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Surface Tension and Refractive Index of Dialkylsulfoxide + Water Mixtures at Several Temperatures

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Surface tensions of binary mixtures of dimethylsulfoxide (DMSO) + water, diethylsulfoxide (DESO) + water, dipropylsulfoxide (DPSO) + water, and diisopropylsulfoxide (DiPSO) + water have been determined at (298.15, 303.15, 308.15, 313.15, 318.15, 323.15, and 328.15) K. The refractive index for the above-mentioned systems has been measured at (298.15, 303.15, and 308.15) K. An unusual behavior of the concentration dependence of surface tension observed for the DMSO + water system is explained on the basis of changing intermolecular interactions involving DMSO self-association and DMSO association with water.

Introduction

Our systematic studies on homologies of well-known dimethylsulfoxide (DMSO), particularly the nearest homologue diethylsulfoxide (DESO), reveal interesting physicochemical features.[1−5] Moreover, recently, the biomedical significance of DESO has been reported.[6,7]

The binary aqueous mixtures of organic nonelectrolytes are typically nonideal, and to describe the dependence of surface tension on composition, one has to use an appropriate model equation.[8]

Surface tension measurements for binary mixtures of DMSO with water over the whole composition range,[9] and in more detail by Cheong and Carr,[10] have been reported.

Karpovich and Ray[11] have investigated the surface of the aqueous DMSO system employing surface second harmonic generation. It was shown that at low concentrations (mole fraction of DMSO up to 0.07) the average orientation of interfacial DMSO does not change.

Also, in ref 12, on the basis of surface tension and surface potential measurements of DMSO + water in the low concentration range, it has been concluded that adsorbed DMSO molecules point their methyl groups toward the exterior of the liquid phase.

Using surface tension measurements together with surface vibration sum frequency generation spectroscopy, it has been shown that for the neat DMSO surface the DMSO methyl groups extend away from the liquid phase.[13] For aqueous solutions of DMSO, it was also shown that DMSO number densities are higher at the surface relative to bulk DMSO concentrations revealing surface partitioning effects.

Knowledge of surface tension and refractive index provides additional and substantial information on the intensity of the interactions in the aqueous solutions of these mixtures. From a fundamental point of view, a study of homologies of dialkylsulfoxides (DASO) allows one to examine in detail the influence of the alkyl chains on the surface tension and refractive index of the DASO + water mixtures.

Experimental

All solutions were prepared by mass using bidistilled water. The composition of each mixture was obtained with an accuracy of $1 \cdot 10^{-4}$ in mole fraction from the measured masses of the components. DMSO was commercially available from LACHEMA N.P. Brno. Other dialkylsulfoxides were synthesized and purified according to the literature.[14] The mass fraction purity of all dialkylsulfoxides, tested by gas chromatography, was found to be greater than 99.5 %.

The surface tension was determined at 5 K intervals, between 298.15 K and 343.15 K, using the method of maximum bubble pressure (SITA Science Line t60). From the measured maximum pressure, P, the surface tension can be calculated employing the Young−Laplace equation, $\gamma = Pr/2$, where r is the radius of the capillary. A detailed instrument design and experimental procedure have been described elsewhere.[15]

The uncertainty of the surface tension measured with this method is $\pm$ 0.1 $\text{mN} \cdot \text{m}^{-1}$, and the temperature was controlled using an MS LAUDA thermostat, with a precision of ± 0.1 K.

Refractive indices were measured with a thermostated refractometer IRF-454, and the uncertainty in the measurements of the refractive index was within $\pm 5 \cdot 10^{-4}$.

Results and Discussion

The surface tensions γ and refractive indices n of the pure components are given in Table 1 and compared with the available literature values.[10,16−20]

Experimental surface tensions and refractive indices for binary x DASO + $(1 - x)$ water mixtures are listed in Tables 2 to 5 and Table 6, respectively. Note that the solubility of diisopropylsulfoxide (DiPSO) in water is limited, mainly in the range $0.1 < x < 0.4$, especially at lower temperatures.

In all systems studied, the surface tension decreased linearly with increasing temperature for any given mole fraction of DASO. As an illustration, Figure 1 shows these dependences for three regions: lower ($x < 0.02$), middle ($0.2 < x < 0.5$), and higher ($x > 0.8$) of DMSO + water. It should be noted that linear variation of the surface tension with temperature has been shown for aqueous mixtures of alkylalkanolamines.[21,22]

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Table 1. Surface Tension γ and Refractive Indices n of Pure Components

	γ/mN·m^{-1}		n			γ/mN·m^{-1}		n	
T/K	exptl value	lit. value	exptl value	lit. value	T/K	exptl value	lit. value	exptl value	lit. value
				water					
298.15	71.6	71.66 ± 0.27[a]	1.3335	1.3329[d]	313.15	69.2	69.6[c]		
		72.01[b]			318.15	68.2	68.77[c]		
		71.98[c]			323.15	67.5	67.94[c]		
303.15	71.1	71.2[c]	1.3320	1.3323[d]	328.15	66.6	67.17[b]		
308.15	70.1	70.4[c]	1.3315	1.3316[d]					
		70.41[b]							
				DMSO					
298.15	41.7	42.7[a,e]	1.4765	1.4765[f]	318.15	39.1			
303.15	41.0	42.05[e]	1.4740		323.15	38.5			
308.15	40.3	40.95[e]	1.4720		328.15	37.9			
313.15	39.7	39.83[e]							
				DESO					
298.15	34.6		1.4680		318.15	32.7			
303.15	34.1		1.6460		323.15	32.4			
308.15	33.7		1.4640		328.15	32.0			
313.15	33.2								
				DPSO					
298.15	32.6		1.4595		318.15	30.5			
303.15	32.0		1.4580		323.15	29.9			
308.15	31.5		1.4560		328.15	29.4			
313.15	31.0								
				DiPSO					
298.15	31.8		1.4645		318.15	29.8			
303.15	31.2		1.4620		323.15	29.5			
308.15	30.7		1.4595		328.15	29.1			
313.15	30.3								

[a] Ref 10. [b] Ref 16. [c] Ref 17. [d] Ref 18. [e] Ref 19. [f] Ref 20.

Table 2. Experimental Surface Tension γ and Surface Tension Deviations $\delta\gamma$ for x DMSO + (1 − x) Water from T = 298.15 K to 328.15 K

T/K	x	γ/mN·m^{-1}	$\delta\gamma$/mN·m^{-1}	x	γ/mN·m^{-1}	$\delta\gamma$/mN·m^{-1}	x	γ/mN·m^{-1}	$\delta\gamma$/mN·m^{-1}	x	γ/mN·m^{-1}	$\delta\gamma$/mN·m^{-1}
298.15	0.0121	71.0	−0.2	0.2507	55.4	−8.7	0.3802	52.0	−8.2	0.5900	46.0	−8.0
	0.0202	69.7	−1.3	0.2999	53.3	−9.3	0.4191	51.0	−8.0	0.7027	44.0	−6.6
	0.1044	61.2	−7.3	0.3187	53.1	−9.0	0.4523	50.3	−7.8	0.8088	42.6	−4.8
	0.1979	56.7	−9.0	0.3536	52.6	−8.6	0.5010	48.3	−8.3	0.8945	42.0	−2.9
303.15	0.0121	70.1	−0.6	0.2507	54.5	−9.0	0.3802	51.2	−8.5	0.5900	45.2	−8.1
	0.0202	68.7	−1.8	0.2999	52.4	−9.7	0.4191	50.0	−8.5	0.7027	43.4	−6.5
	0.1044	60.6	−7.4	0.3187	52.3	−9.2	0.4523	49.9	−7.6	0.8088	42.1	−4.7
	0.1979	55.8	−9.3	0.3536	51.7	−8.8	0.5010	47.4	−8.6	0.8945	41.4	−2.8
308.15	0.0121	69.2	−0.5	0.2507	53.2	−9.4	0.3802	50.3	−8.5	0.5900	44.6	−7.9
	0.0202	67.9	−1.6	0.2999	51.5	−9.7	0.4191	49.2	−8.4	0.7027	42.6	−6.6
	0.1044	59.8	−7.2	0.3187	51.4	−9.2	0.4523	49.1	−7.5	0.8088	41.5	−4.5
	0.1979	54.8	−9.4	0.3536	50.6	−9.0	0.5010	46.7	−8.5	0.8945	40.9	−2.5
313.15	0.0121	67.6	−1.2	0.2507	52.3	−9.5	0.3802	49.5	−8.5	0.5900	43.8	−8.0
	0.0202	66.9	−1.7	0.2999	50.6	−9.8	0.4191	48.4	−8.4	0.7027	42.1	−6.0
	0.1044	58.7	−7.4	0.3187	50.4	−9.4	0.4523	48.2	−7.7	0.8088	40.9	−4.4
	0.1979	53.9	−9.5	0.3536	50.0	−9.9	0.5010	46.0	−8.4	0.8945	40.3	−2.5
318.15	0.0121	66.4	−1.5	0.2507	51.2	−9.7	0.3802	48.6	−8.5	0.5900	43.1	−7.9
	0.0202	65.8	−1.8	0.3218	50.7	−9.5	0.4191	47.5	−8.5	0.7027	41.4	−6.4
	0.1044	57.9	−7.3	0.3506	49.7	−8.3	0.4523	47.3	−7.7	0.8088	40.4	−4.3
	0.1979	53.0	−9.4	0.3549	49.4	−8.5	0.5010	45.1	−8.5	0.8945	39.8	−2.4
323.15	0.0121	65.3	−1.9	0.2507	50.3	−9.9	0.3802	47.7	−8.8	0.5900	42.3	−8.1
	0.0202	64.8	−2.1	0.3218	49.9	−9.4	0.4191	46.7	−8.6	0.7027	40.8	−6.3
	0.1044	57.0	−7.5	0.3506	48.7	−8.6	0.4523	46.3	−8.1	0.8088	39.8	−4.2
	0.1979	52.2	−9.6	0.3549	48.4	−8.8	0.5010	44.4	−8.6	0.8945	39.2	−2.4
328.15	0.0121	65.1	−1.1	0.2507	49.4	−10.0	0.3802	46.8	−8.9	0.5900	41.7	−8.0
	0.0202	63.8	−2.2	0.3218	49.0	−9.0	0.4191	45.9	−8.6	0.7027	40.2	−6.2
	0.1044	55.1	−8.5	0.3506	47.7	−8.8	0.4523	45.3	−8.3	0.8088	39.2	−4.2
	0.1979	51.1	−9.8	0.3549	47.4	−9.0	0.5010	43.5	−8.7	0.8945	38.7	−2.2

Plots of surface tension at 298.15 K as a function of mole fraction of DASO for x DASO + (1 − x) water are presented in Figure 2. The surface tension of the mixture decreases rapidly in dilute solutions but then becomes almost constant in the concentrated solution. The results show that DPSO + water and DiPSO + water mixtures mainly act as surfactants.

The continuous curves in Figure 2 were generated by fitting the Connors and Wright equation[8] (eq 1) to the experimental data

$$\gamma = \gamma_1 - \left[1 + \frac{b_1 x_1}{1 - a x_1}\right] x_2(\gamma_1 - \gamma_2) \qquad (1)$$

Table 3. Experimental Surface Tension γ and Surface Tension Deviations $\delta\gamma$ for x DESO + (1 − x) Water from T = 298.15 K to 328.15 K

T		γ	$\delta\gamma$		γ	$\delta\gamma$	T		γ	$\delta\gamma$		γ	$\delta\gamma$
K	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	K	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$
298.15	0.0099	65.5	−6.1	0.1999	46.0	−18.5	313.15	0.0513	53.1	−14.4	0.4908	38.6	−13.0
	0.0207	62.5	−8.7	0.2999	42.8	−18.0		0.1001	48.4	−17.4	0.7123	36.5	−7.1
	0.0513	55.4	−14.7	0.4908	40.4	−13.2	318.15	0.0099	61.8	−7.4	0.1999	46.1	−16.1
	0.1001	50.9	−17.4	0.7123	37.6	−7.8		0.0207	58.4	−10.4	0.2999	43.2	−15.3
303.15	0.0099	64.8	−5.8	0.1999	45.2	−18.4		0.0513	52.4	−15.3	0.4908	38.0	−13.5
	0.0207	61.5	−8.7	0.2999	42.0	−17.7		0.1001	47.7	−18.2	0.7123	35.7	−7.6
	0.0513	54.9	−14.2	0.4908	39.8	−13.1	323.15	0.0099	60.8	−7.5	0.1999	45.3	−16.1
	0.1001	50.2	−17.1	0.7123	37.1	−7.61		0.0207	56.8	−11.1	0.2999	41.6	−16.2
308.15	0.0099	64.1	−5.9	0.1999	44.2	−18.9		0.0513	50.5	−16.3	0.4908	37.3	−13.6
	0.0207	60.4	−9.2	0.2999	41.9	−17.5		0.1001	46.5	−18.6	0.7123	35.0	−7.8
	0.0513	54.0	−14.5	0.4908	39.3	−13.1	328.15	0.0099	59.9	−7.3	0.1999	43.4	−17.1
	0.1001	49.5	−17.2	0.7123	37.0	−7.3		0.0207	56.4	−10.5	0.2999	40.7	−16.2
313.15	0.0099	62.8	−6.2	0.1999	47.1	−15.1		0.0513	49.7	−16.1	0.4908	36.6	−13.5
	0.0207	59.3	−9.4	0.2999	44.3	−14.2		0.1001	45.7	−18.3	0.7123	34.4	−7.8

Table 4. Experimental Surface Tension γ and Surface Tension Deviations $\delta\gamma$ for x DPSO + (1 − x) Water from T = 298.15 K to 328.15 K

T		γ	$\delta\gamma$		γ	$\delta\gamma$		γ	$\delta\gamma$
K	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$
298.15	0.0105	52.3	−19.9	0.0998	39.6	−29.0	0.3975	35.8	−20.9
	0.0199	47.4	−24.4	0.2019	37.5	−27.0	0.5001	35.4	−17.2
	0.0469	42.2	−28.5	0.2809	37.2	−24.2	0.6818	34.3	−11.0
303.15	0.0105	51.1	−20.3	0.0998	38.9	−28.9	0.3975	35.2	−20.8
	0.0199	46.4	−24.6	0.2019	37.0	−26.8	0.5001	34.9	−17.0
	0.0469	41.5	−28.4	0.2809	36.5	−24.1	0.6818	34.2	−10.5
308.15	0.0105	49.9	−20.5	0.0998	38.1	−28.8	0.3975	34.5	−20.7
	0.0199	45.3	−24.7	0.2019	36.5	−26.4	0.5001	34.3	−16.9
	0.0469	40.7	−28.3	0.2809	36.0	−23.8	0.6818	33.5	−10.5
313.15	0.0105	48.8	−20.7	0.0998	37.3	−28.7	0.3975	34.1	−20.3
	0.0199	44.4	−24.7	0.2019	35.9	−26.1	0.5001	33.8	−16.7
	0.0469	40.0	−28.1	0.2809	35.0	−24.0	0.6818	32.9	−10.5
318.15	0.0105	47.6	−20.9	0.0998	36.6	−28.5	0.3975	33.4	−20.2
	0.0199	44.3	−23.8	0.2019	35.0	−26.1	0.5001	33.3	−16.4
	0.0469	39.3	−27.8	0.2809	34.4	−23.7	0.6818	32.2	−10.5
323.15	0.0105	46.6	−21.0	0.0998	35.7	−28.5	0.3975	32.8	−20.1
	0.0199	43.2	−24.0	0.2019	34.4	−25.9	0.5001	32.7	−16.3
	0.0469	38.5	−27.7	0.2809	33.8	−23.5	0.6818	31.6	−10.4
328.15	0.0105	45.6	−21.1	0.0998	35.0	−28.3	0.3975	32.2	−19.9
	0.0199	42.2	−24.1	0.2019	33.7	−25.8	0.5001	32.1	−16.2
	0.0469	37.8	−27.5	0.2809	33.1	−23.4	0.6818	30.8	−10.6

Table 5. Experimental Surface Tension γ and Surface Tension Deviations $\delta\gamma$ for x DiPSO + (1 − x) Water from T = 298.15 K to 328.15 K

T		γ	$\delta\gamma$		γ	$\delta\gamma$	T		γ	$\delta\gamma$		γ	$\delta\gamma$
K	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	K	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$	x	$\mathrm{mN \cdot m^{-1}}$	$\mathrm{mN \cdot m^{-1}}$
298.15	0.0087	52.5	20.1	0.6002	33.9	−14.4	318.15	0.0087	49.8	−19.8	0.4035	32.8	−20.9
	0.0197	48.8	−23.4	0.7756	32.6	−8.2		0.0197	45.8	−23.3	0.6002	31.5	−14.3
	0.4035	35.9	−20.5	0.8899	32.2	−4.1		0.0505	40.6	−27.1	0.7756	30.3	−8.2
303.15	0.0087	52.4	−19.4	0.6002	33.3	−14.3		0.0987	37.0	−28.9	0.8899	30.0	−4.2
	0.0197	48.1	−23.3	0.7756	32.1	−8.0	323.15	0.0087	48.9	−19.8	0.4035	31.8	−21.3
	0.0505	42.9	−27.2	0.8899	31.7	−4.0		0.0197	45.0	−23.2	0.6002	30.4	−14.9
	0.4035	34.6	−21.1					0.0505	39.9	−25.7	0.7756	29.8	−8.3
308.15	0.0087	51.5	−19.0	0.4035	34.1	−20.5		0.0987	36.7	−28.4	0.8899	29.5	−4.3
	0.0197	47.3	−22.7	0.6002	32.7	−14.0	328.15	0.0087	48	−19.1	0.4035	31.0	−20.9
	0.0505	41.8	−27.0	0.7756	31.5	−7.9		0.0197	43.7	−22.9	0.6002	29.8	−14.6
	0.0987	35.1	−31.7	0.8899	31.1	−4.0		0.0505	39.7	−25.8	0.7756	29.3	−8.1
313.15	0.0087	50.6	−19.1	0.4035	33.4	−20.6		0.0987	36.4	−27.2	0.8899	28.9	−4.4
	0.0197	46.6	−22.6	0.6002	32.1	−14.1							
	0.0505	41.2	−26.8	0.7756	30.9	−8.0							
	0.0987	36.0	−30.1	0.8899	30.6	−4.1							

where a and b are adjustable parameters obtained by nonlinear least-squares. The validity of this equation has been proved by several authors.[18,21,22] The parameters a and b and standard deviations are given in Table 7.

The surface tension deviation ($\delta\gamma$) is defined as the difference between the surface tension of the mixture and that expected on the basis of a mole fraction average

$$\delta\gamma = \gamma - (x_1\gamma_1 + x_2\gamma_2) \tag{2}$$

where γ_1 and γ_2 represent the surface tensions of pure water and pure dialkylsulfoxide, respectively, and x_1 and x_2 represent the mole fractions of water and dialkylsulfoxide. In all systems, the surface tension deviation is negative, indicating an enrichment of one component (component with lower surface tension) in the liquid−vapor interface. Plotting $\delta\gamma$ against the mole fraction of the sulfoxide (Figure 3) shows that the deviation from a mole fraction average increases with increasing length of the DASO carbon chain.

Figure 4 shows the experimental values of changes of refractive indices for the four binary systems. The change of

Table 6. Refractive Indices *n* and Changes of Refractive Indices Δ*n* for Binary Mixtures from *T* = 298.15 K to 308.15 K

T/K	*x*	*n*	Δ*n*	*x*	*n*	Δ*n*	*x*	*n*	Δ*n*
				x DMSO + (1 − *x*) Water					
298.15	0.0121	1.3400	0.0051	0.2959	1.4305	0.0541	0.4301	1.4475	0.0525
	0.0202	1.3440	0.0076	0.3213	1.4345	0.0551	0.5964	1.4610	0.0417
	0.1467	1.3960	0.0411	0.3713	1.4415	0.0549	0.7685	1.4700	0.0264
	0.2455	1.4215	0.0523	0.3967	1.4445	0.0538			
303.15	0.0121	1.3390	0.0056	0.2959	1.4295	0.0549	0.4301	1.4455	0.0524
	0.0202	1.3435	0.0087	0.3213	1.4335	0.0559	0.5964	1.4590	0.0418
	0.1467	1.4005	0.0472	0.3713	1.4405	0.0558	0.7685	1.4680	0.0267
	0.2455	1.4200	0.0525	0.3967	1.4430	0.0542			
308.15	0.0121	1.3395	0.0066	0.2959	1.4280	0.0544	0.4301	1.4445	0.0526
	0.0202	1.3430	0.0087	0.3213	1.4320	0.0554	0.5964	1.4580	0.0422
	0.1467	1.4000	0.0474	0.3713	1.4395	0.0558	0.7685	1.4660	0.0263
	0.2455	1.4190	0.0524	0.3967	1.4420	0.0543			
				x DESO + (1 − *x*) Water					
298.15	0.0099	1.3415	0.0067	0.2999	1.4460	0.0722	0.5803	1.4605	0.0490
	0.0513	1.3735	0.0333	0.4091	1.4570	0.0697	0.7123	1.4645	0.0369
	0.1001	1.3990	0.0521	0.5189	1.4580	0.0547	0.7741	1.4660	0.0284
	0.1999	1.4300	0.0696						
303.15	0.0099	1.3320	0.0072	0.2999	1.4445	0.0723	0.5803	1.4585	0.0487
	0.0513	1.3675	0.0343	0.4091	1.4555	0.0699	0.7123	1.4630	0.0372
	0.1001	1.3730	0.0526	0.5189	1.4570	0.0555	0.7741	1.4640	0.0283
	0.1999	1.4280	0.0692						
308.15	0.0099	1.3315	0.0087	0.2999	1.4430	0.0718	0.5803	1.4565	0.0481
	0.0513	1.3685	0.0339	0.4091	1.4530	0.0685	0.7123	1.4615	0.0373
	0.1001	1.3720	0.0518	0.5189	1.4550	0.0548	0.7741	1.4620	0.0279
	0.1999	1.4265	0.0685						
				x DPSO + (1 − *x*) Water					
298.15	0.0105	1.3440	0.0092	0.2019	1.4305	0.0718	0.5049	1.4502	0.0537
	0.01985	1.3516	0.0156	0.2809	1.4395	0.0707	0.6818	1.4550	0.0358
	0.0469	1.3740	0.0342	0.3975	1.4460	0.0621	0.9002	1.4580	0.0111
	0.0998	1.4009	0.0548						
303.15	0.0105	1.3430	0.0097	0.2019	1.4285	0.0713	0.5049	1.4495	0.0545
	0.01985	1.3510	0.0165	0.2809	1.4375	0.0702	0.6818	1.4540	0.0363
	0.0469	1.3725	0.0342	0.3975	1.4455	0.0631	0.9002	1.4555	0.0101
	0.0998	1.3990	0.0544						
308.15	0.0105	1.3420	0.0093	0.2019	1.4245	0.0681	0.5049	1.4486	0.0549
	0.01985	1.3506	0.0166	0.2809	1.4350	0.0686	0.6818	1.4520	0.0358
	0.0469	1.3711	0.0334	0.3975	1.4445	0.0632	0.9002	1.4540	0.0105
	0.0998	1.3980	0.0541						
				x DiPSO + (1 − *x*) Water					
298.15	0.0087	1.3435	0.0087	0.0987	1.4070	0.0604	0.7756	1.4625	0.0268
	0.0197	1.3530	0.0169	0.4035	1.4530	0.0671	0.8899	1.4635	0.0134
	0.0505	1.3800	0.0400	0.6002	1.4600	0.0479			
303.15	0.0087	1.3430	0.0097	0.0987	1.4060	0.0610	0.7756	1.4610	0.0276
	0.0197	1.3520	0.0174	0.4035	1.4510	0.0670	0.8899	1.4625	0.0148
	0.0505	1.3785	0.0400	0.6002	1.4575	0.0475			
308.15	0.0087	1.3420	0.0092	0.0987	1.4040	0.0597	0.7756	1.4590	0.0277
	0.0197	1.3515	0.0174	0.4035	1.4480	0.0653	0.8899	1.4605	0.0151
	0.0505	1.3775	0.0396	0.6002	1.4560	0.0477			

refractive index (Δ*n*) is defined as

$$\Delta n = n - (n_1 x_1 + n_2 x_2) \qquad (3)$$

where n_1 and n_2 represent the refractive indices of pure water and pure dialkylsulfoxide, respectively, and x_1 and x_2 represent the mole fractions of water and dialkylsulfoxide. Experimental values of changes of refractive indices over the whole mole fraction range were fitted to the Redlich−Kister[23] polynomial equation

$$F(x) = x(1 - x)\sum_{k=0}^{N} A_k (2x - 1)^k \qquad (4)$$

where $F(x)$ represents changes of the refractive index, Δ*n*, and *x* is the mole fraction of DASO. The coefficients A_k of eq 4 were calculated by the method of least-squares. The values obtained for the coefficients A_k along with the standard deviations are given in Table 8.

For DESO + water and DPSO + water mixtures, surface tension first decreases quite abruptly and becomes rather steep in the region where the mole fraction, *x*, of those sulfoxides is > 0.2. These curves are concave in the whole concentration region.

However, among aqueous solutions of dialkylsulfoxides, the DMSO + water system behaves quite differently from the others. For DMSO + water mixtures, both surface tension and surface tension deviation curves exhibit convex curvature when the mole fraction of DMSO varies between 0.3 and 0.5 (Figures 2 and 3).

This observation is similar to the plot of the surface tension deviation of the DMSO + water system presented by Cheong and Carr.[10]

This fact prompts us to investigate this system in more detail, measuring additional compositions, for a total of 18 values and 7 values in this region (see Figure 5).

From the point of view of the surface phenomena, it seems reasonable to also consider the temperature dependences of surface tension, mainly the effect of temperature on the surface

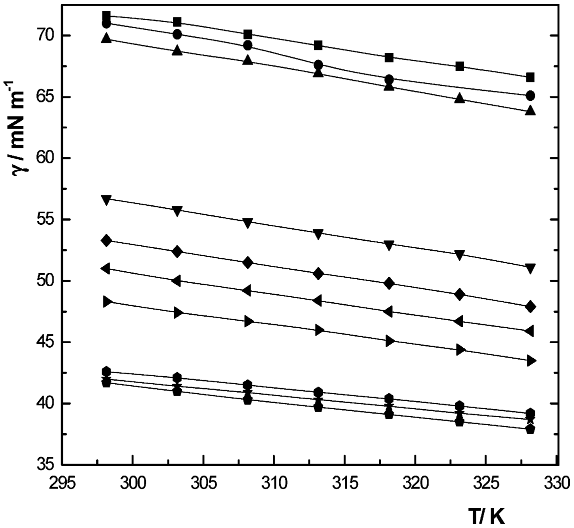

Figure 1. Temperature variation of the surface tension for the *x* DMSO + (1 − *x*) water mixtures. Each line represents a constant mole fraction of DMSO in water: ■, 0; ●, 0.0121; ▲, 0.0202; ▼, 0.1979; ◆, 0.3187; solid arrow pointing left, 0.4191; solid arrow pointing right, 0.5010; ⬢, 0.8088; ★, 0.8945; ⬟, 1.

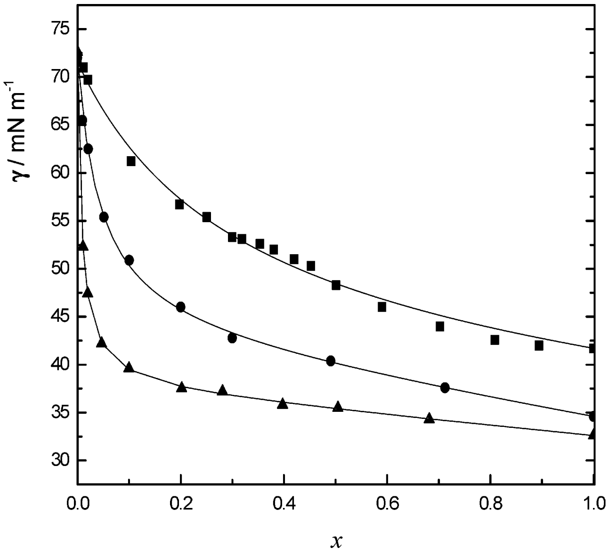

Figure 2. Surface tension of the aqueous solutions at 298.15 K: ■, *x* DMSO + (1 − *x*) water; ●, *x* DESO + (1 − *x*) water; ▲, *x* DPSO + (1 − *x*) water. *x* represents mole fraction of dialkylsulfoxide.

Table 7. Surface Tension Parameters *a* and *b* and Their Standard Deviation from Equation 1

	T/K						
	298.15	303.15	308.15	313.15	318.15	323.15	328.15
			DMSO (1) + Water (2)				
a	−3.32	−3.87	−4.03	−4.54	−4.69	−5.12	−6.26
b	−2.91	−3.23	−3.34	−3.68	−3.65	−3.97	−4.66
SD	0.76	0.71	0.66	0.61	0.71	0.68	0.68
			DESO (1) + Water (2)				
a	−23.24	−22.41	−24.57	−34.76	−38.87	−41.47	−36.61
b	−17.64	−17.19	−18.64	−22.68	−25.93	−28.66	−26.46
SD	0.43	0.41	0.36	0.93	0.87	0.88	0.65
			DPSO (1) + Water (2)				
a	−127.10	−136.63	−144.46	−149.58	−149.96	−155.11	−159.87
b	−110.99	−118.61	−125.52	−130.42	−129.60	−135.85	−140.67
SD	0.16	0.20	0.20	0.17	0.37	0.34	0.33
			DiPSO (1) + Water (2)				
a	−139.27	−131.50	−111.92	−119.37	−134.75	−132.32	−133.46
b	−117.64	−110.27	−99.71	−104.63	−115.54	−115.25	−115.92
SD	0.93	0.91	1.26	1.02	0.92	1.09	1.21

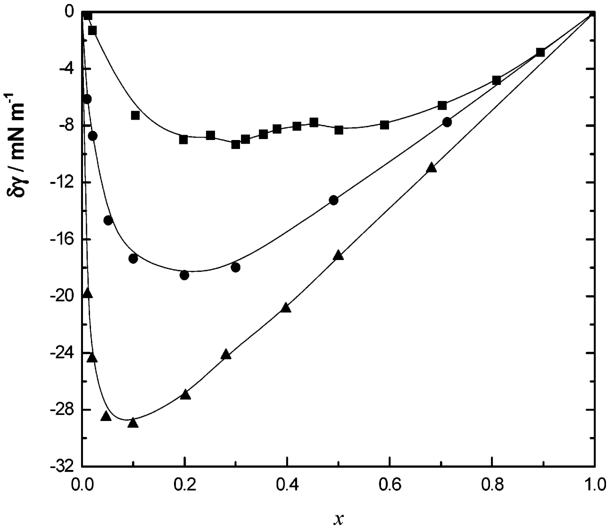

Figure 3. Experimental surface tension deviations at 298.15 K of: ■, *x* DMSO + (1 − *x*) water; ●, *x* DESO + (1 − *x*) water; ▲, *x* DPSO + (1 − *x*) water mixtures. *x* represents mole fraction of dialkylsulfoxide.

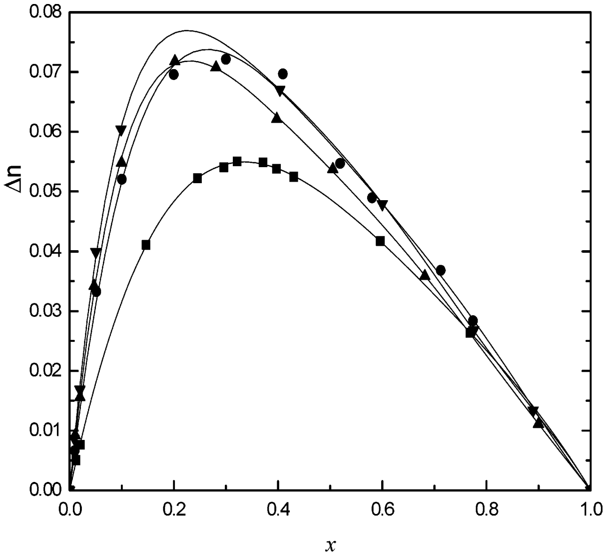

Figure 4. Changes of refractive index at 298.15 K of: ■, *x* DMSO + (1 − *x*) water; ●, *x* DESO + (1 − *x*) water; ▲, *x* DPSO + (1 − *x*) water; ▼, *x* DiPSO + (1 − *x*) water mixtures. *x* represents mole fraction of dialkylsulfoxide.

tension behavior in the concentration range $0.3 < x < 0.5$. To obtain a more clear picture for DMSO + water mixtures, the temperature was raised to 343.15 K.

As depicted in Figure 5, the curve exhibits a slight maximum, which disappears with increasing temperature. To explain this phenomenon, it is reasonable to assume that at higher temperature a decay of DMSO + water complexes occurs resulting in the increase of DMSO concentration on the liquid surface, and hence the lowering of surface tension was observed.

Obviously, this fact shows the nonvalidity of the model equation as was stated by Connors and Wright for binary aqueous + DMSO mixtures at 298.15 K.[8]

In general, this type of nonmonotonous concentration dependence of the surface tension of solutions arises from the change of the difference in the distribution of molecules between the surface and the bulk region of the liquid.

We believe that the formation of such a type of convex could be a result of a strong interaction between DMSO and water molecules which predominates in the concentration range 0.3

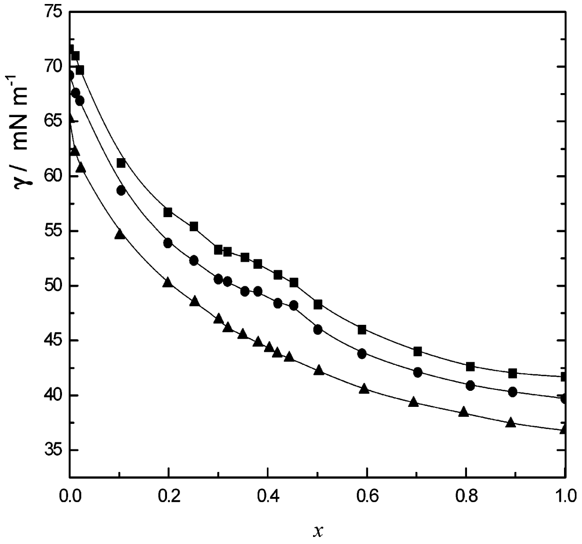

Figure 5. Experimental surface tension of x DMSO + $(1 - x)$ water at: ■, 298.15 K; ●, 313.15 K; ▲, 343.15 K. x represents mole fraction of DMSO.

Table 8. Changes in Refractive Index Parameters A_k and Their Standard Deviation from Equation 4

T/K	A_0	A_1	A_2	A_3	A_4	SD 10^{-3}
			DMSO (1) + Water (2)			
298.15	0.195	−0.130	0.081			0.22
303.15	0.196	−0.132	0.085			0.69
308.15	0.196	−0.132	0.083			0.74
			DESO (1) + Water (2)			
298.15	0.233	−0.190	0.189	−0.148		1.65
303.15	0.230	−0.184	0.191	−0.150		1.86
308.15	0.232	−0.194	0.194	−0.122		1.81
			DPSO (1) + Water (2)			
298.15	0.215	−0.180	0.182	−0.205	0.098	0.62
303.15	0.220	−0.175	0.145	−0.222	0.129	0.68
308.15	0.223	−0.171	0.080	−0.209	0.213	0.35
			DiPSO (1) + Water (2)			
298.15	0.234	−0.192	0.155	−0.229	0.183	0.57
303.15	0.232	−0.194	0.165	−0.216	0.199	0.69
308.15	0.230	−0.174	0.131	−0.230	0.243	0.49

$< x <$ 0.5, and DMSO (component with lower surface tension) tends to prefer the bulk region of the liquid rather than the interface. In this respect, it is important to emphasize a well-known fact for DMSO + water mixtures: the greatest deviations from ideal mixing occur around a DMSO mole fraction of x = 0.33, which suggests the presence of 1 DMSO + 2 water complexes.[24]

For the higher concentration range of DMSO, $x > 0.5$, a significant self-association of DMSO molecules occurs, leading to the redistribution on the surface due to released DMSO molecules. This unique behavior is indicative of changing intermolecular interactions involving DMSO self-association and DMSO association with water. Such self-association could be playing a significant role in the observed changes in DMSO orientation with concentration.

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