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SHORT COMMUNICATION

P.C. Schulz
M.A. Morini

# Styrene solubilization in micelles of dodecyltrimethylammonium hydroxide

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Prof. Dr. P.C. Schulz (✉) · M.A. Morini
Universidad Nacional del Sur
Departamento de Química e Ingeniería Química
Avda. Alem 1253
8000 Bahía Blanca, Argentina

**Abstract** The solubilization of styrene molecules in aqueous dodeciltrimethylammonium Hydroxide (DTAOH) solution was studied by UV-Vis spectroscopy. In short, fully ionized DTAOH aggregates the styrene molecules in the micelle double layer, oriented with their vinyl group to the micelle core and the aryl ring to the intermicellar solution. At increased surfactant concentration, when the aggregates incorporate counterions in their Stern layer, the orientation is maintained, but styrene molecules gradually penetrate into the micelle core as the micelle size and degree of counterion union increased, until they were completely immersed in the hydrocarbon core of rod-like micelles.

**Key words** Solubilization – hydroxide surfactants – styrene – monomers – micelles

## Introduction

The solubilization site and the orientation of solvate monomer molecules in micelles influences the type of polymer which is obtained in both emulsion and microemulsion polymerization [1]. The type and concentration of surfactant determine the rate and mechanism of polymerization, structure and properties of the polymer, and stability of the resulting latex [1]. It was found in previous papers [1] that styrene solubilizes in anionic and cationic micelles following the two-states model [2]. In this model, some of the solvate molecules are adsorbed at the micelle surface, and the others are solubilized in the hydrocarbon micelle core. This is because of the surface activity of aromatic compounds in aliphatic hydrocarbon–water interfaces, since they can form hydrogen bonds with water molecules, *via*, their $\pi$ electrons [3].

In a series of papers we have studied the system dodeciltrimethylammonium hydroxide (DTAOH)–water, [4]. In this way we determined the sites of styrene solubilization in DTAOH micelles. DTAOH aggregates in steps: at $1.3 \times 10^{-3}$ M, small, fully ionized aggregates form which grow with increasing concentration. At $1.11 \times 10^{-2}$ M (CMC) true micelles form with micellized $OH^-$ counterions, and at $3.02 \times 10^{-2}$ M there is a change in micelle structure. At the CMC, DTAOH micelles are small and highly ionized ($\alpha = 0.8$), but the degree of ionization $\alpha$ decreases with increasing concentration [4a]. The goal was to determine the effect of these steps on the solubilization of polymerizable monomers. To follow the path defined in previous papers, we used styrene as a probe, by using the effect of the dielectric constant in the microenvironments on the absorption properties of the solubilized molecules in the UV-Vis spectrum [2a, 5]. This estimation may be made by comparing such characterisitics of the microenvironment of a spectroscopic sensor as chemical shift or the absorbance ratio of a band to the adjacent minimum measurements made in a number of reference solvents.

## Experimental

The preparation of dodecyltrimethylammonium hydroxide solution has been reported elsewhere [4a]. Solutions

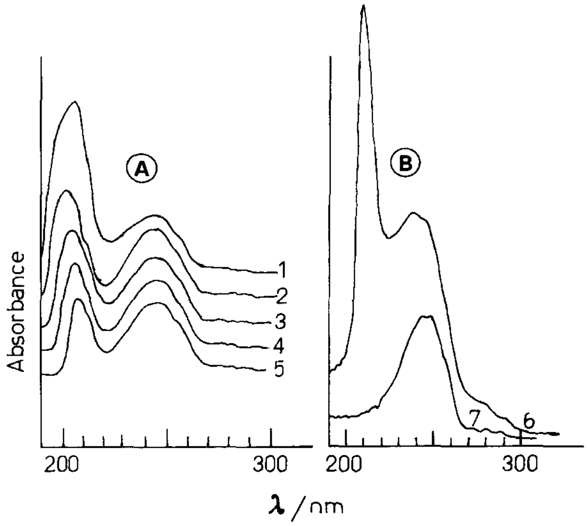

**Fig. 1A** UV-Vis spectra of styrene in methanol–water mixtures: (1) methanol 20 wt.%, $\varepsilon = 72.8$, (2) methanol 40 wt.%, $\varepsilon = 63.0$; (3) methanol 60 wt.%, $\varepsilon = 52.2$; (4) methanol 80 wt.%, $\varepsilon = 42.6$, (5) methanol 100 wt.%, $\varepsilon = 33.8$. **B** styrene spectra of styrene in (6) aqueous 1% urea and (7) *n*-decane

were prepared with double-distilled water, which was degassed and preserved from atmospheric $CO_2$. All chemicals were of analytical grade.

All UV-Vis spectra were studied with a Hewlett Packard HP 8452A spectrometer with a linear diode arrays at 25 °C.

Calibration curves were obtained for $4.8 \times 10^{-5}$ M styrene solutions in n-decane, water + 1 wt.% urea, ethanol, acetone, ethyl ether and different methanol–water mixtures, with dielectric constants ranging from 2 to 81.5 [6]. Figure 1a shows the UV-Vis spectra of styrene in ethanol–water mixtures with different dielectric constants and Fig. 1b the spectra in water with 1% urea and in decane. The ~210 nm band corresponds to transitions $\pi \rightarrow \pi^*$ in the vinyl group, whereas that of ~240 pertains to the transition $\pi \rightarrow \pi^*$ in the aromatic ring (K band). A detailed analysis was made in ref. [1d].

In Fig. 2 the dependence of the absorbance ratio $A_{\sim 210}/A_{\sim 240}$ on the solvent dielectric constant ($\varepsilon$) is plotted. The ratio is a measurement of the average dielectric constant in the microenvironment of the styrene molecules as a whole.

Figure 3 shows the dependence of $\lambda_{mx}$, the position of the maximum at the vinyl $\pi \rightarrow \pi^*$ transition on $\varepsilon$. Figure 4 shows the dependence of the absorbance ratio $A_{\sim 240}/A_{\sim 230}$ between the maximum and the adjacent minimum for the K band. Figure 5 shows the UV-Vis spectra of styrene in (a) $5 \times 10^{-3}$ M DTAOH, (b) $2 \times 10^{-2}$ M DTAOH and (c) $5 \times 10^{-2}$ M DTAOH aqueous solution.

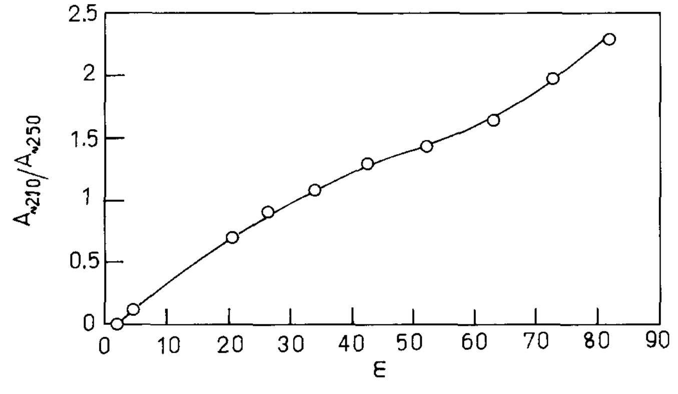

**Fig. 2** Absorbance ratio $A_{\sim 210}/A_{\sim 250}$ vs. solvent dielectric constant

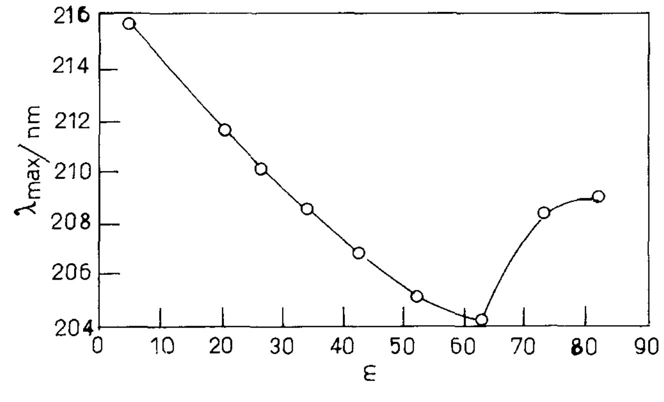

**Fig. 3** Maximum wavelength ($\lambda_{mx}$) or the vinyl $\pi \rightarrow \pi^*$ transition vs. solvent dielectric constant

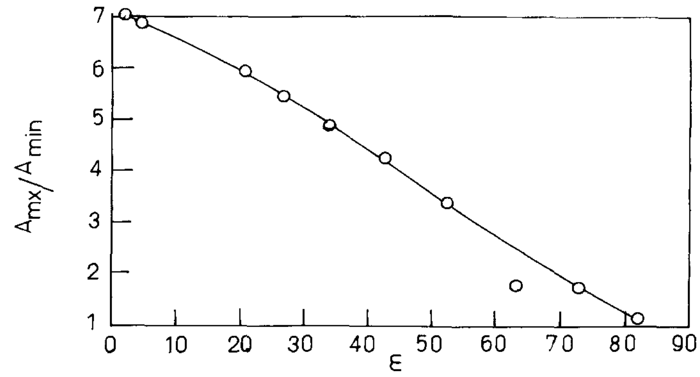

**Fig. 4** Absorbance ratio $A_{mx}/A_{min}$ vs. solvent dielectric constant, for the aryl $\pi \rightarrow \pi^*$ transition

## Results and discussion

- As can be seen in Fig. 5, in all three DTAOH concentrations styrene is associated with aggregates. None of the spectra is similar to that in water. Figure 3 has a

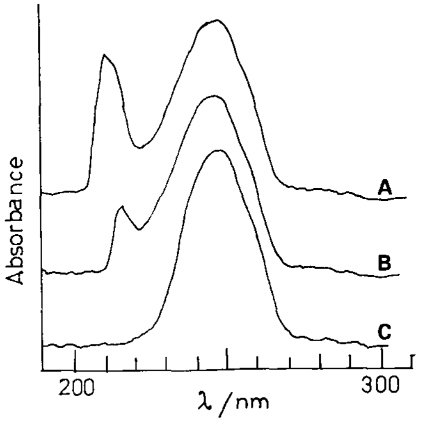

**Fig. 5** Styrene UV-Vis spectra in DTAOH aqueous solution, **A** $5 \times 10^{-3}$ M, **B** $2 \times 10^{-2}$ M, **C** $5 \times 10^{-2}$ M

minimum at $\varepsilon = 63$. This means that except for the minimum, there are two solutions for a given $\lambda_{mx}$ value. The indefinition was avoided by using Fig. 2 to elucidate the average value of $\varepsilon$.

- Solution in $5 \times 10^{-3}$ M DTAOH: At this concentration, DTAOH forms small premicellar aggregates which are almost completely ionized [4a]. From Fig. 2, the average dielectric constant for the whole styrene molecule is about 24. The dielectric constant of the vinyl group microenvironment is $\approx 27$, whereas that of the aromatic ring is $\approx 52$. This situation is compatible with a model in which the styrene molecules are adsorbed at the surface of the aggregates, with the vinyl group closer to the hydrocarbon core than the aromatic ring, which is oriented to the water, as it is shown in Fig. 6. This picture is consistent with a gradual depletion of the dielectric constant when the distance to the surface diminishes [7], and with the affinity between the aromatic $\pi$ electrons and water, by formation of hydrogen bonds [3].
- Solution in $2 \times 10^{-2}$ M DTAOH: From Fig. 2, the average dielectric constant for the whole styrene molecule is about 13. The local dielectric constant for the vinyl group is $\approx 4.3$, whereas that of the aryl group is $\approx 45$. At this concentration there are true micelles, with counterions in the Stern layer [4a]. The dielectric constant of the aryl microenvironments is similar to that found for styrene in DTAB micelles ($\varepsilon \approx 32$).
- Solution in $5 \times 10^{-2}$ M DTAOH: The styrene spectrum is now equal to that in decane, with $\varepsilon \approx 2$. From Fig. 2, the average dielectric constant for the whole styrene molecule is about 2, too. This means that the aggregates have a very high solubilization capacity in the micelle core, with an undetectable (if any) adsorption in the micelle–water interface. This is a surprising result,

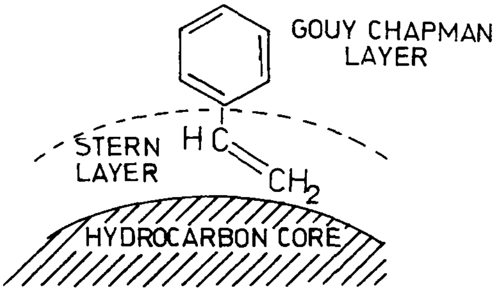

**Fig. 6** Proposed orientation of styrene at the interface of small DTAOH aggregates

because the solubilization of aromatic molecules in micelles (including alkyltrimethylammonium halides) was in the past described by the two-states model: some of the solubilizate was in the micelle interior core, and some adsorbed at the surface, because of the surface activity of aromatic substances at the hydrocarbon–water interface [2b, 8]. This effect is similar to that of acrylic acid on styrene solubilized in cetyltrimethylammonium bromide micelles [1d].

- From the average values of $\varepsilon$ of Fig. 2, the progressive immerison of styrene molecules into the micelle structure may be followed. This average value considers both the vinyl and the aryl micromedia, giving a good measurement of the degree of immersion of the molecule as a whole. It must be reminded that in the two-states model, some molecules are in the micelle core and others are at the interface. Then, the values obtained from Fig. 2 are average values from styrene molecules in both states. The progressive immersion reflects the increased capacity of solubilization of aggregates as they increase in size when counterions join the stern layer.
- The solubilization of styrene in the micelle core without any detectable adsorption at the micelle surface in $5 \times 10^{-2}$ M DTAOH aqueous solution may be due to a combination of effects. Preliminary measurements with laser light scattering in aqueous $5 \times 10^{-2}$ M DTAOH showed very polydisperse rod-like micelles about 300 nm long. The micelle ionization degree at this concentration is $\alpha \approx 0.5$ [4a]. Rod-like micelles have enhanced solubilization capacity, when compared with spherical ones [9]. However, rodlike micelles of other surfactants showed two-states solubilization [2b, 10] We suppose that the highly hydrated $OH^-$ counterions in the Stern layer, with their hydration water molecules strongly oriented, shield the aryl groups from free water molecules. This enables the styrene to form hydrogen bonds with free water molecules. Since the hydrogen bond formation causes for the adsorption of aromatic molecules at the hydrocarbon–water interface, styrene molecules sink into the hydrocarbon micelle core.

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