ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 10, 1993

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STUDIES ON INTERMOLECULAR INTERACTIONS IN MONOETHANOLAMINE-WATER LIQUID MIXTURES BY MEANS OF ^{1}H-NMR SPECTRA AND ELECTRIC PERMITTIVITIES

The ^{1}H-NMR spectra of liquid binary mixtures made of water and monoethanolamine (MEA) at 298.15 K within the nearly whole range of solvent compositions (i.e. from 3.22 to 72.95 mol% of MEA), were recorded. From these experimental data, the chemical shift differences, $\delta(MEA - H_2O)$, between the proton signals of water and the methylene groups of monoethanolamine were determined and, subsequently, the values of the spectral parameter $\Delta\delta(MEA - H_2O)$ were found graphically for the studied mixtures. From the measurements of electric permittivities (ε) at 293.15, 298.15 and 303.15 K and over the whole range of solvent compositions, values of the temperature coefficients of ε, viz. $\alpha = (1/\varepsilon)\cdot[d\varepsilon/d(1/T)]$, were determined.

The thus results obtained would indicate at the formation of some relatively most stable "complexes" (sub-units) $MEA \cdot 2H_2O$ in the liquid mixtures under investigation.

This paper continues my previous studies on the internal structures of various liquid binary mixtures, with emphasis put on mutual intermolecular interactions through the hydrogen bonding [1-4]. The ^{1}H-NMR spectra presented herein were recorded for binary solutions of monoethanolamine (MEA) and water (H_2O) within the nearly full range of compositions. Subsequently, based on these data, the relative differences in the chemical shift values between the center of the proton signal of H_2O and

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the center of the MEA methylene groups signal, δ(MEA - H_2O), were calculated. The graphical method was used as previously [1-4], for determination of the useful spectral parameter Δδ(MEA - H_2O) in the mixtures studied.

Independently, the measurements of electric permittivities (ε) were performed for the analyzed system at three temperatures and the values of the temperature coefficients of ε were calculated at 298.15 K.

The choice of the said binary mixture for the present studies was due to the fact that monoethanolamine, being the simplest aminoalcohol, possesses both the $-NH_2$ and the -OH groups which are apt to strong intermolecular interactions. Thus, it is able to form the fairly stable hydrogen bonding with water molecules, where either the amino or the hydroxyl group is involved or the both [5-10]. The aqueous solutions of MEA were also the "model" system for the studies on some biological objects [11]. They are as well widely used in chemical technology as surfactants [11].

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and the measurements of electric permittivities, monoethanolamine (p.a., Fluka) was used. After its preliminary drying over molecular sieves 4 Å, MEA was purified and dried by a fractional distillation under reduced pressure. For all the experiments, redistilled water from a quartz glass distiller was used.

All the binary solutions studied were prepared by weight. The ^{1}H-NMR spectra (at 298.15 ± 1 K) were recorded on a Tesla spectrometer of the type BS 487C (80 MHz). The chemical shift values for the proton signals of MEA and water in each binary mixture were measured with an accuracy of ±0.2 Hz in relation to an external standard, HMDS (hexamethyldisiloxane).

The electric permittivity measurements were performed with an accuracy of ±0.2%, using a bridge of the type OH-301 (made in Hungary). All the measurements of electric permittivities were performed at 293.15, 298.15 and 303.15 K. Each temperature was maintained with an accuracy of +0.01 K, using a cascade thermostatic system.

RESULTS AND DISCUSSION

Monoethanolamine (MEA) belongs to a group of organic compounds named aminoalcohols. In living organisms it is formed from serine by its decarboxylation [12-13]. The IR studies [14] have revealed that in dilute tetrachloroethylene solutions, three different forms of MEA are simultaneously present Fig. 1.

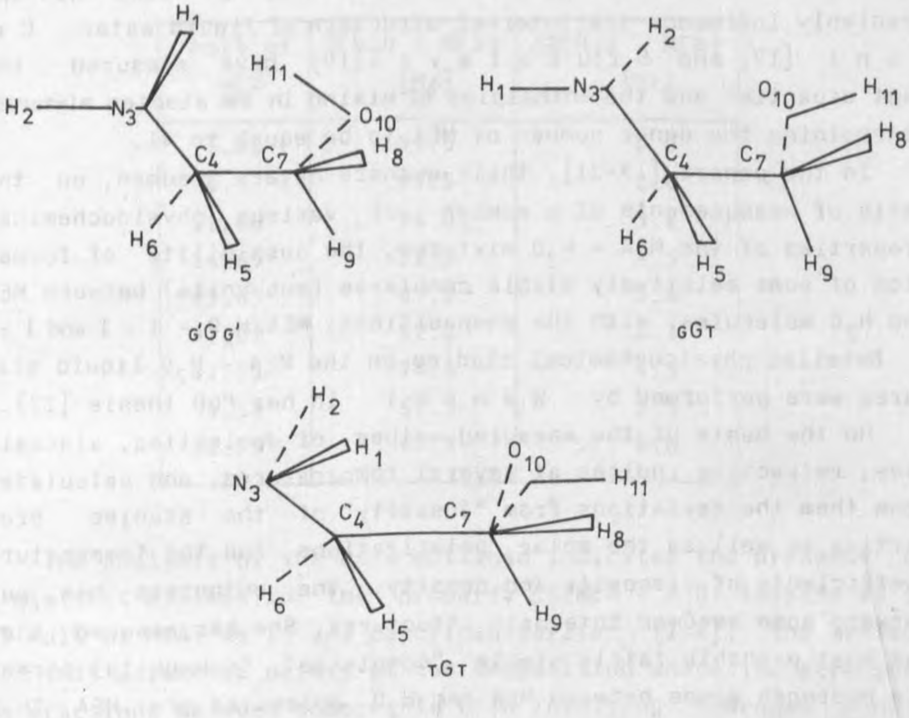

Fig. 1

The most stable is the form ($_{G'}G_{G'}$), in which the internal hydrogen bond, O-H...N, is formed between the hydroxyl group (proton donor) and the amino group (proton acceptor). Two other forms are: the form $_{G}G_{T}$ with no internal hydrogen bond (less stable than the former by ca. 2.8 kJ/mol), and the form $_{T}G_{T}$, where $-NH_2$ is a proton donor and -OH is a proton acceptor (it is less stable than the form $_{G'}G_{G'}$ by 5.6 kJ/mol). The presence and the relative stability of the conformer $_{G'}G_{G'}$ was confirmed both by ab initio calculations [5] and by microwave measurements in the gas phase [6-9] and in the solid phase [10]. The structure of liquid water was briefly discussed in the previous paper [3]. There are several reports in the literature discussing mutual interactions between MEA and H_2O through intermolecular hydrogen bonds [5-10]. Rodnikova [15, 16] has studied dilute aqueous solutions of MEA, using the dielectrometric method. She has concluded that up to 8 mol% of MEA, considering the structure and the directions of bonds in the molecules, MEA does not appreciably influence the internal structure of liquid water. Cabani [17] and Brusaleva [18] have measured the heat capacties and the enthalpies of mixing in the studied mixtures, determining the donor number of MEA to be equal to 41.

In the papers [19-21], their authors have assumed, on the basis of measurements of a number of various physicochemical properties of the MEA - H_2O mixtures, the possibility of formation of some relatively stable complexes (sub-units) between MEA and H_2O molecules, with the compositions: MEA/H_2O = 1 : 1 and 1 : 2.

Detailed physicochemical studies on the MEA - H_2O liquid mixtures were performed by Wencel in her PhD thesis [22].

On the basis of the measured values of denisities, viscosities, refractive indices at several temperatures, and calculated from them the deviations from "ideality" of the studied properties as well as the molar polarizations and the temperature coefficients of viscosity and density, the authoress has put forward some assumed internal structures. She has assumed that the most probable fairly stable "complexes" (sub-units) formed via hydrogen bonds between MEA and H_2O molecules are: MEA $\cdot$ $2H_2O$ and MEA $\cdot$ $3H_2O$.

In order to confirm or to verify the existing literature points of view concerning mutual interactions between MEA and H_2O molecules, in this work I have newly measured the values of chemical shift differences, δ(MEA - H_2O) (in Hz), between the centers of the ^{1}H-NMR signals of water molecules and the centers of the ^{1}H-NMR signals of $-CH_2-$ groups in molecules over a wide range of solvent compositions, 3.22 to 72.95 mol% of MEA.

Subsequently, using the same method as previously [1-4], from these new spectral data the values of the spectral parameter $\Delta\delta$(MEA - H_2O) were graphically determined. The δ(MEA - H_2O)

and the $\Delta\delta(MEA - H_2O)$ values are shown in Tab. 1, and they are visualized in Fig. 2 as a function of the mixture compositions.

Table 1

Relative chemical shifts, $\delta(H_2O - MEA)$, and ^{1}H-NMR spectral parameters, $\Delta\delta(H_2O - MEA)$, measured at 298.15 K

mol% of MEA	$\delta(H_2O - MEA)$ [Hz]	$\Delta\delta(H_2O - MEA)$ [Hz]
3.22	96.5	0.0
6.97	95.5	2.0
11.40	94.0	3.4
16.65	91.5	4.5
23.05	87.5	5.4
31.01	82.0	6.1
41.15	74.0	4.3
54.51	62.5	2.5
72.95	47.5	0.0

The analysis of the data obtained indicates the presence of a distinct maximum for the property $\Delta\delta(MEA - H_2O)$ located at ca 33 mol% of MEA. As it was described earlier [1-4], the maximum for this parameter points at the composition where the strongest interactions between components with involving hydrogen bonds, are displayed. Thus, from the new spectral results thus obtained, the conclusion would be drawn that the most stable "complex" (sub-unit) between MEA and water molecules is of the $MEA \cdot 2H_2O$ - type.

In order to support this conclusion, I also performed the independent measurements of electric permittivities (ε) over the whole range of solvent compositions, at the temperatures 293.15, 298.15 and 303.15 K (the measured values of ε are summarized in Tab. 2). Using these data, I have calculated the values of the temperature coefficients of ε, denoted α, at 298.15 K. This coefficient, in agreement with the results of Raetzsch

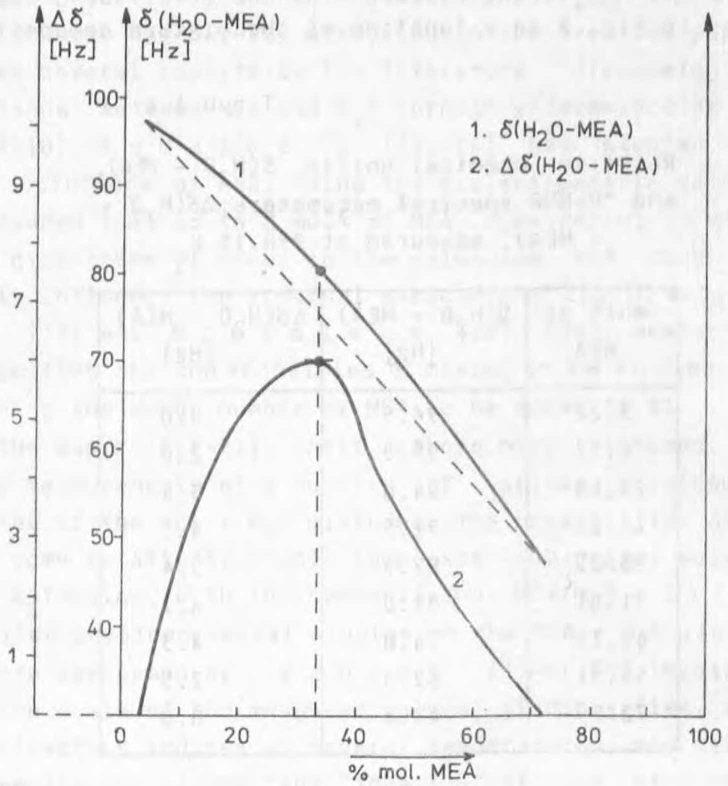

Fig. 2. Changes in the functions, $\delta(H_2O - MEA) = f(mol\%)$ and $\Delta\delta(H_2O - MEA) = f(mol\%)$, for the liquid mixtures water-monoethanolamine, at 298.15 K

[23], should be used as one of the criteria for estimating the mutual interactions between polar components of binary solvents. The composition, where this spectral parameter is displaying a maximum points at the "complex" with a strongest intermolecular hydrogen bond interaction between the components. In the previous papers [1-4] I have shown that there is a fairly good agreement in conclusions drawn from the both maxima: for the spectral parameter $\Delta\delta(MEA - H_2O)$, and for the α property.

Using the experimental values of electric permittivities, I have calculated the values of their deviations from "ideality" as a function of the MEA molar fraction as follows:

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

Table 2

Dielectric permittivities for binary liquid mixtures, H_2O - MEA, measured at 293.15, 298.15 and 303.15 K

mol% of MEA	ε		
	293.15 K	298.15 K	303.15 K
0.00	80.37	78.48	74.95
3.22	78.47	76.51	73.31
6.97	76.18	74.04	70.38
11.40	72.98	70.78	66.79
16.65	69.11	66.87	62.35
23.05	64.28	61.74	55.91
31.01	59.75	56.61	50.36
41.15	55.49	53.43	47.84
54.51	51.07	49.96	45.47
72.95	45.58	44.93	41.89
100.00	38.11	37.70	36.88

The values of ε, α and $(\Delta\varepsilon_{12})_{ideal.}$ as functions of the solvent composition are shown in Fig. 3.

Analysis of the function $\alpha = f(\text{mol\% MEA})$ indicates that the increasing addition of MEA to water up to 10 mol% of MEA nearly does not change the values of α. This suggests lack of appreciable structural changes in liquid water upon addition of such small quantities of MEA, and it also confirms the results of Rodnikova [15, 16].

The values of α reach a maximum at the composition having ca 33 mol% of MEA. Thus, for this composition one would expect the strongest interactions between MEA and water molecules, and the formation of some fairly stable "complex" (sub-unit) of the MEA $\cdot$ H_2O - type.

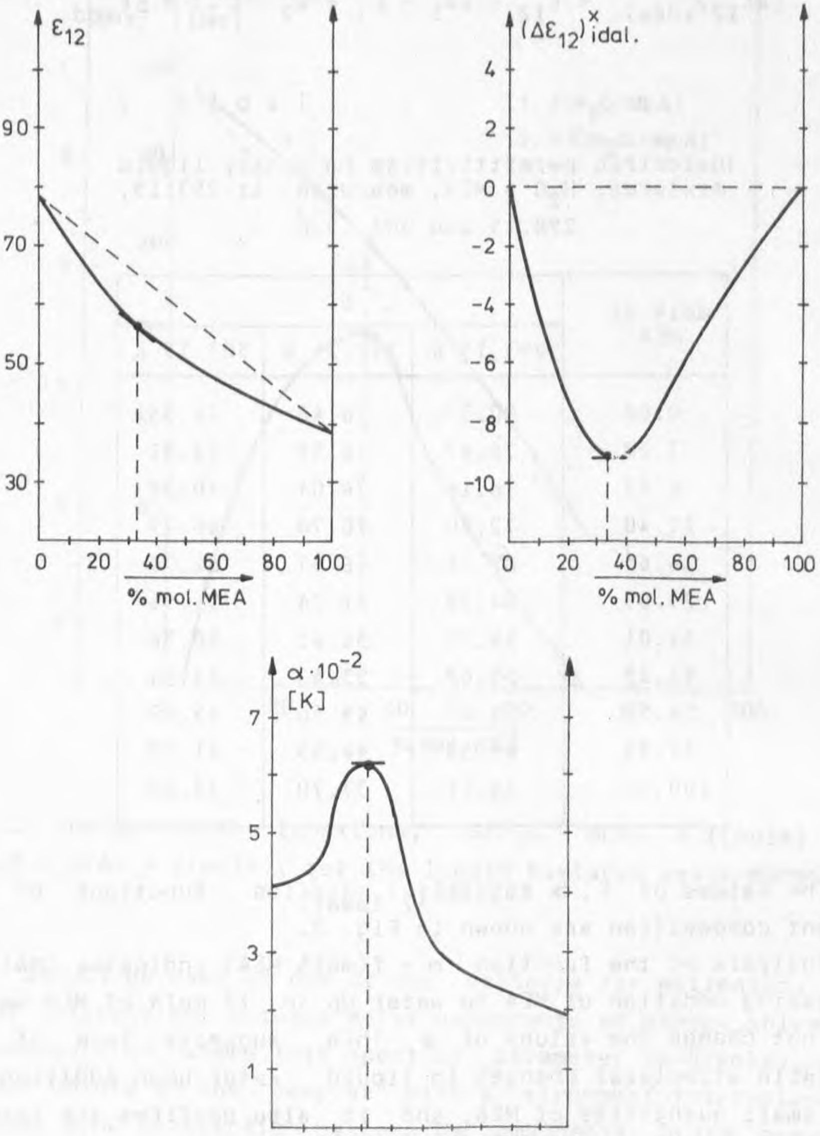

Fig. 3. Changes in temperature coefficients of dielectric permittivity drawn as a function of composition for the liquid mixtures water-monoethanolamine, at 298.15 K

This confirms the former conclusions drawn above and based on the analysis of the ^{1}H-NMR spectral parameter, $\Delta\delta$(MEA - H_2O). In the same area of the concentrations there is also a maximum deviation from "ideality" for electric permittivities as a function of the MEA molar fraction (see Fig. 3).

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 MEA - H_2O liquid binary mixtures are those of the MEA · $2H_2O$ - type. Other "complexes" (sub-units) though they are quite possible, are apparently less stable.

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BADANIA ODDZIAŁYWAŃ MIĘDZYMOLEKULARNYCH W MIESZANINACH MONOETANOLOAMINY Z WODĄ METODĄ POMIARU ICH WIDM ^{1}H-NMR I PRZENIKALNOŚCI ELEKTRYCZNEJ

Zmierzono widma ^{1}H- NMR ciekłych mieszanin wody i monoetanoloaminy (MEA) w temperaturze 298,15 K (w zakresie od 3,22 do 72,95 mol% MEA) oraz wartości przenikalności elektrycznej dla tego układu w temperaturach 293,15, 298,15 i 303,15 K, w pełnym zakresie składu mieszanych rozpuszczalników. Z danych doświadczalnych wyznaczono przebiegi względnych przesunięć chemicznych, δ(MEA - H_2O), pomiędzy środkami sygnałów pochodzących od wody i od grup metylenowych monoetanoloaminy, a następnie wartości parametru spektralnego, $\Delta\delta$(MEA - H_2O), w badanych mieszaninach. Z temperaturowych zależności przenikalności elektrycznej wyznaczono dla badanych układów wartości temperaturowego współczynnika przenikalności elektrycznej α.

Otrzymane wyniki wskazują na tworzenie się względnie trwałych "kompleksów" o składzie MEA · $2H_2O$ w ciekłych mieszaninach wody i monoetanoloaminy.