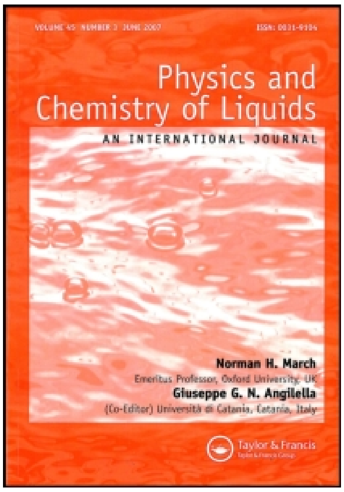

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THE N-METHYLPROPIONAMIDE-WATER SYSTEM. STUDY OF INTERMOLECULAR INTERACTIONS

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The ^{1}H-NMR spectra of liquid binary mixtures, N-methylpropionamide (NMP)-water, were recorded at 298 K over a wide range of mixed solvent compositions. From these data the values of spectral parameter, $\Delta\delta$(NMP-H_2O) were found. The densities (d_{12}) and viscosities (η_{12}) of mixed solvent were measured at 298.15 K, as well as the dielectric permittivities (ε_{12}) at 293.15 K, 298.15 K and 303.15 K. From these new parent data, the values of molar volumes (V_{12}) and their deviations from "ideality" were calculated. Additionally, the values of temperature coefficient of dielectric permittivities (ε_{12}) were found. These structural parameters as functions of concentration suggest the formation of the structures such as clathrate hydrates and the most stable "complexes" (sub-units) of the NMP·$2H_2O$ and 3NMP·$2H_2O$ types.

KEY WORDS: Intermolecular interactions, liquid binary mixtures ^{1}H-NMR spectra.

INTRODUCTION

The N-monosubstituted amides are of interest for their remarkably high dielectric permittivities, a property which has been attributed to extensive chainwise association through hydrogen bonding[1, 2]. Furthermore, the miscibility of these compounds with water and several organic liquids permits the preparation of mixed solvents covering an extremely wide range of dielectric permittivities. The structural properties of the mixed system N-methylpropionamide (NMP)-water are of interest since each component is highly structured through hydrogen bonding, but in different ways. Many of the unique properties of water are determined by its three-dimensional network of bonding[3], while NMP exhibits remarkably long chains of linear associations[4].

Taking into account all the aforementioned literature opinions, as well as those pertaining to the structure of liquid water[3, 4], it may be deduced that in the widely-varied aqueous solution of NMP investigated in the present work, a network of intermolecular H-bonds is formed between water and molecules of NMP under study,sometimes stronger than those responsible for their self-association in the corresponding neat liquids. This opinion seems to be evidenced by our ^{1}H-NMR spectral experiments and supported by parallel analysis of the respective macroscopic characteristics, i.e., the values of viscosity, density, dielectric permittivity, molar volume and temperature coefficient of dielectric permittivity.

EXPERIMENTAL

N-methylpropionamide (Fluka) was stored over molecular sieves and then it was freshly redistilled under vacuum. The water content in the solvent was determined by Karl Fisher method and it was found not to exceed 0.03 wt. %. Water was deionized, distilled over alkaline $KMnO_4$ and finally distilled twice in an argon atmosphere. ^{1}N-NMR spectra were recorded on the Tesla spectrometer of the BS 467 (60 MHz) type, at 298 K. The chemical shift values for proton signals of NMP and water 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 OH-301 type (made in Hungary) with an electric adapter our own construction used to expand its measuring scale of dielectric permittivity up to 220. The viscosities were measured with an accuracy $\pm 0.1\%$, using the Höppler viscosimeter. Solvent densities were measured, using a glass pycnometer of the Lipkin type. The maximum error in the density measurements was $1 \cdot 10^{-4}\,g \cdot cm^{-3}$. All the solutions were prepared by weight.

RESULTS AND DISCUSSION

The review through the literature data indicates that only Hoover[5] in his work attempted to estimate and analyse intermolecular interactions in the liquid mixtures of N-methylpropionamide (NMP) and water. Found by him course of changes of molar volume of transfer of organic component from liquid NMP to aqueous solution at 303.15 K (defined as the volume change of transfering 1 mol of the organic component from the pure liquid to a dilute solution in water) plotted in the function of the composition of the studied mixed solvent NMP-H_2O shows a distinct minimum at the composition corresponding to approximately to 8–10 mol. % of NMP. In his opinion, the most satisfying interpretation lies in the cooperative, specific participation of the solute molecules with water to form a clathrate type of structure[6]. As Franks and Ives[6] are careful to point out, it is not clear what structure is stabilized, since crystalline clathrate hydrates of these solutes are not known but evidently the organic molecules help to form or to stabilize "holes" in the water structure. These holes are able to accommodate, at least partially, the solute molecules with a consequent economy of volume. On this basis, the maximum structural stabilization occurs at the concentrations corresponding to the minimum in the molar volume of transfer curves. These concentrations, representing 6–9 mol of water/mol of organic solute, are consistent with the stoichiometry of known clathrate hydrates[7]. Our studies presented in this work confirm fully conclusions drawn by Hoover referring to the intermolecular interactions between molecules of NMP and H_2O at the composition range corresponding to approximately 10 mol. % of NMP in the studied binary mixture. In this paper, we have measured the values of chemical shift differences $\delta(\mathrm{NMP\text{-}H_2O})$ at 298 K, between the centre of the ^{1}H-NMR signal of the proton of $\text{—N}\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{H}}$ group of the NMP molecules and the centre of the ^{1}H-NMR signal of the water molecules over a wide range of solvent compositions. From these new spectral data the spectral parameters $\Delta\delta(\mathrm{NMP\text{-}H_2O})$ have been found. We have shown in our previous papers[8-10], that the location of this parameter's maximum points at the composition where the strongest intermolecular interactions between the components are displayed. The $\delta(\mathrm{NMP\text{-}H_2O})$ values are shown in Table 1, whereas the $\Delta\delta(\mathrm{NMP\text{-}H_2O})$ values are visualized in Figure 1 as a function of the mixture compositions.

The analysis of the obtained data indicates the presence of maximum of $\Delta\delta(\mathrm{NMP\text{-}H_2O})$ at ca. 8–9 mol. % of NMP. Thus, the conclusion can be drawn that at this composition the strongest interactions between NMP and water molecules and the maximum structural stabilization are displayed.

In our previous paper[8-10] we have shown that the study of changes of temperature coefficient of dielectric permittivity (ε_{12}) plotted in the function of the composition is very useful for analysis of intermolecular interactions present in the binary liquid mixtures. In agreement with the results of Räetzsch[11], the composition where this parameter is displaying a maximum points where the strongest intermolecular interactions between components are displayed.

The newly measured values of dielectric permittivity (ε_{12}) at 293.15 K, 298.15 K and 303.15 K (see Table 2) have been used for calculations of the temperature coefficient of ε_{12}, denoted α_{12}, viz. $\alpha_{12} = (1/\varepsilon_{12})\cdot[d\varepsilon_{12}/d(1/T)]$. Since, values of dielectric permittivity (ε_{12}) at 298.15 K have not been given by Hoover[5] and all other values of

Table 1 Relative ^{1}H-NMR chemical shifts, $\delta(\mathrm{NMP\text{-}H_2O})$, measured at 298 K.

mol. % of NMP	*(NMP-H_2O) [Hz]*	*mol. % of NMP*	*(NMP-H_2O) [Hz]*
1.01	127.5	44.99	121.9
2.10	128.0	47.25	121.6
4.61	129.4	50.01	121.2
7.65	130.5	62.24	119.6
11.41	129.3	66.89	119.0
16.19	127.4	73.49	118.0
22.46	125.5	77.09	117.6
31.07	123.9	83.48	116.7
34.03	123.5	89.09	115.9
37.49	122.9	95.53	115.1
41.51	122.4	98.18	114.5

ε_{12} at other temperatures have been measured with $\pm 3-4\%$ error, we have decided to use our data for calculation of α_{12}. The changes of α_{12} as function of the mixture 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. 9 mol. % of NMP, which confirms the aforementioned conclusion drawn from the ^{1}H-NMR spectral data and Hoover's results[5] on a possibility of formation of the stable clathrate hydrates in the studied mixtures. Further interesting results can be obtained by detailed analysis of the function $\alpha_{12} = f$(mol % of NMP). It indicates that an increasing addition of water to NMP up to ca. 40 mol. % of NMP, where a minimum is reached, causes a rapid drop in the α_{12}values. Further

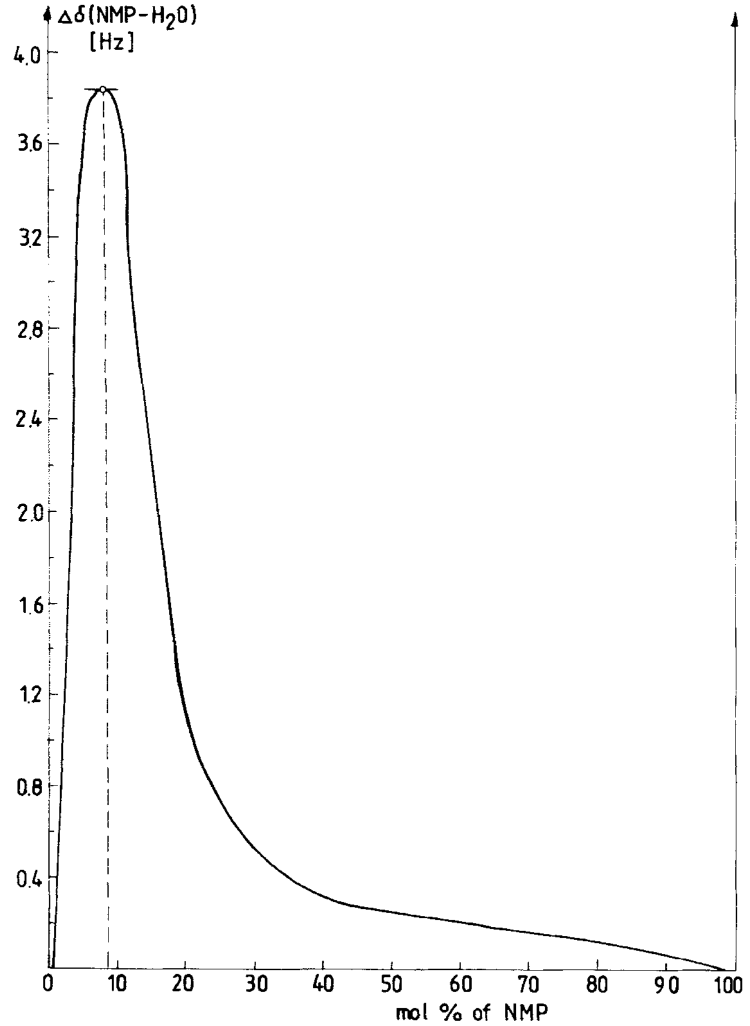

Figure 1 Changes in the function $\Delta\delta(\text{NMP-H}_2\text{O}) = f(\text{mol. \%})$ for the liquid N-methylpropionamide-water mixtures, at 298 K.

Table 2 Dielectric permittivities for the liquid binary mixtures, NMP-H_2O

mol. % of NMP	ε_{12}			*mol. % of NMP*	ε_{12}		
	293.15 K	*298.15 K*	*303.15 K*		*293.15 K*	*298.15 K*	*303.15 K*
0.00	80.09	78.32	76.58	47.25	94.65	92.06	89.58
2.10	80.97	78.92	76.87	50.01	96.12	93.61	91.07
4.61	82.16	79.61	77.06	62.24	106.43	103.13	100.02
7.65	83.05	80.28	77.51	66.89	114.78	111.01	107.21
11.41	83.13	80.98	78.85	73.49	126.87	123.24	118.39
16.19	83.60	81.60	79.61	77.09	134.37	129.61	124.72
22.46	84.58	82.59	80.73	83.48	151.98	141.19	137.18
31.07	87.10	84.92	82.70	89.09	157.22	151.21	145.11
34.03	88.23	85.93	83.72	92.75	164.54	157.91	151.56
37.49	89.61	87.28	84.80	95.53	170.18	163.35	155.95
41.51	91.64	89.06	86.69	98.18	177.91	169.33	161.42
44.99	93.38	90.82	88.40	100.00	185.23	177.11	168.36

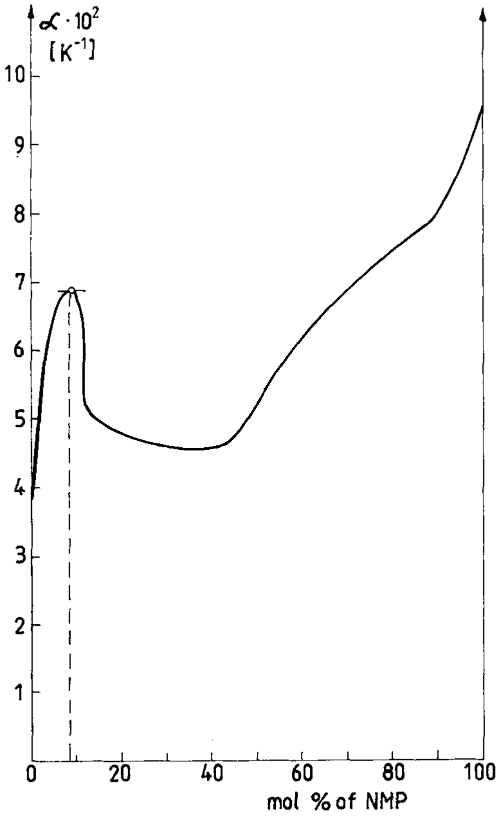

Figure 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid N-methylpropionamide-water mixtures, at 298.15 K.

addition of water to the studied mixtures causes an increase in α_{12}, which results in a maximum at ca. 9 mol. % of NMP. Therefore, it is possible to assume that small amounts of water when being added to neat NMP break its internal structure (composition region up to ca. 40 mol. % of NMP), whereas further addition of water, up to ca. 9 mol. % of NMP, makes the internal structure of the mixed solvent more and more stabilized by formation of hydrogen bonds between molecules of its components. The same analysis made for the water-rich composition region shows a permanent increase of values of the α_{12} coefficient down to ca. 9 mol. % of NMP. Therefore, it seems that molecules of NMP in the studied mixtures, within the composition range between 0 to 9 mol. % of NMP, play role of "structure-makers" in respect to molecules of water of the neat solvent.

In our previous work[12], we have given the literature review of different methods of proper dealing with macroscopic characteristics of liquid binary mixtures and we have calculated from them different structural parameters. The most reliable results for binary liquid systems are obtained from the analysis of deviations from "ideality" of densities $\Delta(d_{12})^{(x)}_{\text{ideal}}$, viscosities $\Delta(\eta_{12})^{(x)}_{\text{ideal}}$, dielectric permittivities $\Delta(\varepsilon_{12})^{(x)}_{\text{ideal}}$ and molar volumes $\Delta(V_{12})^{(x)}_{\text{ideal}}$ (where: x-stands for the mole fraction).

In the present work, using newly measured values of dielectric permittivities (ε_{12}) (see Table 2), viscosities (η_{12}) and densities (d_{12}) (see Table 3), we have calculated the values of all mentioned above deviations from "ideality" from the given below equations:

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

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

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

Table 3 Viscosities (η_{12}) and densities (d_{12}) for the liquid NMP-H_2O mixtures, at 298.15 K.

mol. % of NMP	η_{12} *[cP]*	d_{12} *[g·cm^{-3}]*	*mol. % of NMP*	η_{12} *[cP]*	d_{12} *[g·cm^{-3}]*
0.00	0.8903	0.9971	47.25	2.3236	0.9648
2.10	0.9344	0.9970	50.01	2.4067	0.9630
4.61	0.9941	0.9968	62.24	2.8459	0.9524
7.65	1.0716	0.9964	66.89	3.0523	0.9493
11.41	1.1663	0.9957	73.49	3.3841	0.9461
16.19	1.3284	0.9941	77.09	3.5843	0.9415
22.46	1.5594	0.9909	83.48	3.9778	0.9376
31.07	1.8895	0.9803	89.09	4.3659	0.9351
34.03	1.9644	0.9770	92.75	4.6426	0.9337
37.49	2.0523	0.9735	95.53	4.8657	0.9323
41.51	2.1602	0.9695	98.18	4.0899	0.9314
44.99	2.2566	0.9666	100.00	5.2504	0.9308

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

where:

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

x-stands for the mole fraction.

The nature of the changes of the calculated from these equations values as function of the mixture composition (at 298.15 K) are visualized in Figure 3.

The deviations from "ideality" of density, viscosity and molar volume attain the highest values at the NMP content amounting to about 31–33 mol. %. Thus the NMP-H_2O mixtures with this composition shoud be treated as "dense and viscous to a maximum". This effect, according to suggestions of many researchers[13, 14], can

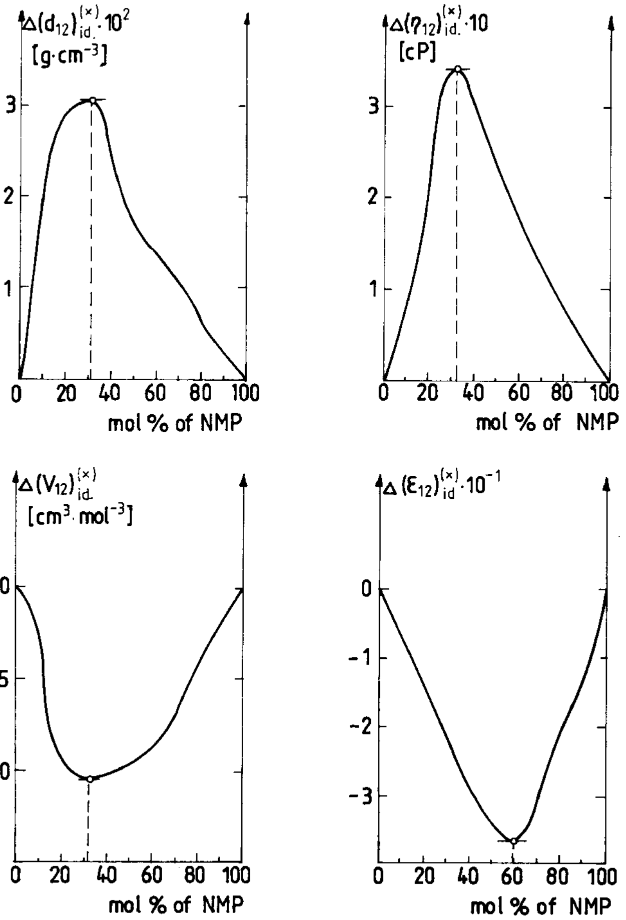

Figure 3 The course of changes of deviations from "ideality" of density, viscosity, molar volume and dielectric permittivity as a function of composition for the liquid N-methylpropionamide-water mixtures, at 298.15 K.

be accounted for by increase in the number of hydrogen bonds between NMP and water molecules, which consequently leads to the formation of stable intermolecular "complex" (sub-unit) of the NMP·2H_2O type. Further increase of NMP in the liquid NMP-H_2O mixtures under investigation brings about the additional structural effects and the appearance of new (with different compositions) intermolecular "complexes" (sub-units). The changes in deviations from "ideality "of dielectric permittivity attain the extreme value at about 60 mol. % of NMP (see Figure 3), which most likely points to the formation of 3 NMP·2H_2O sub-unit in liquid mixtures of NMP and water.

The results of the present study as well as literature data[5] show that in the liquid NMP-H_2O mixtures under investigation, structures such as clathrate hydrates can be formed (at the NMP content up to 10 mol. %) as well as intermolecular "complexes" (sub-units) in which NMP and water molecules are linked by hydrogen bonds, while their stoichiometry is as follows: NMP·2H_2O and 3 NMP·2H_2O. In our opinion the structures as clathrate hydrates are characterized probably by the highest stability.

The structures as clathrate hydrates and the complexes (sub-units) of the NMP·2H_2O and 3 NMP·2H_2O types which are internally H-bonded form subsequently "flickering" internal structures which can mutually convert from one to another. At the present moment it does not seem possible to construct a model of such internal structure and this will require further studies.

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