

Surface Tension of the Dimethylsulfoxide/ Thiophene System at 298.15 K

S. Aznarez, L. Mussari, and M. Postigo*

Cátedra de Fisicoquímica, Departamento de Química, Facultad de Ingeniería,
Universidad Nacional del Comahue, Buenos Aires 1400, 8300-Neuquén, Argentina

Summary. Densities and surface tensions of dimethylsulfoxide (1) + thiophene (2) were determined over the whole composition range at 298.15 K. The densities have been determined with a vibrating tube densimeter and the surface tensions by the differential capillary rise technique. Negative excess surface tensions were observed. From the different equations existing in the literature for estimation of surface tensions of mixtures we have used the equations due to Rice and Teja [1] and Winterfeld, Scriven and Davis [2]. The Rice and Teja's Equation gives better results.

Keywords. Surface tension; Mixtures of non-electrolytes; Thermodynamic excess functions.

Die Oberflächenspannung des binären Systems Dimethylsulfoxid/Thiophen bei 298.15 K

Zusammenfassung. Dichten und Oberflächenspannungen von Dimethylsulfoxid (1) + Thiophen (2) wurden über den gesamten Mischungsbereich bei 298.15 K gemessen. Die Dichten wurden mit einem Vibrationsröhrendensitometer und die Oberflächenspannung mit der differentiellen Kapillaren-Steig-Methode bestimmt. Es wurden negative Zusatzoberflächenspannungen beobachtet. Von den verschiedenen Ansätzen zur Abschätzung von Oberflächenspannungen in Mischungen wurden die Methoden von Rice und Teja [1] und von Scriven und Davis [2] getestet, wobei der Ansatz nach Rice und Teja bessere Ergebnisse erzielte.

Introduction

The excess surface tension σ^E of a binary mixture is defined as the amount by which the surface tension σ of the mixture exceeds the ideal value calculated from the surface tensions of the pure components, assuming additivity on a mole fraction basis. Thus

$$\sigma^E = \sigma - (x_1\sigma_1 + x_2\sigma_2) \quad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2 in the mixtures, and σ_1 and σ_2 are the surface tensions of the pure components. For most nonelectrolyte mixtures, σ^E is negative and this fact is generally attributed to a Gibbs enrichment of the surface region by the component of lower surface tension. However, positive values of σ^E have also been observed for some systems; usually, these involve polar molecules.

This work describes measurements of surface tension for the dimethylsulfoxide (1) + thiophene (2) system at 298.15 K by the differential capillary rise technique.

Different equations exist in the literature which predict the excess surface tensions of mixtures, like those by Shereshefsky [3], Hoar and Melford [4], Eckert and Prausnitz [5], and Flory [6]. In this work, equations due to Rice and Teja [1] and Winterfeld-Scriven and Davis [2] were applied and compared with the experiment.

Experimental Part

The chemicals used in the present study were dimethylsulfoxide supplied by Merck and thiophene supplied by Fluka. All solvents were used from freshly opened bottles without further purification. According to the specification of the suppliers, the purities were better than 99.7 mass % for dimethylsulfoxide and 99.5 mass % for thiophene. All liquids were stored over molecular sieves (Union Carbide Type 4A). The purity of the compounds was checked by determining their refractive indices and densities, which agreed well with the literature values.

Air and bidistilled water were used for densimeter calibration.

All the solutions were prepared by using a Mettler H 315 balance (precision of 1×10^{-4} g) and air-tight stoppered bottles. The more volatile component was poured directly into the bottle. The charged bottle was closed and weighed. The second component was injected into the bottle through the stopper by means of a syringe. This procedure hindered any vapor loss and contamination. Hence the possible error in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

A digital densimeter (Anton Paar Model DMA 45) was employed for the determination of the densities of the pure components and the binary mixtures. Water and air were chosen as calibrating fluids since they span a wide range and their densities are known at a high precision level.

The surface tensions were deduced from our measurements of the capillary length and density measurements. The capillary length parameter is

$$a^2 = 2\sigma/(\rho_l - \rho_v)g. \quad (2)$$

Here, σ is the surface tension; ρ_l and ρ_v are the densities of the liquid and vapor, respectively; and g is the acceleration due to gravity 9.78 m s^{-2} . The capillary length can be determined from a relation derived by Rayleigh [7]:

$$a^2 = r_i \left[h_i - h_0 + \frac{r_i}{3} - 0.1288 \frac{r_i^2}{h_i - h_0} + 0.1312 \frac{r_i^3}{(h_i - h_0)^2} \right] \quad (3)$$

where r_i is the radius of capillary, i , and $h_i - h_0$ is the height of the meniscus in the i th capillary (h_i) above the bulk meniscus (h_0). The liquid-gas contact angle was assumed to be zero. We have used a differential capillary rise technique that avoids the difficult measurement of the location of the bulk meniscus h_0 . h_1 and h_2 were measured for two different capillaries (r_1 and r_2) in the same cell. Then Eq. (3) was written twice (once for each measurement) and h_0 was eliminated from the equations to determine a^2 . The sample cell contains two capillaries of the following bore radii: $r_1 = 0.320 \pm 0.001$ mm and $r_2 = 0.148 \pm 0.002$ mm. Their radii were determined by partially filling the capillaries with plugs of mercury. The plugs were weighed and their lengths were measured with a cathetometer.

The capillary rise h_i was measured (± 0.01 mm) for each capillary with a cathetometer.

All measurements were carried out at atmospheric pressure. The pressure was measured by means of a mercury barometer. A Haake constant temperature bath circulator was used with a temperature control interval of ± 0.01 K. The temperature was detected with a digital thermometer (Digitec) calibrated and checked at the water triple point. The precision of the densities measured is estimated to be better than $\pm 0.2 \text{ kg m}^{-3}$ and the precision of the surface tension better than $\pm 3 \times 10^{-5} \text{ N m}^{-1}$.

Results and Discussion

Densities and surface tensions for the pure components at 298.15 K are given in Table 1, together with literature values for comparison. In general, our results agree fairly well with these already known values.

Densities for the binary mixtures were calculated as a function of the mole fraction of dimethylsulfoxide by the following polynomial equation:

$$\rho = \rho_1 x_1 + \rho_2 x_2 + x_1 (1 - x_1) \sum_{j=1}^n a_j (1 - 2x_1)^{j-1}. \quad (4)$$

The experimental values of the excess surface tensions of the binary mixtures (as determined by Eq. (1)) over the whole concentration range are summarized in Table 2.

The set of results of excess surface tensions was fitted with a Redlich–Kister [8] form of the type:

$$\sigma^E = x_1 (1 - x_1) \sum_{j=1}^n a_j (1 - 2x_1)^{j-1}. \quad (5)$$

The method of least squares was used to determine the values of the coefficients a_j .

Table 1. Density and surface tension of pure substances at 298.15 K

	$\rho \times 10^{-3}/\text{kg m}^{-3}$		$\sigma \times 10^3/\text{N m}^{-1}$	
	Expt.	Lit.	Expt.	Lit.
Dimethylsulfoxide	1.0956	1.09537	43.04	42.98
Thiophene	1.0583	1.05884	32.07	32.0

Literature: Ref. [10]

Table 2. Experimental values of σ^E and the calculated values with Eqs. (7) and (15) at 298.15 K

x_1	10^{-3} N m^{-1}		
	$\sigma^E(\text{Exp.})$	$\sigma^E(\text{Eq. 7})$	$\sigma^E(\text{Eq. 15})$
0.1069	-0.381	-0.336	-0.294
0.2039	-0.618	-0.569	-0.501
0.2876	-0.744	-0.717	-0.644
0.4070	-0.823	-0.843	-0.817
0.5062	-0.834	-0.871	-0.861
0.5800	-0.802	-0.848	-0.873
0.6687	-0.717	-0.769	-0.829
0.7856	-0.549	-0.583	-0.670
0.9046	-0.294	-0.298	-0.368
0.9464	-0.174	-0.175	-0.224

Table 3. Coefficients a_j from Eqs. (4) and (5) and standard deviations ε at 298.15 K

	a_1	a_2	a_3	a_4	a_5	ε
$\rho/(\text{kg m}^{-3})$	12.61	11.83	-1.39	-3.02	-4.33	0.08
$\sigma^E/10^{-3}(\text{N m}^{-1})$	-3.337	-0.432	-0.559	-	-	0.02

The optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate with n :

$$\varepsilon = [\sum (X_{\text{obs}} - X_{\text{cal}})^2 / (n_{\text{obs}} - n)]^{1/2} \quad (6)$$

where X denote the density (ρ) or the excess surface tension (σ^E). The values adopted for the coefficients a_j and the standard error of the estimate are shown in Table 3.

The surface tensions of the solution were calculated in two different ways for comparison with the experimental values.

1) First, we applied Rice and Teja's [1] corresponding states method for the prediction of surface tension of mixtures. These authors proposed the relation:

$$(\sigma\varphi) = (\sigma\varphi)^{(s1)} + \frac{\omega - \omega^{(s1)}}{\omega^{(s2)} - \omega^{(s1)}} [(\sigma\varphi)^{(s2)} - (\sigma\varphi)^{(s1)}] \quad (7)$$

where s1 and s2 refer to the properties of two reference fluids, (in this case, the pure components) and ω is the acentric factor. For mixtures, the pseudocritical equivalent substance replacing the pure fluid are defined as

$$T_{\text{cm}} V_{\text{cm}} = \sum_i \sum_j x_i x_j T_{\text{cij}} V_{\text{cij}} \quad (8)$$

$$V_{\text{cm}} = \sum_i \sum_j x_i x_j V_{\text{cij}} \quad (9)$$

$$\omega_{\text{m}} = \sum_i x_i \omega_i \quad (10)$$

$$T_{\text{cij}} V_{\text{cij}} = \Psi_{ij} (T_{\text{cii}} V_{\text{cii}} T_{\text{cjj}} V_{\text{cjj}}) \quad (11)$$

$$V_{\text{cij}} = (V_{\text{cii}}^{1/3} + V_{\text{cjj}}^{1/3})^3 / 8 \quad (12)$$

where Ψ_{ij} is a binary interaction coefficient which must be evaluated from experimental data. The values of φ from Eq. (7) are obtained as:

$$\varphi = V_{\text{cm}}^{2/3} / T_{\text{cm}} \quad (13)$$

With $\Psi_{12} = 0.961$ we determined for our system the values of excess surface tensions indicated in Table 2.

2) Second, Winterfeld-Scriven and Davis [2] used, for the surface tension of binary solutions, the expression

$$\sigma = (n_1/\rho_1)^2 \sigma_1 + (n_2/\rho_2)^2 \sigma_2 + 2 \delta n_1 n_2 (\sigma_1 \sigma_2)^{1/2} / \rho_1 \rho_2 \quad (14)$$

where σ_i and ρ_i denote the surface tension and saturated liquid density of pure i at

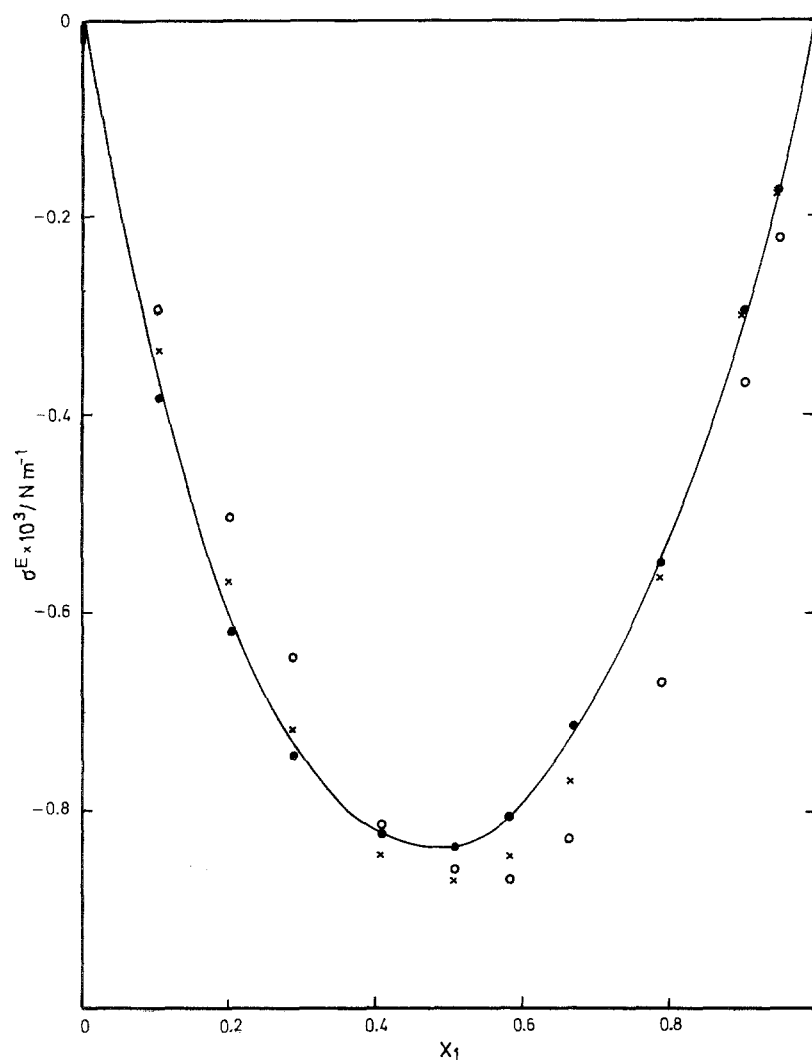


Fig. 1. Comparison of the excess surface tension: ● Experimental values; × Eq. (7). ○ Eq. (14). Solid curve Eq. (5)

the same temperature as the solution, n_i is given by $n_i = x_i$ and ρ denotes the density of component i in the liquid solution.

The unknown parameter of the model is δ . This is the same parameter that Girifalco and Good [9] introduced in relating the interfacial tensions of immiscible liquids to the surface tensions of the pure liquids. Girifalco and Good have given for δ the following estimate

$$\delta_{GG} = \frac{4V_1^{1/3} V_2^{1/3}}{(V_1^{1/3} + V_2^{1/3})}. \quad (15)$$

We determined δ with experimental data at a composition x_1 near the equimolar point. With $\delta = 0.959$ we determined for our system the values of excess surface tensions indicated in Table 2.

In Fig. 1 we also represent Rice–Teja’s and Winterfeld–Scriven–Davis’s values.

Rice–Teja’s equation predicts surface tensions which agree well with the experimental values giving rise to symmetrical curves. The other method is not in agreement with experiment (comp. Table 2), probably because the values of parameter δ do not take into account all important interactions.

References

- [1] Rice P., Teja A. S. (1982) *J. Colloid Interface Sci.* **38**: 294
- [2] Winterfeld P. H., Scriven L. E., Davis H. T. (1978) *AIChE J.* **24**: 1010
- [3] Shereshefsky J. L. (1967) *J. Colloid Interface Sci.* **24**: 317
- [4] Hoar T. P., Melford D. A. (1957) *Trans. Faraday Soc.* **53**: 315
- [5] Eckert C. A., Prausnitz J. M. (1964) *AIChE J.* **10**: 677
- [6] Flory P. J. (1965) *J. Am. Chem. Soc.* **87**: 1833
- [7] Rayleigh O. M. (1916) *Proc. R. Soc. London Ser. A* **92**: 184
- [8] Redlich O., Kister A. T. (1948) *Ind. Eng. Chem.* **40**: 345
- [9] Girifalco L. A., Good R. J. (1957) *J. Phys. Chem.* **61**: 904
- [10] Weissberger A., Riddick J. A., Bunger W. B., Sakano T. K. (1986) *Organic Solvents*. Wiley, Chichester

Received June 24, 1992. Accepted March 22, 1993