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SPECTROSCOPIC INVESTIGATIONS OF AQUEOUS NONELECTROLYTE SOLUTIONS

The observation of changes of water combination band $(\bar{V}_{1,3} + V_2)$ [1] under the influence of organic solvents (ethylene glycol, glycerol, acetone, DMSO, dioxane, DMF) over the whole concentration range was carried out.

INTRODUCTION

Analysing, in our previous works [1, 2] the changes of water spectra parameters caused by the temperature effect on the electrolytes dissolved in it or by monohydric alcohol we have chosen combination band $(\bar{V}_{1,3} + V_2)$ of -OH groups as particularly suitable for the investigations. The changes of half width of this band seemed to fit the criterion of ordering and disordering influence on water structure.

Examining water-alcohol mixtures we have also observed that the band intensity as the function of composition seems to point to the changes of some interactions in the solution.

The combination band of water chosen by us was also examined by Sidorova [3] and Kochnev [4]. Observing the wave number changes of combination band $(\bar{V}_{1,3} + V_2)$ with the composition change of water-alcohol systems, Sidorova et al. [3] came to the conclusion on ordering influence of small portions of monohydric alcohols on water structure similar to those in our works.

The interpretation of the effect of ions on water structure led however to incompatible conclusions relative to the criteria accepted by the mentioned authors and by us.

In this work we present spectroscopic investigations of aqueous solutions of some organic substances often used both in science and technology as solvents.

EXPERIMENTAL

Measurements were carried out using a Unicam SP-700 spectrometer [1, 2] at the temperatur 25°C. The cell path length was 0,2 mm. Stability ±0,5°C.

RESULTS AND DISCUSSION

Ethylene glycol-water

The absorotion in maximum (intensity) dependence of water combination band $(\bar{V}_{1,3} + V_2)$ in binary mixture on ethylene glycol content $E = f(x)$ (x is the mole per cent of organic solvent) is expressed by the line with inflexion points (fig. 1). These points make it possible to divide the whole range of the investigated mixture into four regions: I:0-7 mol. %, II: 7-32 mol. %, III: 32-54 mol. %, IV: 54-100 mol. % of ethylene glycol. The observed changes of the $E = f(x)$ function course suggest certain differences in properties of the mixture relative to the concentration of the components.

The course of relation of the half-width $(W_{1/2})$ of the discussed band and the mixture composition is also illustrated by the broken line (fig. 2) the inflexion points of which divide the whole composition range into four regions. They correspond exactly to the regions indicated by the absorption concentrational relation course.

In the 1st region a slight decrease of the half-width in relation to its value in pure water can be observed. In an ear-

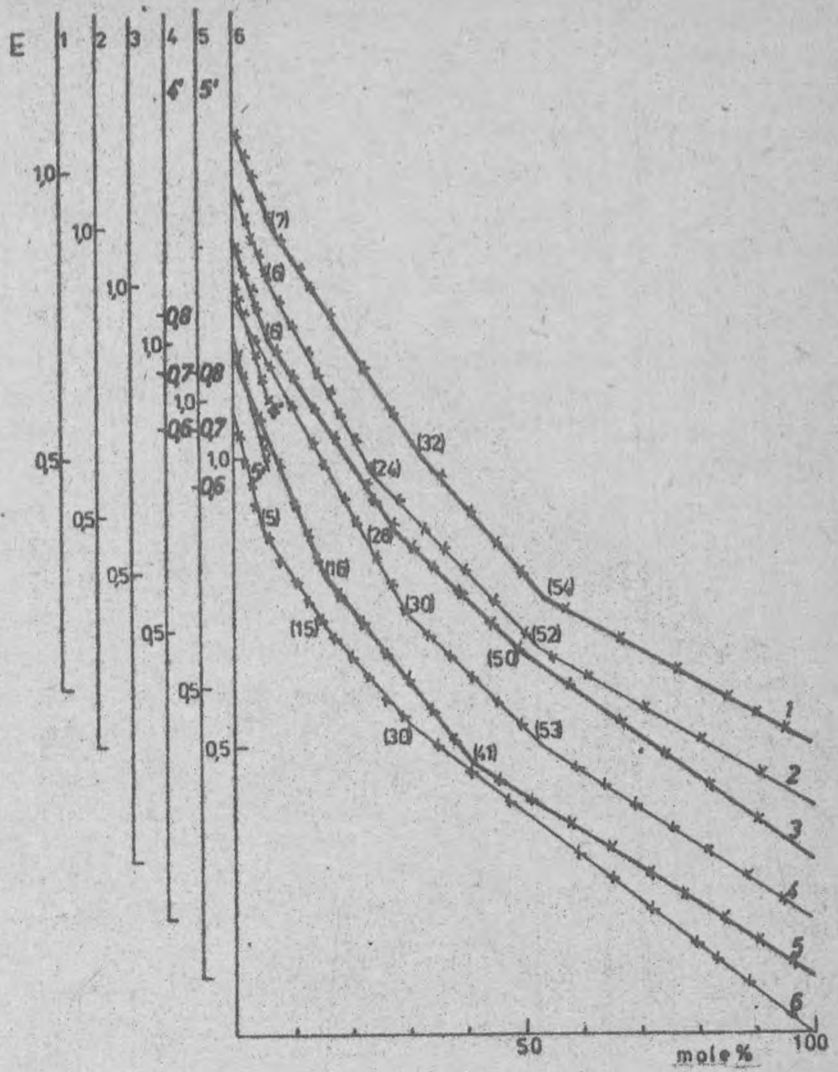

Fig. 1. The dependence of water combination band absorption in maximum on the concentration of organic in mixtures: 1 - water-ethylene glycol; 2 - water--glycerol; 3 - water-aceton; 4 - water-DMSO, 5 - water-dioxane, 6 - water--DMF. The dependence of absorption in maximum of the first overton-OD band on the concentration of organic solvent in mixtures: 4' - water-DMSO; 5' - water-dioxane

lier paper [1] the influence of the temperature changes on the bands of combination vibrations of the OH-group of water has

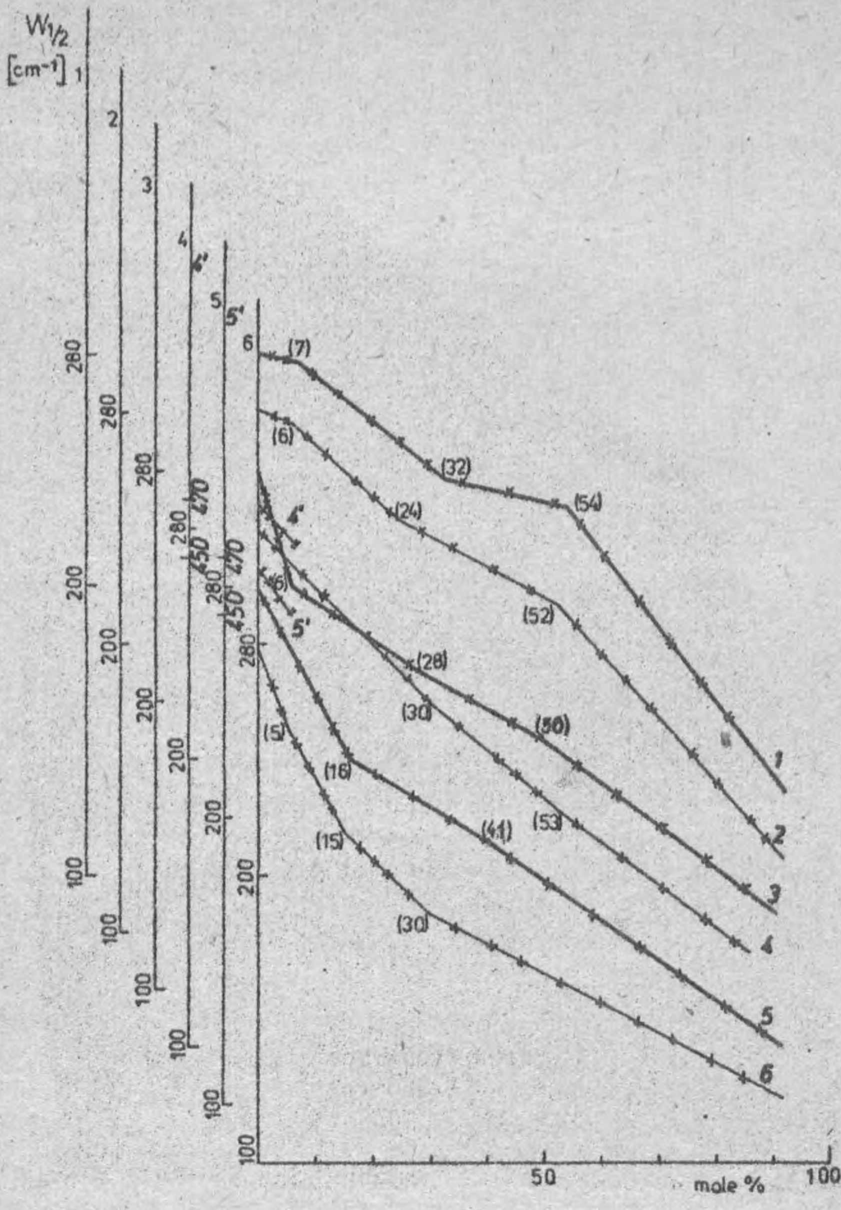

Fig. 2. The course of dependence of half-width of water combination band on the concentration of organic solvent in mixtures: 1 - water-ethylene glycol; 2 - water-glycerol; 3 - water-aceton; 4 - water-DMSO; 5 - water-dioxane; 6 - water-DMF. The dependence of half-width of the first overtone - OD band on the concentration of organic solvent in mixtures: 4' - water-DMSO; 5' - water-dioxane

been investigated. It has been noticed that the half-width may be accepted as the index of "ordering" and "disordering" influence on the water structure. The above criterion has been succesfully applied to the influence of electrolyte and monohydric alcohols on water structure. Taking into consideration the above results it may be assumed that the addition of glycol breaks the structure of water in the system. It reveals in the decrease of the half width of the investigated band over the whole composition range. Krestov [5] has interpreted the relations between argon apparent heat capacity in the discussed system and the mixed solvent composition and he has drawn the conclusion, that glycol exerts destructive effect on water structure.

The acidity functions for water-organic series led Boyer et al. [6] to the conclusion that the addition of diols to water causes the disturbance of the threedimentional water clathrate compounds. The analysis of the relation that holds between wave number ν_{max} variations of the investigated band and the investigated mixture composition (fig. 3) may lead to opposite conclusions. The discussed function is in the 1st region a monotonously decreasing curve.

According to Sidorova [3, 7] the decrease of the wave number of the OH - groups combination band shows that water structure is ordered by the added component. Investigating the wave number concentrational variations in water-glycol mixtures, Kochnev [4] has obtained the course of function similar to that of ours. According to the author the drastic wave number decrease in the first region substantiates the ordering influence of nonelectrolyte as it is in the case of monohydric alcohols. In the II-nd range a drastic decrease of the half - width can be observed which substantiates, assuming the above mentioned criterium [1], the increasing destructive influence of glycol on water structure with the concentration growth.

In this range the occurance of 2 : 1 water-glycol associates is probable. Above the 1-st region the wave number - concentration function has the form of a less rapidly decreasing curve in the whole composition range, which is rather diffi-

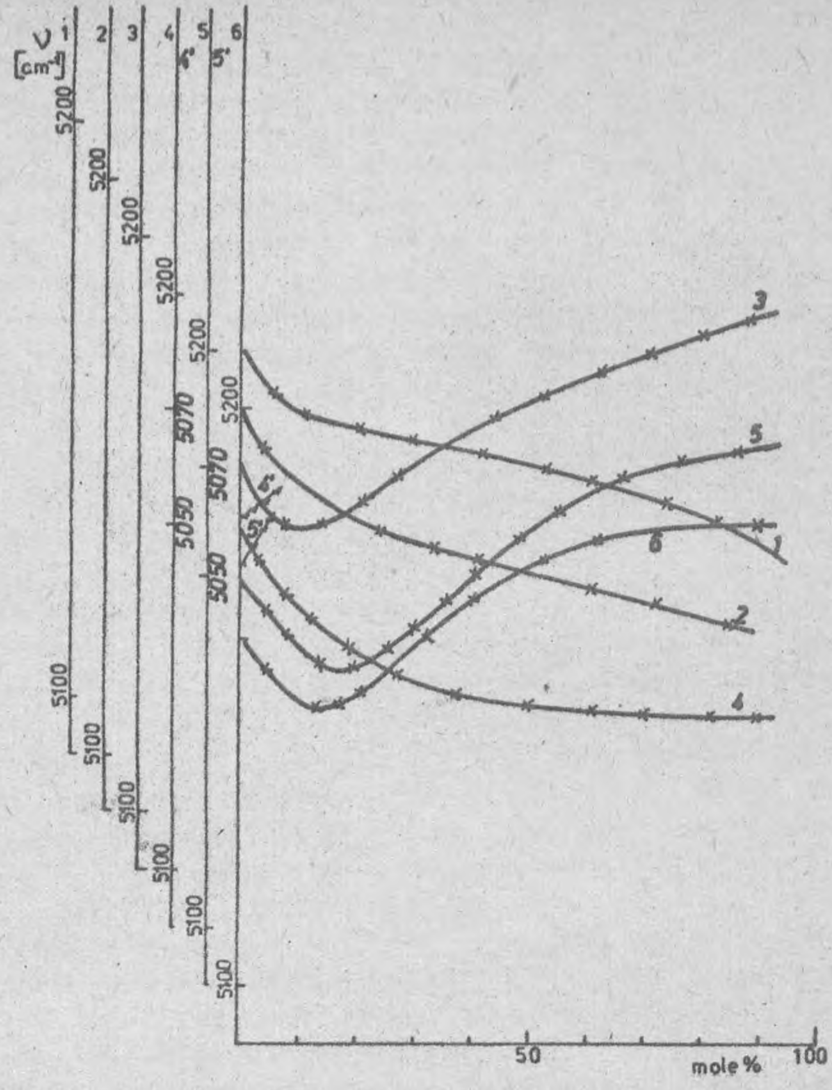

Fig. 3. The course of dependence of wave number ν of water combination band on the concentration of organic solvent in mixtures: 1 - water-ethylene glycol; 2 - water-glycerol; 3 - water-aceton; 4 - water-DMSO; 5 - water-dioxane; 6 - water-DMF. The dependence of wave number ν of the first overtone - OD band on the concentration of organic solvent in mixtures: 4' - water-DMSO; 5' - water-dioxane

cult to explain now. Investigating the viscosity and density of water-glycol mixtures, Irany [8] has observed an increase of viscosity starting with 30 mol. % contents.

The course of these relations may hint at a change of properties between water-like structure solution and associated structure. At about 25 mol. % of ethylene glycol the maximum of water-ethylene glycol [9] mixing heat occurs. In the III-rd region a less drastically decreasing half-width is observed. It can be assumed that the shift from 2 : 1 to 1 : 1 associated structure occurs.

In the IV-th region, above 50 mol. % as the concentration of the organic substance grows, we have probably to do with the glycol-like structure.

Above the concentration of 60 mol. % the diol value of electrolyte solutions activity coefficients is water-glycol mixtures decreases drastically [10].

Basing on the results of free energy of transfer of alcali metal chlorides from water to water-glycol mixtures Wells [11] has observed that in the range of 75 mol. % of organic solvent the stabilization of "extra" water icebergs by ethylene glycol OH-group occurs.

Glycerol-water

Alike in water-glycol systems the relation between the intensity of water combination band and glycerol concentration E = f(x) is expressed by line (fig. 1) with three inflexion points. These points allow to distinguish three water-glycerol mixture composition ranges. They are as follows: I-st range 0-6 mol. % of glycerol, II-nd 6-24 %, III-rd 24-52% and IV-th 52-100 mol. % of glycerol.

The observed changes of the discussed curve course hint, similarly to the case of ethylene glycol-water mixture, at the existance of certain differances in the mixture structure depending on the changes of the component concentration. The division of the whole composition range of glycerol-water mixture may be performed on the basis of the dependence of half-width changes of the investigated band on glycerol content (fig. 2).

In the first range we can observe a slight half - width slope alike in the case of water-glycol mixture. It may be assumed that this slope substanciates a faintly disturbing effect of glycerol on water structure. The acid functions determined by Bayer et al. (6) for the water-organic series lead to a similar conclusion. According to the authors, the addition of trioles causes destruction of three dimensional water clathrates. Calorimetric and densymetric measurements have led Paola and Bellean [12] to the conclusion that in water-glycerol solutions there exists much smaller ordering than in pure water. According to these authors the effect of glycerol on water structure is comparable to that of urea.

A different conclusion may be drawn from the analysis of ν_{max} wave number of the combination band changes relative to the glycerol concentration. Basing on Sidorova's opinion [3, 7] the decreasing values of this function in comparison to the value for pure water show the ordering effect of the added substance on water structure.

Examining the relation between the apparent thermal capacity of argon and the mixed solvent composition, Krestov came to a similar conclusion. In the discussed system the author has observed a similar course of changes of Cp values as it is in the case of monohydric alcohols, which in his opinion order water structure.

Łogwinienko and Pluta [13] have measured KI solution heat in water-glycerol mixtures. The heat isotherms of KI dissolving in the above mentioned system display the shift from type II, occuring only in aqueous solutions, to the character typical for nonaqueous solvents (I-st type). This shift corresponds to about 8 mol. % of glycerol content, near the value corresponding to the mixture composition in the first inflexion point of $E = f(x)$ function.

It may be assumed that starting from the given composition in water-glycerol mixture, water structure is obviously disturbed and this process intensifies, with the organic solvent concentration growth.

In the II-nd range a drastic slope of half-width can be observed. According to the previously expressed opinion it may substantiate a more intensive breaking of water-like structure of a solution by glycerol molecules.

In the above mentioned solution both density and viscosity [14] of the discussed system change their values drastically. It provides a strong argument for a distinct change of structure and properties of mixture.

When the glycerol content reaches 25 mol. % the occurance of 1 : 3 type glycerol-water associates is probable.

The relation between the wave number and concentration both in this range and in the two remaining ones is represented by a monotously decreasing curve.

Examining the standard SEM of glycerol-water and electrolyte system within the range at 0-20 mol. % of glycerol Khoo [15] has noticed some structural changes. According to this author the addition of trioles to water at first causes the growth of the structural order (about 12%) and the further quantities cause structure breaking in relation to water. A slight slope of the half - value width can be observed in the III-rd range. The occuring inflexion at 52 mol. % of glycerol concentration, alike in water-monohydric alcohol systems [16] suggests the possibility of shifting of 1 : 3 associates into 1 : 1 agregates. The IV-th and the last of the ranges is probably the region of passing from mixed associates structure to glycerol-like structure.

Acetone-water

The intensity and half-width dependence of combination band ($\bar{V}_{1,3} + V_2$) of OH group of water on acetone concentration is expressed by the lines [1, 3] with four inflexion points, which make it possible to distinguish four characteristic regions i. e. I: 0-6 mol. %, II: 6-28 mol. %, III: 28-50 mol. %, IV: 50--100 mol. % of acetone.

In the first region a drastic decrease of half-width in comparison to a minimum decrease in glycol and glycerine systems can be observed.

On the grounds of the previously presented point of view

[1] it can be assumed that the addition of acetone causes water structure breaking in the investigated system.

A similar supposition is formulated by Krestov [5] who interpreted the dependence of apparent heat capacity of argon on the acetone-water mixture composition and has drawn the conclusion about acetone distructive influence on water structure. According to our and Kochnev's results, the wave number values rapidly decrease in the discussed region (fig. 3). In Sidorova's et al. opinion [3, 7] this course proves the ordering effect of this substance on water structure. A noticed inflexion of the function of half-width of C = O acetone band at about 8 mol. % of organic solvent i. e. near observed by us (6 mol. %) [17]. According to the author this course of function may be associated with a change of specific nonelectrolyte molecule-water interactions.

In the II-nd region a less drastic decrease of half - width can be obseved (fig. 2). The wave number value in this range increases with acetone concentration. It can be assumed that acetone molecule having two free electrone pairs may form 1 : 2 type associates with two water molecules (which is substantiated by the second characteristic inflexion) (fig. 2). The possibility of existence of such type of complex is also suggested by spectroscopic works of Fox [18] and Nabieruchin [19].

In the discussed concentration range maximum of viscosity and ultrasound velocity [20]; diffusion activation energy [21] and maximum of proton relaxation time of acetone [22] could be found.

In the III-rd region half-width decreases quite rapidly. The shift from 1 : 2 into 1 : 1 water-acetone agregates is possible in this region. This supposition is in accordance with Nabieruchin [19] and Kęcki's [23] opinion.

Above 50 mol. % of acetone concentration the region of aqueous solutions of acetone begins.

Its properties become similar to those of pure acetone when the concentration of nonelectrolyte grows.

DMSO - water

The intensity dependence of $(\bar{V}_{1,3} + V_2)$ water combination band on DMSO concentration $E = f(x)$ in a binary mixture is expressed by the line (fig. 1) with the inflexion points. These points make it possible to divide the whole area of the investigated mixture into three regions. I: from 0 to 30 mol. %, II: from 30 to 53 mol. % and III: from 53 to 100 mol. % of organic solvent. The observed changes of $E = f(x)$ function course suggest certain differences in properties of the mixture relative to the component concentration. The course of relation of the half-width $(W_{1/2})$ curve of the discussed band vs. the mixture composition is also idustrated by the line (fig. 2). The inflexion points of this curve divide the whole composition area into three regions. They correspond exactly to the regions indicated by the absorption relation course.

In the I-st region a drastic change of the half-value width in relation to its volue in pure water can be observed.

The density measurements of this system also [24] suggest the destabilization of structure and hydrogen bonds breaking by DMSO molecules which occur in threedimentional water network.

Basing on the data concerning partial molal entropy and the heat of hydrogen solution in the discussed - mixture, Symons [25] suggests the occurance of 3 : 1, 2 : 2 water-DMSO associates. The viscosimetric investigations by Cowie and Toporovski [26] and Miles [27], spectroscopic and calorimetric works by Fox and Whittingham [28] and Kelm [29] electrochemical works by El - Harakany [30], Lindeberge's magnetic nuclear resonance [31] provide a strong argument for the existance of such associates.

The analysis of the relation between changes of ν_{max} wave number of the examined band and the mixture composition allows to conclude that DMSO affects water structure. This function is a curve decreasing from pure water values up to the concentration of about 30 mol. % of DMSO. According to Sidorova [3, 7] it may substantiate the ordering influence of nonelectrolyte on water structure. The discrepancies arising through the analysis of the changes of half-value width and wave number of the combination band ($\bar{V}_{1/2} + V_3$) made us perform a series of spectroscopic measurements for DMSO - H_2O system within the concentration range 0-6 mol. % of organic solvent. We have examined the dependence of intensity, half-value and wave number on DMSO concentration for the first 2 ν_{OH} band.

Intensity and half-width decrease with the concentration growth (fig. 1, 2), while the value of wave number slightly increases (fig. 3). The interpretation of the above mentioned parameters along the accepted criteria [1, 3, 7] allows us to conclude that nonelectrolyte exerts a distructive influence on water structure.

The viscosimetric and dielectric investigations of water-DMSO system carried out by Kessler et al. [32] have shown, however, the stabilizing influence of organic solvent on water structure below 15 mol. % of DMSO concentration. This suggestion is confirmed by Safford [33], who has examined the discussed system by x - rays. According to him a small portion of DMSO added to water causes water structure ordering.

On the other hand Brink and Falk [34] investigating the discussed system in infra-red came to the conclusion that a small mole per centage of DMSO does not bring about any changes in three dimentional water network.

In the mixtures of about 30 mol. % DMSO concentration (the first inflexion on $E = f(x)$ and $W_{1/2} = f(x)$ functions) characteristic spheres on entropy activation curves [35] and viscosity curves occur [36]. In this region the deviation [37] of dielectric constant from additivity shows maximum [37].

In the II-nd range, where DMSO content varies from [30] to 53 mol. %, the values $W_{1/2}$ decrease less drastically (fig. 2), while the wave number is constant and independent of the composition till 100 mol. % of DMSO.

It may be assumed that with the DMSO concentration the shift of 1 : 2 type DMSO-water associates into 1 : 1 associates takes place. It is also suggested by spectroscopic investigations carried out by Kelm [29]. In the III-rd range, above 50 mol. % of DMSO concentration a moderate slope of half-width can be observed (fig. 2).

In this region the dimethylsulfooxide-water solutions occur. With the growth of concentration of organic solvent their properties become similar to these of pure DMSO.

Dioxane-water

The dependence of concentration and half-width of the combination band $(\bar{V}_{1,3} + V_2)$ of OH-water groups on dioxane concentration is expressed by the lines with three inflection points (fig. 1, 2). These points allow to distinguish three characteristic regions i. e. I: 0-16 mol. %, II: 16-41 mol. % and III: above 41 mol. % to 100 mol. % of dioxane.

In the I-st range a drastic decrease of half-width can be observed in comparison to its value in pure water which substantiates the destructive influence of dioxane on water structure [1]. This suggestion is confirmed by Krestov [5] who interpreting the apparent heat capacity of argon in the discussed mixture on the mixed solvent composition concludes that dioxane affects water destructively. The analysis of the relation wave number $\tilde{\nu}_{max} = f(x)$ of the given band (fig. 3) may lead to different conclusions. The discussed function is at first presented as a curve decreasing to the value corresponding to 16 mol. % of dioxane which may suggest, in accordance with Sidorova's opinion [3, 7], the ordering effect on the of water structure.

In order to account for divergent interpretations of half--width and wave number, we have performed a series of spectroscopic measurements for dioxane - D_2O system.

Considering the changes of stretching vibrations more characteristic for structure observations than deformation vibrations we have chosen the overtone band instead of the combination band.

The intensity of the first overtone OD band and half-width decrease rapidly with the organic solvent concentration growth (fig. 1, 2) while the values of wave number grow (fig. 3). The interpretation of the discussed parameters provides a strong argument for the destabilising influence of dioxane on three dimensional water structure.

Basing on the Arhenius activation energy changes Clemett [38] expresses the opinion about the ordering influence of dioxane. The excess mixing entropy of the discussed system, which shows minimum at about 20 mol. % of organic solvent confirms this opinion. According to Clemett [39] mentioned concentration of dioxane is the border between dioxane solutions in water and water clathrates in dioxane.

Within this concentration range Shkodin [40] has obtained maximum of viscous flow activation energy in the function of composition. Analysing spectroscopy data of water-dioxane and D_2O-dioxane systems, Nabieruchin [41] claims that hydrogen bonds in water strengthen on adding small ammounts of dioxane. Near the characteristic point i. e. at about 20 mol. % of dioxane in the discussed mixture the dielectric constant shows minimum, the self-diffusion activation energy shows maximum [42] and the minimum of maxing heat occurs [43].

The half-width gradually decreases in the II-nd and III-rd regions, and the wave number value in these regions grows with the growth of nonelectrolyte concentration.

Clemett [44] expresses the opinion that in the range of greater nonelectrolyte concentrations water occurs in the form of clusters which disappear when the organic solvent content is below 70 mol. % because dioxane molecules become more effective in destroying the hydrogen bonds in water.

The investigations of this system in infra-red have shown that 4.7 μ band, characteristic for pure water disappears when nonelectrolyte concentration exceeds 70 mol. % [45]. This observation is confirmed by the work of Nabieruchin [19] who claims that the appearing water globules break when dioxane concentration is above 80 mol. %, which is the result of hydrogen bonds weakening.

DMF-water

The functions of density and half-width of $(\bar{V}_{1,3}+V_2)$ OH-group of water combination band in relation to DMF concentration are illustrated by the lines with characteristic regions on them: I: 0-5%, II: 5-15 mol. %, III: 15-30 mol. % and IV: 30-100 mol. % of DMF concentration.

In the first range a drastic decrease of half-width in the relation to this value for pure water can be observed. From the change of this parameter it follows that DMF exerts a destructive influence on hydrogen bonds forming water network.

The analysis of ν_{max} wave number changes of the examined band in relation to water-DMF mixture composition leads to different conclusion. The decrease of this function in the discussed region hints at ordering influence of nonelectrolyte on water structure. Near the first inflexion point (4 mol. % of DMF) Cu and Bi null potential in water-DMF mixtures shows minimum [46].

The second region is characteristic of its drastic decrease of half-width with the growth of nonelectrolyte concentration, while wave number slightly decreases exhibiting minimum at about 15 mol. % of MDF concentration.

Different conclusions follow from the analysis of both these parameters. On the grounds of half-width it can be stated that the breakiñg of water structure is gradually strengthened by the penetrating influence of DMF molecules or by water-dimethylformamide agregates formation.

On the other hand the interpretation of wave number changes allows to assume that a further slight stabilization of water-like structure takes place.

According to Kessler [32] who has investigated the discussed system by viscosimetric and dielectric methods the stabilization of water structure occurs in the solutions containing less than 15 mol. % of DMF.

Larinov [47] has observed density maximum in the solution of the above mentioned concentration.

Namoto and Endo [48] have observed maximum of ultrasounds diffusion and minimum of adiabatic compressibility coefficient in such mixtures [49].

In the III-rd region there is a less drastic change of half--width and wave number grows continuously with nonelectrolyte. concentration growth. In this region the breaking of "water--like" structure probably takes place and what is suggested by spectroscopic works [50], the formation of $DMF.2H_2O$ associates is probable.

Shakhparonov assumes that DMF - water system has a clathrate type structure [51] in a small amide contents range. In the mixture containing about 25 mol. % of DMF all free interstitial spaces of water are filled. According to the author the structure of such a solution is more stable, which is substantiated, among others, by the minimum of isothermic compressibility in the discussed mixture.

Basing on the results of dielectric research, Kessler [52] came to the conclusion that that up to 30 mol. % DMF in the mixture with water causes stabilization of water structure.

Maximum of viscosity in water-dimethylformamide system occurs at the mentioned above concentration [47, 53, 54]. A different opinion on the effect of DMF on water structure was expressed by Fratiello [55]. He has investigated the discussed system by magnetic nuclear resonance method. According to him organic solvent disorders water structure. The measurements of DMF with water mixing heat, vapour pressure and osmotic pressure of water-DMF mixtures [56, 57] carried out by Geller et al. point at the presence of DMF hydrates.

The authors express the opinion that the discussed hydrates have $DMF.nH_2O$ composition, where $n = 2 \div 4$. The existance of $DMF.2H_2O$ hydrates is confirmed also by the results of crioscopic works carried out by Bougard and Jadot [58]. Above 30 mol. % in the discussed mixture the IV-th region begins in which a slight change of half-value width can be observed. It may substantiate the differences in the mixture properties caused by the concentration change of the components.

From the literature data if follows that in the IV-th region i. e. above 50 mol. % of DMF the formation of $H_2O.2DMF$ [50, 59, 60] associates as the result of strong interactions among water and DMF molecules is possible.

On the other hand, in the region of considerable DMF contents the ordering of molecules characteristic for pure DMF occurs.

As the presented material indicates the opinions on nonelectrolyte influence on water structure depend on the experimental method used.

Different kinds of parameters characterizing the influence of solute on solvent structure (breaking, ordering of structure) obtained by spectroscopic method lead very often to incompatible conclusions.

It seems to us that the half-width is a good criterion defining the structural changes taking place in the solution.

Our view is confirmed by spectroscopic investigations of temperature and electrolyte effect on water structure [1, 2].

The criterion of "half-width" seems possible to apply due to its agreement in many systems with thermodynamic characteristics.

The thermodynamic investigations of the change of entropy according to the opinion of Frank, Wen [61] and Mishchenko [62] serve as the best criterion of the effect of ions on the water structure.

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SPEKTROSKOPOWE BADANIA WODNYCH ROZTWORÓW NIEELEKTROLITÓW

W niniejszej pracy ustalono spektroskopowe zależności natężenia, szerokości połówkowej oraz częstości pasma kombinowanego $(\bar{V}_{1,3} + V_2)$ wody w mieszaninach z rozpuszczalnikami organicznymi: glikolem etylenowym, gliceryną, acetonem, DMSO, dioksanem i DMF. Pomiary przeprowadzono w całym zakresie stężeń w temperaturze 25°C. Otrzymane wartości parametrów zanalizowano pod kątem wpływu nieelektrolitów na strukturę wody. Przyjęto szerokość połówkową jako kryterium porządkującego lub zakłócającego działanie substancji rozpuszczonej na wodę. Omawiane rozpuszczalniki organiczne wpływają destrukcyjnie na strukturę wody w całym zakresie składów. Aceton, dioksan, DMF wykazują silniejsze tendencje do niszczenia trójwymiarowej siatki wiązań wodorowych w wodzie niż glikol etylenowy, gliceryna, DMSO.

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СПЕКТРОСКОПИЧЕСКИЕ ИССЛЕДОВАНИЯ ВОДНЫХ РАСТВОРОВ НЕЭЛЕКТРОЛИТОВ

В этой работе изучались спектроскопические зависимости интенсивности, полуширины, частоты комбинированной полосы -OH ($\bar{V}_{1,3} + V_2$) воды в смесях с органическими растворителями: этиленгликолем, глицерином, ДМСО, ацетоном, диоксаном, ДМФ. Опыты проводились во всем диапазоне концентрации при температуре 25°C. Полученные значения параметров проанализированы с точки зрения влияния неэлектролитов на структуру воды. Полуширина полосы рассматривалась как критерий упорядочивающего и разупорядочивающего влияния растворенного вещества на структуру воды. Оказалось, что исследованные органические растворители разупорядочивают сетку водородных связей в воде во всем диапазоние концентрации. Ацетон, диоксан, ДМФ сильнее разрушают структуру воды чем этиленгликоль, глицерин, ДМСО.