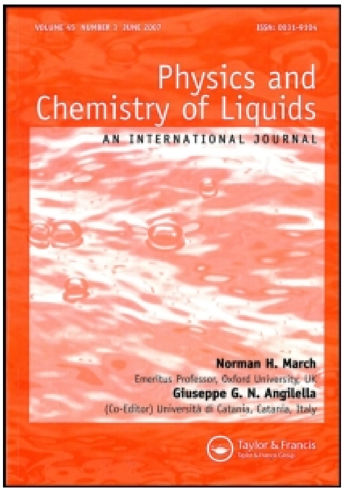

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Study on the Internal Structures of Liquid Formamide-Propane-1,2-Diol Mixtures

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

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The ^{1}H-NMR spectra of liquid binary mixtures, formamide (F)-propane-1,2-diol (PD-1,2), were recorded at 298 K within nearly whole range of the mixed solvent compositions. From these data were found the values of the spectral parameter, $\Delta\delta$(F-PD-1,2). 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 the most stable "complex" (sub-unit) of the 3 F·2 PD-1,2 type.

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

INTRODUCTION

This paper is a continuation of the series of studies on internal structures of some liquid binary mixtures, in which formamide or propane-1,2-diol 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]. In the present work I have analysed the mutual intermolecular interactions in the liquid mixtures of formamide (F) and propane-1,2-diol (PD-1,2). I have newly recorded ^{1}H-NMR spectra of liquid binary F-PD-1,2 mixtures (at 298 K) within nearly the whole range of solvent compositions (i.e. 3.60 to 98.1 mol. % of F). The same graphical method as that used previously[1–3] has been applied for determination of the relative differences in the chemical shift values δ(F-PD-1,2) of the centre of the formyl proton signal of F and the centre of –OH groups signals of PD-1,2. Subsequently, the values of the spectral parameter $\Delta\delta$(F-PD-1,2) have been determined. In order to characterize better the mixtures studied and to pinpoint the composition where the strongest intermolecular interactions are displayed involving hydrogen bonds, I have analysed values of newly measured densities (d_{12}), viscosities (η_{12}) at 298.15 K and dielectric permittivities (ε_{12}) at 288.15 K, 298.15 K and 303.15 K within nearly the entire range of solvent compositions. From all these data, using the previously described method[4], the values of molar volumes (V_{12}), kinematic viscosities (η_{12}/d_{12}), their deviations from "ideality" and the temperature coefficients of dielectric permittivities (α_{12}) for the same binary mixtures, at 298.15 K, have been determined and analysed.

The internal structures of liquid formamide and propane-1,2-diol have already been reviewed in my previous papers[1-3]. Taking into account the published data concerning the structure of liquid F and PD-1,2 it seemed quite interesting to extend these studies onto the F-PD-1,2 mixtures.

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and all the physicochemical measurements, chemical pure formamide (Fluka) and propane-1,2-diol (Polskie Odczynniki Chemiczne-Gliwice) were used. Formamide and propane-1,2-diol were dried and purified according to the known procedure[5].

^{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 formamide and propane-1,2-diol were measured with an accuracy of about ± 0.2 Hz in respect to an external standard HMDS (hexamethyldisiloxane). The viscosities were measured with an accuracy ± 0.1%, at 298.15 K, using Höppler viscometer. Solvent densities were measured, at 298.15 K, using a glass pyknometer of the Lipkin type. The maximum error in the density measurements was 1.10^{-4} g.cm^{-3}. The dielectric permittivity measurements were performed with an accuracy of ± 0.1%, using a bridge of the type OH-301 (made in Hungary), at 288.15 K, 298.15 K and 303.15 K. All the binary solutions made of F 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 formamide with propane-1,2-diol. In this work, with the aim of

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

mol. % of F	δ(F-PD-1,2) [Hz]
3.60	175.50
8.92	172.20
12.51	172.50
17.36	173.50
25.74	175.30
31.59	176.40
41.66	179.00
50.24	181.50
55.18	183.00
60.17	184.50
65.40	189.50
70.51	195.70
73.47	198.50
81.17	205.50
88.08	210.50
94.34	215.30
98.91	218.50

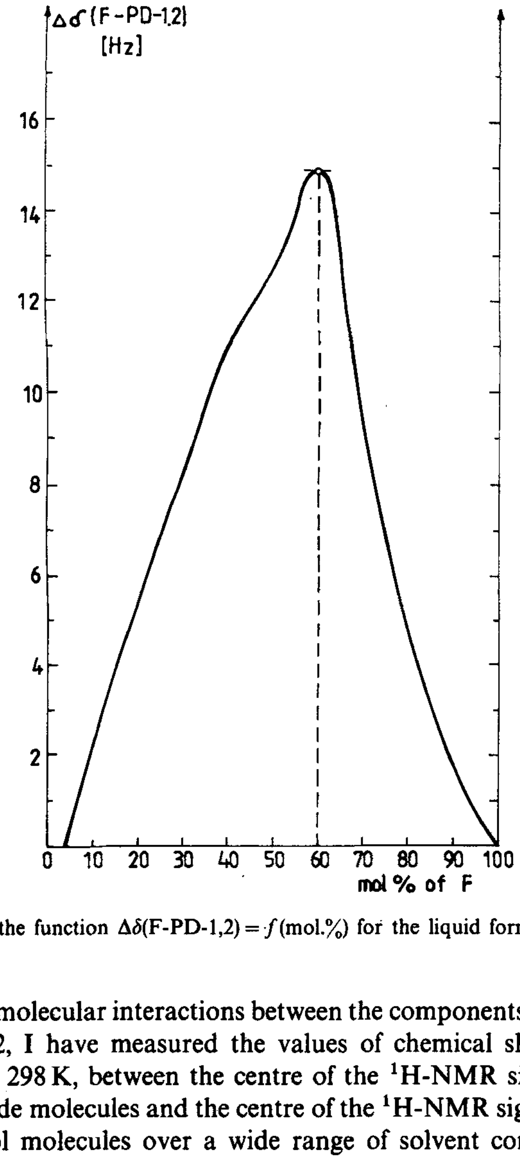


Figure 1 Changes in the function Δδ(F-PD-1,2) = *f*(mol.%) for the liquid formamide-propane-1,2-diol mixtures, at 298 K.

analysing the intermolecular interactions between the components in the liquid binary mixtures F-PD-1,2, I have measured the values of chemical shift differences δ(F-PD-1,2) (in Hz) at 298 K, between the centre of the ^{1}H-NMR signals of the formyl proton of formamide molecules and the centre 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 3.60 mol. % to 98.81 mol. % of F. Subsequently, using the same method as previously[1-3], from these new spectral data the spectral parameter Δδ(F-PD-1,2) has been found. The values of this parameter, or more precisely, the location of its maximum values as has been shown in my previous papers[1-4], are located at the composition with the strongest intermolecular interactions between the components whereby hydrogen bonds are involved. The δ(F-PD-1,2) values are shown in Table 1, whereas the Δδ(F-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 Δδ(F-PD-1,2) at ca. 60 mol. % of F. Thus, the conclusion would be drawn that at this

Table 2 Dielectric permittivities (ε_{12}) for binary liquid mixtures, F-PD-1,2, measured at 288.15 K, 298.15 K and 303.15 K.

mol. % of F	ε_{12} 288.15 K	298.15 K	303.15 K
0.00	32.45	31.36	30.71
3.60	35.02	33.85	32.51
8.92	38.57	37.01	35.48
12.51	41.50	39.41	37.85
17.36	44.48	42.26	40.63
31.59	54.49	52.07	49.25
41.66	61.93	58.65	55.84
55.18	71.88	68.57	64.98
60.17	75.44	72.26	68.50
65.40	79.47	76.47	72.18
73.47	85.96	83.05	79.91
81.17	92.75	89.71	88.23
88.08	99.51	96.92	95.52
94.34	106.94	104.36	102.28
100.00	110.84	109.70	109.44

composition the strongest interactions between components with involving hydrogen bonds, are displayed, and that the most stable "complex" (sub-unit) is of the 3 F·2PD-1,2 type.

I had also performed the independent measurements of dielectric permittivities (ε_{12}) over a whole range of solvent compositions, at 288.15 K, 298.15 K and 303.15 K. The measured values of ε_{12} are summarized in Table 2. Using this data, I have calculated values of the temperature coefficient of dielectric permittivities, denoted α_{12}, viz. $\alpha_{12} = (1/\varepsilon_{12})\cdot[d\varepsilon_{12}/d(1/T)]$. 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 consideration[6]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. It has been shown in our previous papers that there is a full consistence of conclusions drawn from the analysis of changes in spectral parameter $\Delta\delta$ and coefficient α_{12}. Change in the α_{12} value versus compositions of liquid F-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 60 mol. % of F. This would correspond to the formation of a stable intermolecular "complex" (sub-unit) with a composition of 3 F·2 PD-1,2, which has been confirmed by spectral ^{1}H-NMR measurements. Further interesting results can be obtained by detailed analysis of the function $\alpha_{12} = f$(mol. % of F). It indicates that on increasng addition of F to propane-1,2-diol up to 8 mol. % of F, where a minimum is reached, causes a rapid drop in the α_{12} values. Further addition of formamide to the studied mixtures causes an increase in α_{12}, which results in a maximum at ca. 60 mol. % of F. Therefore, it is possible to assume that small amounts of formamide being added to neat propane-1,2-diol break its internal structure (composition region up to 8 mol. % of F), whereas further addition of formamide, up to ca. 60 mol. % of F, makes the internal structure of the mixed solvent more and more stabilized by hydrogen bonds formed between

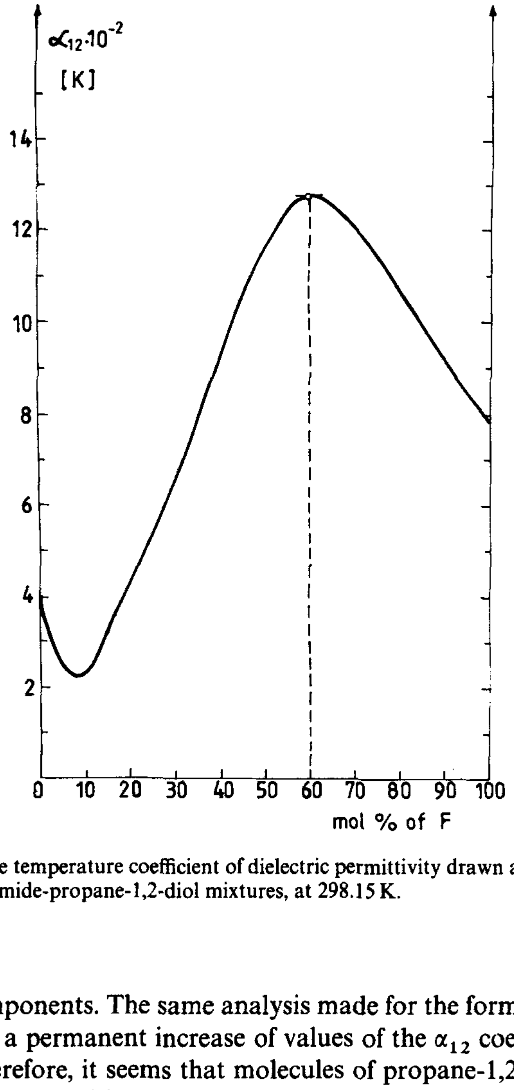


Figure 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid formamide-propane-1,2-diol mixtures, at 298.15 K.

molecules of its components. The same analysis made for the formamide-rich composition region shows a permanent increase of values of the α_{12} coefficient down to ca. 60 mol. % of F. Therefore, it seems that molecules of propane-1,2-diol in the studied mixture, within the composition range between 100 to 60 mol. % of F, play a role of "structure-makers" in respect to molecules of formamide in the neat solvent. Solid formamide has a structure of layers formed by crossing chains of molecules linked by hydrogen bonds[7-9]. This layer arrangement, according to Ladell and Post is partly disturbed on melting[8]. Probably the addition of small quantities of PD-1,2 to F causes the alcohol molecules to become an additional bonding element in the disarranged formamide structure.

Previously[4] a literature review of different methods used for the interpretation of the maxima of deviations from "ideality" of different physico-chemical properties was given. Now using the values of densities (d_{12}) and viscosities (η_{12}) (see Table 3) and dielectric permittivities (ε_{12}) (see Table 2) as a function of composition, at 298.15 K, the deviations from "ideality" of densities $\Delta(d_{12})^{(x)}_{ideal.}$, viscosities $\Delta(\eta_{12})^{(x)}_{ideal.}$, dielectric

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

mol. % of F	d_{12} [g·cm^{-3}]	η_{12} [cP]
0.00	1.0329	41.736
17.36	1.0440	29.684
31.59	1.0549	22.751
41.66	1.0635	18.753
55.18	1.0761	14.590
60.17	1.0813	13.695
65.40	1.0863	12.313
73.47	1.0947	10.264
81.17	1.1039	8.254
88.08	1.1132	6.511
94.34	1.1224	4.916
100.00	1.1295	3.393

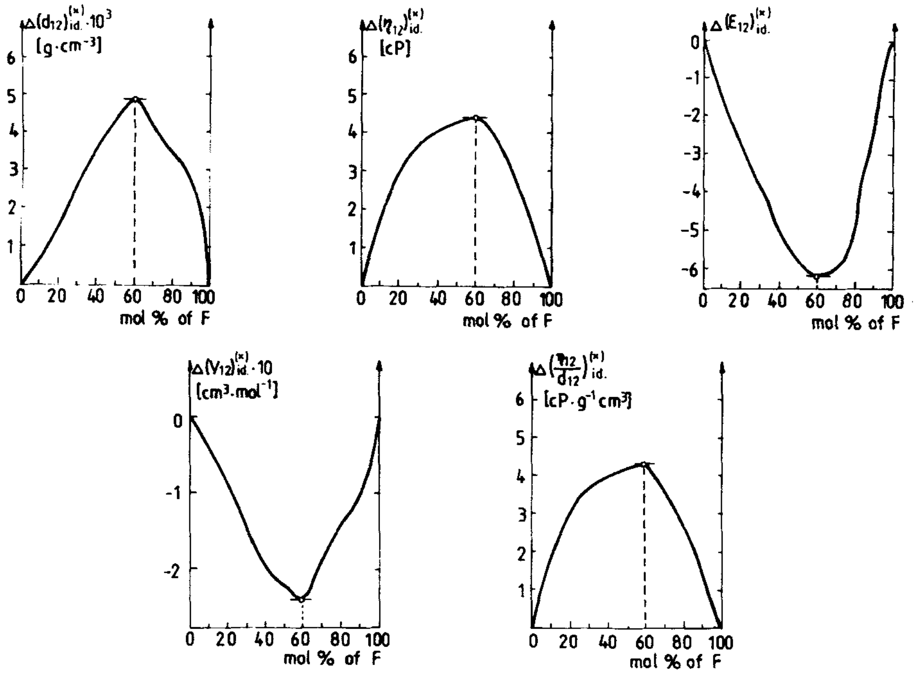


Figure 3 The course of changes of deviations from "ideality" of density, viscosity, dielectric permittivity, molar volume and kinematic viscosity as a function of composition for the liquid formamide-propane-1,2-diol mixtures, at 298.15 K.

permittivities $\Delta(\varepsilon_{12})^{(x)}_{ideal.}$, molar volumes $\Delta(V_{12})^{(x)}_{ideal.}$ and kinematic viscosities $\Delta(\eta_{12}/d_{12})^{(x)}_{ideal.}$ were evaluated by the following equations:

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

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

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

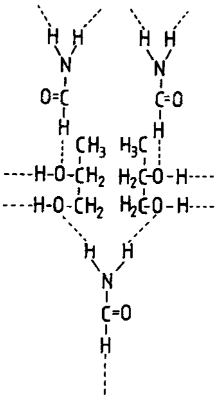
$$\Delta(V_{12})^{(x)}_{ideal.} = (V_{12})^{(x)}_{add.} = V_{12} - (x_1 \cdot V_1 + x_2 \cdot V_2)$$

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

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

These changes as functions of the composition are presented 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. 60 mol.% of F. Thus, this particular composition would correspond to the most viscous and dense system. This effect, according to suggestions of many researchers[10,11], can be accounted for by the increase in the number of hydrogen bonds formed between F and PD-1,2 molecules, which consequently leads to the formation of stable intermolecular "complexes" (sub-units) of the 3 F·2 PD-1,2 type. These



3F·2PD-1,2
sub-unit

Figure 4

results confirm the conclusions drawn from the spectral measurements, changes in the temperature coefficient of dielectric permittivity and the changes in deviations from "ideality" of dielectric permittivity.

Therefore, due to all aforementioned literature data[1-3], concerning the structure of liquid F and PD-1,2 and the present studies, the structure of the mentioned above "complex" (sub-unit) of the 3F·2 PD-1,2 type can be suggested as given on Figure 4.

The "complexes" (sub-units) of this type which are internally H-bonded form subsequently flickering internal structures of type $(3\ F \cdot 2\ PD\text{-}1{,}2)_n$. At the present moment it seems impossible to suggest a model of such internal structure and this will require further studies.

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