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A STUDY OF THE STRUCTURE OF AQUEOUS ETHANOL SOLUTIONS BY THE CORRELATION SPECTROSCOPY AND LUMINESCENT PROBE TECHNIQUES

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The scattered light correlation spectroscopy and luminescent probe techniques have been applied to study aqueous ethanol solutions. It is shown that adding C_2H_5OH to water in concentrations below 10 vol.% results in adsorption of ethanol molecules on the surface of clusters, which causes an increase in their volume. Adding more ethanol destroys the clusters. An analysis of the polarization and kinetic characteristics of eosin luminescence shows microstratification to occur in aqueous ethanol solution in the range of ethanol concentrations from 20 to 80%. The scattered light correlation characteristics have been used to determine the volume of one of the solution microphases.

Aqueous solutions of nonelectrolytes are characterized by a dramatic change of their physico-chemical properties in the region of low concentrations. This concerns the properties that depend on both density of molecular packing and displacements of molecules from the equilibrium positions. Thus the study of solubility of gases in aqueous ethanol solutions [1] has shown that gases and ethanol stabilize the structure of water at a low temperature and alcohol concentrations $x < 0.03$, where x is the molar fraction of ethanol. At $0.03 < x < 0.20$ concentrations, gases have a stabilizing and ethanol a destructive action. At still higher concentrations, both compounds have a destructive action.

In [2], low-concentration solutions of nonelectrolytes have been studied to show that the stabilization of the structure of water is accompanied by the dissociation of water–water H-bonds, which are replaced by weaker water–nonelectrolyte bonds. As regards the region of electrolyte concentrations $x = 0.3$-0.7, it has been suggested that there occur a separation of solutions into microphases (microstratification) [3]. Based on this suggestion, a model of water-rich microphases (globules) has been developed which enables the composition and size of the globules to be determined. The H-bonds between water molecules have been shown to be weaker in a globule than in pure water.

All of the changes in the properties of aqueous alcohol solutions described in the literature cannot be explained by the formation of bonds between H_2O and nonelectrolyte molecules alone. The interpretation of these changes requires taking into consideration the influence of dissolved molecules on the structure of water.

The present work describes an experimental study of the structure of aqueous ethanol solutions using scattered light correlation spectroscopy as well as fluorescence and phosphorescence spectroscopies.

The objects of the study were doubly distilled water (conductivity $\kappa = 1.2 \times 10^{-6}$ ohm^{-1} cm^{-1}) and ethanol, which had been purified and dried following the routine procedures [4]. The ethanol purity was checked by comparing its UV absorption spectra with the reference ones [4]. An anionic dye, eosin, with a concentration $C = 10^{-5}$ mol/liter was used as a luminescent probe.

The absorption spectra were recorded on a Specord-M40 spectrometer and the fluorescence spectra on a Hitachi MPF-4 spectrofluorimeter. The positions of the absorption and fluorescence maxima were measured with an accuracy of ± 0.05 and ± 0.5 nm, respectively. The electronic band halfwidths were determined with an accuracy of ± 0.5 nm. The fluorescence decay kinetics was determined on a picosecond fluorimeter described in [5]. The time resolution of the instrument was $\sim 10^{-11}$ s. The degree of fluorescence polarization was measured on an MPF-4 spectrofluorimeter equipped with an accessory for light polarization. The temperature dependence of fluorescence anisotropy was determined using the accessory described in [6].

The kinetic characteristics of long-lived luminescence of eosin were studied on a pulsed spectrofluorime-

ter with laser excitation. A YAG:Nd^{3+} laser with a modulated Q-quality was used as a pulsed excitation source (20 ns pulses). The samples were excited by the second harmonic of the radiation ($\lambda = 532$ nm), the luminescence spectrum was isolated with the help of an MDR-6 monochromator. The signal was recorded by an FEU-84 photomultiplier and an S8-17 oscilloscope.

A monodynic scattered light spectrometer with a helium-neon laser as a light source ($\lambda = 632.8$ nm) was also used. The laser beam was directed onto a side wall of a 10 × 10 mm cell containing the solution studied. The scattered light intensity was measured at a 90° angle in the photon counting mode by an FEU-79 photomultiplier.

The light scattering data were processed using the correlation-spectral technique, which was based on the calculation of (i) the correlation function $G(\tau)$ [7]:

$$G(\tau) = \int_0^\infty E(t)E(t+\tau)\,dt, \tag{1}$$

where $E(t)$ is an array of data measured with a certain spacing τ, and of (ii) the Fourier spectrum of the function $G(\tau)$ (random quantity power spectrum),

$$I(\omega) = \int_{-\infty}^{\infty} G(\tau)\exp\{i\omega\tau\}\,d\tau. \tag{2}$$

Whatever the spectral technique used, the smallest frequency distance $\Delta\nu$ between the lines that can be resolved is related to the time t of observation as $\Delta\nu t > 1$. From these considerations the mean observation time chosen was $t = 5120$ s to provide a spectral resolution $\Delta\omega = 10^{-4}$ Hz.

If a sample contains M output signal values obtained at a time interval t, the error (root mean square deviation) is determined as $1/\sqrt{M}$. In our measurements, the relative error was 10%.

It has long been assumed that water is close to ideal crystals in its structural homogeneity. However, in [8, 9], the intensity of light scattered by water and its solutions has been found to undergo periodical oscillations with an amplitude that departs by 10-40% from the maximum intensity value. The periods of these oscillations range from tens of seconds to tens of minutes. These results are indicative of structural inhomogeneity of aqueous systems.

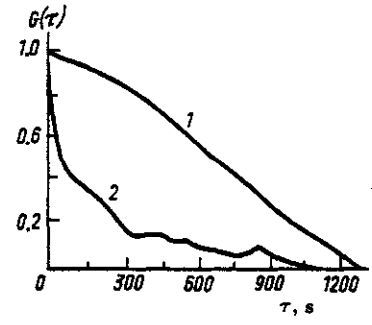

Fig. 1

Correlation function $G(\tau)$ for light scattering by the 3 vol.% (1) and the 8 vol.% (2) aqueous ethanol solution.

It is known [9] that the scattered light correlation function $G(\tau)$ describes variations in scatterer characteristics with time. We have therefore studied the correlation functions $G(\tau)$ of aqueous ethanol solutions. The $G(\tau)$ values for aqueous ethanol solutions of various concentrations are presented in Fig. 1. One can see

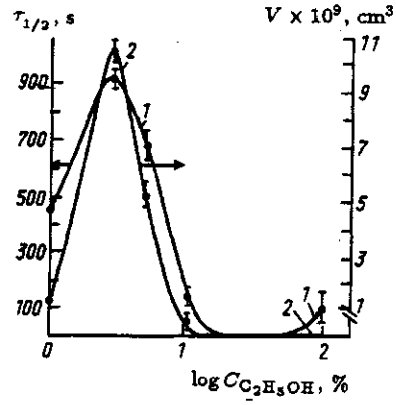

Fig. 2

Dependence of $\tau_{1/2}$ (1) and the volume of the scatterers (2) on the concentration of C_2H_5OH in aqueous ethanol solutions.

that a change in the percentage of alcohol causes a drastic change of the $G(\tau)$ dependence, and the correlation time $\tau_{1/2}$ (equal to the time during which $G(\tau)$ decreases to 0.5) shows a nonmonotonic dependence on the concentration of C_2H_5OH. The dependence of $\tau_{1/2}$ on $C_{C_2H_5OH}$ is plotted in Fig. 2, curve 1.

To determine the sought dynamical characteristics of the object under investigation some model of this object should be chosen to obtain an expression for the power spectrum. The theoretical and experimental spectra should then be compared to determine the object parameters.

A large number of models have been suggested. Unfortunately none of these can be used to describe our system. First, all of them are based on the assumption that the size of scatterers is smaller than the wavelength of the scattered light. Secondly, these models mostly describe noninteracting identical, spherical particles, whereas our system is characterized by strong intermolecular interactions.

For the qualitative analysis purposes, let the scatterers be regarded as spherical formations involved in translational motion only. The correlation time can then be written as [10]:

$$1/\tau_{1/2} = kTg^2/(6\pi R\eta), \tag{3}$$

where k is the Boltzmann constant; T is the temperature; η is the solution viscosity; R is the radius of the scattering particle; and $g = (4\pi n \sin\theta/2)/\lambda$ (the scattering angle $\theta = 90°$; $\lambda = 632.8$ nm is the light wavelength; and n is the refractive index of the medium).

Equation (3) has been used to determine first the radius of the scatterers and then their volume. The dependence of the volume on the alcohol concentration is shown in Fig. 2 (curve 2). It follows from Fig. 2 that large-volume scatterers (clusters) are present in pure water, and radical changes in the dynamical characteristics of the objects under investigation mainly occur at low alcohol concentrations (up to 10% C_2H_5OH). Adding alcohol increases the volume of scatterers (most likely, adsorption of nonelectrolyte molecules on the surface of clusters occurs). The largest volume corresponds to $C_{C_2H_5OH} = 3\%$. A further increase in the concentration of alcohol causes a decrease in the volume of clusters, which collapse when $C_{C_2H_5OH}$ reaches the value of 10%. As has already been mentioned, in the region of alcohol concentrations exceeding 10% one observes the onset of microstratification, and there are globules in the solutions comprising 300 water and 80 ethanol molecules [3]. The volume of these globules as determined by our technique is 3×10^{-12} cm^3.

A further, more detailed study of the structure of aqueous ethanol solutions has been accomplished using the luminescent probe technique (with eosin dye molecules as the probe). It is known that the shift of the absorption and luminescence spectra of dye molecules that occurs on going from one solvent to another is due to changes in the stabilization energies of their ground and excited states caused by differences in the character of dye molecule interactions with medium molecules.

The absorption and fluorescence spectra of eosin molecules have been measured in aqueous ethanol solutions for various alcohol concentrations. The positions of the maxima of the absorption (curve 1) and fluorescence (curve 2) spectra as functions of the concentration of ethanol are shown in Fig. 3. One can see that the positions and half-widths of the maxima (curves 3 and 4) depend strongly on the composition of the solvent mixture. The most pronounced change of these characteristics occurs at alcohol concentrations below 10%. In the concentration range of 10 to 80%, the spectral characteristics of the probe are practically the same, which is indicative of an unchanging structure of the water-alcohol mixture (microstratification occurs in this concentration region). At low H_2O concentrations in the mixture, the eosin absorption and fluorescence spectra again undergo variations.

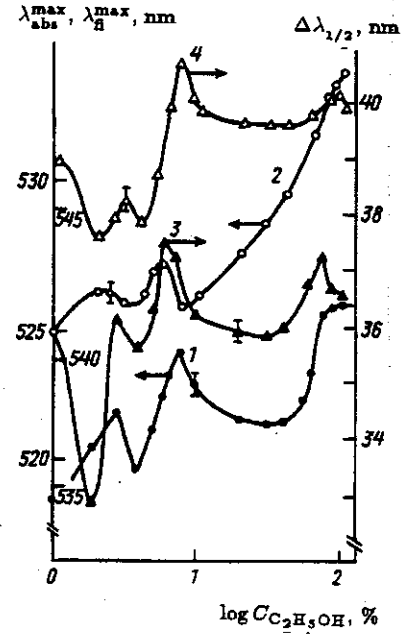

Fig. 3

Positions of the maxima of the eosin absorption (1) and fluorescence (2) spectra and also the eosin absorption (3) and fluorescence (4) line half-widths ($C = 10^{-5}$ mol/liter) as functions of the composition of water-propanol mixtures.

The spectral variations described and also similar data on other organoluminophors reported earlier [11, 12] can be regarded as a result of changes in the positions of the maxima of the eosin absorption and luminescence spectra under the influence of variations in the composition of dye molecule solvation shells (SS). This influence should also be manifested in the kinetics of deactivation of both singlet and triplet dye molecule states. Indeed, experiments have shown that the kinetics of eosin fluorescence decay in aqueous ethanol solutions depends strongly on the binary solvent composition (Fig. 4). This composition affects not only the eosin fluorescence decay rate, K_{fl} (Fig. 4, curve 1), but also the slowed fluorescence decay rate, K_{sfl} (Fig. 4, curve 2).

Slowed fluorescence is determined by diffusion of molecules and, therefore, the $K_{sfl}(C_{C_2H_5OH})$ dependence can be used to draw conclusions on the structure of aqueous ethanol solutions. In the region of alcohol concentrations up to 20%, the K_{sfl} value is practically constant (Fig. 4, curve 2), which is indicative of a constant diffusion coefficient. At the same time, the cluster volume increases in this concentration region (Fig. 2, curve 2). This means that the volume increase is caused by adsorption of C_2H_5OH molecules on the surface of the clusters. At concentrations above 30%, the K_{sfl} constant reaches its minimum. Minimal deactivation rates of the dye triplet state are observed in water-alcohol mixtures which are also characterized by smaller mutual diffusion coefficients of the component molecules. In this region of mixture composition

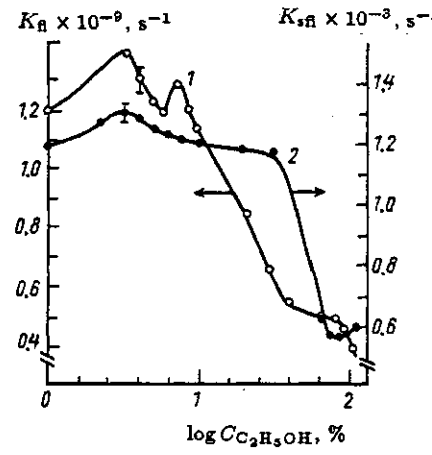

Fig. 4

Decay rates of fluorescence(1) and slowed fluorescence (2) of eosin ($C = 10^{-5}$ mol/liter) versus the percentage of C_2H_5OH in aqueous ethanol mixtures.

variations, clusters collapse and the liquid becomes microheterogeneous. The dye SS composition does not change in these solutions.

A further increase in the percentage of alcohol causes a destruction of the microheterogeneous structure and a decrease in liquid viscosity. Water molecules are completely replaced by alcohol in the SS of eosin molecules. This results in some increase of the eosin triplet state deactivation rate (Fig. 4, curve 2).

Our measurements show that the composition of the solvent mixture affects not only radiative but also nonradiative transitions in eosin molecules. Fluorescence quantum yields, B_{qfl}, and internal conversion constants, K_{ic}, of eosin molecules in various binary H_2O/C_2H_5OH mixtures are listed in Table 1.

Table 1

Eosin Fluorescence Quantum Yields, B_{qfl}, and Internal Conversion Constants, K_{ic}, in H_2O/C_2H_5OH Mixtures

Concentration of C_2H_5OH, %	B_{qfl}	$K_{ic} \times 10^{-8}$, s
0	0.15	5.7
10	0.18	4.2
30	0.3	2.5
70	0.45	1.7
80	0.48	1.5
100	0.60	1.1

It is seen from Table 1 that the internal conversion constant, K_{ic}, decreases, and the fluorescence quantum yield of eosin, B_{qfl}, increases with increasing concentration of alcohol. This suggests that the H-

bonds are not the determining factor in the variations of radiative and nonradiative transition rates caused by substantial changes in the interactions between the molecules of the SS and the dissolved substance. This prompted us to investigate the shape and composition of the SS of eosin molecules by studying the polarization characteristics of luminescence of eosin solutions in aqueous ethanol mixtures, since variations of the SS composition affect the degree of anisotropy, r, of the dye fluorescence.

A qualitative analysis of the SS of eosin molecules can be performed using the relation obtained in [13]:

$$r = r_0 \frac{1 + AkT/V\eta}{1 + [(1+A)k\tau T/V\eta]}, \tag{4}$$

where r and r_0 are the anisotropy and the limiting emission anisotropy coefficients; V is the volume of an eosin molecule together with its SS; τ is the mean lifetime of the eosin excited state; η is the solution dynamic viscosity; T is the solution temperature; $A = I/6kT$ is the parameter characterizing the deviation of the SS shape from spherical; k is the Boltzmann constant; and I is the moment of inertia of an eosin molecule together with its SS.

The r and r_0 values were determined from the dependence $r^{-1}(T/\eta)$, which was approximately linear in the temperature range from +20 to −20° C.

The viscosity of the aqueous ethanol mixture, η_m, was determined using the equation [14]

$$\eta_m^{1/3} = x_1\eta_1^{1/3} + x_2\eta_2^{1/3}, \tag{5}$$

where x_1 and x_2 are the mole fractions of the mixture components and η_1 and η_2 are their dynamic viscosities.

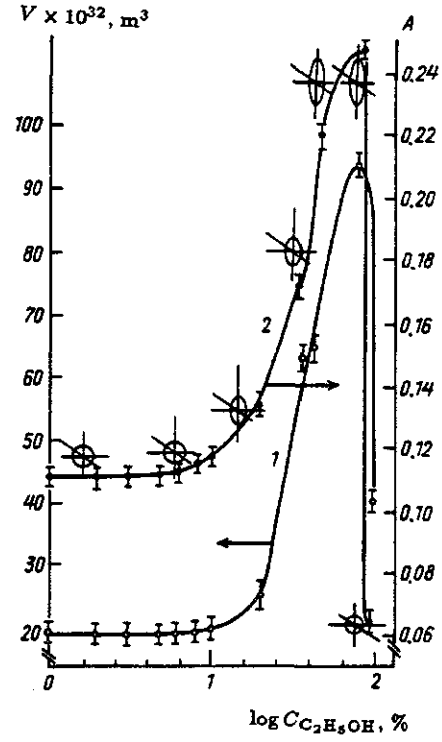

Fig. 5

Volume V of an eosin molecule with the SS (1) and the nonsphericity coefficient A (2) as functions of the composition of the H_2O/C_2H_5OH solvent.

The alcohol concentration dependences of V and A calculated using Eqs. (4) and (5) are shown in Fig. 5. The shapes of eosin SS in solutions with various percentages of C_2H_5OH are drawn schematically in the same figure.

One can see that the eosin SS remains unchanged in the region of alcohol concentrations where clusters increase in size. It follows that alcohol molecules are adsorbed on the surface of clusters and do not affect the luminescent probes present within the clusters. In the region of microstratification where there is no clusters, the alcohol molecules enter into the eosin SS thereby causing it to increase in size and assume an ellipsoidal shape. At higher alcohol concentrations, the water molecules are completely replaced by the alcohol ones in the eosin SS, the SS decreases in size, and its shape again becomes approximately spherical.

The results of the experiments described above suggest the following scheme of physical processes that occur in aqueous ethanol solutions. Water contains species (clusters) up to dozens micrometers in size. The addition of C_2H_5OH results in the adsorption of alcohol molecules on the surface of the clusters, and this causes the clusters to increase. A further increase in the concentration of alcohol is accompanied by collapse of the clusters. In the region of alcohol concentrations about 20-80%, the solutions have two phases (microstratification). At still higher C_2H_5OH concentrations the microheterogeneous structure of solvent mixtures is destroyed.

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