VISCOMETRIC STUDIES
OF BINARY DIMETHYL SULFOXIDE + 1-HEXANOL SYSTEM

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The viscosities of the binary system dimethyl sulfoxide + 1-hexanol have been measured at T = (298.15, 303.15, 313.15 and 323.15) K and atmospheric pressure, over the whole composition range. The excess functions, viscosity deviations (Δv) and excess Gibbs energy of activation of viscous flow (G^{*E}) were calculated from experimental data and have been fitted to Redlich–Kister polynomial equation. The system exhibits negative values for Δv and G^{*E} over the whole composition range at all investigated temperatures. From the experimental data the thermodynamic functions of activation of viscous flow have been estimated by using Eyring viscosity equation. Furthermore, the Gibbs energies, (ΔG^*), enthalpies (ΔH^*) and entropies (ΔS^*) of activation of viscous flow have been evaluated and their variation with concentration were discussed. The viscosity data have also been correlated with semi-empirical equations of Grunberg-Nissan, Soliman and McAllister. The results are discussed in terms of interactions between components.

INTRODUCTION

Well recognized importance of thermodynamic and physico-chemical properties in design calculations involving chemical separations, fluid flow and heat transfer, has motivated our research group for systematic measurements of various thermophysical properties of binary mixtures containing "supersolvents", as dimethyl sulfoxide (DMSO) and *n*-alcohols. We have carried out the volumetric and refractometric study of mixtures of DMSO with 1-hexanol over entire composition range.[1] Continuing with our studies, the present paper reports the viscosity deviations (Δv) and excess Gibbs energy of activation of viscous flow (G^{*E}) at T = 298.15 K, 303.15 K, 313.15 K and 323.15 K with the aim of analyzing the disruption of self-association in 1- hexanol and the breaking both of dipole–dipole interactions and molecular

association in DMSO. DMSO is a typical aprotic self-associated solvent due to S=O group, with large dipole moment (μ =3.96 D at 298.15 K) and 1-hexanol is a self-associated solvent through hydrogen bonding, with relatively low values of dipole moment. The transport properties of binary mixtures of DMSO with 1-hexanol have also been studied by other authors[2-4] at 303.15 K and 313.15 K; no literature data at other temperatures are available for this system.

EXPERIMENTAL

Materials. Dimethyl sulfoxide and 1-hexanol (Merck, purities > 99.5% in mole fraction) were used without further purification. Experimental densities, ρ, and dynamic viscosities, η, of the pure components are in agreement with the literature values, as can be seen in Table 1.

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Table 1

Densities and dynamic viscosities of pure components at 298.15 K

Compound	ρ, g cm^{-3}		η, mPa·s	
	Exp.	Lit.	Exp.	Lit.
Dimethyl sulfoxide	1.09536	1.09533[5], 1.095278[6]	1.991	1.975[9]
1-hexanol	0.81513	0.81494[7] 0.81523[8]	4.589	4.594[8]

Apparatus and procedure. All mixtures were prepared by mixing the appropriate volumes of liquids in airtight glass bottle and weighed using a HR-120 (A&D Japan) electronic balance with a precision of 0.1 mg. The experimental uncertainty in mole fraction was estimated to be less than ± 0.0002.

The kinematic viscosities, ν, of pure solvents and their mixture were measured with an Ubbelohde capillary viscometer. The viscometer was calibrated using double distilled water. The time of fall always exceeded 60 seconds; the accuracy of the flow time was ±0.1 seconds. At least four time flow measurements were performed for each composition and temperature, and the results were averaged. All measurements were performed in a thermostat maintained at desired temperature with accuracy of ± 0.05 K. The uncertainty in the kinematic viscosity was ±0.001 cSt.

Dynamic viscosity, η, was calculated with the following equation:

$$\eta = k \times t \times \rho \qquad (1)$$

where t is the flow time, k is the viscosimeter constant, and ρ is the density. Densities were determined with an Anton Paar digital densimeter, model DMA 4500, with a precision of ±0.00005 g·cm^{-3}.

RESULTS AND DISCUSSION

The experimental data of kinematic viscosities obtained at T = (298.15, 303.15, 313.15 and 323.15) K for the binary system DMSO (1) + 1-hexanol (2) are shown in Table 2.

The values of viscosity deviation, Δv, and the excess Gibbs energy of activation of viscous flow, G^{*E}, were calculated from the experimental data according to the following equations:

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

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

where x_i represent the mole fraction of pure component i, v, η, are the kinematic and dynamic viscosities of mixtures, respectively, and v_i, η_i, the properties of the pure components. R is the gas constant and T the absolute temperature.

The experimental values of Δv and G^{*E} were fitted to the Redlich-Kister type polynomials:

$$Y = x_i x_j \sum_{k=0}^{p} A_k \left(x_i - x_j \right)^k \qquad (4)$$

where Y is Δv or G^{*E} and p is the degree of polynomial expansion. The adjustable parameters A_k obtained by fitting the equations to the experimental values with a least-squares algorithm are given in Table 3, along with the standard deviation, σ, defined as follows:

$$\sigma = \left[\frac{\sum_{i=1}^{n}(Y_i^{\exp} - Y_i^{calc})^2}{n - m} \right]^{0.5} \qquad (5)$$

where n is the number of experimental data and m is the number of parameters. It should be noted that for DMSO + 1-hexanol system three parameters were necessary for correlation to obtain optimum standard deviation.

The variation of the excess or deviation properties along with the smoothed curves using Eq. (4) are presented in Figs. 1 and 2. As can be seen from the figures, the DMSO +1-hexanol system shows negative values for the deviations in viscosity and excess Gibbs energy of activation of viscous flow over the whole composition range, which increase as the temperature of the mixture increases from 298.15 K to 323.15 K.

The positive excess volume variation[1] and negative Δv and G^{*E} values obtained for this system indicate the disruption of the associated molecules in pure state and formation of weak interactions between the components in the mixture, as was suggested by Chowdhury *et al.* for other systems with 1-hexanol. [10] According to Fort and Moore,[11] negative values of excess viscosity are observed for the systems of different molecular size in which the dispersion forces are dominant.

Table 2

Kinematic viscosities, v, for the DMSO (1) + 1-hexanol (2) system at different temperatures

x_1	v, cSt			
	298.15 K	303.15 K	313.15 K	323.15 K
0.0000	5.6299	4.8757	3.6697	2.8667
0.1115	4.4072	4.0142	3.1161	2.4662
0.2124	3.6673	3.2636	2.6023	2.1361
0.3032	3.2321	2.8759	2.3465	1.9428
0.3919	2.9416	2.6449	2.1557	1.8057
0.5036	2.6485	2.3898	1.9707	1.6694
0.6043	2.4425	2.2095	1.8270	1.5550
0.6983	2.2702	2.0352	1.7016	1.4454
0.8008	2.0846	1.9009	1.5917	1.3601
0.8983	1.9553	1.7768	1.4656	1.2967
1.0000	1.8173	1.6579	1.3950	1.2066

Table 3

Parameters A_k and standard deviations of excess functions for DMSO + 1-hexanol system at different temperatures

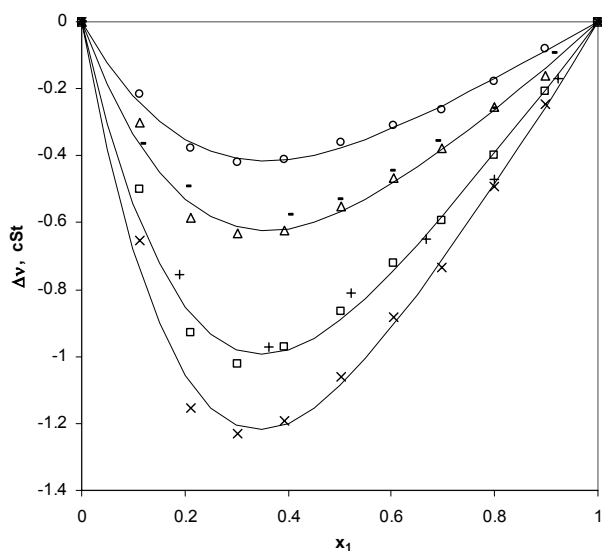|	T, K	A_0	A_1	A_2	σ
Δv, (cSt)	298.15	-3.0806	5.5226	-1.2708	0.0413
G^{*E}, (J·mol^{-1})		-1.7582	1.2782	-0.5322	0.0104
Δv, (cSt)	303.15	-2.6952	4.1403	-0.8727	0.0413
G^{*E}, (J·mol^{-1})		-1.6286	1.2329	-0.4228	0.0098
Δv, (cSt)	313.15	-1.7477	2.4513	-0.5292	0.0296
G^{*E}, (J·mol^{-1})		-1.3359	1.0766	-0.2713	0.0097
Δv, (cSt)	323.15	-1.1811	1.5964	-0.3274	0.0146
G^{*E}, (J·mol^{-1})		-1.0793	0.8509	-0.3263	0.0079

Fig. 1 – Viscosity deviation for DMSO (1) +1-hexanol (2) system at 298.15 K (×); 303.15 K (□); 313.15 K (Δ); 323.15 K (o); correlation with Redlich-Kister equation (—); data from ref. 2. at 303.15 K (+); data from ref. 4. at 313.15 K (-).
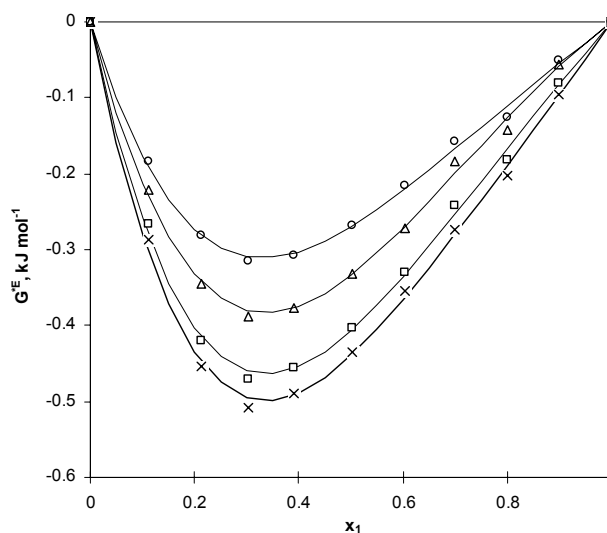
Fig. 2 – Excess molar Gibbs energy of activation of viscous flow for DMSO (1) +1-hexanol (2) system at 298.15 K (×); 303.15 K (□); 313.15 K (Δ); 323.15 K (o); correlation with Redlich-Kister equation (—).

The system exhibits also negative values for excess Gibbs energy of activation of viscous flow over the whole composition range at all investigated temperatures. Negative G^{*E} values indicate that dispersion forces are prevailing in the mixtures, as was suggested in literature.[12] All the obtained excess or deviation properties are in accordance with those reported in literature,[2-4] as is shown in Fig. 1.

The temperature dependence of viscosity was used to estimate ΔH^*, ΔS^* and ΔG^* through Eyring's viscosity equation[13] which is given as:

$$\eta = \frac{h\ N_A}{V} \exp\left(\frac{\Delta G^*}{R\ T}\right) \qquad (6)$$

where h is the Planck's constant, N_A is Avogadro's number, V is the molar volume of the mixture and ΔG^* is the molar Gibbs energy of activation for the viscous flow process. Combining this equation with:

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (7)$$

The equation yields:

$$\ln\left(\frac{\eta\ V}{h\ N_A}\right) = \frac{\Delta H^*}{R\ T} - \frac{\Delta S^*}{R} \qquad (8)$$

A plot of $\ln(\eta V/hN_A)$ as a function of $1/T$ was found to show a quite linear trend for each composition of the system under study. This indicates that the ΔH^* values are almost constant in the studied temperature range. Thus, the values of ΔH^* and ΔS^* were estimated as the slopes and intercepts of the linear plots of $\ln(\eta V/hN_A)$ against $1/T$ by using a linear regression procedure. The values of ΔH^*, $T\Delta S^*$ and ΔG^* along with the linear

regression coefficient, r, are given in Table 4. A perusal of the table indicates that all of the obtained thermodynamic functions of activation vary with mixture composition, decreasing with increasing concentration of DMSO in the mixture. The values of ΔH^* and ΔG^* are positive and of $T\Delta S^*$ are negative (Fig. 3). The enthalpy magnitude of activation for viscous flow is higher than $T\Delta S^*$ values, which indicate that the energetic contribution, corresponding to the enthalpy of activation for viscous flow, is more important than the entropic contribution terms to the Gibbs energy of activation for viscous flow for dimethyl sulfoxide + 1-hexanol system.

The variation of ΔH^* and ΔG^* with the DMSO concentration indicates that the formation of activated species necessary for viscous flow appears difficult in the 1-hexanol rich region and becomes quite easy as the DMSO concentration increases. However, the values of ΔS^* suggest that as the concentration of DMSO increases, the liquid is becoming more structured.

The viscosity data have been correlated using semiempirical or theoretical-based models of Grunberg-Nissan (eq. (9)), McAllister (eq. (10)) and Soliman (eq. (11)) with one or two adjustable parameters.

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2G_{12} \qquad (9)$$

According to Grunberg and Nissan,[14] the adjustable binary parameter, G_{12}, is regarded as measure of the strength of interactions between the mixing species.

Table 4

The thermodynamic functions of activation of viscous flow, ΔH^*, $T\Delta S^*$, ΔG^*, for DMSO (1) + 1-hexanol (2) system at 298.15 K

x_1	ΔH^* / kJ·mol^{-1}	ΔS^* / J·mol^{-1}·K^{-1}	ΔG^* / kJ·mol^{-1}	r
0.0000	21.71	-25.92	29.44	0.9997
0.1115	19.24	-31.95	28.77	0.9998
0.2124	17.37	-36.49	28.25	0.9997
0.3032	16.28	-38.90	27.88	0.9997
0.3919	15.68	-39.94	27.59	0.9996
0.5036	14.95	-41.27	27.26	0.9996
0.6043	14.51	-41.85	26.99	0.9994
0.6983	14.04	-42.63	26.75	0.9999
0.8008	13.71	-42.76	26.46	0.9998
0.8983	13.39	-43.07	26.23	0.9998
1.0000	13.16	-42.96	25.97	0.9992

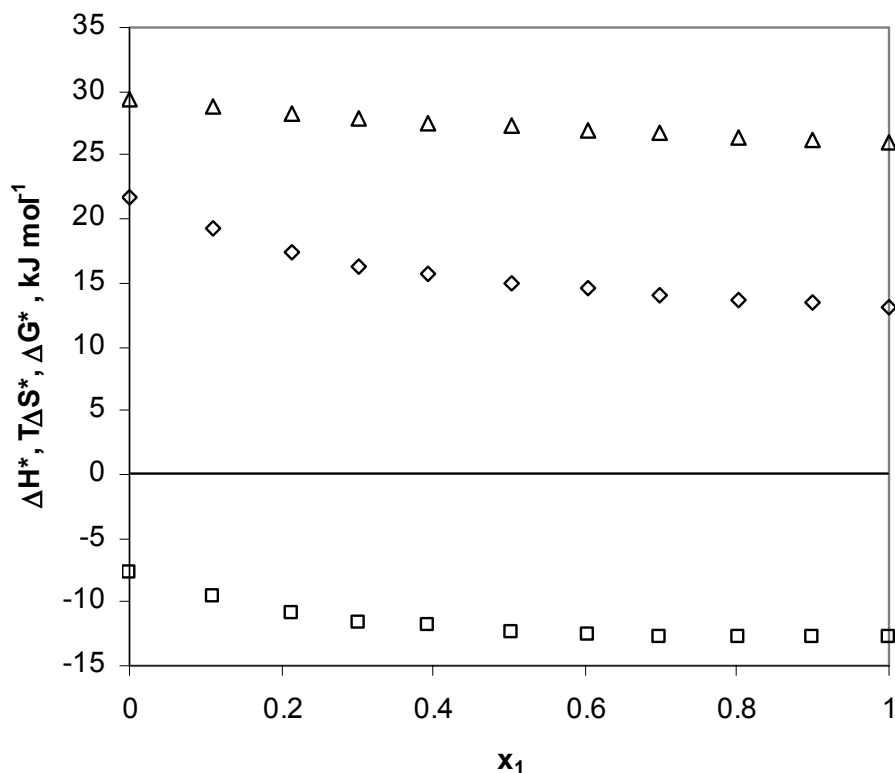Fig. 3 – Thermodynamic functions of activation vs. composition
for dimethyl sulfoxide (1) + 1-hexanol (2) system at 298.15 K: ΔH^* (◊); $T\Delta S^*$ (□) and ΔG^* (Δ).

McAllister's two-parameter equation,[15] based on Eyring's theory of absolute reaction rates, takes into account interactions both of like and unlike molecules by a two-dimensional three-body interaction.

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln \nu_{12} + 3x_2^2 x_1 \ln \nu_{21} + x_1^3 \ln M_1 +$$
$$+ x_2^3 \ln M_2 - \ln\left(x_1 M_1 + x_2 M_2\right) + 3x_1^2 x_2 \ln M_{12} + 3x_1 x_2^2 \ln M_{21}$$
$$M_{12} = \left(2M_1 + M_2\right)/3 \qquad M_{21} = \left(M_1 + 2M_2\right)/3$$

(10)

where ν and ν_i are the kinematic viscosity of the mixture and pure components, respectively.

The data were also correlated with a modified form of the McAllister equation proposed by Soliman,[16] using the form with two-parameters.

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln A_{12} + \frac{\nu_{12} x_1 x_2}{\left(\dfrac{M_1}{M_2}\right)^2 x_1 + x_2}$$

(11)

For all these models the standard deviation (σ) was calculated using type (5) equation, where Y is the kinemativ viscosity.

The values of the Grunberg-Nissan interaction parameter are also negative for this system, which increase as the temperature of the mixture increases from 298.15 K to 323.15 K; this suggests weak interactions between unlike molecules, in accordance with the excess properties analysis. The equations used for viscosity correlation present small deviations, less than 1% (as can be seen from Table 5), with very good results for theoretical based equation of McAllister.

Table 5

Adjustable parameters and standard deviation of the Grunberg-Nissan, Soliman and McAllister equations

Equation	Parameters/ σ	298.15 K	303.15 K	313.15 K	323.15 K
Grunberg-Nissan	A_{12}	-0.9752	-0.9063	-0.7411	-0.6226
	σ	0.0861	0.0743	0.0462	0.0319
Soliman	A_{12}	0.5332	0.5024	0.5452	0.6273
	v_{12}	2.8673	2.7093	2.1892	1.6511
	σ	0.0393	0.0441	0.0318	0.0161
McAllister	A_{12}	2.4636	2.1371	1.7593	1.5205
	A_{21}	2.4960	2.3698	2.0079	1.6919
	σ	0.0195	0.0439	0.0304	0.0147

CONCLUSIONS

New experimental data of kinematic viscosities for the binary systems DMSO + 1-hexanol at 298.15, 303.15, 313.15 and 323.15 K have been reported. The obtained deviations in viscosity and excess Gibbs energy of activation of viscous flow, G^{*E}, are negative over the whole composition range. This suggests that breaking up of self-associated structures of the pure compounds is dominant over the formation of hydrogen bonding and dipole–dipole interaction between unlike molecules. The energetic contribution, corresponding to the enthalpy of activation for viscous flow, is more important than the entropic contribution terms to the Gibbs energy of activation for viscous flow. The Grunberg-Nissan, Soliman and McAllister equations are suitable to estimate the mixing viscosities in terms of the pure component data. Negative values of the Grunberg-Nissan parameter indicate weak interactions between unlike molecules.

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