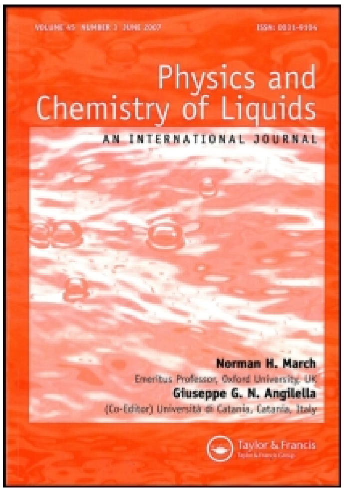

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N,N-Dimethylformamide-methanol Binary Mixtures and their Assumed Internal Structures

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N,N-DIMETHYLFORMAMIDE-METHANOL BINARY MIXTURES AND THEIR ASSUMED INTERNAL STRUCTURES

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The ^{1}H-NMR spectra of liquid binary mixtures, *N,N*-dimethylformamide (DMF)-methanol (MeOH), 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-MeOH) were found. The dielectric permittivities (ε_{12}) of the mixed solvents were measured at 288.15 K, 298.15 K, 303.15 K and 308.15 K. From literature values of density (d_{12}), viscosity (η_{12}) and measured dielectric permittivities the values of molar volumes (V_{12}), kinematic viscosities (η_{12}/d_{12}) and their deviations from "ideality", at 298.15 K, were calculated. Additionally, the values of the temperature coefficients of dielectric permittivity, $\alpha_{12} = (1/\varepsilon_{12}) \cdot [d\varepsilon_{12}/d(1/T)]$, were found. These structural parameters as functions of concentration suggest the formation of the "complexes" (sub-unit) of the DMF · MeOH type.

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

INTRODUCTION

In previous works[1,2] I have studied the mutual intermolecular interactions in the liquid mixtures of *N,N*-dimethylformamide-water and *N,N*-dimethylformamide-dioxane by comparing their ^{1}H-NMR spectral characteristics ($\Delta\delta$, as explained also in this paper) with their corresponding macroscopic characteristics, viz. densities (d_{12}), viscosities (η_{12}), relative dielectric premittivities (ε_{12}), as well as the respective temperature coefficients of ε_{12}, i.e. $\alpha_{12} = (1/\varepsilon_{12}) \cdot [d\varepsilon_{12}/d(1/T)]$, all determined at 298 K. From the corresponding property—composition curves it has been possible to gain some valuable information on the internal structure of the binary solutions investigated[1,2]. The aim of the present paper has been, consequently, to throw some more light on the internal structure of *N,N*-dimethylformamide (DMF)—methanol (MeOH) mixtures over the full concentration range at 298 K—using the same comparative approach as previously[1,2]. The internal structure of neat liquid aliphatic alcohols is still not explained satisfactorily and needs further study. Earlier matrix isolation work on the methanol dimer concluded that the minimum energy configuration was a cyclic structure[3] but more recent calculations by Murthy *et al.*[4] and Hoyland and Kier[5], as well as experimental work by Bellamy and Pace[6], support the view that the methanol dimer is linear instead of cyclic. Experiments by Weltner and Pitzer on gas-phase methanol[7] and recent studies of methanol in various inert solvents[8] support a monomer-tetramer equilibrium (with some presence of dimer and trimer not ruled out). Murthy *et al.* studied methanol cyclic dimers and the linear dimer and trimer by CNDO/2 and EHT molecular orbital methods. The extended Hückel theory calculations predicted a 1.3 kcal/mol stabilization for the linear dimer and 0 for the cyclic; the corresponding values for the CNDO/2 were 6.46 and 1.70 kcal/mol. The linear trimer had a greater energy of stabilization than two dimers. Hoyland and Kier examined the cyclic tetramer of methanol by CNDO/2 and found its energy of formation to be 23.9 kcal/mol, surprisingly less than four times the dimerization energy of methanol. It is possible, however, that the author's use of the experimental monomer geometry (rather than CNDO/2 optimized) as well as incomplete geometry optimization in the tetramer caused this lower stabilization energy. Allen and Kollman found cyclic hexamers of methanol stable by 10 kcal/H bond with respect to six monomers[9].

The two lone electron pairs at oxygen atom as well as a strongly protondonating hydrogen atom of the same OH group create, however, a theoretical possibility of forming as much as three H—bonds by each individual alcohol molecule, Me—O—H, in its neat liquid. However, due to steric and other reasons it has been concluded that usually only two (on average) and no more H—bonds are formed therein[10].

The internal structures of liquid *N*,*N*-dimethylformamide have already been reviewed in previous papers[1,2]. Taking into consideration all the aforementioned literature data regarding the structure of liquid DMF and MeOH, and my own previous works on mixtures of DMF with water[1] and dioxane[2] it seemed quite interesting to extend these studies to the DMF-MeOH liquid mixtures, focusing on the intermolecular interactions of its components.

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and the measurements of dielectric permittivities, chemical pure *N*,*N*-dimethylformamide (Fluka) and methanol (Fluka) were used. DMF and MeOH were dried and purified according to the known procedure[1,11]. ^{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 methanol 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). All the binary solutions made of DMF and MeOH were prepared by weight.

RESULTS AND DISCUSSION

There is a limited number of studies on the structure and intermolecular interactions in the liquid binary (DMF-MeOH) mixtures. Quitzsch[12] analysed changes of values of the heat of evaporation and calculated from it thermodynamic excess functions

Table 1 Relative chemical shifts, δ(DMF-MeOH), measured at 298 K.

Mol. % of MeOH	*δ(DMF-MeOH) [Hz]*
17.43	234.0
32.21	229.0
44.88	224.0
55.85	217.5
65.52	211.0
74.03	204.5
81.06	199.5
88.37	194.5
94.48	190.0

ΔH^E, ΔS^E and ΔG^E plotted in the function of the composition of liquid binary mixtures of DMF-MeOH in the wide range of temperatures. On the base of these results he postulated the existence of an intermolecular complex of DMF · MeOH type in the studied mixtures. Similar conclusion was derived by Winkelmann[13], on the base of measurements of dielectric permittivities carried in the wide range of temperatures in the liquid DMF-MeOH mixtures. Granzhan[14] has assumed on the basis of measurements of a number of various physicochemical properties (viscosities, densities, surface tensions and refractive indices) of the DMF-MeOH liquid mixtures the possibility of formation of some relatively stable complexes between DMF and MeOH molecules, with the compositions: DMF/MeOH = 1:1 and 1:2.

In this work, in order to analyse the intermolecular interactions between the components in the liquid binary mixtures DMF-MeOH, I have measured the values of chemical shift differences, δ(DMF-MeOH) (in Hz) at 298 K, between the center of the ^{1}H-NMR signal of the formyl proton of *N,N*-dimethylformamide molecules and the center of the ^{1}H-NMR signal of —OH groups in methanol molecules over a wide range of solvent compositions, i.e. from 17.43 to 94.48 mol. % of MeOH. Subsequently, using the same method as previously[1,2], from these new spectral data the values of the spectral parameter Δδ(DMF-MeOH) have been found. The values of this parameter, or more precisely, the location of its maximum points, as I have shown in my previous works[1,2,15,16], at the composition where the strongest intermolecular interactions between the components with involving hydrogen bonds are displayed. The δ(DMF-MeOH) values are shown in Table 1, whereas the Δδ(DMF-MeOH) 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(DMF-MeOH) at ca. 50 mol.% of MeOH. 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 · MeOH type.

In order to support this conclusion, I also performed the independent measurements of dielectric permittivities (ε_{12}) over the whole range of solvent compositions,

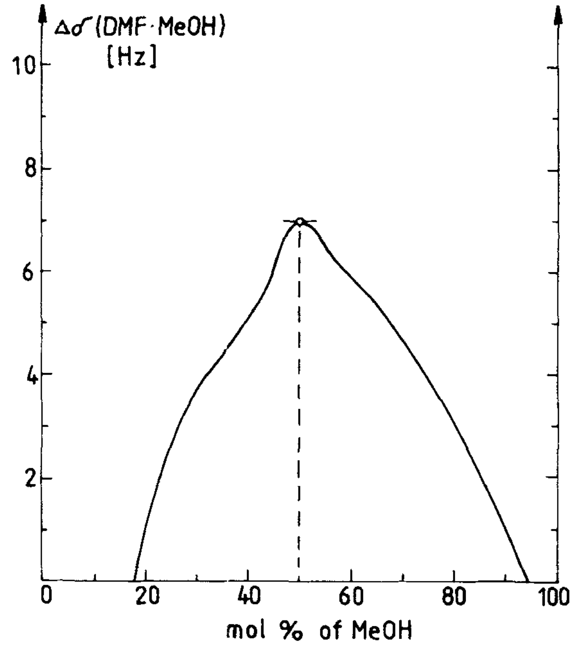

Figure 1 Changes in the function $\Delta\delta$(DM F-MeOH) $= f$(mol.%) for the liquid *N,N*-dimethylformamide-methanol mixtures, at 298 K.

at the temperatures 288.15, 298.15, 303.15 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 coefficient, of ε_{12}, denoted α_{12}, viz. $\alpha_{12} = (1/\varepsilon_{12}) \cdot [de_{12}/d(1/T)]$. This coefficient (or more precisely, the location of its maximum points), in agreement with the results of Räetzsch[11], may be used as a good criterium for estimating the mutual interactions between components of the mixed solvent. In the previous papers[1,2,15,16], I have shown that there is a fairly good agreement in conclusion drawn from the courses of the spectral parameter $\Delta\delta$, and for α_{12} property. The changes of α_{12} as a function of the mixture compositions are visualized in Figure 2.

As it seems in Figure 2, the values of α_{12} reach their maximum at the composition having ca. 50 mol.% of MeOH, which confirms the aforementioned conclusion drawn from the ^{1}H-NMR spectral data on the possibility of formation of a "complex" (sub-unit) of the DMF · MeOH type in the studied mixtures. Parallely, in order to support this conclusion, using values, measured by me, of dielectric permittivities and literature[13] values of viscosities and densities in the whole range of compositions of the DMF-MeOH mixtures at 298.15 K, I 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 fraction]. Previously[9], I have given a 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

Table 2 Dielectric permittivities for binary liquid mixtures, DMF-MeOH, measured at 288.15 K, 298.15 K, 303.15 K and 308.15 K.

Mol. % of MeOH	ε *288.15 K*	ε *298.15 K*	ε *303.15 K*	ε *308.15 K*
0	39.46	37.70	36.87	36.01
5	39.58	37.86	37.01	36.14
10	39.69	37.98	37.14	36.26
20	39.93	38.19	37.34	36.45
30	40.07	38.33	37.46	36.55
35	40.11	38.36	37.48	36.56
40	40.05	38.32	37.45	36.54
45	39.98	38.26	37.42	36.52
50	39.89	38.14	37.31	36.47
55	39.75	37.96	37.14	36.33
60	39.61	37.77	36.91	36.07
70	39.23	37.27	36.35	35.39
80	38.53	36.54	35.60	34.63
90	37.14	35.23	34.32	33.50
100	34.79	32.53	31.38	30.22

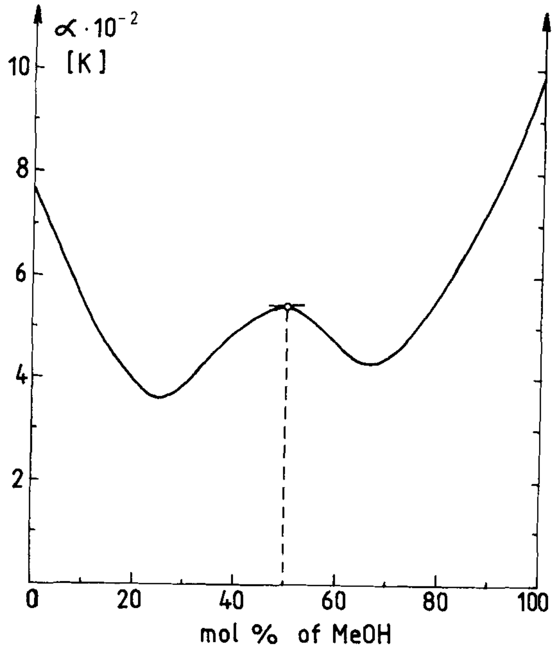

Figure 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid *N,N*-dimethylformamide-methanol mixtures, at 298.15 K.

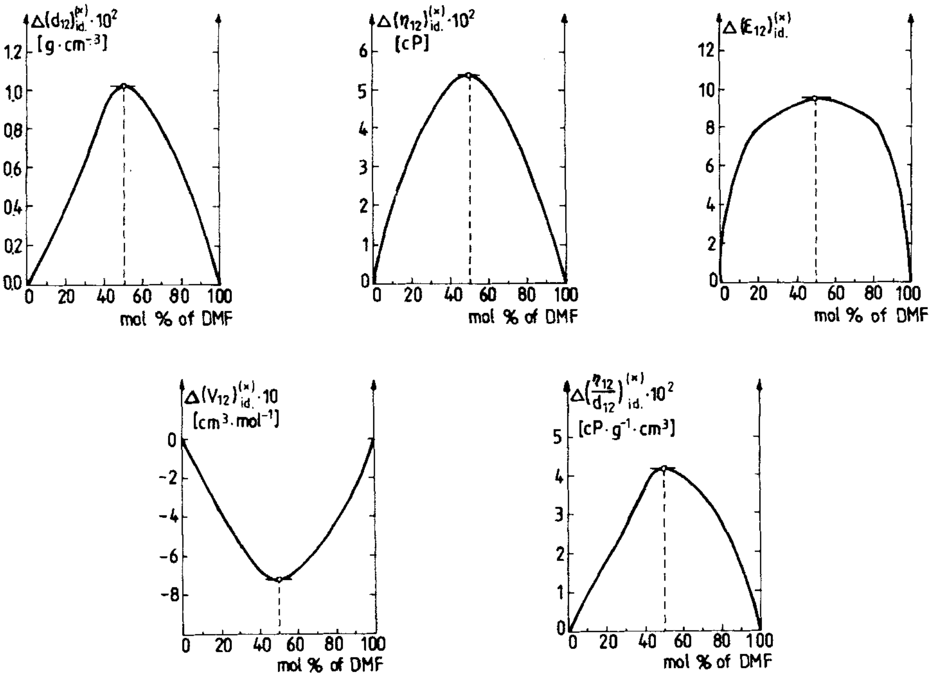

Figure 3 The course of changes of deviations from "ideality" of density, viscosity, dielectric permittivity, molar volume and kinematic viscosity as a function composition for the liquid *N*,*N*-dimethylformamide-methanol mixtures, at 298.15 K.

binary liquid system. The above mentioned values were calculated at 298.15 K using the equations given below:

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

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

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

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

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

where:

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

The course of changes of the calculated values as functions of the mixture compositions, at 298.15 K, are visualized in Figure 3.

All of the functions show the greatest deviations from "ideality" at the composition having ca. 50 mol.% of MeOH which corresponds to the formation of a "complex" (sub-unit) of the DMF · MeOH type in the studied liquid binary 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}. On the basis of the present results, and those found in the literature, it may be concluded that the most stable "complexes" (sub-units) existing in the DMF-MeOH liquid binary mixtures are those of the DMF · MeOH-type. Other "complexes" (sub-units), though they are quite possible, are apparently less stable.

The complexes (sub-units) of the DMF · MeOH type which are internally H-bonded from subsequently "flickering" internal structures of $(\mathrm{DMF \cdot MeOH})_n$ type. At the present moment I am not able to propose a model of such internal structure and further studies are clearly needed here.

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