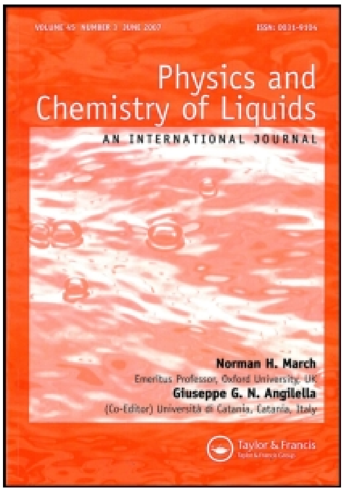

**Physics and Chemistry of Liquids**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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**To cite this Article** Kinart, Cezary M. , Kinart, Wojciech J. and Bald, Adam(1999) 'The Measurements of the Surface Tension of Mixtures of Dimethyl Sulfoxide with Methyl, Ethyl and Propyl Alcohols', Physics and Chemistry of Liquids, 37: 4, 317 — 321

**To link to this Article: DOI:** 10.1080/00319109908031436

**URL:** http://dx.doi.org/10.1080/00319109908031436

*Phys. Chem. Liq.*, 1999, Vol. 37, pp. 317–321
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Printed in Malaysia.

# THE MEASUREMENTS OF THE SURFACE TENSION OF MIXTURES OF DIMETHYL SULFOXIDE WITH METHYL, ETHYL AND PROPYL ALCOHOLS

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*(Received 15 September 1997)*

The surface tension of liquid binary mixtures of dimethyl sulfoxide (DMSO) with methyl (MeOH), ethyl (EtOH) and propyl (PrOH) alcohols was measured at 293.15 K, 298.15 K, 303.15 K, 308.15 K and 313.15 K. From all these data the temperature coefficients of surface tension, $k = -(d\gamma_{12}/dT)$, were calculated.

*Keywords:* Surface tension; intermolecular interactions; binary liquid mixtures

## INTRODUCTION

This work is a continuation of series of studies on the analysis of intermolecular interactions and internal structures of some liquid binary mixtues of dimethyl sulfoxide with aliphatic alcohols based on the correlation of $^1$H-NMR spectral data with macroscopic properties of these mixtures as viscosity, density, dielectric permittivity, molar volume, apparent molar volume and their deviations from ideality as a

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function of the mixture composition [1, 2]. Presently, in purpose to gain further information regarding intermolecular interactions in liquid mixtures of DMSO with methyl, ethyl and *n*-propyl alcohols, we have applied measurements of temperature dependances of the surface tension ($\gamma_{12}$) of these systems. The analysis of changes of the surface tension and its temperature coefficients, denoted $k$, (or more precisely its negative value, *viz.* $k = -(d\gamma_{12}/dT)$, within the whole composition range enables the assessment of intermolecular interactions between components of binary mixtures the more so as it has been shown by Landau [3] and Toriank [4] that the fluctuations of the temperature coefficient of the surface tension should be interpreted as changes of entropies of aggregates forming the free surface of the studied mixture.

## EXPERIMENTAL

For the measurements of surface tensions chemical pure DMSO (Fluka), methanol (Fluka), ethanol (Fluka) and propanol (Fluka) were used. They were dried and purified according to known procedures [5]. The surface tensions were measured with an accuracy ± 0.1%, using a stalagmometer. All the solutions were prepared by weight.

## RESULTS AND DISCUSSION

The values of the temperature coefficients $k$, *viz.* $k = -d\gamma/dT$, have been determined within the whole composition range at 298.15 K (Fig. 1) using measured temperature dependances of the surface tension for mixtures of dimethyl sulfoxide with methyl, ethyl and *n*-propyl alcohols (see Tab. I).

The gradual addition of all three studied alcohols to DMSO results in a sharp decrease of the value of $k$ coefficient (see Fig. 1) which indicates a distinct increase of the entropy of aggregates forming a free surface of studied mixtures.

It is an evidence of the ordering nature of studied alcohols at the internal structure of liquid DMSO. The analogous conclusions can be drawn from the analysis of changes of this function in the opposite case when DMSO is added to the studied alcohols. However, some

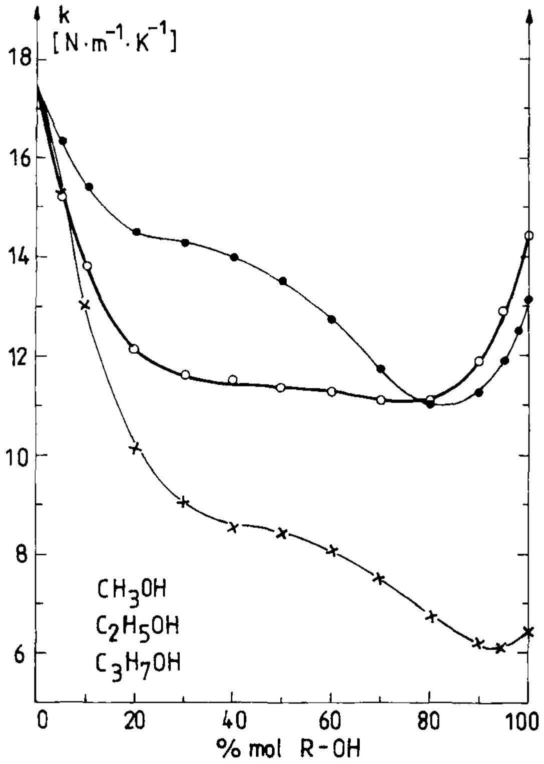

FIGURE 1 Changes in the temperature coefficient of surface tension ($k$) as a function of composition for the liquid DMSO-methanol, DMSO-ethanol and DMSO-*n*-propanol mixtures, at 298.15 K.

differentiation of effects upon the type of alcohol is observed. The addition of DMSO to *n*-propyl alcohol results in the smallest changes of the temperature coefficient $k$. Therefore, it is necessary to assume that one deals here with the weakest ordering effect influenced by molecules of DMSO at the structure of this alcohol.

A distinct minimum of the negative value of entropy within the composition range corresponding to ca. 80 mol. % of alcohol was observed for mixtures of dimethyl sulfoxide with methyl and ethyl alcohols.

Whereas, mixtures of *n*-propyl alcohol exhibit analogous minimum in considerably less pronounced way. It appears within the composition range corresponding to ca. 95 mol. % of *n*-propanol.

TABLE I Surface tensions ($\gamma_{12}$) for binary liquid mixtures DMSO-methanol, DMSO-ethanol and DMSO-*n*-propanol

| *mol. %* *of alcohol* | *DMSO-methanol* $\gamma_{12} \cdot 10^3$ $[N \cdot m^{-1}]$ | | | | | *DMSO-ethanol* $\gamma_{12} \cdot 10^3$ $[N \cdot m^{-1}]$ | | | | | *DMSO-n-propanol* $\gamma_{12} \cdot 10^3$ $[N \cdot m^{-1}]$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 293.15 *K* | 298.15 *K* | 303.15 *K* | 308.15 *K* | 313.15 *K* | 293.15 *K* | 298.15 *K* | 303.15 *K* | 308.15 *K* | 313.15 *K* | 293.15 *K* | 298.15 *K* | 303.15 *K* | 308.15 *K* |
| 0 | 43.36 | 42.70 | 42.05 | 40.95 | 39.83 | 43.36 | 42.70 | 42.05 | 40.95 | 39.83 | 43.36 | 42.70 | 42.05 | 40.95 |
| 2 | 42.93 | 42.30 | 41.71 | 40.60 | 39.52 | 42.51 | 41.93 | 41.29 | 40.29 | 39.21 | 42.48 | 41.98 | 41.32 | 40.23 |
| 5 | 42.35 | 41.77 | 41.20 | 40.15 | 39.08 | 41.32 | 40.83 | 40.19 | 39.28 | 38.27 | 41.29 | 40.82 | 40.26 | 39.31 |
| 10 | 41.42 | 40.89 | 40.37 | 39.35 | 38.32 | 39.49 | 39.10 | 38.47 | 37.67 | 36.75 | 39.49 | 39.12 | 38.60 | 37.82 |
| 15 | 40.50 | 40.00 | 39.48 | 38.52 | 37.51 | 37.85 | 37.50 | 36.89 | 36.17 | 35.31 | 37.89 | 37.57 | 37.10 | 36.43 |
| 20 | 39.58 | 39.10 | 38.59 | 37.66 | 36.66 | 36.38 | 36.02 | 35.43 | 34.77 | 33.96 | 36.46 | 36.15 | 35.71 | 35.13 |
| 25 | 38.66 | 38.19 | 37.68 | 36.76 | 35.77 | 35.04 | 34.66 | 34.09 | 33.47 | 32.68 | 35.18 | 34.85 | 34.44 | 33.91 |
| 30 | 37.72 | 37.25 | 36.74 | 35.83 | 34.85 | 33.81 | 33.39 | 32.84 | 32.25 | 31.48 | 34.01 | 33.66 | 33.28 | 32.78 |
| 35 | 36.76 | 36.28 | 35.78 | 34.87 | 33.91 | 32.69 | 32.22 | 31.69 | 31.11 | 30.35 | 32.95 | 32.56 | 32.21 | 31.71 |
| 40 | 35.76 | 35.28 | 34.79 | 33.88 | 32.97 | 31.64 | 31.13 | 30.61 | 30.06 | 29.30 | 31.96 | 31.55 | 31.21 | 30.72 |
| 45 | 34.73 | 34.26 | 33.76 | 32.87 | 31.96 | 30.66 | 30.12 | 29.61 | 29.07 | 28.31 | 31.04 | 30.61 | 30.28 | 29.79 |
| 50 | 33.67 | 33.21 | 32.72 | 31.84 | 30.97 | 29.73 | 29.17 | 28.67 | 28.14 | 27.38 | 30.17 | 29.74 | 29.42 | 28.92 |
| 55 | 32.58 | 32.12 | 31.64 | 30.79 | 29.95 | 28.84 | 28.29 | 27.79 | 27.22 | 26.51 | 29.34 | 28.92 | 28.61 | 28.11 |
| 60 | 31.46 | 31.02 | 30.55 | 29.72 | 28.93 | 28.00 | 27.45 | 26.96 | 26.44 | 25.68 | 28.54 | 28.14 | 27.84 | 27.36 |
| 65 | 30.32 | 29.90 | 29.44 | 28.64 | 27.89 | 27.18 | 26.66 | 26.16 | 25.60 | 24.83 | 27.77 | 27.40 | 27.11 | 26.64 |
| 70 | 29.16 | 28.76 | 28.32 | 27.55 | 26.85 | 26.39 | 25.91 | 25.40 | 24.89 | 24.12 | 27.04 | 26.71 | 26.42 | 25.97 |
| 75 | 28.00 | 27.62 | 27.19 | 26.45 | 25.75 | 25.62 | 25.18 | 24.66 | 24.15 | 23.38 | 26.32 | 26.04 | 25.75 | 25.34 |
| 80 | 26.85 | 26.48 | 26.06 | 25.35 | 24.66 | 24.89 | 24.44 | 23.95 | 23.41 | 22.64 | 25.64 | 25.40 | 25.11 | 24.73 |
| 85 | 25.72 | 25.36 | 24.95 | 24.24 | 23.54 | 24.19 | 23.81 | 23.26 | 22.63 | 21.89 | 24.99 | 24.79 | 24.49 | 24.14 |
| 90 | 24.63 | 24.26 | 23.85 | 23.13 | 22.39 | 23.52 | 23.14 | 22.58 | 21.93 | 21.13 | 24.40 | 24.20 | 23.90 | 23.57 |
| 95 | 23.60 | 23.20 | 22.79 | 22.03 | 21.21 | 22.91 | 22.48 | 21.90 | 21.15 | 20.33 | 23.87 | 23.63 | 23.32 | 23.01 |
| 98 | 23.02 | 22.59 | 22.17 | 21.37 | 20.48 | 22.57 | 20.09 | 21.50 | 20.67 | 19.83 | 23.57 | 23.30 | 22.98 | 22.67 |
| 100 | 22.66 | 22.20 | 21.77 | 20.94 | 19.99 | 22.35 | 21.83 | 21.23 | 20.34 | 19.48 | 23.40 | 23.09 | 22.76 | 22.45 |

We assume that both mentioned above composition ranges should be treated as regions of the most stable and ordered structures of mixed associates forming the free surface of studied liquid mixtures. The shift of the position of the minimum of the $k$ coefficient with the increase of the length of the aliphatic chain of alcohol is presumably due to the steric affects. The more complete and precise interpretation of observed effects will require further studies, e.g., measurements of heats of evaporation.

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