

Adsorption of anionic and non-ionic surfactants on a cellulosic surface

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Abstract

The adsorption of an anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS) and a non-ionic surfactant, Triton X-100 (TX-100) has been studied on cellulose surfaces with and without the presence of electrolytes by using both spectrophotometric and titrametric methods. The adsorption isotherms are identified with four different regimes for both surfactants. Two important phenomena reflected in the adsorption isotherms are the steep increase in adsorption due to hemimicellisation below the critical micelle concentration (CMC) and the decrease in the adsorption above the CMC. Adsorption of anionic surfactant, NaDBS gets enhanced in presence of monovalent (K^+) or bivalent (Ca^{2+}) cation while for non-ionic surfactant, TX-100 there is no such enhancement in adsorption in presence of salt.

Keywords: Adsorption isotherm; Sodium dodecylbenzenesulfonate; TX-100; Adsorption maxima; Cellulose

1. Introduction

Adsorption of surfactants at the solid–liquid interfaces is an important phenomenon in many practical applications of surfactants areas, such as, detergency, flotation of ore, oil recovery, and dispersions such as paints and pigments. In particular, the adsorption is a crucial step for removal of particulates and oily soils in detergency. This work is focused on the adsorption of surfactants on the cellulosic surface and therefore, we review here the relevant literature of surfactant adsorption on cellulosic or a hydrophilic surface. Previous studies are reported in a number of publications [1–23].

Fig. 1 depicts a typical log–log plot of adsorption isotherm of surfactants on the solid–liquid interface in a rather wide range of concentration of surfactants going beyond the CMC. In general, a typical isotherm can be subdivided into four regions when plotted on a log–log scale [16–22]. In Region I adsorption obeys Henry's law, that is, adsorption increases linearly with concentration. Region II shows a sudden increase in adsorption, while Region III shows a slower rate

of increase in adsorption than Region II. Region IV is the plateau region above the CMC [16–21]. However, depending upon several factors, such as surface-active impurities, solid surface, solid–liquid ratio, etc. this Region IV may show a maximum [1–11,13,22].

The explanations for the nature of adsorption curve in the first three regions are well accepted. The sudden steep rise in Region II is due to formation of small cluster of surfactant molecules onto the surface. These clusters are known as hemimicelles and form beyond a particular concentration below CMC and the formation continued until the surface is saturated with the hemimicelles. In Region III, there occurs a slow down of new surface cluster formation and hence there is a reduction in the slope of isotherm.

The adsorption mechanism in Region IV is not well understood. Ideally, the adsorption is expected to remain unchanged beyond the CMC since the concentration of monomer does not increase beyond the CMC with the increase in bulk concentration of surfactant and the micelles that formed do not adsorb on the surface [5]. The observation of a maximum in Region IV for consistency has drawn attention of some researchers and attempts have been made to explain this occurrence. Presence of trace surface-active impurities in the surfactant sample has been attributed to the

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Nomenclature

a_{sm}	mean area occupied at the solid–liquid interface (\AA^2 per molecule)
a_{smh}	mean area occupied on hydrophobic site at the solid–liquid interface (\AA^2 per molecule)
C_{eq}	equilibrium concentration of surfactant (mM)
C_L, C_S	monomer concentration of surfactant (mM)
C_T	total concentration (mM)
CMC	critical micelle concentration
CMC_{Mix}	mixed CMC
f	fraction of hydrophobic area
f_L, f_S	activity coefficient
M	molecular weight
N_A	Avagadro's number (mol^{-1})
X_S	amount of surfactant adsorbed on solid surface (mg/g)
y_L	micellar mole fraction

Greek letters

$\alpha, \alpha_L, \alpha_S$	mole fraction of surfactants
Γ	amount adsorbed at the interface (mg/g)

occurrence of this maximum. These would be adsorbed below the CMC but would be solubilized in the micelles above the CMC [4,11,12]. In another explanation, it is stated that, ionic strength of the solution, reduces the electrical repulsion between adsorbed ions and the repulsive interaction becomes less than the van der Waals attraction between the paraffin chains, leading to the formation of surface micelles. Desorption of both simple monomer ions and surface micelles occur on collision of micelles in solution with the adsorbing surface and thus decreasing the amount of adsorption on the surface

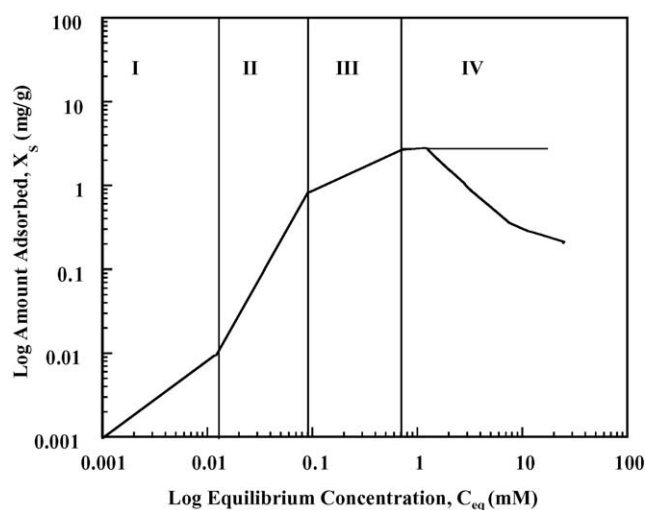


Fig. 1. A typical adsorption isotherm of surfactants on the solid–liquid interface.

[10]. The observation of maximum in case of cotton surface has been attributed to the presence of wax, which gets solubilized beyond CMC [7]. There seems to be a lack of clear understanding of the adsorption of surfactants onto cellulosic surface beyond the CMC (Region IV).

The effect of electrolyte on the adsorption of surfactant onto cellulosic surface has not been studied systematically. It is shown that presence of an electrolyte enhances the adsorption of anionic surfactant onto a gas–liquid interface [24] or solid–liquid interface [2,15]. In case of a non-ionic surfactant, such as TX-100, the adsorption onto a solid–liquid interface containing OH group (quartz, kaoline, silica) changes in presence of electrolyte, when it occurs by means of hydrogen bonding [15,25].

The overall objective of this study is to generate information and generic understandings on the adsorption of surfactants onto cellulosic surface under a wide range of conditions such that practical applications such as detergency can be enhanced. There are situations where removal of soils is extremely difficult due to strong bonding of soil to the fabric and poor penetration and adsorption of surfactant molecules onto soil–surface interface. To solve such problems of difficult detergency, one requires the knowledge of adsorption of surfactants under variety conditions. We have carried out a systematic and comprehensive study of the adsorption of surfactants under a wide range of conditions such as type of surfactant, presence of electrolyte and pH. This paper addresses the equilibrium aspects of adsorption of single surfactant systems under various conditions.

2. Experimental

2.1. Materials

Anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS, shown in Fig. 2(a)) was obtained from Fluka Chemicals. Non-ionic surfactant, polyoxyethylene (number of segments 9.5) glycol *tert*-octylphenyl ether (Triton X-100 or TX-100, shown in Fig. 2(b)) was obtained from Sigma Chemicals.

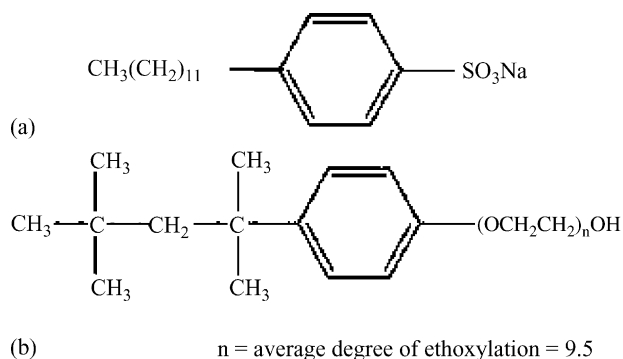


Fig. 2. (a) Chemical structure of sodium dodecylbenzenesulfonate, (b) chemical structure of TX-100.

Surfactants were used as received, without any further purification. Calcium chloride dihydrate and potassium chloride were obtained from E. Merk (India) Ltd. and s.d. fine-chem Ltd., India, respectively. Adsorbent used was Whatman-40 ashless filter paper of 9 cm diameter from Whatman International Ltd., England. The BET multipoint surface area (N_2 adsorption) was $16.5 \text{ m}^2/\text{g}$. The filter paper showed no residue after acetone extract. Double distilled water of pH 5.6 and conductivity $1.2 \text{ }\mu\text{S}$ (μMho) 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 till the conductivity of the washed water became equal to that of the distilled water. Then it was dried in oven for 1–1.5 h at $50\text{--}55^\circ\text{C}$ until the weight of the filter paper became constant.

The concentration of surfactant was determined by measuring UV absorbance at 223 nm wavelength using UV–vis spectrophotometer (Shimadzu, UV-160A model). Quartz glass cells (Hellma) of 10 mm path length were used. The calibration curves (absorbance versus concentration) are linear in nature, and are used to determine the concentration of surfactant. The critical micelle concentration (CMC) at room temperature (25°C) was determined from the break in the surface tension versus concentration plots using a Du-Noüy ring tensiometer (Fisher surface tensiometer, Model 21).

In adsorption study, surfactant solution was prepared by diluting the concentrated stock solution. Amount of adsorbent and the volume of solution were kept constant for each set of experiments. For each set of experiments, 0.580 g of filter paper was used after cutting into small pieces of size 5–10 mm. 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 the glass bottles. Time required for adsorption to reach equilibrium at various conditions is equal to approximately 1 h [26,27]. For the adsorption isotherm, system was kept for 3–4 h for equilibration. Absorbance of concentrated solution was measured after proper dilution and waiting for 1 h. In some cases, absorbance method can give rise to errors due to suspended particles. To get an independent check on the concentration of NaDBS, the concentration was also measured by two-phase titration technique [28,29] by using methylene blue indicator. The precipitation phase diagram (clear to turbid boundary) was determined by measuring turbidity of the solution. For each surfactant concentration, the electrolyte concentration was increased gradually and the turbidity of the solution was measured after 2 h of mixing. The maximum concentration of electrolyte that showed zero turbidity was taken as a boundary between clear to turbidity region. The concentration of electrolyte was taken for boundary also showed not increasing turbidity after keeping for overnight. Acidic and alkaline pH was maintained by adding dilute HCl and Na_2CO_3 , respec-

tively. All the experiments were done at the room temperature (25°C).

3. Results and discussion

3.1. CMC measurements

Critical micelle concentration of surfactant was determined by surface tension measurements. The CMC of TX-100 and NaDBS are 0.25 and 1.2 mM, respectively, as determined from the surface tension data. From the surface tension data of non-ionic and anionic surfactants, surface area occupied by a surfactant molecule at the air water interface was calculated by using Gibb's surface excess equations for non-ionic and ionic surfactants [30]. For TX-100, calculated surface area is 106 \AA^2 per molecule, which compares well with the reported value, of 120.8 \AA^2 per molecule as calculated based on molecular volume [31]. Surface area occupied by one molecule of dodecylbenzenesulfonate is calculated as 54.12 \AA^2 in absence of salt and 49 \AA^2 in presence of 100 mM KCl, and this value compares well with the reported value, of 45 \AA^2 per molecule [30].

3.2. Adsorption isotherms

Figs. 3 and 4 show the adsorption isotherm curves for TX-100 and NaDBS, respectively on filter paper surface, which is negatively charged (zeta potential $\sim -28 \text{ mV}$) in neutral aqueous medium [32]. It is observed from these figures that adsorption isotherms can be divided into three or four regions, for NaDBS and TX-100. Such adsorption behavior has been reported earlier [16–20,33,34]. We further observe from Figs. 3 and 4 that even though the four-region adsorption seems to occur both for TX-100 and NaDBS, there are indeed, some differences. For non-ionic TX-100, the distinctness be-

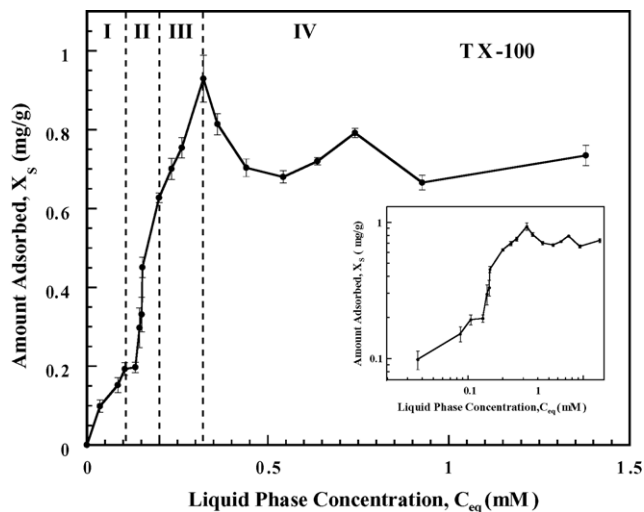


Fig. 3. Adsorption isotherm of TX-100. The inset shows the log–log plot.

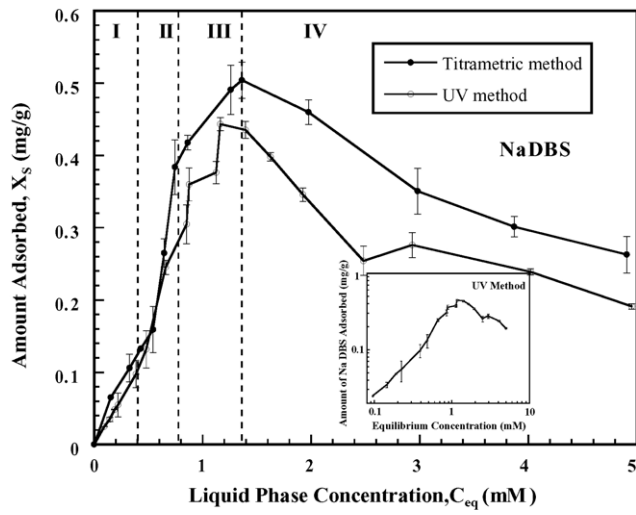


Fig. 4. Adsorption isotherm of NaDBS by UV and titrametric method. The inset shows the log–log plot.

tween Region II with that of Region I is sharper as compared to that for NaDBS. This indicates that the phenomenon that distinguishes Region II is more intense in case of a non-ionic surfactant. In Region III, the slope of X_S versus C_{eq} plot is lower for NaDBS as compared to that for the case of TX-100, indicating the presence of some inhibiting factor for ionic surfactants. One other significant difference is in the Region IV. For NaDBS, the amount of surfactant adsorbed, X_S actually decreases with concentration beyond the CMC, resulting in a maximum at around CMC. The existence of such a maximum is, however, not as definite in case of TX-100 although there seems to some decrease in the extent of adsorption.

In Region I of low concentrations, as expected both NaDBS and TX-100 molecules adsorb in a linear fashion. Beyond a particular concentration, the adsorption is suddenly enhanced as compared to that due to molecular adsorption. Such enhanced adsorption can be attributed to the cluster mode adsorption termed as hemimicellization initiated by some adsorbed TX-100 molecule on the surface [21]. Hemimicellization occurs through hydrophobic interaction between the surfactant chain in bulk and in adsorbed molecules. The concentration beyond which enhancement occurs is known as hemimicellization concentration, HMC. Adsorption isotherm of TX-100 shows that HMC is approximately 0.15 mM. For NaDBS, there is no sharp difference between Regions I and II and hence hemimicellization is absent due to the electrical repulsion between the head group of the adsorbed NaDBS molecules, where the tail is attached to the surface. According to Gao et al. [18], the average hemimicelle aggregation number h is equal to the ratio of the amount of adsorption at the two plateaus, Γ_{max} and Γ_{hmc} of the adsorption isotherm. For TX-100 adsorption, our measurements indicate the hemimicellar aggregation number to be five.

In Region III, the rate of adsorption becomes slower both for NaDBS as well as for TX-100. It is believed that in this region, either the cluster mode adsorption due to surface mi-

cellization (hemimicellization) stops or the rate decreases significantly and adsorption proceeds more or less in a regular way for TX-100. NaDBS adsorbed at slower rate due to the electrical repulsion between the head group of the adsorbed molecules.

In Region IV, adsorption shows a maximum near CMC and there is a subsequent decrease in the extent of adsorption. We believe that the maximum is due to the presence of lower chain length surfactant molecules or isomers as impurities, which has different CMC's than pure NaDBS. Lower chain surfactants (higher CMC) are adsorbed to a less extent on the solid surface than the higher chain surfactants (lower CMC). If we assume for simplification a solution of binary mixture of two different chain length, one long (L) and the other short (S) then, the CMC of the mixed solution will be [35],

$$\frac{1}{CMC_{Mix}} = \frac{\alpha_L}{f_L CMC_L} + \frac{\alpha_S}{f_S CMC_S} \quad (1)$$

CMC_{Mix} is the CMC of the mixed solution, f_L and f_S are the activity coefficients of the surfactants, equal to one for ideal system, α the mole fraction of surfactant in total surfactant. The subscripts L and S represent long and short chain surfactant molecules, respectively. Below the CMC_{Mix} ($C_T \leq CMC_{Mix}$), the monomer concentration of long chain will be,

$$C_L = \alpha_L C_T \quad (2)$$

Above the CMC of the mixture ($C_T \geq CMC_{Mix}$), monomer concentration of long chain in the bulk can be written as [35],

$$C_L = y_L CMC_L \quad (3)$$

$$C_S = (1 - y_L) CMC_S \quad (3a)$$

Micellar mole fraction of long chain component can be written as,

$$y_L = \frac{C_L}{CMC_L} = \frac{\alpha_L C_T - C_L}{C_T - C_L - C_S} \quad (4)$$

Eliminating C_S from Eq. (4), we get the concentration of monomer of long chain component above the mixed CMC [36,37],

$$C_L = \frac{-(C_T - \Delta) + \{(C_T - \Delta)^2 + 4\alpha_L C_T \Delta\}^{1/2}}{2(\Delta/CMC_L)} \quad (5)$$

$$C_L + C_S = CMC_{Mix} \quad (6)$$

where $\Delta = CMC_S - CMC_L$, C_T is the total surfactant concentration, y_L the mole fraction of long chain component in mixed micelle. Fig. 5 shows the plot of C_T versus C_S for a binary mixture of surfactants. Two sets of plots are shown for two concentrations of short chain surfactant of 0.2–0.5. With the increase in the C_T above the mixed CMC of the mixture, monomer concentration of long chain component decreases and that of short chain increases. As micelles do not adsorb and short chain surfactants are less adsorbed, there will be a decrease in the amount of adsorption. Therefore, we

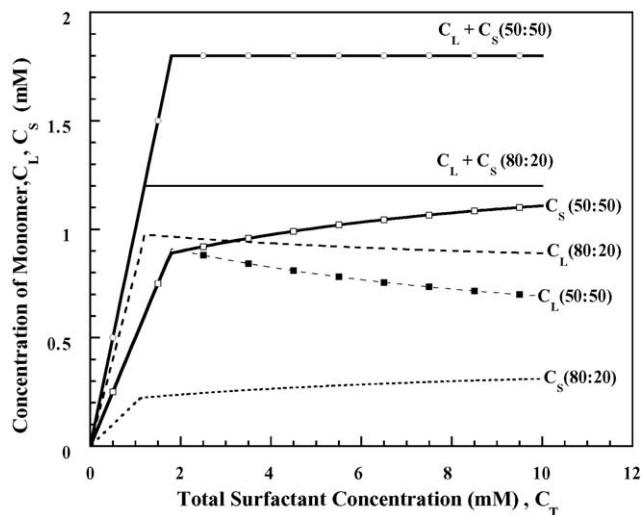


Fig. 5. Plot of total surfactant concentration vs. monomer concentrations, assuming binary surfactant system of ideal mixed micelle. $CMC_L = 1$ mM, $CMC_S = 10$ mM, $CMC_{Mix(80:20)} = 1.2$ mM, $CMC_{Mix(50:50)} = 1.8$ mM, $\alpha_L = 0.8$ and 0.5 , $\alpha_L + \alpha_S = 1$, $C_L + C_S = CMC_{Mix}$.

conclude that the existence of a maximum at around CMC in adsorption isotherm is due to the presence of short chain surfactant molecules. It is important to mention that the ‘impurity’ of the surfactant supply will not, in this case, show the minimum in a surface tension–concentration plot as this minimum is generated by a hydrophobic impurities which can not self-assemble (i.e. does not form micelle on its own). In addition, to produce a surface tension minimum, the impurity must be more surface-active than the major component and be solubilized in the micelles of the major component. Thus the absence of minima is necessary but not sufficient criterion of purity of surface-active agents [38].

To detect the presence of short chain surfactant molecules, we have conducted high performance liquid chromatographic (HPLC) measurements of NaDBS solution at a concentration of 0.5 mM. The chromatograph is presented in Fig. 6. We observe from this figure that there are some 21 percepti-

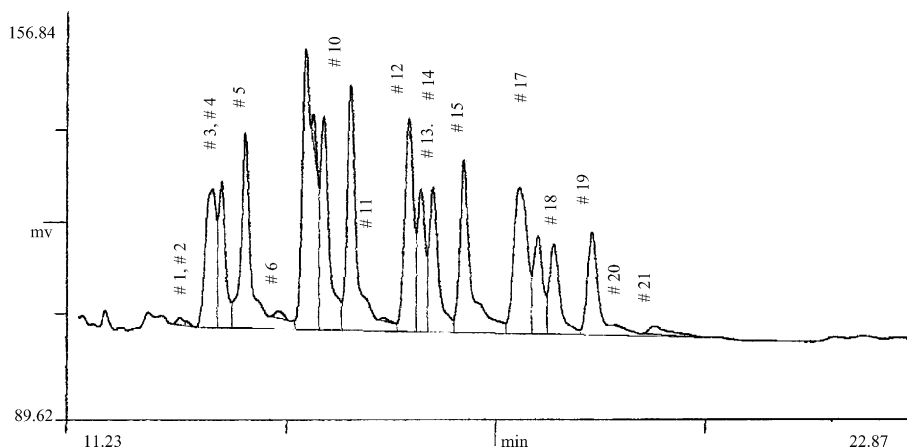


Fig. 6. HPLC chromatograph of NaDBS at 0.5 mM concentration.

Table 1

Percentage of short and long chain surfactants are adsorbed, calculated from HPLC analysis

NaDBS concentration (mM)	Percentage of lower chain surfactant adsorbed (%)	Percentage of long chain surfactant adsorbed (%)
0.5	1.34	14.94
1.0	3.79	13.16
3.0	2.61	6.06
5.0	1.36	3.25

ble peaks, which clearly indicate the presence of surfactant molecules of different chain lengths or isomers. Retention times are supposed to be associated with chain length of the surfactant molecules. Based on the retention time versus percentage area data, we have taken the percentage of surfactant molecules having different short chain lengths (less than C_{12}) as 20%. Fjelde and Austad [39] also reported NaDBS is polydisperse in the alkyl group and the distribution of different chain length is $C_{10} \approx 5\%$, $C_{11} \approx 45\text{--}50\%$, $C_{12} \approx 35\%$, $C_{13} \approx 10\text{--}15\%$ and $C_{14} \approx 0.5\%$. This data indicates that the concentration of surfactant that chain length shorter than that of C_{12} can be as high as 0.5. The effect of short chain surfactants (higher CMC) on adsorption remains the same in nature as shown in Fig. 5 that the monomer concentration of the long chain surfactant decreases beyond CMC of the mixture.

Furthermore, HPLC measurements were conducted using solutions both before and after the adsorption. Using the data, percentage adsorption for short chain and long chain surfactants were calculated. Table 1 presents these values at four different concentrations. We observe from Table 1 that short chain surfactants are adsorbed to less extent than the long chain surfactants. The first two lower values are below CMC while the rest are above CMC. Based on the above experimental measurements, we can conclude that the decrease in extent of adsorption beyond CMC is due to the presence of short chain surfactants.

HPLC measurements of TX-100 by Kamiyuki et al. [40] shows that TX-100 also has some polydispersity in chain

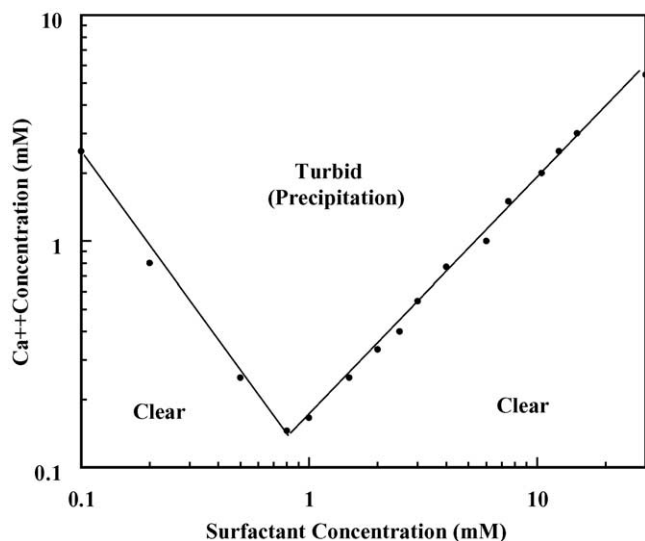


Fig. 7. Precipitation phase diagram of NaDBS in presence of CaCl_2 .

length of octylphenol ethoxylates, which explains the existence of the small peak observed in TX-100 isotherm.

3.3. Adsorption isotherm in presence of electrolytes

3.3.1. Adsorption isotherm in presence of CaCl_2

Fig. 7 shows the precipitation phase diagram of NaDBS in presence of Ca^{2+} ion. We observe from the figure that for lower surfactant concentrations calcium ion tolerance is more, and then the tolerance decreases and goes through a minimum. Beyond this minimum, the borderline is a straight line, that is, the turbid to clear region maintains a particular, surfactant: Ca^{2+} ratio. This study is conducted with in the clear (no precipitation) regime.

Fig. 8 shows the adsorption isotherm of NaDBS in presence of calcium ion. We observe from this figure that, there

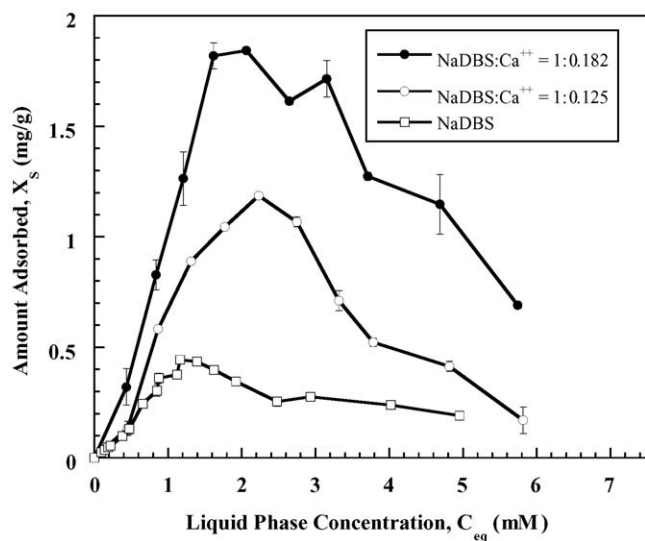


Fig. 8. Adsorption isotherm of NaDBS in presence of CaCl_2 .

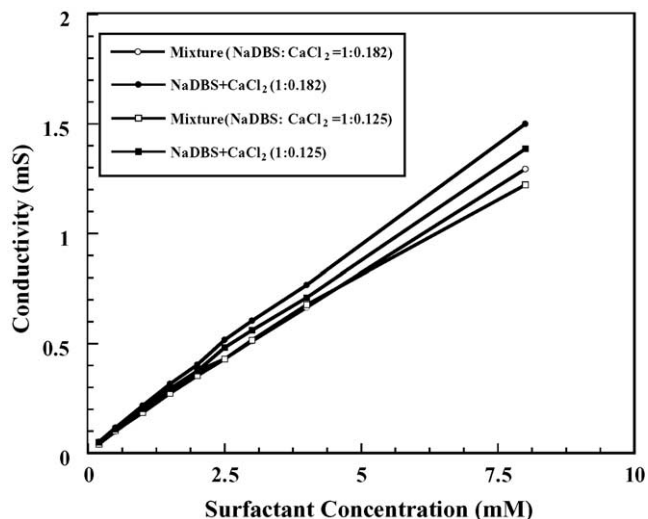


Fig. 9. Comparison of conductivity of NaDBS and CaCl_2 mixture and sum of the conductivities of the individual solutions in same proportions.

occurs a significant increase in adsorption in the presence of even a small amount of Ca^{2+} ions. We further observe that the extent of increase is higher for higher amount of Ca^{2+} ions present. The amount of adsorption at the peak value increases by 167 and 316% for the mixtures containing NaDBS and CaCl_2 in the ratios of 1:0.125 and 1:0.185, respectively. In addition, the extent of enhancement is found to be higher at lower surfactant concentration. Interestingly, in the presence of CaCl_2 the nature of curves, particularly the existence of a maximum remains intact in the presence of Ca^{2+} ions, although there is a shift of the location of the peak to a lower concentration of surfactant at higher Ca^{2+} ion concentration.

We offer the following explanations for this observation in presence of electrolytes. In presence of Ca^{2+} ions, the negative charge of cellulosic surface gets neutralized partially and as a result, anionic surfactant adsorption gets enhanced. Conductivity measurements as presented in Fig. 9, show the conductivity of the mixture of NaDBS, CaCl_2 , and the sum of the individual conductivities of NaDBS and CaCl_2 in the same proportion. It shows that the conductivity of the mixture is less than the sum of the conductivities. Therefore, it can be concluded that the negative charge of the surfactant molecules is shielded by the Ca^{2+} ions. In addition, the compressed electric double layer at the cellulosic surface shields the surface charge. Consequent to this charge shielding, the adsorption of anionic surfactant molecules onto cellulosic surface does not experience any inhibition arising out of electrical repulsion. Hence the extent of adsorption increases. As regards to the shifting of the peak, the peak appears at the changed CMC, which decreases in presence of CaCl_2 .

3.3.2. Adsorption isotherm of NaDBS in presence of KCl, CaCl_2 and their mixture

Fig. 10 shows the adsorption isotherms in the presence KCl, CaCl_2 and mixture of KCl and CaCl_2 . At lower

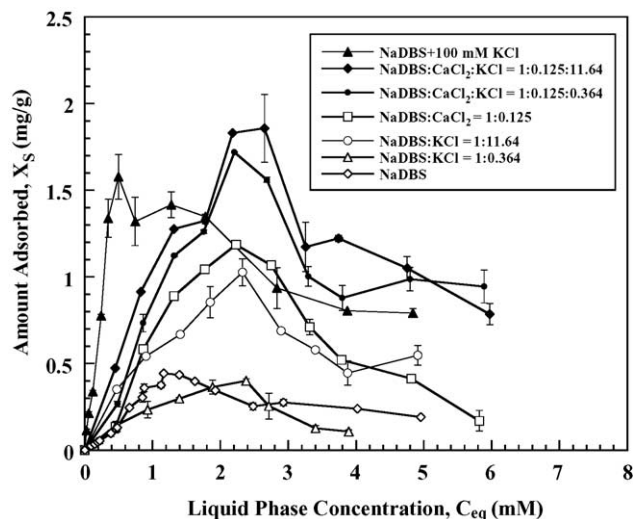


Fig. 10. Adsorption isotherm of NaDBS in presence of KCl and CaCl₂ and their mixture.

concentration of KCl (NaDBS:KCl, 1:0.364), there is negligible increase in adsorption. At higher concentration of KCl (NaDBS:KCl, 1:11.64) and at constant KCl concentration (100 mM KCl), the extent of adsorption is enhanced. Enhancement at this KCl concentration (NaDBS:KCl, 1:11.64) matches with the isotherm for the presence of CaCl₂ at a concentration, which is 93 times less (NaDBS:CaCl₂, 1:0.125). Such observation qualitatively agrees with Schulze–Hardy rule, which states the importance of the effectiveness of valency of the counter ion in shielding the charge. At the lower concentration of KCl (NaDBS:KCl, 1:0.364) there is no enhancement of amount of NaDBS adsorption. However, we observe that, at the same concentration of KCl solution, in the presence of CaCl₂ in the proportion of NaDBS:KCl:CaCl₂, 1:0.364:0.125, the extent of enhancement in adsorption increases as compared to that in case of CaCl₂ alone. This observation is in consistent with the fact that the charge is effectively shielded at higher ionic strength produced by mixing with a bivalent electrolyte.

Interestingly, relatively high concentration of KCl (1:11.64) does not significantly enhance the adsorption as can be seen in the Fig. 10. At higher concentration of KCl, CMC of the surfactant solution decreases (CMC of NaDBS in presence of 100 mM KCl is 0.15 mM) with a consequent increase in the number of micelles. As a result, adsorption of surfactant molecules decreases. This result is also consistent with the DLVO theory and can be explained in terms of energy barrier of total interaction energy between the surface and surfactant molecules in presence of salt. The rate of adsorption depends on the height of the energy barrier in total interaction energy versus distance curve. In the absence of salt, the energy barrier is high. With the addition of small amount of salt, the energy barrier decreases significantly and the extent of such decrease levels off as the salt concentration

increases. Hence, further enhancement in adsorption may not occur at high salt concentration.

3.3.3. Adsorption isotherm of TX-100 in presence of CaCl₂ and KCl

We have carried out the adsorption of TX-100 in presence of KCl (2 mM) and CaCl (1, 10 and 180 mM). We observed from the experiment that there is no significant change in the adsorption isotherms as compared to those without the presence of electrolyte. Note, TX-100 is non-ionic surfactant and hence is not influenced by the electrostatic effects. The enhancement in the case of NaDBS, as seen is primarily an electrostatic effect and it is absent in case of TX-100 adsorption. Furthermore, we can also conclude that, adsorption of TX-100 does not occur due to hydrogen bonding with OH group on the cellulosic surface. If the adsorption was by hydrogen bonding, then in presence of K⁺ or Ca²⁺, the extent of adsorption of TX-100 should decrease due to strong adsorption of K⁺ or Ca²⁺ ion with free OH group of adsorbent [15,25]. Adsorption of TX-100 molecules appears to occur primarily by the interactions between the hydrophobic site and the hydrophobic group of the TX-100.

3.3.4. Adsorption of NaDBS at different pH

Furthermore, the effect of pH on the adsorption isotherm of NaDBS was studied at two different pH 3.0 and 11.0. The isotherms are presented in Fig. 11. We observe from the Fig. 11 that the amount of NaDBS adsorbed at equilibrium decreases at pH equal to 11, compared with same electrolyte concentration. At pH of 11, surface becomes increasingly negatively charged and hence there occurs a decrease in adsorption. The adsorption at pH equal to 3.0 is slightly higher arising out of partial neutralization of negative charge. Therefore, the observed pH effect indicates the significant electrical effects on the adsorption behavior.

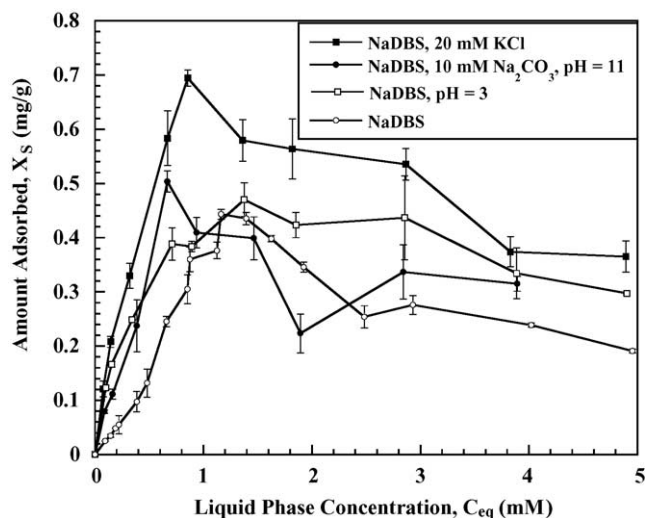


Fig. 11. Adsorption isotherm of NaDBS in presence of different pH.

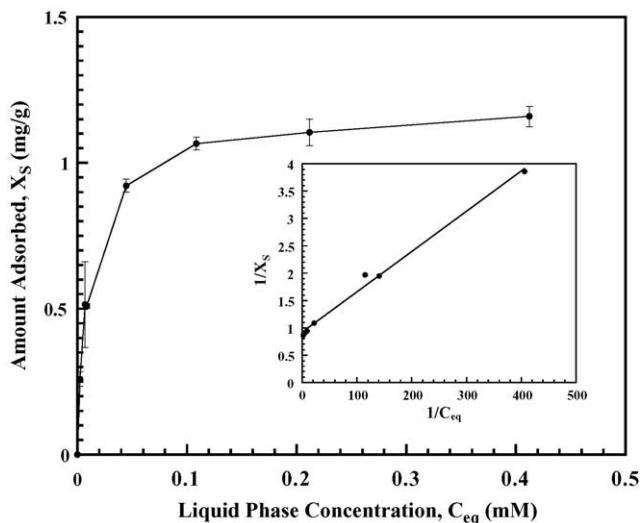


Fig. 12. Adsorption isotherm of methylene blue. The inset shows the plot of $1/X_s$ vs. $1/C_{eq}$.

3.4. Estimation of polar and non-polar sites on the cellulosic surface

The observations relating to the adsorption of NaDBS and TX-100 indicate the presence of both charged and hydrophobic sites on the cellulosic surface. The electrical nature of the surface is manifested in the change in adsorption behavior in presence of electrolyte, while the hydrophobic nature is shown through the adsorption of TX-100. The non-ionic surfactants may also be adsorbed onto charged sites by hydrogen bonding but in this situation the extent of adsorption will depend on the pH of the solution [30] and electrolyte [15,25]. We, therefore, hypothesize that the cellulosic surface consists of two kinds of sites for adsorption: electrically charged sites or polar and hydrophobic sites or non-polar sites.

From the adsorption isotherms, we have determined the effective area occupied (\AA^2) of different surfactant molecules on the filter paper surface. For this calculation, we assumed the monolayer adsorption occur on the cellulose surface. CTAB and TX-100 are forming hemimicelle, but as the hemimicellar aggregation number is very low (~ 5) calculation is carried out considering monolayer. The values for these effective areas are calculated using the following for-

Table 2
Area occupied by one molecule of surfactant and methylene blue on filter paper surface

Molecule	Area occupied per molecule (\AA^2 per molecule)
NaDBS	2000
TX-100	1920
NaDBS + Ca^{2+} (1:0.182)	530
NaDBS + Ca^{2+} + K^+ (1:0.182:11.64)	510
NaDBS + KCl (100 mM)	600
CTAB [27,41]	440
Methylene blue	750

mula:

$$a_{sm} = \frac{M \times S_{BET} \times 10^{23}}{\Gamma \times N_A} \quad (7)$$

where M is the molecular weight of the surfactant, S_{BET} the BET surface area of the filter paper in m^2/g , Γ the amount of surfactant adsorbed in mg/g , a_{sm} the area occupied per molecule in \AA^2 . Based on the observations presented earlier, we assume the filter paper surface to consist of both negatively charged sites as well as neutral hydrophobic sites. Calculations have been conducted to determine the area occupied by surfactant molecules and are presented in Table 2. Table 2 shows that the effective area occupied by a molecule of NaDBS and a molecule TX-100 nearly the same. Such agreement may indicate that NaDBS and TX-100 are mainly adsorbed to the same site, that is, on the hydrophobic sites of the filter paper. The calculated area occupied per molecule on the solid surface is more than the actual molecular area of TX-100 (120\AA^2) and NaDBS (45\AA^2). This clearly shows that even at the maximum adsorption, multilayer adsorption does not occur.

In order to prove the presence of the negatively charged sites, we have conducted the adsorption of a cationic dye, methylene blue. The molecules carry positive charge and hence are expected to adsorb onto the negatively charged sites. Fig. 12 presents the adsorption isotherm, the inset shows linear fit of Langmuir equation. We observe from this figure that unlike the four regime adsorption isotherms of NaDBS and TX-100, methylene blue gives a Langmuir type of isotherm. This is expected as both hemimicellization and micellizations are absent in such system.

Referring back to Table 2, we note that, the effective area occupied by a molecule for anionic surfactant in presence of electrolytes, and the effective area occupied by a cationic surfactant, CTAB are nearly equal to 500\AA^2 . The effective area occupied by a methylene blue molecule 750\AA^2 is higher than that for surfactants in presence of electrolyte and for CTAB. Let us assume that, NaDBS and TX-100 molecules adsorb onto hydrophobic sites only and methylene blue molecules onto negatively charged sites only and NaDBS in presence of electrolyte and CTAB adsorb onto both hydrophobic and negatively charged sites. Let us consider that f is fraction of area that consists of hydrophobic sites. The area occupied by one molecule as calculated assuming that adsorption occurs on the entire area is, $a_{sm} = 500 \text{\AA}^2$. The area occupied by one molecule, as calculated assuming that adsorption occurs on the area consisting of hydrophobic sites only is, $a_{smh} = 2000 \text{\AA}^2$. The number of molecules adsorbed on unit area in case of adsorption on hydrophobic sites is $1/a_{smh}$, which is also equal to f/a_{sm} . Hence, f the fraction of area occupied by hydrophobic sites is equal $a_{sm}/a_{smh} = 0.25$. When adsorption occurs only in the area containing negatively charged sites, it can be easily shown that the area occupied by a molecule will be $a_{sm}/1-f = 500/0.75 = 667 \text{\AA}^2$. This value of 667\AA^2 agrees well with the calculation of 750\AA^2 as shown in Table 2. The surface area of filter paper calcu-

lated from the methylene blue adsorption is $3.5 \text{ m}^2/\text{g}$, which is 21.2% of actual surface area determined by BET method ($16.5 \text{ m}^2/\text{g}$). Which also further support about 25% sites are hydrophilic. Hence it can be concluded that approximately a quarter of the filter paper surface is of hydrophilic in nature and the rest is of hydrophobic in nature.

4. Conclusions

- Equilibrium adsorption isotherms of NaDBS and TX-100 do not show Langmuir-type adsorption but show a typical three or four-region isotherm having a maximum in the Region IV. This can be attributed to the presence of shorter chain (different CMC) surfactant molecules. TX-100 molecules show hemimicelle formation while NaDBS molecules do not form hemimicelles.
- Adsorption studies of surfactant in presence of salt as well as that of methylene blue indicate that the filter paper surface consist of both hydrophilic and hydrophobic sites. The estimation further indicates that 0.25 fraction of filter paper surface consist of hydrophobic site.
- Area per molecule estimated from the adsorption isotherm data indicate that methylene blue molecules adsorb densely on the anionic sites of filter paper. NaDBS and TX-100 molecules adsorb on the hydrophobic sites and NaDBS molecules in presence of Ca^{2+} and K^+ adsorb on both hydrophilic and hydrophobic sites.

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