CHAPTER XI

Thermodynamic and transport properties of binary mixtures of dimethyl sulfoxide with t-butyl alcohol, butyl acetate, 2-butanone and butyl amine at different temperatures*

11.1. Introduction

Dimethyl sulfoxide (DMSO), a typical aprotic solvent having both polar and nonpolar groups, is an important solvent in chemistry, biotechnology, and medicine for the dissolution of various substances and as an antifreeze agent of living cells.[1]

This solvent was chosen particularly for this study because of its wide range of applicability as a solvent in chemical and biological processes. Viscosity and density of binary liquid mixtures are extensively used to understand molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications.[4,5] These have been extensively used to obtain information on intermolecular interactions and stereo chemical effects in these systems.[6] In this paper we extend our studies to the binary mixtures of DMSO, with butyl acetate, tert-butyl alcohol, n-butyl amine and 2-butanone.The various thermodynamic properties such as excess molar volume (V^E) and viscosity deviations ($\Delta\eta$) obtained from experimental observations have been rationalized.

To our knowledge, the experimental data reported in this paper are not available in the literature.

11.2. *Experimental Section*

11.2.1. *Materials*

Dimethylsulfoxide, Merck, India, was kept several days over anhydrous $CaSO_4$, refluxed for four hours over CaO. Finally, it was distilled at low pressure. Details[11] have been described in chapter III. tert-butanol, n-butyl acetate, 2-butanone, n-butylamine (S. D. Fine Chemicals, Analytical Reagent, Purity > 99%) were used. The purity of the solvents was ascertained by comparing experimental values of densities and viscosities with those reported in the literature [12-17] as listed in Table 1.

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11.2.2. *Apparatus and Procedure*

Viscosities (η) have been measured at 298.15 K, 308.15 K and 318.15 K by means of a suspended Ubbelohde type viscometer [7]. Calibration was done at all the experimental temperatures with triply distilled water and purified methanol using density and viscosity values from the literature. Densities (ρ) were measured at the mentioned temperatures with an Ostwald-Sprengel type pycnometer having bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. The flow times were accurate to ± 0.1s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was ± 2 x 10^{-4} mPa.s. The measurements were done in a thermostatic bath controlled to ± 0.01 K. The details of the methods and techniques for determination of these parameters have been described in earlier papers. [6,8,9,10]

The mixtures were prepared by mixing known volumes of pure liquids in air-tight stoppered bottles. The reproducibility in mole fraction was within ± 0.0002 units. The weights were taken on a Mettler electronic analytical balance (AG 285) accurate to 0.02 mg. The precision of the density and viscosity measurements is ± 3 × 10^{-4} g cm^{-1} and ± 2 ×10^{-4} m Pa s respectively. The details of all the experimental methods are described in chapter III.

8.3. *Results and Discussion*

Table 2 lists the experimental values of densities (ρ_i) and viscosities (η_i) of the binary mixtures along with the corresponding mole fractions of DMSO (x_1), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), excess Gibbs energy of activation for viscous flow (G^{*E}) and interaction parameters (d_{12}, T_{12}, H_{12}) at all the experimental temperatures. The plots of V^E, $\Delta\eta$, G^{*E} against x_1 at 298.15 K are represented in fig. 1, 2, 3 respectively. Because of similarity of nature the plots at the other two temperatures are not presented here.

The experimental ρ values have been used to calculate the excess molar volumes (V^E) using the following equation, [5,18]

$$V^E = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \qquad (1)$$

Where, M_i, ρ_i, ρ are mol. Wt., density of the pure components and density of the mixtures respectively.

The deviation in viscosities from linearity ($\Delta\eta$) can be computed using the relationship,

$$\Delta\eta = \eta - \sum_{i=1}^{2} (x_i \eta_i) \qquad (2)$$

Where, η_i, η and are the viscosities of the pure components and of the mixtures respectively.

On the basis of the theories of absolute reaction rates [19], the excess Gibbs energy of activation for viscous flow (G^{*E}) was calculated from the equation, [20]

$$\Delta G^{*E} = RT \left[\ln \eta V - \sum_{i=1}^{2} (x_i \ln \eta_i V_i) \right] \qquad (3)$$

R, T, V, V_i are the Universal gas constant, experimental temperature in absolute scale and molar volumes of pure component and the mixtures respectively.

The excess properties (V^E, $\Delta\eta$ and G^{*E}) were fitted to the Redlich-Kister polynomial equation[21],

$$Y^E = x_1 x_2 \sum_{i=1}^{K} a_i (x_1 - x_2)^i \qquad (4)$$

where Y^E refers to excess properties, x_1 is the mole fraction DMSO and x_2 is that of the other component. The coefficients (a_i) were obtained by fitting eq.6 to experimental results using a least-squares regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The estimated values of a_i along with the tabulated standard deviations (σ) are summarized for all mixtures in table 3. The standard deviation (σ) was calculated using the equation,

$$\sigma = \left[\frac{(Y^E_{\exp} - Y^E_{cal})^2}{(n - m)} \right]^{\frac{1}{2}} \qquad (5)$$

where n is the number of data points and m is the number of coefficients.

The value of the excess molar volume, V^E are found to be negative for mixtures containing DMSO and butyl acetate, butyl amine and 2-butanone and their magnitudes follow the order given below;

Butyl amine > 2-Butanone> Butyl acetate,

But for the mixture of DMSO with tert-butyl alcohol, values of V^E are positive. This indicates that, the interaction occurring between DMSO and butyl amine is the strongest followed by butanone and butyl acetate. Whereas dispersive force plays the main role in case of tert-butyl alcohol.

The values of V^E may be regarded as the result of contributions from several opposing effects[22], namely, physical, chemical, and structural. Physical contributions are nonspecific interactions and contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease. The structural contributions arise especially from geometrical fitting (interstitial accommodation), of one component into other due to the differences in the free volume and molar volume between components lead to negative contribution to V^E.

The largest negative excess volume of DMSO and n- butyl amine system is due to strong interaction between the oxygen atom of DMSO and hydrogen atom of n- butyl amine. This indicates formation of intermolecular hydrogen bonded complexes. The parabolic shapes of V^E versus x_1 plots with well defined minima also indicate the presence of complex formation. It is seen that the values of V^E for the binary mixtures of DMSO with 2-butanone are also negative over the entire range of composition, suggesting specific interactions between the mixing components. These negative values of V^E may be attributed to the dipole-dipole interactions resulting in the formation of electron-transfer complexes between the molecules of mixing components. The molar volumes of DMSO and butyl acetate differ considerably. Hence, smaller DMSO molecules are interstitially accommodated into aggregates of butyl acetate, yielding negative V^E values for DMSO and butyl acetate mixtures .

DMSO+ tert-butyl alcohol mixture is the only exception among the experimental binary mixtures showing positive values of V^E over the entire composition and temperature range. Mixing of DMSO with tert-butyl alcohol would induce dissociation of the hydrogen bonds in the self associated alcohol[23] leading to expansion in volume, and

thus a positive contribution to V^E values. Another equally important contribution leading to the positive V^E values for this mixture arises from the close molecular sizes of DMSO and tert-butyl alcohol. Assarson and Eirich [23] suggested that the liquids of similar molecular sizes usually mix with positive excess volumes.

Large negative values of viscosity deviations $\Delta\eta$ are observed for the binary mixtures of DMSO with t-Butyl alcohol and Butyl acetate. For 2- butanone and butyl amine the $\Delta\eta$ values are negative for lower mole fractions of DMSO but ultimately they turn positive at higher mole fractions of DMSO thereby resulting sigmoid type plots (fig-2).

In general, for systems where dispersion and dipolar interactions are operating, $\Delta\eta$ values are found to be negative, whereas charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules, thereby resulting in positive values[36]. The negative $\Delta\eta$ values of DMSO and t-Butyl alcohol mixtures indicates the dominance of dispersion forces between the unlike molecules in this mixture [35, 36] and supports the conclusion drawn from V^E values.. According to Fort and Moore also $\Delta\eta$ values are negative in systems of unequal molecular size in which dispersion forces are predominant. [39] This explains the negative $\Delta\eta$ values for DMSO and Butyl acetate mixture which also supports the conclusion drawn from V^E values. For 2- butanone and butyl amine mixtures with DMSO positive $\Delta\eta$ values indicate presence of charge transfer interactions leading to the formation of complex species between unlike molecules, [40] This conclusion is in excellent agreement with that drawn from V^E values.

According to Reed and Taylor and Meyer *et al.* positive G^{*E} values indicate specific interactions while negative values indicate the dominance of dispersion forces. [25,27]

It is seen that, for DMSO+ t-butyl alcohol and DMSO+ butyl acetate, the G^{*E} values are negative over the entire range of composition and temperature indicating that, in these mixtures forces of dispersion are dominating. The large and positive G^{*E} values for DMSO + butylamine mixture supports strong specific interactions through complex formation in the system. The value of G^{*E} for DMSO+ 2-butanone mixture is less positive suggesting the presence of weaker interactions.

There is a systematic rise in V^E and $\Delta\eta$ values with a rise in temperature for all the components studied here suggesting an increase in interaction between the component molecules. The effect of temperature increase is to disrupt hetero and homo association of the molecules which causes increase in fluidity of the liquid. So, $\Delta\eta$ values are higher at higher temperatures. Similar results were reported earlier [28].

Apart from expressing η as a polynomial fit, several semi empirical relations have been proposed to estimate the dynamic viscosity η of liquid mixtures in terms of pure component data. [29,30] We have examined equations proposed by Grunberg-Nissan, Tamura-Kurata and Hind et al.

The single parameter Grunberg-Nissan equation [31] reads as:

$$\eta = \exp[\sum_{i=1}^{2}(x_i \ln \eta_i) + x_1 x_2 d_{12}] \qquad (6)$$

where d_{12} is a parameter proportional to the interchange energy and has been regarded as an approximate measure for the non-ideal behaviors of binary mixtures.

Tamura-Kurata [32] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{2} x_i \phi_i \eta_i + 2(x_1 x_2 \phi_1 \phi_2)^{1/2} T_{12} \qquad (7)$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of i[th] pure component in the mixture.

Molecular interactions may also be interpreted by the viscosity model of Hind *et al* [32]

$$\eta = \sum_{i=1}^{2} x_i^2 \eta_i + 2(x_1 x_2 H_{12}) \qquad (8)$$

where H_{12} is interaction parameter.

Among the three parameters determined here, the Grunberg-Nissan parameter provides the best measure to ascertain the strength of interaction. At any given composition, the variation of d_{12} with strength of interaction is similar to that of $\Delta\eta$, being negative for systems in which dispersion forces are dominant, becoming less negative and then increasingly positive as the strength of interaction increases.[26,37,38]

According to Fort and Moore [26] the values of T_{12} and H_{12} are not very different except where the values of the components differ considerably. There is a tendency of T_{12} and H_{12} at a certain composition to increase with the strength of interaction of the components but this is not well defined and T_{12} and H_{12} can not generally be regarded as a measure of the strength of interaction. [38]

A perusal of this table shows that the variations and signs of d_{12} are similar to those of $\Delta\eta$ and thereby supports our conclusion. DMSO + n-butylamine mixture, which involves large specific interaction, shows positive d_{12} values.

T_{12} and H_{12} values are positive for all binary mixtures, almost identical and do not change appreciably with the change of composition of binary mixtures.

4.4. *Conclusion:*

In summary, we can draw some conclusion about the type and nature of molecular interactions occurring in the binary mixtures of DMSO with butyl acetate, tert-butyl alcohol, n-butyl amine and 2-butanone. Specific interaction is present between DMSO and n- butyl amine, DMSO + butyl acetate, DMSO + 2-butanone solvent system but in DMSO + t-butyl alcohol solvent system dispersion forces are prevailing. This study on excess or deviation properties along with acoustic properties seems to be of much use in exploring the nature of interactions present in the experimental binary mixtures; however, more extensive study will have a better in this field.

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Table 1

Comparison of density (ρ), viscosity (η) of the Pure Liquids with Literature Data at 298.15 K.

	Temperature	ρ x 10^{-3}/ (kg.m^{-3})		η / (m Pa.s)	
		Expt.	Lit.	Expt.	Lit.
DMSO	298.15 K	1.0951	1.09568[17]	1.9923	1.991[17]
	308.15 K	1.0839	-	1.7052	-
	318.15 K	1.0757	-	1.4504	-
Butyl acetate	298.15 K	0.8754	0.8761[18]	0.6738	0.674[18]
	308.15 K	0.8646	-	0.6684	-
	318.15 K	0.8565	-	0.5342	-
t-Butyl alchohol	298.15 K	0.7807	0.7799[19]	4.4338	4.433[19]
	308.15 K	0.7705	-	2.7910	-
	318.15 K	0.7610	-	1.8099	-
Butyl amine	298.15 K	0.7312	0.7331[20]	0.4960	0.496[22]
	308.15 K	0.7199	-	0.4195	-
	318.15 K	0.7136	-	0.3600	-
2-Butanone	298.15 K	0.7984	0.7996[21]	0.3784	0.378[21]
	308.15 K	0.7883	-	0.3235	-
	318.15 K	0.7796	-	0.3138	-

Table 2
Measured and Derived Parameters for Various Studied Binary Mixtures at 298.15 K, 308.15 K And 318.15 K

x_1	$\rho \times 10^{-3}$ / (kg.m^{-3})	η / (mPa.s)	V^E x10^6 / (m^3.mol^{-1})	$\Delta\eta$ / (mPa.s)	G^{*E} / J.mol^{-1})	d_{12}	T_{12}	H_{12}
298.15 K								
tert-Butyl alcohol + DMSO								
0.0953	0.8031	3.6683	0.068	-0.533	-270.70	-1.31	-0.41	0.12
0.1917	0.8269	3.0119	0.145	-0.954	-559.55	-1.51	-0.31	0.14
0.2890	0.8521	2.5592	0.225	-1.169	-762.96	-1.55	0.03	0.37
0.3874	0.8791	2.2505	0.276	-1.238	-881.15	-1.55	0.35	0.61
0.4868	0.9083	2.0714	0.296	-1.174	-887.18	-1.49	0.69	0.86
0.5872	0.9399	1.9671	0.281	-1.033	-816.73	-1.41	0.97	1.08
0.6888	0.9743	1.9624	0.222	-0.790	-625.17	-1.23	1.31	1.37
0.7914	1.0115	1.9556	0.148	-0.546	-437.31	-1.12	1.54	1.56
0.8951	1.0518	1.9423	0.065	-0.306	-258.69	-1.16	1.61	1.58
Butyl acetate + DMSO								
0.1418	0.8943	0.6508	-0.140	-0.210	-419.83	-1.55	0.51	0.47
0.2710	0.9137	0.6822	-0.212	-0.349	-617.16	-1.42	0.55	0.45
0.3893	0.9335	0.7441	-0.238	-0.443	-698.62	-1.34	0.56	0.40
0.4979	0.9539	0.8413	-0.226	-0.489	-675.80	-1.27	0.58	0.36
0.5980	0.9750	0.9732	-0.192	-0.489	-583.06	-1.17	0.60	0.32
0.6905	0.9968	1.1292	-0.141	-0.455	-470.78	-1.09	0.62	0.27
0.7763	1.0195	1.3174	-0.089	-0.382	-334.72	-0.99	0.65	0.24
0.8561	1.0434	1.5356	-0.051	-0.267	-192.35	-0.85	0.71	0.25
0.9305	1.0686	1.7657	-0.019	-0.135	-76.24	-0.70	0.80	0.29
Butanone + DMSO								
0.0930	0.8234	0.4384	-0.302	-0.090	-20.99	-0.09	0.70	0.65
0.1875	0.8492	0.5180	-0.520	-0.163	1.37	0.02	0.71	0.65
0.2834	0.8762	0.6758	-0.693	-0.160	263.84	0.54	0.87	0.79
0.3809	0.9041	0.8631	-0.800	-0.130	467.78	0.81	1.00	0.91
0.4799	0.9333	1.0880	-0.854	-0.065	632.84	1.04	1.16	1.06
0.5806	0.9635	1.3404	-0.837	0.025	735.31	1.23	1.34	1.24
0.6829	0.9947	1.5525	-0.737	0.072	679.11	1.28	1.45	1.35
0.7868	1.0274	1.7503	-0.589	0.102	549.37	1.34	1.57	1.49
0.8925	1.0608	1.9089	-0.345	0.090	332.04	1.42	1.72	1.65
Butyl Amine +DMSO								
0.0942	0.7595	0.5608	-0.403	-0.076	-19.60	-0.10	0.87	0.80
0.1896	0.7892	0.6836	-0.711	-0.096	143.36	0.37	1.04	0.93
0.2862	0.8207	0.8842	-0.948	-0.040	448.01	0.88	1.28	1.15
0.3841	0.8540	1.1108	-1.109	0.040	675.78	1.15	1.48	1.32
0.4834	0.8892	1.3283	-1.191	0.109	776.10	1.25	1.61	1.55
0.5839	0.9265	1.5437	-1.185	0.174	801.06	1.33	1.74	1.74

Contd

0.6858	0.9658	1.7132	-1.073	0.191	706.96	1.33	1.81	1.93
0.7891	1.0070	1.8558	-0.845	0.179	548.66	1.34	1.88	2.13
0.8939	1.0503	1.9775	-0.501	0.144	345.03	1.48	2.06	2.07
			308.15 K					
			tert- Butyl alcohol + DMSO					
0.0953	0.7932	2.4965	0.026	-0.191	-156.14	-0.75	0.95	1.14
0.1917	0.8173	2.2559	0.054	-0.327	-286.22	-0.76	1.03	1.19
0.2890	0.8430	2.0712	0.077	-0.406	-376.30	-0.76	1.13	1.26
0.3874	0.8703	1.9334	0.098	-0.437	-423.97	-0.74	1.23	1.33
0.4868	0.8996	1.8355	0.111	-0.427	-429.55	-0.72	1.33	1.39
0.5872	0.9310	1.7704	0.110	-0.383	-395.46	-0.68	1.41	1.46
0.6888	0.9648	1.7292	0.099	-0.314	-330.22	-0.65	1.49	1.51
0.7914	1.0014	1.6867	0.075	-0.245	-270.22	-0.69	1.51	1.51
0.8951	1.0411	1.6621	0.034	-0.157	-186.23	-0.82	1.44	1.41
			Butyl acetate + DMSO					
0.1418	0.8842	0.7177	-0.244	-0.098	-111.00	-0.51	0.90	0.79
0.2710	0.9037	0.7848	-0.335	-0.165	-158.04	-0.47	0.91	0.77
0.3893	0.9238	0.8663	-0.357	-0.206	-167.64	-0.44	0.92	0.75
0.4979	0.9438	0.9507	-0.339	-0.234	-178.27	-0.46	0.92	0.72
0.5980	0.9649	1.0476	-0.299	-0.241	-169.13	-0.46	0.91	0.69
0.6905	0.9869	1.1548	-0.258	-0.229	-149.89	-0.47	0.91	0.65
0.7763	1.0096	1.2712	-0.203	-0.202	-125.88	-0.48	0.90	0.61
0.8561	1.0334	1.4053	-0.144	-0.151	-84.19	-0.48	0.91	0.58
0.9305	1.0580	1.5465	-0.069	-0.087	-47.14	-0.50	0.89	0.52
			Butanone + DMSO					
0.0930	0.8124	0.4090	-0.215	-0.043	204.19	0.95	0.82	0.76
0.1875	0.8380	0.5575	-0.440	-0.025	593.52	1.53	1.01	0.93
0.2834	0.8655	0.7461	-0.692	0.031	927.48	1.80	1.18	1.09
0.3809	0.8940	0.9258	-0.860	0.076	1061.92	1.77	1.27	1.18
0.4799	0.9233	1.1266	-0.940	0.14	1141.60	1.80	1.39	1.29
0.5806	0.9533	1.3117	-0.906	0.186	1102.61	1.79	1.48	1.40
0.6829	0.9842	1.4620	-0.786	0.195	946.45	1.72	1.54	1.46
0.7868	1.0165	1.5877	-0.613	0.177	716.86	1.69	1.60	1.54
0.8925	1.0498	1.6767	-0.360	0.120	409.58	1.69	1.68	1.64
			Butyl Amine + DMSO					
0.0942	0.7489	0.5155	-0.529	-0.025	298.88	0.98	1.02	0.92
0.1896	0.7793	0.6382	-0.927	-0.025	614.32	1.06	1.10	0.98
0.2862	0.8111	0.8425	-1.212	0.055	1091.99	1.49	1.34	1.20
0.3841	0.8451	1.0464	-1.440	0.133	1408.81	1.62	1.49	1.34
0.4834	0.8804	1.2390	-1.509	0.198	1601.54	1.64	1.59	1.46
0.5839	0.9177	1.4212	-1.480	0.251	1709.70	1.67	1.70	1.58
0.6858	0.9567	1.5703	-1.320	0.269	1719.63	1.68	1.78	1.69
0.7891	0.9978	1.6681	-1.056	0.234	1543.01	1.66	1.83	1.77
0.8939	1.0403	1.6887	-0.618	0.12	1078.02	1.48	1.74	1.69
			318.15 K					
			tert-Butyl alcohol + DMSO					

Contd.

0.0953	0.7837	1.7142	0.032	-0.078	-78.06	-0.39	1.22	1.27
0.1917	0.8078	1.5876	0.060	-0.153	-216.16	-0.57	1.08	1.14
0.2890	0.8335	1.4874	0.080	-0.211	-325.19	-0.64	1.05	1.10
0.3874	0.8610	1.4069	0.092	-0.245	-410.41	-0.70	1.04	1.07
0.4868	0.8904	1.3750	0.096	-0.252	-410.63	-0.67	1.09	1.11
0.5872	0.9221	1.3684	0.087	-0.230	-365.21	-0.61	1.15	1.15
0.6888	0.9562	1.3737	0.069	-0.189	-298.64	-0.58	1.20	1.19
0.7914	0.9930	1.3890	0.043	-0.136	-215.40	-0.54	1.24	1.21
0.8951	1.0327	1.4189	0.020	-0.069	-107.35	-0.48	1.29	1.26
			Butyl acetate + DMSO					
0.1418	0.8758	0.5781	-0.212	-0.086	-116.05	-0.51	0.74	-2.39
0.2710	0.8955	0.6605	-0.348	-0.122	-70.40	-0.30	0.82	-0.66
0.3893	0.9158	0.7569	-0.426	-0.134	-1.55	-0.17	0.87	-0.07
0.4979	0.9365	0.8393	-0.443	-0.151	-4.94	-0.18	0.87	0.19
0.5980	0.9579	0.9280	-0.426	-0.154	-3.73	-0.19	0.87	0.34
0.6905	0.9799	1.0308	-0.383	-0.136	20.96	-0.15	0.89	0.45
0.7763	1.0026	1.1374	-0.312	-0.108	38.02	-0.11	0.91	0.54
0.8561	1.0261	1.2444	-0.222	-0.074	41.28	-0.08	0.94	0.61
0.9305	1.0504	1.3507	-0.113	-0.036	31.38	-0.03	0.97	0.68
			Butanone + DMSO					
0.0930	0.8051	0.3725	-0.389	-0.047	71.81	0.35	0.65	0.60
0.1875	0.8312	0.4369	-0.662	-0.091	107.63	0.29	0.64	0.59
0.2834	0.8584	0.5429	-0.870	-0.093	290.81	0.56	0.71	0.65
0.3809	0.8866	0.6887	-1.009	-0.058	523.03	0.86	0.83	0.76
0.4799	0.9161	0.8739	-1.093	0.015	749.95	1.16	0.99	0.91
0.5806	0.9472	1.0807	-1.142	0.107	901.39	1.43	1.17	1.10
0.6829	0.9797	1.2410	-1.128	0.151	989.72	1.76	1.44	1.39
0.7868	1.0127	1.3732	-0.979	0.165	932.08	2.15	1.77	1.75
0.8925	1.0455	1.3853	-0.657	0.057	641.73	2.59	2.14	2.18
			Butyl Amine + DMSO					
0.0942	0.7422	0.4387	-0.510	-0.024	174.36	0.78	0.85	0.76
0.1896	0.7728	0.5147	-0.960	-0.052	242.39	0.61	0.82	0.74
0.2862	0.8050	0.6441	-1.316	-0.028	476.63	0.90	0.94	0.84
0.3841	0.8396	0.8489	-1.623	0.070	841.07	1.36	1.17	1.05
0.4834	0.8762	1.0931	-1.826	0.206	1138.80	1.75	1.43	1.32
0.5839	0.9143	1.2867	-1.866	0.290	1196.30	1.89	1.60	1.50
0.6858	0.9541	1.4169	-1.760	0.309	1073.30	1.92	1.69	1.62
0.7891	0.9945	1.4255	-1.423	0.205	710.87	1.66	1.58	1.52
0.8939	1.0359	1.4277	-0.886	0.093	334.24	1.39	1.44	1.40

Table 3
Redlich-Kister coefficients and standard deviations (σ) for the binary mixtures at 298.15 K, 308.15 K And 318.15 K

Binary mixture	Excess property	Temp. (/K)	a_0	a_1	a_2	a_3	a_4	σ
DMSO + Tert-But. Alcohol.	V^E x10^6/ (m^3.mol^{-1})	298.15	1.183	-0.074	-0.722			0.002
		308.15	0.442	0.121	-0.087	-0.126	-0.124	0.002
		318.15	0.378	-0.100	-0.147	-	-	0.001
	$\Delta\eta$ / (mPa S)	298.15	-4.664	2.294	-	-	-	0.023
		308.15	-1.689	0.711	-0.094	-0.588	-0.502	0.002
		318.15	-0.998	0.220	0.272	-0.182	-	0.001
	G^{*E} /(J.mol^{-1})	298.15	-3553.20	981.45	1660.60	-1224.24	-2480.93	9.21
		308.15	-1707.49	454.38	311.26	-1252.91	-710.67	3.22
		318.15	-1639.09	485.49	-1006.67	-	-	7.39
DMSO + But. Acet.	V^E x10^6/ (m^3.mol^{-1})	298.15	-0.889	0.518	0.257	-	-	0.002
		308.15	-1.351	0.541	-0.436	0.116	-	0.003
		318.15	-1.778	-0.024	-	-	-	0.002
	$\Delta\eta$ / (mPa.S)	298.15	-1.958	-0.373	-	-	-	0.006
		308.15	-0.933	-0.305	-0.177	-	-	0.001
		318.15	-0.615	-0.001	-	-	-	0.007
	G^{*E} /(J.mol^{-1})	298.15	-2688.68	1090.97	370.72	419.07	-	5.51
		308.15	-702.389	35.529	-217.51	218.25	-	3.37
		318.15	-28.83	46.12	675.66			3.57
DMSO + 2-Butanone	V^E x10^6/ (m^3.mol^{-1})	298.15	-3.402	-0.052	-0.205	-	-	0.006
		308.15	0.599	0.931	-0.324	0.215	-	0.005
		318.15	-4.445	-1.210	-0.390	-	-	0.006
	$\Delta\eta$ / (mPa.S)	298.15	-0.177	1.396	-	-	-	0.010
		308.15	0.599	0.931	0.214	-	-	0.005

Contd.

		318.15	0.011	1.886	0.262	-	-	0.004
	G^{*E} /(J.mol^{-1})	298.15	2668.48	2379.35	-2772.74	-999.62		11.44
		308.15	4545.82	-180.14	-242.60	-563.24	-2344.28	16.42
		318.15	3125.33	3726.60	114.70	1235.00	-	6.95
DMSO + n-But.Amine	V^E x10^6/ (m^3.mol^{-1})	298.15	-4.787	-0.437	-0.191			0.003
		308.15	0.858	1.293	-0.563	-0.362	-	0.011
		318.15	-7.327	-2.062	-0.404	-	-	0.012
	$\Delta\eta$ / (mPa.S)	298.15	0.510	1.266	-1.046	0.391	1.166	0.005
		308.15	1.121	1.783	-1.050	-1.39	-	0.014
		318.15	0.890	2.385	-1.662	-3.650	1.228	0.007
	G^{*E} /(J.mol^{-1})	298.15	3205.28	866.70	-2967.24	2496.09	976.64	16.87
		308.15	3808.74	2767.12	-518.58	999.67	-	16.24
		318.15	4644.68	3325.08	-2269.01	6206.62	-2316.12	17.05

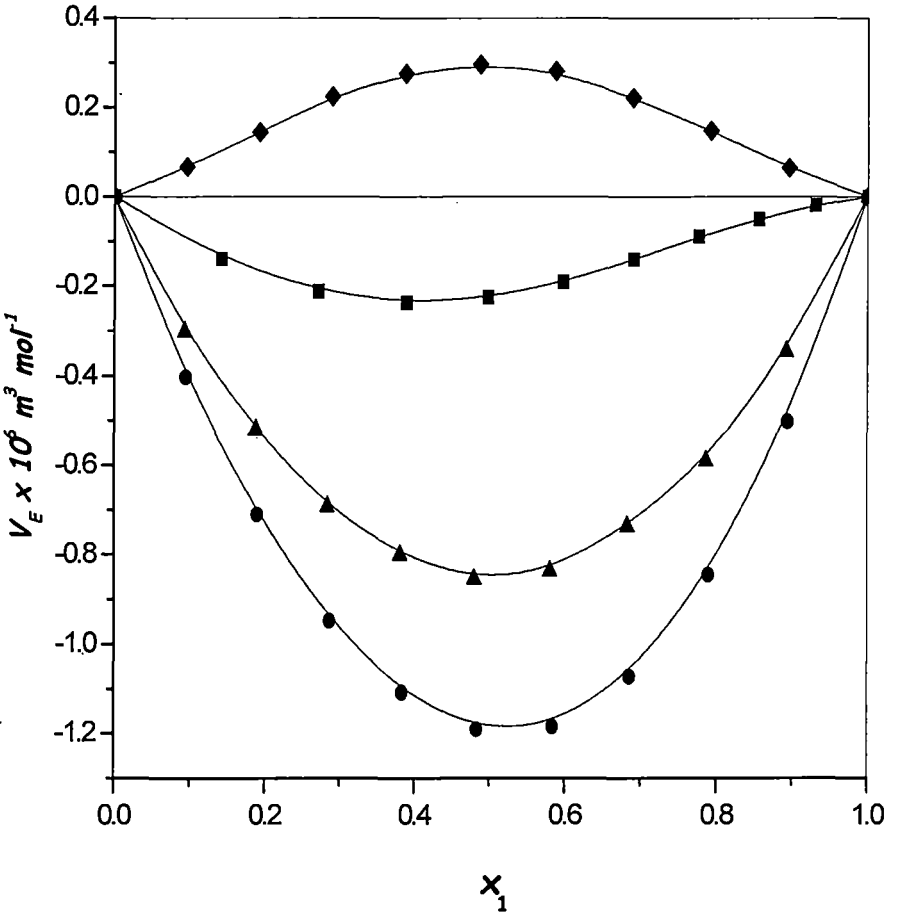

Figure1.

Excess molar volumes (V^E) for binary mixtures of DMSO(x_1) with t-butyl alcohol (♦) n-butyl acetate (■),2-Butanone (▲)and n-butylamine(●);at 298.15K

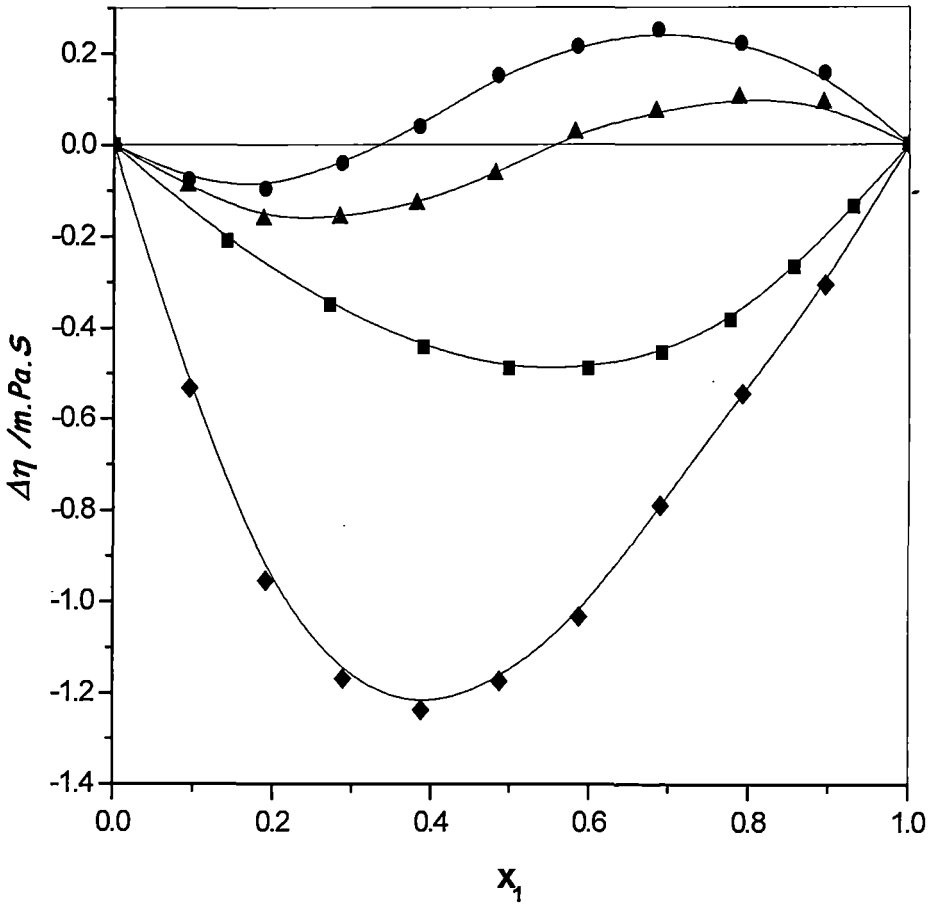

Figure2.

Viscosity deviations ($\Delta\eta$) for binary mixtures of DMSO(x_1) with t-butyl alcohol (♦) n-butyl acetate (■),2-Butanone (▲)and n-butylamine(●);at 298.15K

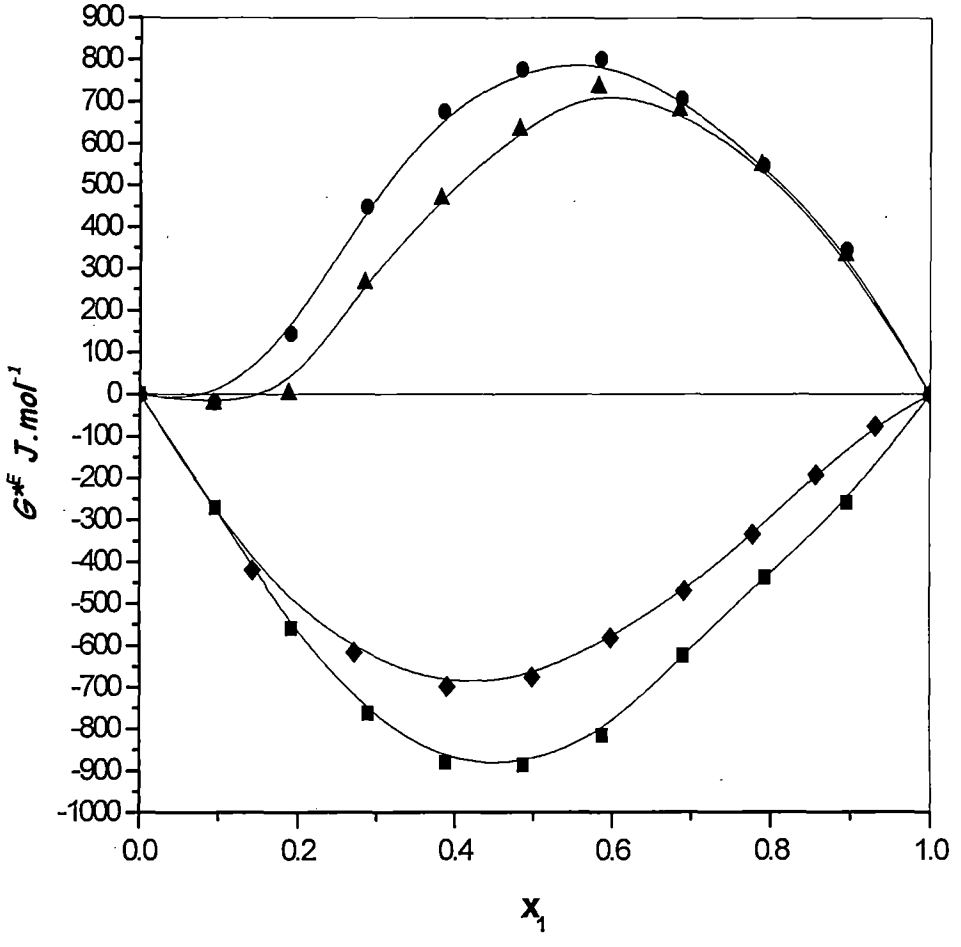

Figure3.

Excess Gibbs free energies for activation of viscous flow (G^{*E}) for binary mixtures of DMSO(x_1) with t-butyl alcohol (♦) n-butyl acetate (■),2-Butanone (▲)and n-butylamine(●);at 298.15K