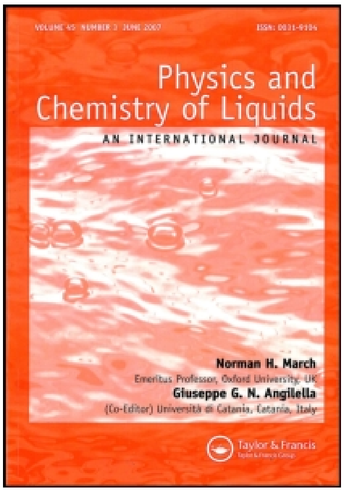

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THE INTERNAL STRUCTURES OF LIQUID N-METHYLFORMIDE -N, N-DIMETHYLFORMAMIDE BINARY MIXTURES

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The ^{1}H-NMR spectra of liquid binary mixtures N-methylformamide (NMF) - N, N-dimethylformamide (DMF), were recorded at 298 K within nearly the whole range of mixed solvent compositions. From these data were found the values of the spectral structural parameter, $\Delta\delta$(NMF - DMF). The viscosities (η_{12}) of the mixed solvents were measured at 298.15 K, as well as the relative permittivities (ε_{12}) and the surface tensions (σ_{12}) at 291.15 K, 298.15 K and 303.15 K. From all these data their deviations from ideality were calculated. Additionally, the temperature coefficients of relative permittivity, $\alpha_{12} = 1/\varepsilon_{12}\,[d\varepsilon_{12}/d(1/T)]$ and temperature coefficients of surface tensions, $\gamma_{12} = -(\sigma_{12}/dT)$, were found. These quantities, as a function of a mole fraction, deviate very little from their molar values, indicating that the mixtures of NMF - DMF can be regarded as almost ideal.

Keywords: ^{1}H-NMR spectra; physicochemical properties; binary liquid mixtures

INTRODUCTION

This paper is a continuation of series of studies on internal structures of some liquid binary mixtures, in which NMF 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 [1–3]. In the present work we have analysed the mutual intermolecular interactions in the liquid mixtures of NMF and DMF. The internal structure of liquid N-methylformamide and N, N-dimethylformamide have already been reviewed [1–2]. Our studies have been inspired by conclusions drawn by de Visser and Somsen [4] from their results. They have studied thermodynamic properties of mixtures of NMF with DMF from the point of view of intermolecular interactions. According to changes of them [4] molar volumes and heat capacities for these mixtures indicate that they can be regarded as almost ideal.

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and the measurements of relative permittivities, viscosities and surface tensions, chemical pure NMF (Fluka) and DMF (Fluka) were used. They were dried and purified according to known procedures [5]. The ^{1}H-NMR spectra were recorded using a Tesla BS 467 (60 Mhz) spectrometer, at 298±1 K. The proton chemical shifts of NMF and DMF were measured with an accuracy of ca. ±0.2 Hz with respect to an external standard HMDS (hexamethyldisiloxane). The relative permittivity measurements were performed with an accuracy of ±0.1%, using a bridge of the type OH-301 (made in Hungary). The viscosities were measured with an accuracy ±0.1%, using a Höppler viscosimeter. The surface tensions were measured with an accuracy ±0.1%, using a stalagmometer. Solvent densities were measured, using a glass Lipkin pycnometer (Carl Zeiss Jena). All the solutions were prepared by weight.

RESULTS AND DISCUSSION

The review of literature data indicates that the only attempt to study intermolecular interactions in binary liquid mixtures of NMF with DMF has been done by de Visser [4]. Presently with the aim of analysing the intermolecular interactions between the components in the binary liquid NMF – DMF mixtures, we measured the values of chemical shift differences δ(NMF – DMF) at 298 K, between the centre of the ^{1}H-NMR signals of the -NHCH$_3$ group of N-methylformamide and the centre of the ^{1}H-NMR signals of the -CH$_3$ groups of N, N-dimethylformamide molecules over a wide range of solvent compositions, i.e. from 2.00 to 98.00 mol. % of DMF. Subsequently, to obtain more conclusive experimental evidence from the chemical shifts δ(NMF – DMF), shown in Table I and explained above, their deviations from the additive properties, viz. Δδ(NMF – DMF) values, have been calculated. The procedure to find these values has been discussed in detail previously [3]. The values of this structural parameter or, more precisely, the location of its maximum values [1 – 3], are located at the composition with the strongest intermolecular interactions between the components, where hydrogen bonds are involved. The course of changes of values of chemical shift differences δ(NMF – DMF) as a function of composition for liquid NMF – DMF mixtures is linear (see Tab. I), within limits of experimental error, and values of the studied by us structural parameter Δδ(NMF – DMF) are equal to zero within the whole range of mixed solvent compositions (see Fig. 1). Therefore, it seems necessary to assume that these mixtures can be regarded as almost ideal.

We wish to underline that the linear course of the spectral parameter, Δδ, as a function of composition for liquid binary mixtures has been observed by us for the first time in spite we have studied

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

DMF (mol %)	*δ(NMF – DMF) [Hz]*
2.0	13.0
5.0	13.0
10.0	13.1
20.0	13.2
30.0	13.3
40.0	13.5
50.0	13.6
60.0	13.7
70.0	13.8
80.0	14.0
90.0	14.1
95.0	14.2
98.0	14.2

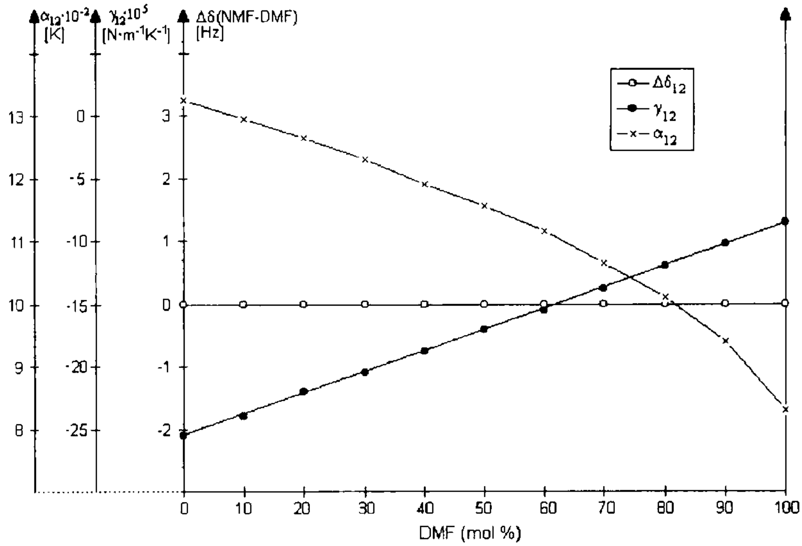

FIGURE 1 Changes in the temperature coefficient of relative permittivity (α_{12}), temperature coefficient of surface tensions (γ_{12}) and the function $\Delta\delta$(NMF–DMF) drawn as a function of composition for the liquid N-methylformamide-N,N-dimethylformamide mixtures, at 298.15 K.

previously more than thirty analogous different mixtures. We have also analysed other structural parameters as changes in the temperature coefficient of relative permittivity and surface tension as a function of composition in purpose to confirm our hypothesis regarding the ideal behaviour of binary liquid mixtures of NMF and DMF.

From the relative permittivity data (see Tab. II) the temperature coefficients of the relative permittivity, denoted α_{12}, viz. $\alpha_{12}=(1/\varepsilon_{12})[d\varepsilon_{12}/d(1/T)]$, were calculated. The composition range of binary liquid mixtures within which α_{12} attains its highest value should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic consideration [6]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. Conclusions drawn from the analysis of changes in $\Delta\delta$ and α_{12} are fully consistent [1–3]. Changes in α_{12} vs. composition of liquid NMF – DMF mixtures are shown in Figure 1.

TABLE II Relative permittivities (ε_{12} and viscosities η_{12}) for binary liquid mixtures NMF – DMF

DMF	ε_{12}				η_{12}
(mol %)	*293.15 K*	*298.15 K*	*303.15 K*	*308.15 K*	*[cP]* *298.15 K*
0.0	197.80	182.40	171.00	159.20	1.6503
2.0	194.63	179.51	168.33	156.73	1.6268
5.0	189.82	175.20	164.32	153.04	1.5921
10.0	181.83	167.91	157.60	146.85	1.5352
20.0	165.92	153.46	144.19	134.51	1.4287
30.0	149.95	139.00	130.77	122.26	1.3294
40.0	134.02	124.52	117.37	109.93	1.2266
50.0	118.07	110.03	103.92	97.62	1.1504
60.0	102.08	95.55	90.50	85.26	1.0707
70.0	86.15	81.12	77.14	72.97	0.9963
80.0	70.21	66.64	63.73	60.65	0.9271
90.0	54.25	52.17	50.31	48.35	0.8622
95.0	46.29	44.91	43.56	42.15	0.8319
98.0	41.51	40.60	39.55	38.47	0.8140
100.00	38.30	37.70	36.87	36.01	0.8024

The temperature coefficient of relative permittivity, α_{12}, as a function of composition do not exhibit any extremum (see Fig. 1), indicating that the mixture can be regarded as almost ideal.

This confirms the conclusion from ^{1}H-NMR spectral data concerning ideality (from the point of view of intermolecular interactions) of liquid binary mixtures of NMF and DMF.

Additionally from the surface tensions data (Tab. III), the temperature coefficient of the surface tensions, denoted γ_{12}, viz. $\gamma_{12}=\mathrm{d}\sigma_{12}/\mathrm{dT}$, were calculated.

The conclusion drawn from the analysis of changes of the temperature coefficient of surface tension seems also to support our hypothesis. The course of changes of the negative value of this coefficient as a function of composition for the binary mixtures is interpreted as the change of the surface entropy of the mixture [7]. Thus, the composition range of binary liquid mixtures within which γ_{12} attains its lowest values has been interpreted as a most stable region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. The function $\gamma_{12}=-(\mathrm{d}\sigma_{12}/\mathrm{dT})$ vs. composition for the liquid binary mixtures of

TABLE III Surface tensions (σ_{12}) for binary liquid mixtures NMF – DMF

DMF *(mol %)*	$\sigma_{12} \cdot 10^3$ $[N \cdot m^{-1}]$ 293.15 K	298.15 K	303.15 K	308.15 K
0.0	40.71	39.58	38.16	36.92
2.0	40.65	39.52	38.13	36.87
5.0	40.52	39.44	38.05	36.85
10.0	40.29	39.28	37.91	36.78
20.0	39.92	38.93	37.72	36.66
30.0	39.51	38.63	37.46	36.52
40.0	38.08	38.33	37.24	36.38
50.0	38.73	37.96	37.05	36.26
60.0	37.32	37.65	36.79	36.12
70.0	37.94	37.33	36.57	36.00
80.0	37.52	37.02	36.30	35.83
90.0	37.14	36.65	36.12	35.71
95.0	36.95	36.49	35.99	35.65
98.0	36.81	36.41	35.90	35.60
100.00	36.73	36.35	35.87	35.58

NMF and DMF (see Fig. 1) is linear, which confirms our assumption regarding the absence of intermolecular interactions between molecules of NMF and DMF in studied mixtures.

Additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of deviations from "ideality" of basic physiochemical properties of these mixtures, i.e. viscosity (η_{12}), relative permittivity (ε_{12}) and surface tensions (σ_{12}). A thorough review of the literature data justifies the correctness of using these parameters in the analysis of intermolecular interactions [3]. In this study, using experimental values of viscosity, relative permittivity and surface tensions at 298.15 K (see Tab. II and Tab. III), deviations from "ideality" of the functions involved have been calculated from equations discussed by us previously [3]. Deviations from "ideality" for all this functions are equal to zero within limits of the experimental error. All these results together with the work of de Visser and Somsen [4] make possible to assume that the NMF – DMF mixtures can be regarded as almost ideal and it is clear that in these mixtures it does not make a great differences if a DMF molecule is surrounded by NMF molecules or by other DMF molecules.

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