

# Kinetics of Adsorption of Anionic, Cationic, and Nonionic Surfactants

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The kinetics of adsorption of anionic, nonionic, and cationic surfactants on a cellulose–water interface were investigated. The effects of monovalent, divalent, and a mixture of mono- and divalent salts on the adsorption kinetics of anionic surfactant were also investigated. The cellulose surface is shown to have dual sites of hydrophobic and hydrophilic nature. It is shown that anionic and nonionic surfactant molecules mostly adsorb on the hydrophobic site while cationic surfactant molecules mostly adsorb on the hydrophilic site. A simple model based on two-site adsorption is developed to describe the kinetics of adsorption. The values of rate constants are determined by using the experimental data and are compared with those reported in the literature. The rate constants show that the rates of adsorption of sodium dodecylbenzenesulfonate (NaDBS) and polyethoxylated *tert*-octylphenol (TX-100) are same and cetyltrimethylammonium bromide is higher than NaDBS and TX-100 at the cellulose–water interface.

## 1. Introduction

Studies of adsorption of a surfactant at the solid–liquid interface find practical applications in many areas such as detergency, ore flotation, oil recovery, and formulation of dispersions such as paints and pigments. Surfactant adsorption kinetics at the cellulose–water interface are of special interest in detergency and textile processing. Surfactant adsorption kinetics at air–liquid and liquid–liquid interfaces have been studied beginning with the initial attempts by Ward and Tordai.<sup>1–14</sup> Studies of surfactant adsorption kinetics on solid–liquid interfaces have also been reported.<sup>15–23</sup> Adsorption kinetics of surfactants at the hydrophilic solid–liquid interface are reviewed by Paria and Khilar.<sup>24</sup>

There seem to be consequences in the literature that the time variations on the extent of adsorption can be divided into three different regimes: (1) a linear increase in adsorption with time; (2) a transition regime where the rate of adsorption decreases; (3) a plateau regime. The range over which the regions extend varies with the bulk concentration, nature of the surfactant, presence of salt, and so on. The nature of the solid surface, that is, the hydrophobicity or hydrophilicity, and the electrical interactions play an important role in the kinetics of adsorption of a surfactant at the solid–liquid interface.

Adsorption and desorption kinetics of different nonionic surfactants on hydrophilic and hydrophobic silica have been studied.<sup>15–21</sup> The adsorption is described by a two-step process, where the first step is diffusion from the bulk solution to a subsurface and the second stage is transport from the subsurface to the surface and subsequent adsorption. The stagnant layer outside the surface is assumed to be finite because of convection caused by stirring, and the concentration at this layer is determined by equilibrium in the sublayer driven by diffusion. The rate of adsorption in the linear region for a pre-micellar solution is found to be a function of the

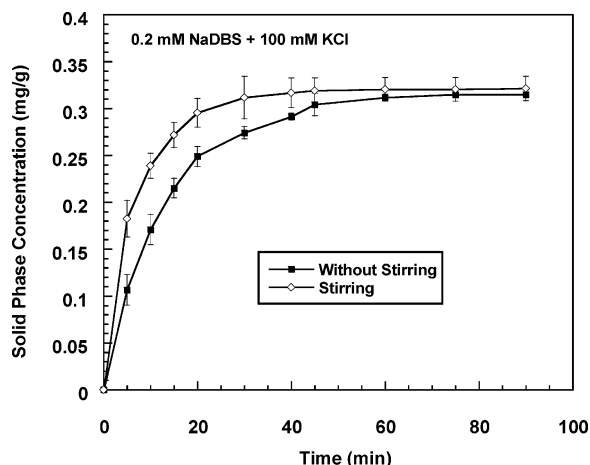
bulk concentration, the critical surface aggregation concentration, the thickness of the stagnant layer, and the diffusion coefficient of the monomer. Surface aggregates are surfactant aggregates similar to the bulk micelle form at the solid–solution interface. The critical concentration of surfactants at which surface aggregates are formed is called critical surface aggregation concentration (csac). A similar relation was found for concentration above the critical micelle concentration (cmc). Biswas and Chattoraj<sup>21</sup> have studied the adsorption of cationic surfactants (C<sub>12</sub>TAB, C<sub>14</sub>TAB, and C<sub>16</sub>TAB) on the silica–water interface at different bulk concentrations, pHs, ionic strengths, temperatures, and electrolyte contents. It is shown that the adsorption follows a two-step first-order rate process with two different process rate constants. Fava and Eyring,<sup>22</sup> and Meader and Fries<sup>23</sup> have studied the adsorption of an anionic surfactant on cotton by the radiotracer method. Fava and Eyring<sup>22</sup> have found that the kinetics of the adsorption of an anionic surfactant on a cotton surface cannot be described by the first-order rate equation.

The adsorption of surfactants onto a cellulose surface is a complex process, and therefore there appear to be conflicting results in the literature. Experimental studies do not cover a wide range of parameters to provide insights into this complex process. We have carried out a systematic and comprehensive study of adsorption of surfactants under a wide range of conditions. In this paper, experimental and modeling studies of adsorption kinetics of anionic, cationic, and nonionic surfactants and an anionic surfactant in the presence of salt are reported.

## 2. Experimental Section

**2.1. Materials.** Anionic surfactants, sodium dodecylbenzenesulfonate (NaDBS), and sodium dodecyl sulfate (SDS), were obtained from Fluka Chemicals, Buchs, Switzerland. Nonionic surfactant, polyethoxylated *tert*-octylphenol (Triton X-100 or TX-100; average 9.5 ethylene oxide groups), was obtained from Sigma Chemicals, St. Louis, MO. NaDBS and TX-100 were used as

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**Figure 1.** Effect of stirring on the adsorption kinetics of NaDBS. 100 mM KCl was used as the background electrolyte.

received, without any further purification. Cationic surfactant, cetyltrimethylammonium bromide (CTAB), was obtained from Ranbaxy Fine Chemicals Ltd., Mumbai, India. It was recrystallized twice from an acetone–methanol (3:1) mixture before use.<sup>25</sup> Calcium chloride dihydrate [E. Merck (India) Ltd.], potassium chloride, and sodium sulfate were obtained from S.D. Fine-Chem Ltd., Mumbai, India. The adsorbent used was Whatman 40 ashless filter paper ( $\varnothing$  9 cm) from Whatman International Ltd., Kent, England. The Brunauer–Emmett–Teller multipoint surface area of this filter paper ( $N_2$  adsorption) was  $16.5 \text{ m}^2/\text{g}$ . Double-distilled water of pH 5.6 and a conductivity of  $1.2 \mu\text{S}$  ( $\mu\text{mho}$ ) was used for the experiment.

**2.2. Methods.** The filter paper was washed thoroughly with double-distilled water to remove the dust and soluble ions from the filter paper until the conductivity of the washed water became equal to that of the distilled water. Then it was dried in an oven for 1–1.5 h at  $50\text{--}55 \text{ }^\circ\text{C}$  to constant weight.

The concentrations of NaDBS and TX-100 were determined by measuring UV absorbance at 223 nm (wavelength) using a UV–vis spectrophotometer (Shimadzu model UV-160A). Quartz glass cells (Hellma) of 10-mm path length were used. The concentration of CTAB was measured by a two-phase titration technique by using methylene blue indicator and standard SDS (99% pure) as the titrate.<sup>26,27</sup> The cmc at room temperature ( $25 \text{ }^\circ\text{C}$ ) was determined from the break in the surface tension vs concentration plots using a Du–Noüy ring tensiometer (Fisher surface tensiometer model 21).

In adsorption studies, surfactant solutions were prepared by diluting the concentrated stock solutions. The amount of adsorbent and the volume of the solution were kept constant for each set of experiments. For each set of experiments, 0.580 g of filter paper was used after cutting it into small pieces of 5–10-mm size. A 10-mL surfactant solution was used for each set of experiments. The adsorption experiments were carried out in a 25-mL stopper glass bottle, and the system was stirred slowly by shaking. All of the experiments were done at room temperature ( $25 \text{ }^\circ\text{C}$ ).

### 3. Experimental Results and Discussion

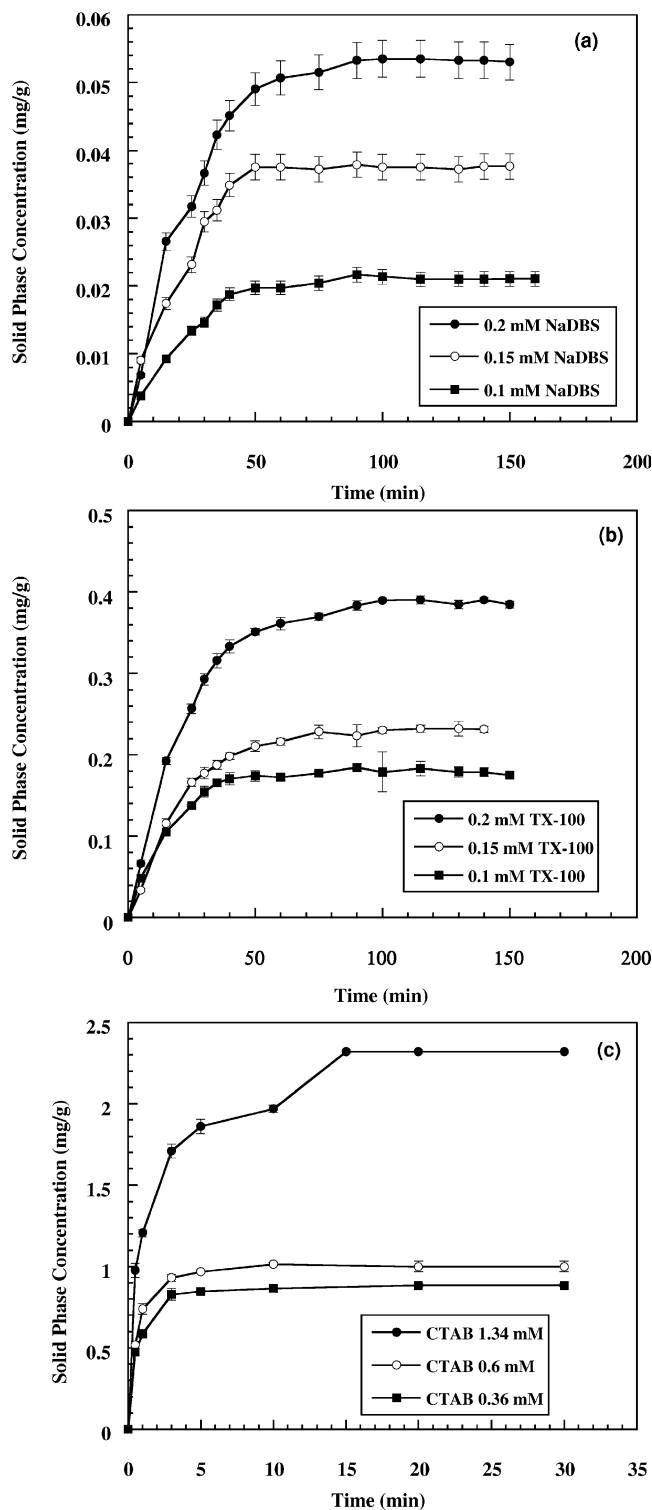
**3.1. Effect of External Mass Transfer on the Adsorption Kinetics of NaDBS.** Figure 1 presents the effect of bulk (external) mass transfer on the kinetics

of NaDBS adsorption on filter paper (surface). The figure presents a comparison between two conditions: without stirring and with stirring. The main objective of this experiment is to determine whether mass transfer is the controlling step in the kinetics of adsorption. As mentioned above, the adsorption can be described as a two-step process. The results presented in Figure 1 indicate that there is a weak effect of stirring (mass transfer). On the other hand, Figure 1 shows that the extent of adsorption at equilibrium is not dependent on stirring. All of the experiments in this study were carried out under identical stirring conditions. The differences in the kinetics of adsorption can, therefore, be attributed to the interactions between the adsorption sites and the surfactant molecules and not to the mass-transfer process.

**3.2. Adsorption Kinetics of NaDBS, TX-100, and CTAB.** The adsorption kinetics of three different surfactants NaDBS, TX-100, and CTAB, were studied on the cellulose–water interface. Parts a–c of Figure 2 graphically present the kinetics of adsorption of NaDBS, TX-100, and CTAB, respectively, at three different initial concentrations in each case. We make the following observations from these figures. The nature of the plots is similar, that is, having a somewhat nonlinear increase in the amount of adsorption followed by a clear leveling off to indicate equilibrium. The amount of adsorption increases with the concentration. Both trends are expected. When the adsorption kinetics between the surfactants are compared, it is noted that the slope of the curve (average rate of adsorption) increases in the following order:  $\text{NaDBS} \approx \text{TX-100} < \text{CTAB}$ . The slope of the curve was determined at  $t_{1/2}$  (half-equilibrium time). In what follows, we give an explanation to the above observations. The cellulosic material such as filter paper is negatively charged ( $\zeta$  potential  $\sim -28 \text{ mV}$ ) in the neutral aqueous medium.<sup>28</sup> A two-site adsorption mechanism describes the kinetics reasonably well. There are two sites (hydrophilic and hydrophobic) present on the cellulose surface, and the hydrophilic sites are negatively charged. CTAB, being a cationic surfactant, adsorbs rapidly onto the negatively charged sites. Anionic and nonionic surfactants are adsorbed on the hydrophobic sites. Anionic surfactants in the presence of salt and cationic surfactants are adsorbed on the hydrophilic sites as well as on the hydrophobic sites. The two-site model is used to describe the kinetics; the necessary details describing the two sites on the filter paper are given elsewhere.<sup>29</sup>

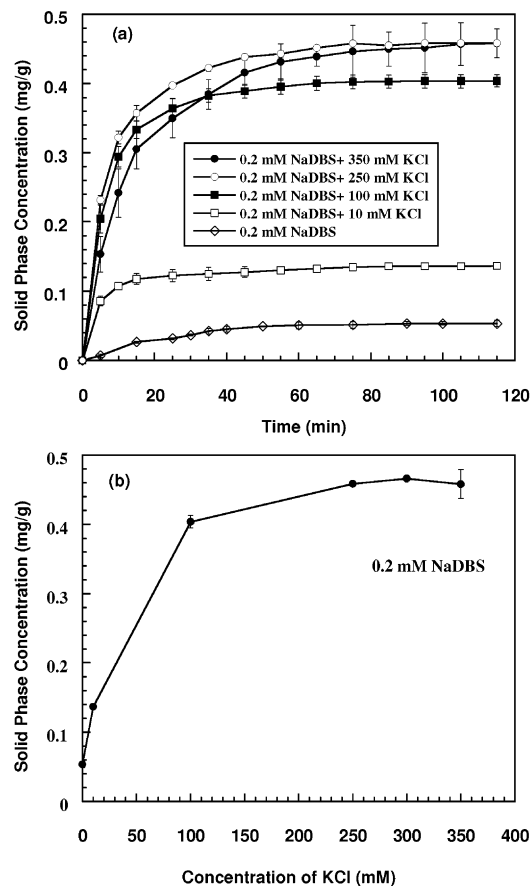
**3.3. Adsorption Kinetics of NaDBS in the Presence of Salt.** Figure 3a shows the adsorption kinetics of NaDBS at four different KCl concentrations. We observe from the figure that there are enhancements in both the rate of adsorption and the equilibrium extent of adsorption at all four KCl concentrations shown. Figure 3b shows that the adsorption kinetics is significantly enhanced for both 10 and 100 mM KCl, while for higher concentrations of 250 and 350 mM, there are no further enhancements as compared to that for the 100 mM KCl solution. The degree of enhancement varies with the electrolyte concentration and levels off at high KCl concentration.

To study the effect of the valency of the counterion (cation for a negatively charged cellulose surface), we have conducted measurements using a  $\text{CaCl}_2$  solution. The results are presented in Figure 4. We observe from

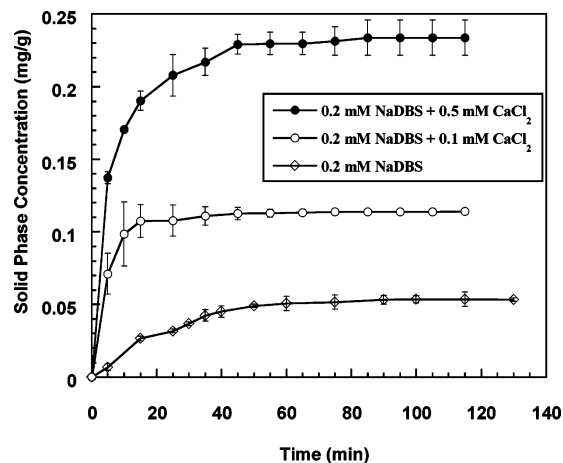


**Figure 2.** (a) Adsorption kinetics of NaDBS. (b) Adsorption kinetics of TX-100. (c) Adsorption kinetics of CTAB.

this figure that there is significant enhancement with an increase in the concentration of  $\text{CaCl}_2$  but only at lower concentrations. This observation is consistent with classical theories such as the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory<sup>30,31</sup> and the Schulze–Hardy rule.<sup>32</sup> The results presented in Figures 3 and 4 strongly indicate that the electric double layer of a charged cellulose surface plays a significant role in adsorption. Significantly, the rates as well as the extent of adsorptions are higher for the conditions of thinner double layers.



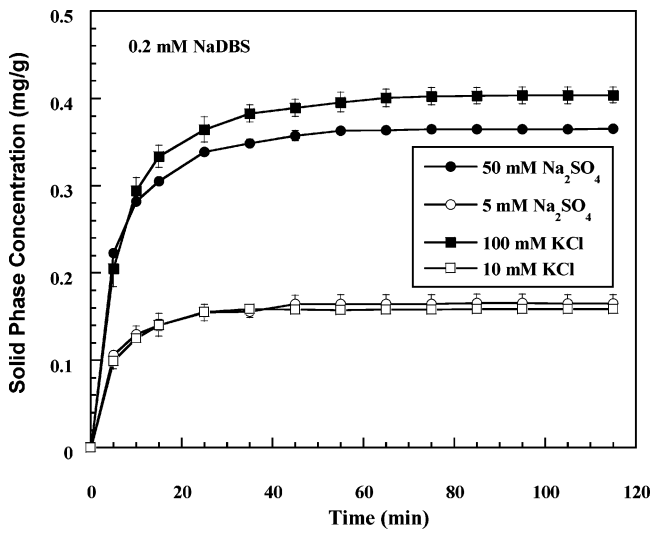
**Figure 3.** (a) Adsorption kinetics of NaDBS in the presence of KCl. (b) Plot of the KCl concentration vs amount of NaDBS adsorbed from a 0.2 mM NaDBS solution.



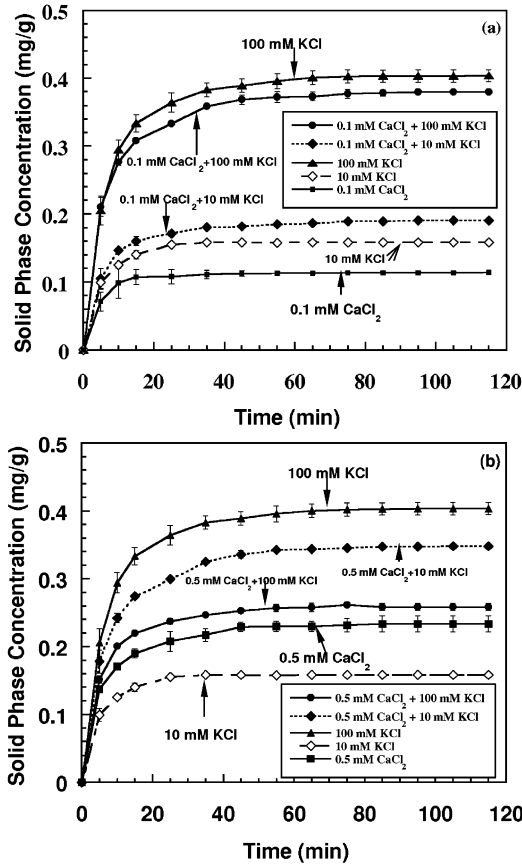
**Figure 4.** Adsorption kinetics of NaDBS in the presence of  $\text{CaCl}_2$ .

Figure 5 shows the effect of the valency of coions on the adsorption at two different counterion concentrations. If the concentration of the monovalent counterion is the same but the coion valence is different, similar adsorption curves were observed. We conclude from this figure that there is no difference in the effects of coions  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . Such observations further support the importance of electric double-layer effects in adsorption on a negatively charged cellulose surface.

**3.4. Adsorption Kinetics of NaDBS in the Presence of Mixed Salt.** In many practical uses, more than one salt are present. Hence, studies were conducted using a mixture of salts. Parts a and b of Figure 6 show



**Figure 5.** Adsorption kinetics of NaDBS in the presence of KCl and  $\text{Na}_2\text{SO}_4$ .



**Figure 6.** Adsorption kinetics of NaDBS in the presence of a mixture of KCl and  $\text{CaCl}_2$ .

the adsorption kinetics in the presence of a mixture of KCl and  $\text{CaCl}_2$ . Mixing was done at two different  $\text{CaCl}_2$  and KCl concentrations. Figure 6a presents the adsorption plots at 0.1 mM  $\text{CaCl}_2$ , while Figure 6b presents the plots at a higher concentration of 0.5 mM  $\text{CaCl}_2$ . We observe from Figure 6a that the addition of 0.1 mM  $\text{CaCl}_2$  to a 10 mM KCl solution enhances the rate and equilibrium extents of adsorption, though there is no significant difference in adsorption with only KCl. However, the effect of the addition 0.1 mM  $\text{CaCl}_2$  to 100 mM KCl shows slight decreases for both the rate and the maximum adsorbed amount, though the difference

**Table 1.** cmc Values of NaDBS in the Presence of Different Salt Concentrations

salt	salt concn (mM)	cmc (mM)
KCl	10	1.2
KCl	20	0.8
KCl	100	0.4
KCl	250	0.15
$\text{Na}_2\text{CO}_3$	10	0.8
$\text{CaCl}_2$	0.1	0.8
$\text{CaCl}_2$	0.5	0.3
KCl + $\text{CaCl}_2$	10 + 0.5	0.3
KCl + $\text{CaCl}_2$	100 + 0.5	0.15

is not significant. The explanation of this fact is given below for the discussion of the results presented in Figure 6b. Figure 6b shows that the addition of 0.5 mM  $\text{CaCl}_2$  to a 10 mM KCl solution enhances the rate and equilibrium extents of adsorption. However, the interesting result that we observe from this figure is that there is certainly no enhancement in adsorption due to the increase in the  $\text{CaCl}_2$  concentration and, in fact, the extent of adsorption actually slightly decreases for the 100 mM KCl + 0.5 mM  $\text{CaCl}_2$  mixture. A similar result is found in a mixture of 250 mM KCl + 0.5 mM  $\text{CaCl}_2$  (figures are not shown here). For the mixture of 250 mM KCl + 0.1 mM  $\text{CaCl}_2$ , enhancement is the same as that for 250 mM KCl. The decrease in adsorption at high salt concentration may be due to the change in the properties of surfactant molecules in bulk. It is known that, at high salt concentration, the hydrophilicity of the surfactant headgroup decreases,<sup>33</sup> which may decrease adsorption on hydrophilic sites; also, in the presence of mixed salt, more stable micelles are formed and, as a result, the monomer concentration in the solution decreases and even the shape of the micelles changes in the presence of high salt concentration. The detailed mechanism of this observation is still unknown to us. The cmc values of NaDBS are changed in the presence of salt; the cmc values of NaDBS at different salt concentrations are given in Table 1.

## 4. Modeling Studies

**4.1. Adsorption Kinetics Model.** We propose a simple two-site model to describe the batch adsorption studies of surfactant on a cellulose surface. We write equations for a system containing  $V \text{ m}^3$  of solution of surfactant at a concentration of  $C_{b0}$  and  $m \text{ kg}$  of fresh filter paper pieces added to it. Assuming a cellulose surface containing two sites, we write

$$X_S = X_{\text{Sh}} + X_{\text{Se}} \quad (1)$$

$$X_{\text{Sm}} = X_{\text{Smh}} + X_{\text{Sme}} \quad (2)$$

$X_S$  is the total concentration of surfactant on the cellulose surface at time  $t$  in kg/kg.  $X_{\text{Sh}}$  and  $X_{\text{Se}}$  are the concentrations of surfactant on the hydrophobic and hydrophilic sites, respectively, at time  $t$ .  $X_{\text{Sm}}$  is the maximum amount of total surfactant adsorbed on the cellulose surface, and  $X_{\text{Sme}}$  and  $X_{\text{Smh}}$  are those on hydrophilic and hydrophobic sites, respectively.

Now, considering the mole balance of the surfactant at any time  $t$ , it can be shown that

$$C_b = C_{b0} - \frac{m(X_{\text{Sh}} + X_{\text{Se}})}{VM} \quad (3)$$

$C_{b0}$  and  $C_b$  are the concentrations of surfactant in solution at time  $t = 0$  and  $t = t$ , respectively, in  $\text{kmol}/\text{m}^3$ ,  $m$  is the mass of the filter paper in  $\text{kg}$ , and  $M$  is the molecular weight of the surfactant.

The rate of adsorption can be expressed for both hydrophilic and hydrophobic sites using the Langmuir equation.

$$dX_{\text{Sh}}/dt = k_{\text{ah}}(X_{\text{Smh}} - X_{\text{Sh}})C_b - k_{\text{dh}}X_{\text{Sh}} \quad (4)$$

$$dX_{\text{Se}}/dt = k_{\text{ae}}(X_{\text{Sme}} - X_{\text{Se}})C_b - k_{\text{de}}X_{\text{Se}} \quad (5)$$

$k_{\text{ah}}$  and  $k_{\text{ae}}$  are the adsorption rate constants at hydrophobic and hydrophilic sites, respectively, in  $\text{m}^3/(\text{kmol min})$ , and  $k_{\text{dh}}$  and  $k_{\text{de}}$  are the desorption rate constants at hydrophobic and hydrophilic sites, respectively, in  $\text{min}^{-1}$ .

Substituting the value of  $C_b$  from eq 3 into eqs 4 and 5, we obtain

$$\begin{aligned} \frac{dX_{\text{Sh}}}{dt} = & k_{\text{ah}}X_{\text{Smh}}C_{b0} + \frac{k_{\text{ah}}m}{VM}X_{\text{Sh}}^2 - \\ & \left( \frac{k_{\text{ah}}X_{\text{Smh}}m}{VM} + k_{\text{ah}}C_{b0} + k_{\text{dh}} \right) X_{\text{Sh}} - \\ & \frac{k_{\text{ah}}X_{\text{Smh}}m}{VM}X_{\text{Se}} + \frac{k_{\text{ah}}m}{VM}X_{\text{Sh}}X_{\text{Se}} \quad (6) \end{aligned}$$

$$\begin{aligned} \frac{dX_{\text{Se}}}{dt} = & k_{\text{ae}}X_{\text{Sme}}C_{b0} + \frac{k_{\text{ae}}m}{VM}X_{\text{Se}}^2 - \\ & \left( \frac{k_{\text{ae}}X_{\text{Sme}}m}{VM} + k_{\text{ae}}C_{b0} + k_{\text{de}} \right) X_{\text{Se}} - \\ & \frac{k_{\text{ae}}X_{\text{Sme}}m}{VM}X_{\text{Sh}} + \frac{k_{\text{ae}}m}{VM}X_{\text{Se}}X_{\text{Sh}} \quad (7) \end{aligned}$$

Equations 6 and 7 are first-order nonlinear differential equations, which are difficult to solve analytically. A numerical method (Euler's method) was used to solve the simultaneous differential equations and to develop a code in C to obtain  $X_S$  as a function of time. The equation can be represented as

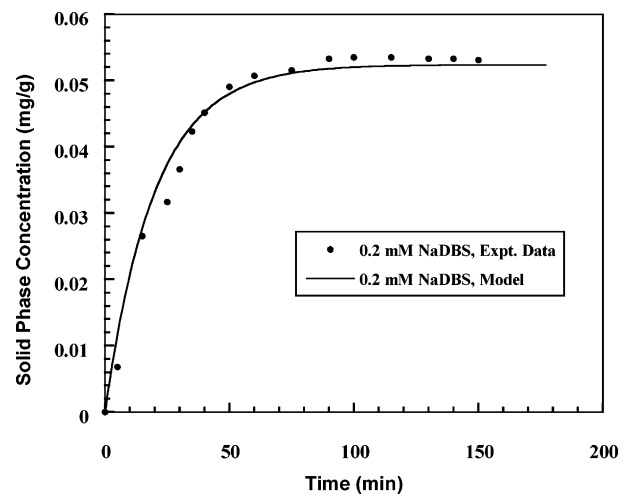
$$dX/dt = f'(X) \quad (8)$$

Our objective is to determine the unknown function  $X(t)$  for  $t \geq t_0$ . Now the value of  $X$  at  $n + 1$  time steps can be calculated as

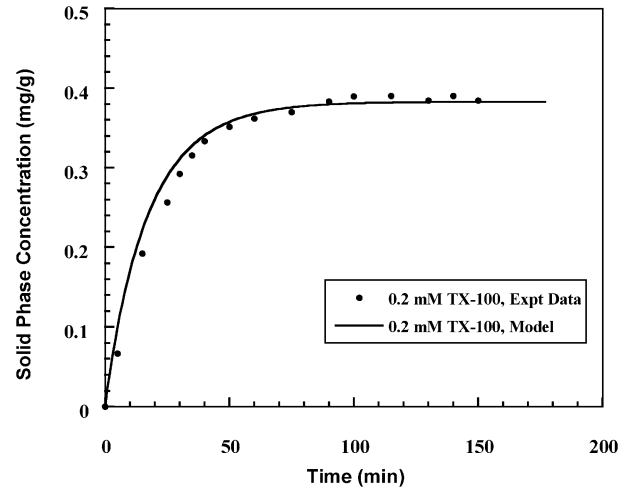
$$X_{n+1} = X_n + f'(X_n) \Delta t \quad (9)$$

where  $\Delta t$  is the time step and  $X_n$  is the value of  $X$  at time step  $n$ . The method is called explicit because the new value of  $X_{n+1}$  is given explicitly in terms of the old value  $X_n$ . The initial values of  $X_{\text{Sh}}$  and  $X_{\text{Se}}$  were taken as zero when  $t$  is zero. The time step of 0.001 was used for the calculations.

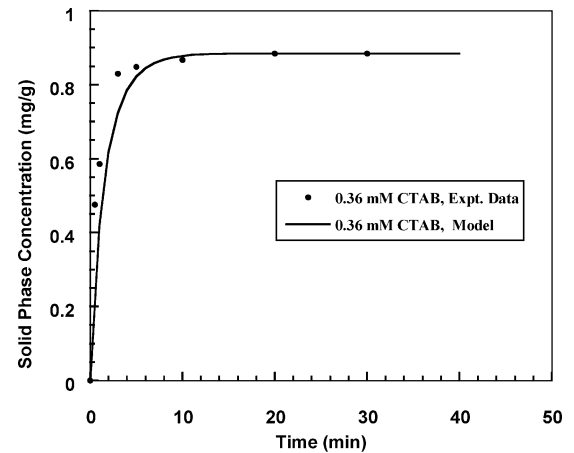
**4.2. Comparison of Measurements with the Predictions of the Model.** Figures 7–9 show comparisons between model and experimental data of the adsorption kinetics of NaDBS, TX-100, and CTAB, respectively. The values for the rate constants were obtained by fitting the experimental data. The sum of the standard deviation between experimental and theoretical plots was kept at a minimum for best fitting. The different rate constants obtained from the fitting are presented in Table 2. For the adsorption of NaDBS and TX-100 in the absence of salt, we have considered that the adsorp-



**Figure 7.** Fitting of experimental data of the adsorption kinetics of NaDBS with the model.



**Figure 8.** Fitting of experimental data of the adsorption kinetics of TX-100 with the model.



**Figure 9.** Fitting of experimental data of the adsorption kinetics of CTAB with the model.

tion only occurs at the hydrophobic sites. The adsorption rate constants of NaDBS and TX-100 are found to be the same, whereas the desorption rate constants are slightly different. In the case of adsorption of CTAB, it is assumed that CTAB adsorbs onto negatively charged sites (hydrophilic) and that desorption can be neglected because of the strong electrical attraction between the site and adsorbed CTAB molecules. The adsorption rate

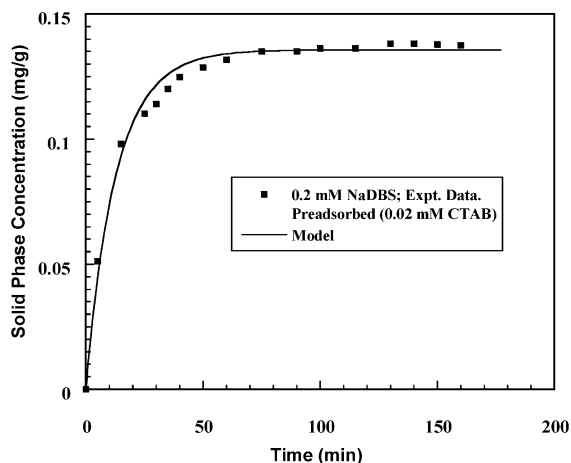
**Table 2. Different Model Parameters Obtained from the Fitting of Experimental Data with the Model**

surfactant	concn of salt (mM)	$k_{ah}$ [m <sup>3</sup> /(kmol min) × 10 <sup>3</sup> ]	$k_{ae}$ [m <sup>3</sup> /(kmol min) × 10 <sup>3</sup> ]	$k_{dh}$ (min <sup>-1</sup> )	$k_{de}$ (min <sup>-1</sup> )
NaDBS (0.2 mM)	0	300		0.002	
TX-100 (0.2 mM)	0	300		0.001	
CTAB (0.36 mM)	0		2000		0
NaDBS (0.2 mM) + KCl	10	300	800	0.002	0
	100	300	850	0.002	0
	250	300	750	0.002	0
	300	300	450	0.002	0
	350	300	400	0.002	0
NaDBS (0.2 mM) + CaCl <sub>2</sub>	0.1	300	900	0.002	0
	0.5	300	1150	0.002	0
NaDBS (0.2 mM) + CTAB (0.02 mM) preadsorbed	0	400		0.001	

constant of CTAB is found to be higher than that of NaDBS or TX-100, which is expected because of favorable electrical effects.

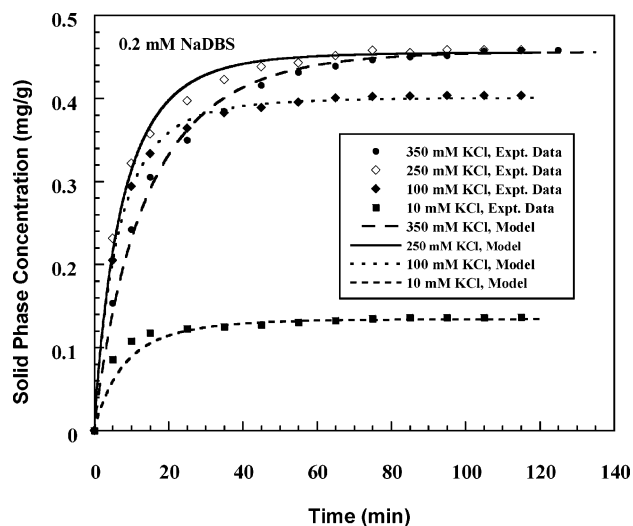
Figure 10 shows the fitting of the adsorption kinetics of NaDBS on filter paper, which is preadsorbed with CTAB to increase the hydrophobicity of the filter paper surface. In this experiment, CTAB was preadsorbed to modify the filter paper surface. The surface is expected to become more hydrophobic with a higher extent of adsorption. First, the filter paper was preadsorbed with a 0.02 mM CTAB solution, and then the filter paper was rinsed with distilled water, dried, and used to study the kinetics of NaDBS adsorption.<sup>34</sup> As the surface becomes more hydrophobic, the rate constant of adsorption obtained from the model on the hydrophobic site increases compared to that on the pure filter paper surface.

Figure 11 shows the fitting of the kinetics of NaDBS in the presence of KCl. We have assumed that the desorption rate constant is negligible on the hydrophilic site in the presence of salt. For the fitting of NaDBS in the presence of salt, two sites were used and the rate constant for hydrophobic sites was used as determined previously for NaDBS in the absence of salt. The rate constant for adsorption on the hydrophilic site for 10 mM KCl is  $800 \times 10^3 \text{ m}^3/(\text{kmol min})$ ; with an increase in the KCl concentration to 100 mM, there is an enhancement in  $k_{ae}$  to  $850 \times 10^3 \text{ m}^3/(\text{kmol min})$ . This result is consistent with the DLVO theory and can be explained in terms of the energy barrier of the total interaction energy between the surface and surfactant molecules in the presence of salt. The rate of adsorption depends on the height of the energy barrier in the total interaction versus distance of the separation curve. In

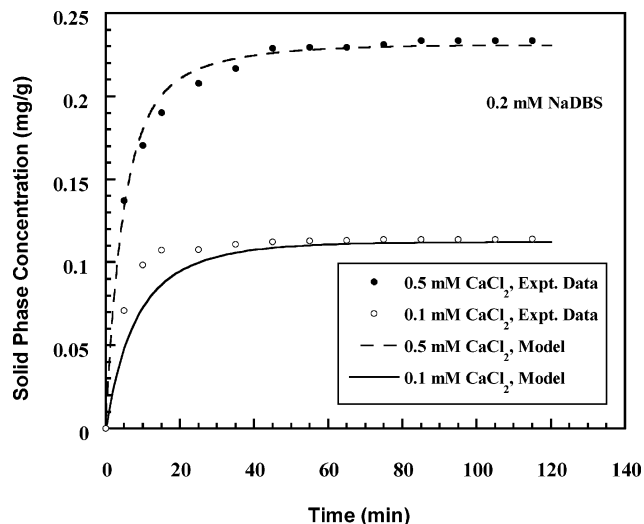


**Figure 10.** Fitting of experimental data of the adsorption kinetics of NaDBS on preadsorbed CTAB filter paper with the model.

the absence of salt, the energy barrier is high. With an increase in the salt concentration, the energy barrier decreases and becomes almost zero at 100 mM KCl.<sup>35</sup> Similar observations are made in the presence of CaCl<sub>2</sub>. The fitting with experimental data in the case of CaCl<sub>2</sub> is shown in Figure 12. If the concentration of KCl is above 100 mM, the rate constant value was found to decrease. The reason may be that in the presence of a high concentration of KCl the surfactant solution used was above the cmc, so micellar dissociation plays an



**Figure 11.** Fitting of experimental data of the adsorption kinetics of NaDBS in the presence of KCl with the model.



**Figure 12.** Fitting of experimental data of the adsorption kinetics of NaDBS in the presence of CaCl<sub>2</sub> with the model.

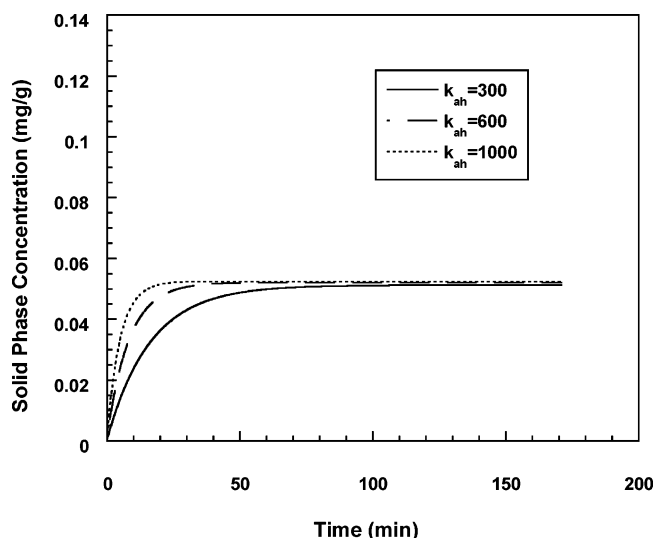


Figure 13. Effect of  $k_{ah}$  on the adsorption kinetics.

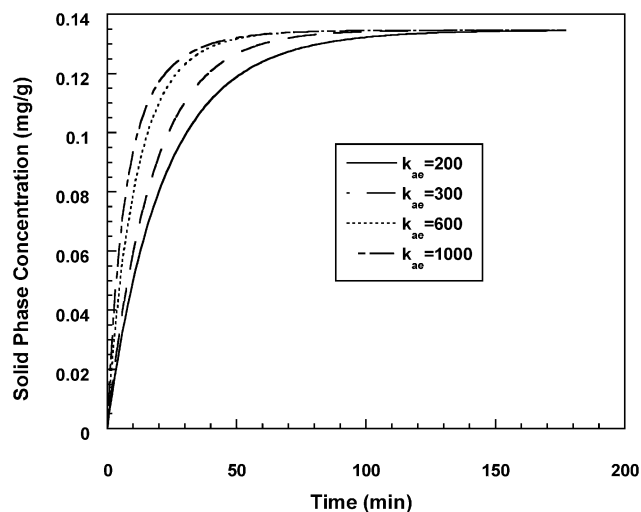


Figure 14. Effect of  $k_{ae}$  on the adsorption kinetics.

important role. There will be a continuous equilibrium between the surfactant monomer and micellar forms.

Figures 13 and 14 show the sensitivity of parameters  $k_{ah}$  and  $k_{ae}$  on adsorption kinetics. We observe from these figures that calculations are sensitive to the values of  $k_{ah}$  and  $k_{ae}$  and therefore the values of  $k_{ah}$  and  $k_{ae}$  are significant.

Let us compare the rate constants obtained in this work with those reported in the literature. Studies reporting the values for adsorption and desorption rate constants are very few in the literature. The values are dependent on the nature of the surfactant and adsorbent. Studies on the adsorption of TX-100 and  $C_{14}E_6$  on two surfaces, carbon black<sup>36</sup> and silica,<sup>16</sup> respectively, report that the value of the adsorption equilibrium constant for carbon black,  $k_a/k_d$ , is  $\approx 20 \times 10^3$  m<sup>3</sup>/kmol and, for silica, it is  $2.9 \times 10^6$  m<sup>3</sup>/kmol. We have determined the value for the adsorption equilibrium constant for TX-100 and the filter paper system as  $3 \times 10^8$  m<sup>3</sup>/kmol, higher than the reported values.

## 5. Conclusions

The adsorption kinetics of anionic (NaDBS), nonionic (TX-100), and cationic (CTAB) surfactants on a filter paper surface were studied at different electrolyte concentrations. CTAB was found to adsorb relatively

faster and to a higher extent than NaDBS and TX-100, with NaDBS showing the least adsorption. The rate and maximum amount adsorbed of NaDBS, however, can be enhanced by adding electrolytes such as KCl and CaCl<sub>2</sub>. The findings are interpreted in terms of a two-site model and the double-layer effects. In the two-site model, the filter paper surface contains both hydrophobic and hydrophilic sites, which carry negative electric charges.

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## Notation

$C_b$  = bulk concentration of adsorbate in solution, kmol/m<sup>3</sup>  
 $C_{b0}$  = initial concentration of adsorbate (surfactant), kmol/m<sup>3</sup>

$k_{ae}$  = adsorption rate constant on the hydrophilic site, m<sup>3</sup>/(kg min)

cmc = critical micellar concentration

$C_{12}$ TAB = dodecyltrimethylammonium bromide

$C_{14}$ TAB = tetradecyltrimethylammonium bromide

$C_{16}$ TAB, CTAB = cetyltrimethylammonium bromide

$k_{ah}$  = adsorption rate constant on the hydrophobic site, m<sup>3</sup>/(kg min)

$k_{de}$  = desorption rate constant on the hydrophilic site, min<sup>-1</sup>  
 $k_{dh}$  = desorption rate constant on the hydrophobic site, min<sup>-1</sup>

$M$  = molecular weight of the surfactant

$m$  = mass of the adsorbent, kg

$t$  = time, min

$V$  = solution volume, m<sup>3</sup>

$X_S$  = total solid-phase concentration of the surfactant (amount adsorbed), kg/kg

$X_{Se}$  = solid-phase concentration of the surfactant on the hydrophilic site, kg/kg

$X_{Sh}$  = solid-phase concentration of the surfactant on the hydrophobic site, kg/kg

$X_{Sm}$  = maximum amount of surfactant adsorbed on the hydrophobic and hydrophilic sites, kg/kg

$X_{Sme}$  = maximum amount of surfactant adsorbed on the hydrophilic site, kg/kg

$X_{Smh}$  = maximum amount of surfactant adsorbed on the hydrophobic site, kg/kg

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