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Excess Molar Volume And Viscosity Studies of Binary Mixtures of MTBE With Anisole, Cyanobenzene,Nitrobenzene And Toulene At Different Temparatures

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ABSTRACT

The density and viscosity of binary mixtures of (Methyl tertary butyl ether (MTBE) +anisole, or +cyanobenzene, or +nitrobenzene, or + toluene) have been measured over the entire range of composition at T=(303.15, 308.15, 313.15, 318.15 and 323.15)K. From the experimental data, excess molar volume, V_m^E and viscosity deviation, Δη over the entire range of composition were calculated. These results were fitted to the Redlich-Kister polynomial equation to estimate the binary interaction parameters. The negative and positive values of deviation or excess parameters observed have been explained on the basis of the intermolecular interactions present in these mixtures.

Keywords: Density, viscosity, excess molar volume, excess viscosity, MTBE.

INTRODUCTION

Due to their unusual behaviour binary liquid mixtures have attracted considerable attention. The physical, chemical and transport properties of fluids assume more importance in chemical and physical processes [1]. In recent years these properties have been adequately used in practical and theoretical point of view in understanding the nature of physicochemical behaviour and molecular systems in binary and ternary liquid mixtures. The present study is a continuation of our earlier studies on understanding the thermodynamic properties of binary mixtures whose components have relative industrial application [2,3]. The detailed literature search shows that binary mixtures containing anisole, cyanobenzene, nitrobenzene, toluene with MTBE have not been reported earlier. MTBE is exclusively used as a fuel component in fuel for gasoline engines. Cyanobenzene is a useful solvent and a versatile precursor to many derivatives. Nitrobenzene is used in shoe and floor polishes, leather dressing, paint solvents, and other materials to mask unpleasant odors. Toluene is a common solvent abele to dissolve paints, paint thinners, many chemical reactants, rubber, printing ink leather tanners and disinfectants. Volumetric properties of binary mixtures are very important because they depend not only on solute-solute, solvent-solvent and solute-solvent interactions but also on the structural effect arising from interstitial accommodation due to the difference in volume between the components present in the solution [4,5]. In the present study, the data on density and

viscosity of binary mixtures of (MTBE +anisole, or+cyanobenzene, or +nitrobenzene, or +toluene) have been measured over the entire range of composition at T= (303.15, 308.15, 313.15, 318.15, and 323.15) K. From these data excess molar volume, V^E and viscosity deviation, $\Delta\eta$ have been calculated and the results have been fitted to Redlich-Kister equation to derive the coefficients and standard deviations.

MATERIALS AND METHODS

Materials: The mass fractions of the materials used (obtained from Merck) were the following: MTBE (0.980), anisole (0.980), cyanobenzene (0.990), nitrobenzene and toluene (0.987). All the liquids used were further purified by standard procedure [6]. The purity of the samples was checked by comparing the experimental values of density and viscosity with those available in the literature [7-10] and these values are compiled in table 1.

Table 1 : Comparison of measured densities, ρ, and viscosities, η, of pure components with literature values.

Liquids	T/K	10^{-3} . ρ/(Kg . m^{-3})		10^3 . η/(Kg . m^{-1} . s^{-1})	
		Experimental	Literature	Experimental	Literature
MTBE	308.15K	0.7253	0.7273[a]	0.4450	-
Anisole	303.15K	0.9844	0.9843[b]	0.9541	-
Cyanobenzene	303.15K	0.9958	0.9964[c]	1.1731	1.1260[c]
Nitrobenzene	308.15K	1.1873	1.1882[d]	1.3245	1.5430[d]
toluene	308.15K	0.8528	0.8528[d]	0.6047	0.4980[d]

[a] Domanska [7], [b] Wen-Lu-Weng [8], [c] Ali *et al*. [9]. [d] Thirumaran *et al.* [10].

Procedure: Job's method of continuous variation was used to prepare the mixtures of required proportions. The prepared mixtures were preserved in well-Stoppard conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to allow them to attain thermal equilibrium. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ± 0.5%. An electronic balance (Shimadzu AUY220, Japan), with a precision of ±0.1 mg was used for the mass measurements. Averages of 4-5 measurements were taken for each sample. Viscosities were measured at the desired temperature using Ostwald's viscometer, which is calibrated using water and benzene. Flow time has been measured, after the mixture had attained bath temperature. An electronic stop watch with a precision of 0.01s was used for the flow measurements. The viscosity is determined using the relation

$$\eta = k\rho t \quad (1)$$

where k, ρ, and t are viscometric constant, density of liquid, and time of efflux for a constant volume of liquid respectively. The values are accurate to ±0.001cP. All the measurements were realized in a constant temperature bath with temperature controlled to ±0.01K.

RESULTS AND DISCUSSION

Molar volumes V_m were calculated from density measurements at each temperature according to the following equation:

$$V_m = (x_1M_1 + x_2M_2)/ \rho \quad (2)$$

where M_1 and M_2 are the molar masses of the pure components, x_1 and x_2 are the corresponding mole fraction and ρ is the density of the solution.

The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality [11]. Excess molar volume, V_m^E, and viscosity deviation, $\Delta\eta$, were calculated through the following equations:

$$V_m^E = \left(\frac{x_1 M_1 + x_2 M_2}{\rho} \right) - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (3)$$

$$\Delta\eta = \eta_m - \sum_{i=1}^{n} x_i \eta_i \quad (4)$$

where x is the mole fraction, M_1, M_2 and ρ_1, ρ_2 are the molecular weights and densities of pure components and ρ is the density of the solution at each temperature. The subscripts i and m represent pure component and mixture respectively.

The excess values of above parameters for each mixture have been fitted to Redlich-Kister [12] polynomial equation

$$Y^E = X_1 . X_2 \sum_{i=0}^{n} A_i \quad X_1 - X_2 \quad ^i \quad (5)$$

The values of the coefficients A_i were calculated by method of least squares along with the standard deviation σ (Y^E). The coefficient is adjustable parameters for a better fit of the excess functions. The standard deviation values were obtained from

$$\sigma(Y^E) = \left[\frac{\sum_{i=1}^{n} (Y_{\exp t}^E - Y_{cal}^E)^2}{m - n} \right]^{1/2} \quad (6)$$

where m is the number of data points, n is the order of the fitting polynomial, Y_{expt} and Y_{cal} are the experimental and calculated parameters, respectively.

Experimental data for density (ρ) and viscosity (η) of the four binary mixtures as a function of mole fraction at temperatures T = (303.15, 308.15, 313.15, 318.15 and 323.15) K are given in table 2. The values of the Redlich-Kister polynomial coefficients A_i evaluated by the method of least squares along with standard deviation are given in table 3. Plots of V^E and Δη against mole fraction of MTBE for all the four mixtures are given in figures 1 (a-d) to 2 (a-d).

Table 2: Densities, ρ, and viscosities, η, for binary mixtures at T=(303.15, 308.15, 313.15, 318.15 and 323.15)K

X_1	ρ/(Kg . m^{-3})					10^3 . η/(Kg . m^{-1} . s^{-1})				
	303.15	308.15	313.15	318.15	323.15	303.15	308.15	313.15	318.15	323.15
{MTBE(1) + anisole(2)}										
0.0000	984.5	979.7	975.0	970.2	965.4	0954	0.895	0.841	0.795	0.751
0.0919	961.0	956.3	951.5	946.6	941.8	0.889	0.834	0.785	0.742	0.706
0.1854	937.0	932.2	927.4	922.5	917.6	0.819	0.773	0.732	0.694	0.664
0.2807	914.4	909.6	904.7	899.8	894.9	0.768	0.730	0.693	0.659	0.632
0.3777	889.1	884.2	879.3	874.3	869.3	0.700	0.664	0.631	0.602	0.579
0.4766	864.0	859.9	855.0	850.0	845.0	0.649	0.618	0.590	0.564	0.541
0.5773	838.7	833.7	828.7	823.6	818.5	0.603	0.583	0.550	0.525	0.508
0.6799	813.8	808.7	803.6	798.5	793.3	0.562	0.540	0.517	0.496	0.478
0.7846	785.3	780.1	774.9	769.6	764.3	0.550	0.526	0.506	0.483	0.472
0.8912	761.9	756.7	751.4	746.0	740.6	0.486	0.467	0.450	0.434	0.419
1.0000	730.6	725.2	719.8	714.4	708.8	0.461	0.445	0.430	0.415	0.403
MTBE(1) + cyanobenzene(2)}										
0.0000	995.8	991.3	986.9	982.4	978.0	1.173	1.098	1.031	0.972	0.919
0.0870	970.4	965.9	961.3	956.8	952.3	1.130	1.060	0.997	0.941	0.893
0.1766	952.1	947.6	943.1	938.5	933.9	1.105	1.036	0.975	0.921	0.872

0.2688	920.8	916.2	911.5	906.9	902..3	0.984	0.936	0.870	0.837	0.779
0.3638	902.2	897.5	892.9	888.2	883.5	0.947	0.892	0.843	0.802	0.779
0.4617	875.6	870.7	865.9	861.2	856.3	0.825	0.785	0.744	0.761	0.673
0.5626	849.5	844.7	839.8	834.9	830.0	0.735	0.697	0.662	0.631	0.603
0.6668	821.3	816.3	811.4	806.4	801.4	0.658	0.632	0.603	0.576	0.553
0.7743	793.3	786.3	783.1	778.0	772.8	0.589	0.565	0.540	0.509	0.489
0.8853	763.6	758.4	753.2	747.9	742.5	0.518	0.497	0.479	0.462	0.445
1.0000	730.6	725.2	719.8	714.4	708.8	0.461	0.445	0.430	0.415	0.403
				{MTBE(1) + nitrobenzene(2)}						
0.0000	1192.3	1187.3	1182.3	1177.3	1172.1	1.444	1.325	1.229	1.148	1.078
0.0868	1151.1	1146.1	1141.1	1136.2	1131.2	1.280	1.186	1.106	1.035	0.972
0.1762	1108.4	1103.5	1098.5	1093.5	1088.5	1.153	1.076	1.003	0.943	0.888
0.2683	1061.0	1056.0	1051.0	1045.9	1040.9	1.045	0.979	0.928	0.874	0.825
0.3632	1021.3	1016.4	1011.3	1006.3	1001.3	0.967	0.911	0.857	0.811	0.769
0.4610	976.8	971.8	966.7	961.7	956.6	0.848	0.800	0.757	0.718	0.685
0.5620	931.8	926.7	921.7	916.5	911.5	0.789	0.745	0.706	0.674	0.646
0.6662	881.7	876.5	871.4	866.3	861.0	0.668	0.635	0.604	0.577	0.560
0.7738	838.3	833.2	827.9	822.7	817.5	0.595	0.569	0.545	0.519	0.514
0.8850	772.6	767.3	761.9	756.6	751.2	0.516	0.492	0.474	0.457	0.442
1.0000	730.6	725.2	719.8	714.4	708.8	0.461	0.445	0.430	0.415	0.403
				{MTBE(1) + toluene(2)}						
0.0000	857.5	852.8	848.1	843.4	838.6	0.632	0.605	0.578	0.555	0.534
0.0900	845.5	840.7	836.0	831.2	826.4	0.604	0.576	0.551	0.529	0.508
0.1821	833.8	829.1	824.3	819.5	814.6	0.591	0.564	0.540	0.517	0.497
0.2762	821.9	817.0	812.2	807.2	802.3	0.576	0.547	0.528	0.508	0.484
0.3725	808.2	803.3	798.3	793.3	788.3	0.552	0.531	0.512	0.494	0.469
0.4711	798.0	793.1	788.1	783.0	777.9	0.548	0.525	0.503	0.484	0.457
0.5719	784.5	779.4	774.4	769.3	764.2	0.515	0.494	0.475	0.457	0.441
0.6751	770.9	765.8	760.7	755.5	750.3	0.499	0.479	0.461	0.444	0.430
0.7808	758.6	753.4	748.2	743.0	737.6	0.489	0.470	0.452	0.436	0.422
0.8891	744.9	739.7	734.4	729.0	723.6	0.471	0.454	0.437	0.422	0.410
1.0000	730.6	725.2	719.8	714.4	708.8	0.461	0.445	0.430	0.415	0.403

Table 3: Coefficients of Redlich-Kister equation, A_i, and standard deviations, σ, for excess molar volume, V^E, and viscosity deviation, Δη, for binary liquid mixtures.

Properties	T/K	A_0	A_1	A_2	A_3	A_4	σ
			{MTBE(1) + anisole(2)}				
$10^6V^E/(m^3 . mol^{-1})$	303.15	-0.397	-0.041	0.419	0.656	-1.150	0.014
	308.15	-0.409	-0.041	0.044	0.672	-1.191	0.014
	313.15	-0.419	-0.039	0.452	0.685	-1.213	0.014
	318.15	-0.431	-0.036	0.461	0.697	-1.235	0.015
	323.15	-0.437	-0.034	0.472	0.709	-1.259	0.015
$10^3\Delta\eta/(Kg.m^{-1}.s^{-1})$	303.15	-20.93	-8.464	40.96	8.642	-70.48	0.817
	308.15	-20.63	-7.064	51.05	8.442	-78.65	0.706
	313.15	-20.43	-4.293	53.89	3.636	-84.79	0.698
	318.15	-22.05	-2.763	46.97	1.323	-74.61	0.589
	323.15	-19.49	-1.810	54.10	3.005	-85.09	0.693
			{MTBE(1) + cyanobenzene(2)}				
$10^6V^E/(m^3 . mol^{-1})$	303.15	-0.657	0.234	0.240	0.249	-0.529	0.027
	308.15	-0.673	0.243	0.229	0.252	-0.516	0.027
	313.15	-0.688	0.251	0.231	0.255	-0.518	0.028
	318.15	-0.706	0.259	0.226	0.258	-0.515	0.028
	323.15	-0.724	0.269	0.221	0.260	-0.508	0.029
$10^3\Delta\eta/(Kg.m^{-1}.s^{-1})$	303.15	-9.657	45.54	71.45	-16.24	-82.33	1.205
	308.15	-8.429	40.76	65.35	-11.93	-75.58	1.105
	313.15	-7.588	38.03	60.04	-12.45	-68.94	1.038

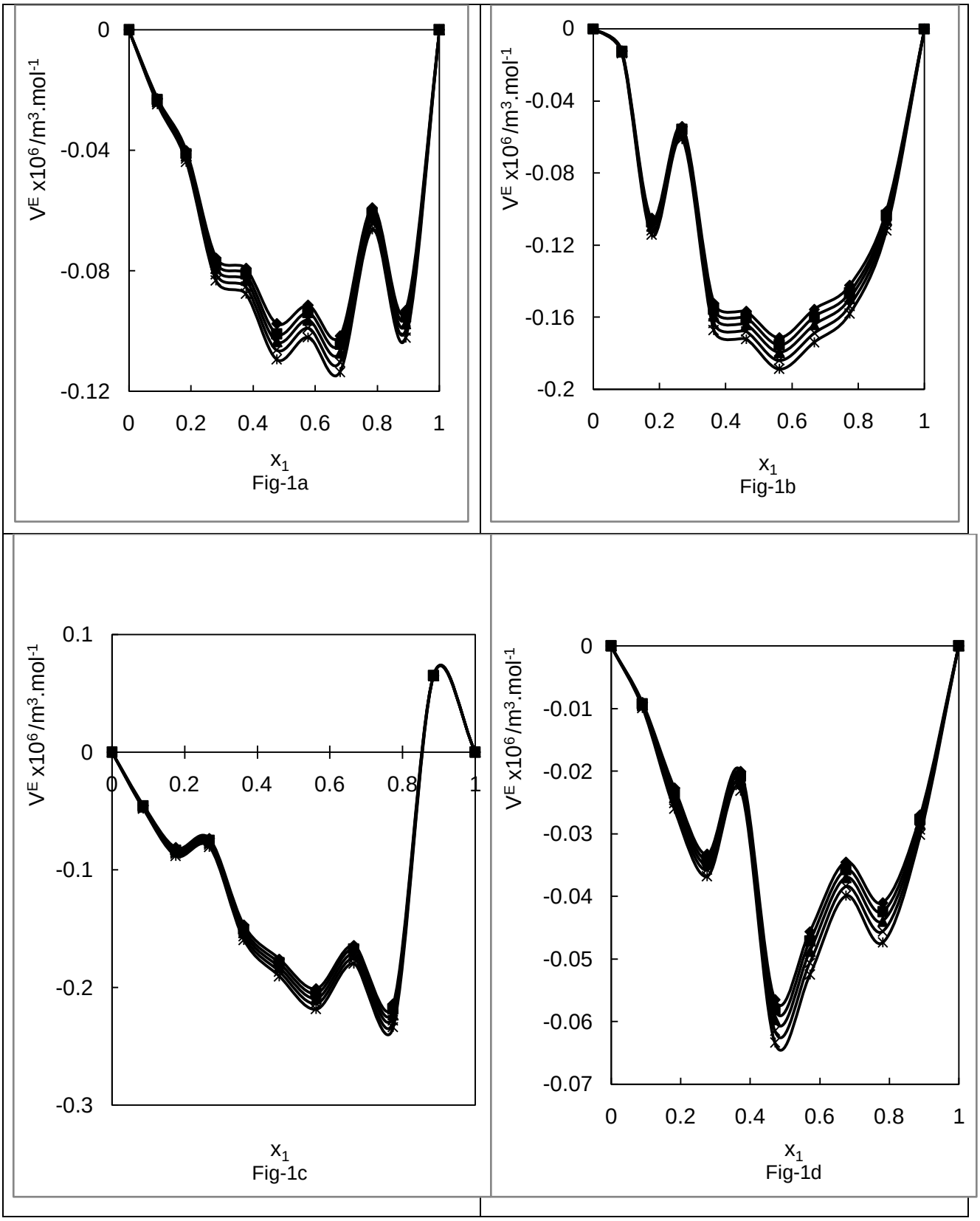
	318.15	-6.368	34.41	47.41	-11.73	-47.92	1.107
	323.15	-5.871	30.35	39.38	-6.294	-34.86	1.051
		{MTBE(1) + nitrobenzene(2)}					
$10^6V^E/(m^3 . mol^{-1})$	303.15	-0.696	1.007	-1.023	-2.582	3.467	0.045
	308.15	-0.710	1.024	-1.045	-2.613	3.525	0.045
	313.15	-0.725	1.043	-1.067	-2.650	3.583	0.046
	318.15	-0.740	1.064	-1.091	-2.689	3.644	0.047
	323.15	-0.756	1.085	-1.114	-2.728	3.705	0.047
$10^3\Delta\eta/(Kg.m^{-1}.s^{-1})$	303.15	-49.06	-12.14	-48.34	-20.34	9.966	1.198
	308.15	-41.12	-7.258	-35.97	-12.48	-2.376	1.118
	313.15	-36.32	-2.666	-25.18	-17.04	-14.28	1.016
	318.15	-31.64	-72.40	-30.69	-18.74	-40.42	0.978
	323.15	-28.15	-9.015	-12.56	-6.861	-33.33	0.947
		{MTBE(1) + toluene(2)}					
$10^6V^E/(m^3 . mol^{-1})$	303.15	-0.178	0.055	0.112	0.061	-0.283	0.009
	308.15	-0.183	0.058	0.111	0.058	-0.284	0.010
	313.15	-0.188	0.063	0.109	0.055	-0.283	0.010
	318.15	-0.195	0.068	0.109	0.052	-0.284	0.010
	323.15	-0.202	0.073	0.011	0.047	-0.283	0.011
$10^3\Delta\eta/(Kg.m^{-1}.s^{-1})$	303.15	-5.426	5.879	-0.0001	-15.89	-12.62	0.516
	308.15	-5.143	6.723	-0.088	-17.76	-12.47	0.494
	313.15	-4.741	8.353	-0.107	-21.29	-12.94	0.438
	318.15	-4.411	8.558	-0.310	-21.27	-13.03	0.421
	323.15	-4.161	8.868	6.108	-22.01	-14.52	0.415

Fig.1(a-d) show that the excess molar volumes V_m^E are negative for all the mixtures over the composition range studied except for MTBE+ Nitrobenzene, at higher mole fraction and become more negative as temperature increases. The negative values are of the order of MTBE+ nitrobenzene > MTBE+ anisole > MTBE+ cyanobenzene > MTBE+ toluene. The negative excess molar volumes in binary mixtures is a consequence of large specific interactions as the result of three contributions [13,14]: a) Structural contributions that arise from the geometrical fitting of one component into other owing to difference in molar volumes and free volumes between the components, (b) hydrogen bond formation between molecules of the mixture making negative contribution towards V_m^E and positive contribution towards $\Delta\eta$ and (c) hydrogen bond breaking in the pure components leading to a positive contribution towards V_m^E and negative contribution towards $\Delta\eta$.

Fig.2(a-d) show that the viscosity deviation $\Delta\eta$ are negative for all the mixtures over the composition range studied except for MTBE+ Cyanobenzene at lower mole fraction and become less negative as temperature increases. Negative viscosity deviations from rectilinear dependence on mole fraction may also occur where dispersion forces are dominant, particularly for the system having different molecular sizes [15].

APPLICATIONS

The results were fitted to the Redlich-Kister polynomial equation to estimate the binary interaction parameters. The negative and positive values of deviation or excess parameters observed have been explained on the basis of the intermolecular interactions present in these mixtures.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-0.08
-0.12
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x_1
Fig-1a
0
-0.04
-0.08
-0.12
-0.16
-0.2
V^E x10^6/m^3.mol^{-1}
0 0.2 0.4 0.6 0.8 1
x_1
Fig-1b
0.1
0
-0.1
-0.2
-0.3
V^E x10^6/m^3.mol^{-1}
0 0.2 0.4 0.6 0.8 1
x_1
Fig-1c
0
-0.01
-0.02
-0.03
-0.04
-0.05
-0.06
-0.07
V^E x10^6/m^3.mol^{-1}
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x_1
Fig-1d

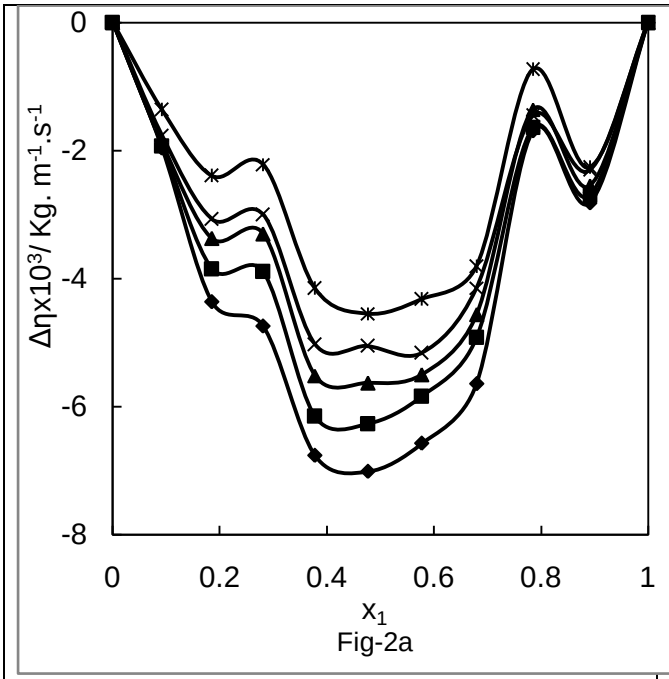

Fig-2a

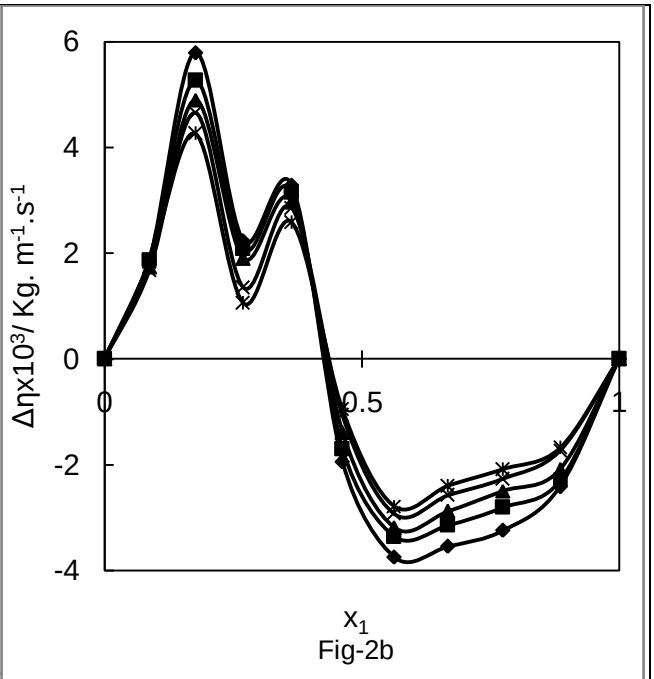

Fig-2b

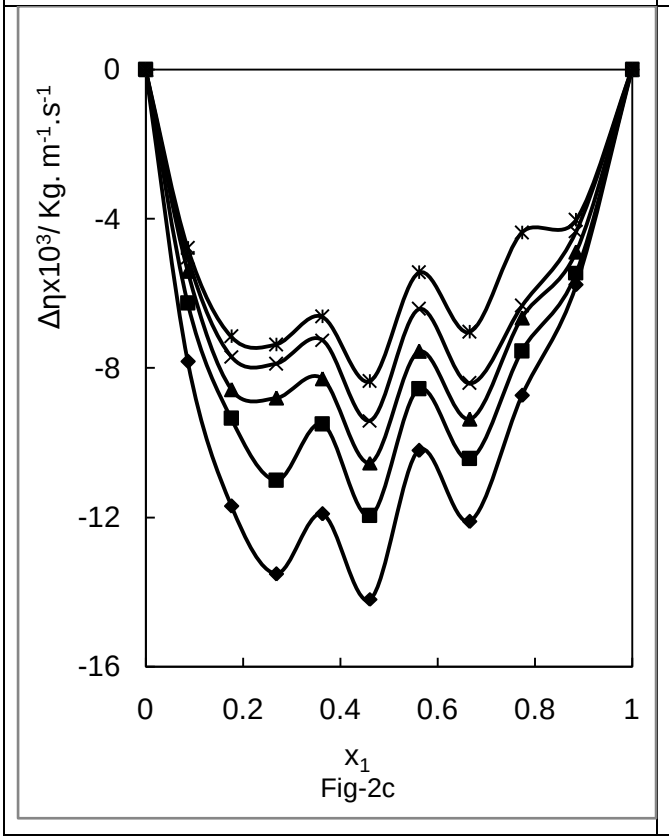

Fig-2c

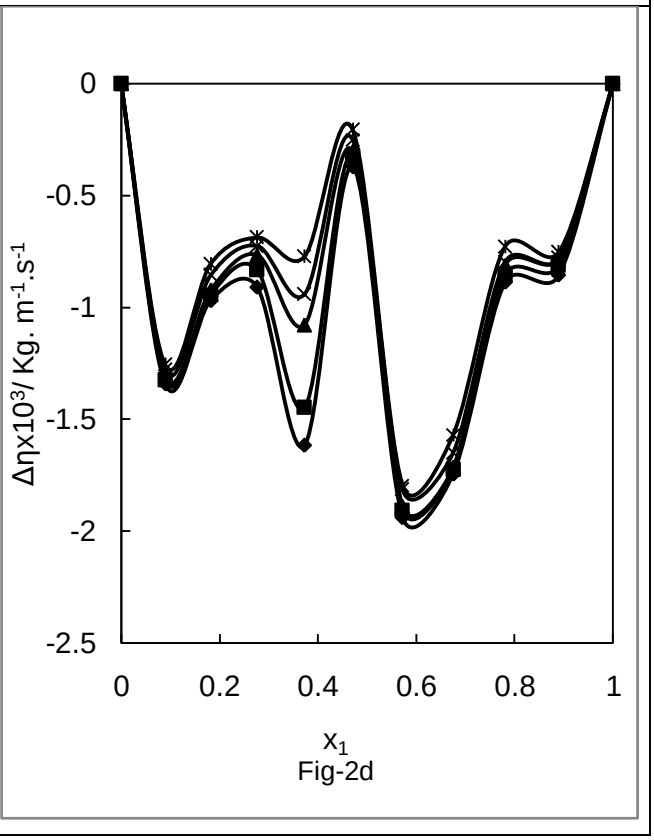

Fig-2d

CONCLUSIONS

The densities and viscosities of mixtures consisting of MTBE+ anisole, or+cyanobenzene, or +nitrobenzene, or +toluene have been measured at different temperatures over the entire range of their

compositions. These data have been used to compute the excess molar volumes and viscosity deviations of the binary systems, and a Redlich-Kister type equation was used for fitting each set of excess properties. Also, it was observed that excess molar volumes and viscosity deviations were negative for almost all the systems examined here. It was also observed that the values of excess properties are dependent on temperature.

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