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Study of Refractive Indices and Its Theories for Mixtures of *N*, *N*-Diethylethanamine and Acetates

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Abstract

This paper reports the refractive indices (n) of *N*,*N*-diethylethanamine + methyl acetate, ethyl acetate, propyl acetate, butyl acetate and pentyl acetate at 298.15 K and at different composition range. The various empirical correlations like Arago-Biot (AB), Gladstone-Dale (GD), Lorentz-Lorenz (L-L) Heller (H), Weiner (W), Newton (Nw) and Erying-John (E-J) were applied to experimental data for estimating theoretical value of refractive indices. For an equimolar mixture, the predicted deviation in refractive index values is consistent well with the experimental data. It has been found that the interactions between amine and different esters decrease when carbon chain length in ester increases. Also refractive indices are affected with change in temperature. To evaluate the standard deviation, RK polynomial equation was fitted to the measured refractive indices data.

Keywords: Refractive index; Triethylamine; Alkyl acetates; Correlations.

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1. Introduction

The excess functions are very useful to understand the nature and magnitude of deviations from ideality and as the non-ideality is directly linked with the intermolecular interactions [1,2].

Recently, we have reported some thermodynamic functions of binary mixtures of aliphatic amine and aliphatic esters [3,4]. Deviation in refractive index of binary mixtures reveals significant information about the structure and molecular interactions [5-7]. From recent research work it was found that some of the polymers in polymer chemistry which are insoluble in pure solvent can be dissolved in a solvent mixture [8]. Also *N*,*N*-diethylethanamine is a very good additive for gasolines. Binary mixtures are used to refine the petroleum product which is very toxic if we use the binary mixtures then we can increase the efficiency of fuel and decrease the toxicity. *N*,*N*-diethylethanamine is a clear

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colorless liquid having fish-like odour. Its vapours are heavier than air also and are used as a food additive. Esters are clear liquid, flavouring ingredient. They can act as a non-polar (lipophilic) as well as weakly polar (hydrophilic) aprotic solvent. It is used as adhesives, sealant chemicals, intermediates, lubricants, lubricant additives, electrical, electronic products, paint, coating additives, floor coverings, plasticizers, lubricants and also used as solvents for cleaning and degreasing. Since the components of these binary mixtures have both proton-donating/accepting abilities, significant interaction through hydrogen bonding between unlike molecules is expected.

2. Experimental

The specifications of all the chemicals are given in Table 1. All the chemicals were purified by standard procedure and their purities were confirmed by comparing the measured density and refractive index (at 298.15 K) data with literature [7-12] are given in Table 2. Refractive indices were measured with refractometer (Anton Paar Abbemat-200) having temperature controlled within ±0.01 K with an accuracy of $\pm 1\times10^{-4}$. The samples were prepared by using electronic balance (CAUW 220 D) with a precision of ±0.005 mg.

Table 1. Sample Information Table.

S. No.	Sample	CAS No.	Make	Initial Mass Fraction Purity
1	N,N-diethylethanamine	121-44-8	Merck, India	≥0. 990
2	Methyl acetate	79-2--0-9	Merck, India	≥0. 995
3	Ethyl acetate	141-78-6	Fisher Scientific, India	≥0. 995
4	Propyl acetate	109-60-4	S.D. Fine Chemicals, India	≥0. 980
5	Butyl acetate	123-86-4	Merck, India	≥0. 995
6	Pentyl acetate	628-63-7	Merck, India	≥0. 990

Table 2. Experimental and literature values of densities, ρ^* and refractive index of pure liquid components at 298.15 K and atmospheric pressure.

	Density ($\rho^*\times10^{-3}$) ($\mathrm{kg\cdot m^{-3}}$)		Refractive Index (n)	
Components	Exp.	Lit.	Exp.	Lit.
N,N-diethylethanamine	0.722430	0.722822 [14]	1.4272	1.4277[13]
Methyl acetate	0.928458	0.92850[14]	1.3594	1.3597[13]
Ethyl acetate	0.894790	0.89471[14]	1.3698	1.3700[13]
Propyl acetate	0.883369	0.8831[14]	1.3818	1.3821[13]
Butyl acetate	0.876399	0.87626[14]	1.3920	1.3922[13]
Pentyl acetate	0.87132	0.87146[14]	1.4049	1.4050[13]

3. Results and Discussion

Deviation in refractive index (Δn) is reported in Table 3 and was calculated as:

$$\Delta n = n_D - \sum_{i=1}^{2} x_i n_{Di} \tag{1}$$

where x_i represent the mole fraction of the i^th^ component. The Δn values were also fitted to Redlich – Kister polynomial Eq.

$$\Delta n = x_1(1-x_1)\left[\sum_{n=1}^{4} A^{(j)}\left(2x_1-1\right)^{(j-1)}\right] \tag{2}$$

where $A^{(j)}$ are the adjustable parameters and calculated by fitting Δn data in Eq. (2). Experimental Δn data at 298.15 K for the studied system together with smoothing curves from Eq. (2) is shown in Fig. 1. Similar trend were observed at all the other temperatures. For quantitative determination of refractive indices following mixing relations were used:

Arago-Biot (A-B)

$$n_D = n_{D1}\phi_1 + n_{D2}\phi_2 \tag{3}$$

Gladstone-Dale (G-D)

$$n_D - 1 = (n_{D1}-1)\phi_1 + (n_{D2}-1)\phi_2 \tag{4}$$

Lorentz-Lorenz (L-L)

$$\frac{n_D^2-1}{n_D^2+2} = \left(\frac{n_{D1}^2-1}{n_D^2+2}\right)\phi_1 + \left(\frac{n_{D2}^2-1}{n_D^2+2}\right)\phi_2 \tag{5}$$

Heller (H)

$$\frac{n_D-1}{n_D} = \frac{3}{2}\left(\frac{\left(n_{D2}/n_{D1}\right)^2-1}{\left(n_{D2}/n_{D1}\right)^2+2}\right)\phi_2 \tag{6}$$

Weiner (W)

$$\frac{n_D^2-n_{D1}^2}{n_D^2+2n_{D2}^2} = \left(\frac{n_{D2}^2-n_{D1}^2}{n_{D2}^2+2n_{D2}^2}\right)\phi_2 \tag{7}$$

Newton (Nw)

$$n_D^2 - 1 = (n_{D1}^2-1)\phi_1 + (n_{D2}^2-1)\phi_2 \tag{8}$$

Eyring and John (E-J)

$$n_D = n_{D1}\phi_1^2 + 2(n_{D1}n_{D2})^{1/2}\phi_1\phi_2 + n_{D2}\phi_2^2 \tag{9}$$

In these equations, n_D, n_{D1} and n_{D2} are the refractive index of the binary mixtures and its components, respectively. ϕ_1 and ϕ_2 represent the volume fraction of pure components and given by

$$\phi_1 = x_1V_1/\sum x_iV_i \text{ and } \phi_2 = x_2V_2/\sum x_iV_i \tag{10}$$

From these mixing rules standard deviation were also calculated. Refractive index values along with deviation in refractive index over the entire composition are given in Table 3. Figs. 1 and 2 show the variations of n and Δn versus x_1 for the binary systems studied at 298.15 K respectively.

Table 3. Refractive Index, n and deviation in refractive index Δn for the binary system TEA + (C_1 – C_5) Acetates at T = 298.15 K.

x_1	n	Δn
	N,N-diethylethanamine+ methyl acetate	
0.0000	1.3594	0.0000
0.0626	1.3608	-0.0012
0.2054	1.3642	-0.0038
0.2770	1.3659	-0.0051
0.3579	1.3684	-0.0060
0.4534	1.3723	-0.0061
0.5106	1.3750	-0.0057
0.6055	1.3794	-0.0053
0.7414	1.3874	-0.0030
0.8495	1.3934	-0.0015
1.0000	1.4012	0.0000
	N,N-diethylethanamine+ ethyl acetate	
0.0000	1.3698	0.0000
0.0578	1.3705	-0.0011
0.1567	1.3722	-0.0025
0.2569	1.3746	-0.0033
0.3538	1.3768	-0.0041
0.4522	1.3796	-0.0044
0.5522	1.3829	-0.0042
0.6588	1.3868	-0.0037
0.7503	1.3902	-0.0032
0.8535	1.3946	-0.0020
1.0000	1.4012	0.0000
	N,N-diethylethanamine+ propyl acetate	
0.0000	1.3698	0.0000
0.0578	1.3705	-0.0011
0.1567	1.3722	-0.0025
0.2569	1.3746	-0.0033
0.3538	1.3768	-0.0041
0.4522	1.3796	-0.0044
0.5522	1.3829	-0.0042
0.6588	1.3868	-0.0037
0.7503	1.3902	-0.0032
0.8535	1.3946	-0.0020
1.0000	1.4012	0.0000
	N,N-diethylethanamine+ propyl acetate	
0.0000	1.3818	0.0000
0.0580	1.3819	-0.0010
0.1072	1.3822	-0.0017
0.2041	1.3837	-0.0021
0.3035	1.3854	-0.0023
0.4012	1.3871	-0.0025
0.5057	1.3891	-0.0025
0.6037	1.3911	-0.0024
0.7066	1.3935	-0.0020
0.8057	1.3961	-0.0013
1.0000	1.4012	0.0000
	N,N-diethylethanamine+ butyl acetate	

0.0000	1.3920	0.0000
0.0596	1.3921	-0.0004
0.1125	1.3924	-0.0006
0.2154	1.3930	-0.0010
0.3300	1.3938	-0.0012
0.4000	1.3943	-0.0014
0.5002	1.3951	-0.0015
0.6151	1.3962	-0.0015
0.7584	1.3977	-0.0013
0.8562	1.3990	-0.0009
1.0000	1.4012	0.0000
	N,N-diethylethanamine+ pentyl acetate	
0.0000	1.4049	0.0000
0.0661	1.4043	-0.0004
0.1006	1.4040	-0.0005
0.2009	1.4034	-0.0008
0.3001	1.4029	-0.0009
0.3909	1.4025	-0.0010
0.5001	1.4021	-0.0009
0.6001	1.4018	-0.0009
0.7504	1.4014	-0.0007
0.8394	1.4013	-0.0005
1.0000	1.4012	0.0000

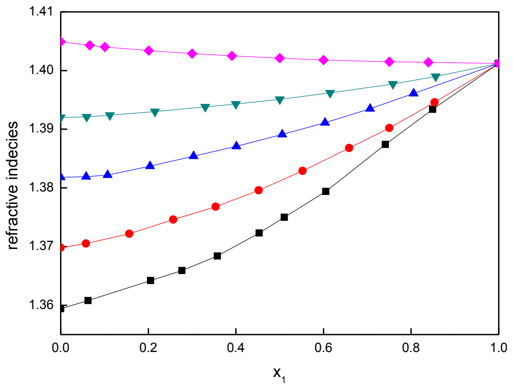

Fig. 1. Refractive index (n) against mole fractions, x_1 *N,N*-diethylethanamine + x_2 methyl acetate (■); x_2 ethyl acetate (●); x_2 propyl acetate (▲); x_2 butyl acetate (▼); x_2 pentyl acetate (◆) at 298.15 K.

From Fig. 1 it can be seen that as we increase the concentration of esters in *N, N*-diethylethanamine, the interactions becomes appreciable. Also it can be noted that the interactions are maximum for methyl acetate and minimum for pentyl acetate i.e. the interactions decreases as we go from methyl acetate to pentyl acetate. These interactions are due to rupture of self-association of amine molecule as well as ester molecule and orientation of antiparellel spin of ester molecule to amine [13-17]. The Δn values for the

N,*N*-diethylethanamine (1) + alkyl (C_1-C_5) acetates (2) binary systems are negative. This indicates that there is specific interaction between these two components.

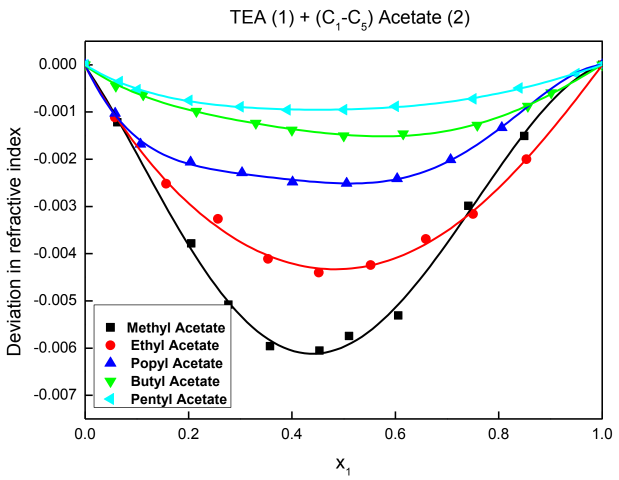

Fig. 2. Deviation in refractive indices against mole fractions of x_1 *N*,*N*-diethylethanamine + x_2 alkyl acetates (C_1-C_5) at 298.15 K. The smoothing of the curve has been drawn from RK equation.

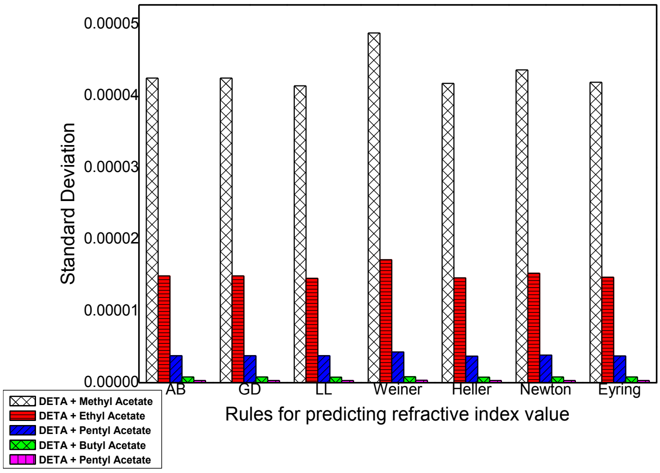

Fig. 3. Standard deviation of calculated values of refractive index using various correlations fractions of x_1 *N*,*N*-diethylethanamine + x_2 alkyl acetates (C_1-C_5) at 298.15 K.

Fig. 3 shows the standard deviation of predicted values of refractive index using various correlations for the binary mixtures at 298.15 K. From these results, it can be seen that Lorentz-Lorentz correlation well explain these binary systems and as the carbon chain is increasing these correlations fits well also Lorentz-Lorentz has minimum standard deviation among all the correlations used.

3. Conclusion

From refractive index data we have measured (Δn) for binary liquid mixtures of amine and aliphatic acetates (methyl acetate, ethyl acetate, propyl acetate, butyl acetate and pentyl acetate) at temperature of 298.15 K over the entire composition range. The Δn results for all the binary mixtures are negative. The negative magnitude of Δn values shows the presence of specific interactions. Also, the predicted result from various correlation of Δn also supports experimental data. Various mixing rules applied for the theoretical estimation of refractive index and have good correlation with experimental data. The interaction decreases as we increase the number of carbon atoms in esters (methyl acetate to pentyl acetate).

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