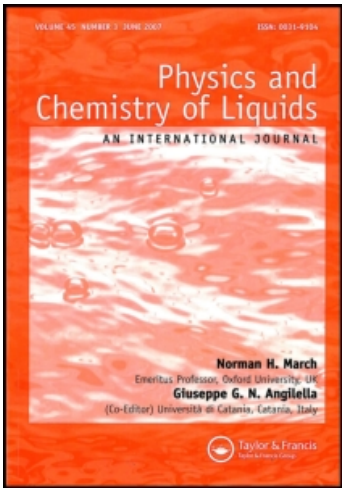

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Intermolecular Interactions in Liquid N-methylformamide-dioxane Mixtures Found by Measuring Their ^{1}H-NMR Spectra, Densities, Viscosities and Relative Dielectric Permittivities

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INTERMOLECULAR INTERACTIONS IN LIQUID N-METHYLFORMAMIDE-DIOXANE MIXTURES FOUND BY MEASURING THEIR ^{1}H-NMR SPECTRA, DENSITIES, VISCOSITIES AND RELATIVE DIELECTRIC PERMITTIVITIES

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The ^{1}H-NMR spectra of liquid binary mixtures, N-methylformamide (NMF)-dioxane (Dx), were recorded at 298 K within nearly the whole range of the mixed solvent compositions. From these data the values of the spectral parameter, $\Delta\delta$(NMF-Dx) were found. The densities and viscosities of the mixed solvents were measured at 298.15 K, as well as the dielectric permittivities at 293.15 K, 298.15 K, 303.15 K and 308.15 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, $\alpha_{12} = (1/\varepsilon) \cdot [d\varepsilon/d(1/T)]$, were found. The scrutiny of all these structural parameters as functions of the mixture composition points to the formation of a "complex" (sub-unit) of the 2NMF · Dx type in the bulk of the mixed solvents.

KEY WORDS: ^{1}H-NMR spectra, intermolecular interactions in the liquid mixtures.

In the present work I have analysed the mutual intermolecular interactions in the liquid mixtures of dioxane (Dx) and N-methylformamide (NMF). I have newly recorded ^{1}H-NMR spectra of liquid binary NMF-Dx mixtures (at 298 K) within nearly the whole range of solvent compositions (i.e. from 7.12 to 86.11 mol.% of Dx). 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(NMF-Dx) of the centre of the formyl proton signal of NMF and the centre of Dx protons signals. Subsequently, the values of the spectral parameter $\Delta\delta$(NMF-Dx) 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 293.15 K, 298.15 K, 303.15 K and 308.15 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 temperature coefficients of dielectric permittivities (α) for the same binary mixtures, at the 298.15 K, have been determined and analysed. The choice of the binary mixture for the present study is due to fact that in my previous works[1–5] I have carried out the analogous studies

of binary liquid mixtures of formamide, N-methylformamide and N,N-dimethylformamide with water, dioxane with water and formamide and N,N-dimethylformamide with dioxane. Therefore, it seemed quite interesting to extend the previous studies to the NMF-Dx liquid system. The literature opinions on the internal structures of neat liquid formamide, N-methylformamide and N,N-dimethylformamide and dioxane are reviewed in my previous works[1–5]. NMF and Dx profoundly differ in their relative dielectric permittivity values (at 298.15 K): $\varepsilon_{NMF} = 182.4$[6], $\varepsilon_{Dx} = 2.21$[7] and their dipole moments (at 298.15 K in benzene): $\mu_{NMF} = 4.8$ D[6], $\mu_{Dx} = 0.4$ D[7] as well as in their abilities to form intermolecular H-bonds. Mono-N-alkylamides, with including NMF, seem to be very strongly chainwise associated with H-bonding[8]. It has been suggested[9] that formation of cyclic dimers by formamide and NMF is less likely, since it would noticeably diminish their ε values and dipole moments, which is not observed experimentally. On melting formamide or N-methylformamide with inert solvents the H-bonded multimeric chain structure is preserved to a considerable extent. Contrariwise, the association is markedly reduced in "active" solvents ($CHCl_3$, dioxane, ketones and particularly dimethyl sulfoxide) because the aggregates are broken up by solute—solvent H-bonding, although some association persists even in relatively dilute solutions[10]. It has been shown[11–13] that the molecule of dioxane is able to form one or two H-bonds. Taking into consideration all aforementioned literature data concerning the structure of liquid NMF and Dx, and my own previous works on mixtures of formamide and N,N-dimethylformamide with dioxane[4,5] it seemed quite interesting to extend these studies to the NMF-Dx liquid mixtures focusing on the intermolecular interactions of its components.

EXPERIMENTAL

For the present ^{1}H- NMR spectral studies and all the physicochemical measurements, chemical pure N-methylformamide (Fluka) and 1,4-dioxane (Polskie Odczynniki Chemiczne-Gliwice) were used. Dioxane and N-methylformamide were dried and purified according to the known procedure[1,2].

^{1}H-NMR spectra were recorded on the Tesla spectrometer of the type BS 467 (60 MHz), at 298 $\pm$ 1 K. The chemical shift values for proton signals of N-methylformamide and dioxane were measured with an accuracy of about $\pm$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 DP-220 (made in Germany), at 293.15 K, 298.15 K, 303.15 K and 308.15 K. The viscosities were measured with an accuracy $\pm$0.1%, at 298.15 K, using the Höppler viscometer. The densities were measured at 298.15 K, with an accuracy of $\pm$0.01%. All the binary solutions made of NMF and Dx were prepared by weight.

RESULTS AND DISCUSSION

There is no literature data concerning the analysis of intermolecular interactions in liquid mixtures of N-methylformamide with dioxane. In this work, with the aim of

Table 1 Relative chemical shifts δ(NMF-Dx), measured at 298.15 K.

mol % of Dx	*δ(NMF-Dx)[Hz]*
7.12	257.5
14.70	261.8
22.81	264.6
31.49	267.6
40.81	268.2
50.84	268.8
61.67	269.3
73.38	269.5
86.11	269.6

analysing the intermolecular interactions between the components in the liquid binary mixtures NMF-Dx, I have measured the values of chemical shift differences δ(NMF-Dx) (in Hz) at 298 K, between the centre of the ^{1}H-NMR signals of the dioxane molecules and the centre of the ^{1}H-NMR signal of the formyl proton of N-methylformamide over a wide range of solvent compositions, i.e. from 7.12 to 86.11 mol.% of Dx. Subsequently, using the same method as previously[1,2], from these new spectral data the values of the spectral parameter $\Delta\delta$(NMF-Dx) have been found.

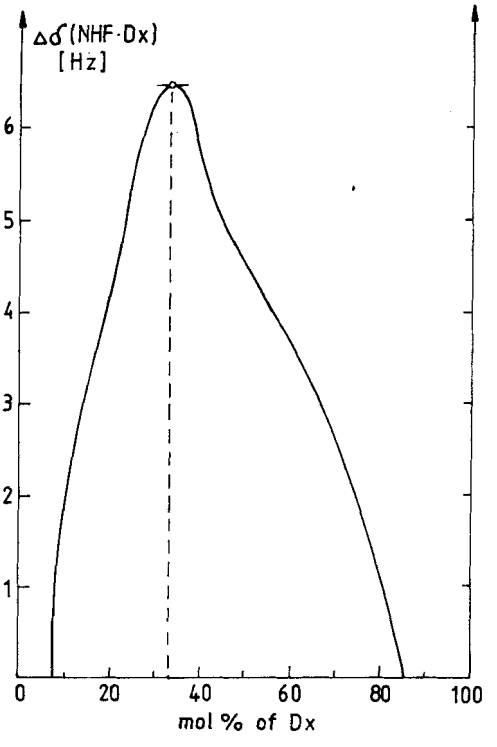

Figure 1

The values of this parameter, or more precisely, the location of its maximum points precisely, as I have shown in my previous works[1–5], at the composition where the strongest intermolecular interactions between the components with involving hydrogen bonds are displayed. The δ(NMF-Dx) values are shown in Table 1, whereas the $\Delta\delta$(NMF-Dx) 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 $\Delta\delta$(NMF-Dx) at ca. 33 mol.% of Dx. Thus, the conclusion can 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 2NMF · Dx type.

I have also performed independent measurements of dielectric permittivities (ε_{12}) over the whole range of solvent compositions, at 293.15 K, 298.15 K, 303.15 K and 308.15 K. The measured values of ε_{12} are summarized in Table 2. Using these data, I have calculated the values of the temperature coefficients of dielectric permittivity, denoted α_{12}, viz. $\alpha_{12} = (1/\varepsilon_{12}) \cdot [d\varepsilon_{12}/d((1/T)]$. This coefficient, in agreement with the results of Räetzsch[14], may be used as a good criterion for estimating the mutual interactions between components of the mixed solvent. The composition where this parameter is displaying a maximum points to the "complex" with the strongest intermolecular hydrogen bond interactions between the components. In the previous papers[1–5] I have shown that there is fairly good agreement between conclusions drawn from the behaviour of the spectral parameter $\Delta\delta$, and for the α_{12} property. The changes of α_{12} as a function of the mixture compositions are visualized in Figure 2. As can be seen in Figure 2, the values of α_{12} reach their maximum at the composition having ca. 33 mol.% of Dx, which confirms the aforementioned conclusion drawn from the ^{1}H-NMR spectral data on a possibility of formation of a

Table 2 Dielectric permittivities for binary liquid mixtures, NMF-Dx, measured at 293.15 K, 298.15 K, 303.15 K and 308.15 K.

mol % of Dx	ε_{12}			
	293.15 K	*298.15 K*	*303.15 K*	*308.15 K*
0.00	197.80	182.40	171.00	159.20
2.51	179.90	161.10	151.40	136.90
4.72	165.30	144.20	134.30	120.60
8.49	143.10	119.90	111.10	105.40
12.25	123.20	97.30	89.10	74.57
16.05	104.80	78.05	69.93	54.02
19.62	86.90	62.51	54.11	41.38
26.98	56.95	38.23	24.85	20.79
31.96	39.12	26.86	17.94	13.51
36.02	33.94	22.94	14.02	11.22
43.25	32.04	21.13	13.18	10.75
61.67	26.79	17.14	12.51	7.93
73.38	20.46	13.92	10.41	6.09
86.11	12.88	8.95	7.15	4.19
100.00	2.39	2.31	2.24	2.22

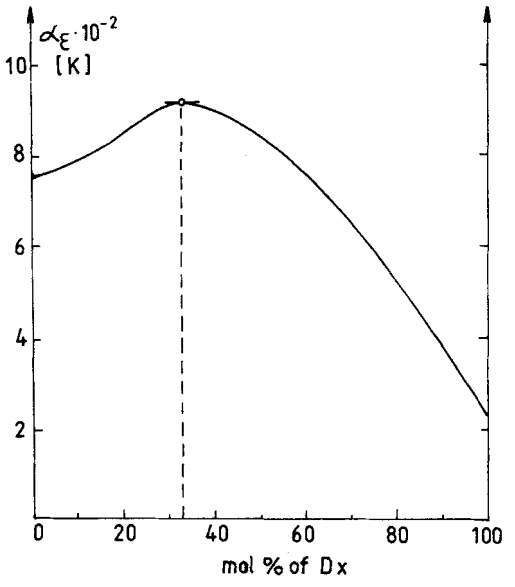

Figure 2

"complex" (sub-unit) of the 2NMF · Dx type in the studied mixtures. In the previous work[3] I 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 liquid system. In the present work, using newly measured values of densities, viscosities and ε_{12} in the whole range of compositions of the mixture NMF-Dx at 298.15 K (see Table 2 and Table 3), I

Table 3 Densities (d_{12}) and viscosities (η_{12}) for binary liquid mixtures, NMF-Dx, measured at 298.15 K.

mol% of Dx	d_{12} [$g \cdot cm^{-3}$]	η_{12} [*cP*]
0.00	0.9986	1.6500
2.51	1.0040	1.5940
4.72	1.0079	1.5621
8.49	1.0136	1.5163
12.25	1.0188	1.4764
16.05	1.0228	1.4395
19.62	1.0260	1.4058
26.98	1.0302	1.3473
31.96	1.0317	1.3127
36.02	1.0316	1.2945
43.25	1.0310	1.2816
61.67	1.0287	1.2660
73.38	1.0278	1.2607
86.11	1.0273	1.2569
100.00	1.0269	1.2550

have calculated deviations from "ideality" of densities $\Delta(d_{12})^x_{\text{ideal.}}$, viscosities $\Delta(\eta_{12})^x_{\text{ideal.}}$, dielectric permittivities $\Delta(\varepsilon_{12})^x_{\text{ideal.}}$, molar volumes $\Delta(V_{12})^x_{\text{ideal.}}$ and kinematic viscosities $\Delta(\eta_{12}/d_{12})^x_{\text{ideal.}}$ [where (x) stands for the mole fractions]. The above-mentioned values were calculated at 298.15 K using the equations given below:

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

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

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

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

where:

$$V = m/d$$

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

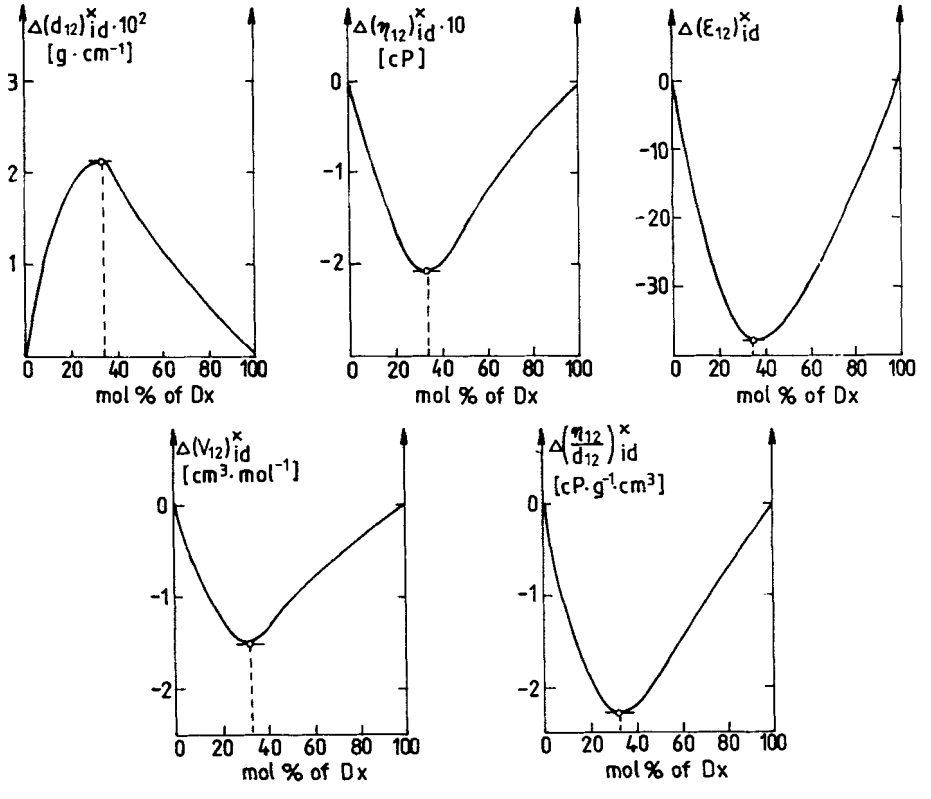

Figure 3

The nature of the changes of the calculated (from these equations) values as functions of the mixture compositions (at 298.15 K) are visualized in Figure 3, and the experimental values of η_{12} and d_{12} (at 298.15 K) are summarized in Table 3.

All of the functions [$\Delta(d_{12})^{x}_{\text{ideal.}}$, $\Delta(\eta_{12})^{x}_{\text{ideal.}}$, $\Delta(\varepsilon_{12})^{x}_{\text{ideal.}}$, $\Delta(V_{12})^{x}_{\text{ideal.}}$ and $\Delta(\eta_{12}/d_{12})^{x}_{\text{ideal.}}$] show the greatest deviations from "ideality" at the composition having ca. 33 mol.% of Dx which corresponds to the formation of a "complex" (sub-unit) of the 2NMF · Dx type in the studied mixtures. It confirms the conclusion drawn from ^{1}H-NMR spectral data and the analysis of the changes of the temperature coefficient of ε_{12}. The complexes (sub-units) of this type which are internally H-bonded form subsequently "flickering" internal structures of $(2\text{NMF} \cdot \text{Dx})_n$ type. At the present moment we are not able to propose a model of such internal structure and further studies are clearly needed here.

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