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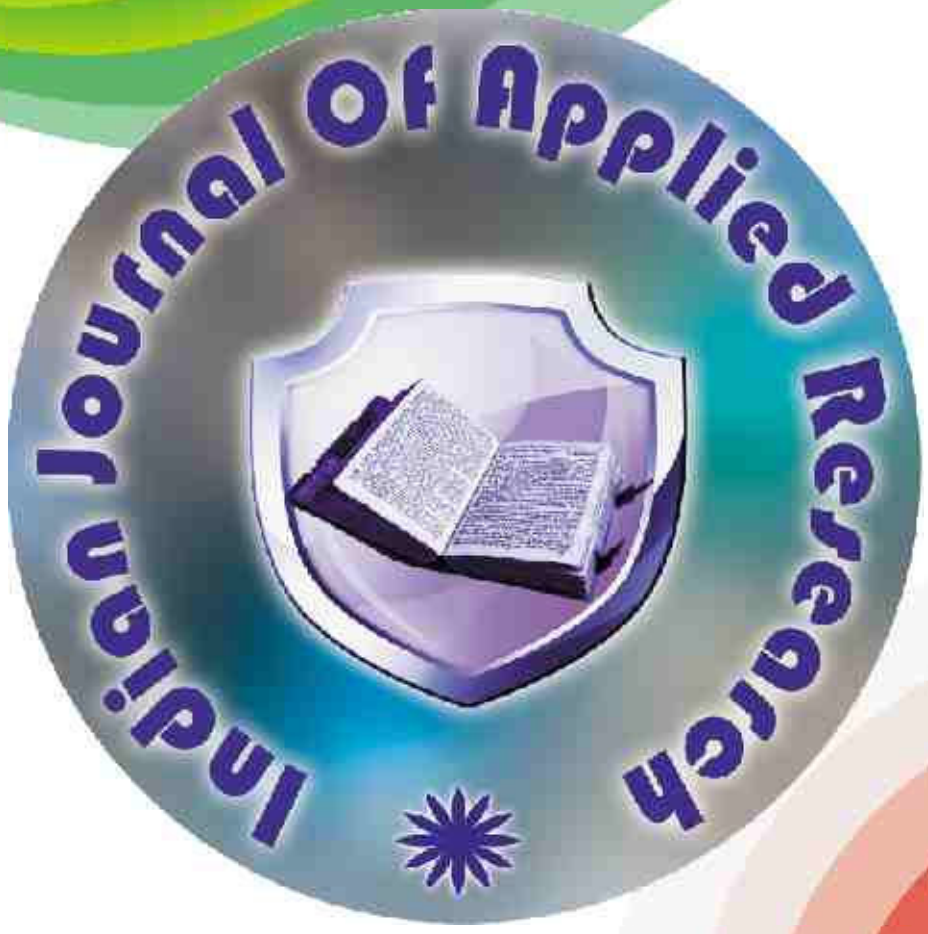

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Research Paper Physics

Study Of Refractive Index And Excess Parameters For Different Liquid Mixtures At Different Temperatures

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ABSTRACT

Refractive index and density have been measured at (293,298,303) K for binary mixtures of 1,4-Dioxane + Ethyl Ethanoate, + Ethanoic Acid, + Butanol over the whole mole fraction range. From these data the excess molar volume, excess molar refraction and excess refractive index were calculated. These quantities are discussed in terms of intermolecular interactions.

Keywords : Refractive index, density, excess parameters, intermolecular interactions.

Introduction

The organic polar and non polar compounds are quite useful in various applications. The studies of organic liquids and liquid mixtures provide a deep knowledge into the molecular structures, which includes the molecular interactions between the molecules of liquid mixtures [1-10]. As a part of our research programme, we present here the experimental results of the refractive index, nm , and the density, ρ , for the binary mixtures of 1,4-Dioxane (D) with Ethyl Ethanoate (EE), Ethanoic Acid (EA) and Butanol (B) at (293,298,303)K over the whole mole fraction range. From these results, the excess molar volume (V^E), excess molar refraction (R^E) and excess refractive index (Δn_m) have been calculated over the whole mole fraction range, from which valuable information about intermolecular interactions between the components can be deduced. The interaction between organic liquids with 1, 4-Dioxane has been carried out by many workers [11-20] but, to the best of our knowledge, a systematic study of a series of liquid mixtures taking under consideration here, with temperature range (293,298,303) K is not present in literature.

Experimental Section

The refractive index of mixtures was measured using Abbe refractometer [13,21]. Before measuring refractive index on Abbe refractometer inspection of scale was made using test piece. The refractometer was calibrated with distilled water before each use. The temperature was maintained constant with the help of thermostatically controlled water bath (accuracy ±0.01K). Our refractive indices are accurate up to ±.0001. The sample mixtures were directly injected into prism assembly of the instrument with the help of a plastic syringe. An average of three measurements was taken for a sample mixture.

The densities were measured with a bicapillary pycnometer having a bulb volume of about 10 cm^3 and an internal diameter of about 1mm. The pycnometer was calibrated at (293,298,303) K with doubly distilled water. The reproducibility of the density measurements was $\pm 3\times10^{-4}$ $gmcm^{-3}$. The pycnometer was immersed in water bath whose temperature was maintained constant by circulating the coolant liquid. All measurements were repeated three times, and then average values were calculated. The chemicals used were of AR/BDH grade. All the chemicals were purified by standard procedures discussed by Perrin and Armarego [23] before use.

Theory

The various physical parameters were calculated from the measured values of refractive index (n_m) and density (ρ) using the following formulae:

Excess molar volume

$$V^E = \left(\frac{X_1M_1 + X_2M_2}{\rho}\right) - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \quad (1)$$

Excess molar refraction

$$R^E = \frac{(n_m^2-1)}{(n_m^2+2)}\left(\frac{X_1M_1+X_2M_2}{\rho}\right) - \left[\frac{(n_1^2-1)}{(n_1^2+2)}\frac{M_1}{\rho_1}\phi_1 + \frac{(n_2^2-1)}{(n_2^2+2)}\frac{M_2}{\rho_2}\phi_2\right] \quad (2)$$

Excess refractive index

$$\Delta n_m = n_m - (x_1 n_1 + x_2 n_2) \quad (3)$$

Where X1 and X2 are mole fractions of respective components; ρ, ρ1, and ρ2 are the densities and nm, n1 and n2 are the measured refractive indices of the mixture and the pure component liquids, respectively. M1, M2 are the molecular weights and ϕ_1, ϕ_2 are volume fractions of respective components in liquid mixtures.

Results

Experimentally find out densities (ρ), refractive indices (n_m) and calculated values of excess molar volume (V^E), excess molar refraction (R^E) and excess refractive index (Δn_m) for system (D+EE), (D+EA) and (D+B) are given in Table 1 to 3 respectively. Values of V^E and R^E for system (D+EE), (D+EA) and (D+B) at T=293 K are plotted with respect to mole fraction of 1,4-Dioxane (X_1) and shown in Fig. 1 and 3, respectively. The variation of V^E and R^E with mole fraction of 1,4-Dioxane (X_1) for system (D+EE) for all the three temperatures viz. 293K, 298K, 303K is shown graphically in Fig. 2 and 4 respectively. Density is expressed in gm cm^{-3} and excess molar volume and excess molar refraction in cm^3 mol^{-1}.

Discussion

Excess parameters provide information about intermolecular interactions to the great extent, the negative values of excess molar volume V^E indicates about the presence of strong intermolecular interactions in the system. There are mainly three factors viz. physical, chemical and structural, which makes positive and negative contributions to the resultant value of excess molar volume and magnitude of contribution depends on mole fraction range [17]. Physical contribution includes non specific physical contribution. Chemical effect appears due to breaking up of the liquid order of associated species. The Structural effects appear due to geometrical fittings of molecules having comparatively small size into the voids created by molecules having comparatively large size. The differences in molar and free volumes are also responsible for structural effect. From figure (1) it is observed that excess molar volume V^E have negative values for mixture (D+EE) and (D+EA) and positive values for system (D+B) over the entire range of mixture composition, for all the selected values of temperature. The large negative values of V^E for mixture (D+EA) over (D+EE) indicate the presence of strong intermolecular interaction in the system (D+EA) in comparison to (D+EE). This may be due to fitting of comparatively smaller molecules of EA (molar volume 57.2505 cm^3 mol^{-1} at 293K) into the voids created by molecules of 1,4-dioxane having comparatively large size (molar volume 84.9759 cm^3 mol^{-1} at 293K). For EE, molar volume at 293K is 98.4801cm^3mol^{-1}. Hence structural effect plays important role for strong intermolecular interaction in system (D+EA). The positive values of V^E for system (D+B) may be due to breaking up of the liquid order i.e. breaking up of the intermolecular hydrogen bonding between Butanol molecules with possible new hydrogen bonding with 1,4-dioxane molecules. The effect of temperature on excess molar volume for system (D+EA) is shown in figure (2). It is observed that excess molar volume decreases systematically with increasing temperature. Similar trends are found for system (D+EE) and (D+B) also.

Excess molar refraction represents the complex electronic perturbation between liquid components due to orbital mixing of components. Excess molar refraction, R^E, gives the strength of interaction in a mixture and is sensitive function of mixture composition along with temperature and wavelength [23,24]. From figure (3) it is observed that excess molar refraction R^E have negative values for mixture (D+EE) and (D+EA) while positive values for system (D+B) over the entire range of mixture composition, for all the selected values of temperatures. The negative values of R^E for system (D+EE) and (D+EA) indicates about strong intermolecular interactions between molecules. The order of negative values of R^E is (D+EA) > (D+EE), similar behavior is found for V^E earlier; hence, this again confirms the existence of strong intermolecular interactions for system (D+EA) over (D+EE). Figure (4) represents the effect of temperature on R^E for system (D+EA). It is observed that excess molar refraction R^E decreases systematically with increasing temperature similar behavior is found for V^E earlier.

Excess refractive index have negative values for system (D+EE) and (D+B) while it has positive values for system (D+EA) over the entire range of mixture composition and for all the selected values of temperatures. It is observed that excess refractive index have very small values which are close to zero. With mole fraction of 1,4-Dioxan(X_1) the negative values of excess refractive index, first, increases then it attains a maximum and thereafter it becomes decreases for system (D+EE) and (D+B), similar behavior is observed for system (D+EA).

Conclusions

Thus from above mentioned discussion, it may be concluded that investigation about the molecular association for liquid mixtures may be studied with the refractometric study of liquid mixtures. This type of investigation provides a better insight for a comprehensive investigation of intermolecular interactions between molecules of mixtures. The variation of excess parameters with concentration and temperature strongly supports the molecular association in these liquid mixtures. This type of result if of much importance for developing mixing rules for mixtures.

Figure1: Excess molar volume vs. mole fraction for mixtures of 1,4Dioxane(X1) with Ethyl Ethanoate ,Ethanoic Acid and Butanol at293K

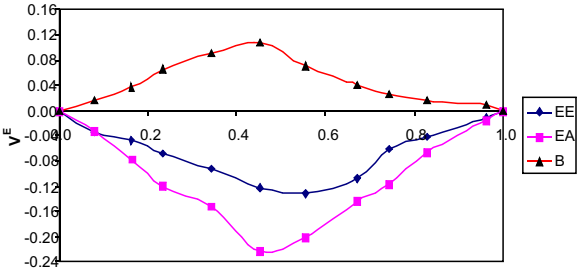

Figure 2 Effect of temperature on excess molar volume for mixture 1,4 Dioxane (X1) with Ethanoic Acid

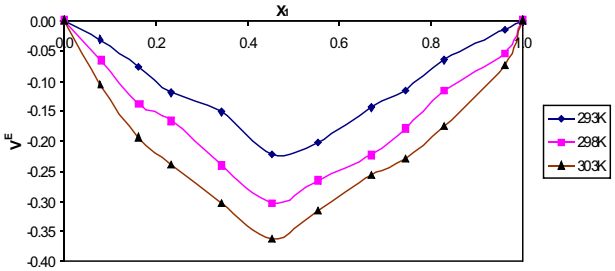

Figure 3 Excess molar refraction vs. mole fraction for mixtures of 1,4Dioxane (X1) with Ethyl Ethanoate, Ethanoic Acid and Butanol at 293K

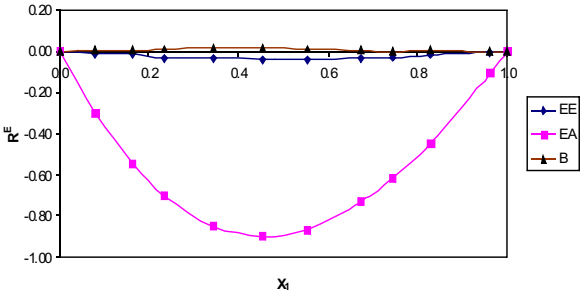

Figure 4 Effect of temperature on excess molar refraction for mixture 1,4Dioxane(X1) with Ethanoic Acid

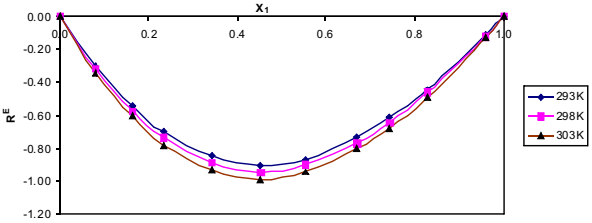

TABLE 1 Refractive index (nm),density (ρ),excess molar volume (VE), excess molar refraction (RE), excess refractive index(Δnm) for mixture 1,4-Dioxane and Ethyl Ethanoate at temperature 293K, 298K, 303K as a function of the mole fraction X1 of 1,4-Dioxane

T	X_1	ρ (g cm $^{-3}$)	n_m	V^E (cm^3 mol^{-1})	R^E (cm^3 mol^{-1})	Δn_m
293K	0.0000	0.8948	1.3711	0.0000	0.0000	0.0000
	0.0660	0.9033	1.3741	-0.0336	-0.0130	-0.0005
	0.1620	0.9156	1.3787	-0.0473	-0.0157	-0.0010
	0.2670	0.9295	1.3836	-0.0680	-0.0334	-0.0016
	0.3582	0.9420	1.3883	-0.0927	-0.0335	-0.0017
	0.4798	0.9591	1.3945	-0.1218	-0.0435	-0.0020
	0.5950	0.9757	1.4007	-0.1320	-0.0420	-0.0019
	0.6590	0.9849	1.4042	-0.1073	-0.0364	-0.0018
	0.7710	1.0013	1.4103	-0.0609	-0.0316	-0.0016
	0.8600	1.0149	1.4156	-0.0418	-0.0163	-0.0010
	0.9200	1.0241	1.4191	-0.0120	-0.0089	-0.0007
	1.0000	1.0370	1.4240	0.0000	0.0000	0.0000
298K	0.0000	0.8939	1.3698	0.0000	0.0000	0.0000
	0.0660	0.9020	1.3727	-0.0426	-0.0124	-0.0004
	0.1620	0.9136	1.3770	-0.0563	-0.0198	-0.0009
	0.2670	0.9267	1.3817	-0.0770	-0.0356	-0.0015
	0.3582	0.9384	1.3862	-0.1017	-0.0334	-0.0016
	0.4798	0.9545	1.3920	-0.1308	-0.0494	-0.0019
	0.5950	0.9701	1.3980	-0.1410	-0.0441	-0.0017
	0.6590	0.9786	1.4011	-0.1163	-0.0474	-0.0018
	0.7710	0.9939	1.4072	-0.0699	-0.0281	-0.0014
	0.8600	1.0066	1.4121	-0.0508	-0.0203	-0.0010
	0.9200	1.0152	1.4155	-0.0210	-0.0104	-0.0006
	1.0000	1.0270	1.4201	0.0000	0.0000	0.0000
303K	0.0000	0.8932	1.3685	0.0000	0.0000	0.0000
	0.0660	0.9008	1.3713	-0.0536	-0.0124	-0.0004
	0.1620	0.9116	1.3752	-0.0740	-0.0320	-0.0010
	0.2670	0.9237	1.3802	-0.0960	-0.0204	-0.0011
	0.3582	0.9345	1.3844	-0.1150	-0.0235	-0.0012
	0.4798	0.9493	1.3897	-0.1509	-0.0503	-0.0017
	0.5950	0.9636	1.3894	-0.1600	-0.3412	-0.0075
	0.6590	0.9714	1.3987	-0.1430	-0.0327	-0.0013
	0.7710	0.9853	1.4041	-0.0910	-0.0325	-0.0013
	0.8600	0.9967	1.4089	-0.0610	-0.0147	-0.0007
	0.9200	1.0044	1.4119	-0.0340	-0.0136	-0.0006
	1.0000	1.0150	1.4163	0.0000	0.0000	0.0000

TABLE 2 Refractive index (nm),density (ρ),excess molar volume (VE), excess molar refraction (RE), excess refractive index(Δnm) for mixture 1,4-Dioxane and Ethanoic Acid at temperature 293K, 298K, 303K as a function of the mole fraction X1 of 1,4-Dioxane

T	X_1	ρ (g cm $^{-3}$)	n_m	V^E (cm^3 mol^{-1})	R^E (cm^3 mol^{-1})	Δn_m
293 K	0.0000	1.0489	1.3722	0.0000	0.0000	0.0000
	0.0793	1.0481	1.3781	-0.0318	-0.2998	0.0018
	0.1620	1.0476	1.3837	-0.0770	-0.5462	0.0031
	0.2348	1.0471	1.3884	-0.1200	-0.7023	0.0040
	0.3430	1.0461	1.3947	-0.1520	-0.8493	0.0046
	0.4528	1.0457	1.4009	-0.2230	-0.9005	0.0051
	0.5538	1.0441	1.4058	-0.2010	-0.8668	0.0047
	0.6711	1.0419	1.4113	-0.1439	-0.7309	0.0041
	0.7440	1.0408	1.4145	-0.1160	-0.6114	0.0035
	0.8280	1.0393	1.4178	-0.0660	-0.4436	0.0025
	0.9612	1.0375	1.4229	-0.0150	-0.1106	0.0006
	1.0000	1.0370	1.4240	0.0000	0.0000	0.0000
298 K	0.0000	1.0471	1.3710	0.0000	0.0000	0.0000
	0.0793	1.0460	1.3765	-0.0660	-0.3201	0.0016
	0.1620	1.0449	1.3820	-0.1380	-0.5709	0.0030
	0.2348	1.0435	1.3863	-0.1660	-0.7341	0.0038
	0.3430	1.0420	1.3925	-0.2400	-0.8835	0.0047
	0.4528	1.0405	1.3980	-0.3020	-0.9467	0.0048
	0.5538	1.0378	1.4029	-0.2660	-0.8959	0.0047
	0.6711	1.0350	1.4079	-0.2230	-0.7685	0.0039
	0.7440	1.0331	1.4108	-0.1800	-0.6453	0.0033
	0.8280	1.0309	1.4141	-0.1150	-0.4616	0.0024
	0.9612	1.0282	1.4188	-0.0540	-0.1226	0.0006
	1.0000	1.0270	1.4201	0.0000	0.0000	0.0000
303 K	0.0000	1.0465	1.3701	0.0000	0.0000	0.0000
	0.0793	1.0447	1.3754	-0.1070	-0.3398	0.0016
	0.1620	1.0426	1.3806	-0.1940	-0.6058	0.0030
	0.2348	1.0404	1.3846	-0.2400	-0.7812	0.0037
	0.3430	1.0372	1.3905	-0.3020	-0.9308	0.0046
	0.4528	1.0343	1.3958	-0.3630	-0.9892	0.0048
	0.5538	1.0304	1.4002	-0.3160	-0.9429	0.0045
	0.6711	1.0261	1.4049	-0.2570	-0.8035	0.0038
	0.7440	1.0238	1.4077	-0.2300	-0.6771	0.0032
	0.8280	1.0210	1.4107	-0.1760	-0.4933	0.0023
	0.9612	1.0167	1.4151	-0.0740	-0.1307	0.0006
	1.0000	1.0150	1.4163	0.0000	0.0000	0.0000

TABLE 3 Refractive index (nm),density (ρ),excess molar volume (VE), excess molar refraction (RE), excess refractive index (Δnm) for mixture 1,4-Dioxane and Butanol at temperature 293K, 298K, 303K as a function of the mole fraction X1 of 1,4-Dioxane

T	X_1	ρ (g cm $^{-3}$)	n_m	V^E (cm^3 mol^{-1})	R^E (cm^3 mol^{-1})	Δn_m	T	X_1	ρ (g cm $^{-3}$)	n_m	V^E (cm^3 mol^{-1})	R^E (cm^3 mol^{-1})	Δn_m
293 K	0.0000	0.8091	1.3985	0.0000	0.0000	0.0000	303 K	0.0000	0.7995	1.3971	0.0000	0.0000	0.0000
	0.0750	0.8249	1.4003	0.0169	0.0021	-0.0001		0.0750	0.8146	1.3984	0.0120	-0.0017	-0.0001
	0.1850	0.8484	1.4030	0.0360	0.0062	-0.0003		0.1850	0.8370	1.4005	0.0273	0.0049	-0.0002
	0.2567	0.8638	1.4047	0.0640	0.0082	-0.0004		0.2567	0.8517	1.4018	0.0500	0.0071	-0.0002
	0.3550	0.8852	1.4072	0.0911	0.0171	-0.0005		0.3550	0.8721	1.4036	0.0731	0.0097	-0.0003
	0.4640	0.9095	1.4099	0.1072	0.0168	-0.0006		0.4640	0.8952	1.4057	0.0785	0.0124	-0.0003
	0.5390	0.9269	1.4119	0.0701	0.0117	-0.0005		0.5390	0.9116	1.4071	0.0485	0.0041	-0.0003
	0.6599	0.9552	1.4151	0.0400	0.0049	-0.0004		0.6599	0.9382	1.4095	0.0260	0.0013	-0.0003
	0.7580	0.9784	1.4176	0.0249	-0.0029	-0.0005		0.7580	0.9600	1.4114	0.0154	-0.0014	-0.0003
	0.8546	1.0015	1.4203	0.0157	0.0010	-0.0002		0.8546	0.9818	1.4133	0.0100	-0.0044	-0.0002
	0.9418	1.0227	1.4227	0.0094	0.0007	-0.0001		0.9418	1.0016	1.4151	0.0031	-0.0008	-0.0001
	1.0000	1.0370	1.4240	0.0000	0.0000	0.0000		1.0000	1.0150	1.4163	0.0000	0.0000	0.0000
298 K	0.0000	0.8017	1.3978	0.0000	0.0000	0.0000							
	0.0750	0.8173	1.3994	0.0146	0.0041	-0.0001							
	0.1850	0.8406	1.4016	0.0320	-0.0011	-0.0003							
	0.2567	0.8559	1.4032	0.0531	0.0053	-0.0003							
	0.3550	0.8771	1.4053	0.0760	0.0096	-0.0004							
	0.4640	0.9012	1.4077	0.0862	0.0108	-0.0004							
	0.5390	0.9184	1.4094	0.0560	0.0040	-0.0004							
	0.6599	0.9462	1.4122	0.0350	0.0031	-0.0003							
	0.7580	0.9691	1.4144	0.0215	-0.0010	-0.0003							
	0.8546	0.9920	1.4166	0.0100	-0.0045	-0.0003							
	0.9418	1.0129	1.4187	0.0044	-0.0016	-0.0001							
	1.0000	1.0270	1.4201	0.0000	0.0000	0.0000							

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