

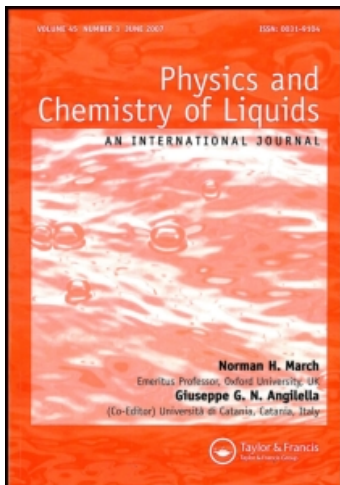
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VISCOSITIES OF AQUEOUS SOLUTIONS OF DIMETHYLSULFOXIDE, 1,4-DIOXANE AND TETRAHYDROFURAN

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Viscosities of the systems, water(W) + dimethylsulfoxide(DMSO), W + 1,4-dioxane (DXN) and W + tetrahydrofuran(THF), are measured at temperatures ranging from 303.15–323.15 K. Viscosities and excess viscosities are plotted against the mole fraction of the organic solutes. On addition of solutes to water, viscosities first increase rapidly, pass through maxima and then decline continuously until the pure state of solutes is reached. Excess viscosities are found to be positive and large in magnitude and their curves are similar to those of the viscosity curves. The ascending part of the viscosity curves in the water-rich region is accounted for by both the hydrophobic effect of forming cage structures around solutes and the hydrophilic effect forming H-bonds between water and organic solutes. The descending part of the viscosity curves is explained by the continuous destruction of cages formed. The maxima are thought to be due to competing processes of formation and destruction of cage structures.

Keywords: Excess viscosity; Dimethylsulfoxide; 1,4-dioxane and tetrahydrofuran

1. INTRODUCTION

This is a part of our ongoing research of the volumetric and viscometric properties of aqueous solutions of organic substances with particular reference to hydrophobic solutes. Literature survey shows that, very limited studies are so far reported relevant to our

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present investigation. However, notable amongst them are the works of Sacco *et al.* [1] and Tamura *et al.* [2] describing volumetric and viscometric properties of DMSO+W. Here, we report on the viscosities of aqueous systems formed by DMSO, DXN and THF covering the whole range of composition with a view to understand the nature of interaction of these substances with water. Apart from the objective analysis of experimental results an additional but useful outcome of this is the presentation of viscosity data of the systems which we believe will make some contribution to database.

2. EXPERIMENTAL

The organic liquids under investigation were procured from Aldrich, with the following quoted purity: dimethylsulfoxide (99.9%), 1,4-dioxane (99.8%), and tetrahydrofuran (99.5%). The substances were used without any further purification except that each of the liquids was kept over molecular sieves (4A) for at least two weeks prior to use. Thrice distilled water was used in the preparation of the solutions. The

TABLE I Density $d(\text{g cm}^{-3})$ and viscosity $\eta(\text{mp})$ of pure liquids

T/K	DMSO		DXN		THF	
	<i>d</i>	η	<i>d</i>	η	<i>d</i>	η
303.15	1.0896 (1.0910) ^a (1.0906) ^b (1.090269) ^c	17.979 (17.9) ^a	1.0225 (1.02225) ^f (1.02223) ^g (1.0224) ^h	10.958 (10.937) ^g (10.86) ^h	0.8759 (0.8773) ^h	4.496 (4.50) ^h
308.15	1.0847 (1.0870) ^a (1.0856) ^b	16.092 (16.05) ^k (15.9) ^a	1.0168 (1.01650) ^o (1.01689) ^g (1.0167) ^h	10.122 (10.112) ^g (10.000) ^h	0.8702 (0.8718) ^h (0.87033) ⁱ	4.277 (4.277) ⁱ (4.29) ^h
313.15	1.0797 (1.0806) ^b (1.08046) ^d	14.492	1.0110 (1.01157) ^f	9.376	0.8649 (0.86567) ^j	4.066
318.15	1.0748	13.173 (13.10) ^k	1.0052 (1.00514) ^o	8.714	0.8600 (0.86140) ⁱ	3.901 (3.902) ⁱ
323.15	1.0698 (1.06062) ^d	12.214	0.9995 (1.00028) ^f	8.121	0.8541	3.696

^a Ref. [4]; ^b Ref. [5]; ^c Ref. [2]; ^d Ref. [6]; ^e Ref. [7]; ^f Ref. [8]; ^g Ref. [9]; ^h Ref. [10]; ⁱ Ref. [11]; ^j Ref. [12]; ^k Ref. [13].

TABLE II Coefficient of viscosity η (mp) and excess viscosity η^E (mp) of aqueous solutions of organic solutes for different molar ratios at different temperatures

T/K	303.15		308.15		313.15		318.15		323.15	
	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
Water (X_1) + Dimethylsulfoxide (X_2)										
0.0000	8.006	0.000	7.226	0.000	6.557	0.000	5.994	0.000	5.501	0.000
0.1000	16.095	7.414	14.210	6.382	12.600	5.502	11.305	6.485	10.189	4.231
0.2003	25.390	15.976	22.168	13.685	19.372	11.686	17.128	10.110	15.208	8.755
0.3023	31.493	21.269	27.253	18.048	23.772	15.439	20.933	13.328	18.551	11.550
0.3494	32.173	21.552	27.856	18.298	24.439	15.789	21.532	13.640	19.075	11.806
0.4044	31.915	20.800	27.742	17.754	24.472	15.435	21.640	13.400	19.419	11.824
0.5003	29.833	17.833	26.274	15.488	23.252	13.502	20.760	11.872	18.526	10.327
0.5974	26.741	13.763	23.724	12.066	21.189	10.658	19.103	9.508	17.209	8.350
0.6975	23.641	9.565	21.282	8.651	19.119	7.718	17.376	6.994	15.735	6.140
0.7981	21.269	5.999	19.173	5.483	17.423	5.075	15.879	4.642	14.538	4.140
0.8999	19.107	2.527	17.366	2.513	15.836	2.450	14.571	2.396	13.387	2.110
1.0000	17.979	0.000	16.092	0.000	14.492	0.000	13.173	0.000	12.214	0.000
Water (X_1) + 1,4-Dioxane (X_2)										
0.0999	14.365	6.099	12.734	5.261	11.379	4.586	10.229	4.013	9.254	3.536
0.1999	17.240	8.711	15.271	7.542	13.611	6.571	12.219	5.766	11.017	5.071
0.2998	17.255	8.455	15.372	7.378	13.768	6.471	12.408	5.708	11.243	5.061
0.3982	16.111	7.036	14.447	6.184	13.019	5.461	11.804	4.852	10.744	4.321
0.4981	14.701	5.337	13.281	4.735	12.041	4.207	10.987	3.769	10.061	3.383
0.5981	13.409	3.747	12.181	3.342	11.119	3.000	10.204	2.710	9.385	2.441
0.6997	12.377	2.403	11.314	2.167	10.375	1.955	9.556	1.771	8.833	1.609
0.7996	11.591	1.300	10.633	1.172	9.799	1.072	9.063	0.980	8.408	0.897
0.9000	11.070	0.450	10.203	0.417	9.430	0.384	8.757	0.364	8.148	0.337
1.0000	10.891	0.000	10.122	0.000	9.376	0.000	8.714	0.000	8.121	0.000

TABLE II (Continued)

T/K	303.15		308.15		313.15		318.15		323.15	
	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
X_2										
Water (X_1) + Tetrahydrofuran (X_2)										
0.0971	14.439	6.870	12.556	5.689	10.772	4.512	9.839	4.099	8.801	3.509
0.1497	15.232	7.888	13.291	6.611	11.707	5.602	10.415	4.794	9.355	4.173
0.2011	14.772	7.643	13.006	6.504	11.537	5.581	10.373	4.875	9.367	4.289
0.3057	12.570	5.859	11.198	5.043	10.105	4.439	9.172	3.915	8.382	3.511
0.3979	10.398	4.035	9.414	3.549	8.555	3.133	7.829	2.776	7.216	2.521
0.4978	8.602	2.596	7.881	2.316	7.240	2.071	6.687	1.846	6.210	1.698
0.6026	7.189	1.298	6.666	1.217	6.175	1.119	5.760	1.027	5.365	0.934
0.7025	6.137	0.597	5.723	0.569	5.361	0.554	5.036	0.512	4.716	0.483
0.8003	5.413	0.216	5.085	0.220	4.788	0.225	4.520	0.201	4.277	0.221
0.8978	4.813	0.044	4.554	0.042	4.306	0.037	4.089	0.013	3.879	0.030
1.0000	4.496	0.000	4.277	0.000	4.066	0.000	3.901	0.000	3.696	0.000

density was measured by using a 5 ml bicapillary pycnometer previously calibrated by distilled water. An Ostwald U-tube viscometer with sufficiently long efflux time was used in viscosity measurement. The time of flow was recorded by a timer accurate up to ± 0.1 s. An analytical balance (Mettler Toledo) of accuracy ± 0.0001 g was used in density measurement. For every measurement, a thermostatic water bath controlled to $\pm 0.05^\circ$ C was used. The average uncertainty in the measured viscosity was estimated to be less than 6×10^{-3} mp.

3. RESULTS AND DISCUSSION

Densities(d) and viscosities(η) of pure liquids, dimethylsulfoxide (DMSO), 1,4-dioxane(DXN) and tetrahydrofuran(THF), at different temperatures are listed in Table I together with the available literature data. The results show satisfactory agreement with literature values. The viscosities and excess viscosities(η^E) are shown in Table II for all

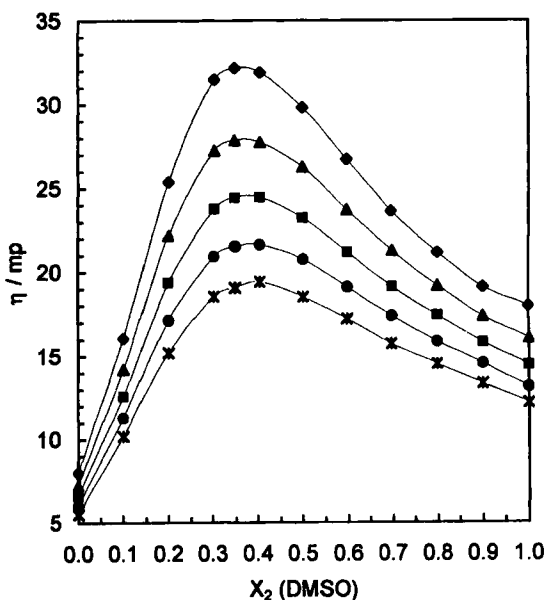


FIGURE 1 Viscosity as a function of mole fraction of DMSO of W + DMSO system at different temperatures. \blacklozenge - 303.15 K; \blacktriangle - 308.15 K; \blacksquare - 313.15 K; \bullet - 318.15 K; $*$ - 323.15 K.

the systems. Viscosities *vs.* composition curves of the systems water (W)+DMSO, W+DXN and W+THF at different temperatures are represented by Figures 1–3, respectively. Viscosity data for W+THF at 303.15K between 0.1–0.4 mole fraction of THF of Ref. [3] as plotted in Figure 3 are found to fit well with our viscosity curve. However, an examination of the figures reveals the following characteristics:

- On addition of organic liquids to water, η increase quite rapidly, pass through maxima and then decline continuously until the pure state of the liquids is reached.
- Heights of the maxima are different for different systems and, found to be in the order: W+DMSO > W+DXN > W+THF.
- Maxima occur at ~ 0.35 , 0.30 and 0.15 mole fractions of DMSO, DXN and THF, respectively, and the positions of the maxima virtually do not change with temperature.

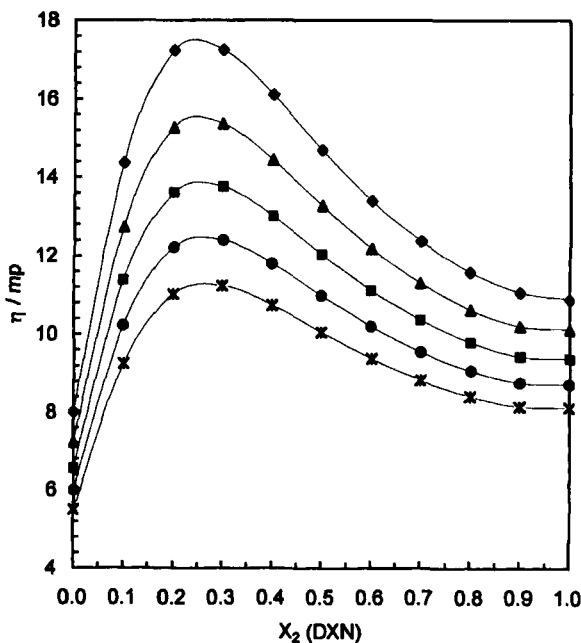


FIGURE 2 Viscosity as a function of mole fraction of DXN of the W+DXN system at different temperatures. Symbols are the same as in Figure 1.

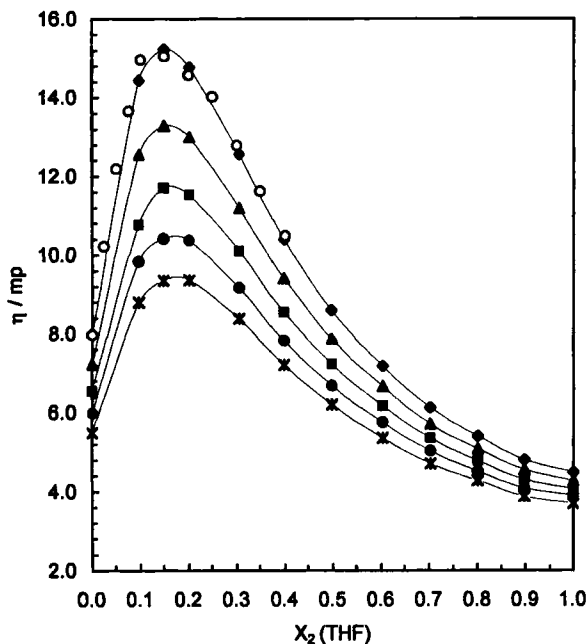


FIGURE 3 Viscosity as a function of mole fraction of THF of W + THF system at different temperatures. Symbols are the same as in Figure 2. \circ —data at 303.15 K of Ref. [3].

Excess viscosities were calculated using the following equation,

$$\eta^E = \eta - \exp(X_1 \ln \eta_1 + X_2 \ln \eta_2) \quad (1)$$

Here, η is the measured viscosity of the mixtures, η_1 and η_2 are the viscosity of water and organic liquid, respectively, and X_1 and X_2 are the corresponding mole fractions. All the excess viscosity curves were fitted to the polynomial equation of the form,

$$\eta^E = X_1 X_2 \sum_{i=0}^n A_i (2X_1 - 1)^i \quad (2)$$

Here, A_i is the i th fitting coefficient and other terms have their usual significance. Using $n=3$, at each temperature values for four A_i and the standard deviation, σ , were obtained through the least squares method. The fitting coefficients and the standard deviations are shown in Table III. The plots of excess viscosities against mole fraction of the

TABLE III Fitting coefficients A_i of Redlich–Kister Eq. (2) and standard deviation σ in mp for water + organic solute systems

System	T/K	A_0	A_1	A_2	A_3	σ
W + DMSO	303.15	73.5524	-80.6153	-18.8801	74.5907	0.5559
	308.15	63.4411	-65.0943	-14.1706	60.1465	0.4328
	313.15	55.2636	-54.0433	-11.4880	52.0898	0.3212
	318.15	47.7719	-40.6543	-0.6146	23.7051	0.3135
	323.15	42.3005	-37.9606	-7.6876	36.9387	0.1941
W + DXN	303.15	21.4732	-34.9809	25.5255	-7.8214	0.1331
	308.15	19.0294	-30.1940	21.3994	-6.3860	0.1114
	313.15	16.9160	-26.1202	18.2309	-5.5611	0.0904
	318.15	15.1380	-22.7864	15.5760	-4.6813	0.0749
	323.15	13.5674	-19.9555	13.4112	-4.0456	0.0596
W + THF	303.15	9.3312	-26.5080	43.9719	-34.3814	0.1603
	308.15	8.4685	-22.8858	35.7569	-27.2233	0.1183
	313.15	7.7907	-20.6907	28.6866	-18.9805	0.1057
	318.15	6.9738	-17.7184	24.7473	-17.7165	0.0527
	323.15	6.4371	-16.1028	21.0480	-13.5966	0.0425

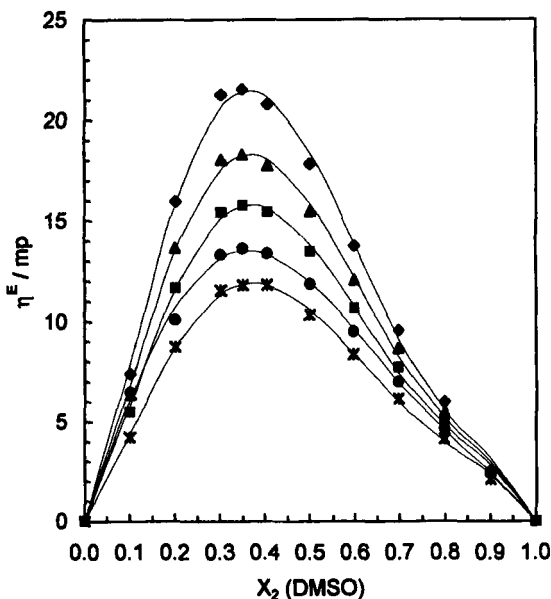


FIGURE 4 Excess Viscosity vs. composition curves of the W + DMSO system at different temperatures. Symbols are the same as in Figure 1.

organic solutes for the systems, DMSO + W, DXN + W and W + THF, are shown in Figures 4–6, respectively. For comparison η vs. composition at 303.15 K are plotted in Figure 7. An examination of

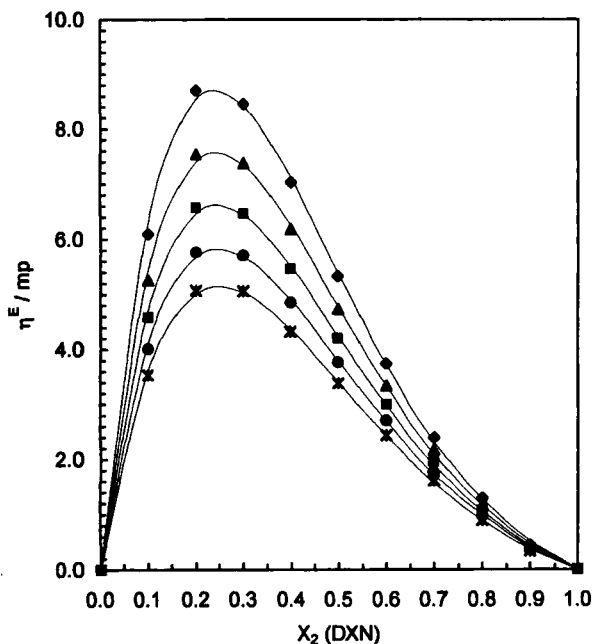


FIGURE 5 Excess Viscosity vs. composition curves for the W+DXN system at different temperatures. Symbols are the same as in Figure 1.

the curves shows that:

- (a) η^E s are positive for all the systems in the whole range of composition. The values are relatively high and they decrease with the rise of temperature.
- (b) There are well-defined maxima occurring in the water-rich regions of the systems. The maxima for W+DMSO, W+DXN and W+THF appear at ~ 0.35 , 0.25 and 0.15 mole fractions, respectively, of the solutes. The maxima do not change their positions noticeably with the change of temperature.

The initial rise of viscosity, existence of maxima in the water-rich region and continuous decline of viscosity afterwards, are typical characteristics of the viscosity of aqueous solutions of well-known hydrophobic solutes, such as, acetone [14], mono- and di-substituted amides [15, 16], alcohols [17–19], glycol ethers [20], *n*-alkoxyethanols [21], amines [22], *etc.* Two effects, (i) hydrophobic hydration and (ii) hydrophilic bonding, are considered to be the primary reasons for the

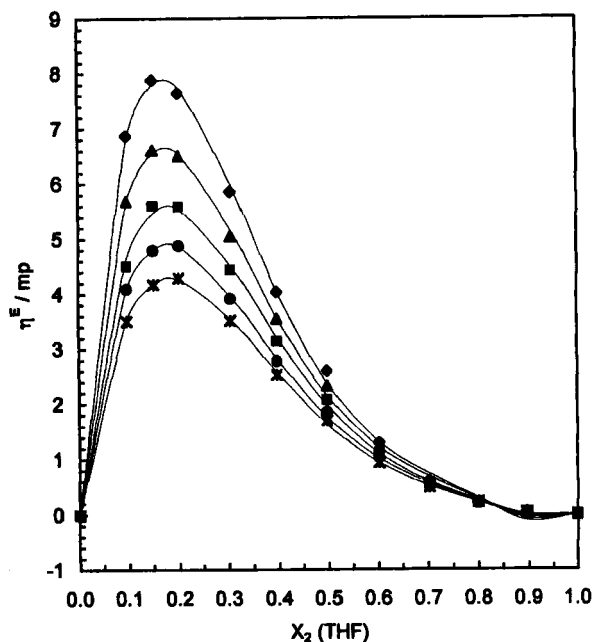


FIGURE 6 Excess Viscosity vs. composition curves of the W + THF system at different temperatures. Symbols are the same as in Figure 1.

ascending part of viscosity of these systems. In the dilute regions, where water exists in large concentration, solute molecules are considered to be surrounded by highly structured water molecules forming cages known as hydrophobic hydration. As this process leads to the decrease of entropy, it is not thermodynamically favourable. The hydrophobic hydration always requires large amounts of water, and therefore, it occurs only in the water-rich or moderately water-rich regions of solutions. However, when the solute is gradually added, a composition is reached when the number of water molecules available is not sufficient enough for the hydration to proceed further. Beyond this concentration, hydrophobic bonds forming the cage structures are broken down continuously giving rise to the reformation of normal water structures. This accounts for almost a monotonous decline in viscosity. The maximum in the viscosity curve is thought to be the result of an equilibrium state of two competing processes, the formation and the destruction of the cage structures. The characteristic

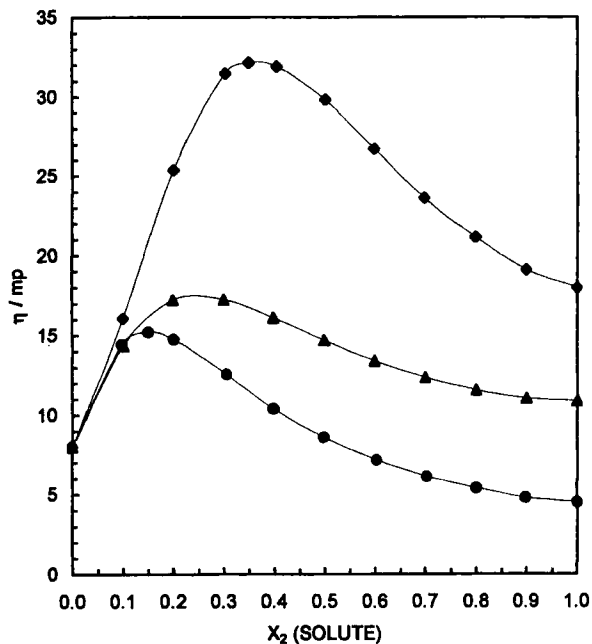


FIGURE 7 Comparison of Viscosity as a function of mole fraction of the organic solute. \blacklozenge - W+DMSO; \blacktriangle - W+DXN; \bullet - W+THF.

features of the excess viscosity curves are basically similar to those of viscosity curves. The interpretation put so far for the observed viscosity behaviour may well be applied to the excess viscosity curves. Recent studies of volumetric and viscometric properties by Sacco and Matteoli [1] and the nuclear magnetic relaxation studies by Holz *et al.* [23] on the aqueous solutions of DMSO have unambiguously indicated to some moderate to weak hydrophobicity of DMSO. Again, large negative excess enthalpies [24] of the mixtures of DMSO and water suggest for strong hydrophilic interaction of DMSO. From the excess volume studies on W+DMSO Tamura *et al.* [2] concluded that, in the water-rich region water molecules are reoriented to form hydrophobic hydrogen bonds around the two methyl groups of a DMSO molecule. Moreover, hydrophobic interaction studies on a large number of aqueous solutions of alkan-1,2-diols by Andini *et al.* [25] strongly suggest that the methyl group is the most potent hydrophobic group. However, hydrophobicity of the methyl groups of the particular case

of DMSO is thought to be reduced substantially due to the close proximity of the hydrophilic $>S=O$ group. A comprehensive paper on water shell stabilization by interstitial non-electrolytes by Glew, Mak and Rath [26] and the references therein explicitly pointed to the formation of solid clathrates by THF and DXN, giving unambiguous evidence to the cavity solution model. The authors concluded further that, DXN and THF form relatively weak H-bonds with water as indicated by the n.m.r. spectroscopy and by the endothermic heats of mixing of the dilute solutions of water.

4. CONCLUSION

All the three aqueous systems of DMSO, DXN and THF exhibit similar viscosity behaviour. DMSO is thought to be rather a moderately or weakly hydrophobic but strongly hydrophilic solute. The other two solutes DXN and THF on the other hand are supposed to be much strongly hydrophobic but relatively weakly hydrophilic towards W. The ascending parts of viscosity curves of these systems are accounted for by both hydrophobic and hydrophilic effects. The maximum in viscosity curves is thought to be the resultant of two competing processes – one the formation and the other the destruction of the cage structures around the hydrocarbon moieties of organic solutes. Declining part of the viscosity following the maximum, on the other hand, is due to the continuous break down of cages formed as well as simultaneous reformation of the normal water structures.

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References

- [1] Sacco, A. and Matteoli, E. (1997). *J. Solution Chem.*, **26**, 527.
- [2] Tamura, K., Nakamura, M. and Murakami, S. (1997). *J. Solution Chem.*, **26**, 1199.
- [3] Nowicka, B., Kacperska, A., Barczynska, J., Bald, A. and Taniewska-Osinska, S. (1988). *J. Chem. Soc., Faraday Trans. 1*, **84**, 3877.

- [4] Ritzoulis, G. (1989). *Can. J. Chem.*, **67**, 1105.
- [5] Aznarez, S. B., Mussari, L. and Postigo, M. A. (1993). *J. Chem. Eng. Data*, **38**, 270.
- [6] Pruet, D. J. and Felker, L. K. (1985). *J. Chem. Eng. Data*, **30**, 452.
- [7] Sakurai, M. (1992). *J. Chem. Eng. Data*, **37**, 492.
- [8] Ruostesuo, P. and Mattila, T. (1987). *J. Chem. Eng. Data*, **32**, 241.
- [9] Papanastasiou, G. E. and Ziogas, I. I. (1992). *J. Chem. Eng. Data*, **37**, 167.
- [10] Aralaguppi, M. I., Jadar, C. V. and Aminabhavi, T. M. (1996). *J. Chem. Eng. Data*, **41**, 1307.
- [11] Muhuri, P. K., Das, B. and Hazra, D. K. (1996). *J. Chem. Eng. Data*, **41**, 1473.
- [12] Suri, S. K. (1981). *Can. J. Chem.*, **59**, 2839.
- [13] Gokavi, G. S., Raju, J. R., Aminabhavi, T. M., Balundgi, R. H. and Muddapur, M. V. (1986). *J. Chem. Eng. Data*, **31**, 15.
- [14] Saleh, M. A., Biswas, D., Ahmed, O., Akhtar, S. and Habibullah, M. (1993). *Chittagong Univ. Stud., Part II: Sci.*, **17**(2), 127.
- [15] Assarson, P. and Eirich, F. R. (1968). *J. Phys. Chem.*, **72**, 2710.
- [16] Volpe, C. D., Guarino, G., Sartorio, R. and Vitagliano, V. (1986). *J. Chem. Eng. Data*, **31**, 37.
- [17] Akhtar, S., Bhuiyan, M. M. H., Uddin, M. S., Sultana, B., Nessa, M. and Saleh, M. A. (1999). *Phys. Chem. Liq.*, **37**, 215.
- [18] Tanaka, Y., Matsuda, Y., Fujiwara, H., Kubota, H. and Makita, T. (1987). *Int. J. Thermophys.*, **8**, 147.
- [19] Wolf, D. and Kudish, A. I. (1980). *J. Phys. Chem.*, **84**, 425.
- [20] Pal, A. and Singh, Y. P. (1996). *J. Chem. Eng. Data*, **41**, 425.
- [21] Pal, A. and Singh, Y. P. (1996). *Indian J. Chem.*, **35A**, 137.
- [22] Saleh, M. A., Akhtar, S. and Khan, A. R. (2000). *Phys. Chem. Liq.*, **38**, 137.
- [23] Holz, M., Grunder, R., Sacco, A. and Meleleo, A. (1993). *J. Chem. Soc. Faraday Trans.*, **99**, 1215.
- [24] Christensen, C., Gmehling, J., Rasmussen, P. and Weidlich, U., *Heats of Mixing Data Collection, Binary Systems*, Chemistry Data Series, Vol. III (Part 1) (Dechema, Frankfurt am Main, Germany, 1984).
- [25] Andini, S., Castronuovo, G., Elia, V. and Fasano, L. (1990). *J. Chem. Soc. Faraday Trans.*, **86**, 3567.
- [26] Glew, D. N., Mak, H. D. and Rath, N. S., *Aqueous Non-electrolyte Solutions. Part VII, Water Shell Stabilization by Interstitial Non-electrolytes*, In: *Hydrogen-bonded Solvent Systems*, Eds. Covington, A. K. and Jones, P. Taylor and Francis Ltd., London, 1968.