Effect of temperature and composition on the surface tension and surface properties of binary mixtures containing DMSO and short chain alcohols

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A B S T R A C T

Surface tension of binary mixtures of methanol, ethanol and isopropanol with DMSO (dimethyl sulfoxide) was measured over the whole range of composition at atmospheric pressure of 82.5 kPa within the temperatures between (298.15 and 328.15) K. The experimental measurements were used to calculate in surface tension deviations ($\Delta\sigma$). The sign of $\Delta\sigma$ for all temperatures is negative (except of methanol/DMSO system) because of the factors of hydrogen bonding and dipole–dipole interactions in the DMSO-alcohol systems. Surface tension values of the binary systems were correlated with FLW, MS, RK and LWW models. The mean standard deviation obtained from the comparison of experimental and calculated surface tension values for binary systems with three models (FLW, MS and RK) at various temperatures is less than 0.83. Also, the results of the LWW model were used to account for the interaction energy between alcohols and DMSO in binary mixtures. The temperature dependence of σ (surface tension) at fixed composition of solutions was used to estimate surface enthalpy, H^s, and surface entropy, S^s. The results obtained show that the values of the thermodynamic parameters for alcohol/DMSO mixtures decrease with increasing alkyl chain length of alcohol. Finally, the results are discussed in terms of surface mole fraction and lyophobicity using the extended Langmuir (EL) isotherm.

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1. Introduction

Among the various experimental methods, surface tension is one of the most powerful techniques that provide information about surfaces and intermolecular interaction. The study of the surface properties in liquid mixtures is of great interest from both scientific and industrial points of view [1–3].

Dimethyl sulfoxide (DMSO) is a non-aqueous dipolar aprotic solvent used in pharmaceuticals, surface cleaners, extraction, electrochemistry and as a solvent for polymers. As pure solvent, DMSO has a large dipole moment and high dielectric constant (the relative dielectric constant $\varepsilon = 46.50$ and dipole moment $\mu = 4.06$ D at 298.15 K) [4–6].

Also, alcohols are considered to be a water-like solvent in terms of hydrogen-bonding ability and are an important solvent due to their use in the chemical, pharmaceutical, fuel cell, cosmetic industries and others [7–10].

This study is a continuation of our systematic experimental research on surface properties of binary liquid mixtures that contain polar or polar aprotic solvents [1–3,11,12]. The experimental values of surface tension of the binary systems consisting of DMSO with methanol, ethanol and isopropanol were determined over the whole range of composition at (298.15, 308.15, 318.15 and 328.15) K.

After surveying the literature, a number of research studies have been located on the surface tensions of DMSO with alkanols binary mixtures at various temperatures. However, no surface tension values were previously reported for DMSO with isopropanol at different temperatures and DMSO with methanol and ethanol at (308.15, 318.15 and 328.15) K [1,2,13–15].

After experimental measurements, the data obtained were analysed using various methods. In the first section, the concentration dependence of the surface tension of binary DMSO-alcohol mixtures at various temperatures are correlated using Fu et al. (FLW) [16], the Myers-Scott (MS) [17] and Redlich-Kister (RK) [18] and Li et al. (LWW) equations, and then in a new approach, the effect of alcohol structure on the interaction energy values (between alcohols and DMSO) is discussed in the binary systems [19,20].

In the second section of this work, by employing the measured surface tensions at various temperatures, the thermodynamic

properties of the surface (H^s and S^s) have been obtained. Finally, a Langmuir type isotherm model (or the extended Langmuir (EL)) is employed to determine the surface concentrations from the knowledge of the bulk mole fractions. The results provide information on the molecular interactions between the unlike molecules that exist at the surface and the bulk at various temperatures [20,21].

2. Experimental

2.1. Materials

All compounds were purchased from Merck and used without any further purification. Purity of each compound was ascertained by gas chromatography (GC type Agilent 7820A Agilent Technologies). The water mass fraction of the all components was determined by Karl Fisher (K.F.) titration, and it was found to be less than 0.0008 for DMSO and less than 0.004 for alcohols. Chemicals were kept in dark bottles. The detailed information of the materials used in the experiment is listed in Table 1.

The purity of components was checked by comparing the measured surface tension with those reported in the literature [13–15,22–29]. The resultant values are in good agreement with values found in the literature and reported in Table 2 [14]. Bi-distilled water has been used for checking the performance of the tensiometer instrument in previous publication [25].

Table 1
Specification of the chemicals employed in this work.

Component	CAS number	Supplier	Purity (mass fraction)		Water content (mass fraction)	
			Supplier	GC	Supplier	K.F.
DMSO[a]	67-8-5	Merck	>0.995	0.995	<0.001	0.0008
Methanol	67-56-1	Merck	>0.995	0.996	⩽0.0002	0.0002
Ethanol	64-17-5	Merck	>0.995	0.997	<0.0005	0.0003
Isopropanol	67-63-0	Merck	>0.99	0.990	<0.005	0.0035

[a] Dimethyl sulfoxide.

Table 2
Comparison of experimental surface tension, σ, of pure components with literature values at atmospheric pressure of 82.5 kPa within the temperatures between (298.15 and 328.15) K.[a]

Component	T/K	σ/(mN·m^{-1})	
		Exptl.	Lit.
DMSO	298.15	42.426	42.65[14], 42.78[22]
	308.15	41.295	40.95[13], 41.62[22]
	318.15	40.173	40.41[23]
	328.15	39.081	39.38[23]
Methanol	298.15	22.241	22.20[13], 22.18[24]
	308.15	21.413	21.52[25], 21.35[26]
	318.15	20.530	20.61[25], 20.33[24]
	328.15	19.541	19.39[24]
Ethanol	298.15	21.658	21.74[27], 21.80[28]
	308.15	21.011	21.04[25], 21.03[29]
	318.15	20.189	20.22[25]
	328.15	19.235	19.38[14]
Isopropanol	298.15	21.146	21.22[25]
	308.15	20.286	20.23[25], 20.20[15]
	318.15	19.525	19.47[15]
	328.15	18.512	18.4[14]
Water	298.15	72.05	72.01[25]

[a] Standard uncertainties u are $u(T) = 0.01$ K, $u(P) = 10$ kPa, $u(x) = 0.001$ and the combined expanded uncertainty U_c is $U_c(\sigma) = 0.114$ mN·m^{-1} (0.95 level of confidence).

2.2. Apparatus and procedure

The surface tension of each sample liquid (pure or mixture) was measured using the platinum-iridium ring method with a PC controlled KSV Sigma 701 tensiometer. The ring was thoroughly cleaned and flamed before each measurement. The measurements were automatically corrected to the actual values by means of the Huh and Mason compensation for interface distortion [30,31]. The use of boiling distilled water can be a good (alternative) procedure (for checking the performance of the instrument). The uncertainty in the calculated surface tensions (the mean value from 7 points) was estimated to be ±0.04 mN·m^{-1}. The measurements were carried in the temperature range from 298.15 K to 328.15 K and at pressure of 82.5 kPa. The sample under measurement was kept thermostatted in a double-jacketed glass cell by means of a water bath, using a LAUDA circulator (model ECO RE415) equipped with a Pt100 probe, immersed in solution, and able to control the temperature within ±0.01 K.

The binary mixtures were prepared by mass using a Sartorius analytical balance (model BP 121S, accurate to ±0.1 mg). The standard uncertainty of the mole fractions is ±1.000 × 10^{-3}.

3. Results and discussion

3.1. Correlation of surface tension and concentration in binary mixtures

The concentration dependence of the surface tension of mixtures can be represented in terms of the surface tension deviation, $\Delta\sigma$, defined as:

$$\Delta\sigma = \sigma - \sum_{i=1}^{n} x_i \sigma_i^* \tag{1}$$

where σ is the surface tension of the mixture, and σ_i^* is the surface tension of the pure component I at the same temperature and pressure of the mixture, x_i is the mole fraction of the component I and n is the number of components.

A few empirical and thermodynamic-based equations are available to correlate the surface tension; some of them have recently proposed and are well founded on a thermodynamic basis. Fu et al. (FLW) proposed a two-parameter equation to correlate the surface tension with the composition in the binary systems which is based on the local composition concept due to the Wilson equation [16]. Another surface tension correlation was proposed by Li et al. (LWW) for liquid mixtures, which is based on the Wilson equation for the excess Gibbs energy [19,32]. Other empirical equation such as Myers-Scott (MS) has been applied for the correlation of binary surface tension values [17]. The relevant equations for all the models for surface tension (or the surface tension deviation) correlation, in this work, are summarized in Table 3.

In Table 4, the measured surface tension is presented for binary systems over the range T = (298.15–323.15) K at intervals of 10 K as a function of mole fraction.

Figs. 1–3 show the behaviour of surface tension of alcohol in DMSO at various temperatures. In all systems, the surface tension, σ, decreased with increasing alcohol concentration. This trend is non-linear, with the change in surface tension caused by a given change in alcohol mole fraction being greater at low mole fraction than at high mole fraction. On the other hand, as discussed above, DMSO and alcohol interact strongly and mixtures form non-ideal solutions particularly in the low concentration regime. This behaviour is typically explained by a difference in distribution of molecules between the surface and the bulk of the liquid. In a characteristic case, the compound having a lower surface tension