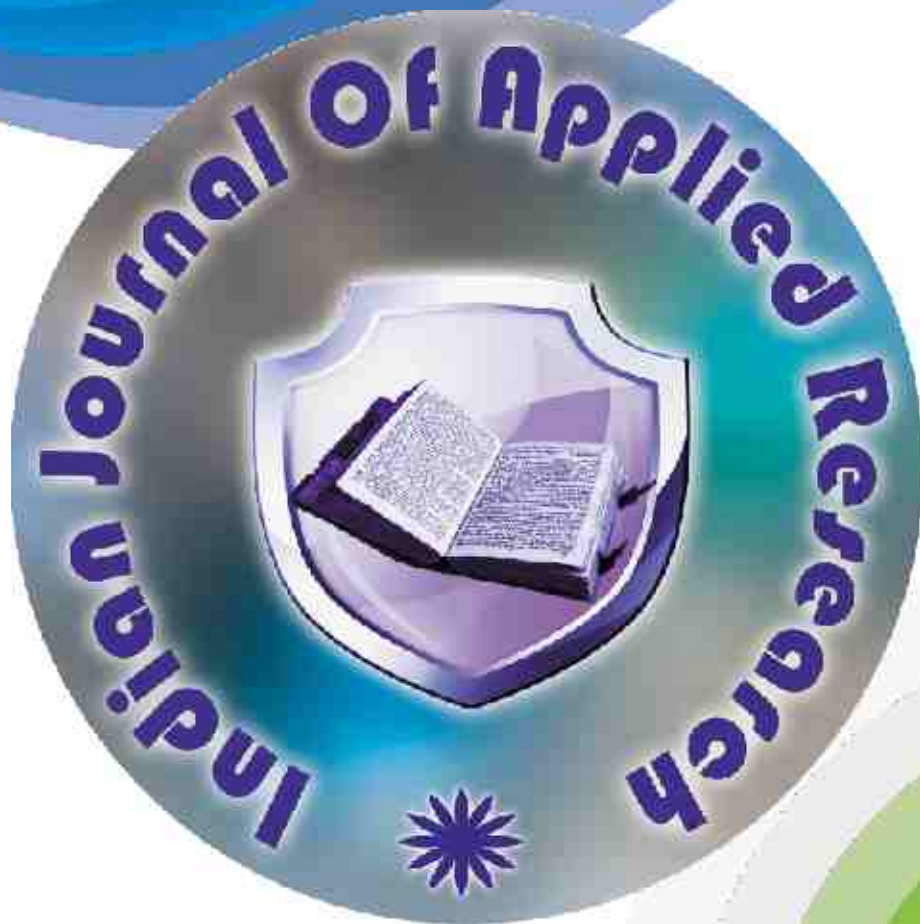


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Refractive Index, Density, Excess Molar Volume, Excess Molar Refraction For Liquid Mixtures (ethyl Ethanoate + Benzene Derivatives) At Different Temperatures

* Sheeraz Akbar ** Mahendra Kumar

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ABSTRACT

Refractive index and density have been measured at (293,298,303) K for binary mixtures of Ethyl Ethanoate + Benzene and its derivatives 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 investigation of molecular interaction in different types of liquid mixtures with varying temperatures and compositions helps to predict the behavior of molecules after mixing very clearly. The excess properties viz. excess molar volume; excess molar refraction and excess refractive index are of great importance in supplying valuable information about the intermolecular forces and the behavior of attached functional groups of molecules in solutions. The non-zero value of these parameters gives deep insight into the molecular interactions, arrangements and structural behavior. We present here the experimental results of the refractive index, n_m , and the density, ρ , for the binary mixtures of Ethyl Ethanoate (EE) with Benzene (BN), Toluene (T) and p-Xylene (X) 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.

Experimental Section

The refractive index of mixtures was measured using Abbe refractometer. 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 ± 0.01 K). Our refractive indices are accurate up to ± 0.0001 . The densities were measured with a bipycnometer 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 pycnometer was immersed in water bath whose temperature was maintained constant by circulating the coolant liquid.

Theory

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

$$V^E = \left(\frac{X_1 M_1 + X_2 M_2}{\rho} \right) - \left(\frac{X_1 M_1}{\rho_1} + \frac{X_2 M_2}{\rho_2} \right) \quad (1)$$

$$R^E = \frac{(n_m^2 - 1)}{(n_m^2 + 2)} \left(\frac{X_1 M_1 + X_2 M_2}{\rho} \right) - \left[\frac{(n_1^2 - 1)}{(n_1^2 + 2)} \frac{M_1}{\rho_1} \phi_1 + \frac{(n_2^2 - 1)}{(n_2^2 + 2)} \frac{M_2}{\rho_2} \phi_2 \right] \quad (2)$$

$$\Delta n_m = n_m - (X_1 n_1 + X_2 n_2) \quad (3)$$

Where X_1 and X_2 are mole fractions of respective components; ρ , ρ_1 , and ρ_2 are the densities and n_m , n_1 and n_2 are the measured refractive indices of the mixture and the pure component liquids, respectively. M_1 , M_2 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 V^E , R^E and Δn_m for binary mixtures (EE+BN), (EE+T) and (EE+X) are given in Table 1 to 3 respectively. Values of V^E and R^E for (EE+BN), (EE+T), and (EE+X) at $T=293 \text{ K}$ are plotted with respect to mole fraction of Ethyl Ethanoate (X_1) and shown in Fig. 1 and 3 respectively. The variation of V^E and R^E with mole fraction of Ethyl Ethanoate (X_1) for system (EE+BN) for all the three temperatures viz. 293K, 298K, 303K is shown graphically in Fig. 2 and 4 respectively.

Discussion

With the help of excess parameters we can investigate about the intermolecular interactions to the great extent. The negative values of V^E indicate the presence of strong intermolecular interactions in the system. The results of V^E as a function of mole fraction of Ethyl Ethanoate presented in Fig (1) indicates that V^E have positive values for system (EE+BN) and negative values for system (EE+T) and (EE+X) over the entire range of mixture composition. It is found that negative values of V^E for system (EE+T) and (EE+X) have the order (EE+T) > (EE+X). It is well known that negative values of excess molar volume represent the strong intermolecular interactions in the system. Therefore for present system (EE+T) and (EE+X),

there exists strong intermolecular interactions. Due to mixing of two liquids, interactions between the component molecules occur. Negative deviation of V^E confirms the more efficient packing of molecules. There exists systematic symmetric changes in excess molar volume V^E versus X_1 graph for (EE+BN) over entire composition range and for all the temperature values as shown in fig(2). As temperature values becomes increases, values of excess molar volume decreases. Similar trends are found for (EE+T) and (EE+X) mixtures. It is well established that the complex electronic perturbation between liquid components due to orbital mixing of components may be attributed by excess molar refraction. From figure (3) it is observed that R^E have the same trends as discussed for V^E above i.e. it has positive values for mixture (EE+BN) while have negative values for mixture (EE+T) and (EE+X) over the entire range of mixture composition. This further supports the existence of strong interaction in these systems. It is also seen from fig (3) that for the binary mixtures (EE+T) and (EE+X) excess molar refraction R^E

decreases as a function of mole fraction (X_1) of Ethyl Ethanoate, attains a minimum and then further increases with X_1 . Figure (4) represents the effect of temperature on R^E for system (EE+BN). It is observed that excess molar refraction R^E increases systematically with increasing temperature.

Conclusions

From the above investigation it may be concluded that the variation of excess parameters with concentration and temperature strongly supports the molecular association in these liquid mixtures. The effects observed for all the systems under investigation show dependence on hydrogen bonding of components of mixture. It may also be concluded that refractometric study of liquid mixtures provides a better insight for a comprehensive investigation of molecular association between molecules of mixtures.

Figure1 V^E vs. mole fraction(X_1) for mixtures of Ethyl Ethanoate with Benzene (BN), Toluene (T) and Xylene(X) at 293K

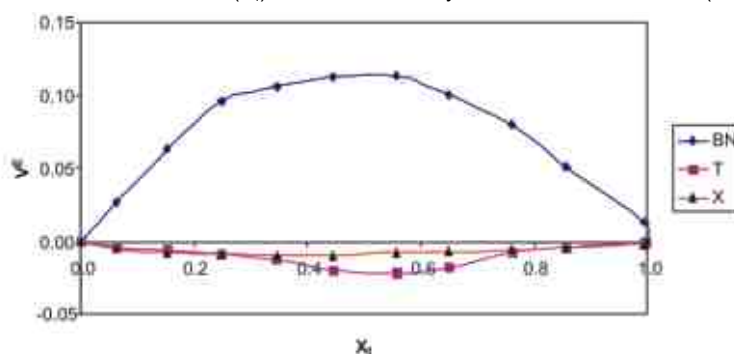


Figure2 Effect of temperature on V^E for mixture (EE+BN)

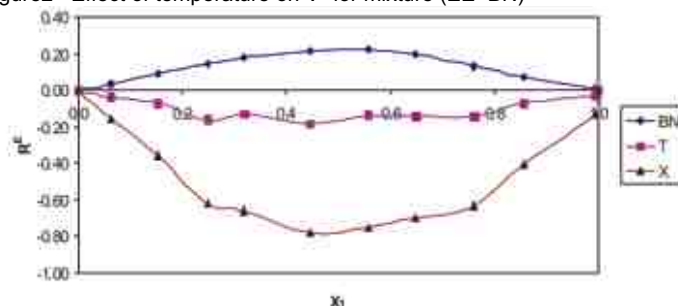


Figure3 R^E vs. mole fraction (X_1) for mixtures of Ethyl Ethanoate with Benzene (BN), Toluene (T) and Xylene(X) at 293K

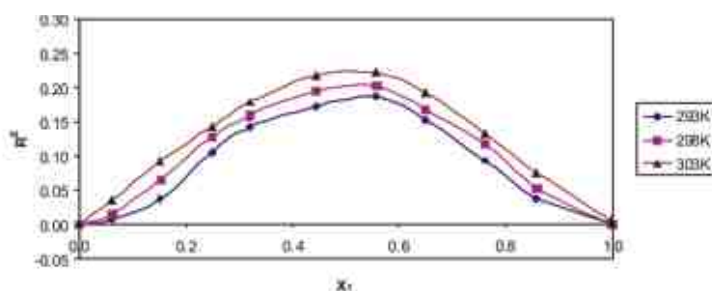


Table1 Refractive index (n_m), density (ρ), excess molar volume (V^E), excess molar refraction (R^E), excess refractive index (Δn_m) for mixture Ethyl Ethanoate and Benzene at 293K, 298K, 303K as a function of the mole fraction X_1 of Ethyl Ethanoate

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	0.8737	1.4991	0.0000	0.0000	0.0000
	0.0623	0.8749	1.4900	0.0271	0.0309	-0.0011
	0.1531	0.8766	1.4775	0.0630	0.0911	-0.0020
	0.2478	0.8784	1.4634	0.0962	0.0776	-0.0040
	0.3468	0.8805	1.4513	0.1061	0.1539	-0.0034
	0.4456	0.8825	1.4375	0.1137	0.1234	-0.0046
	0.5573	0.8849	1.4242	0.1140	0.1657	-0.0036
	0.6499	0.8869	1.4124	0.1013	0.1378	-0.0035
	0.7609	0.8894	1.3985	0.0796	0.0847	-0.0032
	0.8574	0.8916	1.3876	0.0513	0.0745	-0.0018
298K	0.9952	0.8946	1.3716	0.0130	0.0026	-0.0001
	1.0000	0.8948	1.3711	0.0000	0.0000	0.0000
	0.0000	0.8734	1.4978	0.0000	0.0000	0.0000
	0.0623	0.8746	1.4891	0.0194	0.0482	-0.0007
	0.1531	0.8763	1.4757	0.0536	0.0661	-0.0025
	0.2478	0.8780	1.4632	0.0898	0.1288	-0.0029
	0.3468	0.8800	1.4492	0.0971	0.1165	-0.0042
	0.4456	0.8820	1.4377	0.1059	0.1960	-0.0031
	0.5573	0.8843	1.4220	0.1031	0.1212	-0.0045
	0.6499	0.8863	1.4113	0.0956	0.1468	-0.0033
303K	0.7609	0.8887	1.3982	0.0672	0.1359	-0.0022
	0.8574	0.8908	1.3859	0.0423	0.0537	-0.0022
	0.9952	0.8938	1.3703	0.0051	0.0002	-0.0001
	1.0000	0.8939	1.3698	0.0000	0.0000	0.0000
	0.0000	0.8730	1.4965	0.0000	0.0000	0.0000
	0.0623	0.8743	1.4876	0.0117	0.0358	-0.0009
	0.1531	0.8760	1.4734	0.0422	0.0160	-0.0035
	0.2478	0.8776	1.4635	0.0788	0.2026	-0.0013
	0.3468	0.8797	1.4478	0.0850	0.1066	-0.0043
	0.4456	0.8816	1.4358	0.0993	0.1638	-0.0037

Table 2 : Refractive index(n_m), density (ρ), excess molar volume (V^E), excess molar refraction (R^E), excess refractive index(Δn_m) for mixture Ethyl Ethanoate and Toluene at 293K, 298K, 303K as a function of the mole fraction X_1 of Ethyl Ethanoate

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	0.8622	1.4945	0.0000	0.0000	0.0000
	0.0574	0.8640	1.4877	-0.0040	-0.0378	0.0003
	0.1478	0.8668	1.4772	-0.0064	-0.0721	0.0009
	0.2643	0.8704	1.4623	-0.0090	-0.1657	0.0004
	0.3556	0.8733	1.4524	-0.0131	-0.1276	0.0018
	0.4311	0.8757	1.4424	-0.0198	-0.1806	0.0011
	0.5849	0.8807	1.4243	-0.0216	-0.1335	0.0020
	0.6598	0.8832	1.4146	-0.0179	-0.1418	0.0015
	0.7389	0.8858	1.4042	-0.0079	-0.1446	0.0009
	0.8552	0.8898	1.3900	-0.0046	-0.0699	0.0010
298K	0.9505	0.8931	1.3776	-0.0018	-0.0275	0.0004
	1.0000	0.8948	1.3711	0.0000	0.0000	0.0000
	0.0000	0.8619	1.4929	0.0000	0.0000	0.0000
	0.0574	0.8636	1.4862	-0.0060	-0.0303	0.0004
	0.1478	0.8663	1.4742	-0.0084	-0.1440	-0.0005
	0.2643	0.8699	1.4632	-0.0110	-0.0318	0.0028
	0.3556	0.8728	1.4500	-0.0175	-0.1734	0.0009
	0.4311	0.8751	1.4417	-0.0238	-0.1344	0.0019
	0.5849	0.8800	1.4225	-0.0256	-0.1487	0.0016
	0.6598	0.8825	1.4152	-0.0239	-0.0308	0.0035
303K	0.7389	0.8851	1.4035	-0.0109	-0.1066	0.0016
	0.8552	0.8890	1.3886	-0.0056	-0.0715	0.0010
	0.9505	0.8922	1.3767	-0.0028	-0.0037	0.0008
	1.0000	0.8939	1.3698	0.0000	0.0000	0.0000
	0.0000	0.8615	1.4918	0.0000	0.0000	0.0000
	0.0574	0.8632	1.4850	-0.0090	-0.0354	0.0003
	0.1478	0.8659	1.4745	-0.0114	-0.0681	0.0009
	0.2643	0.8694	1.4596	-0.0160	-0.1615	0.0004
	0.3556	0.8722	1.4497	-0.0222	-0.1224	0.0017
	0.4311	0.8746	1.4398	-0.0288	-0.1724	0.0012

Table 3 : Refractive index(n_m), density(ρ), excess molar volume (V^E), excess molar refraction(R^E), excess refractive index (Δn_m) for mixture Ethyl Ethanoate and p-Xylene at 293K, 298K, 303K as a function of the mole fraction X_1 of Ethyl Ethanoate

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	0.8563	1.4947	0.0000	0.0000	0.0000
	0.0562	0.8581	1.4889	-0.0050	-0.1533	0.0011
	0.1511	0.8611	1.4791	-0.0081	-0.3576	0.0031
	0.2643	0.8649	1.4657	-0.0086	-0.6216	0.0037
	0.3532	0.8680	1.4568	-0.0096	-0.6622	0.0058
	0.4449	0.8714	1.4453	-0.0095	-0.7770	0.0056
	0.5504	0.8755	1.4332	-0.0084	-0.7536	0.0065
	0.6727	0.8803	1.4173	-0.0072	-0.7000	0.0057
	0.7467	0.8833	1.4070	-0.0060	-0.6332	0.0046
	0.8538	0.8880	1.3927	-0.0038	-0.4058	0.0035
298K	0.9614	0.8930	1.3769	-0.0020	-0.1277	0.0010
	1.0000	0.8948	1.3711	0.0000	0.0000	0.0000
	0.0000	0.8559	1.4931	0.0000	0.0000	0.0000
	0.0562	0.8577	1.4873	-0.0023	-0.1542	0.0011
	0.1511	0.8607	1.4776	-0.0045	-0.3541	0.0031
	0.2643	0.8644	1.4641	-0.0055	-0.6228	0.0036
	0.3532	0.8675	1.4553	-0.0071	-0.6595	0.0057
	0.4449	0.8709	1.4438	-0.0069	-0.7768	0.0056
	0.5504	0.8748	1.4318	-0.0057	-0.7443	0.0066
	0.6727	0.8797	1.4158	-0.0044	-0.7040	0.0056
303K	0.7467	0.8826	1.4056	-0.0038	-0.6316	0.0046
	0.8538	0.8872	1.3914	-0.0023	-0.4006	0.0036
	0.9614	0.8921	1.3756	-0.0012	-0.1255	0.0010
	1.0000	0.8939	1.3698	0.0000	0.0000	0.0000
	0.0000	0.8552	1.4918	0.0000	0.0000	0.0000
	0.0562	0.8570	1.4860	-0.0014	-0.1542	0.0011
	0.1511	0.8600	1.4763	-0.0018	-0.3542	0.0031
	0.2643	0.8638	1.4628	-0.0030	-0.6268	0.0036
	0.3532	0.8669	1.4540	-0.0039	-0.6633	0.0057
	0.4449	0.8702	1.4425	-0.0052	-0.7772	0.0056

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