

Comparison Between Aqueous and Nonaqueous AOT-Heptane Reverse Micelles Using Acridine Orange as Molecular Probe

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Abstract: Aqueous and nonaqueous AOT/n-heptane reverse micelles were characterized by UV-Visible and fluorescence spectroscopy of AO. The study shows the presence of the dimer in aqueous reverse micelles which is not present in the nonaqueous systems. It seems that there is a conversion of the dimer to monomer in the aqueous reverse micelles at high AOT concentration. In the nonaqueous systems, there is only partition of the monomer. The apparent constants of these processes were calculated.

Introduction

Reverse micelles are aggregates of surfactant molecules with their polar groups concentrated in the interior while the hydrophobic moieties extend into and are surrounded by, the bulk apolar solvent. Thus, water or other polar solvent with high dielectric constants and unmiscible in the hydrocarbon solvent such as ethyleneglycol (EG), N,N-Dimethylformamide (DMF), glycerol (GY), Propileneglycol (PE) can be solubilized in the polar core. The last ones are called nonaqueous microemulsions and present a series of advantages over the aqueous reverse micelles for example can be useful media for organic reaction such as Diels-Alder [1] and others.

The microemulsions can be characterized by using molecular probes such as: 1-methyl-8-oxyquinolinium betaine (QB) or the free base of the dye acridine orange AO [2]. The aim of the present contribution is to investigate the properties of the base AO in aqueous and nonaqueous AOT/n-heptane microemulsions. Thus, the spectroscopic behavior of AO in AOT/n-heptane using water, DMF and EG as polar solvents has been studied by the absorption and fluorescence spectra.

Experimental

Sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) from SIGMA was dried under vacuum over P₂O₅. The molar ratio between polar solvent and AOT is defined as $W_s = [\text{polar solvent}]/[\text{AOT}]$. The free base of AO from SIGMA was used as received. The polar solvent ethyleneglycol (EG) and N,N-

Dimethylformamide (DMF) all from ALDRICH (more than 99% of purity) were used without further purification. Ultrapure water was obtained from Labonco equipment model 90901-01.

Results and discussion

The absorption spectra of AO in water [3] at pH <10 (cationic form, AOH^+), show two bands, at 468 and other at 490 nm which can be attributed to the dimer and monomer specie respectively. At pH >10 (basic form) only the monomer's band is present. Thus, only AOH^+ is the species that can suffer the dimerization process.

In aqueous reverse micelles systems, there are four processes that AO can suffer, a) distribution between the organic phase and the micellar interface; b) protonation to give AOH^+ ; c) dimerization of AOH^+ and d) conversion of the dimer to monomer by the micelle. The spectra of AO with AOT concentration show the disappearance of the band originally present in n-heptane ($\lambda = 417$ nm) and the appearance of the dimer band at 462 nm. The monomer band appears at $[\text{AOT}] > 3.4 \times 10^{-4} \text{ M}$. There are two isosbestic points, at 427 and 467 nm. The fluorescence spectra show the band of the dimer at 644 nm at low $[\text{AOT}]$ and the band of the monomer at 544 nm. On the other hand, in the nonaqueous microemulsion, AOH^+ was not detected and only the distribution of the AO between the two pseudo-phases is observed. The absorption and the emission spectra are consistent with these facts.

The value of the distribution constant, K_{dist} for the process a) was calculated by the Ketelaar approach [4] and, the value of the dimer dissociation K_{des} for the process d) was calculated by the method showed in Ref [5].

The values of K_{dist} show the following order: $K_{\text{dist}}^{\text{Water}} > K_{\text{dist}}^{\text{EG}} > K_{\text{dist}}^{\text{DMF}}$. This can be explained considering the micropolarity of the interfaces and hydrogen bond interactions.

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References and Notes

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