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Refractivity Studies of Binary and Ternary Solutions

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Introduction

The knowledge of refractive index (n) and molar refraction (R_m) is useful for predicting many physico-chemical properties of liquid mixtures. Refractive index is used to evaluate the molar refraction and molecular connectivity which are used in predicting the structure of the liquid and their solutions. There are several empirical and semi empirical mixing rules for evaluating the refractive index of binary liquid solutions. The validity of various mixing rules as proposed by Lorentz-Lorenz (L-L), Gladstone-Dale (G-D), Weiner (W), Heller (H), Arago-Biot (A-B), Eykman (Eyk) and Oster (Os) relation has been tested by various workers during recent years.

It was found that the L-L, G-D, Eyk and Os relations have performed well with less deviation from experimental values whereas W, H and A-B are found to be unsatisfactory, but deviations are not out of the experimental precision. Recently Pandey et al[5.15-16] and other workers [6-7] have also studied the relative validity of refractive index mixing rules for multicomponent liquid systems. Refractive index measurements in binary and multicomponent liquid mixtures have been made by several workers[3.8-13]. The values of refractive index of multicomponent systems have also been evaluated theoretically from the respective data of their binaries constituents[17].

In the present work refractive indices (n) of two binary liquid solutions viz. ethanol+hexane and ethanol+dodecane, and one ternary solution ethanol+hexane+decane are measured along with all the pure components at 308.15K. Using experimental values of refractive index, change in refractive indices An, and change in molar refraction ΔR_m values have been calculated for all the systems and the results are fitted to Redlich-Kister polynomial equation. The refractive indices of all binary and ternary solutions have been evaluated theoretically using various mixing rules (L-L, G-D, W, H, A-B, Eyk and Os) from the experimental values of pure components of the mixtures. A comparative study of the validity, merits and demerits of all the mixing rules have also been made.

Theoretical

The most important basis of various mixing rules[13], which are used to calculate refractive index of binary and ternary liquid mixtures is the electromagnetic theory of light in which molecules are considered as dipoles or assemblies of dipole induced by an external field. The mixing rules which are used to calculate the refractive index of binary and ternary liquid solutions are as follows:

Lorentz-Lorenz (L-L) relation:

L-L relation has widest applicability in predicting the refractive index of mixture from the refractive index and density of pure components. For ternary mixture it can be represented in weight fraction form as,

$$\left[\frac{n_m^2-1}{n_m^2+2}\right]\frac{1}{\rho_m}=\left[\frac{n_1^2-1}{n_1^2+2}\right]\frac{W_1}{\rho_1}+\left[\frac{n_2^2-1}{n_2^2+2}\right]\frac{W_2}{\rho_2}+\left[\frac{n_3^2-1}{n_3^2+2}\right]\frac{W_3}{\rho_3} \qquad (1)$$

In terms of volume fraction form it can be written as,

$$\left[\frac{n_m^2-1}{n_m^2+2}\right]=\left[\frac{n_1^2-1}{n_1^2+2}\right]\phi_1+\left[\frac{n_2^2-1}{n_2^2+2}\right]\phi_2+\left[\frac{n_3^2-1}{n_3^2+2}\right]\phi_3 \qquad (2)$$

where n_m, n_1, n_2 and n_3 are the refractive index of the liquid mixture and its pure components 1, 2 and 3 in the mixture respectively. P_m, p_1, p_2, and P_3 are their respective densities. W_1, W_2, W_3 and $\phi 1$, $\phi 2$, 3 are the weight fractions and volume fractions of the pure components in liquid mixtures, which can be calculated from the relation

$$W_i=\frac{\phi_i\rho_i}{\rho_m}=\frac{x_iM_i}{M_{mix}}=\frac{x_iM_i}{\sum x_iM_i} \qquad (3)$$

The volume fraction is obtained as

$$\phi_i=\frac{c_i}{\rho_i} \qquad (4)$$

Gladstone-Dale [G-D] relation:

It can be expressed as,

$$(n_m-1)=\phi_1(n_1-1)+\phi_2(n_2-1)+\ldots \qquad (5)$$

$$\frac{n_m}{\rho_m}=\left[\frac{(n_1-1)}{\rho_1}\right]W_1+\left[\frac{(n_2-1)}{\rho_2}\right]W_2+\left[\frac{(n_3-1)}{\rho_3}\right]W_3 \qquad (6)$$

ing (1-ϕ_1) in

$$\left[\frac{(n_m^2-1)}{(n_m^2+2)}-\frac{(n_1^2-1)}{(n_1^2+2)}\right]=\left[\frac{(n_2^2-1)}{(n_2^2+2)}-\frac{(n_1^2-1)}{(n_1^2+2)}\right]\phi_2+\left[\frac{(n_3^2-1)}{(n_3^2+2)}-\frac{(n_1^2-1)}{(n_1^2+2)}\right]\phi_3 \qquad (7)$$

$$\left[\frac{(n_m^2-n_1^2)}{(n_m^2+2n_1^2)}\right]=\left[\frac{(n_2^2-n_1^2)}{(n_2^2+2n_1^2)}\right]\phi_2+\left[\frac{(n_3^2-n_1^2)}{(n_3^2+2n_1^2)}\right]\phi_3 \qquad (8)$$

It is clear from the above discussion that both Wiener and L-L relations give the same results if solution is ideal.

Heller's (H) relation:

Heller relation can be obtained by substituting $n_2 / n_1 = m_1$ and $n_3 / n_2 = m_2$ assuming $n_m \approx n_1$ in the above mentioned Wiener relation (8)

$$\left[\frac{(n_m-n_1)(n_m+n_1))}{(n_m^2+2n_1^2)}\right]=\left[\frac{(n_2^2/n_1^2-1)}{(n_2^2/n_1^2+2)}\right]\phi_2+\left[\frac{(n_3^2/n_1^2-1)}{(n_3^2/n_1^2+2)}\right]\phi_3$$

on rearranging the above equation, we get Heller's relation
The basis of the above equation is the Debye equation of light scattering.

$$\frac{n_m - n_1}{n_1} = \frac{3}{2}\left[\left\{\phi_2\left(\frac{m_1^2-1}{m_1^2+2}\right)\right\} + \left\{\phi_3\left(\frac{m_2^2-1}{m_2^2+2}\right)\right\}\right] \quad (9)$$

e. ϕ_i

$$\phi_i = \frac{V_i}{\sum V_i}$$

Arago-Biot proposed independently a relation for the evaluation of refractive index of binary and multicomponent liquid mixtures assuming volume additivity, which is given below

$$n_m = \phi_1 n_1 + \phi_2 n_2 + \ldots \quad (10)$$

Eykman's (Eyk) relation:

It can be expressed as

$$\left[\frac{n_m^2-1}{n_m+0.4}\right] = \left[\frac{n_1^2-1}{n_1+0.4}\right]\frac{V_1}{V_m} + \left[\frac{n_2^2-1}{n_2+0.4}\right]\frac{V_2}{V_m} + \left[\frac{n_3^2-1}{n_3+0.4}\right]\frac{V_3}{V_m} \quad (11)$$

aning.

Oster (Os) relation:

Refractive index of mixture can be computed using Os relation as

$$\left[\frac{(n_m^2-1)(2n_m^2+1))}{n_m^2}\right] = \left[\frac{(n_1^2-1)(2n_1^2+1)}{n_1^2}\right]\phi_1 + \left[\frac{(n_2^2-1)(2n_2^2+1)}{n_2^2}\right]\phi_2 \quad (12)$$

The molar refraction (R_m) can be calculated from refractive index values using the relation[16]

$$R_m = \frac{n^2-1}{n^2+2}V_m \quad (13)$$

$$V_m = \frac{\sum x_i M_i}{\rho_m}$$

n the x_1 mixture

The deviation in molar refraction, ΔR_m can be evaluated from the expression

$$\Delta R_m = R_m - \sum R_{m,i} x_i \quad (14)$$

where $R_{m,i}$ is the molar refraction of pure component i.
The deviation in refractive index has been calculated using equation

$$\Delta n = n_m - n_{id} \quad (15)$$

where n_m is the refractive index of mixture and n_{id} is the ideal refractive index, which can be obtained as,

$$n_{id} = \sum x_i n_i \qquad (16)$$

The values of Δn and ΔRm of all binary mixtures have been fitted by least square method using Redlich-Kister type polynomial equation

$$Y^E = x(1-x)\sum_{i=0}^{n} A_i (1-2x)^i \qquad (17)$$

where Y^E may be Δn or ΔRm

The values of the coefficients A_i of the above equation were obtained by the least square fit. The standard deviations were calculated using equation,

$$\sigma(Y^E) = \left[\sum Y^E_{obs} - Y^E_{cal} / (m-n)\right]^{1/2} \qquad (18)$$

where m is the total number of experimental points and n is the number of coefficients considered (n = 5) in the present calculation.

Results and discussion

The experimental values of refractive index (n), change in refractive index (Δn) and change in molar refraction (ΔR_m) upon mixing were calculated using experimental data of refractive indices of two binary solutions viz. ethanol+hexane and ethanol+dodecane and one ternary solution namely ethanol+hexane+decane at 308.15K. The results are summarized in tables 1, 2 and 3 respectively. The refractive index has also been computed theoretically using various mixing rules viz. L-L, G-D, W, H, A-B, Eyk and Os for the same solutions at 308.15K and reported in table 1. The results of computation of refractive index using various mixing rules have been discussed in terms of average percentage deviations (APD).

The values of change in refractive index (Δn) and change in molar refraction (ΔR_m) upon mixing were fitted to Redlich-Kister polynomial type equation. The coefficients A_i and standard deviations were estimated by least square method and listed in table 4.

A careful study of table 1 shows that for the system ethanol+hexane, the values of change in refractive index and change in molar refraction are negative over the entire composition range, except two mole fractions (x_1= 0.1259 and 0.3513), the values of Δn are positive.

As table 2 shows that for the system ethanol+dodecane, both positive and negative values of Δn and ΔR_m were obtained. It is also observed that the magnitudes of Δn and ΔR_m are greater in system ethanol+dodecane than those of system ethanol+hexane. It may be due to the increase in size of alkane molecules.

For ternary system (table 3) viz. ethanol+hexane+decane, the values of Δn and ΔR_m are positive over the entire range of concentration. But ΔR_m values are negative at two mole fractions (x1=0.7173 and 0.9441).

The deviation in molar refraction, ΔR_m gives more information than the change in refractive index (Δn), about the mixture process because it takes into account the electronic perturbation of molecular orbital during liquid mixture process,[4] and molar refraction is also directly related to the dispersion forces. The positive values of ΔR_m for mixtures indicate towards the higher dispersion forces in the mixtures than in pure liquids, whereas negative ΔR_m values of mixtures indicate that the dispersion forces are lower in the mixtures than in pure liquids.[10]

The results of refractive index calculated theoretically using various mixing rules for two binary and one ternary mixtures have been analysed in terms of average percentage deviations (APD) deviations which are tabulated in tables 1, 2 and 3. A comparison of experimental results of refractive index, and the results obtained from various mixing rules indicate that there is a good agreement between the experimental and theoretical values. For the system ethanol+hexane the order of APD is H<G-D<Eky<L-L<Os<W<A-B, whereas for system ethanol+dodecane the order is as follows H<G-D<Eyk<Os<L-L<W<A-B. The order of APD shows that H,G-D and Eky mixing rules provide excellent agreement with the experimental values than the other relations, but the deviations resulted from other relations are not out of the experimental precision. It is also observed that the magnitude of APD for system ethanol+dodecane is higher than the system ethanol+hexane like the magnitude of Δn and ΔR_m.

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Table - 2

Values of refractive indices, change in refractive indices (Δn) and change in molar refraction (ΔR_m) upon mixing for ethanol+dodecane solution at 308.15K

x_1	n_{exp}	$R_{m,exp}$	Δn	ΔR_m	L	-D	W	H	A-B	Eyk	Os
0.2989	1.4145	44.9602	0.0154	0.3364	1.4	107	1.4110	1.4107	1.4111	1.4111	1.4111
0.4002	1.4083	40.0709	0.0153	0.0193	1.4081	1.4076	1.4082	1.4078	1.4082	1.4082	1.4083
0.5001	1.3945	34.7612	0.0075	-0.7814	1.4045	1.4039	1.4047	1.4044	1.4048	1.4047	1.4049
0.5488	1.3855	32.0930	0.0014	-1.2514	1.4025	1.4017	1.4026	1.4024	1.4027	1.4027	1.4029
0.6001	1.3750	29.4801	-0.0060	-1.5489	1.4001	1.3992	1.4002	1.4000	1.4003	1.3976	1.3981
0.6996	1.3551	24.3195	-0.0199	-2.2185	1.3943	1.3935	1.3945	1.3943	1.3946	1.3919	1.3924
0.8001	1.3429	19.8785	-0.0261	-2.1234	1.3863	1.3858	1.3865	1.3864	1.3866	1.3843	1.3848
0.9002	1.3508	16.5330	-0.0122	-0.9508	1.3749	1.3747	1.3750	1.3750	1.3751	1.3736	1.3740
0.9502	1.3670	15.2586	0.0070	0.0316	1.3670	1.3669	1.3671	1.3671	1.3672	1.3663	1.3665
				APD	-1.1286	-0.0109	-1.1378	-0.0112	-1.1436	-1.0577	-1.0789

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Table - 1

Values of refractive indices, change in refractive indices (Δn) and change in molar refraction (ΔR_m) upon mixing for ethanol+hexane solution at 308.15K

x_1	n_{exp}	$R_{m,exp}$	Δn	ΔR_m	L-L	G-D	W	H	A-B	Eyk	Os
0.0486	1.3710	29.3624	-0.0003	-0.0039	1.3717	1.3738	1.3717	1.3716	1.3717	1.3711	1.3711
0.1529	1.3700	27.5115	0.0003	-0.0583	1.3709	1.3728	1.3709	1.3709	1.3709	1.3709	1.3709
0.3513	1.3670	24.0312	0.0003	-0.1213	1.3691	1.3703	1.3691	1.3691	1.3691	1.3691	1.3691
0.5001	1.3640	21.4127	-0.0005	-0.1769	1.3674	1.3683	1.3674	1.3674	1.3674	1.3674	1.3674
0.6472	1.3620	18.9046	-0.0003	-0.1513	1.3652	1.3663	1.3652	1.3652	1.3653	1.3652	1.3653
0.7996	1.3590	16.2933	-0.0010	-0.1377	1.3624	1.3639	1.3624	1.3624	1.3624	1.3624	1.3624
0.9469	1.3570	13.8342	-0.0008	-0.0580	1.3587	1.3602	1.3587	1.3587	1.3587	1.3587	1.3587
				APD	-0.1598	-0.0027	-0.1603	-0.0016	-0.1607	-0.1544	-0.1557

Table - 3

Values of refractive indices, change in refractive index (Δn) and change in molar refraction (ΔRm) upon mixing for the system ethanol+hexane+decane at 308.15K

x_1	x_2	n_{exp}	R_{mexp}	Δn	ΔR_m	L-L	G-D	W	H	A-B	Eyk	Os
0.0492	0.2480	1.4020	42.5922	0.0061	0.2157	1.4069	1.3998	1.3998	1.3873	1.3998	1.3934	1.3941
0.1826	0.2132	1.4000	38.4332	0.0096	0.1812	1.3905	1.3962	1.3962	1.3849	1.3962	1.4032	1.4026
0.3298	0.1748	1.3980	34.0304	0.0136	0.3294	1.3809	1.3922	1.3921	1.3821	1.3922	1.4045	1.4035
0.4715	0.1378	1.3950	29.7050	0.0164	0.3844	1.3694	1.3873	1.3872	1.3788	1.3873	1.4069	1.4052
0.6265	0.0974	1.3850	24.5578	0.0127	0.0301	1.3533	1.3804	1.3804	1.3740	1.3804	1.4121	1.4093
0.7175	0.0737	1.3770	21.4299	0.0085	-0.2835	1.3415	1.3753	1.3753	1.3705	1.3753	1.4180	1.4141
0.9441	0.0146	1.3640	14.6922	0.0047	-0.0150	1.3001	1.3575	1.3575	1.3581	1.3575	1.4302	1.4231
					APD	2.3506	0.7896	0.7902	1.1346	0.7896	-1.5699	-1.3722

Table - 4

Parameters of equation (17) and standard deviations

Ethanol+hexane

	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
Δn	0.0025	0.0098	-0.0074	-0.0046	-0.0106	0.0001
ΔR_m	-0.6438	0.0412	-0.1762	0.6709	0.219	0.009

Ethanol+dodecane

	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
Δn	0.0318	0.2216	-0.3474	-0.1024	0.3481	0.0006
ΔR_m	-0.3089	2.2949	-3.7473	-0.7115	7.5684	0.0048