Properties of AOT Aqueous and Nonaqueous Microemulsions Sensed by Optical Molecular Probes

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Nonaqueous microemulsions of AOT in *n*-hexane and *n*-heptane by using six polar solvents as water substitutes such as glycerol (GY), ethylene glycol (EG), propylene glycol (PG), formamide (FA), dimethylformamide (DMF), and dimethylacetamide (DMA) were studied and compared with the corresponding aqueous reverse micelles. The microenvironment generated by these systems was sensed by following the solvatochromic behavior of 1-methyl-8-oxyquinolinium betaine (QB). By varying W_s (W_s = [polar solvent]/[AOT]), the existence of an interaction between the hydrogen bond donor solvents EG, PG, and FA and QB was detected by the changes in the absorption spectra. These changes were interpreted as caused by the partition of the probe between the micelle interface and the polar solvent core by hydrogen bond interactions. The hydrogen bond association constants were calculated, being the largest for FA. In the case of GY, as well as for water, QB seems to be anchored at the interface and no partition was detected. For solvents with no hydrogen bond donor ability such as DMF and DMA the polarity sensed by QB increases with W_s being always larger than the polarity of the neat solvent. The value of the critical micellar concentration (cmc) was also investigated by using acridine orange base as absorption and fluorescence probe. The values of the cmc found for these systems are around $(7 \pm 2) \times 10^{-3}$ M which are higher than those for AOT in comparable aqueous systems.

Introduction

Reverse micelles and water-in-oil microemulsions have attracted considerable attention due to their ability to host hydrophilic components in organic solvents. These systems are suitable media for processes that involve hydrophobic and hydrophilic reactants providing "microreactors" for a variety of chemical and biological reactions. The majority of the studies in these systems use water as the polar component. Among the surfactants capable of forming reversed micelles, the most widely used is sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT).[1,2] AOT has a remarkable ability to solubilize large amounts of water, being able to reach W_o (W_o = [H_2O]/[AOT]) as large as 40−60, depending on the surrounding nonpolar organic medium.[1,2b]

In recent years, attempts have been made to prepare and study waterless microemulsions. In this effort, water has been replaced by polar solvents, which have relatively high dielectric constants and are immiscible in hydrocarbon solvents.[3] These nonaqueous microemulsions are essentially oil continuous[4] and have attracted much recent interest from both theoretical (thermodynamics, particle interactions) and practical (potential use as novel reaction media) viewpoints.[5] These systems are also interesting due to their application in a large number of fields such as cosmetics, solar energy conversion, semiconductors, and microcolloids whose sizes can be controlled by that of the droplets used in their formation and in biological systems.[6] There seems to be a number of distinct advantages of the nonaqueous microemulsions systems over the aqueous ones particularly because they can be used as good reaction media. They are, of course, specially attractive for those reactants that may react with water.[7]

Despite of their potential use the literature about these waterless microemulsions is scarce. The most common polar solvents used include formamide (FA), dimethylformamide (DMF), dimethylacetamide (DMA), ethylene glycol (EG), propylene glycol (PG), and glycerol (GY).[4,5,8−11]

Most of the studies give information about phase and viscous behavior, conductance, and some reactions occurring in the microheterogeneous environment.[4,5,8,12−19] In a recent study[9] dynamic light scattering (DLS) and steady-state absorption spectra of Coumarin 433 have been used to characterize nonaqueous microemulsions in isooctane and decane using AOT and FA, EG, DMF, PG, acetonitrile, and methanol as polar solvents. They give

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evidence that the character of these microemulsions depends partially upon the solubility of the polar solvent in the hydrocarbon. In addition, Laia et al.[11] have studied by DLS isooctane/AOT and *n*-heptane/AOT microemulsions using GY, EG, and FA as polar solvents and found that the interaction between droplets are more attractive than the ones observed in water-in-oil microemulsions, being larger in FA and smaller in GY. Although the droplet structure seems to remains spherical, evidence of cluster formation was obtained in all systems and attributed to strong attractive interactions.

The aim of this work is to obtain some insight about the microenvironment created by the polar solvent in the micelle interior, such as polarity and hydrogen bond interactions, using an optical probe.

Previously, we have studied the micropolarity of AOT aqueous reverse micelles[20,21] by following the solvatochromic behavior of 1-methyl-8-oxyquinolinium betaine (QB). QB presents two electronic absorption bands. The band in the visible, B_1, is sensitive mainly to polarity, while the band in the UV, B_2, is most sensitive to the hydrogen bond donor capability of the solvent. Moreover, the intensity of B_2 has a higher sensitivity than B_1 to the hydrogen bond donor ability of the environment. Hence, the absorbance ratio ($AbsB_2/AbsB_1$) is used in combination with the absorption bands shifts to determine the properties of the microenvironment surrounding the probe.[20]

In the present contribution we have studied nonaqueous microemulsions of AOT in *n*-hexane and *n*-heptane using polar solvents such as GY, EG, PG, FA, DMF, and DMA as water substitutes. These microemulsion's microenvironments were sensed following the solvatochromic behavior of QB. The value of the critical micelle concentration (cmc) was also investigated by using acridine orange free base as absorption and fluorescence probe as was done before in benzene/AOT reverse micelle systems.[22] The properties of aqueous and nonaqueous systems are compared.

Experimental Section

Sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT) from Sigma was purified by the procedure described in ref 23.[23] It was kept under vacuum over P_2O_5. The absence of acidic impurities was checked by using QB as indicator.[20,21]

1-Methyl-8-oxyquinolinium betaine (QB) was prepared by a procedure reported previously.[24] *n*-Hexane and *n*-heptane (Sintorgan HPLC) were dried by distillation over metallic sodium before use. Acridine orange (AO) base was from Sigma and used as received. Ultrapure water was obtained from Labonco equipment model 90901-01. The polar solvents dimethylformamide (DMF), dimethylacetamide (DMA), formamide (FA), ethylene glycol (EG), and propylene glycol (PG) all from Aldrich (more than 99% of purity) were used without further purification. Glycerol (GY) from Merck (fluorescence spectroscopy quality) was eluted through basic alumina to remove detected acid impurities and water.

The solutions of AOT in the hydrocarbon solvents were prepared by weighing and dilution. To introduce the probe, a concentrated solution of QB was prepared in methanol (Sintorgan HPLC quality). The appropriate amount of the methanolic solution to obtain a given concentration of the probe in the micellar medium was transferred into a volumetric flask, and the methanol was evaporated by bubbling dry N_2; the hydrocarbon/AOT solution was added to the residue. The addition of the polar solvents was performed by using a calibrated microsyringe. The molar ratio between polar solvent and AOT is defined as W_s = [polar solvent]/[AOT]. The W_s was varied between 0 and 4.5 or 0 and 2, depending on the polar solvent used. Higher values of W_s were not possible to reach due to turbidity problems. The lowest value for $W_s = 0$ corresponds to a system with no addition of the polar solvent but with the presence of water corresponding to the intrinsic humidity of the system ($W_o \sim 0.3$). This was checked by measuring the λ_{B1} of QB in the stock solutions of AOT/*n*-hexane.[20]

The absorption spectra were measured by using HP 8452A or Shimadzu 2401 at 32 ± 0.1 °C unless otherwise indicated. A Spex Fluoromax apparatus was employed for the fluorescence measurements. The path length used in absorption and emission experiments was 1 cm.

Table 1. B_1 Band of QB in the Neat Polar Solvents and the Nonaqueous Microemulsions

polar solvents	solvatochromic params[a]		λ_{max} (B_1)/nm		
	π^*	α	neat solvents	micelles	Ws^b
DMF	0.88	0.00	546	489 (*n*-heptane)	3.5
				486 (*n*-hexane)	4.0
DMA	0.88	0.00	548	484 (*n*-hexane)	4.2
FA	0.97	0.71	478	478 (*n*-hexane)	2.2
				478 (*n*-heptane)	2.2
PG			462	462 (*n*-heptane)	1.5
				463 (*n*-hexane)	2
EG	0.92	0.90	456	456 (*n*-heptane)	2.2
				455 (*n*-hexane)	2.6
GY	0.62	1.21	452	456 (*n*-hexane)	5
water	1.09	1.17	441	456 (*n*-hexane)	10[c]

[a] From ref 27. [b] Maximum obtained value. [c] See ref 20.

Results and Discussion

I. QB in Nonaqueous AOT Microemulsions. QB is quite soluble in all the polar solvents studied. The λ_{max} of the B_1 band is reported in Table 1. The spectra of QB in the micelles were studied by varying the [AOT] at constant W_s. No significance variation, at least in the range of concentration measured (i.e., 0.02−0.2 M) was observed. Similar results were found previously for QB in *n*-hexane/AOT/water micelles.[20] Thus, in these nonaqueous systems as well as in the aqueous ones QB resides in the micelle polar interior and no partition with the nonpolar medium is detected.[20]

On the other hand, significant changes are observed in the QB spectra when W_s is varied, at constant [AOT]. These changes are different depending upon the hydrogen bond donor capabilities of the polar solvents as follows.

Non-Hydrogen-Bond Donor Solvents (nonHBD). Figure 1 shows typical spectra of QB varying W_s for nonHBD solvents. Only a hypsochromic shift is detected on increasing W_s. As could be expected for this kind of solvents, where there are no possibilities of hydrogen bond interaction with QB, the ratio $AbsB_2/AbsB_1$ gives practically a constant value (i.e., ∼3.2) with W_s.

In Table 1 are gathered the values of λ_{max} (B_1) in the micelles at the maximum value of W_s. As can be observed, the nonHBD solvents which have the same π^* (dipolarity/polarizability) parameter have similar values of λ_{max} (B_1) in the neat solvent. They also reach a similar value of micropolarity as sensed by QB in the micelle at the highest W_s. No significant effect is found on changing the hydrocarbon solvent from *n*-hexane to *n*-heptane in all the systems studied.

It should be noted that QB senses a more polar environment in the micelle than in the pure solvent even at the maximum W_s (Table 1). This is a very novel and

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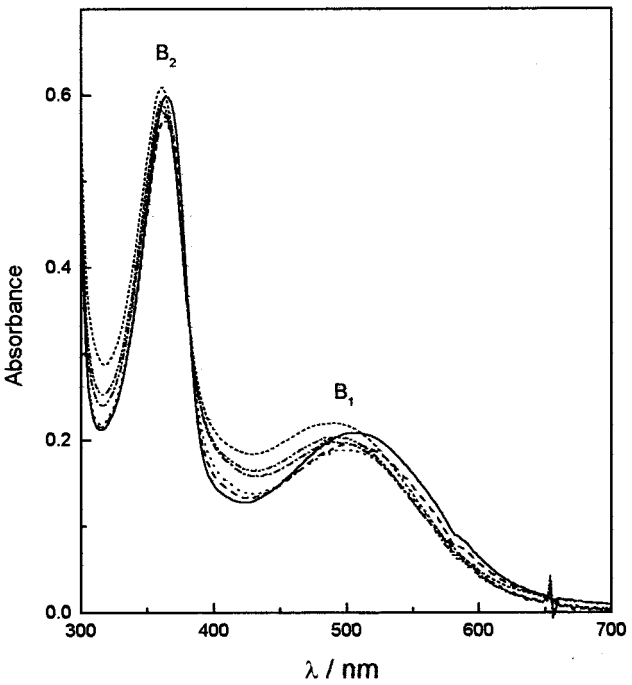

Figure 1. QB absorption spectra in *n*-hexane/AOT/DMF as a function of W_s. [AOT] = 0.15 M; [QB] = 3×10^{-4} M. W_s: (—) 0; (– – –) 0.2; (• • •) 0.8; (- • -) 1.7; (- • • -) 2.2; (- - -) 4.

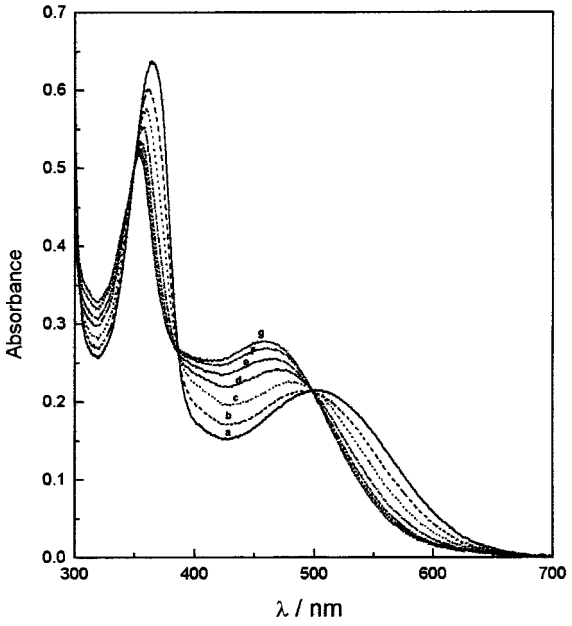

Figure 2. QB absorption spectra in the system *n*-hexane/AOT/EG as a function of W_s. [AOT] = 0.15 M; [QB] = 1.2×10^{-4} M. W_s: a = 0; b = 0.2; c = 0.5; d = 1.0; e = 1.5; f = 2; g = 2.5.

interesting result, which may be indicating a particular structured solvent by strong dipolar interactions, constrained in the droplet. Moreover, an increase of attractive interaction between micelles is expected to accompany the decrease of the hydrogen bond donor ability of the polar solvent.[11] Hence, it is unlikely the formation of monodisperse reverse micelles with nonHBD solvents and larger aggregates may be preferred instead.

Hydrogen Bond Donor Solvents (HBD). Figure 2 shows typical QB absorption spectra in HBD solvents varying W_s at constant [AOT]. Both, B_1 and B_2 bands shift hypsochromically when W_s is increased. These shifts show an increment of the polarity of the interface in the microemulsion when the polar solvent concentration is

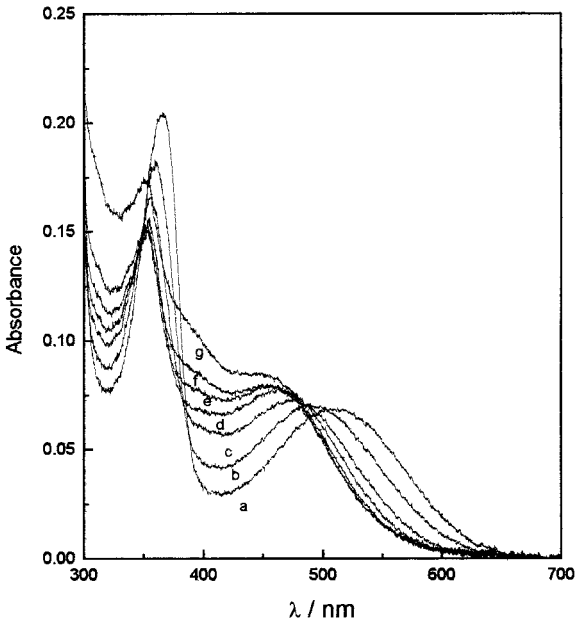

Figure 3. QB absorption spectra in the system *n*-hexane/AOT/GY as a function of W_s. [AOT] = 0.15 M; [QB] = 4×10^{-5} M. W_s: a = 0; b = 0.2; c = 0.5; d = 1.0; e = 2.0; f = 3.0; g = 5.0.

increased. An isosbestic point is observed for EG, PG, and FA, which indicates equilibrium of QB between two environments. Since QB cannot be solubilized in *n*-hexane, these microenvironments should be the interface and the HBD solvent core. An important decrease on the intensity of the band B_2 is also found, showing that there are hydrogen bond interactions involved between QB and the HBD solvents.

When GY is used as solvent (Figure 3) the spectra of QB varying W_s show also a strong hypsochromic shift of the bands B_1 and B_2 and the decrease of the intensity of the B_2 band but they lack an isosbestic point. This behavior is similar to that observed when water is the HBD solvent[20] where QB is in the interface and there is no partition with the water pool. Thus, for the *n*-hexane/AOT/GY system it seems that QB is anchored to the interface and there is no partition with the polar core.

Figure 4 shows typical trends for the B_1 band on changing W_s for some of the solvents used. The trend for similar aqueous reverse micelles with W_0 is also shown for comparison. As can be observed the hypsochromic shift is more notorious below $W_s \sim 2$ for every solvent. In addition, GY shows a very similar trend to water, the greatest shift being below 2 for GY and 10 for water, thereafter the properties detected show practically no variation. This behavior is quite characteristic of a solute which is located in the interface of reversed micelles of AOT.[20,25] For FA, a gradual shift is observed until the maximum experimental value of W_s is reached. Thus, it seems that the solute instead of being anchored in the interface is driven to the polar core when W_s increases. An intermediate behavior is observed for EG and PG.

The shift of the band B_1 for *n*-hexane/AOT/water has been explained considering that the more significant changes in polarity occur when water is involved in the hydration of the AOT polar heads.[20] In the same way, in the nonaqueous system, most of the shift could be due to the solvation of the AOT headgroup by the polar solvent.

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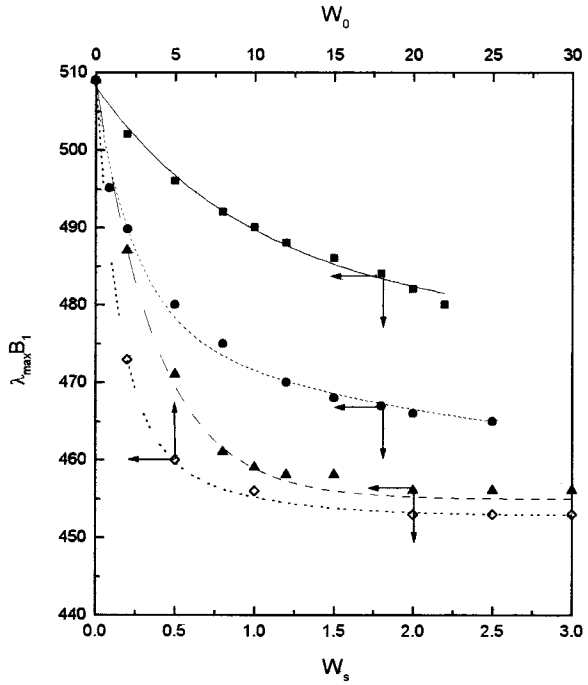

Figure 4. Variation of the B_1 band as a function of W_s in *n*-hexane/AOT/(■) FA, (●) EG, and (▲) GY and (◇) W_o in *n*-hexane/AOT/water.[20] [AOT] = 0.15 M; [QB] = 3×10^{-4} M.

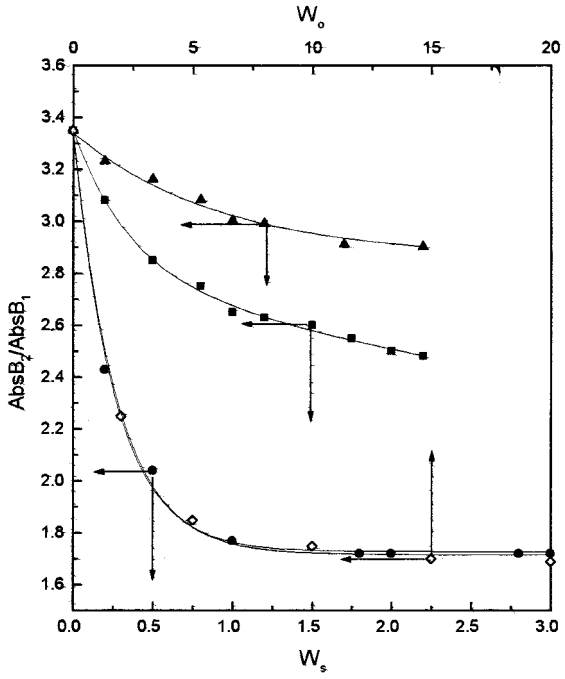

Figure 5. Variation of $AbsB_2/AbsB_1$ as a function of W_s in *n*-hexane/AOT/(▲) FA, (■) PG, and (●) GY and (◇) W_o in *n*-hexane/AOT/water.[20] [AOT] = 0.15 M; [QB] = 3×10^{-4} M.

It is known[26] that alcohols form complexes with AOT via hydrogen bond interaction between a hydroxyl group and the ionic head of the AOT. Moreover, it has been shown[11] that the formation of "solvated" reverse micelles or microemulsions is likely to be associated with the ability of the encapsulated polar solvents to form a large number of hydrogen bonds. From Figure 4 it can be inferred that the solvation of the AOT polar headgroup by HBD solvents follows the order water > GY> EG ∼ PG > FA, which agrees with their HBD abilities as measured Kamlet and Taft's α scale rather than the polarity−polarizability, π^*, parameter[27] (Table 1). It should be noted that at $W_s \cong 2$ the nonaqueous microemulsions reach sizes similar to or greater than the aqueous ones at $W_0 \cong 10$.[9,11] Hence, it can be inferred that QB senses the greatest changes in the microenvironment until a similar size is reached in the polar core of both types of micelle and despite the fact that the AOT seems to be more packed in the nonaqueous ones.[11]

The effect of the hydrogen bonding interaction is more effectively revealed[20,21] when the variation of $AbsB_2/AbsB_1$ is plotted as a function of W_s (Figure 5). This ratio diminishes according to the solvent's α values, being smallest and similar for water and GY. Moreover, from Figure 4 it can be deduced that the solubilization effects of QB (located in the interface) by GY at $W_s = 0.2-3.0$ are similar to water at $W_o = 0.3-20$. For the other HBD solvents, the interaction with QB is much weaker within the experimental ranges of W_s.

Analyzing Table 1 similar conclusions can be reached. At the highest W_s, QB senses the same polarity as the neat solvent for FA, EG, and PG. Thus, QB, which at $W_s = 0$ is located at the interface, seems to be driven to the polar core when the HBD solvent concentration increases as discussed before. Consequently, QB is completely solvated by the polar solvent within the micelle, which seems to have identical properties to the free solvent. This is not the case for water and it seems it is not for GY either. For the aqueous reverse micelle, QB never senses the value of pure water even at very high values of W_0.[20,21] The properties of water confined in reversed micelles are known to be quite peculiar. A study of the dielectric properties of water in AOT reverse micelles in *n*-heptane, using terahertz time-domain spectroscopy, has shown that the amplitude of the dielectric relaxation is substantially smaller than that observed in bulk water.[28] This discrepancy has been attributed to the effect of the confinement, which disrupts the long-range collective modes normally present in the bulk liquid. The polar solvent has to solvate the polar heads of AOT in order to form the micelle.[11] Strong HBD solvents such as water and GY solvate strongly the AOT heads changing consequently its bulk properties inside the micelle. QB seems to be less solvated by this type of solvent and remains anchored at the interface. It is known that water in oil/AOT/water micelles, never reaches bulk properties inside the pool. In addition, viscosity, conductivity, and relaxation studies[10] have shown that isooctane/AOT/GY and oil/AOT/water have similar behavior relative to percolation properties.

On the other hand, for less HBD solvents such as FA, EG, and PG, it is expected to solvate less strongly AOT and maintain most of their bulk structure. In the case of FA, the vibrational spectra in isooctane/AOT and CCl_4/AOT reverse micelles[19] indicate that the intramicellar FA retains a large degree of hydrogen bonding character, it does not interact strongly with AOT polar headgroups, and its structure appears less perturbed than that of water in similar surfactant/hydrocarbon systems. Thus, in less HBD solvents QB is more easily solvated inside the polar core.

Calculation of the QB−HBD Binding Constant. Since the spectra of QB in the micelles with EG, PG, and FA as a function of W_s show neat isosbestic points, the equilibrium of the probe between the two environments can be

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Table 2. Equilibrium Constants (*K*) for the Interaction between QB and HBD Solvents at 32 °C

polar solvent	K (M^{-1})[a]		K (M^{-1})[b]	
	$W_o = 0$	$W_o \sim 1$	$W_o = 0$	$W_o \sim 1$
FA	23.6 ± 2.4	3.5 ± 0.3	22.4 ± 2.2	3.8 ± 0.3
PG	10.9 ± 1.1	2.6 ± 0.3	6.0 ± 0.6	2.8 ± 0.3
EG	8.3 ± 0.8	3.4 ± 0.3	5.0 ± 0.5	2.9 ± 0.3

[a] Equation 2. [b] Equation 5.

quantified. Hence, to evaluate the interaction between QB and these HBD solvents in the micelles a 1:1 interaction was assume (eq 1):

$$QB + SH \overset{K}{\rightleftharpoons} SH\cdots QB \quad (1)$$

Then, the equilibrium constant K can be defined as (eq 2):

$$K = \frac{[QB_b]}{[QB_i][SH]_o} \quad (2)$$

$[QB_b]$ represents [SH·QB]; $[QB_i]$ is the concentration of QB in the interface. $[SH]_o$ is the analytical concentration of SH, the HBD solvent. The value of K was calculated by first obtaining the values of $[QB_b]$ and $[QB_i]$ by measuring the absorbance at two different wavelengths.[29]

$$A_{\lambda 1} = \epsilon_i^{\lambda 1}[QB_i] + \epsilon_b^{\lambda 1}[QB_b] \quad (3)$$

$$A_{\lambda 2} = \epsilon_i^{\lambda 2}[QB_i] + \epsilon_b^{\lambda 2}[QB_b] \quad (4)$$

The values of ϵ_i for QB located in the interface (QB_i) and ϵ_b located in the polar phase of the microemulsion (QB_b) are calculated from the spectrum of QB at $W = 0$ and in the pure polar solvent, respectively. The plots of $[QB_b]/[QB_i]$ vs $[SH]_o$ give very good straight lines ($r > 0.99$) for several sets of wavelengths. From the slope of these plots, the values of K were calculated and they are shown in Table 2.

K was also determined by using the well-known Ketelaar's equation[30,31] (eq 5)

$$\frac{[QB]_o}{A_o - A_{exp}} = \frac{1}{(\epsilon_i - \epsilon_b)} + \frac{1}{(\epsilon_i - \epsilon_b)K[SH]_o} \quad (5)$$

where $[QB]_o$ is the total concentration of the probe, A_o is the absorbance at $W_s = 0$, A_{exp} is the absorbance at different W_s, and the other variables were defined before.

Plotting the left-hand side term of eq 5 vs $1/[SH]_o$ the value of K can be calculated from the slopes and the intercepts. The plots were found linear ($r > 0.99$) and independent of the λ used in the calculation. As can be seen in Table 2 the values of K obtained by this method are in good agreement, within the experimental error, with the ones calculated by the other approach.

Since no isosbestic point is observed for GY, the value cannot be calculated from the spectra of QB in the system. In this sense as discussed in the previous analyses, GY behaves as water and QB seems to be anchored to the interface. This is not the case for the other HBD solvents, which have lower values of α (Table 1). As can be observed in Table 2, the K values follow the order: FA > PG ∼ EG. Thus, FA has the greater value of K even though it has the lower value of α. This is an indication that solvent parameters obtained in homogeneous solutions may not be reflecting the properties of a confined solvent in the microheterogeneous system.

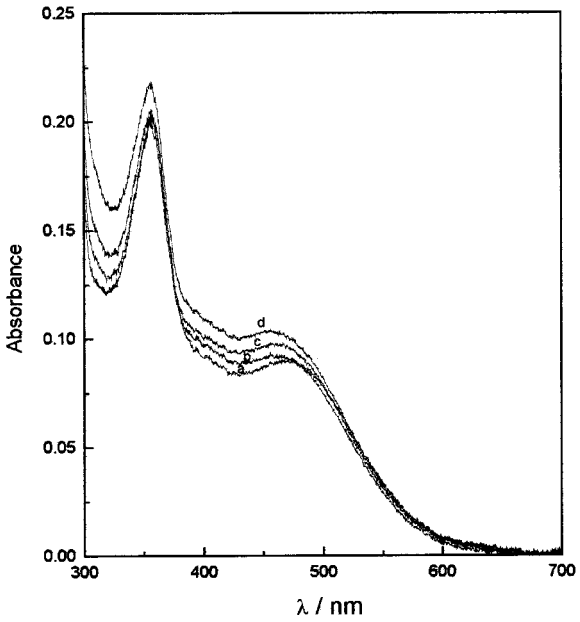

Figure 6. QB absorption spectra in the system *n*-hexane/AOT/FA as a function of W_s. [AOT] = 0.15 M; [QB] = 5×10^{-5} M, $W_o = 3$. W_s: a = 0; b = 1.0; c = 1.5; d = 2.0.

On the other hand, it is known that in benzene/AOT/water system at $W_o = 0$,[24] QB partitions between the nonpolar solvent (in which is much more soluble that in *n*-hexane) and the micelle interface. However, when water is added to the system[21] QB is anchored to the micellar interface. Considering these aspects, water was added to the systems with FA, EG, and PG. Microemulsions where EG was added to water have been reported to be quite monodisperse and EG solubilized cooperatively.[32] Thus, the polar organic solvent solubilizes primarily in the water pool by strong hydrogen bond interactions.

Upon addition of water to values of $W_o \sim 1$, the spectra of QB varying AOT concentration still show the isosbestic point but the value of K is lower (see Table 2) than the obtained in the "dry" systems. When more water is added, the isosbestic point is no longer observed and no partition is detected for QB. A typical result is shown in Figure 6 for FA, at $W_o = 3$. Consequently, when the right amount of water is added, QB senses a mostly aqueous environment and remains anchored at the interface.

II. Determination of cmc Using AO Base as Molecular Probe. To determine the values of cmc of this type of microemulsions, AO base was chosen to perform the study. This probe is quite soluble in *n*-hexane and it can be solubilized well below the value of cmc. It should be pointed that this is not the case for QB, which is completely insoluble in *n*-hexane and in *n*-hexane/AOT at [AOT] < 0.02 M. In addition AO base can be used to detect surfactant aggregation following the absorption and emission spectrum.[22]

Figure 7 shows the absorption and the emission spectra of the AO base *n*-hexane/AOT/DMF as a function of [AOT]. Comparable spectra are observed for the other solvents.

If the apparent molar extinction coefficient of reverse micelles−AO solutions, $\epsilon_{app} = (A\,[AOT]^{-1})$ where A is the absorbance of the AO base, is plotted vs [AOT], graphs of the type shown in Figure 8A are obtained. The intersection of the tangents of the linear portions of the curves is

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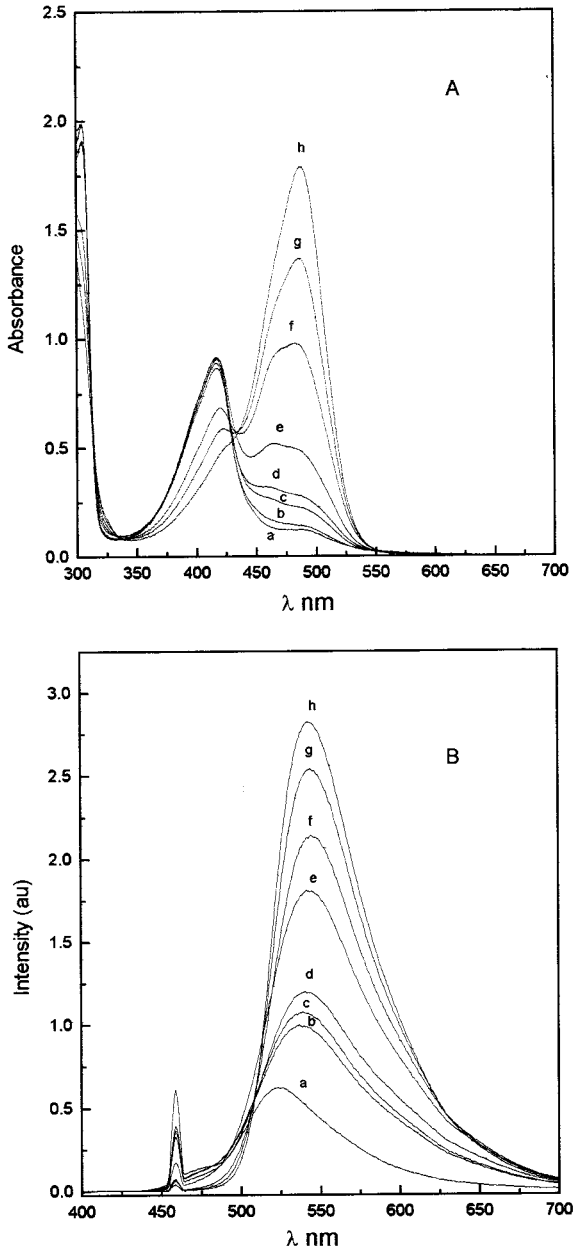

Figure 7. (A) Absorption spectra of AO base in *n*-hexane/AOT/DMF as a function of [AOT]. [AO] = 2×10^{-5} M. $W_s = 2$. [AOT]/M: a = 4.5×10^{-5}; b = 1×10^{-3}; c = 6×10^{-3}; d = 1×10^{-2}; e = 3×10^{-2}; f = 6×10^{-2}; g = 0.10; h = 0.15. (B) Fluorescence spectra of AO base in *n*-hexane/AOT/DMF as a function of [AOT]. [AO] = 2×10^{-5} M. $\lambda_{exc} = 460$ nm. $W_s = 2$. [AOT]/M: a = 4.5×10^{-5}; b = 7×10^{-3}; c = 9×10^{-3}; d = 1×10^{-2}; e = 3×10^{-2}; f = 6×10^{-2}; g = 0.10; h = 0.15.

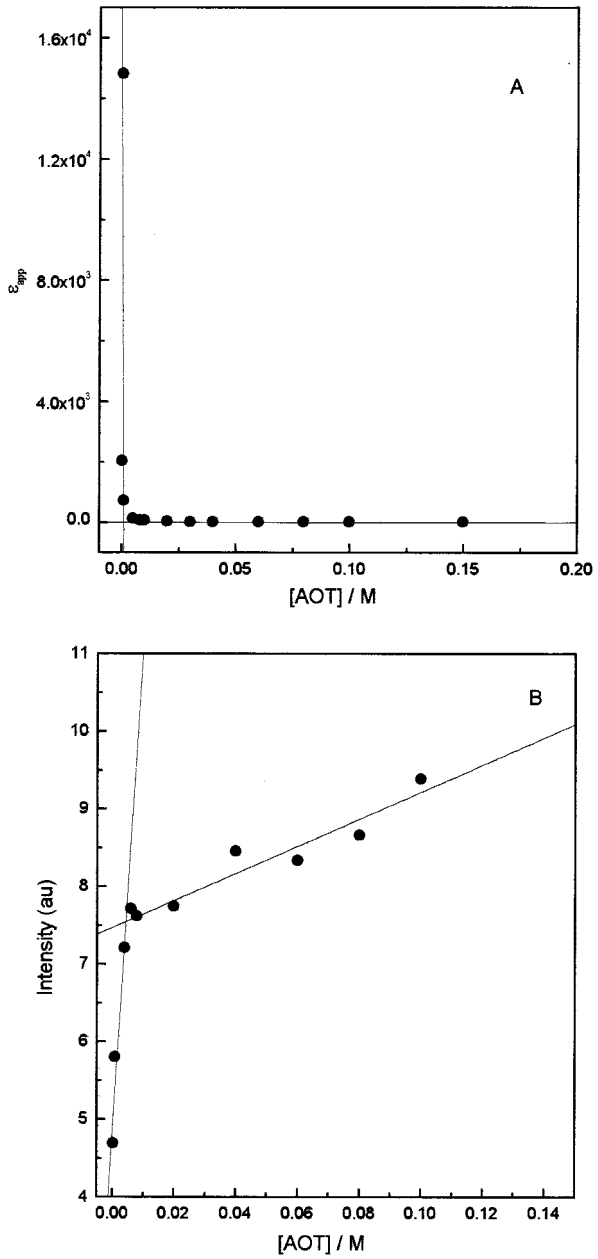

Figure 8. (A) Apparent molar extinction coefficient ($\lambda = 417$ nm) ϵ_{app} of AO base in *n*-hexane/AOT/EG vs [AOT]. $W_s = 2$, [AO] = 2×10^{-5} M. (B) Fluorescence intensity *I* (in arbitrary units) for AO base in *n*-hexane/AOT/EG vs [AOT]. $W_s = 2$. $\lambda_{em} = 530$ nm. $\lambda_{exc} = 417$ nm. [AO] = 2×10^{-5} M.

traditionally interpreted as the cmc of the particular surfactant.[33] In the same way if the fluorescence intensity (*I*) is plotted vs ln[AOT], again, the intercept of the linear portions of the curves can be designated as the operational cmc (Figure 8B).

By use of both methods the value of cmc was calculated for every polar solvent study in *n*-hexane/AOT at $W_s = 2$. Values around $(7 \pm 2) \times 10^{-3}$ M were obtained and no differences within the experimental error were found among the polar solvents. These values are higher than those of in *n*-hexane/AOT aqueous systems,[34] but in the order expected for reverse micelles.[1,2b]

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Conclusions

The microenvironment of the polar core of nonaqueous AOT microemulsions in *n*-hexane and *n*-heptane was investigated by using the solvatochromic behavior of QB as absorption probe. NonHBD solvents DMF and DMA and HBD solvents such as EG, PG, FA, and GY were used as polar solvents. In this type of systems QB is located in the interface of the reverse micelle at $W_s = 0$. In general, addition of the polar solvent causes an hypsochromic shift of both B_1 and B_2 bands of QB showing the expected increase in the micropolarity of the interface. Furthermore, when FA, PG, and EG are the polar solvents, the probe is displaced to the polar core of the aggregate by hydrogen bond interaction. The isosbestic point found in the absorption spectra is consistent with this fact. For these three solvents at the highest value of W_s reached, QB senses the same "polarity" as that in the free solvent. The

interaction was quantified from the absorption spectra by measuring the equilibrium constant K for the association (eq 1) by two different approaches, which give coherent results. FA has the greatest value and it is considered the less perturbed solvent but more able to drive the molecular probe to the polar core. By adding water to these systems, the K values decrease probably due to the solvent association with water.

For GY, as was previously observed for water, there are no isosbestic points in the spectra indicating that there is not partitioning of QB. The molecular probe remains anchored at the interface unable to disrupt the solvation of the polar head of the surfactant.

For nonHBD solvents, QB detects increase in polarity with W_s. Moreover, the micropolarity of the reverse micelle at the maximum W_s reached is higher than that of the neat solvent, a property that may have interesting applications when these systems are used as microreactors.

The values of the cmc for all these system were measured by using the absorption and emission spectrum of AO base at $W_s = 2$ being in the range expected for reverse micelles.

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