Colloid Polym Sci 276:278–281 (1998)
© Steinkopff Verlag 1998

SHORT COMMUNICATION

P.C. Schulz
R.M. Minardi
B. Vuano

Solubilization of styrene in the catanionic system dodecyltrimethylammonium hydroxide–*n*′-dodecanephosphonic acid

Received: 2 September 1997
Accepted: 20 October 1997

P.C. Schulz (✉) · R.M. Minardi · B. Vuano
Departamento de Química
e Ingeniería Química
Universidad Nacional del Sur
Avda. Alem 1253
8000 Bahía Blanca
Argentina

Abstract The solubilization of styrene in micelles of the catanionic surfactant dodecyltrimethylammonium hydroxide (DTAOH)–*n*-dodecanephosphonic acid (DPA) was studied by UV–Vis. spectrometry, as a function of the DTAOH:DPA proportion in the surfactant mixture. The styrene molecules are adsorbed at the surface of the micelles, with the vinyl group closer to the hydrocarbon core than the aromatic ring, which is oriented to the water. In micelles with an excess of DTAOH, the dielectric constant of the water surrounding the micelles was strongly affected by the non-neutralized $-N(CH_3)_3^+$ groups at the Stem layer. In micelles with an excess of DPA, the $-PO_3H_2$ groups which are not neutralized by $-N(CH_3)_3^+$, remain almost unionized and hydrogen-bonded. The effect of the micellar surface on the surrounding water dielectric constant dropped sharply. The dielectric constant in the hydrogen-bonded polar layer is ~65, rising to the value of pure water very close to the micellar surface.

Key words Solubilization – styrene – catanionic surfactants – dodecyltrimethylammonium hydroxide – dodecanephosphonic acid

Introduction

The site of solubilization of monomer molecules and their orientation in surfactant micelles influences the kind of polymer obtained in emulsion or microemulsion polymerization [1]. The nature and concentration of the surfactant determine the polymerization mechanism. The structure and properties of the products are also influenced [1]. In previous work it was found that styrene solubilized in common ionic micelles (cationic or anionic) followed the two-states model [2]. In this model, some styrene molecules are solubilized in the micelle hydrocarbon core, whereas others remain adsorbed at the micelle surface. This adsorption is because of the surface activity of aromatic compounds at the hydrocarbon–water interface, caused by the capacity of the aromatic π-electrons to form hydrogen bonds with water [3].

In a previous work we have studied the catanionic system dodecyltrimethylammonium hydroxide (DTAOH) –*n*-dodecanephosphonic acid (DPA). It was found that the structure of micelles changes dramatically with the DTAOH:DPA proportion in the system [4]. These changes may modify the solubilization characteristics of polymerizable monomers in micelles. The study of these characteristics are of interest to design new polymers as well as to follow changes in micelle structure when the DTAOH:DPA proportion is changed in the system. We used styrene as a probe because this monomer was previously studied in cationic and anionic micelles [5, 6]. The study was carried out by analyzing the spectral changes in the UV–Vis. styrene spectra caused by changing the solvent dielectric constant [2]. This allowed us to determine the dielectric constant of the microenvironment of different parts of the styrene molecule. The position of the absorption bands maxima (λ_{max}) and the maximum/

CPS 934

adjacent minimum absorbance ratio (A_{max}/A_{min}) depend on the dielectric constant in the environments of each group.

Experimental

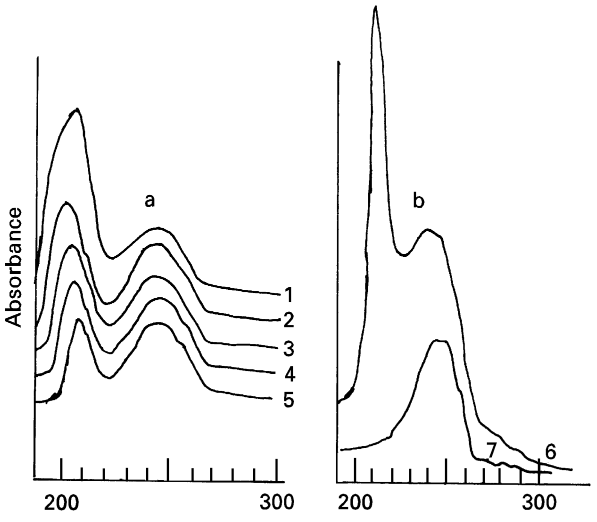
The preparation of pure surfactants and the catanionic mixtures were detailed elsewhere [4]. Double-distilled, CO_2-free water was employed.

UV–Vis. spectra were carried out in a Hewlett–Packard HP 8452 A spectrometer with linear diode array at 25.0 ± 0.1 °C.

Calibration curves were made on styrene solutions (4.8×10^{-5} mol dm^{-3}) in *n*-decane, water +1% urea, ethanol, acetone, ethyl ether and methanol–water mixtures [7]. The solvent dielectric constants (ε) ranged between 2 and 81.5. Figure 1a shows the styrene spectra in several methanol–water solutions, and Fig. 1b, those in water and decane. The ~210 nm band belongs to the $\pi \to \pi^*$ transition in the vinyl group, and that of ~240 nm to the $\pi \to \pi^*$ transition in the aromatic ring (K-band).

Figure 2 shows the $A_{\sim 210}/A_{\sim 240}$ ratio vs. the solvent dielectric constant (ε). This curve is related to the "average" dielectric constant in the microenvironment of the styrene molecules as a whole. Figure 3 shows the dependence of the vinyl $\pi \to \pi^*$ transition λ_{max} on ε. In Fig. 4 the A_{max}/A_{min} ratio for the aryl $\pi \to \pi^*$ transition was plotted vs. ε. The maximum at ~240 nm and the minimum ~230 nm were used.

Fig. 1 UV–Vis spectra of styrene in (a) 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) in (6) water +1% urea and (7) *n*-decane



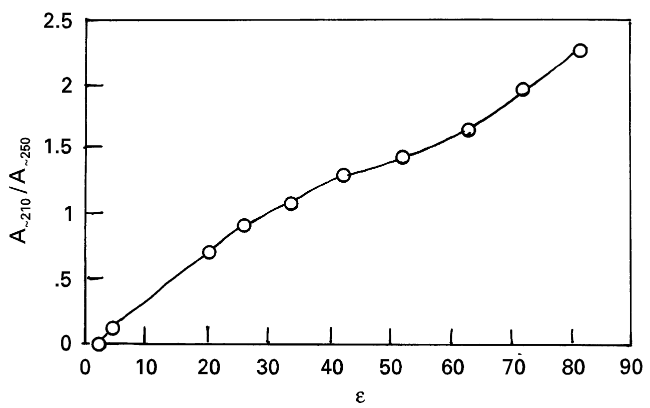


Fig. 2 Absorbance ratio $A_{\sim 210}/A_{\sim 240}$ vs. solvent dielectric constant

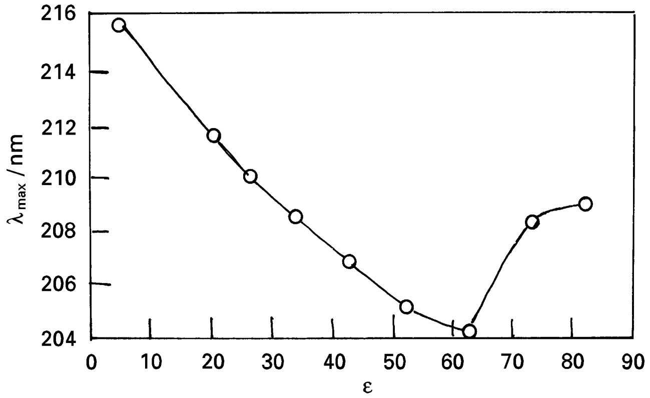


Fig. 3 Maximum wavelength (λ_{max}) for the vinyl $\pi \to \pi^*$ transition vs. solvent dielectric constant

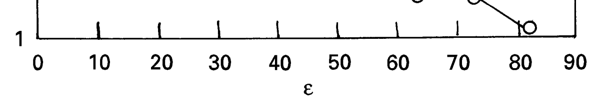


Fig. 4 Absorbance ratio A_{max}/A_{min} vs. solvent dielectric constant for the aryl $\pi \to \pi^*$ transition

Figure 3 has a minimum which gives poor definition between $\varepsilon \approx 33$ and 82. This poor definition was corrected by using Fig. 2. In this figure, the "average" value of ε is not the arithmetic average of the values for vinyl and aryl groups. It may be regarded as a sort of weighed average whose weight factors are not known. By combination of the three figures, it was possible to eliminate the poor definition.

Results and discussion

Figure 5 shows the microenvironment dielectric constant ε for the vinyl and the aryl styrene groups in the catanionic system, plotted vs. the DPA mole fraction in the surfactant (y_{DPA}). To compute this mole fraction water was not taken into account, therefore,

$$y_{\mathrm{DPA}} + y_{\mathrm{DTAOH}} = 1 \qquad (1)$$

In Fig. 5 it may be seen that ε values are lower for the vinyl than for the aryl group. This is consistent with a model in which the styrene molecules are adsorbed at the surface of the micelles, with the vinyl group closer to the hydrocarbon core than the aromatic ring, which is oriented to the water, as it was found in pure DTAOH micelles [8]. There was no significant amount of styrene solubilized in the hydrocarbon micelle core.

Micelles with an excess of DTAOH ($y_{\mathrm{DPA}} < 0.33$) have ionized, non-neutralized $-N(\mathrm{CH}_3)_3^+$ groups at the Stern layer, which affect the dielectric constant of water by electrostatic influence on its structure. Following Danielewicz–Ferchmin [9], the vinyl microenvironment ε value of ~26 corresponds to a distance of about 0.21 nm between $-N(\mathrm{CH}_3)_3^+$ and the vinyl groups. The value of $\varepsilon \approx 50$ for the aryl group corresponds to a distance of about 0.23 nm. The radius of the "bare" $-N(\mathrm{CH}_3)_3^+$ group is 0.209 nm (computed with internuclear distances and atomic radii), whereas that of the micellized group is 0.296 ± 0.014 nm (5c). By comparison with the distances derived from microenvironment dielectric constant measurements, it follows that styrene molecules are inserted in the Stern layer, among the trimethylammonium hydrated groups, with the aryl plane perpendicular to the micelle surface. Due to the aryl size, it cannot be completely immersed into the Stern layer, giving an ε value larger than that of the vinyl. Because the aryl π-electrons system have affinity with water [3], this group is naturally sited close to the aqueous intermicellar solution.

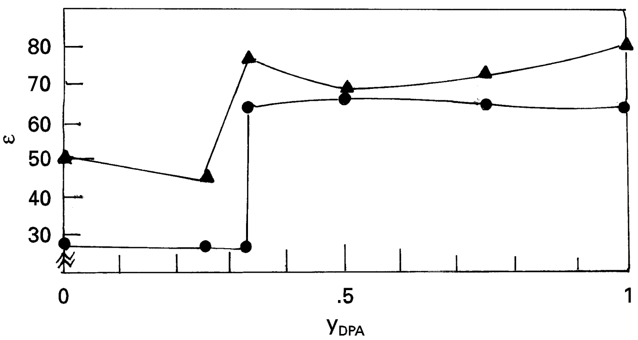


Fig. 5 Dielectric constant of the styrene (●) vinyl (▲) aryl microenvironments in micellar solutions in the system DTAOH–DPA vs. the mole fraction of DPA in the surfactant mixture (y_{DPA})

In DPA-rich micelles ($y_{\mathrm{DPA}} > 0.33$) there is a remarkable change in the styrene microenvironment dielectric constant. That of the vinyl group is still lower than the ε value for the aryl. However, both ε values are higher and closer to each other than in DTAOH-rich micelles.

The ε value of ~65 for the vinyl group, whereas it rises from ~70 ($y_{\mathrm{DPA}} \approx 0.33$) to ~80 ($y_{\mathrm{DPA}} = 1$). This change in the microenvironment dielectric constant is consistent with the micellization behavior of this system [4]. The micelle ionization sharply drops for ($y_{\mathrm{DPA}} \geq 0.33$, which means that the $-\mathrm{PO}_3\mathrm{H}_2$ groups which are not neutralized by $-N(\mathrm{CH}_3)_2^+$ groups remain almost unionized, as it was previously found by ion-selective electrodes measurements [4]. The $-\mathrm{PO}_3\mathrm{H}_2$ groups form a hydrogen-bonded system at the aggregate–water interface in DPA lamellar liquid crystals [10] and micelles [11]. This means that the larger y_{DPA} is, the more extended the hydrogen-bonded structure at the micelle–water interface in this system. Hydrogen-bonded systems have high dielectric constant [12]. The dielectric constant of the vinyl microenvironment is almost constant (~65) and is probably that of the surface hydrogen-bonded system. This is only effective at short distances. The micellar ionization degree gradually falls from $y_{\mathrm{DPA}} \approx 0.33$ to $y_{\mathrm{DPA}} = 1$ [4]. This situation gradually reduces the electrostatic effect on the surrounding water dielectric constant, giving the rise in ε for the aryl group up to about that of pure water in pure DPA micelles. This means that the aryl groups are outside the micelles polar interface.

Acknowledgements One of us (R.M.M.) had a fellowship of the Consejo Nacional de Investigaciones Cientificas y Técnicas de la República Argentina. This work was supported by a grant of the Universidad Nacional del Sur.

References

1. (a) Corona-Galván S, Martínez-Gómez A, Castañeda-Pérez J, Puig JE, Schulz PC, Domínguez JM, Ruano A (1991) Polym Eng Sci 31(6):404; (b) Corona-Galván S, Maldonado A, Schulz PC, Puig JE, Rodríguez BE, Kaler EW ((1990) In: Avances en Ingeniería Química AMIDIQ, Puebla, México, p 167; (c) Corona-Galván S, Castañeda-Pérez J, Martínez-Gómez A, Puig JE, Schulz PC (1990) Colloid Polym Sci 268:1; (d) Puig JE, Corona-Galván S,

Maldonado A, Schulz PC, Rodríguez BE, Kaler EW (1990) J Colloid Interface Sci 137:308; (e) Piirma A (1982) Emulsion Polymerization, Academic Press, New York; (f) Kine B, Redlich GH (1988) In: Wasan T, Ginn ME, Shah DO (eds) Surfactants in Chemical Process Engineering. Marcel Dekker, New York

2. (a) Cardinal JR, Mukerjee P (1978) J Phys Chem 82:1614; (b) Mukerjee P, Cardinal JR (1978) J Phys Chem 82:1620
3. Némethy G, Scheraga HA (1962) J Phys Chem 36:3382
4. Minardi RM, Schulz PC, Vuano B (1996) Colloid Polym Sci 274:669
5. (a) Schulz PC, Morini MA, Minardi RM, Puig JE (1995) Colloid Polym Sci 273(10):959; (b) Morini MA, Schulz PC, Puig JE (1996) Colloid Polym Sci 274:662; (c) Morini MA, Minardi RM, Schulz PC, Rodríguez JL (1996) Colloid Polym Sci 274:854
6. (a) Schulz PC, Fernández-Band BS, Paloemeque M, Allan AL (1990) Colloids & Surf 49:321; (b) Riegelman A, Allawela NA, Hrenoff MK, Streit LA (1958) J Colloid Sci 13:208; (c) LeRosen AL, Reid CE (1952) J Phys Chem 20:233; (d) Brooker LCS, Sprage RH (1941) J Am Chem Soc 63:3214
7. Washburn EW (1929) International Critical Tables of Numerical Data, Vol VI. McGraw Hill, New York, p 100
8. Schulz PC, Morini MA (1997) Colloid Polym Sci 275/6:604
9. Danielewicz I, Ferchmin E (1995) J Phys Chem 99:5688
10. Schulz PC, Abrameto M, Puig JE, Soltero-Martínez FA, González-Alvarez A (1996) Langmuir 12:3082
11. Minardi RM, Schulz PC, Vuano B (1996) Colloid Polym Sci 274:1089
12. Goldman S, Joslin C (1993) J Phys Chem 97:12 349