

# Adsorption of Ionic Surfactant on Polystyrene Particles in the Absence and Presence of Cosurfactant

G. Tuin and H. N. Stein\*

Laboratory of Colloid Chemistry and Thermodynamics, Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received July 12, 1993. In Final Form: December 16, 1993\*

The adsorption of sodium dodecylbenzenesulfonate (SDBS) on polystyrene particles was investigated. Monodisperse polystyrene particles were prepared by a one-step surfactant-free emulsion polymerization and their particle size varied from 0.4 to 3  $\mu\text{m}$ . The surface charge density varies with particle size. Differences in the surface charge density have an effect on the adsorption behavior of surfactants at very high surface charge densities only. The areas per adsorbed SDBS molecule were determined by Maron's soap titration method and were 50–60  $\text{\AA}^2$  at 22  $^\circ\text{C}$  and 60–80  $\text{\AA}^2$  at 60  $^\circ\text{C}$  for the latices depending on the surface charge density. The higher areas per adsorbed molecule at higher temperatures are explained by the larger thermal motion of the adsorbed molecules. The addition of long chain fatty alcohols (cosurfactants) such as dodecanol or cetyl alcohol influences the adsorption behavior of the surfactants. When the alcohols are added at low cosurfactant/surfactant ratios, there is only little influence, whereas at higher ratios the average area per adsorbed molecule of SDBS decreases sharply. This is explained by the fact that when adding alcohols there is a positive attraction between the tails of surfactant and alcohol, without simultaneously introducing additional repulsion through negatively charged groups. This positive effect is more pronounced at larger ratios of cosurfactant/surfactant than at lower ratios. At higher temperatures smaller average areas per adsorbed SDBS molecule are found.

## Introduction

During emulsion polymerization reactions, the surfactant used plays an important role. It emulsifies the monomer, influences the polymerization rate and morphology of the product, and also stabilizes the formed polymer particles. The adsorption behavior of ionic surfactants on polymer particles has therefore been investigated extensively.<sup>1–10</sup> The adsorption of ionic surfactants on polymer particles is due to their amphipathic nature: the polar headgroups are bound to the water phase, while the apolar tails are bound by the apolar polymer surface. In a similar way surfactant molecules also are adsorbed at the water–air interface. If an aqueous dispersion of polystyrene (PS) is in contact with a gas phase, an equilibrium of surfactant molecules adsorbed at the water–air and at the water–polymer interface will be established. The concentration of surfactants in the water phase can be determined by surface tension measurements, because the surface tension is determined predominantly by the amount of surfactant molecules adsorbed at the water–air interface. This principle was already used by Maron et al.<sup>1</sup> in their “soap-titration” technique. The addition of surfactant is continued up to a concentration at which the surface tension reaches an almost constant value, because the surfactant molecules aggregate and form micelles. By measuring the surface tension at different solids percentages, they were able to determine the amount of adsorbed surfactant molecules

at the polymer surface. Since then many investigations have been done for the adsorption behavior of various surfactants on different polymer surfaces.<sup>2–10</sup> The differences found were attributed to various factors, such as polarity of the polymer surface, the number of ionic groups (initiator fragments) on the polymer surface, and the salt present in the aqueous phase.

In microemulsions<sup>11–13</sup> and miniemulsions<sup>14–17</sup> so-called cosurfactants are used to stabilize the emulsion droplets. In microemulsions mostly short chain alcohols (such as pentanol) are used as cosurfactant, whereas in miniemulsions long chain alcohols (such as dodecanol or cetyl alcohol) are used. The cosurfactants used change the adsorption behavior of the surfactants at the oil–water (L1/L2) interface. Most research on the adsorption behavior of mixed emulsifier systems has been done at the L1/L2 interfaces. However, it is expected that addition of a cosurfactant (a higher alcohol or amine) can change the adsorption behavior of anionic surfactants on polymer surfaces as well. There has been little research on this subject. Chou<sup>18</sup> found that SDS (sodium dodecyl sulfate) has a larger molecular area per surfactant molecule on the PS latex in the presence of cetyl alcohol on the PS surface than in its absence. This means that there is a simple replacement of SDS by cetyl alcohol taking place.

The molecular area per surfactant molecule,  $A_m$ , here means: the total area of the interface divided by the number of adsorbed surfactant molecules in absence of

- \* Abstract published in *Advance ACS Abstracts*, March 1, 1994.  
 (1) Maron, S. H.; Elder, M. E.; Ulevitch, I. N. *J. Colloid Interface Sci.* 1954, 9, 89.  
 (2) Paxton, T. R. *J. Colloid Interface Sci.* 1969, 31, 19.  
 (3) Vijayendran, B. R.; Bone, T.; Gajria, C. *J. Appl. Polym. Sci.* 1981, 26, 1351.  
 (4) Maurice, A. M. *J. Appl. Polym. Sci.* 1985, 30, 473.  
 (5) Ali, S. I.; Steach, J. C.; Zollars, R. L. *Colloids Surf.* 1987, 26, 1.  
 (6) Vijayendran, B. R. *J. Appl. Polym. Sci.* 1979, 23, 733.  
 (7) Piirma, I.; Chen, S. R. *J. Colloid Interface Sci.* 1980, 74, 90.  
 (8) Painter, D.; Hall, D. G.; Wyn-Jones, E. *J. Chem. Soc., Faraday Trans 1* 1988, 84, 773.  
 (9) Urban, P. C. *J. Dispersion Sci. Technol.* 1981, 2, 233.  
 (10) Connor, P.; Ottewill, R. H. *J. Colloid Interface Sci.* 1971, 37, 642.

- (11) Gan-zuo, L.; Friberg, S. E. *J. Dispersion Sci. Technol.* 1983, 4, 19.  
 (12) Guo, J. S.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem. Ed.* 1989, 27, 691.  
 (13) Verhoeckx, G. J.; De Bruyn, P. L.; Overbeek, J. Th. G. *J. Colloid Interface Sci.* 1987, 119, 409.  
 (14) Tadros, Th. F. *Colloids Surf.* 1980, 1, 3.  
 (15) El-Aasser, M. S.; Lack, C. D.; Vanderhoff, J. W.; Fowkes, F. M. *Colloids Surf.* 1988, 29, 103.  
 (16) Brouwer, W. M.; El-Aasser, M. S.; Vanderhoff, J. W. *Colloids Surf.* 1988, 21, 69.  
 (17) El-Aasser, M. S.; Lack, C. D.; Choi, Y. T.; Min, T. I.; Vanderhoff, J. W.; Fowkes, F. M. *Colloids Surf.* 1984, 12, 79.  
 (18) Chou, Y. J. Ph.D. Thesis, Lehigh University, 1978; Chapter 3.  
 (19) Sharma, M. K.; Shiao, S. Y.; Bansal, V. K.; Shah, D. O. In *Macro- and Microemulsions, Theory and Applications*; Shah, D. O., Ed.; ACS Symposium Series 272; Washington, DC, 1985; p 91.

cosurfactants. This has to be distinguished from the effective molecular area per surfactant molecule, which is the molecular area of the surfactant in the presence of cosurfactants. In the presence of cosurfactant, the effective molecular area per surfactant molecule,  $A_a$ , is calculated as  $(A_{\text{total}} - N_{\text{cosurf}}A_{\text{cosurf}})/N_{\text{surf}}$ , where  $A_{\text{total}}$  is the total area,  $N_{\text{cosurf}}$  is the number of cosurfactant molecules,  $A_{\text{cosurf}}$  is the area per adsorbed cosurfactant molecule for both dodecanol and cetyl alcohol ( $20 \text{ \AA}^2$ ),<sup>18,24</sup> and  $N_{\text{surf}}$  is the number of surfactant molecules.

The present investigation concerns (i) the effect of the solids percentage on the adsorption of the surfactant, (ii) the effect of the PS particle size on the adsorption of the surfactant, (iii) the influence of cosurfactants on the adsorption of surfactants, and (iv) the influence of the temperature on the adsorption.

### Theory

**Soap Titration Method.** By this method, developed by Maron et al.,<sup>1</sup> the molecular area ( $A_m$ ) of an adsorbed surfactant can be determined. The method involves the titration of a latex with surfactant until the critical micelle concentration (cmc) of the surfactant in solution is attained. The cmc can be determined by either surface tension or conductivity measurements. At the cmc it is assumed that the aqueous phase as well as the interfacial layers (air/liquid and polymer/liquid) have become saturated with surfactant. Because of the large difference between the magnitudes of the air/liquid and polymer/liquid interfacial areas, the amount of surfactant adsorbed at the air/liquid interface can be neglected.

However, the amount of surfactant in the aqueous phase may be significant compared with the adsorbed quantity, especially for large PS particles ( $\geq 1 \mu\text{m}$ ). Therefore it is necessary to subtract this amount from the total surfactant added in order to obtain the amount of surfactant adsorbed on the particle surface.

The amount of surfactant dissolved in the aqueous phase can be determined by titrating several samples of the same latex at different solids percentages. Neglecting the surfactant adsorbed at the air/liquid interface, the total amount of surfactant present in a latex at the titration end point  $C_t$  is given by

$$C_t = C_a + C_f \quad (1)$$

where  $C_t$  is the total concentration of surfactant (moles per liter of suspension),  $C_a$  is the concentration of adsorbed surfactant (moles per liter of suspension), and  $C_f$  is the concentration unadsorbed surfactant (moles per liter of suspension). On division and multiplication of  $C_a$  in eq 1 by  $m$  (grams of polymer per liter of suspension), we obtain

$$C_t = \left(\frac{C_a}{m}\right)m + C_f = S_a m + C_f \quad (2)$$

where  $S_a$  is the surfactant added that has been adsorbed on the latex particles (moles per gram of polymer). Maron assumed that  $C_f$  is constant and equal to  $I$ , the cmc of surfactant in pure water (moles per liter). As shown by Abbey et al.<sup>20</sup> it is more reasonable to assume that the aqueous concentration of the free surfactant at the cmc is a constant quantity and is equal to  $I$ . Therefore the corrected Maron equation becomes

$$C_t = I\left(1 - \frac{m}{\rho}\right) \quad (3)$$

where  $\rho$  is the density of the latex particles (1.05 g/L). Combining eq 2 and eq 3, the corrected Maron equation is obtained:

$$C_t = \left(S_a - \left(\frac{I}{\rho}\right)\right)m + I \quad (4)$$

When various end points are plotted as a function of the amount of polymer, a straight line is obtained.  $S_a$  can be calculated from this plot by adding the intercept  $I$  divided by  $\rho$  to the slope. This intercept  $I$  corresponds with the cmc of the aqueous phase. From the value of  $S_a$  the molecular area of the surfactant can be calculated.

If  $A_i$  is the molecular area in  $\text{\AA}^2$  of surfactant or cosurfactant initially present on the latex particles and  $A_a$  is the molecular area of added surfactant, then the surface area  $A$  in  $\text{\AA}^2$  per gram of polymer is given by

$$A = (S_i A_i + S_a A_a) N_A \quad (5)$$

where  $N_A$  is Avogadro's number and  $S_i$  is the amount of surfactant or cosurfactant initially present. The volume  $V$  of 1 g of polymer in  $\text{\AA}^3$  is

$$V = 10^{24}/\rho \quad (6)$$

where  $\rho$  is the density of the polymer particles (g/mL). Combining eqs 5 and 6 we find for  $V/A$

$$\frac{V}{A} = \frac{10^{24}}{(S_i A_i + S_a A_a) N_A \rho} \quad (7)$$

For spherical monodisperse particles with diameter  $D_s$  (surface average diameter)  $V/A$  equals  $D_s/6$ . Substitution of this relation in eq 7 then gives for  $A_a$  the molecular area of the added surfactant

$$A_a = \frac{9.961}{S_a \rho D_s} - \frac{S_i A_i}{S_a} \quad (8)$$

For particles prepared by surfactant-free emulsion polymerization  $S_i$  is zero (because there are no surfactant or cosurfactant molecules initially present at the latex surface) and eq 8 can be simplified into

$$A_m = A_a = \frac{9.961}{S_a \rho D_s} \quad (9)$$

Relationship 9 is used to calculate the  $A_m$  (molecular area of the adsorbed surfactant) for the adsorption of surfactant in the absence of cosurfactant. In the case of adsorption of surfactant in the presence of cosurfactant, the values of  $S_i$  (the amount of cosurfactant present) and  $A_i$  (the area per adsorbed alcohol molecule) can be substituted in eq 8 and by measurement of  $S_a$  it is possible to calculate  $A_a$ .  $A_m$  is used for the molecular area of a surfactant in the absence of cosurfactants, whereas  $A_a$  is used for the effective molecular area of a surfactant in the presence of cosurfactants.

### Experimental Section

**Materials.** Sodium dodecylbenzenesulfonate (SDBS), ex. Albright and Wilson (Nansa 1260, 25 % (w/v) in water), was used without further purification, because surface tension ( $\gamma$ ) measurements showed no minimum in the  $\gamma$  vs concentration curves, indicative for the absence of surface active impurities.

(20) Abbey, K. J.; Erickson, J. R.; Seidewand, R. J. *J. Colloid Interface Sci.* 1978, 66 (1), 203.

**Table 1. Characterization of the PS Latices**

latex	$D_n$ (nm)	$D_s$ (nm)	$D_v$ (nm)	$P_n$	$\sigma_0$ ( $\mu\text{C}/\text{cm}^2$ )
L-78 <sup>a</sup>	669	690	701	1.05	8.63
L-80 <sup>a</sup>	404	422	432	1.07	2.52
L-86 <sup>b</sup>	1288	1335	1362	1.06	7.18
L-88 <sup>b</sup>	2157	2204	2241	1.04	8.23
L-89 <sup>b</sup>	3230	3278	3308	1.02	9.56

<sup>a</sup> The particle size was determined by the Coulter LS-130.<sup>21</sup> <sup>b</sup> The particle size was determined by the Coulter Counter.<sup>21</sup>

Dodecanol and cetyl alcohol, ex Merck (purity > 98%), were used without further purification.

Water was twice distilled using an all glass apparatus.

**PS Latices.** In this study five different PS latices are used. Their preparation and characterization are described elsewhere.<sup>21,22</sup> The diameters of the latices were measured shortly before use. In Table 1 the properties of these latices are given: number average diameter ( $D_n$ ), surface average diameter ( $D_s$ ), volume average diameter ( $D_v$ ), degree of polydispersity ( $P_n = D_w/D_n$ ) and the surface charge density ( $\sigma_0$ ).

**Cleaning of the Latices.** All latices were dialyzed by the well-known serum replacement technique as described by Vanderhoff<sup>23</sup> in Amicon serum replacement cells. For a description of the serum replacement cells see ref 24. The latex was first diluted to a solid content of a few percent with double-distilled water. Then a volume of 300 cm<sup>3</sup> of the latex was placed in the stirred cell. This cell was equipped with a Nucleopore membrane (Poretics Corp.) with a pore size somewhat smaller than the particle size of the latex. Then a continuous stream of twice distilled water was flowed through the cell until the conductivity of the outlet water reached the same value as that of the inlet double-distilled water (ca.  $0.8 \mu\Omega^{-1} \text{cm}^{-1}$ ).

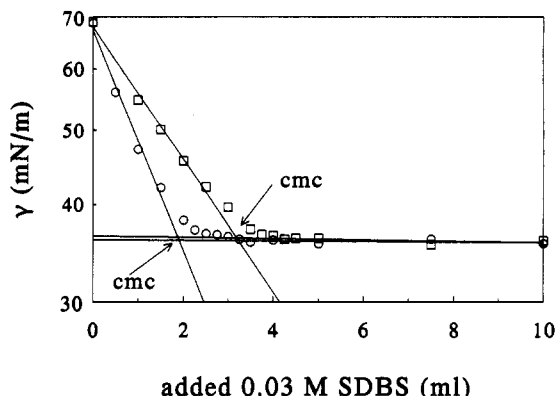
Normally this took about 24 h. All the dissolved electrolyte had then been removed and then the latex was removed from the cell. This procedure was repeated with a new sample of uncleaned latex.

**Determination of Solids Content.** The solids percentage of the different PS latices were determined by drying a known amount of the latex in an oven at 105 °C, until constant weight was reached.

**Procedure of the Surface Tension Measurement.** Surface tension measurements were performed using a Krüss K10T automatic tensiometer (Krüss GmbH, Hamburg) equipped with a Du Nouy ring. Before the measurements the glass vessel (diameter 4 cm, height 2 cm, ground upper edges) was cleaned using chromic acid and washed with double distilled water. The dry vessel was then heated in the gas flame of a Bunsen burner. During a measurements series the Du Nouy ring was also heated in a gas flame between measurements.

After 20.0 g of PS latex was added to the glass vessel and a 10-min wait for thermal equilibrium, the surface tension was measured twice. Then 0.5 mL of 0.03 M SDBS solution in water was added and after 10 min the surface tension was measured. This procedure was repeated until the cmc was reached (the point where further addition of SDBS solution effects only a very slight surface tension decrease). All surface tension measurements were performed at 22 °C.

**Procedure of the Conductivity Measurements.** Conductivity measurements were performed using a conductivity meter (Radiometer Copenhagen). In a thermostated measurement cell of 50 cm<sup>3</sup>, 20.0 g of latex, with known polymer content, was placed. A small magnetic stirrer was added and the conductivity electrode was immersed in the latex. Under stirring, a small amount (0.25 or 0.50 mL) of SDBS solution (0.01 or 0.03 M) was added and after every increment the conductivity was measured. The



**Figure 1.** Surface tension ( $\gamma$ ) vs added 0.03 M SDBS for latex L-78: O, 3.60% solids; □, 17.43% solids. Arrows indicate the cmc.

addition of SDBS solution was continued until 10–15 mL of SDBS solution were added. Conductivity measurements were performed at 22 °C and at 60 °C.

**Procedure of measurements with Cosurfactants.** In the case of the added cosurfactant the measurements were performed by measuring the conductivity. Precise amounts of cosurfactant were added to the latex in glass bottles, in such a way that different percentages of coverage of the PS particles were obtained. The glass bottles were then placed in a water bath at 60 °C (above the melting point of the cosurfactants) for at least 1 day. The measurements were performed in the same way as without cosurfactant at temperatures of 22 and 60 °C.

## Results and Discussion

In Table 1 the parameters of the used PS latices are given. As can be seen from table 1 the latices are monodisperse, indicated by the value of  $P_n$ . This is especially the case for the larger particles. It can also be seen in table 1, that the surface charge density  $\sigma_0$  is rather different for the used latices. The surface charge density arises from the initiator fragments depending on the polymerization procedure and is larger for larger particles. The only exception to this trend is latex L-78, which has a larger surface charge density than expected from its diameter. This latex was prepared in a slightly different way.<sup>21</sup> The surface charge density can have an influence on the molecular areas of surfactants.<sup>4,5</sup>

In Figure 1 a typical example is shown of a titration curve obtained by surface tension measurements of latex L-78. The logarithm of the surface tension is plotted versus the added amount of SDBS solution. As can be seen from Figure 1 the surface tension ( $\gamma$ ) decreases as more SDBS solution is added. This decrease continues up to the point where further addition of SDBS solution results in a much smaller decrease in surface tension (the critical micelle concentration, cmc). In the presence of a larger solids percentage of PS particles, a larger amount of SDBS solution has to be added to reach the cmc. The cmc is indicated in Figure 1 by the two arrows.

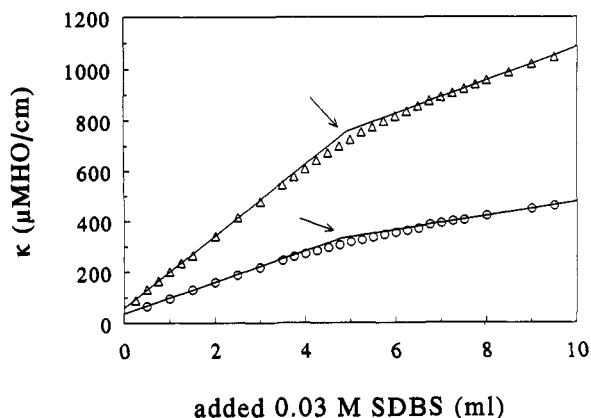
The determination of the cmc was performed from a graph of  $\log(\gamma)$  vs the quantity of SDBS solution added, by approximating the data points not very close to the cmc by straight lines, using linear regression (see Figure 1). There is some uncertainty with regard to the exact position of the cmc, which is related in final instance to the fact that the cmc is an idealization of what is in reality a gradual transition from a micelle-poor to a micelle-rich situation. Errors with regard to the position of the cmc are not considered to be serious, since only the difference between the values of SDBS solution added, in the absence and presence of PS particles, is important in the context

(21) Tuin, G.; Peters, A. C. I. A.; van Diemen, A. J. G.; Stein, H. N. *J. Colloid Interface Sci.* 1993, 158 (2), 508.

(22) Tuin, G.; Stein, H. N. To be submitted for publication in *J. Colloid Interface Sci.*

(23) Vanderhoff, J. W.; Van de Hul, H. J.; Tausk, R. J. M.; Overbeek, J. Th. G. In *Clean surfaces: Their preparation and characterization for interfacial studies*; Goldfinger, G., Ed.; Marcel Dekker, Inc.: New York, 1970; p 15.

(24) Ahmed, S. M.; El-Aasser, M. S.; Pauli, G. H.; Poehlein, G. W.; Vanderhoff, J. W. *J. Colloid Interface Sci.* 1980, 73, 388.



**Figure 2.** Specific conductivity ( $\kappa$ ) vs added 0.03 M SDBS for latex L-80: O, conductivity measurement at 22 °C;  $\Delta$ , conductivity measurement at 60 °C. Arrows indicate the cmc.

of the present paper. The procedure used in the present work was preferred over that used in the work of Maurice,<sup>4</sup> because the latter relies heavily on the data points close to the cmc, in which case the errors of the fitted curve are more pronounced.

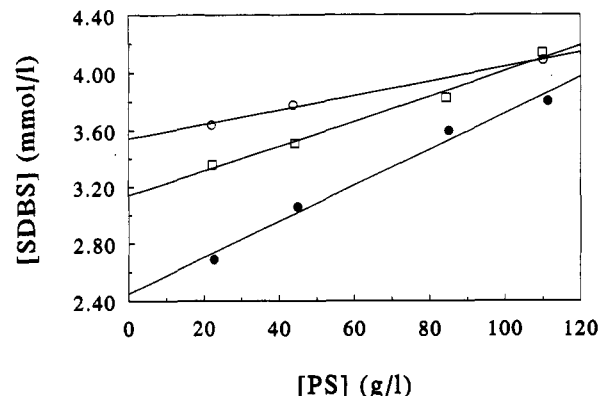
The error in the determination of the surface tension is 0.2 mN/m, which is less than 1%. However, the error in the determined end point is larger than the error in the surface tension measurements, because of the gradual character of the transition at the cmc. Duplicate values differ by less than 6%.

Surface tension measurements were only performed at room temperature (22 °C), because experimentally it was not possible to perform them at higher temperatures. Therefore conductivity measurements were performed both at room temperature (22 °C) and at 60 °C. The conductivity measurements were performed at these two temperatures, for comparing both the difference in  $A_m$  obtained with two different techniques at the same temperature and the difference in  $A_m$  obtained with the same technique at two different temperatures.

In Figure 2 a typical conductivity measurement is shown for latex L-80 for the two different temperatures. As can be seen from Figure 2 the conductivity increases as more SDBS solution is added. The increase is less pronounced after the cmc has been passed. The conductivity versus added quantity of SDBS solution can be represented very well by two straight lines, if the data points close to the cmc are omitted. The best fit of these lines was determined using linear regression. The line before the free surfactant concentration reaches the cmc has a larger slope than the line after the cmc has been passed. The cmc is located at the intersection point of these two lines. With regard to the exact position of the cmc, the same restrictions apply as in the case of cmc determination by surface tension measurements; but again this will not lead to serious errors, since it is the difference between values obtained in the absence and presence of PS particles which is important. Duplicate values differed by less than 5%. Again a higher solids percentage results in more SDBS solution to be added to reach the cmc.

In this way the determined cmc varied between 2 and 3.5 mmol/L; these values show reasonable agreement with literature values ranging from  $3.2 \times 10^{-4}$  mol/L<sup>25</sup> to  $2.0 \times 10^{-2}$  mol/L.<sup>26</sup>

The cmc's obtained with the two different techniques (surface tension and conductivity measurements) and at



**Figure 3.** Plot of the concentration of SDBS vs concentration of PS for the determination of  $S_m$ :  $\bullet$ , surface tension at 22 °C;  $\square$ , conductivity at 22 °C;  $\circ$ , conductivity at 60 °C.

**Table 2.** Molecular Area ( $A_m$ ) for different Latices Measured at Different Temperatures and with Different Techniques

latex	$A_m$ ( $\text{\AA}^2$ ), $\gamma$ , 22 °C <sup>a</sup>	$A_m$ ( $\text{\AA}^2$ ), $\Delta$ , 22 °C <sup>b</sup>	$A_m$ ( $\text{\AA}^2$ ), $\Delta$ , 60 °C <sup>c</sup>
L-78	80	92	117
L-80	49	52	64
L-86	48	60	84
L-88	56	d	d
L-89	78	d	d

<sup>a</sup> Surface tension measurement at 22 °C. <sup>b</sup> Conductometric measurement at 22 °C. <sup>c</sup> Conductometric measurement at 60 °C. <sup>d</sup> Not measured.

different temperatures can be used to calculate  $S_m$ , from which  $A_m$  (the molecular area per adsorbed SDBS molecule) can be calculated. This is shown in Figure 3, where the concentration of SDBS solution at the cmc is plotted versus the concentration of PS particles at the cmc. As can be seen from Figure 3 all obtained points are on straight lines, in agreement with the theory. This confirms the absence of serious errors in the determination of the cmc. The slope of these lines and the intersection points (the cmc) are used to calculate  $A_m$  using eq 9.

In Table 2 the obtained values for  $A_m$  are given for the different techniques and the different temperatures used. The  $A_m$  values are too low to be compatible with an adsorption of the surfactant in the form of trains and loops, as postulated in the Scheutjens-Fleer theory.<sup>27</sup> At least at large surface coverages, adsorption cannot involve more than one or two  $-\text{CH}_2-$  or  $-\text{CH}_3$  groups.

$A_m$  values obtained by surface tension measurements depend on the particle size or the surface charge density. In literature, different values of  $A_m$  are reported for SDBS on PS (in absence of added electrolyte), 62  $\text{\AA}^2$ <sup>2</sup> and 81  $\text{\AA}^2$ ,<sup>4</sup> and for SDS, 14.5  $\text{\AA}^2$ ,<sup>3</sup> 14.5 and 32.7  $\text{\AA}^2$ ,<sup>5</sup> and 47.1  $\text{\AA}^2$ .<sup>7</sup> An  $A_m$  of 53  $\text{\AA}^2$  for SDBS on PS in 0.005 N salt is reported by Paxton.<sup>2</sup> The differences are described to various factors, such as the presence of charged surface groups,<sup>4,5</sup> surface irregularities,<sup>5</sup> and polymer surface polarity.<sup>5</sup> The differences found for the value of  $A_m$  found in the presence of salt are explained by the shielding of the charged head groups of the surfactant.<sup>2</sup>

All values found in the present investigation are very close to the literature values. The values of  $A_m$  for the latices L-80, L-86, and L-88 are very close to each other. Although the surface charge density increases from 2.52 to 8.23  $\mu\text{C}/\text{cm}^2$ , the value for  $A_m$  increases only by 14%. The appearance of charged groups on the surface has only

(25) Jindal, V. K.; Bahadur, P. *Indian J. Technol.* 1982, 20, 66.

(26) Abe, M.; Ohsato, M.; Suzuki, N.; Ogino, K. *Bull. Chem. Soc. Jpn.* 1984, 57, 831.

(27) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* 1980, 84, 178.

a small effect on the adsorption area of the surfactant. The values of  $A_m$  obtained for latex L-78 and L-89 can therefore not be explained by the appearance of charged groups at the surface. A possible explanation for the difference for  $A_m$  for latex L-89 is that the total adsorbing surface area per gram PS is much smaller than for the other latices, because of the larger diameter. The possibility of errors by determining the cmc is therefore increased and the value of  $S_a$  (determined by the position of the cmc) is subject to serious error. However, for latex L-78 this cannot be the explanation, because the surface area is much larger than for latex L-89. The surface charge densities of latex L-78 and L-88 are comparable, but the values for  $A_m$  differ by as much as 66%. The only explanation for this difference which we can see is the surface area used for the calculations. This surface area was determined from the diameter of the latex measured by the Coulter Counter and thus is related to the macroscopic area. Adsorption, however, is related to a surface area on a molecular scale.

Surface irregularities may explain the difference between the calculated surface area (macroscopic) and the real surface area (microscopic). On SEM photographs this kind of surface roughness could be seen only for latex L-78. All other latices used showed no surface roughness.

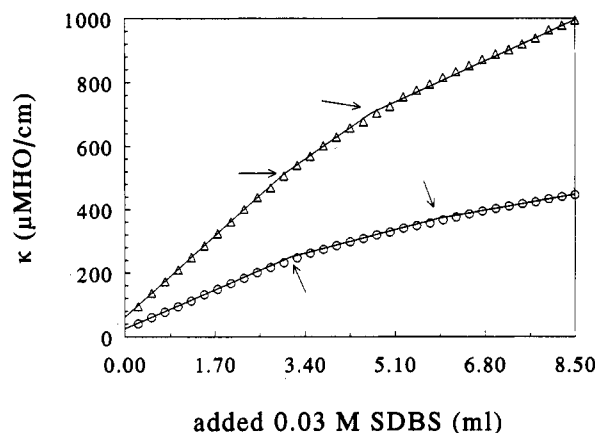
In Table 2 also the values of  $A_m$  obtained with conductometric measurements are listed, at both 22 and 60 °C. The latices used for the conductometric measurements are L-78, L-80, and L-86: with latices L-88 and L-89, the increase in conductivity on SDBS addition up to the cmc was too small for accurate determination of the end point of the titration. This is ascribed to the smaller surface area per gram PS of these latices.

Comparing the results of the surface tension measurements and the conductometric measurements at 22 °C in Table 2 shows that there is some difference between the values of  $A_m$  determined. The values obtained with conductometric measurements are larger than those obtained with surface tension measurements. This is in agreement with data reported by Urban<sup>9</sup> (compare, however, ref 1). The difference between the values of  $A_m$  obtained by conductometric and surface tension measurements is, however, rather small in the experiments reported here.

The values of  $A_m$  obtained with conductometric titrations at 60 °C are all larger than those obtained at 22 °C. This is in agreement with data reported by Piirma and Chen.<sup>7</sup> They studied the adsorption of SDS on PS particles at temperatures varying from 22 to 47 °C. Raising the temperature from 22 to 47 °C resulted in an increase of  $A_m$  from 47.1 to 52.4 Å<sup>2</sup>. This difference was attributed to the larger thermal motion of the molecules. In our case the temperature is even more raised and consequently an even larger value of  $A_m$  was found.

**Results in the Presence of Cosurfactants.** For the measurements with cosurfactants two latices were chosen, latex L-80 and L-86. These latices have a relatively large surface area per gram and the values for the adsorption without cosurfactant are very close to literature values. In Figure 4 the titration of latex L-86 with a surface coverage of dodecanol of  $1.5 \times 10^{-6}$  mol/m<sup>2</sup> is shown as an example. This titration and the titrations without cosurfactants are very similar, with the exception that in the case with cosurfactants, the transition from the situation poor in micelles to that rich in micelles, can be approximated by three straight lines with two intersection points. These are indicated in Figure 4 with the two arrows.

Such a more complicated character of the conductivity



**Figure 4.** Specific conductivity ( $\kappa$ ) vs added 0.03 M SDBS for latex L-86: O, conductivity measurement at 22 °C;  $\Delta$ , conductivity measurement at 60 °C. Arrows indicate the intersection points.

vs added amount of surfactant in the presence of alcohol is ascribed to the excess of alcohol being solubilized in the micelles. In view of the (in reality) gradual character of the transition from solutions poor in micelles to solutions rich in micelles, it is plausible that solubilization of the alcohols in the micelles is more pronounced at surfactant concentrations which exceed the cmc by some amount, than at surfactant concentrations which only slightly exceed the cmc. That such a gradual transition can be approximated, when following the electrical conductivity as a function of added amount of surfactant, by three straight lines was already observed by Chou.<sup>18</sup> The first intersection point found in the latex titration with cosurfactant can be regarded as the cmc.

Such two intersection points are found for both cosurfactants used (dodecanol and cetyl alcohol), the two temperatures studied (22 and 60 °C), and the two surface coverages studied ( $1.5 \times 10^{-6}$  mol/m<sup>2</sup> and  $5 \times 10^{-6}$  mol/m<sup>2</sup>). The first intersection points are used to determine the value of  $S_a$ , similar as described before.

In order to determine  $A_a$  (the adsorption area of SDBS in presence of cosurfactant), some additional assumptions are needed:

1. All the cosurfactant added is assumed to be adsorbed on the PS particles. The solubility of the cosurfactants (dodecanol and cetyl alcohol) in water is very low, as long as the cosurfactants are not solubilized in the micelles. The addition of the cosurfactants refers to the situation before adding surfactants; therefore it is reasonable to assume that all the alcohol molecules are adsorbed on the PS particles. Desorption of the alcohol even after addition of surfactant is only expected to a significant degree at surfactant concentrations larger than the cmc. Measurements of the surface tension after the alcohols had been adsorbed gave the same surface tension, as in the case where no alcohols were used. The decrease in surface tension at very low concentrations of dodecanol is very pronounced. In our case no surface tension decrease was found. This confirms, that the alcohols are indeed all adsorbed on the PS particles.

2. The cosurfactants are assumed to be adsorbed in a monolayer. Absorption of cetyl alcohol or dodecanol by the PS particles is excluded, since it is very unlikely that diffusion of such large molecules into solid PS particles might be fast enough to lead to any perceptible absorption at the time scale of our experiments.

3. The added cosurfactants are assumed to be adsorbed in a random way on PS particles and not patchwise.

If the first two assumptions are granted, the smallest surface area per adsorbed alcohol molecule before addition

**Table 3. Values of  $A_m$ , Effective Molecular Area of SDBS ( $\text{\AA}^2$ ), in the Presence of Different Initial Surface Coverages, Different Cosurfactants, and Different Temperatures, Assuming a Molecular Area of the Cosurfactant of  $20 \text{ \AA}^2$** 

latex	temperature (°C)	without cosurfactant	dodecanol $1.5 \times 10^{-6} \text{ mol/m}^2$	cetyl alcohol $1.5 \times 10^{-6} \text{ mol/m}^2$	dodecanol $5 \times 10^{-6} \text{ mol/m}^2$	cetyl alcohol $5 \times 10^{-6} \text{ mol/m}^2$
L-80	20	52	51	59	45	31
L-86	20	60	59	51	31	24
L-80	60	64	85	103	40	31
L-86	60	84	64	63	25	29

of surfactant becomes  $33 \text{ \AA}^2$ . This value was calculated by the amount of alcohols added divided by the calculated surface area. This is larger than the value of  $20 \text{ \AA}^2$  reported by Chou<sup>18</sup> for cetyl alcohol in a close packed monolayer. A similar value was found by Sharma et al.<sup>19</sup> for  $\text{C}_{18}\text{H}_{37}\text{OH}$  at air/water interfaces.

The third assumption is confirmed by the fact that at the highest surface coverage, the molecular area of an alcohol molecule is larger than that in a close packed monolayer. Then at the titration end point the cosurfactant and surfactant molecules are adsorbed in a mixed close packed monolayer with the alkyl chains standing straight up with their polar heads pointing to the water phase.

In the mixed close packed monolayer the alcohol molecules occupy an area of  $20 \text{ \AA}^2$ . This value was found by Chou<sup>18</sup> for cetyl alcohol. If our assumptions are right, then dodecanol should also occupy an area of  $20 \text{ \AA}^2$ . From this assumption, the obtained values of  $A_a$  (the adsorption area of SDBS in the presence of cosurfactants) are listed in Table 3. It is seen that  $A_a$  values indeed approach  $20 \text{ \AA}^2$  when cetyl alcohol is the cosurfactant; when dodecanol is the cosurfactant, this is only observed with latex L-86. Again, the surface area per adsorbed surfactant or cosurfactant molecule is too low to be compatible with a Scheutjes-Fleer-like adsorption by way of trains and loops.

The data in Table 3 can be understood in the following manner: The temperature of  $22^\circ\text{C}$  is below the melting point of the alcohols, whereas the temperature of  $60^\circ\text{C}$  is above the melting point of the alcohols. From Table 3 it can be seen that at  $22^\circ\text{C}$  the values of  $A_a$  for the two latices studied, at low surface coverage of both alcohols, are very similar to the values obtained without cosurfactant. This would imply that at low surface coverage the effect of the added alcohols is of minor importance only. At these low surface coverages of cosurfactant the amounts of alcohol and SDBS molecules are more or less equal. The electrostatic repulsion between the charged groups of SDBS is still very important. At high surface coverages of cosurfactants the values of  $A_a$  are much smaller than at low surface coverage. In this case the introduction of cosurfactant molecules into a surfactant surface layer leads to additional attraction between the alkyl chains of surfactant and cosurfactant, without simultaneously introducing additional negatively charged ionic head groups. At low temperatures the surface coverage of surfactant can be increased significantly by the presence of cosurfactant, as long as the cosurfactant/surfactant ratio is larger than 1.

At  $60^\circ\text{C}$  a different picture is found. At low surface coverage of cosurfactant the value of  $A_a$  for latex L-80 is

larger and the value of  $A_a$  latex L-86 is smaller than the values obtained without cosurfactants. At this moment it is not quite clear which of these values is the right one.

The values of  $A_a$  obtained at high surface coverage are even lower than those at  $22^\circ\text{C}$ . In spite of the larger thermal motion of both the surfactant and cosurfactant molecules at higher temperatures, the value of  $A_a$  is smaller. The mixed monolayer may be better packed than at lower temperatures. At temperatures of  $60^\circ\text{C}$  it is also important that the ratio of cosurfactant/surfactant should be larger than 1 for reaching a higher surface coverage of surfactant.

### Conclusions

The adsorption of SDBS on PS particles is only slightly influenced by the charged surface groups, arising from initiator fragments. At higher temperatures, the molecular area of SDBS increases, because of the larger thermal motion of the ionic head groups of SDBS. The values found in literature for  $A_m$ , determined from measurement of adsorbed amounts of surfactant and particle sizes, are very different (refs 2–5 and 7). In this study it is shown that the differences in  $A_m$  found are only scarcely influenced by the presence of charged surface groups. A possible explanation for this difference is the surface roughness of the PS particles used.

For this study two cosurfactants (higher alcohols) were chosen, viz. dodecanol and cetyl alcohol. These two cosurfactants were chosen because in miniemulsions such cosurfactants are used for their stabilizing properties. Our results show that these alcohols can change the adsorption behavior of surfactants on solid surfaces as well.

At low surface coverages of cosurfactants little influence on the adsorption of SDBS was found, both at low temperature ( $22^\circ\text{C}$ , below the melting point of the cosurfactant) and  $60^\circ\text{C}$  (above the melting point of the cosurfactants). In this case the electrostatic repulsion of the ionic head groups of SDBS is still very important.

At high surface coverages the adsorption of SDBS is significantly increased (at both temperatures). This may probably be explained by the fact that the positive interaction of the alkyl chains is increased, without simultaneously introducing charged ionic head-groups.

The addition of a cosurfactant can stimulate the adsorption of surfactant only at rather high cosurfactant/surfactant ratios.

**Acknowledgment.** We thank A. C. I. A. Peters for performing the experiments. The financial support of the Foundation of Emulsion Polymerization (SEP) is gratefully acknowledged.