

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

Physicochemical Properties and Internal Structures of Dimethyl Sulfoxide-1-Propanol Liquid Mixtures

Cezary M. Kinart^a; Wojciech J. Kinart^b

^a Department of Chemical Education, University of Lodz, Pomorska 163, Poland ^b Department of Organic Chemistry, University of Lodz, Narutowicza 68, Poland

To cite this Article Kinart, Cezary M. and Kinart, Wojciech J.(1996) 'Physicochemical Properties and Internal Structures of Dimethyl Sulfoxide-1-Propanol Liquid Mixtures', *Physics and Chemistry of Liquids*, 33: 3, 151 — 158

To link to this Article: DOI: 10.1080/00319109608039816

URL: <http://dx.doi.org/10.1080/00319109608039816>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PHYSICOCHEMICAL PROPERTIES AND INTERNAL STRUCTURES OF DIMETHYL SULFOXIDE-1-PROPANOL LIQUID MIXTURES

CEZARY M. KINART^a and WOJCIECH J. KINART^b

^a*Department of Chemical Education, University of Lodz, 90–236 Lodz,
Pomorska 163, Poland;* ^b*Department of Organic Chemistry, University
of Lodz, 90–136 Lodz, Narutowicza 68, Poland*

(Received 10 June 1996)

The ¹H-NMR spectra of liquid binary mixtures of dimethyl sulfoxide (DMSO) and 1-propanol (PrOH), were recorded at 298 K over almost the whole range of the mixed solvent compositions. From these data were found the values of the spectral parameter, $\Delta\delta(\text{DMSO-PrOH})$. The densities (d_{12}) and viscosities (η_{12}) of the mixed solvent were measured at 298.15 K, as well as the relative permittivities (ϵ_{12}) at 293.15 K, 298.15 K and 303.15 K. From all these data, the molar volumes (V_{12}) and their deviations from ideality were calculated. Additionally, the temperature coefficients of relative permittivity, α_{12} , were found. These structural parameters of functions of concentration suggest the formation of stable DMSO-PrOH, DMSO-2PrOH and DMSO-3PrOH type complexes.

Keywords: ¹H-NMR spectra; physicochemical properties; binary liquid mixtures

INTRODUCTION

This paper is a continuation of series of studies on intermolecular interactions and internal structures of some liquid binary mixtures of dimethyl sulfoxide (DMSO) and different aliphatic alcohols, based on the correlation existing between the ¹H-NMR spectral results and some physicochemical intensive properties of the same binary mixtures. In the present work we have analysed the mutual intermolecular interactions in the liquid mixtures of DMSO and 1-propanol (PrOH).

Previously [1], we have analysed intermolecular interactions in the liquid binary mixtures of DMSO-methanol (MeOH) using analogous research methods. The conclusion has been drawn from obtained results that the stable intermolecular "complexes" of DMSO·MeOH and DMSO·2 MeOH types are formed in the studied system. In the present work we have attempted to find out whether the increase of the length of the aliphatic chain of alcohols influences intermolecular interactions and the internal structure of the liquid mixtures of alcohol and DMSO.

EXPERIMENTAL

For the present $^1\text{H-NMR}$ spectral studies and the measurements of relative permittivities, densities and viscosities, chemical pure DMSO (Fluka) and PrOH (Fluka) were used. They were dried and purified according to the known procedures [2]. The $^1\text{H-NMR}$ spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 ± 1 K. The proton chemical shifts of DMSO and PrOH were measured with an accuracy of ca. ± 0.2 Hz with respect to an external standard HMDS (hexamethyldisiloxane). The relative permittivity measurements were performed with an accuracy of $\pm 0.1\%$, using a bridge of the type OH-301 (made in Hungary). The viscosities were measured with an accuracy $\pm 0.1\%$, using a Höppler viscosimeter. Solvent densities were measured, using a glass Lipkin pycnometer (Carl Zeiss, Jena). The maximum error in the density measurements was $1 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}$. All the solutions were prepared by weight.

RESULTS AND DISCUSSION

Lindberg [3], Narayana *et al.* [4] and Lindberg and Pietilä [5] measured heats of mixing, density, viscosity and speed of propagation of ultrasound for the binary mixtures DMSO -1-propanol. However, they did not interpret their results in terms of stoichiometry and internal structure of intermolecular "complexes" formed by molecules of PrOH and DMSO. Also, measurements of relative permittivity, density and refractive index of the liquid mixtures of PrOH and DMSO, carried out over a wide temperature range by Himienko [6]

are only available in the monograph by Krestov *et al.* [7] in the form of numerical values collected in tables. However, these results seem to be uncertain. We found out that obtained from them values of deviations from additivity of these physicochemical properties attain surprisingly the sinusoidal course. It may be a consequence of improper drying of both solvents reflected by considerably higher values of physicochemical parameters found for pure solvents in comparison to other literature data. In this work, with the aim of analysing the intermolecular interactions between the components in the liquid DMSO-PrOH mixtures, we measured the values of chemical shift differences $\delta(\text{DMSO-PrOH})$ at 298 K, between the centre of the $^1\text{H-NMR}$ signals of the -OH group of 1-propanol and the centre of the $^1\text{H-NMR}$ signals of $-\text{CH}_3$ groups of DMSO molecules over a wide range of solvent compositions, i.e. from 5.04 to 96.52 mol.% of PrOH (see Tab. I). Subsequently, using the same method as previously [1, 7] from these new spectral data the spectral parameter $\Delta\delta(\text{DMSO-PrOH})$ has been evaluated. The values of this parameter or, more precisely, the location of its maximum values, are located at the composition with the strongest, intermolecular interactions between the components, where hydrogen bonds are involved [1, 8, 9]. The $\Delta\delta(\text{DMSO-PrOH})$ values are visualized in Figure 1 as a function of the mixture compositions.

The analysis of the data indicates the presence of a maximum $\Delta\delta(\text{DMSO-PrOH})$ at ca. 75 mol. % PrOH. Thus, at this composition

TABLE I Relative $^1\text{H-NMR}$ chemical shifts, $\delta(\text{DMSO-PrOH})$, measured at 298 K

mol.% of PrOH	$\delta(\text{DMSO-PrOH})$ [Hz]
5.04	52.50
10.23	55.25
15.11	58.00
21.04	61.25
30.52	66.25
37.53	70.00
45.75	74.50
50.04	77.25
56.25	81.50
65.51	88.25
73.94	95.00
81.49	95.50
88.76	96.00
96.52	96.50

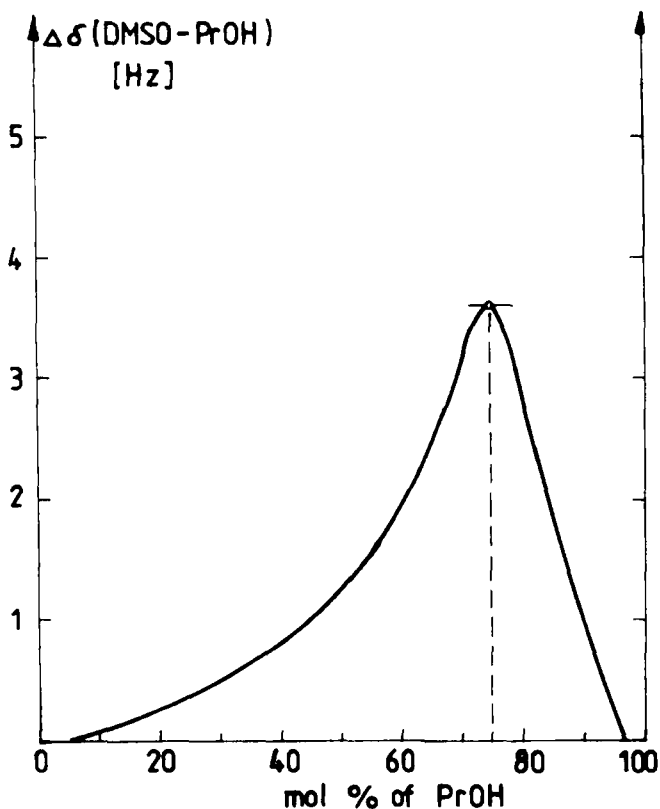


FIGURE 1 Changes in $\Delta\delta$ (DMSO-PrOH) for liquid DMSO-PrOH mixtures, at 298 K.

the strongest interactions between components involving hydrogen bonds, are displayed, and that the most stable "complex" is DMSO · 3 PrOH.

From the relative permittivity data (see Tab. II), the temperature coefficients of the relative permittivity, denoted α_{12} , viz. $\alpha_{12} = (1/\epsilon_{12}) \cdot [d\epsilon_{12}/d(1/T)]$, were calculated. The composition range of binary liquid mixtures within which α_{12} attains its highest value, should be interpreted (as shown in Rätzsch *et al.*'s thermodynamic consideration [10]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. Conclusions drawn from the analysis of changes in $\Delta\delta$ and α_{12} are fully consistent [1, 8, 9]. Changes in α_{12} vs. composition of liquid DMSO-PrOH mixtures are shown in Figure 2.

TABLE II Dielectric permittivities for binary liquid mixtures, DMSO-PrOH, measured at 293.15 K, 298.15 K, 303.15 K and 308.15 K

mol.% of PrOH	ϵ_{12}			η_{12}	d_{12}
	293.15 K	298.15 K	303.15 K	[cP] 298.15 K	[g·cm ⁻³] 298.15 K
0.00	46.61	45.91	45.16	2.0100	1.0958
5.04	46.24	45.41	44.64	1.8203	1.0803
10.23	45.68	44.89	43.98	1.7729	1.0656
15.11	45.08	44.28	43.38	1.7391	1.0515
21.04	44.34	43.48	42.52	1.6932	1.0348
30.52	43.09	42.10	41.13	1.6110	1.0174
37.53	42.03	41.06	40.09	1.5525	0.9985
45.75	40.67	39.71	38.70	1.5042	0.9736
50.04	39.81	38.95	37.91	1.4836	0.9615
56.25	38.39	37.28	36.20	1.4621	0.9427
65.51	35.29	34.06	32.87	1.4490	0.9154
73.94	31.42	30.02	29.11	1.4581	0.8764
81.49	27.81	26.77	25.83	1.5253	0.8651
88.76	24.72	24.04	23.01	1.5874	0.8411
96.52	21.95	21.32	20.32	1.6465	0.8141
100.00	20.74	20.13	19.35	2.0040	0.7995

The maximum of α_{12} is found at ca. 75 mol.% of PrOH. This confirms the conclusion from ¹H-NMR spectral data concerning the formation of a "complex" of DMSO·3PrOH. Further interesting results can be obtained by detailed analysis of the function $\alpha_{12} = f$ (mol.% of PrOH). This indicates that increase addition of DMSO to PrOH up to ca. 10 mol.% of DMSO, where a minimum is reached, causes a rapid drop in α_{12} . Further addition of DMSO to the mixtures causes an increase in α_{12} , which results in a maximum at ca. 75 mol.% of PrOH. Therefore, it is possible to assume that the internal structure of PrOH is disrupted by the addition of small amounts of DMSO (up to 10 mol. % of DMSO), whereas further addition of DMSO, up to ca. 75 mol.% of PrOH, stabilizes the internal structure of the mixed solvent increasingly by hydrogen bonding between the component molecules. The same analysis made for the dimethyl sulfoxide-rich composition region shows a continuous increase in α_{12} down to ca. 75 mol.% of PrOH. Therefore, it seems that molecules of PrOH, within the composition range 0–75 mol.% of PrOH, act as "structure-makers" with respect to molecules of DMSO in the neat solvent.

Additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of deviations from "ideal-

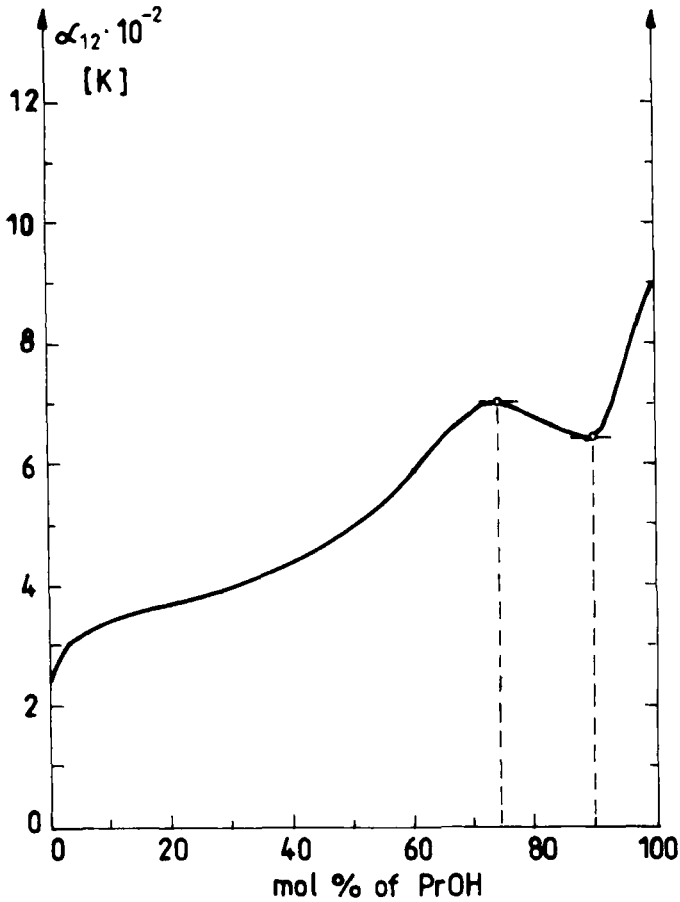


FIGURE 2 Changes in the temperature of relative permittivity as a function of composition for the liquid DMSO-PrOH mixtures, at 298.15 K.

ity” of basic physicochemical properties of these mixtures, i.e. density (d_{12}), viscosity (η_{12}), relative permittivity (ϵ_{12}) and molar volumes (V_{12}). A thorough review of the literature justifies the correctness of using these parameters in the analysis of intermolecular interactions [8]. In this study, using experimental values of relative permittivity, viscosity and density at 298.15 K (see Tab. II), the deviations from “ideality” of the functions involved have been calculated from the

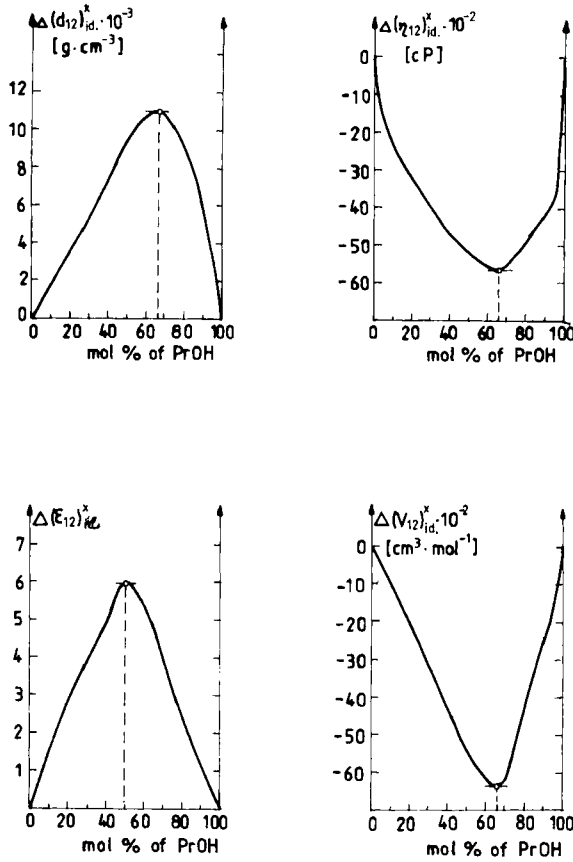


FIGURE 3 The course of changes of deviations from "ideality" of physicochemical properties of DMSO-PrOH mixtures as a function of composition for the liquid DMSO-PrOH mixtures, at 298.15 K.

following equations:

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

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

$$\Delta(\epsilon_{12})_{\text{ideal}}^{(x)} \cong \Delta(\epsilon_{12})_{\text{add}}^{(x)} = \epsilon_{12} - (x_1 \cdot \epsilon_1 + x_2 \cdot \epsilon_2)$$

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

Values calculated from the above equations over a range of DMSO-PrOH mixtures are shown in Figure 3.

Deviations from "ideality" in densities, viscosities and molar volumes attain their highest values at ca. 66 mol.% PrOH. Thus, this particular composition would correspond to the most viscous and dense system. This effect can be accounted for by the increase in the number of hydrogen bonds formed between PrOH and DMSO molecules [11, 12], which leads to the formation of stable intermolecular "complexes" of the type DMSO·2PrOH. The changes in deviations from "ideality" of relative permittivity attain their extreme values at ca. 50 mol.% of PrOH, which most likely points to the formation of DMSO·PrOH "complexes" in liquid mixtures of PrOH and DMSO.

It can be concluded from the given in the present work results and comparison of them with analogous data for the mixture of DMSO-methanol (see Ref. 1) that the increase of the length of the aliphatic chain in the alcohol molecule has an important influence on its intermolecular interactions. Results given in the work of Lindberg [5] based on the comparison of changes heats of mixing drawn as the function of composition for binary systems containing DMSO and methanol, ethanol or 1-propanol fully confirm our conclusions.

References

- [1] Romanowski, S. J., Kinart, C. M. and Kinart, W. J. (1995). *J. Chem. Soc. Faraday Trans.*, **91**(1), 65.
- [2] Roddick, J. A., Bunger, W. B. and Sakano, T. K. (1988). "Organic Solvents. Physical Properties and Method of Purification", *Ed. J. Wiley and Sons*, N.Y.
- [3] Lindberg, J. J. (1962), *Suomen Kemi*, **71**(3), 77.
- [4] Narayana, G. S., Dharmarjn. G. and Raman, G. K. (1981). *Acoust. Lett.*, **4**(10), 210.
- [5] Lindberg, J. J. and Pietilä, I. (1962). *Suomen Kemi*, **B30**, 35.
- [6] Litovskaya, W. W. and Himienko, O. N. (1984), *Sistiema DMSO-PrOH*, Harkov Dep. VIINTI, p. 25.
- [7] Krestov, G. A., Afanasiev, W. N. and Jefremova, L. S. (1988). *Fizikihimitscheskiye Svoistva Binarnykh Rostvoriteli*, *Chemia Leningrad*, p. 149.
- [8] Kinart, C. M., Kinart, W. J. and Skulski, L. (1986), *Pol. J. Chem.*, **60**, 879.
- [9] Kinart, C. M. (1993), *Phys. Chem. Liq.*, **26**, 209
- [10] Rätzsch, M. T., Kehlen, H. and Rosner, H. (1974). *Z. Phys. Chem.*, (Leipzig), **255**, 115.
- [11] Anosov, V. Ya., Ozerova, M. J. and Fialkova, Yu. Ya. (1976). *Osnovy Fizikohimicheskovo Analiza*, Nauka, Moscow and references therein.
- [12] Seip, H. M. (1969), *Acta Chim. Scand.*, **23**, 2741 and references therein.