atom of C=O group of FA molecules and hydrogen atom of -OH groups of dialkylethanolamines molecules. The hydrogen bonds between hydroxyl groups and carbonyl oxygen atoms are stronger than those formed between homo cooperative hydroxyl molecules³⁸. The sign and magnitude of Δn_D also varies with the structural characteristics of the liquid components arising from the geometrical fitting of one component into the structure of other component due to difference in the molecular size and shape of the components. If the unlike molecules have almost the same molar volumes, this effect should be insignificant. However, even if slight difference in the free volume between different species could facilitate the penetration of one component into the other and as the difference of the free volumes of the two pure species increases, the more positive should be the contribution to Δn_D . The interstitial accommodation of the small molecules of FA (V_m (FA)= 40.02 cm³ mol⁻¹ at 303.15 K) in the large dialkylethanolamines molecules (V_m (DMEA)=101.39 cm³ mol⁻¹ and V_m (DEEA)=133.35 cm³ mol⁻¹ at 303.15 K) will also make the deviations Δn_D positive.

Hence, it seems quite reasonable to assume that there is an extensive hydrogen bonding between oxygen atom of C=O group of FA and hydrogen atom of the H-O group of dialkylethanolamines molecules. The values of refractive index (Tables 2 and 3) and its deviation (Fig. 1) are found to be higher for FA+DEEA system than FA+DMEA system. The refractive index of a compound describes its ability to refract light as it moves from one medium to another and thus, the higher the refractive index of a compound, the more the light is refracted. As stated by Deetlefs *et al.*³⁹, the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser. Hence, a perusal of Tables 2 and 3 reveals that refractive index is higher for FA + DEEA than FA + DMEA system

indicating to the fact that these molecules are more tightly packed in the solution. The probable reason for this may be the fact that + I effect of ethyl group is of comparatively greater extent than that of the methyl group. The oxygen of diethylethanolamine should attack more readily to the carbonyl group of FA because ethyl group is a better electron donor than the methyl group. Thus, the DEEA molecules may form hydrogen bond with FA molecules easily, giving rise to higher refractive index and Δn_D values than DMEA.

The strength of intermolecular interactions between FA and dialkylethanolamines molecules is in order: FA + DEEA > FA + DMEA. In both the cases, the refractive index and its deviation decrease with an increase in temperature because of the increase in the velocity of light in the liquid medium. The position of Δn_D maxima does not change with an increase in temperature. Sengwa *et al.*⁴⁰ studied the dielectric behavior of binary mixtures of FA with 2-alkoxyethanols (2-ME, 2-EE and 2-BE (2-butoxyethanol)) at 303.15 K. The magnitude and variation of observed dielectric parameter confirm that the strength of H-bond connectivity between unlike molecules is found to increase with an increase of molecular size of 2-alkoxyethanols. The results obtained from dielectric studies are in close agreement with our results using refractometric technique.

Figure 2(a and b) show the deviation in molar refraction (ΔR_m) with mole fractions (x_1) of FA. The molar refraction is a sensitive function of wavelength, temperature and solution composition. A negative non-linear trend is observed in ΔR_m values, for both the binary liquid mixtures, over the entire concentration range. The negative value of ΔR_m suggests the presence of strong intermolecular interactions between the components of the liquid mixtures. The values of ΔR_m slightly decrease with increase in the temperature³³.

Figure 3(a and b) present the deviations of reduced molar free volume versus mole fraction of FA. The values of deviations of reduced molar free volume $\Delta(V_m/R_m)$ are negative and nonlinear over the whole concentration range, at all temperatures, for both the systems. Brocos *et al.*²⁹ stated that the molar refraction deviation function must be calculated on mole fraction basis and refractive index deviation function on volume fraction basis, which makes it directly interpretable as a sign-reversed measure of

the deviations of reduced free volumes from ideality. According to their suggestions, we have evaluated all the deviation functions, Δn_D , ΔR_m and $\Delta(V_m/R_m)$ and found that deviations in refractive index Δn_D have the opposite sign to the deviation in reduced free molar volume, $\Delta(V_m/R_m)$, for the present binary system^{14,33}. Negative values of $\Delta(V_m/R_m)$ show the minima at the same concentrations where positive values of Δn_D maxima occur. Negative values of $\Delta(V_m/R_m)$ show strong molecular interactions between the components of the liquid mixtures³³.

Figure 4 (a and b) show the trends of deviation of internal pressure versus mole fraction of FA for both the liquid mixtures, respectively. The internal pressure is defined as the energy required vaporising a unit volume of a substance. The values of P_{int} increase with increase in mole fractions of FA. The internal pressure for pure alcohols decreases with increasing chain length⁴¹. The value of internal pressure is found to be greater for FA + DMEA than FA + DEEA system. The deviations of internal pressure (ΔP_{int}) are negative and non-linear in nature over the complete composition range. The effect of temperature is not very significant for ΔP_{int} values^{33,42}. The predicted refractive indices of the binary mixtures at each temperature studied were compared with the experimentally measured values and the results are presented in terms of APD. The APD values for A-B, Nw, H, G-D, E-J, Eyk, L-L, W and Os relations are presented in Table 4. A close perusal of Table 4 reveals that all the mixing rules show good agreement with experimental values for the both FA + DMEA and FA + DEEA systems.

The results show the W, Nw, Os, A-B, G-D, Eyk and E-J relations with minimum percentage deviations, providing excellent agreement for the present systems. This may be because W's relation is based on the assumption that the molecules are spherically symmetrical, whereas in the case of Nw's and Os's relations, this is not so. Furthermore, the APD values of A-B and G-D are similar for the systems studied, as expected, as Eq. 13 reduces to Eq. 10 if we assume volume additivity. However, L-L and H relations show relatively large percentage deviations for the both systems.

4 Conclusions

The refractive indices (n_D) of binary mixtures of formamide with dialkylethanolamines have been measured over the whole composition range at 303.15, 313.15 and 323.15 K. The variations of

refractive index and related parameters with composition and temperature of the mixtures are discussed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules. The outcome were analyzed in terms of the molecular characteristics of the interacting molecules and found to exhibit an extensive hydrogen bonding between oxygen atom of C=O group of FA and hydrogen atom of the H-O group of dialkylethanolamines molecules in the binary liquid mixtures.

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