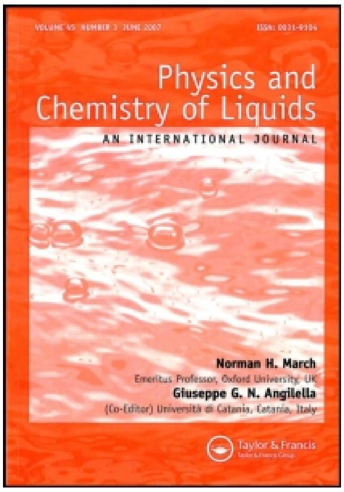

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THE INTERNAL STRUCTURES OF LIQUID DIMETHYLSULFOXIDE-ACETONE MIXTURES

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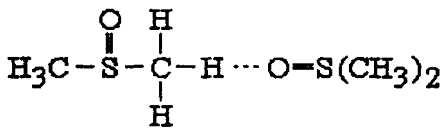
The ^{1}H-NMR spectra of the liquid binary mixtures, dimethylsulfoxide-acetone, were recorded at 298 K within nearly the whole range of mixed solvent compositions. From these data the values of the spectral parameter, $\Delta\delta$(DMSO-A) were found. The viscosities (η_{12}) and surface tensions (γ_{12}) of the mixed solvents were measured at 298.15 K. From all these new parent data, the values of molar volumes (V_{12}) and their deviations from "ideality" were calculated. Additionally, the values of the temperature coefficients of dielectric permittivity, α_{12}, were found. These structural parameters as functions of concentration suggest the formation of the most stable "complex" (sub-unit) of the DMSO·A type.

KEY WORDS: ^{1}H-NMR spectra, binary liquid mixtures, intermolecular interactions, physicochemical properties.

INTRODUCTION

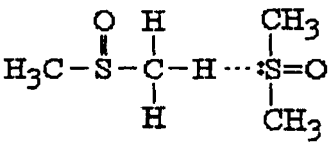
In this paper the intermolecular interactions in the mixtures of dimethylsulfoxide (DMSO)-acetone (A) will be analysed from the point of view of correlations existing between the ^{1}H-NMR spectral results and some physicochemical intensive properties of the same binary mixtures.

Dimethylsulfoxide has been found as the strongly polar solvent: $\mu = 4.3$ D[1] and $\varepsilon = 48.9$[1] (at 298.15 K), and with excellent electron-donor properties (see for more details[1–5]). Its strongly polar SO bond contains O being the most electronegative site of DMSO with respect to S. Several physicochemical characteristics show that neat liquid DMSO is highly associated; the associated DMSO molecules dissociate in part on increasing the temperature. Theoreticaly, the self-association may take place by means of O—H-bridging (2), and S—H-bridging (2) S—O-bridging (3 and 4), viz. The self-association types 1 and 2 seem to be highly improbable because of the very low C—H acidity of DMSO[1,2]: it is less acid than acetone by the factor of 10^7 and less acid than diphenylmethane by the factor of about 10^3. Probably[1], in CCl_4 solutions of DMSO it is mostly monomeric up to a concentration of 0.08 molar; at higher DMSO concentrations (0.08–0.3 molar) the cyclic dimers 3 predominate, and at still higher DMSO concentrations the cyclic dimers 3 break open



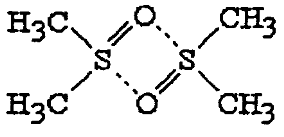
$\mathrm{H_3C{-}S({=}O){-}CH_2{-}H\cdots O{=}S(CH_3)_2}$

1

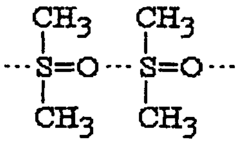


$\mathrm{H_3C{-}S({=}O){-}CH_2{-}H\cdots S(CH_3)_2{=}O}$

2



3

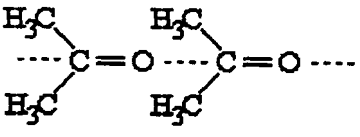


$\cdots\mathrm{(CH_3)_2S{=}O}\cdots\mathrm{(CH_3)_2S{=}O}\cdots$

4

to form polymeric chains of type 4; see, however, Reference.[6] on DMSO-CCl_4 complexes.

Acetone belongs also to the group of strongly polar solvents: $\mu = 2.8D$[7] and $\varepsilon = 20.7$[8] at 298.15 K which results from the difference between the electronegativities of carbon and oxygen. The strong polarity of the C=O bond has an impact on several physicochemical characteristics of acetone (e.g. it exhibits the raise of boiling point in comparison to other less polar solvents with the similar molecular weight[9].) It may be explained as the result of self-association of acetone molecules due to the electrostatic interactions, as it has been shown below[10-11].



However, the self association of acetone by means of formation of the hydrogen bonding of the C—H····O type seems to be highly improbable because of the very low C—H acidity ($pK_a = -3.7$[12]).

EXPERIMENTAL

DMSO (Nationale Petrols, France) was purified by distillation in a vacuum and repeated crystallization until the melting point was at least 18.5°. Acetone (Fluka) was treated with anhydrous potassium carbonate and kept for a few hours over molecular sievs (Type 4 Å from BDH). ^{1}H-NMR spectra were recorded on the Tesla spectrometer of the type BS 467 (60 MHz), at 298 K. The chemical shift values for proton signals of dimethylsulfoxide and acetone were measured with accuracy of about ± 0.2 Hz in respect to external standard HMDS (hexamethyldisiloxane). The viscosities were measured with an accuracy ± 0.1% using the Höppler viscosimeter. The surface tensions were measured with an accuracy ± 0.1% by the maximum bubble pressure method. All the binary solutions made of DMSO and A were prepared by weight.

RESULTS AND DISCUSSION

There is no literature data concerning the analysis of intermolecular interactions in liquid mixtures of dimethylsulfoxide with acetone. Haynes[13], Tommila[14] and Himyenko[15] measured density, dielectric permittivity and surface tension for the studied binary mixtures. However, they have not interpreted their results in terms of stoichiometry and internal structure of intermolecular "complexes" formed by molecules of DMSO and A. In this paper, with the aim of analysing the intermolecular interactions between the components in the liquid binary mixtures DMSO-A, we have measured the values of chemical shift differences δ(DMSO-A) at 298 K, between the centre of the ^{1}H-NMR signal of the DMSO molecules and the centre of the ^{1}H-NMR signal of the A molecules over a wide range of solvent compositions. From these new spectral data the values of the spectral parameter $\Delta\delta$(DMSO-A) have been found. The location of this parameter maximum points, as we shown in our previous papers[16-18], at the composition where the strongest intermolecular interactions between the components are displayed. The δ(DMSO-A) values are shown in Table 1, whereas the $\Delta\delta$(DMSO-A) values are visualized in Figure 1 as a function of the mixture compositions.

The analysis of the obtained data indicates the presence of a maximum $\Delta\delta$(DMSO-A) at ca. 50 mol.% of DMSO. Thus, the conclusion can be drawn that at this composition the strongest interactions between DMSO and A molecules are displayed, and that the most stable "complex" (sub-unit) is of the DMSO·A type.

In addition to the spectral examinations, taking the literature values of dielectric permittivities[14], the temperature coefficients of ε_{12}, denoted α_{12}, viz. $\alpha_{12} = (1/\varepsilon_{12})\cdot[d\varepsilon_{12}/d(1/T)]$, was calculated.

Table 1 Relative ^{1}H-NMR chemical shifts, δ(DMSO-A), measured at 298 K.

mol. % of DMSO	*δ(DMSO-A) [Hz]*	*mol. % of DMSO*	*δ(DMSO-A) [Hz]*
1.11	52.5	50.92	58.5
5.23	53.5	52.91	57.0
10.33	54.5	55.90	55.5
15.48	55.0	60.88	53.5
20.60	55.5	65.86	51.0
25.71	56.0	70.77	49.0
30.88	56.5	75.74	48.0
35.84	56.5	80.58	47.0
40.88	57.0	90.33	46.0
45.91	58.0	99.28	44.5

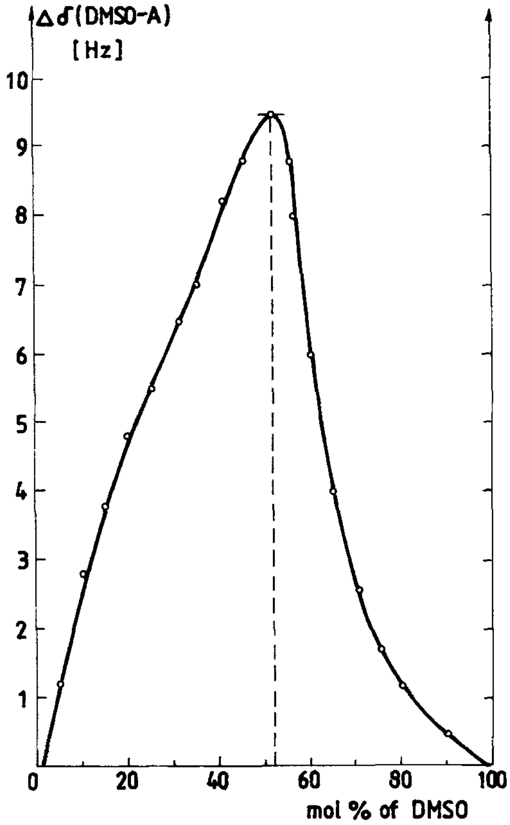


Figure 1 Changes in the functions Δδ(DMSO-A) = *f*(mol. %) for the liquid dimethylsulfoxide-acetone mixtures, at 298 K.

In agreement with the results of Räetzsch's[19] the composition where this parameter is displaying a maximum points the strongest intermolecular interactions between components are displayed. In the previous papers[16-18] we have shown that there is fairly good agreement between conclusions drawn from the behaviour of the spectral parameter Δδ, and for the α_{12} property. The changes of α_{12} as a function of the mixture compositions are visualised in Figure 2.

As can be seen in Figure 2, the values of α_{12} reach their maximum at the composition having ca. 50 mol.% of DMSO, which confirms the aforementioned conclusion drawn from ^{1}H-NMR spectral data on a possibility of formation of the stable "complex" (sub-unit) of the DMSO·A type in the studied mixtures.

In addition, the analysis of changes in the values of temperature coefficient of ε_{12} (see Fig. 2) shows that low additions of DMSO to A as well as of A to DMSO improve the order in the structure of both liquid solvents (increase in values of α_{12} in both cases). Previously[16], we have given the literature review of different methods used by several authors to interpret maxima at the functions of deviations from "ideality" of different physicochemical properties characterizing the given binary

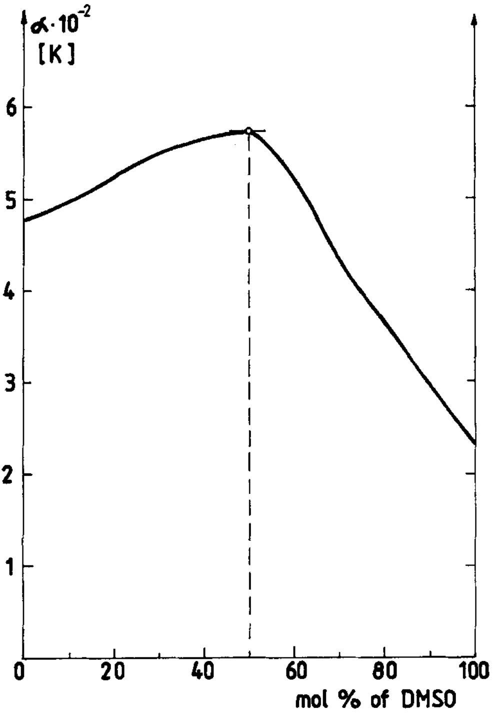


Figure 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid dimethylsulfoxide-acetone mixtures, at 298.15 K.

liquid mixtures. In the present work, using newly measured values of viscosities, surface tensions and literature values of densities[14] and dielectric permittivities[14] in the whole range of compositions of the DMSO-A mixtures (see Table 2), we have calculated deviations from "ideality" of densities $\Delta(d_{12})^{(x)}_{\mathrm{ideal}}$, viscosity $\Delta(\eta_{12})^{(x)}_{\mathrm{ideal}}$, dielectric permittivities $\Delta(\varepsilon_{12})^{(x)}_{\mathrm{ideal}}$, molar volumes $\Delta(V_{12})^{(x)}_{\mathrm{ideal}}$ and surface tensions $\Delta(\gamma_{12})^{(x)}_{\mathrm{ideal}}$; where x stands for the mole fractions.

The above mentioned values were calculated at 298.15 K using the equations given below:

$$\Delta(d_{12})^{(x)}_{\mathrm{ideal}} \cong \Delta(d_{12})^{(x)}_{\mathrm{add}} = d_{12} - \frac{x_1 \cdot M_1 + x_2 \cdot M_2}{x_1 \cdot \frac{M_1}{d_1} + x_2 \cdot \frac{M_2}{d_2}}$$

where: M – molecular weight

$$\Delta(\eta_{12})^{(x)}_{\mathrm{ideal}} = \Delta(\eta_{12})^{(x)}_{\mathrm{add}} = \eta_{12} - (\eta_1)^{x_1} \cdot (\eta_2)^{x_2}$$

$$\Delta(\varepsilon_{12})^{(x)}_{\mathrm{ideal}} \cong \Delta(\varepsilon_{12})^{(x)}_{\mathrm{add}} = \varepsilon_{12} - (x_1 \cdot \varepsilon_1 + x_2 \cdot \varepsilon_2)$$

$$\Delta(V_{12})^{(x)}_{\mathrm{ideal}} = \Delta(V_{12})^{(x)}_{\mathrm{add}} = V_{12} - (x_1 \cdot V_1 + x_2 \cdot V_2)$$

Table 2 Viscosities (η_{12}), surface tensions (γ_{12}) and the values of deviations from "ideality" of viscosity, surface tension, density, dielectric permittivity and molar volume as a function of concentration for the liquid DMSO-A mixtures, at 298.15 K.

mol.% of DMSO	η_{12} [cP]	$\gamma_{12}\cdot 10^{-3}$ [$N\cdot m^{-1}$]	$\Delta(\eta_{12})^{(x)}_{\text{ideal}}$ [cP]	$\Delta(\gamma_{12})^{(x)}_{\text{ideal}}$ [$N\cdot m^{-1}$]	mol.% of DMSO	$\Delta(d_{12})^{(x)}_{\text{ideal}}$ [$g\cdot cm^{-1}$]	$\Delta(\varepsilon_{12})^{(x)}_{\text{ideal}}$	$\Delta(V_{12})^{(x)}_{\text{ideal}}$ [cm^3 mol^{-1}]
0.00	0.3052	22.74	0.0000	0.00	0.00	0.0000	0.00	0.00
10.33	0.3765	23.95	0.0058	−0.25	10.25	0.0026	0.06	−0.24
20.68	0.4580	25.27	0.0088	−0.60	20.99	0.0046	0.21	−0.40
30.80	0.5555	26.64	0.0106	−1.01	30.93	0.0059	0.40	−0.49
35.84	0.6118	27.35	0.0127	−1.25	44.37	0.0066	0.60	−0.52
40.88	0.6731	27.96	0.0144	−1.51	51.22	0.0074	0.75	−0.57
45.91	0.7406	28.70	0.0165	−1.77	61.12	0.0068	0.73	−0.50
50.92	0.8140	29.52	0.0183	−1.88	70.71	0.0059	0.66	−0.42
55.91	0.8914	30.60	0.0175	−1.81	80.69	0.0053	0.54	−0.37
60.88	0.9754	31.77	0.0158	−1.71	90.37	0.0028	0.34	−0.19
70.77	1.1678	34.33	0.0119	−1.42	100.00	0.0000	0.00	0.00
80.58	1.4694	36.96	0.0791	−1.04				
90.33	1.7206	39.74	0.0504	−0.59				
100.00	2.0037	42.98	0.0000	0.00				

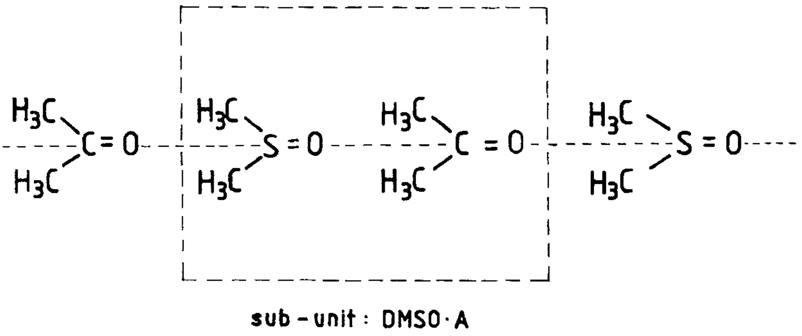


Figure 3

where:

$$V = \frac{M}{d}$$

$$\Delta(\gamma_{12})^{(x)}_{\text{ideal}} \cong \Delta(\gamma_{12})^{(x)}_{\text{add}} = \gamma_{12} - (\gamma_1)^{x_1} \cdot (\gamma_2)^{x_2}.$$

The values calculated from above equations versus the composition of DMSO-A mixtures (at 298.15 K) are shown in Table 2.

All the functions attain the highest values at the composition having ca. 50 mol.% of DMSO. Thus, this particular composition would correspond to the most viscous and dense system. This effect can be accounted for by the strongest intermolecular interactions between DMSO and A molecules, which consequently leads to the formation of stable intermolecular "complex" (sub-unit) of the DMSO·A type. These results confirm the conclusions drawn from the spectral measurements and the changes in the temperature coefficient of dielectric permittivity.

Therefore, due to all aforementioned literature data, concerning the structure of liquid DMSO and A, and the present studies, the structure of the mentioned above "complex" (sub-unit) of the DMSO·A type can be suggested as given on Figure 3.

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