

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/216658209>

Effect of Electrolyte Solutions on the Adsorption of Surfactants at PTFE–Water Interface

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · AUGUST 2010

Impact Factor: 2.59 · DOI: 10.1021/ie100812k

CITATIONS

9

READS

500

2 AUTHORS:



Nihar Ranjan Biswal

Indian Institute of Technology Kanpur

8 PUBLICATIONS 135 CITATIONS

SEE PROFILE



Santanu Paria

National Institute of Technology Rourkela

52 PUBLICATIONS 1,783 CITATIONS

SEE PROFILE

Effect of Electrolyte Solutions on the Adsorption of Surfactants at PTFE–Water Interface

Nihar Ranjan Biswal and Santanu Paria*

Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa, 769008, India

Adsorption of ionic and nonionic surfactants on low surface energy hydrophobic PTFE–water interfaces in the absence and presence of electrolytes have been studied here. The objective of this study is to see the surfactant adsorption behavior in the presence of electrolytes that may reduce the consumption of surfactants. The kinetics of adsorption fits well pseudo-second-order kinetic model for the three surfactants studied here. Adsorption isotherms of TX-100 follow Langmuir type, whereas sodium dodecylbenzene sulfonate (SDBS) and cetylpyridinium bromide (CPB) follow Freundlich type. However, in the presence of electrolytes both the ionic surfactants show better fitting with Langmuir type isotherm. The effect of electrolytes on the surfactant concentration far below the CMC shows there is a linear increase in amount adsorbed with the increase in ionic strength of the electrolyte mainly due to reduction in headgroup repulsion and finally reaches a plateau level when the equilibrium concentration reaches CMC at that electrolyte concentration.

1. Introduction

Surfactant adsorption at solid–liquid interfaces has been extensively studied by many researchers for a long period of time because of its versatile applications. The adsorption of surfactants at the interfaces is always there whenever they are used in different applications. Surfactants can change the solid surface property from hydrophilic to hydrophobic and vice versa by adsorption. There are many studies available on the surfactant adsorption at hydrophilic surfaces, compared to only a few at hydrophobic surfaces. Surfactant adsorption at hydrophobic solid–water interfaces has applications such as wetting,¹ stabilization of polymer suspension,² surface cleaning,³ etc. To see the effectiveness of these applications there are also some studies available on contact angle and wetting properties of different hydrophobic polymer surfaces such as polytetrafluoroethylene (PTFE)^{4–8} and both PTFE and polymethyl methacrylate (PMMA)^{9,10} where surfactant adsorption is inherently involved. In general, hydrophobic or polymer surfaces have low surface energy and are difficult to suspend or wet by aqueous media for different applications. The adsorption of surfactants on hydrophobic surfaces overcomes those difficulties by changing the surface properties. In this regard, apart from the adsorption at solid–liquid interface, surface tension of the aqueous solution which is related to the adsorption at air–liquid interface is equally important. The effect of ionic strength or electrolytes can significantly influence the critical micellar concentration (CMC), surface tension value at CMC, and adsorption densities at air–liquid and solid–liquid interfaces which may have great importance in many applications.

Surfactant adsorption studies on polymer surfaces are mainly reported at PTFE,^{11–15} polystyrene,^{2,16–19} polyvinyltoluene (PVT),²⁰ and PMMA²¹ surfaces. Dixit and co-workers studied single cationic surfactants¹⁴ and cationic–nonionic mixed surfactants systems on PTFE surface.^{13,15} In a single cationic surfactant system they have studied the effects of chain length of alkyltrimethyl ammonium bromide and pyridinium chloride surfactants. The isotherm consisted of two plateau regions due to formation of hemimicelle. In the cationic–nonionic (CTAB–

NP_n) mixed surfactant system adsorption of either cationic or nonionic was enhanced below the CMC¹³ and adsorption of CTAB decreased with the increase in mole fraction of nonionic surfactants (NP_n) above the CMC due to formation of mixed micelle. Connor and Ottewill¹⁶ showed the formation of hemimicelle for cationic surfactant on polystyrene surface; they suggested that the particles have two types of sites for adsorption: charged sites which interact with the cationic headgroup of the surfactant and adsorption through tailgroup on the hydrophobic sites. The adsorption of nonionic nonylphenol polyethylene oxide of different chain lengths on PMMA surface shows Langmuir isotherm due to the formation of monolayer.²¹

Regarding the effect of electrolytes on surfactant adsorption, it is observed that although there is much literature available on hydrophilic surfaces^{22–26} there is not any on hydrophobic surfaces. Atkin et al.²³ found the addition of electrolytes shifted the adsorption isotherm of CTAB toward lower concentration with increase in maximal surface excess at silica–water interface and Br[–] ion was more effective to increase the surface excess of CTAB than that of Cl[–] to the CTAC system. Paria and Yuet²⁵ concluded the adsorption of cationic surfactant on negatively charged hydrophilic surface (sand) linearly increased with the increasing electrolyte concentration at a constant surfactant concentration below the CMC mainly due to reduction of repulsion between the surfactant headgroups. Also, between the two forces (i) attraction between the solid surface and surfactant headgroups and (ii) repulsion between the headgroups, the latter was predominant for increasing the surface excess in the presence of electrolytes. Howard et al.²⁶ showed that there exists a common intersection point (CIP) at which a particular surfactant concentration below this point an increase in electrolyte concentration reduced surfactant surface excess, and at concentrations above this point an increase in electrolyte concentration led to an increase in surfactant surface excess.

From the literature it is clear that limited studies are available on the adsorption of surfactants (kinetics and isotherm) at PTFE surface. Although there are some studies available on the effect of electrolytes on surfactant adsorption at the hydrophilic solid–liquid interface, there are no studies on PTFE or other hydrophobic surfaces to the best of our knowledge. In this paper,

* To whom correspondence should be addressed. E-mail: santanuparia@yahoo.com or sparia@nitrkl.ac.in; Fax: +91 661 246 2999.

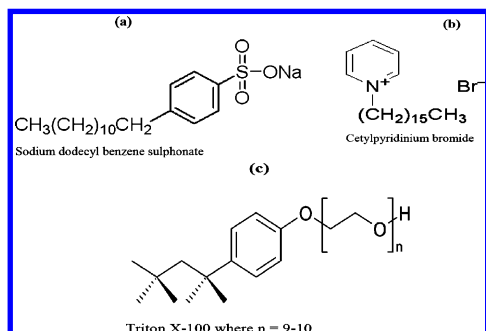


Figure 1. Structures of the surfactant molecules: (a) SDBS, (b) CPB, (c) TX-100.

we have studied the adsorption kinetics and the isotherms of three different surfactants (anionic, SDBS; cationic, CTAB; and nonionic, TX-100; Figure 1) at PTFE surface. In addition, electrolytes effects have also been studied on the adsorption of anionic and cationic surfactants at PTFE–water interface. The objective of this paper is to study the adsorption behavior of surfactants in the presence of electrolytes to reduce the surfactant consumption. Food processing and many other industrial operations use PTFE-coated reactors and pipes; regular cleaning of those is essential, especially in food processing operations. The presence of electrolyte along with the surfactants in the cleaning process may reduce the consumption of surfactant along with the increase in adsorption and wetting properties. In many cases, after the cleaning process surfactants are disposed in the environment; in this situation, less consumption of surfactant may also reduce environmental problems.

2. Materials and Methods

2.1. Materials. Triton X-100 (TX-100; 99% purity) was purchased from Loba Chemicals Pvt. Ltd., India. Cetylpyridinium bromide (CPB, 99%) from Rankem, India and sodium dodecylbenzene sulfonate (SDBS) of technical grade (Cat no. 28 995-7) from Sigma-Aldrich chemicals, Germany were purchased and used without any further purification. The electrolytes NaCl and Na₂SO₄ were purchased from Rankem and CaCl₂ was from Merck, India. The PTFE powder used for adsorption experiments was purchased from Pragati Plastics Pvt. Ltd., Delhi, India. Aqueous solutions of individual surfactants were made by ultrapure water (Sartorius, Germany) of 18.2 MΩ·cm resistivity, 71.5 mN/m surface tension, and 6.5–7 pH at 25 ± 0.5 °C. For all the experiments, a single surfactant solution of desired concentration was prepared by diluting a concentrated stock solution.

2.2. Methods. The surface tension of aqueous solutions of surfactants was measured at 25 ± 0.5 °C by the Wilhelmy plate technique with a surface tensiometer (DCAT 11EC, Data physics, Germany). After measurement of each concentration, the platinum plate was cleaned with water followed by acetone and burned in alcohol flame for complete removal of adsorbed surfactant. The particle size of the PTFE powder was measured using a particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., U. K.) and found that the average particle size 115.7 μm. The zeta potential of PTFE powder was measured by equilibrating 5 mg of powder in 50 mL of 0.01 M KCl solution using Zetasizer Nano ZS (Malvern, U.K.). The zeta (ζ) potential was calculated from the electrophoretic mobility using Smoluchowski's equation and found to be −4.82 mV. The specific surface area (BET) of the PTFE powder was measured twice by N₂ adsorption–desorption studies at liquid nitrogen temperature (−195.8 °C) using Autosorb-1 (Quantach-

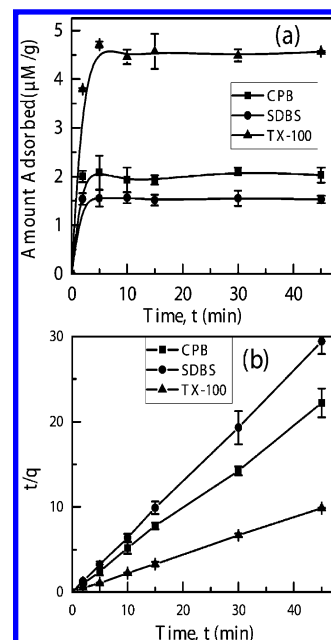


Figure 2. (a) Adsorption kinetics of CPB, SDBS, and TX-100 on PTFE powder using 0.2 mM surfactant concentration. (b) Linear fitting of pseudo-second-order kinetics.

rome, USA) and the average value was found to be 4.3 m² g^{−1}. Prior to the analysis, samples were degassed at 200 °C. Low nitrogen adsorption at relative pressure (*P/P*₀) values <0.2 indicates the absence of microporosity, which is also reflected in the low value of the BET surface area, 4.3 m² g^{−1}.

For the adsorption experiments a volume of 10 mL of surfactant solution of different concentrations was taken in 60-mL plastic bottles, and 0.1 g of PTFE powder was used for all the experiments. The adsorption isotherm was constructed using nine different surfactant concentrations (0.05, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1, 2 mM) from below to above CMC. All the measurements were carried out at neutral pH 6.5–7. For the electrolyte effect, the desired concentration of electrolyte was mixed with the surfactant solution before addition of solid. The bottles were shaken well for 2 h at 25 ± 0.5 °C on an incubator shaker. PTFE particles were separated from the mixture by centrifugation at 5000 rpm. The concentrations of the surfactants solutions before and after the adsorption were determined by UV–vis spectrophotometer (Jasco, V-530, Japan) at λ_{max} 223, 224, and 258 nm for TX-100, SDBS, and CPB, respectively, using their respective calibration curves (absorbance vs concentration) constructed from the known concentrations. The experiments were repeated at least thrice and the average data were plotted. The amount of surfactant adsorbed was determined by the following equation

$$\Gamma = \frac{(C_i - C_{eq})V}{1000m} \quad (1)$$

where *C_i* and *C_{eq}* are the initial and equilibrium concentrations (mM), *V* is the volume of surfactant solution (mL), and *m* is the mass of the adsorbent (g).

3. Results and Discussion

3.1. Adsorption Kinetics. Adsorption kinetics of three different surfactants (CPB, SDBS, and TX-100) at 0.2 mM concentration at PTFE–water interface are presented in Figure 2a. The adsorption kinetics are studied to know the rate as well

Table 1. Pseudo-First-Order and Pseudo-Second-Order Kinetic Parameters for SDBS, CPB, and TX-100

surfactant	pseudo-first-order			pseudo-second-order		
	k_1 (min ⁻¹)	q_e (μM·g ⁻¹)	R^2	k_2 (g·(μM·min) ⁻¹)	q_e (μM·g ⁻¹)	R^2
CPB	0.035	0.148	0.297	0.976	1.074	0.999
SDBS	0.064	0.084	0.140	0.811	1.102	0.998
TX-100	0.115	0.189	0.617	0.914	1.217	0.999

as equilibrium time for the adsorption process. At very low surfactant concentration the amount of surfactant adsorbed as well as the differences among the surfactants are less, hence the concentration was chosen for kinetics where the difference is more. It is found from the figure that within 10 min all three surfactants reached equilibrium and the rate of adsorption is also very fast. Figure 2a shows that at 0.2 mM concentration the surfactants are following the order of amount adsorbed at equilibrium TX-100 > CPB > SDBS. To know the rate at which adsorption takes place there are generally two commonly used kinetic models, i.e., pseudo-first-order and pseudo-second-order, to identify the nature of surfactant adsorption. The pseudo-first-order kinetics can be presented as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

Equation 2 is then integrated for the conditions $t = 0$ to t and $q = 0$ to q_t and rearranged to get

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

The pseudo-second-order kinetics can be presented as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

The eq 4 is then integrated for the conditions $t = 0$ to t and $q = 0$ to q_t and rearranged to get

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (5)$$

or

$$\frac{q_t}{t} = \frac{h}{1 + k_2 q_e t} \quad (6)$$

where q_t and q_e are amount of surfactant adsorbed at time t and at equilibrium in μM·g⁻¹, and k_1 (min⁻¹) and k_2 (g·μM⁻¹·min⁻¹) are adsorption rate constants for pseudo-first-order and pseudo-second-order, respectively. h (μM·g⁻¹·min⁻¹) can be regarded as the initial sorption rate as q_t/t , when t approaches 0. Hence,

$$h = k_2 q_e^2 \quad (7)$$

The adsorption rate constants of both the models calculated by eqs 3 and 5 as shown in Table 1. The high values of correlation coefficient (R^2) for the fitting obtained from the kinetic plots using the second model suggest that adsorption of surfactants on PTFE surface can be better expressed by the pseudo-second-order model as shown in Figure 2b. The results show the order of initial adsorption rates, TX-100 > SDBS > CPB.

3.2. Adsorption Isotherm. Figure 3 represents the adsorption isotherms of three surfactants on PTFE surface. From the figure it is clear that the shapes of three different isotherms are not

similar with different maximum amount adsorbed at saturation. The nature of the adsorption isotherm for TX-100 is apparently different, whereas, the other two ionics are close to similar. At lower surfactant concentration the change in amount adsorbed is not significant, whereas at higher concentration there is a significant change among the three surfactants. The order of equilibrium amount adsorbed at the plateau level is CPB > TX-100 > SDBS.

There are two types of models, Langmuir and Freundlich isotherms, generally used to correlate the amount adsorbed and the equilibrium concentration for the adsorption of surfactant molecules on a solid surface. The Langmuir and Freundlich isotherms may be expressed as the following equations:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (8)$$

$$\log q_e = \log a + \frac{1}{n} \log C_e \quad (9)$$

where q_m is equilibrium amount adsorbed (μM·g⁻¹), b is the adsorption constant of Langmuir equation (mM⁻¹), C_e is the equilibrium concentration of surfactants in the solution (mM), a is a constant or coefficient of Freundlich isotherm equation representing the adsorption capacity, and n is a constant (reciprocal of the exponent of the Freundlich isotherm equation) depicting the adsorption intensity. When there is a negligible intermolecular interaction between the adsorbed surfactant molecules i.e., only monolayer of adsorbate is formed, the Langmuir model works quite well. In this study we have applied two models to test the better fitting of these isotherms. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients (R^2) are listed in Table 2.

From Table 2, it is clear that TX-100 is following Langmuir isotherm with a R^2 value close to 1 and indicates a monolayer formation on the PTFE surface probably by adsorbing the tailgroup on the surface. Initially the adsorption density increases linearly with the equilibrium concentration, i.e., it follows Henry's law due to formation of monolayer, and ultimately reaches a plateau region at about 0.38 mM equilibrium concentration. Whereas for SDBS, both the models are almost equally fitted with an R^2 value above 0.94. For CPB there is a significant difference between the two isotherms with a higher

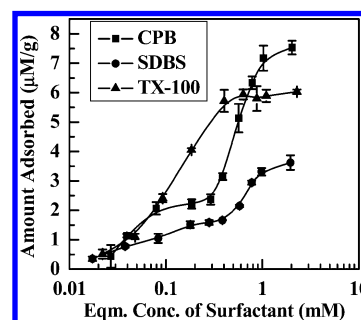


Figure 3. Adsorption isotherms of CPB, SDBS, and TX-100 on PTFE powder.

Table 2. Parameters of Langmuir and Freundlich Isotherm Equations

surfactant	Langmuir			Freundlich		
	$q_m (\mu\text{M}\cdot\text{g}^{-1})$	$b \times 10^{-3} (\text{mM}^{-1})$	R^2	$a (\mu\text{M}\cdot\text{g}^{-1})$	n	R^2
TX-100	6.622	0.301	0.990	6.382	1.879	0.848
CPB	10.101	0.18	0.895	6.309	1.647	0.914
SDBS	4.115	0.048	0.946	2.99	2.141	0.96
CPB + NaCl	10.638	0.462	0.971	8.260	2.469	0.939
CPB + Na ₂ SO ₄	12.5	0.357	0.891	7.638	2.604	0.858
SDBS + NaCl	14.285	1.190	0.987	13.031	2.164	0.924

R^2 value (~ 0.914) for Freundlich type. The ζ potential of PTFE particles show that the surface is having low negative charge, -4.82 mV, indicating it is mostly hydrophobic in nature, so we are expecting the majority of SDBS and CPB molecules also adsorb through the tailgroup. The shape of the isotherm indicates the sudden change in adsorption amount is more sharp for CPB than SDBS and may be due to formation of hemimicelle. To support the higher hemimicellar aggregation number for CPB we have also calculated the hemimicellar aggregation number according to Gao et al.²⁷ for both the surfactants and found the values are ~ 4 and ~ 2 for CPB and SDBS, respectively. So the aggregation of SDBS is not significant. In summary, we conclude SDBS isotherm follows mainly Langmuir type isotherm and the similar fitting with Freundlich type model may be due to a small experimental error in the isotherm. The formation of hemimicelle on PTFE surface by the cationic surfactant (CTAB) is also reported by Dixit et al.¹⁵ and Vanjara and Dixit,¹⁴ with an aggregation number 7. For the isotherms with hemimicelle formation at low surfactant concentration, amount adsorbed increases with the concentration and reaches an intermediate plateau region due to the saturation of monolayer, then with further increases in concentration there is a sudden rise in amount adsorbed due to the formation of hemimicelle. The critical concentration where hemimicelle formation occurs is called critical hemimicellar concentration (CHMC). In general, the driving force of hemimicelle formation is the hydrophobic interaction between the surfactant chains. At low concentration, however, the solution activity of the surfactant may not be sufficient to form any aggregation at the interface, thus the surfactants are still adsorbed as monomers. Above the CHMC the concentration of surfactants in solution is sufficient for formation of hemimicelle due to attraction of adsorbed molecule and the molecules present in the solution. The CHMC found from the isotherm is about 0.38 mM for CPB. The adsorption of three synthetic surfactants on PTFE surface may be predominated by hydrophobic interaction and there may be some other interactions such as electrostatic attraction, hydrogen bonding, and dispersion forces. There is a difference in amount adsorbed between these two ionic surfactants, having higher adsorption density for CPB. This may be attributed in terms of longer chain length of CPB than SDBS. In addition, as the surface is little negatively charged there will be repulsion between the SDBS molecules and the surface; whereas, there will be attraction between that of CPB and the solid surface. Ultimately, some CPB may also adsorb through the headgroup on the negatively charged sites and some on the hydrophobic sites through the tailgroup, finally they are also forming hemimicelle on the surface. These may be the reasons the adsorption of CPB is more than SDBS.

3.3. Effect of Electrolytes. **3.3.1. Effect of Electrolytes on CMC.** The solution property of surfactants also plays a major role in the adsorption behavior at the solid–liquid interface. Effects of three different salts NaCl, Na₂SO₄, and CaCl₂ on solution property and adsorption behavior of SDBS and CPB are studied here. Before studying the adsorption behavior in

the presence of electrolytes we have studied the change in surface tension for a particular surfactant concentration with increasing electrolyte concentration as shown in Figure 4a and b. When the surface tension becomes constant we assume CMC is reached at that particular surfactant and electrolyte concentration. The CMCs of CPB and SDBS are 0.9 and 1.5 mM, respectively, in the absence of electrolytes. In the presence of electrolytes CMC was reached at concentration far below that of the original CMC, depending on the concentration of the electrolytes, as charge screening of the ionic surfactants headgroups and close packing of the surfactants occur at the air–liquid interface. Thus, inorganic salts have a significant impact on the adsorption of ionic surfactants at air–water as well as that in solid–water interfaces. According to the Schulze–Hardy rule, the charge screening efficiency or ability to reduce the Debye length of a multivalence ion is much more than a monovalence, so to get same CMC the required concentration of a multivalence salt required is significantly less than a monovalence. Table 3 shows the concentration of electrolytes required for getting CMCs of SDBS and CPB of 0.05 and 0.1 mM, respectively. SDBS and CPB have surface tension values at CMC in the absence of electrolytes 36.51 and 37.14 mN/m, respectively. The surface tension values of starting surfactant concentrations (0.05 mM and 0.1 mM) for SDBS and

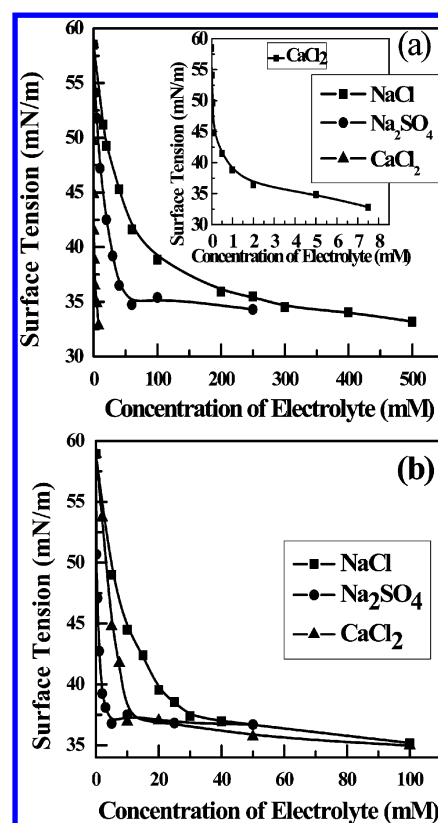
**Figure 4.** Surface tension reduction of surfactants solution in the presence of electrolytes: (a) SDBS, (b) CPB.

Table 3. Concentration of Electrolytes for Reaching the CMC at a Particular Concentration of SDBS and CPB, and Their Surface Tension (γ) Values at Initial Concentration and at CMC

electrolytes	SDBS (0.05 mM)		CPB (0.1 mM)	
	electrolyte concn. (IS)	γ (mN/m), initial value 58.50	electrolyte concn. (IS)	γ (mN/m), initial value 58.92
NaCl	200 mM (IS = 200)	35.94	30 mM (IS = 30)	37.39
Na ₂ SO ₄	60 mM (IS = 180)	35.26	5 mM (IS = 15)	36.79
CaCl ₂	2 mM (IS = 6)	36.25	10 mM (IS = 30)	36.91

CPB are 58.50 and 58.97 mN/m, respectively. Table 3 shows surface tension values reached at CMC in the presence of electrolytes are very close to that of CMC in the absence of electrolytes. From the table it is clear that for CPB when the counterion is monovalence but co-ion is not monovalence a particular CMC value is reached when the ionic strengths (IS) of the electrolyte solutions are similar, for SDBS there is a little difference but it is close to the expected value (66 mM). In contrast, when the bivalence counterion is there for SDBS the concentration required is very close to that calculated according to Schulze–Hardy rule (according to this rule CaCl₂ concentration required is $200/2^6 = 3.12$ mM). Whereas, CPB in the presence of bivalence counterion does not follow this rule, the concentration required is less than that of electrolyte having monovalence counterion but more than that according to Schulze–Hardy rule ($30/2^6 = 0.468$ mM).

3.3.2. Electrolytes Effect on SDBS Adsorption at a Constant Concentration. Figure 5a and b shows the effect of electrolytes on adsorption of SDBS using a constant initial surfactant concentration at PTFE surface below and above the saturation. In this study a constant surfactant concentration (0.05 mM) is used and the electrolytes concentrations are increased to see the change in adsorption. From Figure 5a, it is found that for all three electrolytes there is a linear increase in amount adsorbed with the increase in ionic strength of the electrolyte solution, with a correlation coefficient ~ 0.99 for all the three

cases. First, we have done the adsorption study up to the electrolyte concentration where the CMC reached that particular surfactant concentration from the surface tension plot (Figure 4a, b), and found until that concentration there is no saturation in adsorption. This can be attributed as the initial concentration is constant in the presence of higher electrolyte concentration more surfactant molecules are getting adsorbed and ultimately the equilibrium concentration becomes still below the CMC at that electrolyte concentration, as a result, in this case we need to go to electrolyte concentration of far above than that shown in Table 3, to get the plateau. Figure 5b shows that with further increasing the concentration of electrolytes there indeed is a plateau level reached when the total surface of PTFE is covered. It is also worthy to observe that the maximum amount adsorbed at the plateau is very close for the three electrolytes, and that the amount is less than the plateau of the original adsorption isotherm in the absence of electrolytes above the CMC. It may also be interesting to note, at a constant surfactant concentration the effect of electrolytes show similar effect on amount adsorbed to that of increasing surfactant concentration, but in contrast, their nature of the curves are totally different. In the presence of electrolyte, there is a stiff linear rise in amount adsorbed until below the CMC then reached to a saturation level. From the linear fitting of the experimental data (ionic strength vs amount adsorbed) we found the increasing order of the slopes are Na₂SO₄ < NaCl < CaCl₂. In the presence of CaCl₂ the slope is 1 order of magnitude higher than those of the other two electrolytes. Quantitatively the slope in the presence of CaCl₂ is 35.87 times higher than that of Na₂SO₄ and 32.16 than NaCl. As we have mentioned before, since the surface is almost hydrophobic, adsorption may occur by the hydrophobic attraction between the tailgroup and the solid surface, in this situation reduction in headgroup repulsion or screening of headgroup charge in the presence of electrolyte is responsible for adsorption enhancement. The presence of bivalence counterion (Ca²⁺) can effectively reduce the surface charge of the headgroup and show highest slope. Between NaCl and Na₂SO₄ bivalence co-ion has a negative effect on adsorption, so the slope is a little less in the presence of Na₂SO₄.

3.3.3. Electrolytes Effect on CPB Adsorption at a Constant Concentration. Figure 5c and d shows the adsorption behavior of CPB in the presence of electrolytes using a constant surfactant concentration below and above the saturation level, respectively. From the figure it can be seen that similar natures of the curves are obtained for CPB and SDBS. Figure 5c shows similar to SDBS there is a linear increase in the amount adsorbed with the increase in ionic strength of electrolytes solutions until below the CMC. The increasing orders of the slopes of the linear lines in the presence of electrolytes are NaCl < CaCl₂ < Na₂SO₄. The slope in the presence of Na₂SO₄ is 2.65 times higher than that of CaCl₂ and 3.34 times than that of NaCl. So, similar to the previous study the rate of increase in adsorption is more when bivalence counterion is present than that of monovalence and less when bivalence co-ion is present. Comparing with the SDBS results we can also conclude the slope change is more sensitive to anionic surfactant and bivalence counterion com-

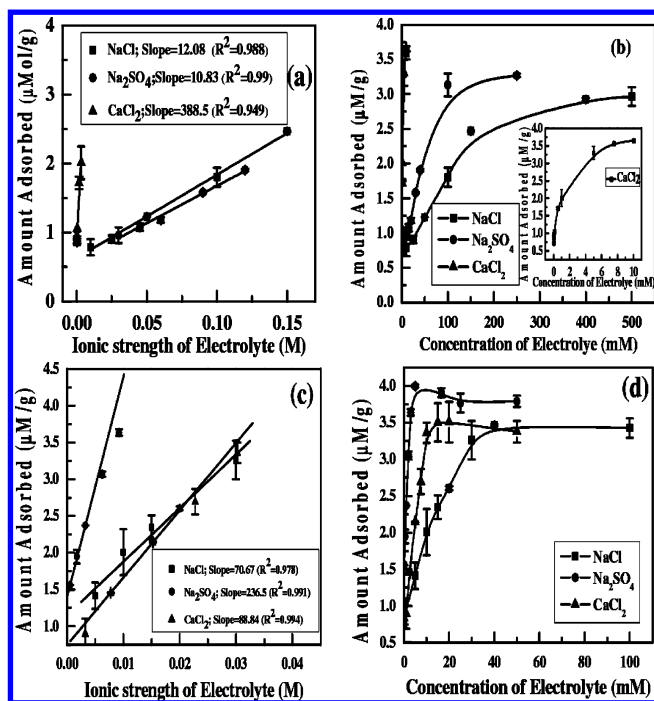


Figure 5. (a) Linear increase of SDBS amount adsorbed with the increase in ionic strength of electrolyte solutions. (b) Plateau level of SDBS adsorption in the presence of different electrolytes solutions at higher concentration. (c) Linear increase of CPB amount adsorbed with the increase in ionic strength of electrolyte solutions. (d) Plateau level of CPB adsorption in the presence of different electrolytes solutions at higher concentration.

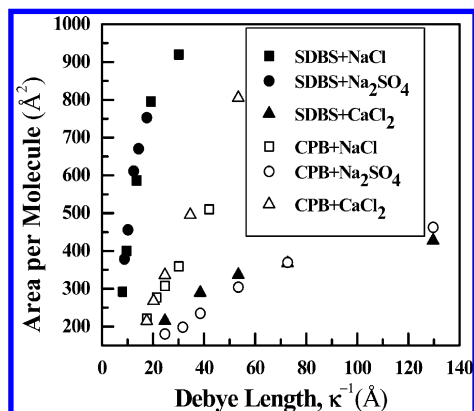


Figure 6. Area occupied per molecule of SDBS and CPB surfactants vs Debye length, κ^{-1} (Å). Areas occupied per molecule in absence of electrolyte are 996.40² and 859.37 Å² for SDBS and CPB, respectively.

bination rather than with cationic surfactant. The above results indicate the decrease in the electrostatic repulsion between the surfactant headgroups is the main mechanism here to increase the amount adsorbed due to closer packing at the surface. Figure 5d shows the amount adsorbed at the plateau is similar for NaCl and CaCl₂ and the difference is not significant from that in the presence of Na₂SO₄. Similar to anionic surfactants it can be seen that the maximum amount adsorbed is lower than that plateau of the isotherm in the absence of electrolyte. Since the amount adsorbed increases linearly and then reaches a plateau level, probably the monolayer formation is there in this surfactant concentration with a closer packing in the presence of electrolytes. In the earlier publication it was reported that during the adsorption of cationic surfactant in the presence of electrolytes on a hydrophilic surface the reduction in headgroup repulsion is important for adsorption enhancement.²⁵

3.3.4. Area Occupied Per Molecule in the Presence of Electrolytes. Debye length (κ^{-1}), defined as the inverse of the Debye–Huckel parameter, is the measure of screening of the electrical double layer in the presence of electrolyte. The Debye–Huckel parameter is represented as

$$\kappa = \left[\frac{1000e^2N_A}{\epsilon_r\epsilon_0k_BT} \sum_i z_i^2 C_i \right]^{1/2} \quad (10)$$

where e is the elementary charge, N_A is Avogadro's number, ϵ_r is the dielectric constant, ϵ_0 is the permittivity in vacuum, k_B is the Boltzmann constant, T is the absolute temperature, and z_i and C_i are the valence and molar concentrations of ionic species i , respectively. The area per molecule is calculated as

$$A_m = \frac{S \times 10^{26}}{\Gamma N_A} \quad (11)$$

where A_m is the area occupied per surfactant molecule in Å², S is the specific surface area of PTFE in m² g⁻¹, and Γ is the amount of surfactant adsorbed at saturation in μmol·g⁻¹. From Figure 6, it can be seen that the area occupied per SDBS molecule linearly increases with the increase in Debye length. It is also found that the area occupied is very similar for a particular Debye length in the presence of NaCl and Na₂SO₄ but different for CaCl₂, especially at higher Debye length. For a constant Debye length the area occupied per SDBS molecule is less in the presence of CaCl₂ than in the presence of NaCl or Na₂SO₄. Figure 6 also shows a similar type of observation obtained for CPB. The area occupied per CPB molecule linearly increases in the presence of electrolytes and is almost similar

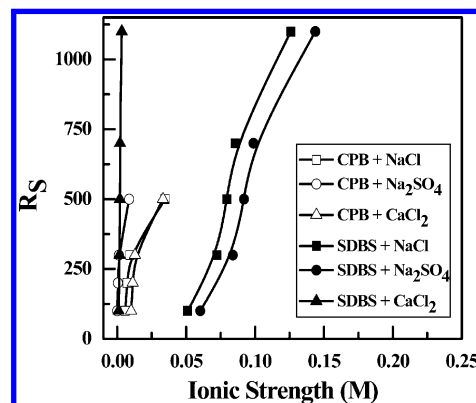


Figure 7. Reduction of surfactant consumption (R_S) with the increase in ionic strength of electrolyte solutions.

with the variation of Debye length when the electrolytes have monovalence counterion. In the presence of bivalence counterion (SO_4^{2-}) the area occupied per CPB molecule is less and the difference from the monovalence counterion is more at higher Debye length. This similar behavior for both the anionic and cationic surfactants is mainly due to the similar adsorption pattern of the molecules at the hydrophobic solid surface. Comparisons of both the surfactants together show there is a difference between the monovalence counterions for SDBS and CPB, but when bivalence counterion is present difference in area occupied by the two surfactants is almost similar.

3.3.5. Reduction in Surfactant Concentration. Since the amount adsorbed significantly increases in the presence of electrolyte, the reduction in surfactant concentration to obtain the same amount adsorption was calculated and presented in Figure 7. For the calculation of percent reduction, first the amount adsorbed for a particular initial concentration was taken from the adsorption isotherm data and the required electrolyte concentration to reach that amount adsorbed was calculated from the linear plot of amount adsorbed vs ionic strength. The percent reduction of surfactant (R_S) was calculated according to the equation

$$R_S = \frac{(C_i - C_E)}{C_i} \times 100 \quad (12)$$

where C_i is the particular initial surfactant concentration from the isotherm, C_E is the concentration of surfactant used for study of electrolyte effect (0.05 mM for SDBS and 0.1 mM CPB). C_i was chosen in a particular range where the amount adsorbed fell in the linear range of Figure 5a and c. From Figure 7 it can be seen that there is a significant increase in R_S with the increase in ionic strength and the reduction efficiency is more for SDBS systems, especially in the presence of CaCl₂.

3.3.6. Effect of Electrolytes on Surfactant Adsorption Isotherm. Figure 8 represents the adsorption isotherm of CPB in the presence of 50 mM NaCl and 16.5 mM Na₂SO₄ each having equal ionic strength to study the counterion valence effect on the isotherm. The isotherms are then fitted with Langmuir and Freundlich model and the parameters are listed in Table 2. From the table it is observed that for both the cases Langmuir isotherm fits better than Freundlich isotherm. In the presence of electrolytes the negative surface charge of PTFE surface may be reduced further, as a result the surfactants are mostly adsorbing like a uniform hydrophobic surface. That may be the reason why the isotherm is shifted from Freundlich to Langmuir type. The increase in amount adsorbed in the plateau region is mainly due to reduction in headgroup repulsion as explained

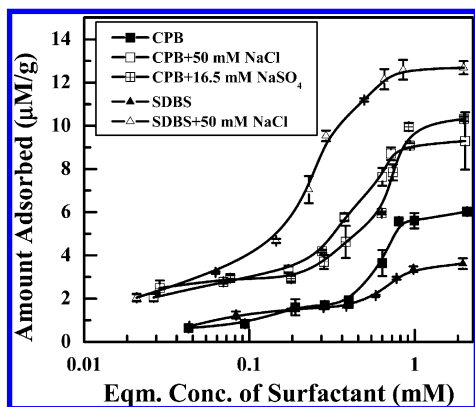


Figure 8. Adsorption isotherms of CPB, CPB + 50 mM NaCl, CPB + 16.5 mM Na₂SO₄, SDBS, and SDBS + 50 mM NaCl on PTFE powder.

before. Higher adsorption amount in the presence of Na₂SO₄ shows counterion valence effect is more important, although the ionic strength is the same. Throughout the isotherm since the ionic strength is constant the difference in amount adsorbed between NaCl and Na₂SO₄ is less.

Figure 7 also depicts the adsorption isotherm of SDBS without electrolyte and at 50 mM NaCl. For SDBS we have not studied the effect of CaCl₂ due to formation of precipitate at 16.5 mM concentration. Similar to CPB adsorption isotherm of SDBS also shows better fitting with Langmuir model may be due to similar reason. The amount adsorb increased also due to further decrease in surface potential and also reduction in headgroup repulsion between the adsorbed molecules. The adsorption of pure surfactants show CPB has higher adsorption capacity than SDBS, whereas in the presence of NaCl the trend is reversed. This observation can be attributed in the following ways: (i) in the presence of NaCl for CPB when the surface charge is reduced, the number of molecules adsorbed due to oppositely charged surface is reduced, and the adsorption enhancement is only due to the reduction in headgroup repulsion; (ii) for SDBS adsorption, the repulsion between same charged surface and headgroup is reduced, which is favorable for adsorption in addition to reduction in headgroup repulsion. As a result, SDBS shows higher adsorption capacity at the plateau level in the presence of NaCl than that of CPB.

4. Conclusion

The rate of adsorption of three synthetic surfactants TX-100, SDBS, and CPB on PTFE surface is very fast; within 10 min the equilibrium is reached. Pseudo-second-order kinetic model fits well for the adsorption kinetics of all three surfactants with the following order of rate constant values with a minimum difference: CPB > TX-100 > SDBS. The adsorption isotherms of TX-100 show Langmuir type but SDBS and CPB are better fit with Freundlich type model. In the presence of electrolytes, isotherms of both the ionic surfactants show better fitting with Langmuir type isotherm. When the initial concentration of the ionic surfactant is constant and far below the CMC, the addition of electrolytes shows there is a linear relationship between the amount of surfactant adsorbed and ionic strength of the electrolyte solutions. The increasing order of the slopes in the linear portion for SDBS is Na₂SO₄ < NaCl < CaCl₂, and that for CPB is NaCl < CaCl₂ < Na₂SO₄. The area occupied per molecule (A_m) also changes linearly with the Debye length in the presence of electrolytes for both the ionic surfactants. The A_m is mainly dependent on Debye length but independent of the types of electrolytes when monovalence counterion is

present. Whereas in the presence of bivalence counterion, for a particular Debye length the difference in A_m is observed. The difference in A_m in the presence of mono- and bivalence counterion is more at higher Debye length. The main mechanism of increase in amount adsorbed for both the surfactants can be attributed to the decrease in the electrostatic repulsion between the surfactant headgroups, and as a result, closer packing of the surfactant molecules at the surface.

This study gives an idea about the adsorption behavior of anionic and cationic surfactants on a hydrophobic surface in the presence of electrolytes. The study may be useful in some applications such as wetting, colloid stability, and dispersion of polymers, etc., where surfactant adsorption is an important parameter; moreover, surfactant consumption can also be reduced by adding small amount of electrolytes to the surfactant solutions.

Acknowledgment

Financial support from University Grants Commission (U.G.C), Grant F. 32-96/2006 (SR), New Delhi, India, for this project is gratefully acknowledged. N.R.B thanks U.G.C, India, for Junior Research Fellowship.

Literature Cited

- (1) Janczuk, B.; Chibowski, E. Influence of n-alkanes on Wettability and Zeta Potential of Quartz. *Mater. Chem. Phys.* **1985**, *12*, 367.
- (2) Romero-Cano, M. S.; Martin-Rodriguez, A.; Chauveteau, G.; De las Nieves, G. F. J. Colloidal Stabilization of Polystyrene Particles by Adsorption of Nonionic Surfactant. II. Electrosteric Stability Studies. *J. Colloid Interface Sci.* **1998**, *198*, 273.
- (3) Wu, W.; Zhu, Q.; Qing, F.; Han, C. C. Water Repellency on a Fluorine-Containing Polyurethane Surface: Toward Understanding the Surface Self-cleaning Effect. *Langmuir* **2009**, *25*, 17.
- (4) Zdziennicka, A.; Janczuk, B.; Wojcik, W. Wettability of Polytetrafluoroethylene by Aqueous Solutions of Two Anionic Surfactant Mixtures. *J. Colloid Interface Sci.* **2003**, *268*, 200.
- (5) Szymczyk, K.; Janczuk, B. The Wettability of Polytetrafluoroethylene by Aqueous Solution of Cetyltrimethylammonium Bromide and Triton X-100 Mixtures. *J. Colloid Interface Sci.* **2006**, *303*, 319.
- (6) Szymczyk, K.; Janczuk, B. Wettability of a Polytetrafluoroethylene Surface by an Aqueous Solution of Two Nonionic Surfactant Mixtures. *Langmuir* **2007**, *23*, 8740.
- (7) Zdziennicka, A.; Janczuk, B. The Adsorption of Cetyltrimethylammonium Bromide and Propanol Mixtures with Regard to Wettability of Polytetrafluoroethylene II. *J. Colloid Interface Sci.* **2008**, *318*, 15.
- (8) Chaudhuri, R. G.; Paria, S. Dynamic Contact Angles on PTFE Surface by Aqueous Surfactants Solution in Absence and Presence of Electrolytes. *J. Colloid Interface Sci.* **2009**, *337*, 555.
- (9) Szymczyk, K.; Zdziennicka, A.; Janczuk, B.; Wojcik, W. The Wettability of Polytetrafluoroethylene and Polymethyl Methacrylate by Aqueous Solution of Two Cationic Surfactants Mixture. *J. Colloid Interface Sci.* **2006**, *293*, 172.
- (10) Harkot, J.; Janczuk, B. The Role of Adsorption of Dodecylethylidimethylammonium Bromide and Benzylidimethyldodecylammonium Bromide Surfactants in Wetting of Polytetrafluoroethylene and Poly(methyl methacrylate) Surfaces. *Appl. Surf. Sci.* **2009**, *255*, 3623.
- (11) Yao, J.; Strauss, G. Adsorption of Quaternary Ammonium Surfactants on Poly(tetrafluoroethylene) Surfaces. *Langmuir* **1991**, *7*, 2353.
- (12) Yao, J.; Strauss, G. Adsorption of Cationic Surfactants on Medical Polymers: Effects of Surfactant and Substrate Structures. *Langmuir* **1992**, *8*, 2274.
- (13) Desai, T. R.; Dixit, S. G. Co-adsorption of Cationic-nonionic Surfactant Mixtures on Polytetrafluoroethylene (PTFE) Surface. *J. Colloid Interface Sci.* **1996**, *179*, 544.
- (14) Vanjara, A. K.; Dixit, S. G. Adsorption of Alkyltrimethylammonium Bromide and Alkylpyridinium Chloride Surfactant Series on Polytetrafluoroethylene Powder. *J. Colloid Interface Sci.* **1996**, *117*, 359.
- (15) Dixit, S. G.; Vanjara, A. K.; Nagarkar, J.; Nikoorazm, M.; Desai, T. Co-adsorption of Quaternary Ammonium Compounds–Nonionic Surfactants on Solid-Liquid Interface. *Colloids Surf., A* **2002**, *205*, 39.

- (16) Connor, P.; Ottewill, R. H. The Adsorption of Cationic Surface Active Agents on Polystyrene Surfaces. *J. Colloid Interface Sci.* **1971**, *37*, 642.
- (17) Zhao, J.; Brown, W. Dynamic Light Scattering Study of Adsorption of a Nonionic Surfactant (C₁₂E₇) on Polystyrene Latex Particles: Effects of Aromatic Amino Groups and the Surface Polymer Layer. *J. Colloid Interface Sci.* **1996**, *179*, 281.
- (18) Martin-Rodriguez, A.; Cabrerizo-Vilchez, M. A.; Hidalgo-alvarez, R. A Comparative Study on the Adsorption of Triton X-100 and Tween 20 onto Latexes with Different Interfacial Properties. *J. Colloid Interface Sci.* **1997**, *187*, 139.
- (19) Romero-Cano, M. S.; Martin-Rodriguez, A.; De las Nieves, F. J. Adsorption and Desorption of Triton X-100 in Polystyrene Particles With Different Functionality. 1. Adsorption Study. *J. Colloid Interface Sci.* **2000**, *227*, 322.
- (20) Santhanalakshmi, J.; Balaji, S. Adsorption Studies of Nonionic Surfactants onto Polyvinyltoluene Microlatexes in Aqueous Medium. *J. Colloid Interface Sci.* **2000**, *232*, 219.
- (21) Steinby, K.; Silveston, R.; Kronberg, B. Effect of Temperature on Adsorption of a Nonionic Surfactant on a PMMA Latex. *J. Colloid Interface Sci.* **1993**, *155*, 70.
- (22) Subramanian, V.; Ducker, W. A. Counterion Effects on Adsorbed Micellar Shape: Experimental Study of the Role of Polarizability and Charge. *Langmuir* **2000**, *16*, 4447.
- (23) Atkin, R.; Craig, V. S. J.; Wanless, E. J.; Biggs, S. The Influence of Chain Length and Electrolyte on the Adsorption Kinetics of Cationic Surfactants at the Silica-Aqueous Solution Interface. *J. Colloid Interface Sci.* **2003**, *266*, 236.
- (24) Paria, S.; Manohar, C.; Khilar, K. C. Adsorption of Anionic and Nonionic Surfactants on a Cellulosic Surface. *Colloids Surf., A* **2005**, *252*, 221.
- (25) Paria, S.; Yuet, P. K. Effects of Chain Length and Electrolyte on the Adsorption of *n*-Alkylpyridinium Bromide Surfactants at Sand-Water Interfaces. *Ind. Eng. Chem. Res.* **2006**, *45*, 712.
- (26) Howard, S. C.; Atkin, R.; Craig, V. S. J. Effect of Electrolyte Species on the Adsorption of a Cationic Surfactant to Silica: The Common Intersection Point. *Colloids Surf., A* **2009**, *347*, 109.
- (27) Gao, Y.; Du, J.; Gu, T. Hemimicelle Formation of Cationic Surfactants at the Silica Gel-Water Interface. *J. Chem. Soc. Faraday Trans.* **1987**, *83*, 2671.

Received for review April 4, 2010

Revised manuscript received June 18, 2010

Accepted June 21, 2010

IE100812K