Fluorimetric and conductometric study of water—*n*-octane—sodium dodecyl sulfate—*n*-pentanol microemulsions

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The influence of the water concentration in the water—*n*-octane—sodium dodecyl sulfate—*n*-pentanol microemulsions on the polarity index I_1/I_3, the efficiency of formation of the fluorescent probe (pyrene) excimers I_{ex}/I_m, and the conductivity of the system in a wide interval of water—oil ratios was studied. Analysis of changes in the polarity index shows that in all types of the microemulsions pyrene is solubilized in the hydrophobic part of the water—oil interface between the surfactant hydrocarbon radicals. Depending on the water—oil ratio, the site of its localization changes, and the effective permittivity of the medium ε_{eff} varies from 5 to 11. Variations of the conductivity and polarity index allow one to observe three structures in the mucroemulsion, *viz.*, water—oil, bicontinual region, and oil—water. Variation of the I_{ex}/I_m ratio reveals only the transition from the water—oil microemulsion to the oil—water microemulsion.

Key words: microemulsion, structure, conductivity, fluorimetry, pyrene.

Fluorescent probes are widely used for studying the structure of active sites of proteins, enzymes, and various types of surfactant-based liquid organized media, including microemulsions.[1—4] The position of the maximum in the fluorescence spectrum, the quantum yield of fluorescence, the ratio of intensities of vibrational bands in the spectrum, or the formation of excimers are indicators for changes in the local microenvironment (polarity, viscosity) of the probe.[4,5]

Pyrene is the most convenient and frequently used fluorescent probe. Its emission spectrum is characterized by a fine vibrational structure, whose shape depends on the polarity of local microenvironment.[6] The parameter of medium polarity is the ratio of intensities of the first (372 nm) and third (383 nm) peaks in the spectrum (I_1/I_3).[6]

Another characteristic of pyrene, efficiency of excimer formation, is sensitive to a change in the microviscosity in the site of its localization.[4,5] It can be estimated from a change in the ratio of intensities of the fluorescence maximum of the excimer and the fifth fluorescence peak of the monomer (I_{ex}/I_m parameter).

A few studies[7—12] are known that are devoted to the use of the I_1/I_3 and I_{ex}/I_m parameters for investigation of structural changes and estimation of the localization site and polarity of pyrene microenvironment in microemulsions with variation of the water content in a wide concentration interval. Only in sole cases,[11,12] the I_{ex}/I_m parameter was applied to the study of the transition of one type of the microemulsion to another.

Unlike fluorimetry, measurement of conductivity is one of the main methods for studying structural changes in microemulsions with variation of the water concentration or temperature.[13,14] A structural change is usually considered from the viewpoint of the percolation transition. The latter implies that nanodrops of water, which form cores of reverse water—oil microemulsions, join to form clusters with an increase in the water content or temperature accompanied by a jump in the conductivity of the solution by three to four orders of magnitude.[13,14] The sharp increase in the conductivity above the percolation threshold is attributed to migration (jump) of conducting surfactant ions and their counterions from one drop to another through water channels between the drops. Analysis of published data showed that the shape of the conductivity curve for each microemulsion is individual. However, one can always distinguish three regions in this curve indicating three types of microemulsions, *viz.*, reverse water—oil microemulsion, bicontinual structure, and direct oil—water microemulsion.

The purpose of this work is the fluorimetric and conductometric study of the structure of the water—*n*-octane—sodium dodecyl sulfate (SDS)—*n*-pentanol microemulsion at different water : oil ratios using the

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I_1/I_3 and I_{ex}/I_m indices. We have previously[15] observed the photosensitized phosphorescence of pyrene at room temperature in a similar system for the first time.

Experimental

Pyrene (purum, Fluka) was used without additional purification. Its concentration in solvents and microemulsions was $2 \cdot 10^{-5}$ and $1 \cdot 10^{-3}$ mol L^{-1}, respectively. "Chromatographically pure" sodium dodecyl sulfate (SintezPAV Research-and-Production Association), whose background fluorescence was virtually absent from solutions, was used. *n*-Pentanol (co-surfactant) was distilled before use with a drying agent according to a described procedure.[16] *n*-Octane (oil) was purified by distillation.[16] Doubly distilled water was used to prepare microemulsions. Microemulsions (ME) were prepared by weighting and mixing of the components: SDS, water, octane, and pentanol. The content of SDS in all microemulsions was 7.77 wt.%, and that of *n*-pentanol was 14.49 wt.%; the water : octane weight ratio was varied from 0.05 to 4, thus varying the water content from 3.89 to 62.19 wt.% and octane content from 73.86 to 15.55 wt.%. The studied microemulsions remained macroscopically uniphase and transparent in the whole concentration interval under study at 25 °C.

Luminescence spectra were obtained on a spectrofluorimeter based on a DFS-24 monochromator. To eliminate reabsorption appeared at high pyrene concentrations, frontal irradiation was performed and luminescence was detected from the front surface of the cell. The conductivity of a solution was measured on an OK-102-1 conductometer (Radelkis, Hungary).

Results and Discussion

Conductivity. The plot of the conductivity of the microemulsion *vs.* water content is presented in Fig. 1. It is seen that the conductivity for the reverse water—oil microemulsion, whose dispersion medium is octane, is very low. The increase in the conductivity at the water content of 7—8 wt.% suggests that the system contains the percolation threshold corresponding to the beginning of joining the water cores of the reverse microemulsion. The further sharp jump of the conductivity by more than three orders of magnitude with an increase in the water content to 16—17 wt.% corresponds to the percolation region in which the bicontinual structure of the microemulsion forms.

The interval with the water content in the microemulsion from 16 to 40 wt.% corresponds, most likely, to the bicontinual structure, which is characterized only by a slight increase in the conductivity with an increase in the water concentration. It is known[13,17,18] that the bicontinual structure is usually characterized by a high viscosity due to the formation and joining of the water and oil clusters or appearance of the liquid-crystalline state. As we have shown previously,[19] the kinematic viscosity of the system in fact increases sharply in this water concentration interval to confirm the formation of the bicontinual structure. At the water content >40 wt.% it becomes a disperse medium, and the oil—water microemulsion forms; the conductivity of the system remains virtually unchanged.

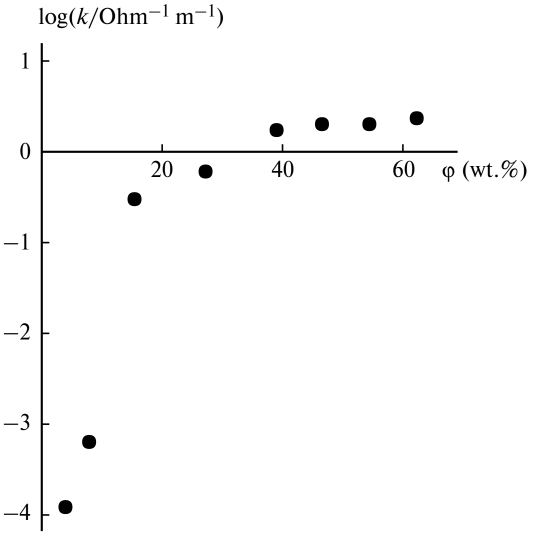

Fig. 1. Plot of the microemulsion conductivity *vs.* water content.

The same conclusion on the transition of the water—oil microemulsion to the bicontinual structure and then to the oil—water microemulsion with an increase in the water concentration in the Aerosol OT—water—0.5% NaCl—decane and water—dodecane—SDS—pentanol systems was made from the results of conductivity and viscosity studies.[10,20]

Parameter I_1/I_3 for pyrene. Let us consider the shape of the fine structure of the fluorescence spectrum for pyrene in individual components of the microemulsion (pentanol, octane, and a micellar solution of SDS) and in the microemulsion itself. A comparison of the spectra (Fig. 2) shows that with the polarity decrease in the series SDS > pentanol > octane the ratio of intensities of the first and third maxima I_1/I_3 in the fluorescence spectra decreases.

Analysis of the spectra in Fig. 2 and changes in the I_1/I_3 polarity index with variation of the water : oil ratio (Table 1) suggests that pyrene is solubilized near the water—oil interface of the microemulsion nanodrops, regardless of the microemulsion type. This agrees with the published data[6,7] and is favored by the comparison of the interval of experimental I_1/I_3 values (0.70—0.85) in the

Table 1. Influence of the water content in the water—*n*-octane—SDS—*n*-pentanol microemulsions on the I_1/I_3 parameter and effective permittivity of the medium (ε_{eff}) in the site of pyrene localization

φ (wt.%)	I_1/I_3	ε_{eff}	φ (wt.%)	I_1/I_3	ε_{eff}
3.89	0.76	7.5	38.88	0.82	9.8
7.77	0.79	8.6	46.64	0.85	11.0
15.55	0.70	5.2	54.42	0.80	9.0
27.20	0.72	6.0	62.18	0.79	8.6

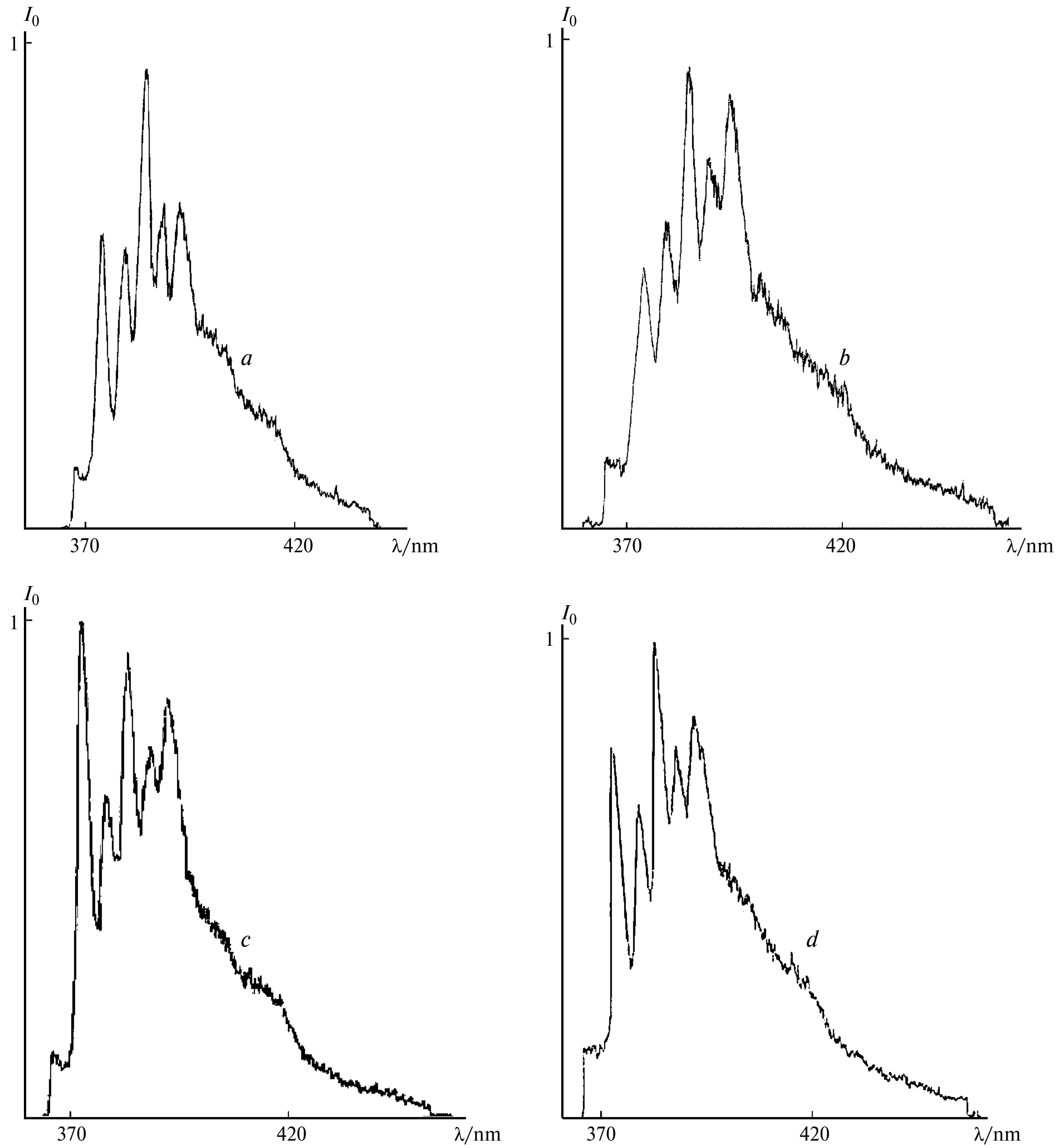

Fig. 2. Fluorescence spectra for pyrene ($C = 1 \cdot 10^{-5}$ mol L^{-1}) in *n*-pentanol (*a*), *n*-octane (*b*), a micellar solution of SDS ($C = 0.2$ mol L^{-1}) (*c*), and the water—*n*-octane—SDS—*n*-pentanol microemulsion (*d*).

microemulsions and those for octane (0.62), pentanol (0.93), a 0.3 *M* micellar solution of SDS (1.07), and water (1.87).[7]

We can draw two conclusions from this comparison. First, the microenvironment of pyrene in the microemulsion is much less polar than that in the SDS micelle. This agrees with both our and published data[7] on the hydrophobization influence of the alcohol molecules on the micelle—water interface for their radial incorporation as co-surfactants into a micelle. Second, the microenvironment of pyrene in the water—oil microemulsion is also less polar than that in *n*-pentanol. The authors[11] explained this phenomenon by specific features of pyrene localization. In a reverse microemulsion pyrene is localized between the hydrocarbon chains of SDS directed to the oil phase, probably, containing octane (between the SDS chains), which diminishes the medium polarity. Thus, it seems reasonable[11] that in the reverse microemulsion pyrene is localized at the outer surface of the interface directed to the low-polarity disperse oil phase.

At the same time, pyrene is not completely immersed into octane, otherwise the polarity index (0.76—0.79) would be much lower. It is noteworthy that in the percolation region (7—16 wt.% of water) an increase in the size of water drops and a decrease in the octane concentration are accompanied by a decrease in the I_1/I_3 parameter to 0.70. Such an additional decrease in polarity of the microenvironment is probably related to a change in the site of pyrene localization.

It also follows from Table 1 that an increase in the water concentration in the 16—40 wt.% interval again enhances the I_1/I_3 ratio and the polarity of the pyrene microenvironment, *i.e.*, the site of its localization once more changes. Comparing this result with the conductivity data, one can assume that in this region of water concentrations the microemulsion is characterized by the bicontinual structure. At the water content above 40 wt.%, the I_1/I_3 parameter and conductivity remain almost unchanged. At this water : oil ratio, the solution contains a direct microemulsion in which pyrene is localized in its hydrophobic core at the internal side of the water—oil interface.[7] Thus, although changes in the I_1/I_3 parameter in the whole interval of water concentrations in the microemulsions are not significant, they are regular and agree with a change in the conductivity and results of other works[8—11] for similar microemulsions.

A relation between the I_1/I_3 ratio of pyrene and permittivity of the medium (ε) is known[6] for homogeneous solvents and their mixtures. This allows one to find the effective permittivity (ε_{eff}) of the medium in the site of probe localization from the I_1/I_3 ratio of pyrene in the microemulsion under study. Using the ε values and I_1/I_3 ratio for pyrene in hexane, *n*-butanol, and *n*-pentanol, we constructed the ε—I_1/I_3 plot, which is described by the equation $y = 37.9x - 21.3$ ($R = 0.999$). It is almost identical to the equation $y = 37.6x - 20.8$ ($R = 0.999$) obtained by the published data.[6]

The ε_{eff} values calculated using these equations for the microenvironment of pyrene localized in different sites of the interface vary from 5 to 11 with an increase in the fraction of water from 3.89 to 62.2 wt.% and a threefold change in the microemulsion type (see Table 1). It is noteworthy that the same ε_{eff} values in the site of pyrene localization are obtained when the I_1/I_3 values for pyrene presented[8,10] for similar (in composition) water—hexane—SDS—pentanol and water—dodecane—SDS—pentanol microemulsions are inserted in our equation.

It follows from the obtained results that the pyrene microenvironment in the site of its localization in the microemulsion is hydrophobic and the variation of the water : oil ratio in a wide concentration interval does not significantly change ε_{eff}.

Parameter I_{ex}/I_m for pyrene. The fluorescence spectra of the pyrene monomers and excimers for one of the microemulsions are presented in Fig. 3. The concentration of pyrene in a solution was $1 \cdot 10^{-3}$ mol L^{-1}; at a lower pyrene concentration the excimers of pyrene do not form, as in Ref. 11. The fluorescence spectrum of the pyrene monomers contains five pronounced peaks. The fluorescence spectrum of the excimers is a broad band with a maximum at 475 nm.

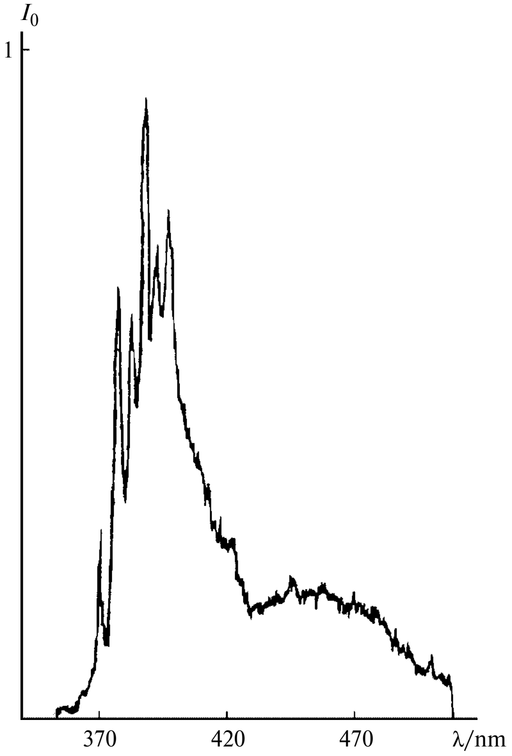

Fig. 3. Fluorescence spectrum for pyrene ($C = 1 \cdot 10^{-3}$ mol L^{-1}) in the water—*n*-octane—SDS—*n*-pentanol microemulsion.

The change in the I_{ex}/I_m ratio, as a function of the water content in the microemulsion, is shown in Fig. 4. This relation is rather simple: it contains only one break at the water content of 40 wt.% at which the concentration of the pyrene excimers begins to increase. This plot shows that the I_{ex}/I_m ratio in our system makes it possible to detect only the transition of the bicontinual structure to the oil—water microemulsion.

According to Ref. 11, formation of the pyrene excimers in our microemulsion can be affected by several factors: the pyrene concentration near the interface of microemulsion drops, the lifetime of the excited state of pyrene, and the microviscosity in the site of probe localization. It has been shown[11] that the lifetime of pyrene in the excited singlet state increases with an increase in the water concentration in the microemulsion. The latter can increase the probability of excimer formation. However, the influence of this factor was not evaluated. In the authors′ opinion,[11] the effect of the microviscosity should be excluded because pyrene is always localized at the water—oil interface predominantly near the oil phase.

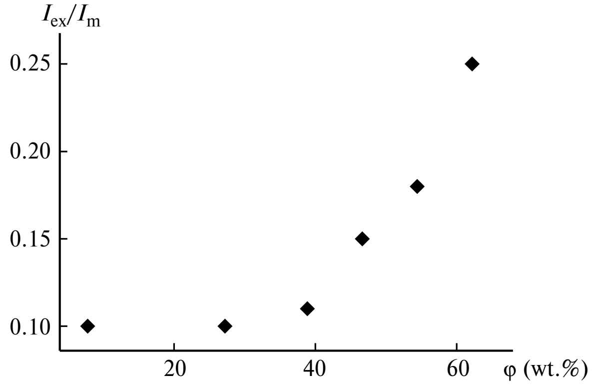

Fig. 4. Plot of I_{ex}/I_m of pyrene ($C = 1 \cdot 10^{-3}$ mol L^{-1}) *vs.* water content in the water—*n*-octane—SDS—*n*-pentanol microemulsion.

Let us consider the effect of the concentration factor. The overall concentration of pyrene in all types of microemulsions is constant and equal to $1 \cdot 10^{-3}$ mol L^{-1}. The concentration of octane in the series under study continuously decreases. Therefore, if the concentration of pyrene localized near the water—oil interface in the microemulsions increases, then the I_{ex}/I_m ratio would also increase due to an increase in the number of collisions between the excited and nonexcited pyrene molecules. This regularity was observed, for example, in the work.[11] In our case (see Fig. 4), the I_{ex}/I_m ratio remained unchanged up to a water concentration of ~40 wt.%, *i.e.*, the excimer concentration did not virtually increase. The concentration of the pyrene excimers did not increase either in the test experiment in which the medium in the site of pyrene localization was simulated in the water—oil microemulsion and bicontinual structure. In the homogeneous pentanol—octane mixtures taken at the same ratio of components as in the microemulsions, I_{ex}/I_m = 0.10±0.01 remained almost unchanged. It can be asserted that the increase in I_{ex}/I_m at the water concentration >40 mol.% is a result of structural changes associated with the transition from the bicontinual structure to the oil—water microemulsion. In the oil—water microemulsion, the pyrene molecules are localized inside the nanosized hydrophobic core near the interface.[6,7] This type of localization sharply increases their local concentration and probability of pyrene excimer formation.

Thus, the comparison of the results of fluorimetric and conductometric studies of the water—*n*-octane—sodium dodecyl sulfate—*n*-pentanol microemulsions with wide variation of the water : oil ratio suggests the following.

1. Changes in the conductivity and polarity index I_1/I_3 of pyrene occur at the same ratios of water and oil concentrations in the microemulsions. They indicate the subsequent structural transitions of the water—oil microemulsion to the bicontinual structure and further to the oil—water microemulsion. Conductometry provides more detailed information on changes that occur during bicontinual structure formation.

2. The I_{ex}/I_m ratio of pyrene in this microemulsion is an efficient indicator for the transition from the bicontinual structure to the oil—water microemulsion. The increase in the local concentration of the pyrene excimers is likely caused by its transition into the core of the direct microemulsion when water, in which pyrene is virtually insoluble, becomes the disperse medium.

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