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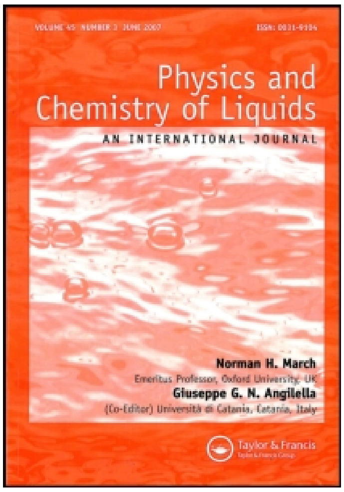

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Study on the Internal Structures of Liquid N,N-dimethylformamidepropane-1,2-diol Mixtures

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STUDY ON THE INTERNAL STRUCTURES OF LIQUID N,N-DIMETHYLFORMAMIDE-PROPANE-1,2-DIOL MIXTURES

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The ^{1}H-NMR spectra of the liquid binary mixtures, N,N-dimethylformamide (DMF)-propane-1,2-diol (PD-1,2), were recorded at 298 K within nearly the whole range of the mixed solvent compositions. From these data the values of the spectral parameter, $\Delta\delta$(DMF-PD-1,2) were found. The densities (d_{12}) and viscosities (η_{12}) of the mixed solvents were measured at 298.15 K, as well as the dielectric permittivities (ε_{12}) at 288.15 K, 298.15 K and 303.15 K. From all these new parent data, the values of molar volumes (V_{12}), kinematic viscosities (η_{12}/d_{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 "complexes" (sub-units) of the DMF·2 PD-1,2 and 3 DMF·2 PD-1,2 types.

KEY WORDS: ^{1}H-NMR spectra, intermoleular interactions.

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INTRODUCTION

This paper is a continuation of the series of studies on the internal structures of some liquid binary mixtures, in which N,N-dimethylformamide or aliphatic alcohol is one of the two constituents, 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[1–3]. Now the intermolecular interactions in the mixtures of N,N-dimethylformamide (DMF) and propane-1,2-diol (PD-1,2) will be analysed, with using the some comparative approach as previously[1–3].

The propanediols have long been known as substances showing clear evidence of intermolecular hydrogen bonds. When dissolved in inert solvents at low, but not too low concentrations, they yield three distinct bands in their infrared spectra, which are unambiguously assigned to the stretching vibration of the free O–H group, the intramolecularly hydrogen bonded O–H and the intermolecularly hydrogen bonded O–H. For a comprehensive review of the spectral and conformational criteria for the formation of intermolecular H-bonds the reader is referred to Chapter 5 of The Hydrogen Bond by Pimentel and McClellen[4]. Of special interest to these studies is the series of papers on frequency shifts, energies and geometries of diols by Kuhn[5–10] as well as the paper of Buc[11]. Using molecular models, these authors have sought for general relations between internuclear distances, bond angles, frequency shifts and energies in systems which engage in intermolecular hydrogen bonding.

The internal structures of liquid N,N-dimethylformamide have already been reviewed in my previous papers[1,2]. Taking into consideration all aforementioned literature data regarding the structure of liquid DMF and PD-1,2 it seemed quite interesting to extend this studies onto the DMF-PD-1,2 liquid mixtures focusing onto the intermolecular interactions of its components.

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and all the physicochemical measurements, chemical pure N,N-dimethylformamide (Fluka) and propane-1,2-diol (Polskie Odczynniki Chemiczne-Gliwice) were used. N,N-dimethylformamide and propane-1,2-diol were dried and purified according to the known procedure[12].

^{1}H-NMR spectra were recorded on the Tesla spectrometer of the type BS 467 (60 MHz), at 298 ± 1 K. The chemical shift values for proton signals of N,N-dimethylformamide and propane-1,2-diol were measured with an accuracy of about ± 0.2 Hz in respect to an external standard HMDS (hexamethyldisiloxane). The dielectric permittivity measurements were performed with an accuracy of $\pm 0.1\%$, using a bridge of the type OH-301 (made in Hungary), at 288.15 K, 298.15 K and 303.15 K. The viscosities were measured with an accuracy $\pm 0.1\%$, at 298.15 K, using the Höppler viscometer. Solvent densities were measured, at 298.15 K, using a glass pycnometer of the Lipkin type. The maximum error in the density measurements was $1 \cdot 10^{-4}\,\mathrm{g\,cm^{-3}}$. All the binary solutions made of DMF and PD-1,2 were prepared by weight.

RESULTS AND DISCUSSION

There is no literature data concerning the analysis of intermolecular interactions in liquid mixtures of N,N-dimethylformamide with propane-1,2-diol. In this work, with the aim of analysing the intermolecular interactions between the components in the liquid binary mixtures DMF-PD-1,2, I have measured the values of chemical shift differences δ(DMF-PD-1,2)(in Hz) at 298 K, between the center of the ^{1}H-NMR signals of the formyl proton of N,N-dimethylformamide molecules and the center of the ^{1}H-NMR signals of –OH groups of propane-1,2-diol molecules over a wide range of solvent composition, i.e. from 9.54 mol. % to 88.77 mol. % of DMF. Subsequently, using the same method as previously[1-3], from these new spectral data the spectral parameter $\Delta\delta$(DMF-PD-1,2) have been found. The values of this parameter, or more precisely, the location of its maximum values as has been shown in my previous papers[1-3], are located at the composition with the strongest intermolecular interactions between the components whereby hydrogen bond are involved. The δ(DMF-PD-1,2) values are shown in Table 1, whereas the $\Delta\delta$(DMF-PD-1,2) 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 of $\Delta\delta$(DMF-PD-1,2) at ca. 33 mol.% of DMF. Thus, the conclusion would be drawn that at this composition the strongest interactions between components with involving hydrogen bonds, are displayed, and that the most stable "complex" (sub-unit) is of the DMF·2 PD-1,2 type.

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Table 1 Relative ^{1}H-NMR chemical shifts, δ(DMF-PD-1,2), measured at 298 K.

mol. % of DMF	*δ(DMF-PD-1,2)* [Hz]
9.54	174.5
19.31	175.5
28.99	177.5
33.92	178.0
35.87	179.5
38.89	181.5
48.72	187.5
58.78	195.0
68.93	201.5
78.82	207.0
88.70	212.5

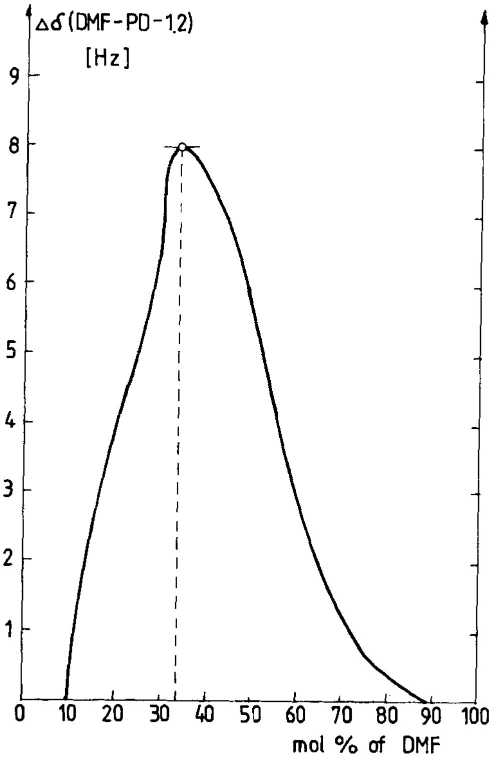

Figure 1 Changes in the function $\Delta\delta$(DMF-PD-1,2) = f(mol.%) for the liquid N,N-dimethylformamide-propane-1,2-diol mixtures, at 298 K.

In addition to spectral examinations, the dielectric permittivity (ε_{12}) of the liquid DMF-PD-1,2 mixtures under investigation was measured within full composition range at 288.15 K, 298.15 K and 303.15 K (see Table 2). This made it possible for me to determine the temperature coefficient of dielectric permittivity α_{12}, viz. $\alpha_{12} = (1/\varepsilon_{12})\cdot$

Table 2 Dielectric permittivities for binary liquid mixtures, DMF-PD-1,2, measured at 288.15 K, 298.15 K and 303.15 K.

mol. % of DMF	ε_{12}		
	288.15 K	*298.15* K	*303.15* K
0.00	32.45	31.36	30.71
9.54	33.98	32.36	31.08
19.31	35.10	33.28	31.83
28.99	36.03	34.09	32.53
38.89	36.89	34.87	33.47
48.72	37.46	35.62	34.31
58.78	37.81	36.37	35.11
68.93	38.05	36.69	35.66
78.82	38.17	36.82	36.02
88.70	38.22	36.95	36.31
100.00	38.31	37.15	36.65

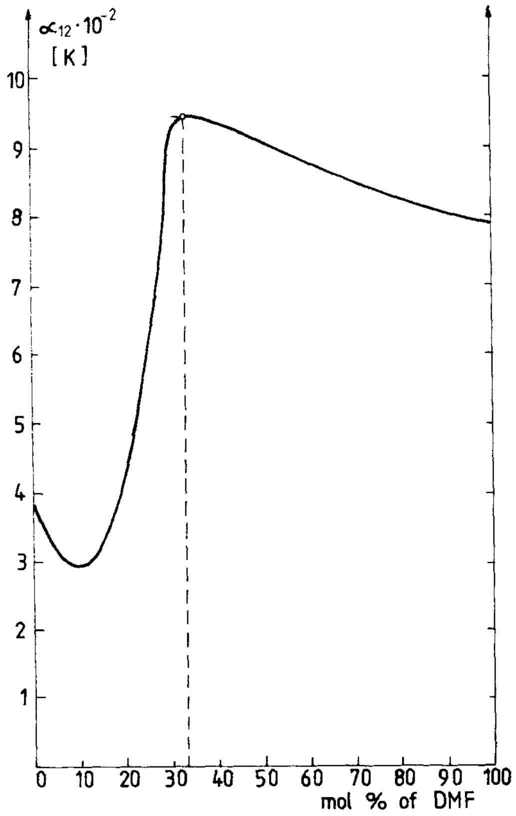

Figure 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid N,N-dimethylformamide-propane-1,2-diol mixtures, at 298.15 K.

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$[d\varepsilon_{12}/d(1/T)]$. The composition range of liquid binary mixtures, within which coefficient α_{12} attains the highest value, should be interpreted (as shown in Räetzsch's thermodynamic considerations[13]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. It has been shown in may previous papers[1-3] that there is a full consistence of conclusions from the analysis of changes in spectral parameter $\Delta\delta$ and coefficient α_{12}. Changes in the α_{12} value versus composition of liquid DMF-PD-1,2 mixtures are shown in Figure 2.

As can be seen from Figure 2, the temperature coefficient of dielectric permittivity attains the highest value within the composition range corresponding to about 33 mol.% of DMF. This would correspond to the formation of a stable intermolecular "complex" (sub-unit) with a composition of DMF·2 PD-1,2, which has been confirmed by spectral ^{1}H-NMR measurements. The consideration of the dependence of temperature coefficient α_{12} versus the composition of DMF-PD-1,2 mixtures leads at the same time to conclusions about the effect of PD-1,2 additives on the structure of pure DMF and vice versa. The α_{12} values are increased when PD-1,2 is added to DMF, which points to an increased degree of the N,N-dimethylformamide structure. It follows from the findings of Rabinowitz and Pines[14,15] as well as Razay[16] and Shakhparonov[17] that chain dimers can be formed in liquid DMF solutions. These authors assumed that the dimers can originate from the formation of weak hydrogen bonds between oxygen of the carbonyl group in one DMF molecule and hydrogen of the methyl group in the second molecule, as well as between oxygen atom of one and formyl hydrogen of the second molecule. They also suggest the possibility of DMF dimers formation by electrostatic dipole–dipole interaction between the oxygen charge in one DMF molecule and nitrogen charge in the other. Probably the addition of small quantities of PD-1,2 to DMF causes the alcohol molecules to become an additional bonding element in the loose N,N-dimethylformamide structure. When small quantities of DMF are added to PD-1,2, coefficient α_{12} is rapidly decreased (see Figure 2), thus pointing to a disturbed structure of the propane-1,2-diol.

As has been shown in my previous papers[1-3], additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of deviations from "idelaity" of different physicochemical properties characterizing the given binary liquid system, i.e density (d_{12}), viscosity (η_{12}), dielectric permittivity (ε_{12})

Table 3 Densities (d_{12}) and viscosities (η_{12}) for binary liquid mixtures, DMF-PD-1,2, measured at 298.15 K.

mol. % of DMF	d_{12}	η_{12}
0.00	1.0329	41.7600
9.54	1.0255	31.7800
19.31	1.0183	22.9500
28.99	1.0098	17.2200
38.89	1.0007	11.8020
48.72	0.9909	7.9470
58.78	0.9817	5.3414
68.93	0.9724	3.4461
78.82	0.9633	2.3432
88.70	0.9542	1.3680
100.00	0.9438	0.8024

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and calculated from these data molar volumes (V_{12}) and kinematic viscosities (η_{12}/d_{12}). In this study, using experimental values of dielectric permittivity (see Table 2) and viscosity and density (see Table 3) the deviations from "ideality" of the functions involved have been calculated, at 298.15 K from the following relations:

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

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

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

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

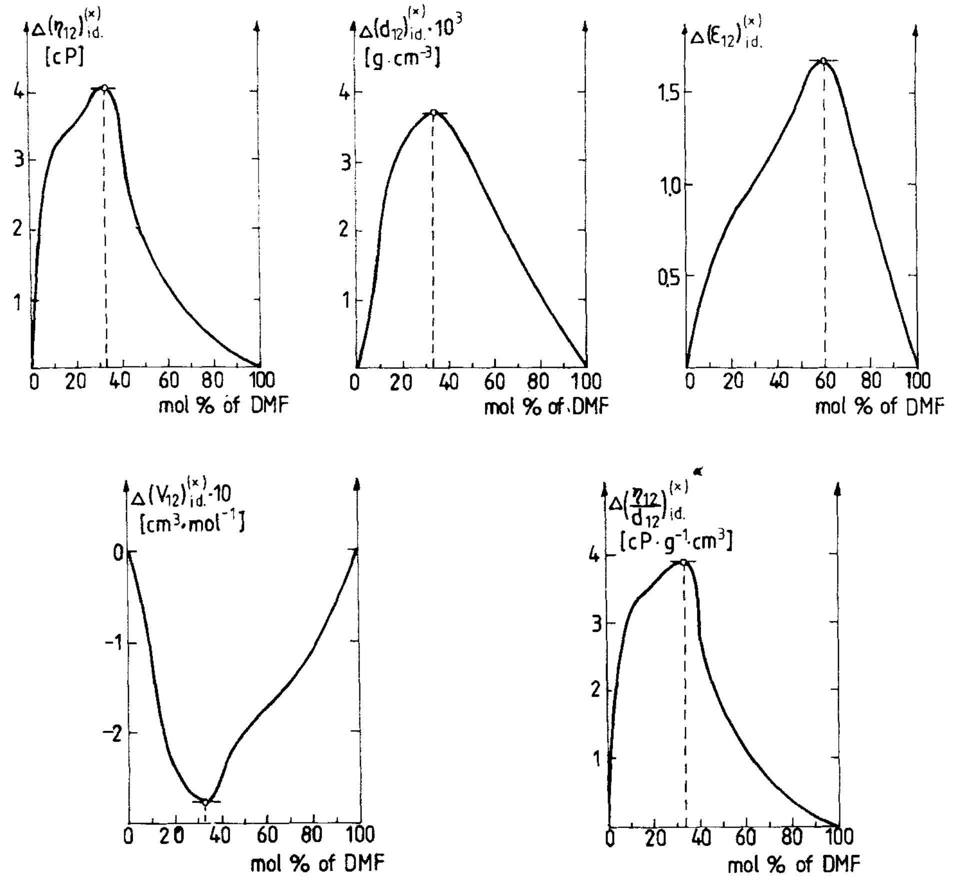

Figure 3 The course of changes of deviations from "ideality" of density, viscosity, dielectric permittivity, molar volume and kinematic viscosity as a function of composition for the liquid N,N-dimethylformamide-propane-1,2-diol mixtures, at 298.15 K.

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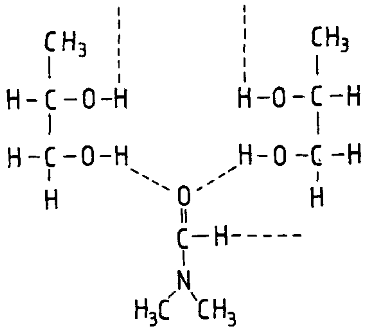
where $V=\frac{M}{d}$

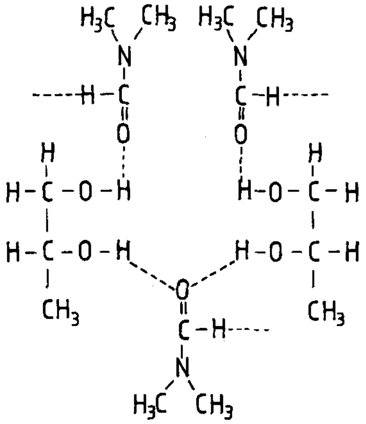
$$\Delta\left(\frac{\eta_{12}}{d_{12}}\right)^{(x)}_{\text{ideal.}} \cong \Delta\left(\frac{\eta_{12}}{d_{12}}\right)^{(x)}_{\text{add.}} = \frac{\eta_{12}}{d_{12}} - \left(\frac{\eta_1}{d_1}\right)^{x_1}\left(\frac{\eta_2}{d_2}\right)^{x_2}$$

Changes in the values calculated from the above equations versus the composition of DMF-PD-1,2 mixtures at 298.15 K are shown in Figure 3.

The values of deviations from "ideality" of densities, viscosities, kinematic viscosities and molar volumes attain the highest values at the compositions having ca. 33 mol.% of



DMF·2PD-1,2
sub-unit



3DMF·2PD-1,2
sub-unit

Figure 4.

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DMF. Thus, this particular composition would correspond to the most viscous and dense system. This effect according to suggestions of many researchers[18,19], can be accounted for by the increase in the number of hydrogen bonds formed between DMF and PD-1,2 molecules, which consequently leads to the formation of stable intermolecular "complexes" (subunit) of the DMF·2 PD-1,2 type. These results confirm entirely the conclusions from the spectral measurements and changes in the temperature coefficient of dielectric permittivity. Further increase of DMF in the liquid DMF-PD-1,2 mixtures under investigation brings about additional structural effects and appearance of new (with different compositions) intermolecular "complexes" (subunits). The changes in deviations from "ideality" of dielectric permittivity attain the extreme value at about 60 mol.% of DMF (see Figure 3), which most likely points to the formation of 3 DMF·2 PD-1,2 sub-unit in liquid mixtures of DMF-PD-1,2. Assumed structures of the sub-units of the DMF·2 PD-1,2 and 3 DMF·2 PD-1,2 types are shown in Figure 4.

The complexes (sub-units) of DMF·2 PD-1,2 and 3 DMF·2 PD-1,2 types which are internally H-bonded form subsequently "flickering" internal structures of the $(\mathrm{DMF}\cdot 2\,\mathrm{PD}\text{-}1,2)_n$ and $(3\,\mathrm{DMF}\cdot 2\,\mathrm{PD}\text{-}1,2)_m$ which can mutually convert from one to another. At the present moment it does not seem possible to construct a model of such internal structure: this will require further studies.

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References

1. C. M. Kinart, W. J. Kinart, L. Skulski, *Pol. J. Chem.*, **59**, 591 (1985).
2. C. M. Kinart, *Phys. Chem. Liq.*, in press
3. C. M. Kinart, *Phys. Chem. Liq.*, in press
4. G. Pimentel, A. McClellen, W. H. Freeman, *The Hydrogen Bond*, (1960).
5. L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).
6. L. P. Kuhn, *J. Am. Chem. Soc.*, **76**, 4323 (1954).
7. L. P. Kuhn, *J. Am. Chem. Soc.*, **80**, 5950 (1985).
8. L. P. Kuhn, *Spectrochim. Acta*, **17**, 650 (1961).
9. L. P. Kuhn, *J. Am. Soc.*, **86**, 1650 (1964).
10. L. P. Kuhn, R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).
11. H. Buc, *Ann. Chim.*, **8**, 409 (1963).
12. J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents, Physical Properties and Method of Purification*, Editor J. Wiley and Sons, New York 1988.
13. M. T. Räetzsch, H. Kehlen, H. Rosner, *Z. Phys. Chem.*, *(Leipzig)*, **255**, 115 (1974).
14. M. Rabinowitz, A. Pines, *J. Am. Chem. Soc.*, **91**, 1585 (1969).
15. M. Rabinowitz, A. Pines, *J. Am. Chem. Soc.*, **B**, 1110 (1968).
16. W. T. Raynes, M. A. Raza, *Mol. Phys.*, **20**, 339 (1971).
17. M. J. Shakhparonov, *Fizika i fizikokhimya zidkostei*, Moscow 1973.
18. V. Ya. Anosov, M. J. Ozerova, Yu. Ya. Fialkova, *Osnovy Fizikokhimitcheskovo Analiza*, "Nauka", Moscow 1976.
19. H. M. Seip, *Acta Chem. Scand.*, **23**, 2741 (1969).