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THE STUDY OF *n*-HEPTANE/AOT/WATER+DIMETHYLSULFOXIDE REVERSE MICELLES USING ACRIDINE ORANGE BASE AS MOLECULAR PROBE

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Acridine orange base (AOB) was used as molecular probe to study the properties of *n*-heptane/sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/water+dimethylsulfoxide (DMSO) reverse micelles using UV-vis absorption, steady-state fluorescence spectroscopy and fluorescence anisotropy measurements at different polar phase contents. The obtained results were compared with those of bulk aqueous and DMSO aqueous solutions to reveal the effect of confined media. From the absorption spectra it was shown that even at high concentrations of DMSO the basic form of acridine orange was not observed. In micellar solution both absorption and fluorescence emission maxima were red shifted. However with the increase of polar phase content the shifts towards blue side occur. Even at the highest obtained values of *W* (*W*=[polar phase]/[surfactant]) the absorption and fluorescence emission maxima of protonated dye molecules have not achieved that in bulk media. This indicates that the microenvironment around dye molecules in AOT reverse micelles is significantly different from that in bulk water and water-DMSO solution. From the anisotropy measurements it was found that the dye molecules exhibit a marked increase in the fluorescence anisotropy with increasing DMSO content, implying that DMSO increases the overall motional restriction experienced by the dye molecule due to the increase of rigidity of the interface of micelles.

Figs. 4, table 1, references 25.

Introduction

It is well known that acridine orange base (AOB) serves as a molecular probe to characterize sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles [1,2]. To study the properties of AOB in *n*-heptane/AOT/water reverse micelles several methods such as UV-vis absorption and fluorescence spectroscopy have been used by other researchers [1]. Acridine orange is a type of cationic-basic dye. Its basic form (AOB), as a proton acceptor, may penetrate into the membranes of some cells accepting proton, while its cationic form ($AOBH^+$) has no similar properties. It

remains within the cell and can cause a variation in the ion local concentration [1]. The property of a dye depends on whether it resides at the interface or in the bulk or is partitioned between both. Depending on the place of location of the dye in micelles it can show different behavior [3,4]. The spectroscopic and photophysical data of these molecular systems in microheterogeneous media are very useful for a better understanding of the biodistribution of these dyes inside the living cells.

Reverse micelles are nanopools of polar solvent surrounded by surfactant monolayer and dispersed in continuous oil phase. Among different surfactants the most common and widely used is Aerosol-OT because of its ability to solubilize a large amount of water with value of W=40-60 ($W = [pol.phase]/[AOT]$) depending on temperature and the surrounding nonpolar solvent. In addition there are numerous investigations with nonaqueous polar solvents such as ethylene glycol (EG), glycerol (GY), formamide (FA), dimethylformamide (DMF), dimethylsulfoxide (DMSO), which have high dielectric constant and very low solubility in hydrocarbon solvents [5-7]. The dielectric constants at the interface of aqueous organized media are lower than in water, therefore the use of nonaqueous solvents that increase the solubility and reactivity in microheterogeneous media such as microemulsions, is in the focus of many researchers [8]. The mixed solvent glycerol (GY)+*N*,*N*-dimethylformamide (DMF) was used as a polar phase in AOT/*n*-heptane reverse micelles and it was shown that in microemulsion, unlike that of bulk media, GY and DMF behave practically as noninteracting solvents [9]. There are several studies regarding DMSO+water mixtures encapsulated within reverse micelles [7, 10,11]. The effect of DMSO on volumetric and rheological behavior of AOT reverse micelles was revealed [11]. It was shown that DMSO increases the apparent molar volume of polar phase. Moreover the presence of DMSO in the system tends to the formation of micellar aggregates at lower concentrations of AOT comparing with aqueous system. Using the DLS technique it was shown that DMSO+water mixture is effectively entrapped by the surfactant layer forming reverse micelles [10]. Moreover using UV-vis spectroscopy it was shown that in micellar system the enzymatic reaction was accomplished at that amount of DMSO, which inhibited the enzymatic reaction in homogeneous media. These results show how the confined microenvironment can impact solvent properties.

The present study deals with the photophysical behavior of AOB in AOT reverse micelles containing water+dimethylsulfoxide (DMSO) mixture as a polar phase at increasing nanopool size (W). Recently the effect of DMSO on the acid-base equilibrium of AOB in aqueous solution has been reported [12]. It is interesting to reveal the effect of DMSO on the above mentioned equilibrium in organized media such as reverse micelles. Here we report the results obtained in AOT microemulsions. Unlike that of bulk DMSO-water mixtures in micellar system we should take into account the influence of the confined microenvironment.

The photophysical properties of AOB in AOT reverse micelles have been studied using absorption and steady state fluorescence spectroscopies as well as

steady-state anisotropy measurements. Since AOT forms negatively charged reverse micelles the interaction of the cationic probes with the surfactant head group is expected to be remarkable. It will therefore be interesting to find out how the added nonaqueous polar solvent (DMSO), droplet size and electrostatic interaction influence the rotation of the solute in the AOT reverse micellar nanopools. An organized molecular assembly is often known to impose restriction on the dynamics and mobility of the probe trapped in it. Depolarization of the fluorescence of the probe has been established to be the most sensitive and powerful technique to elucidate the dynamical information about the fluorophore in the complex microhetergeneous environments.

Experimental

Sodium bis (2-ethylhexyl) sulfosuccinate (AOT 98%) and acridine orange base (AOB) were obtained from Sigma-Aldrich, USA and were used as received. DMSO was purchased from Alfa Aesar (99.9%), Germany and *n*-heptane from Macrochem, Holland. The double distilled water was used with conductance less than 2 $\mu S \cdot cm^{-1}$ at 25^{o}C.

The reverse micellar systems of AOT were prepared by dissolving calculated amount of AOT in *n*-heptane keeping the molal concentration of AOT constant (0.106 *mol/kg*). The ratio of concentrations of polar solvents (water, water+DMSO) and AOT was changed using a calibrated microsyringe. The limited values of *W* for each system were caused by the turbidity of solutions. The volume ratios of components of polar solvents (DMSO to water) were 1/1, 3/1, 5/1, 7/1 and 9/1. AOB was dissolved in *n*-heptane and the desired concentration of AOB was obtained by dilution (about 4.23×10^{-5} *M* for UV-Vis measurements and 1.18×10^{-5} *M* for fluorescence and anisotropy measurements).

The absorption spectra were recorded using Specord 50 Analytic Jena equipment, for fluorescence measurements Varian Cary Eclipse fluorescence spectrophotometer was used with excitation wavelength 425 *nm* for micellar solutions and 417 *nm* in *n*-heptane. The fluorescence emission spectra were recorded in the range of 470-700 *nm* with slit width of 5 *nm* for both the excitation and emission monochromators. To measure steady-state anisotropy typical bandwidths of 5 and 10 *nm* were used for excitation and emission spectra, respectively. The path length used in absorption and emission experiments was 1 *cm*. All experiments were carried out at 25 ^{0}C.

For the anisotropy measurements we used the same apparatus with Cary Eclipse manual polarizer for excitation and emission analyzer. Steady-state fluorescence anisotropy (r) was determined according to the expression:

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad , \qquad (1)$$

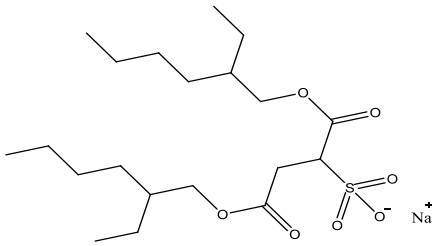
where I_{VV} corresponds to the intensity obtained when the excitation and the emission polarizers are oriented vertically. I_{VH} is the intensity obtained for vertical excitation polarizer and horizontal emission polarizer. The *G* factor was defined as

$$G = I_{HV} / I_{HH} . \quad (2)$$

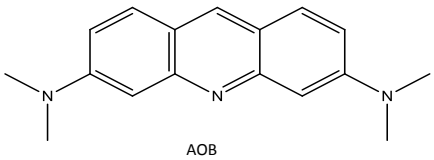
I_{HV} and I_{HH} refer to similar parameters as above for the horizontal positions of the excitation polarizer [13].

Results and Discussion

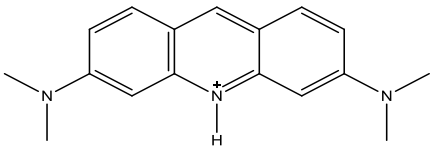
The structural peculiarities of microemulsions rising from strong water-DMSO interaction and on the other hand from the effect of organized media were revealed on the basis of spectral behavior (UV-vis absorption, steady-state fluorescence and fluorescence anisotropy) of AOB in *n*-heptane/AOT/water+DMSO reverse micelles. The molecular structures of AOT, AOB and its protonated monomeric form $AOBH^+$ are depicted in Scheme 1.



Aerosol OT



AOB



$AOBH^+$

Scheme 1. Molecular structures of anionic surfactant AOT, acridine orange base (AOB) and protonated monomer ($AOBH^+$).

Absorption spectra of AOB. Fig. 1 shows the normalized absorption and steady-state fluorescence spectra of AOB in *n*-heptane. The absorption spectrum of AOB in *n*-heptane shows one absorption band at 417 *nm*. The fluorescence emission

spectrum is more structured showing two maxima at 474 and 498 *nm*. Similar results were obtained previously [1]. The structured emission spectra were characteristic for some dyes in nonpolar solvents due to emission from ^1L_b state [14].

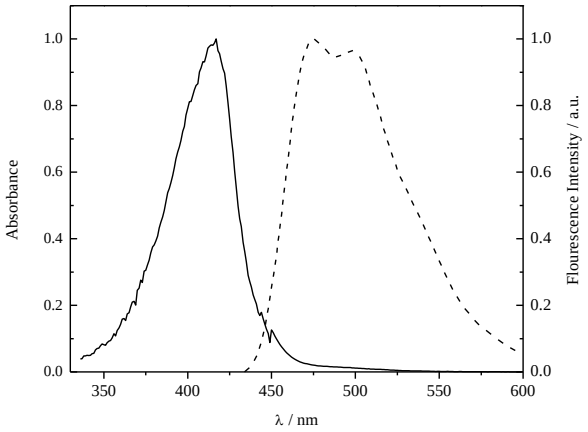


Fig. 1. Normalized absorption (solid line) and fluorescence emission (dashed line) spectra of AOB in *n*-heptane, [AOB]=4.23×10^{-5} *M* for absorption measurements and [AOB]=1.18×10^{-5} *M* for fluorescence measurements.

AOB is cationic-basic type fluorescence dye, which is very sensitive to the presence of protons within the system. At the presence of H^+ ions the protonation of AOB takes place. After the protonation the dimerization of $AOBH^+$ ions occurs and the whole process may be presented by three sequential steps:

$$AOB_f \Leftrightarrow AOB_b \tag{3}$$

$$AOB_b + H^+ \Leftrightarrow AOBH^+ \tag{4}$$

$$2AOBH^+ \Leftrightarrow (AOBH)_2^{2+} \tag{5}$$

where AOB_f and AOB_b are AOB molecules in *n*-heptane (free state) and inside micelle (bound state) respectively.

As it is known the absorption spectrum of AOB in water shows two maxima at 468 and 490 *nm* which can be assigned to the dimeric ($(AOBH)_2^{2+}$) and protonated monomeric ($AOBH^+$) species respectively [12].

Fig. 2 describes the visible absorption spectra of AOB in *n*-heptane/AOT/water and *n*-heptane/AOT/water+DMSO reverse micellar systems at different volume ratios of DMSO and water and different values of *W*. With the increase of *W* the absorption band of $(AOBH)_2^{2+}$ at 468 *nm* decreases and $(AOBH)^+$ band at 490 *nm* increases (Fig. 2). For all the systems there is an isosbestic point at 470 *nm* which indicates that there is equilibrium in reaction (5) and the equilibrium constant may be calculated according to the equation (6)

$$K_D = \frac{\left[(AOBH)_2^{2+}\right]}{\left[AOBH^+\right]^2}. \tag{6}$$

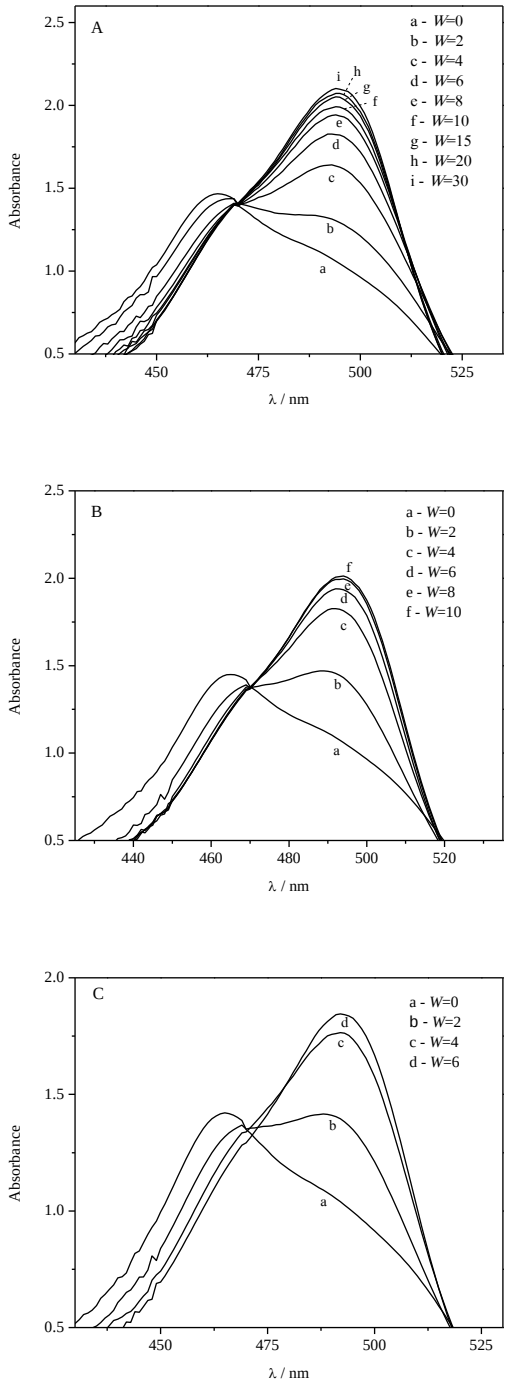


Fig. 2. Absorption spectra of AOB in *n*-heptane/AOT/water (A), *n*-heptane/AOT/1water+ 3DMSO (v/v) (B) and *n*-heptane/AOT/1water+9DMSO (v/v) (C) reverse micellar systems at different *W*, [AOB]=4.23×10^{-5} *M*.

It is known that the observed bands do not obey Lambert-Beer's low, thus to calculate [$(AOBH)_2^{2+}$] and [$(AOBH)^+$] we measure the absorbance (A) for monomeric and dimeric species at each W and the values of concentrations may be determined solving equations (7) and (8) [1]

$$A_{\lambda 1} = \varepsilon^{\lambda 1}_{AOBH^+}\left[AOBH^+\right] + \varepsilon^{\lambda 1}_{(AOBH)_2^{2+}}\left[(AOBH)_2^{2+}\right], \quad (7)$$

$$A_{\lambda 2} = \varepsilon^{\lambda 2}_{AOBH^+}\left[AOBH^+\right] + \varepsilon^{\lambda 2}_{(AOBH)_2^{2+}}\left[(AOBH)_2^{2+}\right], \quad (8)$$

$$\left[AOB\right]_{tot} = \left[AOBH^+\right] + 2\left[(AOBH)_2^{2+}\right], \quad (9)$$

where $A_{\lambda 1}$ and $A_{\lambda 2}$ are optical densities at 468 and 490 *nm* respectively, $\varepsilon^{\lambda_i}_{(AOBH^+)}$ and $\varepsilon^{\lambda_i}_{(AOBH)_2^{2+}}$ are taken from the literature [15] assuming similar values as in water.

Taking into account that in micellar solution absorption band at 417 *nm* is not observed (figure not shown) it can be suggested that all the molecules of acridine orange base are protonated and located within the polar phase.

After the determination of the concentrations of monomeric and dimeric species the values of K_D were calculated at 298.15 K. From the K_D values the standard Gibbs free energy change (ΔG^0) was determined according to the standard thermodynamic expression [16]:

$$\Delta G^0 = -RT \ln K_D . \quad (10)$$

Thermodynamic parameters for the formation of dimeric form of acridine orange (AO) were summarized in Table.

Analysis of the table reveals that at each W the addition of DMSO to micellar solution tends to the decrease of K_D. It can be suggested that DMSO prevents the formation of dimeric species in micellar systems similar to that in bulk solvent [12]. However unlike that of bulk media, where K_D decreases about four times (from 4.04×10^4 M^{-1} to 1×10^4 M^{-1}), in micellar solution K_D decreases only two times (from 6.67×10^4 M^{-1} to 3.90×10^4 M^{-1}) at the same quantity of added DMSO. Moreover in micellar system even at high concentrations of DMSO the basic form of AO was not observed. It shows that in micelles DMSO can influence only the equilibrium (5). It may be explained in terms of the interactions between molecules of AOT and AO. Fig. 2 shows that in the absence of polar phase all AO is protonated and the dimeric species of AO were formed due to residual water in AOT ($W\approx0.3$ [17]). The addition of water decreases the amount of dimeric form and the concentration of protonated monomeric form increases. Both dimeric and protonated monomeric forms were charged positive and were bound with oppositely charged AOT head groups. It can be suggested that DMSO cannot influence the (4) equilibrium as in bulk media due to the strong electrostatic interactions between polar head groups of AOT and $AOBH^+$. As a result the basic form of AO did not form.

K_D decreases rapidly with the increase of W values for all the compositions of polar phase. Similar results were obtained for dimerization of $AOBH^+$ in *n*-

heptane/AOT/water system [1]. It may be concluded that the addition of polar phase changes the micellar size and leads to an easier access of water to the interface. Therefore the increase of the amount and mobility of water favors the dissociation of dimeric species.

Table

Thermodynamic parameters for the dimerization of AOB in *n*-heptane/AOT/water+DMSO reverse micelles at different molar fractions of DMSO and polar phase content, T=298.15 K

X_{DMSO}	*W*	$K \times 10^{-4}$, M^{-1}	(-)ΔG, *kJ mol*$^{-1}$
0	0	18.39	30.05
	2	6.67	27.54
	4	1.85	24.36
	6	0.81	22.30
	8	0.42	20.66
	10	0.30	19.86
	15	0.14	18.00
	20	0.13	17.75
	30	0.08	16.61
0.20	2	3.90	26.21
	4	0.82	22.35
	6	0.32	20.04
	8	0.18	18.52
	10	0.10	17.21
	12	0.07	16.13
	15	0.06	15.92
	20	0.01	12.09
0.43	2	3.22	25.74
	4	0.67	21.84
	6	0.29	19.75
	8	0.16	18.25
	10	0.12	17.51
0.56	2	3.10	25.64
	4	0.63	21.67
	6	0.25	19.38
0.64	2	3.48	25.92
	4	0.69	21.91
	6	0.28	19.70
0.69	2	3.66	26.05
	4	0.72	22.01
	6	0.25	19.40

The values of ΔG^0 reveal that the spontaneous dye aggregation process is predominant at minimum contents of polar phase and in the absence of DMSO. With addition of DMSO the ΔG^0 values increase.

It should be noted that at high concentrations of DMSO the isosbestic point is not observed as clearly as at lower concentrations (Fig. 2C) due to self-association of DMSO molecules [18,19].

Steady-state fluorescence measurements. Fig. 3 shows the fluorescence spectra of AO in *n*-heptane/AOT/water and *n*-heptane/AOT/water+DMSO reverse micelles at different water pool sizes. It should be mentioned that the only emitting specie in AOT reverse micelles is $AOBH^+$, as from the absorption spectra it is evident that all the basic form of AO is protonated. In addition for the detection of fluorescence of dimeric form the initial concentration of AOB must be higher than 1×10^{-3} *M* [12].

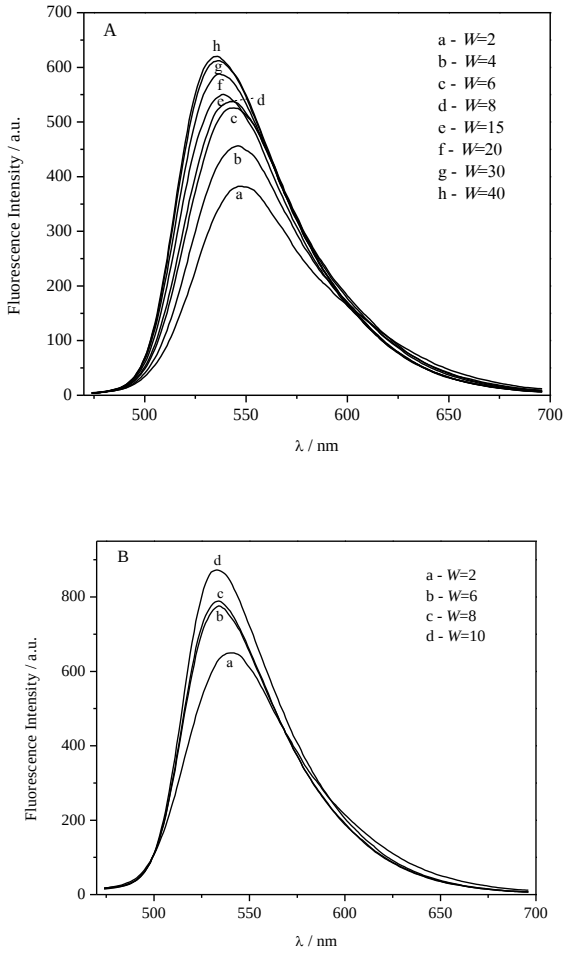


Fig. 3. Fluorescence emission spectra of AOB in *n*-heptane/AOT/water (A) and *n*-heptane/AOT/1water+3DMSO (v/v) (B) reverse micelles at different *W*. Emission spectra were recorded at 425 *nm* excitation wavelength, [AOB]=1.18×10^{-5} *M*.

It follows from Fig. 3 that with the increase of nanopool size the fluorescence intensity increases. Moreover fluorescence intensity increases with the addition of DMSO at each *W*. These results confirm the data obtained from absorption measurements. The increase of the concentration of DMSO leads to the displacement of protonated monomer-dimer equilibrium (5) into left. It results the decrease of the concentration of dimeric form and the concentration of protonated monomeric form increases. The same equilibrium shifts into left with increasing the nanopool size. Therefore the fluorescence intensity increases with increasing *W*.

The fluorescence maximum of $AOBH^+$ in water is at 529 *nm* [12], which shows a large bathochromic shift in AOT reverse micelles. Upon increase in the nanopool size the spectrum gets progressively blue shifted. It should be noted that the absorption maxima of $AOBH^+$ were also red shifted in AOT reverse micelles. With the increase of *W* from 2 to 20 it is evident that the absorption maxima shift towards blue. Even at the highest obtained values of *W* for each system the absorption and fluorescence emission maxima of $AOBH^+$ have not achieved that in bulk media, which indicates that the microenvironment around dye molecule in AOT reverse micelles is significantly different from that in bulk water and water-DMSO solution. The absorption maximum of $AOBH^+$ in AOT reverse micelles at the highest *W* value is about 82 cm^{-1} higher than that in W=2 AOT reverse micelles, and the fluorescence emission maximum of $AOBH^+$ is about 448 cm^{-1} higher than that of W=2 AOT reverse micelles. This different variation value in the absorption and fluorescence emission maxima between highest obtained *W* ($6 \leq W \leq 30$ at different contents of DMSO) and W=2 reveals that the first electronic exited-state dipole moment of $AOBH^+$ is slightly larger than its electronic ground-state dipole moment. It should be mentioned that at the presence of DMSO the shifts in wavelength were the same. Since the solubility of $AOBH^+$ in *n*-heptane is very low it is unlike that $AOBH^+$ will be distributed in the nonpolar *n*-heptane phase of AOT reverse micelles. Thus, it is expected that the dye molecules will mainly reside in the water pool or the interfacial region of AOT reverse micelles. To better inspect the possible localization of dye molecules the fluorescence anisotropy measurements were carried out.

Steady-state fluorescence anisotropy measurements. Fluorescence anisotropy provides important information about the micro-viscosity of the medium around a fluorescent dye molecule. When a dye molecule binds to oppositely charged micelle, the micro-viscosity of the dye-micelle interface gets significantly changed [16]. AOB in *n*-heptane has an anisotropy value of 0.00034, which is in agreement with the value reported earlier [2]. In water the anisotropy value of AO is 0.013. A mild increase in the anisotropy value was observed in DMSO solution (0.013 in water and 0.016 in DMSO). The increase in fluorescence anisotropy of AOB in DMSO was a direct consequence of viscosity enhancement of solvent. Surfactants could significantly alter the anisotropy value of AOB.

It is evident from Fig. 4 that throughout the range of *W* studied the value of anisotropy is quite high compared to that in free aqueous and DMSO solutions. In AOT/*n*-heptane/water system fluorescence anisotropy decreases with an increase in *W* suggesting that the probe molecule experiences an increase in the rotational freedom with an increase in the *W* value, i.e. with increasing size of nanopool. At the highest *W*, the observed anisotropy is still higher than the anisotropy in pure solvent (water and water-DMSO mixture) indicating that the dye molecules in the reverse micelles experience reasonable restriction compared to the situation in bulk media. This indicates that the microenvironment inside this bound water is quite different from that of bulk water, due to which the observed anisotropy at considerably high values of *W* is still much above the value observed in bulk media.

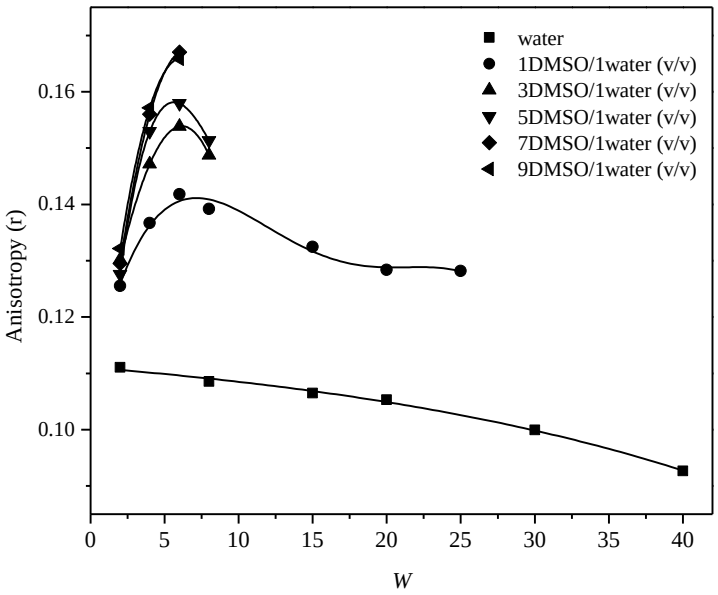


Fig. 4. Variation in fluorescence anisotropy (r) of AOB in *n*-heptane/AOT/polar phase reverse micelles as a function of *W.* The line provides only a guide to the trend of the experimental data points.

The addition of DMSO tends to the increase in fluorescence anisotropy, which indicates that with increasing DMSO concentration the strong hydrogen binding between molecules of water and DMSO makes the microenvironment of dye molecules more rigid. Previously we have shown that the addition of DMSO tends to the hindrance of percolation of conductance due to the increase of the rigidity of micellar interface [20]. The absorption measurements show that the dye is mainly located at the interface of reverse micelles. Moreover it was shown that with addition of DMSO a less hydration of surfactant head groups occurs [21]. Therefore it is reasonable to assume that DMSO promotes the binding of $AOBH^+$ with

surfactant head groups causing the more restriction of rotational freedom of dye molecule.

For all the concentrations of DMSO there is a changeover point in the plots of anisotropy against *W* at around *W*=6. In AOT reverse micelles it was reported that one AOT molecule can be hydrated by as much as 12 water molecules [22]. The counterion Na^+ in AOT can account for 6 water molecules in its solvation shell [23,24]. Thus AOT head group could bind as much as 6 water molecules to get complete hydration, i.e. *W*=6.

In the study reported previously [25] it has been shown that all the photophysical parameters of dye molecules in AOT reverse micelles as a function of *W* have a distinct changeover point at around *W*=8. Moreover it has been suggested that molecular size and property of the probe do not affect the sudden change in the property of the water confined in AOT reverse micelles. These reports are quite consistent with our currently observed changeover point.

Conclusions

The properties of *n*-heptane/AOT/water+DMSO reverse micelles were studied using AOB as molecular probe at different nanopool sizes (different *W* values) by absorption, steady-state fluorescence spectroscopy and steady-state fluorescence anisotropy measurements. The structural peculiarities of reverse micelles were discussed on the basis of the photophysical behaviour of AOB. We obtained the thermodynamic parameters for dimerization process such as dimerization constant, standard Gibbs free energy change, as well as the photophysical parameters such as absorption maxima, fluorescence emission maxima and fluorescence anisotropy of acridine orange in AOT reverse micelles. The results were compared to that of bulk media and the effect of confined media was discussed. The photophysical behaviour of AOB is found to be significantly modified in the reverse micelles from those in the bulk aqueous and DMSO aqueous phases. The study suggests the probable location of the probe in the reverse micellar environment and the more appropriative explanation of the effect of added DMSO on its location.

Acknowledgements

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Ն-ՀԵՊՏԱՆ/AOT/ՋՈՒՐ+ԴԻՄԵԹԻԼՍՈՒԼՖՕՔՍԻԴ ՇՐՋՎԱԾ ՄԻՑԵԼՆԵՐԻ ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ՝ ԿԻՐԱՌԵԼՈՎ ԱԿՐԻԴԻՆԱՅԻՆ ՆԱՐՆՋԱԳՈՒՅՆԻ ՀԻՄՔԸ ՈՐՊԵՍ ՆՇԱԿԻՐ

Գ. Ա. ՇԱՀԻՆՅԱՆ և Շ. Ա. ՄԱՐԳԱՐՅԱՆ

Ակրիդինային նարնջագույնի հիմքն օգտագործվել է որպես մոլեկուլային նշակիր բևեռային ֆազի տարբեր պարունակությամբ ն-հեպտան/նատրիումի բիս(2-էթիլհեքսիլ) սուլֆոսուկցինատ (AOT)/ջուր+դիմեթիլսուլֆօքսիդ (ԴՄՍՕ) շրջված միցելների հատկու-

թյունների ուսումնասիրության համար էլեկտրոնային կլանման, ֆլուորեսցենտային սպեկտրոսկոպիկ մեթոդների և ֆլուորեսցենտային անիզոտրոպիայի չափումների միջոցով: Ստացված արդյունքները համեմատվել են ծավալային ջրում և ԴՄՍՕ-ի ջրային լուծույթներում ստացված տվյալների հետ՝ սահմանափակված միջավայրի ազդեցությունը բացահայտելու համար: Կլանման սպեկտրներից երևում է, որ նույնիսկ ԴՄՍՕ-ի բարձր կոնցենտրացիաների դեպքում ակրիդինային նարնջագույնի հիմնային ձևը չի առաջանում: Միցելային լուծույթում և կլանման, և ֆլուորեսցենտային առաքման մաքսիմումների մոտ ի հայտ է գալիս կարմիր չեզոք: Այնուամենայնիվ, բևեռային փազի քանակության մեծացման հետ կապույտ չեզոքն է դիտվում: Նույնիսկ W-ի (W=[բևեռային փազ]/[ՄԱՆ]) ստացված ամենամեծ արժեքների դեպքում պրոտոնացված ներկանյութի մոլեկուլների կլանման և ֆլուորեսցենտային առաքման մաքսիմումները չեն համընկնում ծավալային միջավայրում ունեցած նույն արժեքների հետ: Սա վկայում է այն մասին, որ AOT-ի չրջված միցելներում ներկանյութի մոլեկուլների միկրոմիջավայրը խիստ տարբերվում է ծավալային ջրում և ջուր-ԴՄՍՕ լուծույթում եղած միկրոմիջավայրից: Անիզոտրոպիայի չափումներից ստացվել է, որ ԴՄՍՕ-ի պարունակության մեծացման հետ տեղի է ունենում ներկանյութի մոլեկուլների ֆլուորեսցենտային անիզոտրոպիայի նշանակալի աճ, ինչից կարելի է ենթադրել, որ ԴՄՍՕ-ն մեծացնում է ներկանյութի մոլեկուլի ընդհանուր չարժողական սահմանափակումը՝ չնորհիվ միցելների մակերևույթի կոշտության մեծացման:

ИССЛЕДОВАНИЕ ОБРАЩЕННЫХ МИЦЕЛЛ *n*-ГЕПТАН/AOT/ВОДА+ ДИМЕТИЛСУЛЬФОКСИД С ИСПОЛЬЗОВАНИЕМ АКРИДИНОВОГО ОРАНЖЕВОГО В КАЧЕСТВЕ МОЛЕКУЛЯРНОЙ ПРОБЫ

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Акридиновый оранжевый использовался в качестве молекулярной пробы для исследования свойств обращенных мицелл *н*-гептан/натриевая соль бис(2-этилгексил) сульфоянтарной кислоты/вода+диметилсульфоксид (ДМСО) методами УФ-виз поглощения, флуоресцентной спектроскопии и флуоресцентной анизотропии при разных содержаниях полярной фазы. Чтобы выявить влияние ограниченной среды, полученные результаты сравнивались с таковыми, полученными для объемной воды и водных растворов ДМСО. Из спектров поглощения видно, что даже при высокой концентрации ДМСО основная форма акридинового оранжевого не наблюдается. В мицеллярном растворе наблюдается красное смещение максимумов поглощения и флуоресцентной эмиссии. Однако при повышении содержания полярной фазы наблюдаются синие смещения. Даже при полученном высшем значении *W* (*W*=[полярная фаза]/[ПАВ]) максимумы поглощения и флуоресцентной эмиссии молекул протонированного красителя не достигают своих значений, полученных в объемной среде. Это означает, что микросреда молекул красителя в обращенных мицеллах AOT значительно отличается от микросреды в объемной воде и растворе вода−ДМСО. Измерения анизотропии показали, что при возрастании содержания ДМСО молекулы красителя проявляют значительно повышенную флуоресцентную анизотропию, подразумевая, что ДМСО увеличивает общее двигательное ограничение молекулы красителя за счет повышения твердости поверхности мицелл.

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