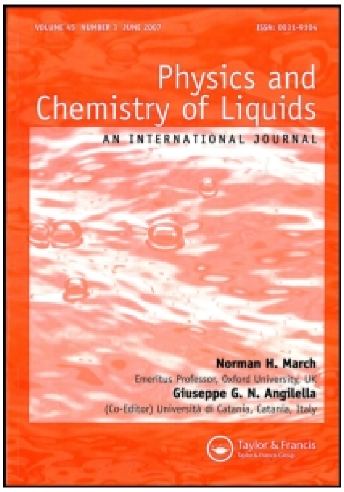

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Internal Structures of Liquid N,N-Dimethylformamideformamide Binary Mixtures

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INTERNAL STRUCTURES OF LIQUID N,N-DIMETHYLFORMAMIDE-FORMAMIDE BINARY MIXTURES

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The ^{1}H-NMR spectra of liquid binary mixtures of formamide (F) and N,N-dimethylformamide (DMF), 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, $\Delta\delta$(F–DMF). The densities (d_{12}), viscosities (η_{12}) of the mixed solvent were measured at 298.15 K, as well as the relative permittivities (ε_{12}) at 288.15 K, 293.15 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} at 298.15 K were found. These structural parameters as functions of concentration suggest the formation of stable 2F • 3DMF, F • DMF, 3F • 2DMF and 2F • DMFx type complexes.

Keywords: ^{1}H-NMR spectra; physiochemical properties; intermolecular interactions

INTRODUCTION

In the present work we have analysed the mutual intermolecular interactions in the liquid mixtures of formamide (F) and N,N-dimethylformamide (DMF). It is a continuation of series of stuides of internal structures of some liquid binary mixtures, in which F or DMF is one of the two constituents, based on the correlation existing between the ^{1}H-NMR spectral results and some physicochemical intensive properties of the same binary mixtures [1]. The internal structures of pure liquid F and DMF have already been reviewed in [1–3]. These two strongly polar liquids (in benzene at 303.15 K: $\mu_F = 3{,}37$ D, $\mu_{DMF} = 3{,}92$ D) are miscible mutually in all proportions and their binary mixtures are stabilized internally mainly by a network of intermolecular hydrogen bonds as well as by fairly strong non-specific van der Waals interactions. It is, therefore, of considerable interest to find out, experimentally, which of the F-DMF mixtures are better or lesser stabilized internally. This is well-visualized by their aforementioned ^{1}H-NMR spectral as well as macroscopic physical characteristics.

EXPERIMENTAL

The two title amides (F and DMF) of analytical reagent grades were commercially available. They were stored, at first, over molecular sieves and then freshly redistilled under vacuum.

^{1}H-NMR spectra were recorded on the Tesla Spectrometer of the type BS 487C (80 MHz), at 298 K. The chemical shift values for proton signals of formamide and N,N-dimethylformamide 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 the Hoppler viscosimeter. Solvent densities were measured at 298.15 K, using a glass pycnometer of the Lipkin type. The maximum error in the density measurements was $1 \cdot 10^{-4}$ g.cm^{-3}. The relative 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 mixtures made of F and DMF were prepared by weight.

RESULTS AND DISCUSSION

There is no literature data concerning the analysis of intermolecular interactions and internal structures in liquid mixtures of formamide with N,N-dimethylformamide. In this work, with the aim of analysing the intermolecular interactions between the components in the binary liquid F–DMF mixtures, we measured the values of chemical shift differences, δ(F–DMF) at 298 K, between the center of the ^{1}H-NMR signals of -NH_2 group of F and the center of the ^{1}H-NMR signals of -CH_3 groups of DMF molecules over a wide range of solvent compositions, i.e. from 2,50 to 98.50 mol.% of F (see Tab. I). From these new spectral data the spectral parameter $\Delta\delta$(F–DMF) has been found (using the same method of previously [1–3]). 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 [1–3]. The $\Delta\delta$(F–DMF) values are visualized in Figure 1 as a function of the mixtures compositions.

The analysis of the data indicates the presence of maximum $\Delta\delta$(F–DMF) at ca. 60 mol.% of F. Thus, at this composition the strongest interactions between components involving hydrogen bonds are observed, and the most stable "complex" is 3 F • 2 DMF.

From the measured values of the relative permittivity at 288.15 K, 298.15 K and 303.15 K (see Tab. II), the temperature coefficients of the

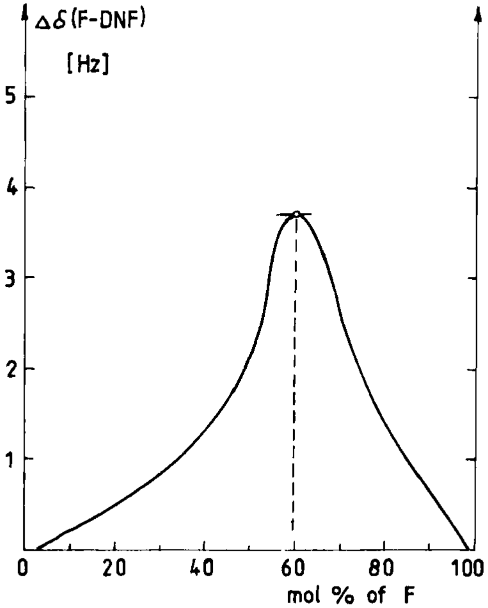


FIGURE 1 Changes in $\Delta\delta$(F–DMF) for liquid F–DMF mixtures, at 298 K.

TABLE I Relative ^{1}H-NMR chemical shifts, δ(F–DMF), meausred at 298 K

mol.% of DMF	*δ(F–DMF)[Hz]*
2.5	400.4
5.0	401.3
10.0	402.9
20.0	406.2
30.0	409.4
40.0	413.2
50.0	416.9
60.0	420.4
70.0	422.1
80.0	423.9
90.0	426.0
95.0	427.0
98.5	427.0

TABLE II Relative permittivities (ε), densities (d_{12}) and viscosities (η_{12}) for liquid binary mixtures F–DMF

mol.%		ε_{12}		$d_{12}[g.cm^{-3}]$	$\eta_{12}[cp]$
of F	288.15 K	298.15 K	303.15 K	298.15 K	298.15 K
0.0	38.31	37.70	36.87	0.9438	0.8024
5.0	39.92	38.38	37.61	–	–
10.0	41.56	39.74	38.64	0.9560	1.0412
15.0	43.18	41.20	40.23	–	–
20.0	44.10	42.77	42.01	0.9695	1.2698
25.0	46.91	44.41	43.18	–	–
30.0	48.83	46.09	44.71	0.9825	1.4721
40.0	52.85	49.58	48.02	0.9983	1.6983
50.0	57.26	53.27	51.24	1.0141	1.9391
60.0	62.10	57.21	54.68	1.0283	2.1980
70.0	68.12	63.65	61.42	1.0498	2.4830
80.0	77.80	74.02	72.16	1.0719	2.8170
90.0	91.24	89.58	88.59	1.1015	3.1910
100.00	110.84	109.70	109.44	1.1295	3.3930

relative permittivity, denoted α_{12}, viz. $\alpha_{12} = (1\,\varepsilon_{12}).[d\varepsilon_{12}/d(1/T)]$ at 298.15 K were calculated. The composition range of binary liquid mixtures within which α_{12} attains its highest value should be interpreted (as shown in our previous work [1–3]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixtures. Changes in the α_{12} vs. compositions of liquid F mixtures are shown in Figure 2.

The maximum value of α_{12} is found at ca. 60 mol.% of F. This confirms the conclusion from ^{1}H-NMR spectral data concerning the formation of a "complex" of 3 F • 2 DMF. Further interesting results can be obtained by detalied analysis of the function $\alpha_{12} = f$(mol% F). This indicates that increasing addition of DMF to F up to 10 mol.% of DMF, where a minimum is reached, causes a rapid drop in α_{12}. Further addition of DMF to the 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 the internal structure of F is disrupted by the addition of small amounts of DMF (up to 10 mol.%), whereas further addition of DMF, up to ca. 60 mol.% of F, stabilizes the internal structure of the mixed solvent increasingly by hydrogen bonding between the component molecules. The same analysis made for the DMF-rich composition region shows a continuous increase in α_{12} down to ca. 60 mol.% of F. Therefore, it seems that molecules of F,

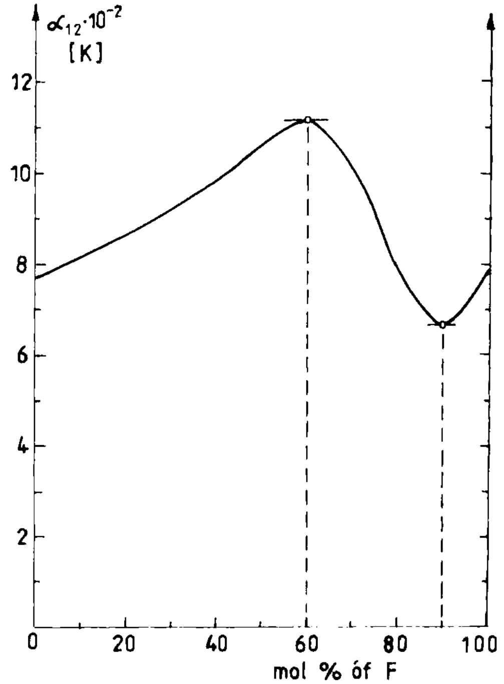


FIGURE 2 Changes in the temperature coefficient of relative permittivity as a function of composition for the liquid F–DMF mixtures, at 298.15 K.

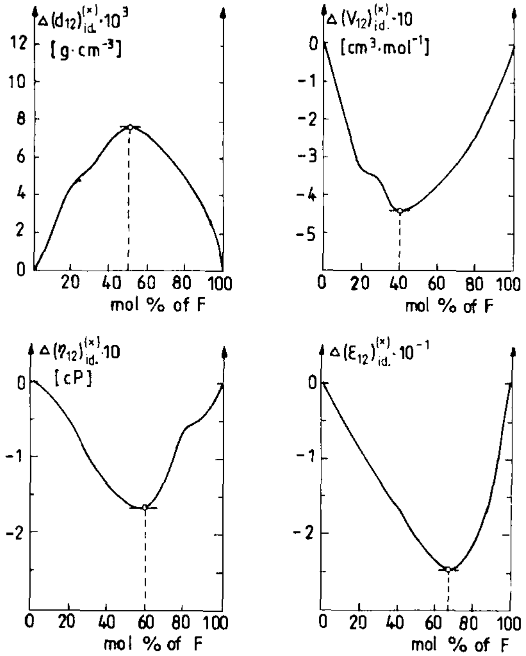
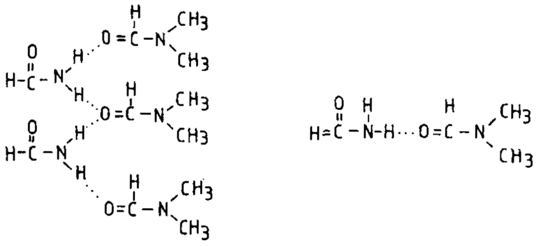


FIGURE 3 The course of changes of deviations from "ideality" of physicochemical properties of F–DMF mixtures as a function of compositon for the liquid F–DMF mixtures, at 298.15 K.

within the composition range 100-60 mol.% of F, act as "structure-makers" with respect to molecules of DMF in the neat solvent.

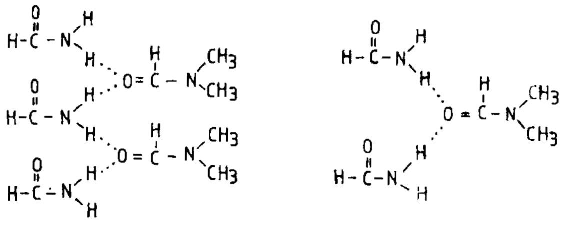
Additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of deviations from "ideality" of basic physicochemical properties of these mixtures, i.e. density (d_{12}), viscosity (η_{12}), relative permittivity (ε_{12}) and molar volumes (V_{12}) [1–3]. A thorough review of the literature justifies the correctness of using these parameters in the analysis of intermolecular interactions [1]. In this paper, using the experimental values of density, viscosity and relative permittivity at 298.15 K (see Tab. I) the values of deviations of "ideality" of analysed physicochemical properties were calculated, using equations discussed in our previous works [1–3]. These values are shown in Figure 3.

The values of $\Delta(d_{12})_{id}^{(x)}$ have maximum at ca.50 mol.% of F, what suggest the formation of the "complex" of F • DMF type. Deviations from "ideality" in molar volumes, viscosity and relative permittivity attain their highest values at ca.40 mol.% of F, 60 mol% of F and 67



complex : 2F·3DMF

complex : F·DMF



complex : 3F·2DMF

complex : 2F·DMF

FIGURE 4 Complexes of the 2 F• 3 DMF, F• DMF, 3 F• 2 DMF and 2 F• DMF types.

mol. % of F what suggest the formation of the "complexes" of: 2 F• 3 DMF, 3 F• 2 DMF and 2 F• DMF types.

The comparison of the present results with earlier works [4–6] devoted to the analysis of the structure of liquid F and DMF leads to the conclusion that the structure of the mentioned above "complexes" of the 2 F• 3 DMF, F• DMF, 3 F • 2 DMF and 2 F • DMF type can be assumed as it has been shown in Figure 4.

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