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Binding Constant of Amines to Water/AOT/n-Hexene Reverse Micelles. Influence of the Chemical Structure

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Abstract: The distribution of different amines between n-hexane bulk and the micellar pseudophase of AOT reverse micelles were measured by a fluorometric method. An independent method was used to corroborate the incorporation of the amines to the interface. The effect of the amine structure on the binding constant was analysed.

Introduction

The increase of the solubility in the presence of supramolecular aggregates is an important phenomenon in a variety of scientific and technological areas. Even though, there are extensive data regarding to the solubilization of small molecules in biological membranes, liposomes and direct micelles. However, in reverse micelles systems data are scanty [1]. In our group we have studied the binding constant of nitroanilines and diphenylamines to water/AOT/n-hexane reverse micelles [2,3].

The aim of the present contribution was to determine the binding constant of different aliphatic and aromatic amines to water/AOT/ n-hexane reverse micelles by steady-state fluorescence measurements. The formation of the $Ru(bpy)_3^{+1}$ ion by laser flash photolysis of a mixture of $Ru(bpy)_3^{+2}$ and amines was used as a further confirmation of the distribution of the amines between the micellar pseudophase and the organic bulk.

Experimental

The following amines: n-butylamine, isobutylamine, tert-butylamine and piperidine from Fluka, N,N-dimethylaniline (BDH) and N-methylaniline (Riedel de Haën) were distilled from sodium under nitrogen atmosphere prior to be used. The binding constants were measured by two different approaches: a) a direct method where the amine act as a quencher of a fluorophore incorporated to the micelle [4]; b) Abuin and Lissi's method [5] for compounds that do not fluoresce or act as quenchers, provided that they modified the bimolecular rate between a microphase incorporated fluorophore

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 $(Ru(bpy)_3^{+2})$ and a quencher $(Fe(CN)_6^{-3})$.

For the radical ion determination, the samples were excited with a Nd:YAG laser operated at 355 nm. The signal was transfer from the oscilloscope to the PC through and IEEE interface.

Results and Discussion

The results show the importance of the hydrogen bond interaction of the amines with the AOT polar heads in the their distribution between the two pseudophases. Similar behaviour was found before with other substrates. In this way, primary amines has the larger binding constant, while the tertiary amines are not incorporated to the micellar pseudophase. The influence of the amine solubility in the organic phase, as an extra driving force for the distribution, should be taking into account.

The laser flash photolysis experiments allowed us to confirm that tertiary amines, aliphatic and aromatics, are not incorporated to the micellar pseudophase since the $Ru(bpy)_3^{+1}$ ion, previously observed in water, was not detected in the micellar media

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