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Theoretical Evaluation of Refractive Index in Binary Liquid Mixtures

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Abstract: The density and refractive index (RI) for four binary liquid mixtures : diethyl malonate + dimethylformamide (DEM+DMF), diethyl malonate + Hexane (DEM + HEX), diethyl malonate + tetrahydrofuran (DEM+ THF), diethyl malonate + 1,4-dioxane (DEM+DO) have been measured. The experimental values are compared with those calculated from Lorentz-Lorentz, Heller, Newton and Gladstone – Dale mixing rules.

Key words: Theoretical Evaluation , Refractive Index, Binary Liquid Mixtures

Introduction

A literature survey shows that physicochemical properties of various liquid mixtures have been studied by several workers[1-5]. It has been reported that refractive index measurement in combination with density, boiling point, melting point and other analytical data are useful industrially[6]. Various empirical and semi-empirical relation have been used to predict refractive index in binary systems[7-10]. The validity of these mixing rules has been tested for some binary systems by few researchers[11,12].

Experimental

All the solvents were of Analar grade and their purity was greater than 99%. The purity was checked by density and RI values of pure liquids with those reported in literature[13]. The values for pure liquids are given in **Table 1**.The mixtures were prepared (v/v) in air tight stoppered bottles to minimize evaporation losses. Densities and refractive index of all the mixtures were measured by pykuometer and Abbe's refractometer with an accuracy of $\pm$0.0001 gm and $\pm$0.0005 respectively.

Results and Discussion

The experimental refractive index and density of four binary mixtures are given in **Table 2**.
From the following mixing rules, refractive index for all the mixtures was calculated:

Table-1. Refractive index of pure liquids at 303.15K.

Liquid	DEM	HEX	THF	DO	DMF
RI	1.405	1.361	1.388	1.400	1.412

Table 2. Experimental and Theoretical values of refractive index of binary liquid systems at 303.15K

		Hexane			
			RI		
X_{DEM}	**Exptl**	**LL**	**N**	**H**	**GD**
0.1051	1.3770	1.3651	1.3652	1.3650	1.3664
0.2137	1.3800	1.3692	1.3694	1.3692	1.3694
0.3072	1.3830	1.3726	1.3728	1.3726	1.3719
0.4035	1.3845	1.3760	1.3762	1.3761	1.3662
0.5026	1.3860	1.3794	1.3796	1.3795	1.3537
0.6048	1.3930	1.3828	1.3830	1.3829	1.3569
0.7102	1.3985	1.3862	1.3864	1.3863	1.3874
0.7979	1.4020	1.3890	1.3891	1.3890	1.4027
0.9088	1.4040	1.3923	1.3924	1.3923	1.3935
		THF			
0.0656	1.3900	1.3888	1.3888	1.3888	1.3906
0.1514	1.3905	1.3898	1.3898	1.3897	1.3915
0.2431	1.3910	1.3906	1.3906	1.3906	1.3928
0.3486	1.3915	1.3915	1.3915	1.3915	1.3937
0.4714	1.3920	1.3924	1.3924	1.3924	1.3945
0.5777	1.3925	1.3930	1.3930	1.3930	1.3949
0.7893	1.3935	1.3941	1.3941	1.3941	1.3969
0.8892	1.3945	1.3946	1.3946	1.3946	1.3967
		1,4-dioxane			
0.0968	1.3995	1.3992	1.3992	1.3992	1.3992
0.1943	1.3990	1.3985	1.3985	1.3985	1.3983
0.2524	1.3985	1.3981	1.3981	1.3981	1.3976
0.3601	1.3980	1.3975	1.3975	1.3975	1.3987
0.4840	1.3975	1.3969	1.3969	1.3969	1.3980
0.6280	1.3970	1.3962	1.3962	1.3962	1.3970
0.7975	1.3960	1.3956	1.3956	1.3956	1.3971
0.8941	1.3955	1.3953	1.3953	1.3953	1.3971
		DMF			
0.1130	1.4215	1.4086	1.4086	1.4086	1.4111
0.1935	1.4200	1.4065	1.4066	1.4065	1.4091
0.3200	1.4170	1.4038	1.4038	1.4040	1.4064
0.3935	1.4150	1.4024	1.4025	1.4024	1.4037
0.4974	1.4120	1.4007	1.4008	1.4007	1.4032
0.6175	1.4100	1.3990	1.3991	1.3991	1.4001
0.7280	1.4085	1.3977	1.3977	1.3977	1.3998
0.8210	1.4075	1.3966	1.3967	1.3966	1.3990
0.9244	1.4070	1.3957	1.3957	1.3957	1.3977

1. Lorentz-Lorentz (L-L): It is given by:

$$(n^2_{12}-1)/(n^2_{12}+2) = \phi_1 (n^2_1-1/n^2_1+2) + \phi_2 (n^2_2-1)/(n^2_2+2)$$

where n_{12} is refractive index of the mixture, n_1 and n_2 are refractive indices of pure components 1 and 2 respectively. ϕ_1 and ϕ_2 are volume fractions of components 1 and 2 respectively and is given by :

$$\phi_i = x_i Vi/\sum x_i V_i$$

where x_i and V_i are the mole fraction and molar volume of i^{th} constituent of binary mixture.

2. Newton relation (N):

It applies to isotropic bodies of spherically symmetrical shape and proposes volume additivity and is given by:

$$(n^2_{12}-1) = (n^2_1-1)\phi_1 + (n^2_2-1)\phi_2$$

3. Heller relation (H):

It is based on light scattering equation of Debye and Rayleigh and is given by

$$(n_{12}-n_1)/n_1 = 3/2\,\phi_2 ((n_2/n_1)^2-1)/((n_2/n_1)^2+2)$$

4. Gladstone – Dale equation : It is given by:

$$(n_{12}-1)/\rho_{12} = (n_1-1/\rho_1) w_1 + (n_2-1/\rho_2) w_2$$

where ρ_{12} is the density of liquid mixture. ρ_1, w_1 and ρ_2, w_2 are the density and weight fraction of pure components 1 and 2 respectively.

Using these four mixing rules of Lorentz-Lorentz, Newton, Heller and Gladstone – Dale, refractive index for all the binary liquid mixtures has been evaluated and are reported in **Table 2**. It is observed from **Table 2** that the values of refractive index calculated by Lorentz-Lorentz, Heller and Newton mixing rules are almost same for all the four systems. However, slight variation is observed in theoretical values calculated by Gladstone- Dale equation.

The experimental values of refractive index are compared with the predicted results from the above mentioned mixing rules and the average % deviations were determined and are given in **Table 3**.

Table-3. Percentage deviation between theoretical and experimental values of refractive index of binary liquid systems at 303.15K

		% Deviation		
		Hexane		
X_{DEM}	LL	N	H	GD
0.1051	0.8633	0.8569	0.8687	0.7706
0.2137	0.7813	0.0768	0.7833	0.7720
0.3072	0.7496	0.0738	0.7495	0.8050
0.4035	0.6110	0.0599	0.6092	1.3189
0.5026	0.4733	0.0462	0.4705	2.3335
0.6048	0.7297	0.0718	0.7266	2.5908
0.7102	0.8778	0.0865	0.8748	0.7935
0.7979	0.9300	0.0920	0.9275	0.0465
0.9088	0.8319	0.0826	0.8365	0.7450
		THF		
0.0656	0.0855	0.0855	0.0857	-0.0635
0.1514	0.0539	0.0539	0.0540	-0.0699
0.2431	0.0269	0.0269	0.0269	-0.1282
0.3486	0.0034	0.0034	0.0000	-0.1587
0.4714	-0.0269	-0.0269	0.0270	-0.1776
0.5777	0.0038	0.0038	0.0383	-0.1730
0.7893	-0.0448	-0.0448	0.0449	-0.2441
0.8892	-0.0045	-0.0045	0.0045	-0.1582

		1,4-dioxane		
0.0982	0.0218	0.0218	0.0219	0.0243
0.1997	0.0364	0.0364	0.0364	0.0488
0.2524	0.0275	0.0275	0.0275	0.0652
0.3601	0.0365	0.0365	0.0364	-0.0512
0.4840	0.0454	0.0454	0.0454	-0.0374
0.6280	0.0542	0.0542	0.0542	0.0009
0.7975	0.0272	0.0272	0.0271	-0.0787
0.8941	0.0136	0.0136	0.0136	-0.1116
		DMF		
0.1130	0.9075	0.9075	0.9075	0.7316
0.1935	0.9507	0.9526	0.9507	0.7676
0.3200	0.9315	0.9315	0.9174	0.7480
0.3935	0.8904	0.8912	0.8904	0.7986
0.4974	0.8003	0.7932	0.8003	0.6232
0.6175	0.7801	0.7730	0.7730	0.7021
0.7280	0.7668	0.7668	0.7668	0.6177
0.8210	0.7744	0.7673	0.7744	0.6039
0.9244	0.8031	0.8031	0.8031	0.6610

It is evident from **Table 3** that in all these systems, there is good agreement between experimental and theoretical values of refractive index calculated by four different mixing rules. Comparison of deviations in the four systems shows that deviation is higher in DEM+HEX and DEM+DMF systems than those in DEM+THF and DEM+DO systems. Excellent agreement between theoretical and experimental values is observed in DEM+DO system followed by DEM+THF system. In both 1,4-dioxane and THF, there is ring structure which may be responsible for minimum deviation in these systems. In DEM+THF system, the values calculated by Gladstone-Dale mixing rule are found to be negative whereas in DEM+DO system, the values are positive at low X_{DEM} and then become negative. However, in DEM+HEX and DEM+DMF systems, positive deviations are observed between experimental and theoretical values calculated from Gladstone-Dale relation.

Thus, from the above investigation, it can be concluded that the above mentioned theoretical mixing rules perform well within the limits of experimental error. The deviation between the theoretical and observed values of refractive index for all the systems can be reduced by taking excess volume in to consideration [14], which is an indirect measure of interaction.

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