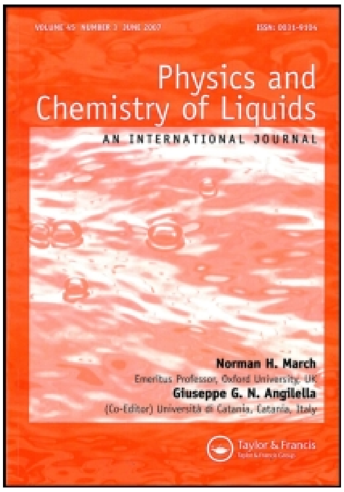

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Excess Molar Volumes and Thermal Expansivities of Aqueous Solutions of Dimethylsulfoxide, Tetrahydrofuran and 1,4-Dioxane

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To cite this Article Saleh, Muhammad A. , Akhtar, Shamim , Ahmed, M. Shamsuddin and Uddin, Mohammad Hemayet(2002) 'Excess Molar Volumes and Thermal Expansivities of Aqueous Solutions of Dimethylsulfoxide, Tetrahydrofuran and 1,4-Dioxane', Physics and Chemistry of Liquids, 40: 5, 621 — 635

To link to this Article: DOI: 10.1080/0031910029001/0473

URL: http://dx.doi.org/10.1080/0031910029001/0473

Phys. Chem. Liq., 2002, Vol. 40(5), pp. 621–635

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EXCESS MOLAR VOLUMES AND THERMAL EXPANSIVITIES OF AQUEOUS SOLUTIONS OF DIMETHYLSULFOXIDE, TETRAHYDROFURAN AND 1,4-DIOXANE

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Densities, ρ, of the systems water (W) + dimethylsulfoxide (DMSO), W + tetrahydrofuran (THF) and W + 1,4-dioxane (DO) have been determined in the temperature range 303.15–323.15 K. Excess molar volumes, V_m^E, have been found to be negative and large in magnitude. Thermal expansivities, α, and excess thermal expansivities, α^E, have been calculated. Densities, excess molar volumes, thermal expansivities and excess thermal expansivities have been plotted against mole fraction of solutes. All these properties have been expressed satisfactorily by appropriate polynomials. Attempt has been made to explain V_m^E in terms of hydrophobic hydration and hydrophilic effect of the solutes.

Keywords: Excess molar volume; Thermal expansivity; Dimethylsulfoxide; Tetrahydrofuran; 1,4-Dioxane

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ISSN 0031-9104. Online ISSN: 1029-0451
DOI: 10.1080/0031910029001/0473

1. INTRODUCTION

The present study is a part of our continuous endeavour to investigate interactions of hydrophobic solutes with water through measurement of volumetric and viscometric properties of their aqueous solutions. In the recent past, we reported the volumetric and viscometric properties of aqueous solutions of hydrophobic solutes such as, acetone [1], alcohols [2,3], diols [4], amines [5,6] and amides [7]. Recent publications on volumetric properties of mixtures of 1,4-dioxane by Matsuo *et al.* [8] and excess partial molar volumes of DMSO in aqueous solution by Lai *et al.* [9] are considered very useful in connection with our work. The main purpose of our study is to collect data on as many systems as possible and attempt to develop a model that can satisfactorily explain the volumetric and viscometric properties of aqueous solutions of hydrophobic solutes of diverse chemical and structural characteristics. The knowledge of interaction of smaller hydrophobic molecules with water, as involved in our studies, may well be useful in understanding the interaction of large biomolecules with water.

2. EXPERIMENTAL

The chemicals used were procured from Aldrich, with the following quoted purities: dimethylsulfoxide (99.9%), 1,4-dioxane (99.8%) and tetrahydrofuran (99.5%). These were used without any further purification except that each of the liquids was kept over molecular sieves (4A) for at least 2 weeks prior to use. Thrice distilled water was used in the preparation of the solutions. An analytical balance (Mettler Toledo) of accuracy ± 0.0001 g was used for density measurement. The solutions were prepared by weighing the two pure components of the systems concerned. Care was taken to minimise evaporation. The mole fraction was accurate up to fourth place of decimal. The density was measured by using a 5 mL bicapillary pyknometer previously calibrated with distilled water. For every measurement a thermostatic water bath controlled to ± 0.05 K was used. The average uncertainty in the measured density was less than $1.4 \times 10^{-7}\,\mathrm{kg\,m^{-3}}$.

3. RESULTS AND DISCUSSION

Densities of the systems water (W) + dimethylsulfoxide (DMSO), W + tetrahydrofuran (THF) and W + 1,4-dioxane (DO) were determined at temperatures ranging from 303.15 to 323.15 K with an interval of 5 K. The densities of the pure components are shown in Table I together with literature values, wherever possible for comparison, in which the agreement between the measured values and literature values has been found to be satisfactory. The densities of the systems have been shown in Table II at different temperatures. The densities, ρ, and thermal expansivities, α, have been correlated with mole fraction of solutes by a polynomial equation of the form,

$$\rho/\mathrm{kg\,m^{-3}} \quad \text{or} \quad \alpha/\mathrm{K^{-1}} = \sum_{i=0}^{n} a_i X_2^i, \tag{1}$$

The least-squares fits of this equation have been found to be excellent as can be seen from the very large values of r^2. The densities of the pure water and pure solutes obtained by putting $X_2 = 0$ and $X_2 = 1$ in Eq. (1), respectively, correspond well with the experimental values. The coefficients of this equation for densities are listed in Table III.

TABLE I Densities, $\rho \times 10^3$ (kg m^{-3}), of pure liquids at different temperatures

Compounds	*Temperature* (K)				
	303.15	308.15	313.15	318.15	323.15
DMSO	1.0896 1.0910[a] 1.0906[b] 1.090269[c]	1.0847 1.0870[a] 1.0856[b]	1.0797 1.0806[b] 1.08046[d]	1.0748 1.0756[e]	1.0698 1.06062[d]
DO	1.0225 1.02225[f] 1.02223[h] 1.0224[i]	1.0168 1.0165[g] 1.01689[h] 1.0167[i]	1.0110 1.01157[f]	1.0052 1.00514[g]	0.9995 1.00028[f]
THF	0.8759 0.8773[i]	0.8702 0.8718[i] 0.87033[j]	0.8649 0.86567[k]	0.8600 0.86140[j]	0.8541

[a][10]; [b][11]; [c][12]; [d][13]; [e][26]; [f][15]; [g][14]; [h][16]; [i][17]; [j][18]; [k][19].

TABLE II Densities, $\rho \times 10^3$ (kg m^{-3}), excess molar volumes, $V_m^E \times 10^6$ (m^3 mol^{-1}), of the systems, W + DMSO, W + THF and W + DO at different temperatures

T/K	303.15		308.15		313.15		318.15		323.15	
x_2	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
Water (X_1) + Dimethylsulfoxide (X_2)										
0.0000	0.9957	0.000	0.9941	0.000	0.9922	0.000	0.9903	0.000	0.9881	0.000
0.1000	1.0398	−0.347	1.0369	−0.342	1.0340	−0.340	1.0310	−0.338	1.0278	−0.340
0.2003	1.0680	−0.689	1.0641	−0.675	1.0603	−0.666	1.0565	−0.660	1.0528	−0.654
0.3023	1.0840	−0.917	1.0798	−0.905	1.0756	−0.897	1.0713	−0.888	1.0670	−0.884
0.3494	1.0882	−0.970	1.0838	−0.955	1.0795	−0.949	1.0751	−0.941	1.0707	−0.936
0.4044	1.0914	−0.993	1.0868	−0.977	1.0824	−0.973	1.0779	−0.965	1.0734	−0.962
0.5003	1.0942	−0.965	1.0896	−0.956	1.0850	−0.952	1.0804	−0.945	1.0757	−0.941
0.5974	1.0944	−0.845	1.0898	−0.842	1.0851	−0.840	1.0804	−0.836	1.0756	−0.834
0.6975	1.0931	−0.648	1.0884	−0.646	1.0836	−0.645	1.0788	−0.638	1.0739	−0.635
0.7981	1.0919	−0.444	1.0871	−0.440	1.0823	−0.436	1.0773	−0.431	1.0724	−0.429
0.8999	1.0905	−0.213	1.0856	−0.211	1.0806	−0.208	1.0758	−0.204	1.0709	−0.201
1.0000	1.0896	0.000	1.0847	0.000	1.0797	0.000	1.0748	0.000	1.0698	0.000
Water (X_1) + Tetrahydrofuran (X_2)										
0.0971	0.9778	−0.534	0.9743	−0.526	0.9708	−0.521	0.9672	−0.510	0.9635	−0.510
0.1497	0.9662	−0.679	0.9622	−0.672	0.9580	−0.659	0.9540	−0.647	0.9498	−0.645
0.2011	0.9560	−0.788	0.9517	−0.768	0.9472	−0.766	0.9430	−0.755	0.9383	−0.748
0.3057	0.9367	−0.843	0.9317	−0.830	0.9269	−0.815	0.9220	−0.798	0.9170	−0.787
0.3979	0.9238	−0.850	0.9186	−0.841	0.9135	−0.820	0.9087	−0.805	0.9033	−0.796
0.4978	0.9126	−0.821	0.9073	−0.814	0.9021	−0.800	0.8971	−0.777	0.8915	−0.766
0.6026	0.9029	−0.751	0.8975	−0.744	0.8924	−0.734	0.8874	−0.722	0.8817	−0.713
0.7025	0.8945	−0.593	0.8889	−0.586	0.8836	−0.575	0.8786	−0.559	0.8727	−0.540
0.8003	0.8877	−0.436	0.8820	−0.430	0.8767	−0.417	0.8716	−0.396	0.8660	−0.400
0.8978	0.8807	−0.161	0.8752	−0.177	0.8698	−0.157	0.8650	−0.166	0.8591	−0.152
1.0000	0.8759	0.000	0.8702	0.000	0.8649	0.000	0.8600	0.000	0.8542	0.000
Water (X_1) + Dioxan (X_2)										
0.0999	1.0224	−0.425	1.0191	−0.421	1.0157	−0.419	1.0123	−0.419	1.0089	−0.421
0.1999	1.0311	−0.641	1.0271	−0.641	1.0229	−0.639	1.0188	−0.643	1.0145	−0.640
0.2998	1.0323	−0.695	1.0277	−0.692	1.0233	−0.701	1.0186	−0.701	1.0140	−0.704
0.3982	1.0316	−0.682	1.0267	−0.680	1.0218	−0.683	1.0169	−0.689	1.0119	−0.688
0.4981	1.0297	−0.600	1.0246	−0.600	1.0194	−0.601	1.0143	−0.609	1.0092	−0.613
0.5981	1.0279	−0.499	1.0227	−0.503	1.0174	−0.509	1.0122	−0.522	1.0069	−0.524
0.6997	1.0257	−0.347	1.0202	−0.342	1.0148	−0.350	1.0093	−0.353	1.0038	−0.350
0.7996	1.0246	−0.244	1.0190	−0.239	1.0133	−0.234	1.0077	−0.237	1.0021	−0.234
0.9000	1.0231	−0.093	1.0174	−0.088	1.0118	−0.097	1.0061	−0.099	1.0004	−0.094
1.0000	1.0225	0.000	1.0168	0.000	1.0110	0.000	1.0052	0.000	0.9995	0.000

The excess molar volumes, V_m^E, were calculated by using the equation,

$$V_m^E = (X_1M_1 + X_2M_2)/\rho_{\text{mix}} - (X_1M_1/\rho_1 + X_2M_2/\rho_2) \qquad (2)$$

where X_1, M_1 and ρ_1 are the mole fraction, molar mass and density respectively, of component 1 (water) and X_2, M_2 and ρ_2 are the corresponding values of component 2 (organic solutes). ρ_{mix} is the density of mixture. The V_m^E data are presented in Table II. The V_m^E

TABLE III Coefficients, a_i, of Eq. (1) expressing $\rho \times 10^3$ in $\mathrm{kg\,m^{-3}}$ and the square of the regression coefficient, r^2 for different systems

Systems	*Temperature* (K)	a_0	a_1	a_2	a_3	a_4	a_5	a_6	r^2
Water + Dimethylsulfoxide	303.15	0.9957	0.5374	− 1.0191	0.6283	0.3627	− 0.6545	0.2392	1.0000
	308.15	0.9941	0.5215	− 0.9937	0.6305	0.3216	− 0.6217	0.2325	1.0000
	313.15	0.9922	0.5098	− 0.9868	0.6797	0.2028	− 0.5186	0.2007	1.0000
	318.15	0.9903	0.4999	− 1.0119	0.8818	− 0.2285	− 0.1278	0.0710	1.0000
	323.15	0.9882	0.4835	− 0.9589	0.8104	− 0.2535	0.0000	0.0000	1.0000
Water + Tetrahydrofuran	303.15	0.9957	− 0.1431	− 0.6628	2.6361	− 4.1023	3.0112	− 0.8590	1.0000
	308.15	0.9941	− 0.1663	− 0.6079	2.6026	− 4.1781	3.1393	− 0.9135	1.0000
	313.15	0.9923	− 0.1917	− 0.5200	2.4209	− 3.9472	2.9738	− 0.8633	1.0000
	318.15	0.9903	− 0.2112	− 0.4733	2.3924	− 4.0087	3.0781	− 0.9075	1.0000
	323.15	0.9881	− 0.2338	− 0.3876	2.1751	− 3.6898	2.8396	− 0.8375	1.0000
Water + Dioxan	303.15	0.9957	0.4110	− 1.8009	4.0395	− 5.0592	3.3217	− 0.8853	0.9998
	308.15	0.9940	0.3902	− 1.7350	3.9044	− 4.8897	3.2029	− 0.8500	0.9997
	313.15	0.9922	0.3660	− 1.6317	3.6384	− 4.5188	2.9440	− 0.7792	0.9998
	318.15	0.9902	0.3494	− 1.6000	3.6299	− 4.5761	3.0184	− 0.8066	0.9997
	323.15	0.9881	0.3330	− 1.5674	3.6173	− 4.6267	3.0874	− 0.8323	0.9997

TABLE IV Coefficients, a_i, of Redlich–Kister Eq. (3) expressing $V_m^E \times 10^6$ in $\mathrm{m^3\,mol^{-1}}$ and standard deviation, σ, for the systems

Systems	*Temperature* (K)	a_0	a_1	a_2	a_3	σ
Water + Dimethylsulfoxide	303.15	− 3.8686	1.7550	1.0666	− 1.2598	0.00723
	308.15	− 3.8318	1.6609	1.0889	− 1.1533	0.00773
	313.15	− 3.8193	1.6125	1.1420	− 1.0773	0.00655
	318.15	− 3.7902	1.5838	1.1540	− 1.0132	0.00669
	323.15	− 3.7777	1.5670	1.1759	− 1.9718	0.00720
Water + Tetrahydrofuran	303.15	− 3.2881	0.9562	− 1.1337	2.5788	0.01616
	308.15	− 3.2457	0.9527	− 1.1622	2.3819	0.01197
	313.15	− 3.1920	0.8840	− 1.0792	2.6368	0.01482
	318.15	− 3.1153	0.9359	− 1.0971	2.4438	0.01347
	323.15	− 3.0697	0.9177	− 1.1027	2.5439	0.01797
Water + Dioxan	303.15	− 2.3971	1.9371	− 0.8374	0.5133	0.01134
	308.15	− 2.4012	1.9244	− 0.7592	0.5897	0.01337
	313.15	− 2.4186	1.9562	− 0.7455	0.4503	0.00986
	318.15	− 2.4499	1.9266	− 0.7048	0.5020	0.01266
	323.15	− 2.4606	1.9224	− 0.6387	0.5728	0.01301

and α^E are fitted to a Redlich–Kister polynomial equation of the type,

$$V_m^E/\mathrm{m^3\,mol^{-1}} \quad \text{or} \quad \alpha^E/\mathrm{K^{-1}} = X_1 X_2 \sum_{i=0}^{n} a_i (1 - 2X_1)^i \tag{3}$$

Using $n = 3$, four a_i coefficients were obtained. For V_m^E these coefficients are shown in Table IV along with standard deviations.

Figure 1 shows the plots of densities as a function of mole fraction of DMSO. The curves show rapid rise in density on addition of DMSO, and are followed by slower and slower rates over the rest of the region, giving ill-defined maxima. Figure 2 on the other hand, shows rapid decrease in density initially on addition of THF. The decrement continues until the pure state of THF is reached, but at a slower rate. Figure 3 shows a somewhat similar variation of density as of Fig. 1 against the mole fraction of DO, exhibiting fairly well-defined maxima.

Excess molar volumes, V_m^E, for the systems W + DMSO, W + THF and W + DO have been plotted in Figs. 4–6, respectively. The solid lines are generated by the polynomial equation (Eq. (3)). In order to avoid unnecessary crowding of the curves, only those at three temperatures 303.15, 313.15 and 323.15 K have been plotted. Examination of

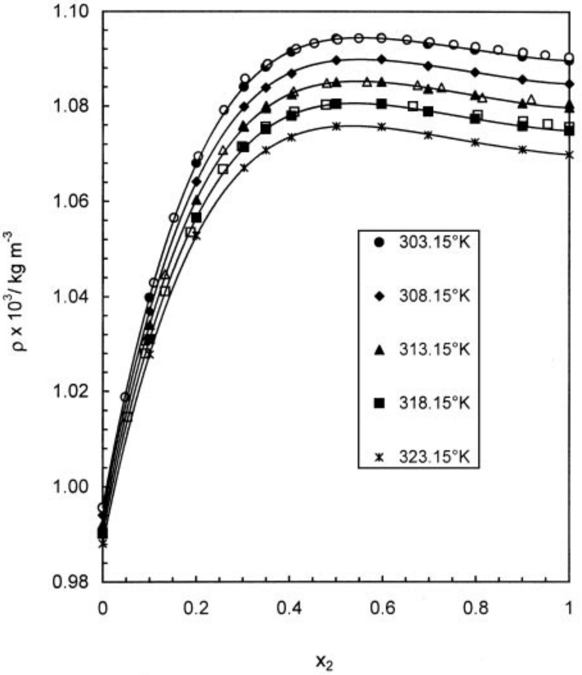

FIGURE 1 Densities of the system water (X_1) + DMSO (X_2) for different molar ratios. ○ – ([12]), 303.15 K; Δ – ([13]), 313.15 K; □ – ([26]), 318.15 K.

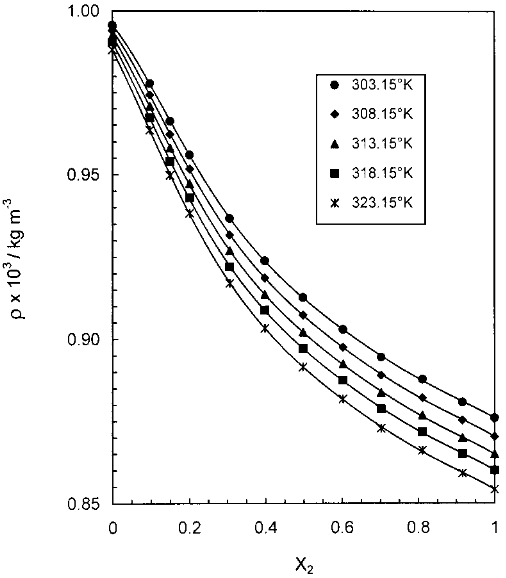

FIGURE 2 Densities of the system water (X_1) + THF (X_2) for different molar ratios.

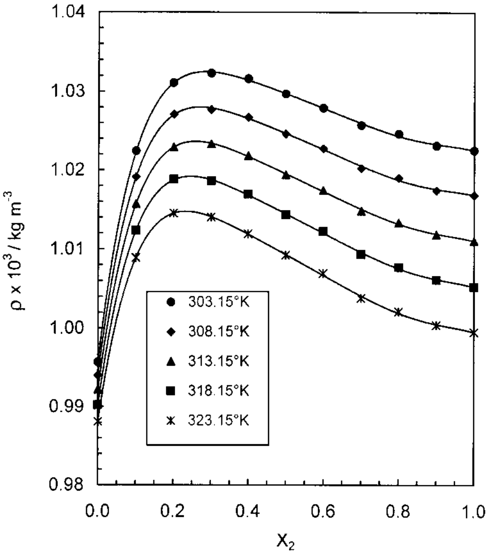

FIGURE 3 Densities of the system water (X_1) + DO (X_2) for different molar ratios.

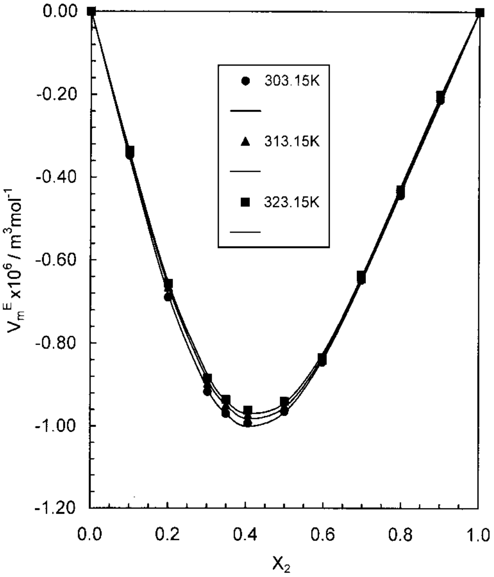

FIGURE 4 Excess molar volume of the system water (X_1) + DMSO (X_2) for different molar ratios.

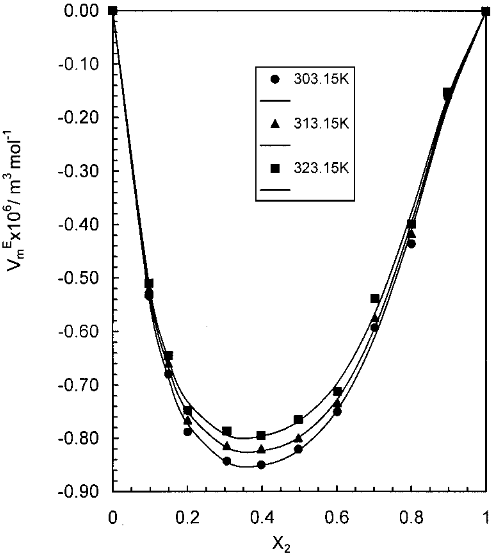

FIGURE 5 Excess molar volume of the system water (X_1) + THF (X_2) for different molar ratios.

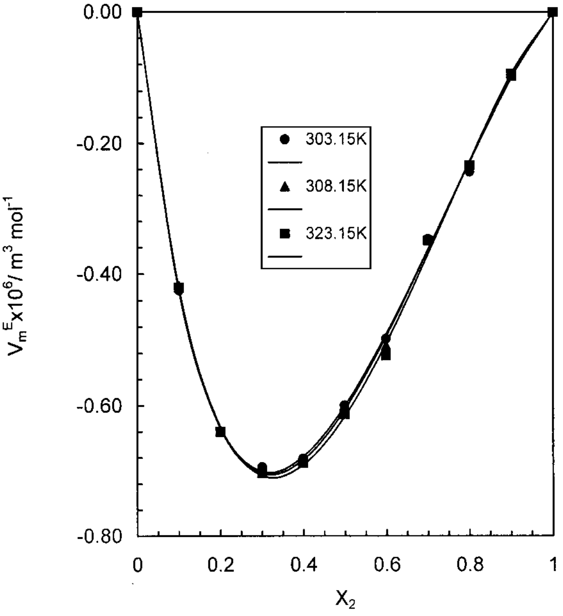

FIGURE 6 Excess molar volume of the system water (X_1) + DO (X_2) for different molar ratios.

these figures reveals the following characteristics:

(a) V_m^E are negative and large in magnitude.
(b) Temperature effect on V_m^E is not much significant.
(c) All systems show well-defined minima occurring in between 0.3 and 0.4 mole fraction of the solutes.

In general, the sign of V_m^E depends upon the relative magnitude of contractive and expansive effects that arise on mixing of the components. The factors that cause contraction on mixing are:

(a) Strong specific interaction, usually a kind of chemical interaction.
(b) Strong physical interaction, such as dipole–dipole or dipole–induced dipole interaction.
(c) Favourable geometrical fitting of component molecules.
(d) Occupation of void spaces of one component by the other. This is expected when the molecular sizes of the compounds differ by a large magnitude.

(e) Hydrophobic hydration. This is a special type of interaction which occurs in water-rich region when an organic solute molecule is surrounded by a network of highly ordered water molecules.

The factors that causes expansion of volume on mixing of the components are:

(a) Dissociation of one component or both of the components.
(b) Steric hindrance due to branching of chains.
(c) Geometrical mismatch of molecules.
(d) Formation of weaker solute–solvent bond than solute–solute and solvent–solvent bonds.

The large negative V_m^E of the systems, a typical characteristic of hydrophobic solutes, lead to the conviction that the factors causing the volume contraction far outweigh the factors responsible for volume expansion. It is not possible to assess the contribution of the individual factor to contraction. Of the contractive factors, perhaps the hydrophobic hydration is by far the most effective one in volume reduction, as by this process the hydrophobic molecules occupy the spaces inside the so-called cages formed by the highly structured water molecules, and thus ensue maximum economy of volume. Whereas in other cases, shrinkage takes place through strong interaction or attractive forces whose contribution to volume reduction is only relatively small. There are convincing evidences that the molecules DMSO, THF and DO are hydrophobic compounds. Recent studies of volumetric and viscometric properties by Sacco and Matteoli [20], volumetric studies by Tamura *et al.* [12] and the nuclear magnetic relaxation studies by Holz *et al.* [21] on aqueous solutions of DMSO have unambiguously indicated that DMSO is weakly or moderately hydrophobic. In their recent paper, To *et al.* [22] analysed the volumetric properties of aqueous solutions of 1-propanol and DMSO and concluded that DMSO is a structure maker. The large negative excess enthalpies of mixtures of DMSO and water suggest strong hydrophilic bond interaction of DMSO [23]. A comprehensive paper on water shell stabilization by interstitial non-electrolytes by Glew *et al.* [24] and references therein explicitly pointed to the formation of solid clathrates by THF and DO, giving credence to cavity solution model. These authors concluded further from NMR spectroscopy and the endothermic heats of mixing of dilute solution of water that, THF and DO also form relatively weak H-bonds with water.

The average thermal expansivities, α, over the range of temperature studied were calculated by using the equation,

$$\alpha = -d \ln \rho / dT \tag{4}$$

According to this equation the α values are the negative slopes of the linear variation of $\ln \rho$ against T. The slopes have been determined by the least-squares method, with high correlation coefficients for all solutions. The expansivity data are shown in Table V, together with their excess values, α^E, calculated as,

$$\alpha^E = \alpha - (X_1\alpha_1 + X_2\alpha_2) \tag{5}$$

The subscripts 1 and 2 refer to water and organic solutes, respectively. The thermal expansivities have been correlated with mole fraction by the polynomial equation (Eq. (1)). The coefficients of Eq. (1) expressing α for the systems are shown in Table VI, together with the

TABLE V Experimental thermal expansivity, $\alpha \times 10^4$ (K^{-1}), and excess thermal expansivity, $\alpha^E \times 10^4$ (K^{-1}), of aqueous dimethylsulfoxide, tetrahydrofuran and 1,4-dioxan for different molar ratios

X_2	α	α^E	X_2	α	α^E
Water (X_1) + Dimethylsulfoxide (X_2)			Water (X_1) + Tetrahydrofuran (X_2)		
0.0000	3.8107	0.0000	0.0000	3.8107	0.0000
0.1000	5.7844	1.4378	0.0971	7.3974	2.7667
0.2003	7.1673	2.2833	0.1497	8.5595	3.4846
0.3023	7.8960	2.5554	0.2011	9.3120	3.8030
0.3494	8.0969	2.4139	0.3057	10.5954	4.2031
0.4044	8.2966	2.3189	0.3979	11.0107	3.8397
0.5003	8.5166	2.0250	0.4978	11.5058	3.4912
0.5974	8.6506	1.6387	0.6026	11.8117	2.9120
0.6975	8.7850	1.2367	0.7025	12.2000	2.4567
0.7981	8.9172	0.8298	0.8003	12.3181	1.7489
0.8999	9.0500	0.4171	0.8978	12.2773	0.8847
1.0000	9.1693	0.0000	1.0000	12.2557	0.0000
Water (X_1) + 1,4-Dioxan (X_2)					
0.0000	3.8107	0.0000	0.5981	10.3206	1.9656
0.0999	6.6559	2.0693	0.6997	10.7813	1.6577
0.1999	8.1149	2.7719	0.7996	11.1120	1.2328
0.2998	8.9334	2.8347	0.9000	11.2087	0.5701
0.3982	9.6307	2.7877	1.0000	11.3951	0.0000
0.4981	10.0645	2.4659			

TABLE VI Coefficients, a_i, of Eq. (1) expressing $\alpha \times 10^4$ in K^{-1} and the square of the regression coefficient, r^2 for the systems

Systems	a_0	a_1	a_2	a_3	a_4	a_5	a_6	r^2
W + DMSO	3.8071	23.217	− 30.261	− 36.408	139.72	− 134.93	44.027	0.9999
W + THF	3.8038	47.308	− 132.06	202.91	− 155.81	46.093	0.0000	0.9995
W + DO	3.8167	38.17	− 121.01	234.37	− 254.05	142.65	− 32.56	0.9995

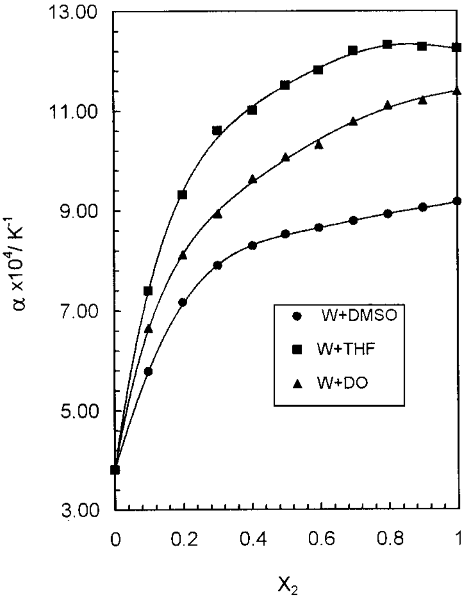

FIGURE 7 Thermal expansivity of the systems, water (X_1) + organic solutes (X_2).

values of r^2. The fitting of the data has been found to be extremely satisfactory as can be seen by very large values of r^2 and also by close correspondence of α values for pure components obtained experimentally and theoretically by using Eq. (1).

The thermal expansivities for the systems W + DMSO, W + THF and W + DO are plotted in Fig. 7 as a function of mole fraction of the solutes. On addition of the solutes the expansivities increase steeply up to ~ 0.3 mole fraction of the solutes for all the systems. Beyond this concentration α increases almost linearly for W + DMSO, but for the other two systems the non-linear increase of α is observed. The curve for W + DMSO shows a very good qualitative agreement with the

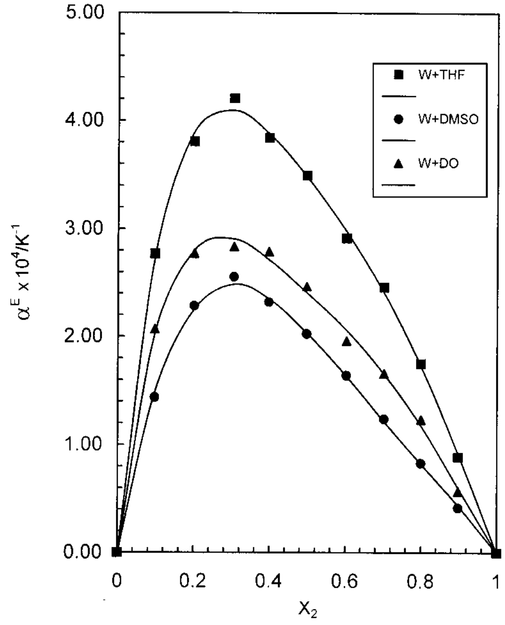

FIGURE 8 Excess thermal expansivity of the systems, water (X_1) + organic solutes (X_2).

TABLE VII Coefficients, a_i, of Redlich-Kister Eq. (3) expressing $\alpha^E \times 10^4$ in K^{-1} and standard deviation, σ, for the systems

Systems	a_0	a_1	a_2	a_3	σ
Water + Dimethylsulfoxide	8.1439	– 7.7249	3.9927	0.7118	0.04578
Water + Tetrahydrofuran	13.8823	– 8.9364	10.2518	– 6.4512	0.07370
Water + Dioxan	9.60778	– 6.6178	7.7975	– 5.1199	0.07869

curves reported by Westh [25]. Unfortunately for the other two systems α values could not be found and hence no comparison could be made.

The excess thermal expansivities, α^E, of the systems have been shown in Fig. 8. The curves have been fitted by a polynomial equation (Eq. (3)). The coefficients of this equation for α^E and the standard deviations are listed in Table VII. The α^E values have been found to be positive for the whole range of composition with maxima occurring at ~ 0.3 mole fraction of the solutes. The excess thermal expansivity is the difference between the sum of the thermal expansions of the species present in solutions and the combined thermal expansions of the pure components. As we do not know exactly what species are formed in the solution systems, nor do we know about their concentration and thermal behaviour, at the present stage we restrict ourselves from attempting to interpret the α and α^E properties of the systems.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the Ministry of Science and Technology, Govt. of People's Republic of Bangladesh, for this work under the research project "Physical Properties and Molecular Interactions in Liquid Systems".

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