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A Volumetric and Viscosity Study for the Binary Mixtures of Dimethylsulfoxide with Benzene, Ethyl benzene, Chlorobenzene and Bromobenzene at Temperatures of (303.15, 308.15 and 313.15) K and a Pressure of 0.1MPa

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ABSTRACT

Viscosities (η) and densities (ρ) of binary mixtures of dimethylsulfoxide with benzene, ethylbenzene, chlorobenzene and bromobenzene have been measured as a function of mole fraction at atmospheric pressure and at different temperatures of (303.15, 308.15, and 313.15) K. Using the experimental data, excess volumes (V^E) and deviations in viscosity ($\Delta\eta$) have been calculated. McAllister's three-body-interaction model, Krishnan and Laddha model and Jouyban Acree model were used to correlate the kinematic viscosity of the systems. The excess volume data was fitted by means of the Redlich-Kister equation. It was found that in all cases the experimental data obtained fitted with the values correlated by the corresponding model very well.

Keywords: *Viscosity; Density; Molecular Interactions; Deviations; Binary Mixture*

1. INTRODUCTION

Binary liquid mixtures due to their unusual behavior have attracted considerable attention [1]. In chemical process industries materials are normally handled in fluid form and as a consequence, the physical, chemical, and transport properties of fluids assume importance. Thus data on some of the properties associated with the liquids and liquid mixtures like density and viscosity find extensive application in solution theory and molecular dynamics [2]. Such results are necessary for interpretation of data obtained from thermo chemical, electrochemical, biochemical and kinetic studies [3]. Dimethylsulfoxide is used as an Anti-inflammatory agent and analgesic. Dimethylsulfoxide + benzene mixture is used as insecticides, pesticides and comprising gel formations for vapor producing systems. Dimethylsulfoxide + ethylbenzene, chlorobenzene, bromobenzene mixture is used in dyes, pigments, perfume and pharmaceutical industry. The present study is a continuation of our earlier studies [4, 5] on understanding the thermodynamic properties of binary mixtures whose component has relevant industrial applications. In the present paper, we have re-ported density (ρ) and viscosity (η) of pure dimethylsulfoxide and benzene, ethylbenzene, chlorobenzene and bromobenzene as well as for the binary system constituted by these two chemicals at temperatures of 303.15 K, 308.15 K and 313.15 K. The viscosity values have been fitted to McAllister [6] model and Krishnan and Laddha [7] model. The Jouyban –Acree model [8] has also been extended to density and viscosity of binary mixtures. The deviation values have been fitted to Redlich-Kister type [9] equation. Literature survey showed that no measurements have been previously reported for the mixture studied in this paper.

2. MATERIALS AND METHOD

2.1 Materials

The chemicals used were of analytical reagent grade obtained from lobo chemicals and purified by standard procedures [10]. All the components were dried over anhydrous calcium chloride and fractionally distilled [11]. Binary solutions were prepared on percentage basis (v/v) by dissolving known volume of dimethylsulfoxide in appropriate volume of benzene, ethylbenzene, chlorobenzene and bromobenzene and measuring their masses on a Shimadzu Corporation Japan Type BL 2205 electronic balance with an uncertainty of 0.01%. All the measurements described below were per-formed at least three times and the results were averaged to give the final values.

2.2 Apparatus and Procedure

Densities were determined by using a 25 cm^3 bicapillary pycnometer and calibrated with deionized double distilled water with a density of 996.0 kg $\cdot m^{-3}$ at a temperature of 303.15 K. The pycnometer was thermostatted in a transparent walled water bath (maintained constant to ± 0.01 K) for 15 min to attain thermal equilibrium and the liquid level in the two arms was obtained with a traveling microscope which could read to 0.01 mm.

The Kinematic viscosities were measured at the desired temperature using Ostwald viscometer. The

viscometer was calibrated using water. The liquid mixture was charged into the viscometer. After the mixture had attained bath temperature (Technico India, Madras), flow time has been measured. The flow measurements were made with an electronic stopwatch with a precision of 0.01sec. In the calculation of viscosity, two constants a and b of the viscometer in the relation

$$\nu = (at) - (b/t) \quad (1)$$

It is obtained by measuring the flow time with high purity benzene at the working temperature. The calculated viscosities were fitted in Eq. (1) and constants were determined.

3. RESULTS AND DISCUSSION

Measured values of densities and viscosities of dimethylsulfoxide with benzene, ethylbenzene chlorobenzene and bromobenzene at temperatures of (303.15, 313.15, and 323.15) K are listed in Table 2-5. The density values have been used to calculate excess molar volumes V^E using the following equation

$$V^E=(x_1M_1+x_2M_2)/\rho_m-(x_1M_1/\rho_1+{}_2M_2/\rho_2) \quad (2)$$

where x_1 and x_2 refer to the mole fraction of components 1 and 2. ρ_1, ρ_2, and ρ_m refer to the density of components 1 and 2 and the density of the mixture, respectively. The uncertainty in the calculation of V^E from density measurements was estimated to be ±0.0001.The viscosity deviations $\Delta\eta$ were calculated from the viscosity values using

$$\Delta\eta=\eta-(x_1\eta_1+x_2\eta_2) \quad (3)$$

where η, η_1, and η_2 are the viscosity of the mixture and the viscosity of pure components 1 and 2, respectively.

The kinematic viscosities were correlated by means of the McAllister model considering a three-body-interaction model, which for two-component mixtures gives

$$\ln\nu = x_1^3 \ln\nu_1 + 3x_1^2 x_2 \ln\nu_{12} + 3x_1 x_2^2 \ln\nu_{21} + x_2^3 \ln\nu_2 - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln((2 + M_2/M_1)/3) + x_2^3 \ln(M_2/M_1) + 3x_1 x_2^2 \ln((1+\square 2M_2/M_1)/3) \quad (4)$$

where ν refers to the kinematic viscosity of the mixture of components 1 and 2 having mole fractions x_1 and x_2 respectively ν_1 and ν_2 refers to the kinematic viscosity of pure liquids 1 and 2 respectively ν_{12} and ν_{21} represent the interaction parameters obtained by multiple regression analysis. M_1 and M_2 refer to the molecular weight of the two components respectively. The values of the parameters are given in Table-6.

The kinematic viscosity was correlated by means of the Krishnan and Laddha model for a two component mixture, which gives:

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 + \ln(x_1M_1+x_2M_2 - 2.30x_1x_2(B+C(x_1-x_2)...)) \quad (5)$$

where B and C are interaction parameters. The values of the parameters and standard deviations are given in Table-7. Jouyban et. al proposed a model for correlating the thermal properties of liquid mixtures at various temperatures.

$$\ln Y_{m,T} = f_1 \ln y_1 + f_2 \ln y_2 + f_1 f_2 \Sigma[A_J (f_1-f_2)^J/T] \quad (6)$$

Where $Y_{m,T}$, $y_{1,T}$, and $y_{2,T}$ are the viscosity of the mixture and solvents 1 and 2 at temperature T, respectively. A_J is the model constant. The values of the parameters and standard deviations are given in Table.8. The excess molar volume and viscosity deviations were fitted to a Redlich- Kister equation of the type

$$Y= x_1x_2 \Sigma A_i(x_1-x_2)^i \quad (7)$$

Where Y is either V^E or $\Delta\eta$ and n is the degree of polynomial. Coefficients A_i were obtained by fitting equation (7) to experimental results using a least square regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation(S) was calculated using the relation

$$S(Y) = [\Sigma(A_{exp}-A_{cal})^2/(N-n)]^{1/2} \quad (8)$$

where N is the number of data points, and n is the number of coefficients. The calculated values of coefficients (A_i) along with the standard deviations (S) are given in table.9.

The variation of excess volumes with the mole fraction of dimethylsulfoxide with benzene, ethylbenzene, chlorobenzene and bromobenzene at (303.15, 308.15 and 313.15) K are represented in figures.1-4. The excess molar volume of dimethylsulfoxide with benzene is positive (12, 13), but for the other binary mixtures containing ethylbenzene, chlorobenzene and bromobenzene is negative over the whole range of mole fraction. The sign of excess volume of a system depends on the relative magnitude of expansion/contraction on mixing of two liquids. If the factors causing expansion dominate the contraction factors, the V^E becomes positive. On the other hand if the contraction factors dominate the expansion factors, then V^E become negative. The factors that are responsible for expansion in volume are as follows. (1) Loss of dipolar association (2) The geometry of molecular structure, which does not allow fitting of one component into other component. (3) Steric hindrance, which opposes the proximity of the constituent molecules. The negative V^E values arise due to dominance of the following factors. (1) Chemical interaction between constituent chemicals. (2) Accommodation of molecules

of one component into the interstitials of the molecules of the other component. (3) Geometry of the molecular structure that favors fitting of the component molecules with each other. The negative V^E values in the mixtures under study indicate that interactions between molecules of the mixtures are stronger than interactions between molecules in the pure liquids and that associative force dominate the behavior of the solution.

The results of variation in viscosity deviations of binary systems consisting of dimethylsulfoxide with benzene, ethylbenzene, chlorobenzene and bromobenzene at temperatures of 303.15K, 308.15K, and 313.15K as displayed in figure 5-8 show negative deviations (14) over the entire range of mole fraction. The viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid's structure and enthalpy. Consequently with the molecular interactions between the components of the mixtures. Therefore the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules.

4. CONCLUSIONS

Viscosities (η) and Densities (ρ) for the binary liquid mixture of dimethylsulfoxide with benzene, ethylbenzene, chlorobenzene and bromobenzene system were found out as a function of mole fraction at atmospheric pressure and at temperatures of 303.15K, 308.15K, and 313.15K. From the density (ρ) and viscosity (η) data, the values of excess molar volumes (V^E) and the viscosity deviations ($\Delta\eta$) were determined at 303.15K, 308.15K, and 313.15K. Excess molar volumes (V^E) and the viscosity deviations ($\Delta\eta$) were used to predict the intermolecular interactions in the mixtures. McAllister's three-body-interaction model, Krishnan-Laddha model and Jouyban-Acree model were used to correlate the kinematic viscosity of the systems. The excess molar volume and viscosity deviation data were fitted by means of the Redlich-Kister equation. It was found that in all cases the experimental data obtained, matches with the McAllister model and Redlich-Kister equation with a high degree of precision.

ACKNOWLEDGEMENT

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Table 1: Comparison of experimental density and viscosity of pure liquids with literature values at 303.15 K

Pure liquids	ρ / g ·cm^{-3}		η/(mPa · s)	
	lit	Exp	lit	Exp
Dimethylsulfoxide	1.0905[16]	1.0899	1.7880[16]	1.7824
Benzene	0.8682[17]	0.8672	0.5630[17]	0.5810
Ethylbenzene	0.8670[5]	0.8513	0.5770[5]	0.5890
Chlorobenzene	1.1000[4]	1.1100	0.7053[4]	0.7050

Table-2: Densities ρ and viscosities η for the dimethylsulfoxide (1) + benzene (2) mixture at T= (303.15, 308.15, and 313.15) K and 0.1 MPa

x_2	ρ / g ·cm^{-3}	η/ (mPa·s)	ρ / g ·cm^{-3}	η/ (mPa·s)	ρ / g ·cm^{-3}	η/ (mPa.s)
	303.15 K		308.15K		313.15K	
0	1.0899	1.7824	1.0811	1.6648	1.0731	1.5412
0.0813	1.0639	1.5621	1.0477	1.4824	1.0436	1.4018
0.1446	1.0427	1.3683	1.0261	1.3279	1.0221	1.2382
0.2098	1.0303	1.2179	1.0006	1.1839	1.0013	1.1230
0.3234	1.0105	1.0564	0.9716	1.0219	0.9704	0.9609
0.4434	0.9957	0.9453	0.9437	0.9003	0.9427	0.8471
0.5704	0.9863	0.8527	0.9215	0.8272	0.9206	0.7608
0.7050	0.9796	0.7620	0.9017	0.7484	0.8997	0.7119
0.8480	0.9720	0.7076	0.8828	0.6761	0.8788	0.6364
1	0.8672	0.5810	0.8601	0.5983	0.8544	0.5486

Table-3: Densities ρ and viscosities η for the dimethylsulfoxide (1) + ethylbenzene(2) mixture at T= (303.15, 308.15, and 313.15) K and 0.1 MPa

x_2	ρ / g ·cm^{-3}	η/ (mPa·s)	ρ / g ·cm^{-3}	η/ (mPa·s)	ρ / g ·cm^{-3}	η/ (mPa·s)
	303.15 K		308.15K		313.15K	
0	1.0899	1.7824	1.0811	1.6648	1.0731	1.5412
0.0604	1.0712	1.6300	1.0619	1.5457	1.0629	1.5329
0.1265	1.0520	1.4736	1.0431	1.4077	1.0417	1.4136
0.1989	1.0337	1.3327	1.0234	1.2953	1.0230	1.3014
0.2786	1.0124	1.2227	1.0020	1.1604	0.9988	1.1681
0.3668	0.9886	1.1080	0.9784	1.0644	0.9751	1.0464
0.4650	0.9619	0.9784	0.9514	0.9570	0.9481	0.9348
0.5748	0.9359	0.8740	0.9242	0.8520	0.9199	0.8406
0.6986	0.9091	0.7476	0.8975	0.7585	0.8910	0.7409
0.8391	0.8799	0.6720	0.8691	0.6428	0.8629	0.6313
1	0.8513	0.5890	0.8390	0.5631	0.8311	0.5288

Table-4: Densities ρ and viscosities η for the dimethylsulfoxide (1) +chlorobenzene (2) mixture at T= (303.15, 308.15, and 313.15) K and 0.1 MPa

x_2	ρ / g ·cm^{-3}	η/ (mPa·s)	ρ / g ·cm^{-3}	η/ (mPa·s)	ρ / g ·cm^{-3}	η/ (mPa.s)
	303.15 K		308.15K		313.15K	
0	1.0899	1.7824	1.0811	1.6648	1.0731	1.5412
0.0721	1.0922	1.6843	1.0924	1.5827	1.0828	1.4239
0.1489	1.0948	1.5811	1.0962	1.4832	1.0873	1.3344
0.2308	1.0989	1.4709	1.1011	1.3790	1.0928	1.2435
0.3182	1.1036	1.3620	1.1063	1.2752	1.0985	1.1537
0.4118	1.1053	1.2513	1.1095	1.1689	1.1009	1.0580
0.5122	1.1064	1.1378	1.1105	1.0603	1.1015	0.9652
0.6203	1.1042	1.0354	1.1088	0.9560	1.1002	0.8755
0.7368	1.1034	0.9361	1.1076	0.8665	1.0989	0.7960
0.8630	1.1005	0.8238	1.1040	0.7666	1.0953	0.7163
1	1.1100	0.7050	1.1003	0.6637	1.0913	0.6390

Table-5. Densities ρ and viscosities η for the dimethylsulfoxide (1) + bromobenzene (2) mixture at T= (303.15, 308.15, and 313.15) K and 0.1 MPa

x_2	ρ / g ·cm^{-3}	η/ mPa·s	ρ / g ·cm$^{-3.}$	η/ mPa·s	ρ / g ·cm^{-3}	η/ mPa.s
	303.15 K		308.15K		313.15K	
0	1.0899	1.7824	1.0811	1.6648	1.0731	1.5412
0.0698	1.1314	1.7121	1.1262	1.5935	1.1205	1.4527
0.1445	1.1745	1.6331	1.1689	1.5127	1.1614	1.3820
0.2246	1.2202	1.5664	1.2123	1.4345	1.2041	1.3082
0.3106	1.2672	1.4931	1.2554	1.3513	1.2481	1.2417
0.4033	1.3135	1.4240	1.2987	1.2776	1.2873	1.1737
0.5034	1.3551	1.3578	1.3383	1.2009	1.3236	1.1151
0.6120	1.3906	1.3085	1.3718	1.1345	1.3558	1.0616
0.7300	1.4205	1.2491	1.4011	1.0687	1.3847	1.0071
0.8588	1.4551	1.1856	1.4294	0.9942	1.4094	0.9502
1	1.4862	1.1227	1.4493	0.9260	1.4267	0.9079

Table.6 Parameters of McAllister constants and standard deviations S

T /K	A	B	S
Dimethylsulfoxide(1) + Benzene(2)			
303.15	0.8241	0.9078	0.0159
308.15	0.8631	0.9389	0.0164
313.15	0.8209	0.8924	0.0235
Dimethylsulfoxide(1) + Ethylbenzene(2)			
303.15	0.8139	1.1169	0.0353
308.15	0.8566	1.0869	0.0257
313.15	0.7431	.9319	0.0353
Dimethylsulfoxide(1) +Chlorobenzene(2)			
303.15	0.6706	0.9097	0.0082
308.15	0.6482	0.8762	0.0047
313.15	0.7229	0.9621	0.0021
Dimethylsulfoxide(1) +Bromobenzene(2)			
303.15	0.6706	1.3154	0.0065
308.15	0.7875	1.0293	0.0031
313.15	0.7431	0.9319	0.0034

Table.7 Parameters of the Krishnan and Laddha Constants and standard deviations S

T/K	A 1	A2	A3	A4	S
Dimethylsulfoxide(1) + Benzene(2)					
303.15	0.2491	-0.2478	-0.1009	0.2688	0.0165
308.15	-0.2870	-1.1905	0.0747	0.2210	0.0575
313.15	-1.1309	-1.8552	0.1185	-0.1401	0.0331
Dimethylsulfoxide(1) + Ethylbenzene(2)					
303.15	0.0532	0.4091	0.0974	-0.1222	0.0514
308.15	-01250	0.6273	0.0416	-0.1885	0.0151
313.15	0.026	0.7303	-0.0286	-0.1485	0.0654
Dimethylsulfoxide(1) +Chlorobenzene(2)					
303.15	-0.1883	-0.0913	-0.0176	0.0186	0.024
308.15	-0.0287	-1.185	0.4747	0.1521	0.0095
313.15	-.0748	-5.195	1.7470	2.521	0.0511
Dimethylsulfoxide(1) +Bromobenzene(2)					
303.15	- 0.037	0.1817	- 0.0276	- 0.1316	0.0438
308.15	- 0.1491	0.5243	0.1091	- 0.2299	0.0034
313.15	- 0.2631	1.0204	0.2455	- 0.3406	0.0159

Table.8. Parameters of the Jouyban Acree model Constants and standard deviations S for the viscosity

T /K	A 1	A2	A3	A4	S
	Dimethylsulfoxide(1) + Benzene(2)				
303.15	210.78	-190.2	-59.411	194.23	0.0122
308.15	146.32	-145.2	-6.8144	142.36	0.0038
313.15	-56.835	-170.24	201.710	160.870	0.0118
	Dimethylsulfoxide(1) + Ethylbenzene(2)				
303.15	269.66	35.339	-219.48	-32.837	0.0062
308.15	99.414	-26.624	-89.547	18.515	0.0087
313.15	-231.63	-22.327	227.11	8.4823	0.0079
Dimethylsulfoxide(1) +Chlorobenzene(2)					
303.15	-177.24	-52.561	165.87	52.949	0.0039
308.15	-74.275	-9.1059	84.065	10.224	0.0022
313.15	47.677	16.394	-13.294	-12.906	0.0025
Dimethylsulfoxide(1) +Bromobenzene(2)					
303.15	178.27	-46.599	-76.579	53.776	0.0083
308.15	218.28	-26.848	-118.65	35.064	0.0081
313.15	276.7	-10.569	-153.19	-15.717	0.0069

Table.9.Parameters of the Redlich Kister constants and standard deviations S for viscosity Deviation

T /K	A 1	A2	A3	A4	A5	S
Dimethylsulfoxide(1) + Benzene(2)						
303.15	-1.1796	0.8961	-1.7342	-0.0669	2.8154	0.0122
308.15	-0.7517	0.3880	-0.3781	-0.3783	0.3029	0.0070
313.15	-0.9146	0.8600	-0.6801	-0.7100	1.7391	0.0188
Dimethylsulfoxide(1) + Ethylbenzene(2)						
303.15	-0.9443	0.1035	-0.9573	0.5639	1.3039	0.1753
308.15	-0.7517	0.388	-0.3781	-0.3783	0.3029	0.1374
313.15	-0.6731	0.3222	0.1366	-0.5789	0.1675	0.1106
Dimethylsulfoxide(1) +Chlorobenzene(2)						
303.15	-0.2	0.6556	0.0975	-1.2112	-0.661	0.0626
308.15	-0.4024	0.0184	0.2021	0.0624	-0.175	0.0566
313.15	-0.4135	-0.015	0.1227	0.1174	-0.176	0.0655
Dimethylsulfoxide(1) +Bromobenzene(2)						
303.15	-0.3409	0.188	0.0633	-0.194	0.0106	0.0439
308.15	-0.3881	0.1518	0.1589	-0.1076	-0.278	0.0545
313.15	-0.4401	0.1628	0.1703	-0.0555	-0.514	0.0665

FIGURES

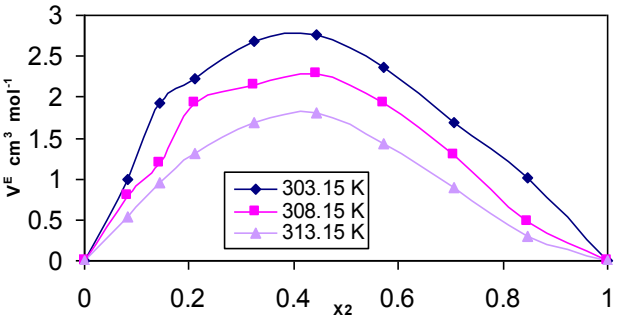

Figure.1. Excess molar volume (V^E) for dimethylsulfoxide(1)+benzene(2) at ♦, 303.15 k; ■, 308.15 k; ▲, 313.15 k.

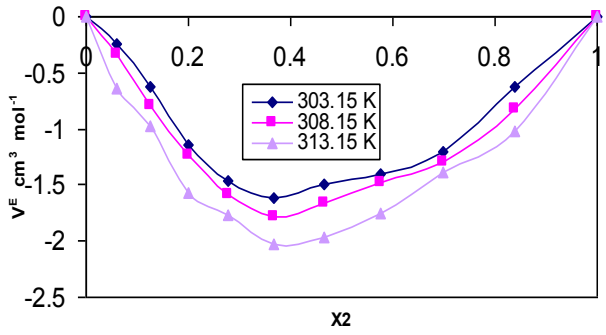

Figure.2. Excess molar volume (V^E) for dimethylsulfoxide(1)+ethylbenzene(2) at ♦, 303.15 k; ■, 308.15 k; ▲, 313.15 k.

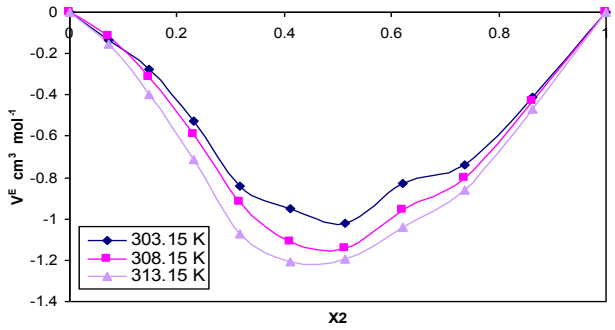

Figure.3: Excess molar volume (V^E) for dimethylsulfoxide(1)+chlorobenzene(2) at ♦, 303.15 k; ■, 308.15 k; ▲, 313.15 k.

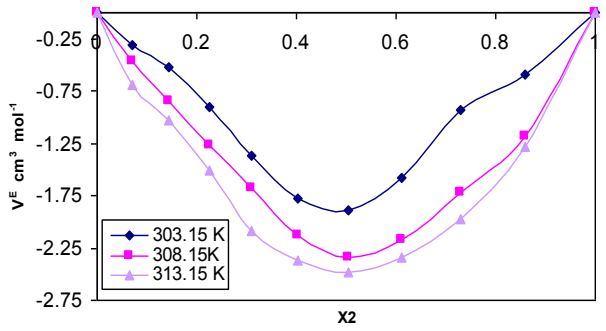

Figure.4: Excess molar volume(V^E) for dimethylsulfoxide(1)+bromobenzene(2) at ♦, 303.15 k; ■, 308.15 k; ▲, 313.15 k.

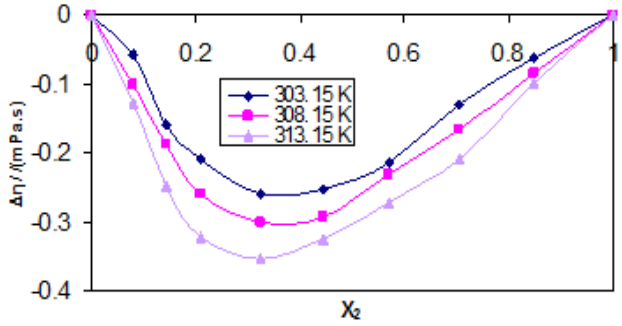

Figure.5. Viscosity deviation (Δη) for dimethylsulfoxide(1)+benzene(2) at ♦, 303.15 k; ■, 308.15 k; ▲, 313.15 k.

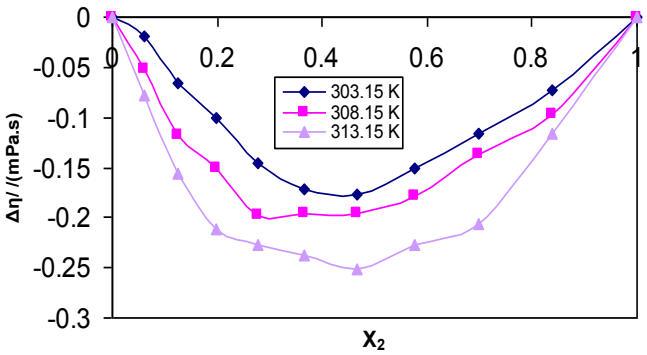

Figure.6. Viscosity deviation (Δη) for dimethylsulfoxide(1)+ethyl benzene(2) at ♦, 303.15 k; ■, 308.15 k; ▲, 313.15 k.

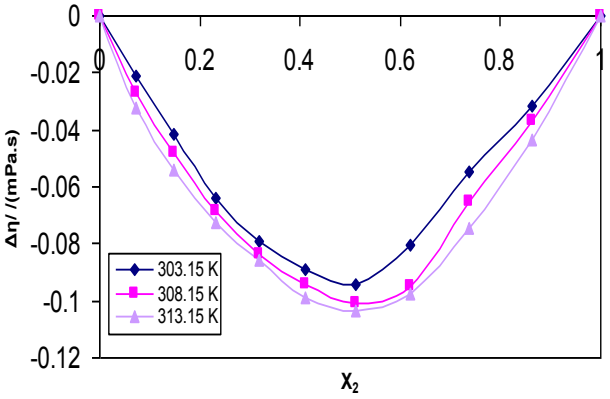

Figure.7. Viscosity Deviation (Δη) for Dimethyl sulfoxide(1)+ Chlorobenzene(2) at ♦, 303.15 k; ■, 308.15 k; ▲, 313.15 k.

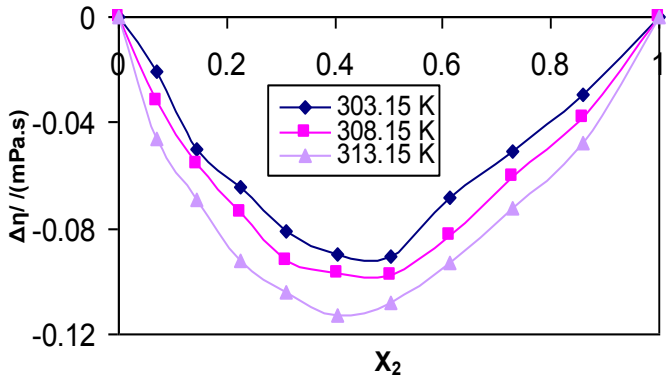

Figure.8. Viscosity deviation (Δη) for dimethylsulfoxide(1)+bromobenzene(2) at ♦, 303.15 k; ■, 308.15 k; ▲, 313.15 k.

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