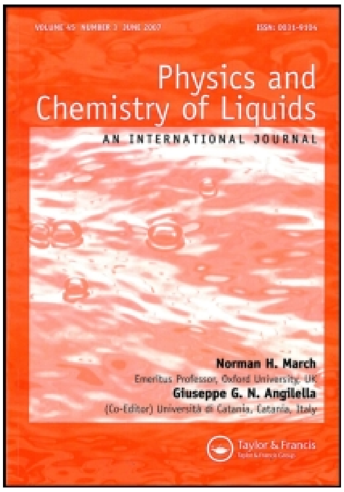

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Cezary M. Kinart[a]; Wojciech J. Kinart[b]; Adam Bald[a]; Adam Szejgis[a]
[a] Department of Chemical Education, University of Lodz, Lodz, Lindleya, Poland [b] Department of Organic Chemistry, University of Lodz, Lodz, Narutowicza, Poland

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STUDY OF THE INTERMOLECULAR INTERACTIONS IN LIQUID N,N-DIMETHYLACETAMIDE–WATER MIXTURES

CEZARY M. KINART*(·), WOJCIECH J. KINART**, ADAM BALD*
and ADAM SZEJGIS*

**Department of Chemical Education, University of Lodz,*
90–136 Lodz, Lindleya 3, Poland
***Department of Organic Chemistry, University of Lodz,*
90–136 Lodz, Narutowicza 68, Poland

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The ^{1}H-NMR spectra of the liquid binary mixtures, N,N-dimethylacetamide (DMA)-water, were recorded at 298 K within nearly the whole range of the mixed solvent compositions. From these data the values of the spectral parameter, $\Delta\delta$(DMA-H_2O) were found. The viscosities and surface tensions of the mixed solvents were measured at 298.15 K, as well as the dielectric permittivities at 288.15 K, 298.15 K and 303.15 K. From all these new parent data, the values of molar volumes and their deviations from "ideality" were calculated. Additionally, the values of the temperature coefficients of dielectric permittivity were found. These structural parameters as functions of concentration suggest the formation of the most stable "complex" (sub-unit) of the DMA·$2H_2O$ type.

KEY WORDS: Intermolecular interactions, physicochemical properties, ^{1}H-NMR spectra.

INTRODUCTION

This paper is a continuation of the series of studies on the internal structures in the liquid binary mixtures, in which amide is one of the two constituents[1–4], from the point of view of correlations existing between the ^{1}H-NMR spectral results and some physicochemical properties of the same binary mixtures (i.e. their densities, dynamic viscosities, relative dielectric permittivities, surface tensions, etc.). Now, the intermolecular interactions in the mixtures of N,N-dimethylacetamide (DMA) and water will be analysed, with using the some comparative approach as previously[1–4]. The internal structures of liquid N,N-dimethylacetamide and water have already been reviewed in our previous papers[1–2]. Taking into account the published data concerning the structure of liquid DMA and H_2O it seemed quite interesting to extend these studies onto all these binary mixtures.

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* To whom correspondence should be addressed.

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and the measurements of dielectric permittivities, viscosities and surface tensions, chemical pure N,N-dimethylacetamide (Fluka) was used. DMA was dried and purified according to the known proc edure[1]. Water was deiomized, distilled over alkaline $KMnO_4$ and finally distilled twice in an argon atmosphere. The ^{1}H-NMR spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 ± 1K. The chemical shift values for proton signals of DMA and H_2O were measured with an accuracy of about ± 0.2 Hz in respect to an external 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). The viscosities were measured with an accuracy $\pm 0.1\%$, using Höppler viscosimeter. The surface tensions measurements were performed with an accuracy $\pm 0.1\%$, using a stalagmometer. All the solutions were prepared by weight.

RESULTS AND DISCUSSION

Petersen[5], Kawaizimi[6] and Nakanishi[7] measured viscosity, density, dielectric permittivity for the studied binary mixtures. However, they have not interpreted their results in terms of stoichiometry and internal structure of intermolecular "complexes" formed by molecules of DMA and water. Also results of measurements of viscosity, density and refractive index of the liquid mixtures of DMA and H_2O carried in the wide temperature range by Himyenko[8] are only available in the monography by Afanasyev[9] in the form of numerical values collected in tables. Similarly as in the previously mentioned works no interpretation of results is given from the point of view of analysis of intermolecular interactions in the studied binary mixtures.

In this work, with the aim of analysing the intermolecular interactions between the components in the liquid binary mixtures DMA-H_2O, we have measured the values of chemical shift differences δ(DMA-H_2O) (in Hz) at 298 K, between the center of the ^{1}H-NMR signals of the methyl groups of DMA molecules and the center of the H_2O protons signal over a wide range of solvent compositions, i.e. from 2.25 mol.% to 99.50 mol.% of DMA. Subsequently, using the same method as previously[1-4], from these new spectral data the spectral parameter $\Delta\delta$(DMA-H_2O) have been found. The δ(DMA-H_2O) values are shown in Table 1 whereas the $\Delta\delta$(DMA-H_2O) values are visualized in Fig. 1 as a function of the mixture compositions.

The location of this parameter maximum values, as has been shown in our previous paper[1-4], are located at the composition with the strongest intermolecular interactions between the components in the liquid binary mixtures. The analysis of the obtained data indicates the presence of maximum $\Delta\delta$(DMA-H_2O) at ca. 33 mol.% of DMA. Thus, the conclusion would be drawn that at this composition the strongest interactions between components are displayed, and that the most stable "complex" (sub-unit) is of the DMA$\cdot$2H_2O type.

In addition to the spectral examinations, the dielectric permittivities of the liquid DMA-H_2O mixtures under investigation were measured within the full composition range at 293.15 K, 298.15 K and 303.15 K (see Table 2).

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

mol. % of DMA	*$\delta(DMA\text{-}H_2O)$ [Hz]*
2.25	162.70
5.83	161.50
9.51	160.50
14.75	159.50
19.01	157.50
25.03	156.00
28.11	155.00
30.09	154.50
33.12	153.50
36.74	151.00
45.08	144.00
56.48	136.00
79.70	121.50
87.32	117.00
98.50	116.50

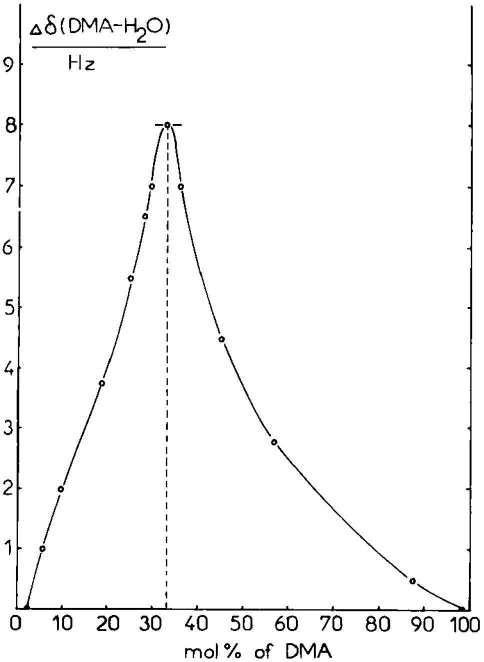

Figure 1 Changes in the function $\Delta\delta(DMA\text{-}H_2O) = f(\text{mol.}\%)$ for the liquid DMA-H_2O mixtures, at 298 K.

From these data, the temperature coefficients of dielectric permittivity, denoted α_{12}, viz.$\alpha_{12} = (1/\varepsilon_{12}) \cdot [d\varepsilon_{12}/d(1/T)]$ were calculated. The composition range of liquid binary mixtures, within which coefficient α_{12} attains the highest value, should be interpreted (as shown in Räetzsch's thermodynamic considerations[10]) as a region

Table 2 Dielectric permittivities for binary liquid mixtures, DMA-H_2O, measured at 293.15 K, 298.15 K and 303.15 K.

mol. % of DMA	ε_{12}		
	293.15K	*298.15K*	*303.15K*
0.00	80.38	78.56	76.74
2.25	78.25	76.49	74.76
5.83	74.98	73.51	71.73
7.11	73.82	72.42	70.61
9.51	72.07	70.49	68.68
11.49	70.53	68.98	67.04
14.75	68.12	66.35	64.59
19.01	65.18	63.48	61.70
22.24	63.07	61.51	59.57
25.03	61.26	59.83	58.01
28.11	59.31	58.19	56.27
30.09	58.29	57.24	55.30
33.12	56.62	55.62	53.76
36.74	55.09	54.16	52.50
41.03	53.49	52.49	51.07
45.08	51.98	51.01	49.77
50.25	50.39	49.05	48.24
56.48	48.55	47.31	46.51
63.81	46.71	45.49	44.60
71.01	44.95	43.72	42.82
79.70	42.91	41.75	40.88
87.32	41.33	40.03	39.25
92.54	40.26	39.05	38.24
98.50	39.20	37.98	37.08
100.00	38.91	37.76	36.80

characterized by maximal intermolecular interactions between two different components of the given liquid mixture. It has been shown in our previous papers$^{1-4}$ that there is a full consistence of conclusions drawn from the analysis of changes in spectral parameter $\Delta\delta$ and coefficient α_{12}. Changes in the α_{12} value versus compositions of liquid DMA-H_2O mixtures are shown in Fig. 2.

The maximum value of α_{12} is found at ca. 33 mol.% of DMA. This confirms the aforementioned conclusion drawn from ^{1}H-NMR spectral data concerning the formation of a "complex" (sub-unit) of the DMA·2 H_2O type. Further interesting results can be obtained by detailed analysis of the function $\alpha_{12} = f$(mol. % of DMA). It indicates that increasing addition of DMA to H_2O up to 8 mol.% of DMA, where a minimum is reached, causes a rapid drop in the α_{12} values. Further addition of methanol to the studied mixtures causes an increase in α_{12}, which results in a maximum of α at ca. 33 mol.% of DMA. Therefore, it is possible to assume that small amounts of DMA when being added to neat H_2O break its internal structure(composition region up to 8 mol.% of DMA), whereas further addition of DMA, up to ca. 33 mol.% of DMA, makes the internal structure of the mixed solvent more and more stabilized by hydrogen bonds between molecules of its components. The same analysis made for the DMA-rich composition region shows a permanent increase of values of the α_{12} coefficient down to ca. 33 mol % of DMA. Therefore, it

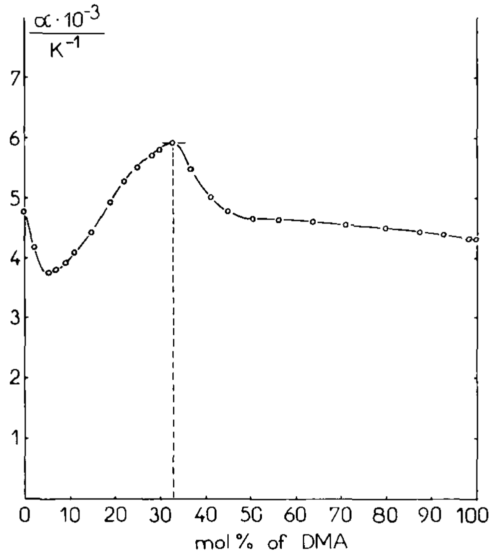

Figure 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid DMA-H_2O mixtures, at 298.15 K.

seems that molecules of H_2O in the studied mixture, within the composition range between 100 to 33 mol.% of DMA, play a role of "structure-makers" in respect to molecules of DMA in the neat solvent.

As has been shown in our previous papers$^{1-3}$, 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}), dielectric permittivity (ε_{12}), molar volume (V_{12}) and surface tension (σ_{12}). In this study, using experimental values of dielectric permittivity (see Table 2), viscosity and surface tension (see Table 3) and literature values of density^5 at 298.15 K, the deviations from "ideality" of the functions involved have been

Table 3 Viscosities (η_{12}) and surface tensions (σ_{12}) for binary liquid mixtures, DMA-H_2O, measured at 298.15 K.

mol. % of DMA	η_{12} *[cP]*	$\sigma_{12}\cdot 10^3$ *[N·m^{-1}]*
0.00	0.8937	71.89
2.12	1.2500	71.99
7.69	2.0249	72.27
16.30	3.2134	74.69
22.72	3.8000	75.45
31.31	3.8668	73.59
42.99	3.2107	67.06
63.73	2.0824	55.44
78.81	1.5800	47.28
100.0	1.0093	36.43

calculated from the following equations:

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

where: M – *molecular weight*

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

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

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

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

$$\Delta(\sigma_{12})^{(x)}_{ideal.} = \Delta(\sigma_{12})^{(x)}_{add.} = \sigma_{12} - (x_1 \cdot \sigma_1 + x_2 \cdot \sigma_2)$$

The values calculated from above equations versus the composition of DMA-H_2O mixtures (at 298.15 K) are shown in Fig. 3.

The values of deviations from "ideality" of densities, viscosities, molar volumes, dielectric permittivities and surface tensions attain the highest values at the composition having ca. 33 mol.% of DMA. Thus, this particular composition would correspond to the most viscous and dense system. This effect can be accounted for by the increase in the number of hydrogen bonds formed between DMA and H_2O molecules which consequently leads to the formation of stable intermolecular

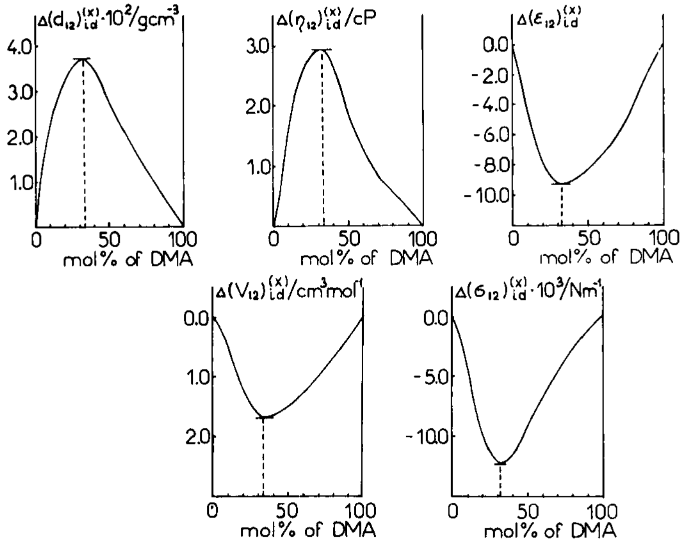

Figure 3 Changes of deviations from "ideality" of density, viscosity, dielectric permittivity, molar volume and surface tension as a function of composition for the liquid DMA-H_2O mixtures, at 298.15 K.

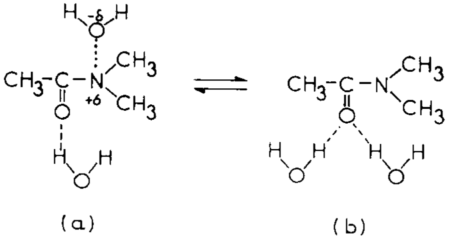

Figure 4

"complexes" of the DMA·2 H_2O type. These results confirm the conclusions drawn from the spectral measurements and the changes in the temperature coefficient of dielectric permittivity.

The hypothetical structures of intermolecular DMA·2H_2O "complexes" (sub-units) formed in the liquid DMA-H_2O system are shown in Fig. 4

In our opinion the "complex" (sub-unit) which hipothetical structure is shown in diagram **b** is considerably more stabilized by the hydrogen bonds $\begin{smallmatrix}\mathrm{O} & \cdot\mathrm{H} \\ \mathrm{O} & -\mathrm{H}\end{smallmatrix}\ \mathrm{O}$ than by the hydrogen bond and electrostatic interaction appearing in structure **a**.

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