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EXPERIMENTAL STUDIES ON ADSORPTION OF SURFACTANTS ONTO CELLULOSIC SURFACE AND ITS RELEVANCE TO DETERGENCY

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ABSTRACT

The adsorption of anionic - sodium dodecylbenzenesulfonate (NaDBS), cationic – cetyl trimethyl ammonium bromide (CTAB) and nonionic - Triton X-100 (TX-100) surfactants under different conditions on cellulose-water interface are investigated.

The adsorption isotherms in general, show four different regimes for the three types of surfactant, such as anionic, cationic and nonionic with some differences. Two important phenomena reflected in the adsorption isotherms are the steep enhancement in the extent of adsorption due to hemimicellization below the critical micellar concentration (CMC) and the reduction in the extent of adsorption above the CMC. The adsorption isotherm for NaDBS shows a maximum at CMC and beyond CMC it shows a decrease in the extent of adsorption. However, for TX-100 and CTAB, hemimicellization occurs with steep enhancement below CMC and the adsorption isotherm levels off without showing a maximum. Adsorption of anionic surfactant, NaDBS gets enhanced in presence of monovalent (K^+) or bivalent (Ca^{++}) cation while for nonionic surfactant, TX-100 there is no such enhancement in adsorption in presence of salt. An analysis of adsorption data indicates approximately 25% of the sites are hydrophobic in nature and the rest 75% of sites are hydrophilic in nature and negatively charged.

The detergency experiments are conducted to correlate the adsorption of surfactant on cellulose water interface to the removal of particulate and composite soil (particulate and oily) from cotton. Two different soiled cotton, terrace and WFK-10D show the maximum in detergency similar to maximum in adsorption isotherm. Adsorption of NaDBS on cellulose surface is enhanced with increasing ionic strength, but the effect of ionic strength in particulate soil detergency is reverse.

KEY WORDS

adsorption isotherm, sodium dodecylbenzenesulfonate, TX-100, adsorption kinetics, cellulose, detergency.

INTRODUCTION AND BACKGROUND LITERATURE.

Surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to a interface. Studies of adsorption of surfactant at the solid-liquid interface find practical applications in many areas such as detergency, floatation of ore, oil recovery and making of dispersions such as paints and pigments. Surfactant adsorption at the hydrophilic surfaces such as cellulose-water interface is of special interest in detergency and textile processing. In particular, the adsorption is an important step for removal of particulates and oily soils in detergency. This work is concerned with a study of adsorption of surfactants on the cellulosic surface and its application in detergency.

Equilibrium adsorption of surfactant (adsorption isotherm)

In general, a typical isotherm of surfactant on a solid surface can be subdivided into four regions (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Gao et al., 1987; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988; Chander et al., 1983). 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 (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988). However, depending upon several factors region IV may show a maximum (Fava and Eyring, 1956; Meader and Fries, 1952; Pagac et al., 1998; Ginn et al., 1961; Biswas and Chattoraj, 1997; Sexsmith and White, 1959a, 1959b; Vold and Sivaramakrishnan, 1958; Furst et al., 1996; Trogus et al., 1978; Arnebrant et al., 1989; Evans, 1958).

The explanations for the nature of adsorption curve in the first three regimes are well accepted. The sudden rise in adsorption in region II is due to formation of surface aggregate

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of the surfactant molecules on the solid surface. These surface aggregates are known as 'hemimicelles' (Gaudin and Ferstenau, 1955); which form beyond a critical concentration below the CMC, and is known as critical hemimicellar concentration (HMC). Hemimicellization was first hypothesized (for the adsorption of dodecylammonium ions on quartz) by Gaudin and Ferstenau (1955); the later by others (Somasundaran et al., 1964; Somasundaran and Fuerstenau, 1966; Gao et al., 1987; Gu et al., 1988). Mane et al. (1994) have reported the first direct AFM imaging of 'hemimicelle' on graphite surface using cationic surfactant (CTAB). In region III, there occurs a slowdown of surface cluster formation and hence there is a reduction in 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 CMC and the micelles that form do not adsorb on the surface (Brinck et al., 1998). The observation of a maximum in region IV 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 have been attributed to the occurrence of this maximum. These would be adsorbed below the CMC but would be solubilized in the micelles above the CMC (Pagac et al., 1998; Furst et al., 1996; Trogus et al., 1978). In some cases as reported in the literature, additional surfactant purification was found to decrease the amplitude of the adsorption maximum but could not completely eliminate it (Arnebrant et al., 1989). In an 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 micelle occurs on collision of micelles in solution with the adsorbing surface and thus decreasing the amount of adsorption on the surface (Vold and Sivaramakrishnan, 1958). The observation of a maximum in case of cotton surface has been attributed to the presence of wax, which gets solubilized beyond CMC (Ginn et al., 1961). There seems to be a lack of clear understanding of the adsorption of surfactants on the solid 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 (Cross and Jayson, 1994) or solid/liquid (Meader and Fries, 1952; Nevskaia et al., 1998) interface. 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 (Nevskaia et al., 1998; 1995).

Particulate and oily soil detergency

The particulate soils are siliceous minerals, such as clays, as well as carbonaceous materials such as soot and carbon black, and inorganic oxide such as iron oxide. The removal mechanism also may differ depending on the type of soil. Anionic surfactants generally increase particulate soil removal. Removal of particulate soil in aqueous medium occurs by the formation of electrical double layers of similar sign on the substrate and particle with a resulting mutual repulsion, which reduces the net adhesion of soil (Rosen, 1978). Adsorption of surfactant and inorganic ions at the substrate/liquid and particle/liquid interface causes a decrease in the work required to remove the particle from the substrate. This repulsive force can be quantified using DLVO theory for forces between double layers. There are some studies related to zeta potential and particulate soil removal (Yoneyama and Ogino, 1982; Batra et al., 2001). The detergency of oily soils involves several mechanisms, but in general, oily soils are removed by (i) rolling up and (ii) solubilization mechanism (Kissa, 1987).

Kinetics of detergency can provide useful information about the detersive process being studied (Bacon and Smith, 1948; Schott, 1975, 1976; Kissa, 1975, 1978, 1979; Vaughn et al., 1941). The kinetics of soil removal is complicated by the heterogeneity of the soil, shape, size, chemical composition and location of soil. Most of the reported results of kinetics of particulate soil removal follow first order kinetics (Bacon and Smith, 1948; Hart and Compton, 1952).

Kissa (1979) has studied the effect of soiling conditions on particulate soil detergency. The soil removal rate decreases with increasing soiling time and intensity of mechanical action during soiling. The removal of soil also increases with increasing mechanical action (Bacon and Smith, 1948) and temperature (Morris and Prato (1982) during laundering.

Removal of oily soil increases with increasing temperature and mechanical action (Scott, 1963). Addition of electrolyte initially decreases the oily soil removal, but at higher concentration of electrolyte it is increased. In this respect, divalent ions are much more effective than the univalent ions (Scott, 1963).

The adsorption of surfactants onto cellulosic surface is a complex process. There is no reported study conducted using all three types of surfactants under a wide range of conditions. We have carried out a systematic and comprehensive study of adsorption of surfactants under a wide rage of conditions. The overall objective of this study is to generate useful information and generic understandings on the adsorption of surfactants onto cellulosic surface under a wide range of conditions such that practical applications such as enhancement of detergency, in general and solving the problem of difficult detergency in particular can be attempted.

EXPERIMENTAL

Materials

Anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS) was obtained from Fluka Chemicals. Nonionic surfactant, polyoxyethylene (number of segments 9.5) glycol tert-octylphenyl ether (Triton X-100 or TX-100) was obtained from Sigma Chemicals. NaDBS and TX-100 were used as received, without any further purification. Cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) was obtained from Ranbaxy Fine Chemicals Ltd., India. It was recrystalized twice from an acetone: methanol (3:1) mixture before use (Desai and Dixit, 1996). Calcium chloride di-hydrate and chloroform were obtained from E. Merk (India) Ltd. Potassium chloride, sodium sulfate and methylene blue were obtained from S. D. Fine-chem Ltd, India. Adsorbent used was Whatman-40 ashless filter paper of 9 cm dia from Whatman International Ltd., England. The BET multipoint surface area of this filter paper (N2 adsorption) was 16.5 m^2/gm. Double distilled water of pH 5.6 and conductivity 1.2 μS (μ Mho) was used for the experiment.

Methods

Adsorption

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 hours at 50-55°C until the weight of the filter paper became constant.

The concentration of NaDBS and TX-100 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. A calibration plot (absorbance vs. concentration) was obtained by measuring absorbance of known concentration surfactant solution used for determine the unknown concentration. The concentrations of CTAB, NaDBS and SDS were measured by two-phase titration technique (Rosen and Goldsmith, 1972; ASTM, 1959) by using methylene blue indicator.

In the 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 gm 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 system was stirred slowly at regular intervals. All the experiments were done at the room temperature (25 ± 3°C). For the adsorption isotherm, experiments were continued for 3-4 hours for equilibration. Amount of surfactant adsorbed was calculated according to,

$$X_S = \frac{(C_{b0} - C_t)M.V}{1000.m} \qquad (1)$$

where, X_S is the solid phase concentration of surfactant (amount adsorbed) in gm/gm, C_t and C_{b0} are the concentration of surfactant in moles/liter at time t and initial respectively. M is the molecular weight of surfactant, V is the volume of solution used, and m is the mass of filter paper used.

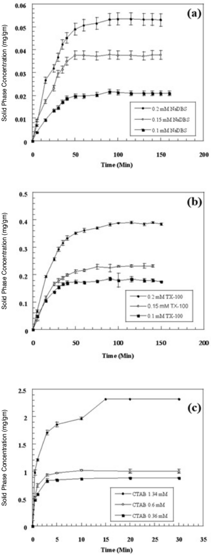

Figure 1: Adsorption kinetics of (a) NaDBS, (b) TX-100 and (c) CTAB on filter paper surface.

Detergency

Two types of artificially soiled cotton, terrace (soiled with carbon black particulate) and WFK-10D (mixed oily and particulate soil) were used for the detergency experiments. The WFK-10D contains kaolin + lampblack + black and yellow iron oxide as particulate soil and wool fat oily soil (Schott, 1975). Each swatch was cut into 8 x 8 cm small pieces. A reflectometer (Gretagmacbeth, Model- 7000A) was used to measure reflectance before and after the detergency tests. Reflectance was taken at 460 nm wavelength excluding UV absorbance. The instrument was standardized using standard white ceramic plate. The swatches were made four fold and reflectance was taken as the average of four places of each swatch before and after detergency. Detergency experiments were done in an Atlas Launder-Ometer. The Launder-Ometer has eight steel jars including nine steel balls in each jar. Launder-Ometer was run at 45 r.p.m and 28 ˚C for 40 minute. For the detergency experiment, five swatches of each sample were taken in the jar and then the swatches were soaked for 30 minute in the surfactant solution. After completing the laundering for 40 minute each swatch was rinsed for four times with fresh deionized water. The swatch was then dried in a rotary drier and final reflectance was measured. The change in reflectance before and after detergency, ΔR, was used to measure detergency. The detergency experiments were conducted using the facilities in Unilever Research Laboratory, Bangalore, India.

RESULTS AND DISCUSSION

Kinetics of adsorption

Adsorption kinetics of three different surfactants NaDBS, TX-100 and CTAB was studied at three different initial concentrations on the cellulose-water interface to measure the equilibrium time. Figures-1 (a), (b) and (c) graphically present the kinetics of adsorption of NaDBS, TX-100 and CTAB respectively. Following observations can be noted from these figures. The natures of the plots are similar, having a somewhat non-linear increase in the amount of adsorption followed by a clear leveling off to indicate equilibrium, which is obtained within one hour. The amount of adsorption increases with increase in the concentration. Both these trends are expected. Comparing adsorption kinetics between the surfactants, it is noted that both the amount and rate of adsorption increase in the following order NaDBS < TX-100 < CTAB. It has been observed that the agitation does not show any effect on the rate of adsorption kinetics indicating that the rate of diffusion and mass transfer of surfactant molecules is very fast and is not the rate-determining step in the adsorption.

Equilibrium adsorption (adsorption isotherm)

Figures-2, 3 and 4 show the adsorption isotherm curves for TX-100, NaDBS and CTAB respectively on the filter paper surface. We observe from these figures that adsorption isotherm can be divided into four regions for the three surfactants, NaDBS, TX-100 and CTAB. Such adsorption

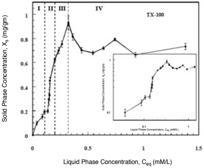

Figure 2 : Adsorption isotherm of TX-100 on filter paper surface. The inset shows the log-log plot.

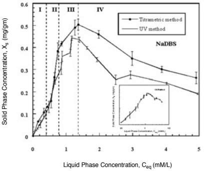

Figure 3 : Adsorption isotherm of NaDBS on filter paper surface by UV and titrametric method. The inset shows the log-log plot.

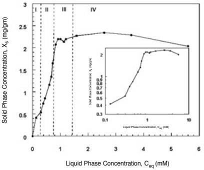

Figure 4 : Adsorption isotherm of CTAB on filter paper surface. The inset shows the log-log plot.

behavior has been reported earlier (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Gao et al., 1987; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988; Chander et al., 1983). In further, it is observed from the figures that even though the four-region adsorption seems to occur for the three cases, there are indeed some differences. For non-ionic TX-100, and cationic CTAB, the distinctness between region II with that of region I is sharper as compared to that for NaDBS. This indicates that the phenomenon distinguishing region II is more intense in case of non-ionic and cationic surfactants. In region III, the slope of X_S vs. C_{eq} plot is lower for NaDBS as compared to that for the case of TX-100, indicating presence of some inhibiting factor for ionic surfactants. One other significant difference is in the region IV. For NaDBS, the solid phase concentration, 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 and CTAB although there seems to be some decrease in the extent of adsorption.

In region I of low concentrations, as expected NaDBS, CTAB 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 surfactant molecules on the surface (Gaudin and Fuerstenau, 1955). Hemimicellization occurred 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 isotherms of TX-100 and CTAB show that hemimicellar concentration (HMC) is approximately 0.15 mM and 0.4 mM respectively. For NaDBS, there seems to be no sharp difference between regions I & II, and hence, HMC cannot be determined accurately. According to Gao et al. (1987) the average hemimicellar aggregation number n_{hm} is equal to the ratio of the amount of adsorption at the two plateaus, Γ_∞ and Γ_{hm} of the adsorption isotherm.

$$n_{hm} = \frac{\Gamma_\infty}{\Gamma_{hm}} \tag{2}$$

For TX-100 and CTAB adsorption, our measurements indicate the hemimicellar aggregation number to be 5.

In region III, the rate of adsorption becomes smaller both for NaDBS as well as for TX-100. It is believed that in this region either the cluster mode adsorption due to surface micellization (hemimicellization) stops or the rate decreases significantly and adsorption proceeds more or less in a regular way. Anionic NaDBS is adsorbed at slower rate than nonionic TX-100 and cationic CTAB.

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 as impurities. Lower chain surfactants are adsorbed to a less extent on the solid surface than the higher chain surfactants. If we assume a surfactant solution of mixture of different chain length, the CMC of the mixed solution can be calculated using mixed micellar theory (Holland and Rubingh, 1983),

$$\frac{1}{CMC_{Mix}} = \sum_{i=1}^{n} \frac{\alpha_i}{f_i CMC_i} \tag{3}$$

CMC_{Mix} is the CMC of the mixed solution, f_i is the activity coefficient of surfactant i in the mixed micelle, equal to one for ideal system, α_i is the mole fraction of surfactant i in total surfactant.

Above the CMC of the binary mixture ($C_T \geq CMC_{Mix}$) monomer concentration of long chain in the bulk can be written as (Holland and Rubingh, 1983),

$$C_L = y_L CMC_L \tag{4}$$

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

$$y_L = \frac{(\alpha_L C_T - C_L)}{C_T - C_L - C_S} \tag{5}$$

Eliminating C_S from equation 5 we get the concentration of monomer of long chain component above the mixed CMC (Clint, 1975; Nishikido, 1993),

$$C_L = \frac{-(C_T - \Delta) + \left\{(C_T - \Delta)^2 + 4.\alpha_L.C_T.\Delta\right\}^{\frac{1}{2}}}{2\left(\frac{\Delta}{CMC_L}\right)} \tag{6}$$

$$C_L + C_S = CMC_{Mix} \tag{7}$$

where, $\Delta = CMC_S - CMC_L$, C_T is the total surfactant concentration, y_L is the mole fraction of long chain component in mixed micelle. The subscripts L and S represent long and short chain surfactant molecules. Figure-5 shows the plot of C_T vs. C_L, C_S for a binary mixture of surfactants. 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 assuming the solution behave ideally. As micelles are not adsorbed and short chain surfactants are less adsorbed, there will be a decrease in the amount of adsorption. Therefore, we 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 hydrophobic impurities which can not self-assemble (i.e. does not form micelle on its own). In addition, to produce a 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 a sufficient criterion of purity of surface-active agents (Elworthy and Mysels, 1966).

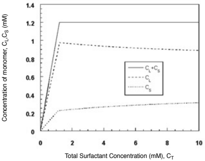

Figure 5 : Plot of total surfactant concentration vs. monomer concentrations, assuming a binary surfactant system forming ideal mixed micelle. $CMC_L = 1$ mM, $CMC_S = 10$ mM, $CMC_{Mix} = 1.2$, $\alpha_L = 0.8$, $\alpha_L + \alpha_S = 1$, $C_L + C_S = CMC_{Mix}$.

Adsorption isotherms of TX-100 and SDS from their mixture on the filter paper surface were carried out to test the effects of bulk mixed micelle formation on adsorption at the solid-liquid interface. In this case, TX-100 and SDS have the different CMCs and both the compounds form micelles individually. No surface tension minimum is observed in the SDS-TX-100 mixed surfactant system. Figures-6 (a) and (b) show the adsorption isotherm of TX-100 and NaDBS from their 80:20 and 70:30 mixtures respectively. In both the cases, TX-100 isotherms show maximum in adsorption nearer to concentration of mixed CMC and SDS isotherms show increasing amount adsorbed above the mixed CMC of the solution.

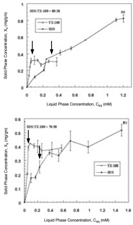

Figure 6 : Adsorption isotherm of (a) SDS and TX-100 from their 80:20 mixture, (b) SDS and TX-100 from their 70:30 mixture on filter paper surface. Arrow indicates the CMC of surfactant in the mixture.

To detect the presence of short chain surfactant molecules, we have conducted high performance liquid chromatographic (HPLC) measurements of NaDBS solution at different concentrations. The chromatograph is presented in Figure-7. One can observe from this figure that there are many peaks, which clearly indicate the presence of surfactant molecules of different chain lengths. Retention times are supposed to be associated with chain length of the surfactant molecules. Based on the retention time vs. percent area data, we have taken the percentage of surfactant molecules having short chain lengths as 20 %.

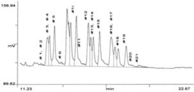

Figure 7 : HPLC chromatograph of NaDBS at 0.5 mM concentration.

Furthermore, HPLC measurements were conducted using solutions 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. It is observed 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 the extent of adsorption beyond CMC is due to the presence of short chain surfactants.

Table 1: Percentage of short and long chain surfactants adsorbed, calculated from HPLC analysis.

NaDBS concentration (mM)	Percentage of short 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

Influence of salt in equilibrium adsorption

Figure-8 shows the adsorption isotherm of NaDBS in presence of KCl and $CaCl_2$. This range of Ca^{++} ion was selected to avoid the precipitation of NaDBS. From Figure-8 we can observe that there occurs a significant increase in adsorption in the presence of even a small amount of Ca^{++} ions. Further, it is observed that the extent of increase is higher for higher amount of Ca^{++} ions present. The extent of adsorption at the maximum is increased by 167 % and 316 % for NaDBS in presence of $CaCl_2$ 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, the nature of curves, particularly the existence of maximum remains intact in the presence of Ca^{++} ions, although there is a shift of the location of the peak to a lower concentration of surfactant at higher Ca^{++} ion concentration.

Following explanations can be offered for this observation in presence of Ca^{++}. In presence of Ca^{++} ions, the negative charge of cellulosic surface gets neutralized partially and as a result, anionic surfactant adsorption gets enhanced. Another reason is negatively charged head group of the surfactant molecules is shielded by the Ca^{++} ions. In addition, the compressed electric double layer at the cellulosic surface shields the charge. Consequent to this charge shielding, the adsorptions of surfactant molecules onto cellulosic surface do 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 CMC, which decreases in presence of $CaCl_2$.

The effect of KCl on the adsorption isotherm of NaDBS is also presented in Figure-8. At lower concentration of KCl (NaDBS: KCl = 1:0.364) there is a negligible enhancement in the extent of adsorption, however, the extent of adsorption is enhanced at higher concentration of KCl (NaDBS: KCl = 1:11.64), and at constant KCl concentration (20mM and 100 mM KCl). Enhancement at KCl concentration of NaDBS: KCl = 1:11.64 matches with the isotherm for the presence of $CaCl_2$ at a concentration, which is 93 times less (NaDBS: $CaCl_2$ = 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. The shifting of adsorption maximum towards lower concentration is due to lowering of CMC when ionic strength is constant.

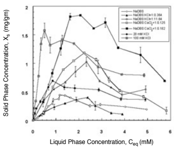

Figure 8 : Adsorption isotherm of NaDBS in presence of KCl and $CaCl_2$ on filter paper surface.

Figure-9 presents the plot on adsorption of TX-100 in presence of KCl and $CaCl_2$. The figure shows 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 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 Ca^{++}, the extent of adsorption of TX-100 should decrease due to strong adsorption of K^+ or Ca^{++} ion with free OH group of cellulose (Nevskaia et al., 1998; 1995). Adsorption of TX-100 molecules appears to occur primarily by the interactions between the hydrophobic site and the hydrophobic group of *the TX-100.*

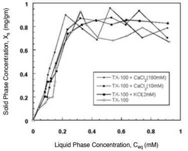

Figure 9 : Adsorption isotherm of TX-100 in presence of $CaCl_2$ and KCl on filter paper surface.

Calculation of polar and non-polar sites on the cellulosic surface from the adsorption data

From the adsorption isotherms we have calculated the area occupied (nm²) by different surfactant molecules on the filter paper surface. The values are calculated using the equation

$$a_{sm} = \frac{M \times S_{BET} \times 10^{21}}{\tilde{A} \times N_A} \qquad (8)$$

where, M is the molecular weight of the surfactant, S_{BET} is the BET surface area of the filter paper in m²/gm, Γ is the amount of surfactant adsorbed in mg/gm, a_{sm} is mean area occupied per molecule in nm² and N_A is the Avogadro's number. Based on the observations presented earlier, we expect the filter paper surface to consist both negatively

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

Molecule	Area occupied per molecule (nm²/molecule)
NaDBS	20.0
TX-100	19.2
NaDBS + Ca^{++} (1 : 0.182)	5.3
NaDBS + Ca^{++} + K^+ (1 : 0.182 : 11.64)	5.1
NaDBS + KCl (100mM)	6.0
CTAB	4.4
Methylene Blue	7.5

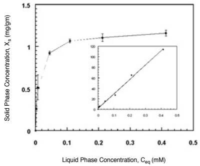

Figure 10 : Adsorption isotherm of methylene blue. The inset shows the plot of $\frac{C_{eq}}{n}$. vs. C_{eq}, where n is the number of moles of methylene blue adsorbed per gram of filter paper.

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 area occupied by a molecule of NaDBS and a molecule TX-100 are nearly 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.

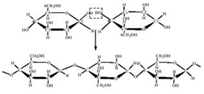

Figure 11 : Structure of cellulose (Dorée, 1950).

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 on to the negatively charged sites. Figure-10 presents the adsorption isotherm. We observe from this figure that unlike the four regime adsorption isotherms of NaDBS, CTAB and TX-100, methylene blue gives a Langmuir type of isotherm. This is expected as both hemimicellization and micellizations are absent in such system. The possibility of hydrophilic and hydrophobic site can be seen from the structure of cellulose molecule also. The negatively charged hydrophilic sites on the cellulose surface is mainly due to presence of hydroxyl groups and the hydrophobic sites is due to the carbon atoms in the cellulose structure. The structure of cellulose is shown in Figure-11.

Referring back to Table-2, we note that, the area occupied by a molecule for anionic surfactant in presence of electrolytes, and the area occupied by a cationic surfactant, CTAB are nearly equal to 5 nm². The area occupied by a molecule of methylene blue 7.5 nm², 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 site only and NaDBS in presence of electrolyte and CTAB adsorb onto both hydrophobic and negatively charged site. Let us further assume that f is fraction of area occupied by the hydrophobic sites. The area occupied by one molecule as calculated assuming that adsorption occurs on the entire area is, $a_{sm} = 5$ nm². The area occupied by one molecule, as calculated assuming that adsorption occurs on the area consisting of hydrophobic sites only is, $a_{smh} = 20$ nm². The number of molecules adsorbed on unit area in case of adsorption on hydrophobic sites is $\frac{1}{a_{smh}}$, which is also equal to $\frac{f}{a_{sm}}$. Hence, f the fraction of area occupied by hydrophobic sites is equal $\frac{a_{sm}}{a_{smh}}$ =0.25. When adsorption occurs only in the area containing negatively charged sites, it can easily shown that the area occupied by a molecule will be $\left(\frac{a_{sm}}{1-f}\right) = \frac{5}{0.75} = 7$ nm². This value of 7 nm² agrees well with the calculation of 7.5 nm² as shown in Table-2. Hence it can be concluded that the filter paper surface consists of approximately 25 % hydrophobic sites and 75 % negatively charged sites.

Detergency

Detergency is a complex process due to the interplay of a large number of parameters relating the nature of textile, the nature of soil, and types of components present in the detergent. Surfactant adsorption is considered an important step in the process of detergency. Therefore in this study we have made some attempts to determine the dependency of detergency on surfactant adsorption.

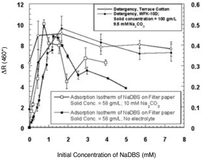

Figure 12 : Relation between adsorption isotherm of NaDBS on cellulose-water interface and detergency of terrace and WFK-10D.

Influence of surfactant adsorption in detergency

The adsorption isotherm of NaDBS shows a maximum at the CMC and beyond the CMC it shows decrease in extent of adsorption. Detergency experiment was carried out with NaDBS to find the correlation with adsorption. Figure-12 shows the plot of ΔR with varying NaDBS concentration using two different types of soiled cotton, terrace and WFK-10D. Figure-12 also presents the adsorption isotherms of NaDBS onto filter paper with and without Na_2CO_3. Adsorbent concentration was used 100 gm/lit and 9.5 mM Na_2CO_3 was used to maintain alkaline pH (pH = 10-11). We observe from Figure-12 that the detergency, in general, increases with increase in adsorption of surfactants. Interestingly, we further observe from the Figure-12 that in both the cases of soiled cottons the maximum in detergency occur virtually at the same concentration at which the maximum in adsorption occur. It can be noted here that, in general, a maximum in detergency may occur, in a binary mixtures of surfactants of different CMC. The commercial detergents in general, contain mixture of different surfactants to improve the efficiency of the detergent. Improvement in detergency may result from the enhancement in adsorption. It should be further noted that maximum adsorption occurs at a particular concentration and this concentration can be taken as the optimum concentration of surfactant in detergent mixture.

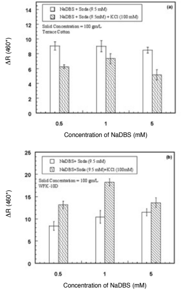

Figure 13 : (a) Effect of ionic strength in detergency of NaDBS, terrace cotton. (b) Effect of ionic strength in detergency of NaDBS, WFK-10D cotton.

Influence of electrolyte in detergency

Adsorption isotherm of NaDBS in presence of KCl shows the extent of adsorption of NaDBS enhanced 275% in presence of 100 mM KCl. The reason for enhancement is the negative charge of the surfactant molecules is shielded by the Na^+ ions. In addition, the compressed electric double layer at the cellulosic surface results in shielding the charge on the surface. Consequent to this charge shielding, the adsorption of surfactant molecules onto cellulosic surface does not experience any inhibition arising out of electrical repulsion. It is expected that detergency may be enhanced in presence of electrolyte. Figures-13 (a) & (b) show the detergency of terrace and WFK-10D cotton with and without the presence of 100 mM KCl respectively at pH 10 – 11. The pH was maintained by adding 9.5 mM Na_2CO_3. Figure-13 presents an interesting observation. From the figures we observe that the detergency of terrace cotton decreases in presence of KCl. The detergency, however, increases for WFK-10D cotton. The explanation for the observed decrease in detergency in terrace cotton can be attributed to the decrease of electrical double layer force that inhibits soil removal. The addition of an electrolyte causes a decrease of the repulsive force between the soil and substrate, and as a result removal of particulate soil becomes difficult, although adsorption of surfactant is enhanced on both the soil and fabric surface. Furthermore, it is reported that deposition of particle, suspended in a moving phase, on to a surface increases dramatically with ionic strength (Marshall and Kitchener, 1966; Hull and Kitchener, 1969; Clint et al., 1973) and the removal of particle decreases (Sharma et al., 1992), resulting in decrease in detergency.

Detergency with WFK-10D cotton is found to increase with increasing electrolyte concentration. For the case of composite soil such as WFK-10D not only electrical double layer but also surfactant adsorption plays an important role. In the composite soil, particulate is hydrophobic in nature and contains oil. Hence, for the removal of composite soil, enhancement of surfactant adsorption plays an important role in wetting of fiber and soil leading enhancement in detergency.

CONCLUSIONS

Following conclusions emerge from this work.

1. Equilibrium adsorption isotherms of NaDBS, CTAB and TX-100 show a typical four-region isotherm. The presence of maximum in region IV can be attributed to the presence of shorter chain surfactant molecules. CTAB and TX-100 molecules show hemimicelle formation while NaDBS molecules do not form hemimicelles.
2. Adsorption of cationic molecules, CTAB and methylene blue is strong, indicating that the charged sites on filter paper surface is negative and they dominate over the smaller number of hydrophobic sites. Estimation shows that approximately 25 % sites are hydrophobic in nature and the rest 75 % sites are negatively charged sites.

3. Estimated area per molecule on the filter paper surface from the adsorption isotherm data indicate that methylene blue molecules adsorb densely on the anionic sites of filter paper. NaDBS molecules do so only in presence of Ca^{++} and K^{+}. NaDBS and TX-100 molecules adsorb on the hydrophobic sites and CTAB molecules adsorb on both hydrophilic and hydrophobic sites.
4. Terrace and WFK-10D soils show maximum detergency with NaDBS at alkaline pH nearer to CMC. This maximum in detergency is very similar to maximum in adsorption on cellulose-water interface due to presence of short chain surfactant impurity.
5. The effects of electrolyte are different for the two types of soil. It adversely affects the detergency of terrace cotton, while it promotes the detergency of WFK-10D.

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REFERENCE

Arnebrant, T.; Backstrom, K.; Jonsson, B. and Nylander, T. (1989). An Ellipsometry Study of Ionic Surfactant Adsorption on Chromium Surfaces, J. Colloid Interface Sci. 128, 303 – 312.

ASTM D1681-59T. (1959). Synthetic Anionic Active Ingredient in Detergents by Cationic Titration Procedure, Part-10, p-276.

Batra, A.; Paria, S.; Manohar, C. and Khilar, K. C. (2001). Removal of Surface Adhered Particles by Surfactants and Fluid Motions, AIChE J. 47, 2557-2565.

Bacon, O. C. and Smith, J. E. (1948). Detergent Action – Mechanical Work as a Measure of Efficiency of Surface Active Agents in Removing Soil, Ind. Eng. Chem. 40, 2361 - 2370.

Biswas, S. C. and Chattoraj, D. K. (1997). Kinetics of Adsorption of Cationic Surfactants at Silica-Water Interface, Langmuir 13, 4505 – 4511.

Brinck, J.; Jönsson, B. and Tiberg, F. (1998). Kinetics of Nonionic Surfactant Adsorption and Desorption at the Silica-Water Interface: One Component, Langmuir 14, 1058 – 1071.

Clint, G. E.; Clint, J. H.; Corkill, J. M. and Walker, T. (1973). Deposition of Latex Particles onto a Planer Surface, J. Colloid Interface Sci. 44, 121 – 131.

Clint, J. H. (1975). Micellization of Mixed Nonionic Surface Active Agents, J. Chem. Soc. 71, 1327 – 1334.

Cross, A. W. and Jayson, G. G. (1994). The Effect of Small Quantities of Calcium on the Adsorption of Sodium Dodecyl Sulfate and Calcium at the Gas-Liquid Interface, J. Colloid Interface Sci. 162, 45 – 51.

Desai, T. R. and Dixit, S. G. (1996). Coadsorption of Cationic-Nonionic Surfactant Mixtures on PolytetraFluoroethylene (PTFE) Surface, J. Colloid Interface Sci. 179, 544 – 551.

Elworthy, P. H. and Mysels, K. J. (1966). The Surface Tension of Sodium Dodecylsulfate Solutions and the Phase Separation Model of Micelle Formation, J. Colloid Interface Sci. 21, 331 – 347.

Evans, H. C. (1958). Fiber Swelling and Detergent Adsorption in Detergent/Textile Fiber Systems, J. Colloid Sci. 13 537 – 552.

Fava, A. and Eyring, H. (1956). Equilibrium and Kinetics of Detergent Adsorption – A Generalized Equilibration Theory, J. Phy. Chem. 60, 890 – 898.

Furst, E. M.; Pagac, E. S. and Tilton, R. D. (1996). Coadsorption of Polylysine and the Cationic Surfactant Cetyltrimethylammonium Bromide on Silica, Ind. Eng. Chem. Res. 35, 1566 – 1574.

Chander, S.; Fuerstenau, D. W. and Stigter, D. (1983). Adsorption from Solution, Ottewill, R. H., Rochester C. H. and Smith, A. L. eds., Academic Press, New York, 197.

Gao, Y.; Du, J. and Gu, T. (1987). Hemimicelle Formation of Cationic Surfactants at the Silica Gel-Water Interface, J. Chem. Soc. Faraday Trans-1 83, 2671 – 2679.

Gaudin, A. M. and Fuerstenau, D. W. (1955). Quartz Flotation with Cationic Collectors, Trans. AIME 202, 958 – 962.

Ginn, M.E.; Kinney, F. B. and Harris, J. C. (1961). Effect of Cotton Substrate Characteristics upon Surfactant Adsorption, J. Am. Oil Chem. Soc. 38, 138 – 143.

Gu, T.; Gao, Y. and He, L. (1988). Hemimicelle formation of Cationic Surfactants at the Silica Gel-Water Interface, J. Chem. Soc. Faraday Trans-1 84, 4471 – 4473.

Harwell, J. H. and Scamehorn, J. F. (1993). Mixed Surfactant Systems, Onigo, K. and Abe, M. eds., Marcel Dekker, New York, Chapter-9.

Harwell, J. H.; Roberts, B. L. and Scamehorn, J. F. (1988). Thermodynamics of Adsorption of Surfactant Mixtures on Minerals, Colloids Surf. 32, 1 – 17.

Hart, W. J. and Compton, J. (1952). Soiling and Soil Retention in Textile Fibers, Ind. Eng. Chem. 44, 1135- 1141.

Holland, P. M. and Rubingh, D. (1983). N. Nonideal Multicomponent Mixed Micelle Model, J. Phy. Chem. 87, 1984 – 1990.

Hull, M. and Kitchener, J. A. (1969). Interaction of Spherical Colloidal Particles with Planer Surfaces, Trans. Faraday Soc. 65, 3093 – 3104.

Kissa, E. (1975). Kinetics and Mechanism of Detergency. Part-I: Liquid Hydrophobic (Oily) Soils, Textile Res. J. 45, 736 – 741.

Kissa, E. (1978). Kinetics and Mechanism of Detergency. Part-II: Particulate Soil, Textile Res. J. 48, 395 – 399.

Kissa, E. (1979). Kinetics and Mechanism of Detergency. Part-III: Effect of Soiling Conditions on Particulate Soil Detergency, Textile Res. J. 49, 384 – 389.

Kissa, E. (1987). Detergency: Theory and Technology, Cutler, W. G. and Kissa, E. eds., Marcel dekker, New York.

Koopal, L. K.; Lee, E. M. and Bohmer, M. R. (1995).

Adsorption of Cationic and Anionic Surfactants on Charged Metal Oxide Surfaces, J. Colloid Interface Sci. 170, 85 – 97.

Lopata, J. J.; Harwell, J. H. and Scamehorn, J. F. (1988). ACS Symposium Series 373, American Chemical Society, Washington D. C., Chapter-10.

Manne, S.; Cleveland, J. P.; Gaub, H. E.; Stucky, G. D. and Hansama, P. K. (1994). Direct Visualization of Surfactant Hemimicelles by Force Microscopy of the Electrical Double Layer, Langmuir 10, 4409 – 4413.

Meader, A. L. and Fries, B. (1952). Adsorption in the Detergent Process, Ind. Eng. Chem. 44, 1636 – 1648.

Morris, M. A. and Prato, H. H. (1982). The Effect of Wash Temperature on Removal of Particulate and Oily Soil from Fabrics of Varying Fiber Content, Textile Res. J. 52, 280 – 286.

Nevskaia, D. M.; Guerrero-Ruíz, A. and López-González, J. de D. (1998). Adsorption of Polyoxyethylenic Nonionic and Anionic Surfactants from Aqueous Solution: Effects Induced by the Addition of NaCl and $CaCl_2$, J. Colloid Interface Sci. 205, 97 – 105.

Nevskaia, D. M.; Cervantes, M. L. R.; Ruíz, A. G. and López-González, J. de D. (1995). Interaction of TX-100 on Silica: a Relationship between Surface Characteristics and Adsorption Isotherms, J. Chem. Tech. Biotechnol. 63, 249 – 256.

Nishikido, M. (1993). Mixed Surfactant Systems, Ogino, K. and Abe, M. eds., Marcel Dekker, New York, Chapter-2.

Pagac, E. S.; Prieve, D. C. and Tilton, R. D. (1998). Kinetics and Mechanism of Cationic Surfactant Adsorption and Coadsorption with Cationic Polyelectrolytes at the Silica-Water Interface, Langmuir 14, 2333 – 2342.

Rosen, M. J. (1978). Surfactants and Interfacial Phenomena, Wiley-Interscience Publication, New York, Chapter-10.

Rosen, M. J. and Goldsmith, H. A. (1972). Systematic Analysis of Surface-Active Agents, Wiley-Interscience Publication, New York, Chapter-V.

Ruckenstein, E. and Prive, D. C. (1976). Adsorption and Desorption of Particles and Their Chromatographic Seperation, AIChE J. 22, 276 – 283.

Scamehorn, J. F.; Schechter, R. S. and Wade, W. H. (1982a). Adsorption of Surfactants on Mineral Oxide Surfaces from Aqueous Solutions. I. Isomerically Pure Anionic Surfactants, J. Colloid Interface Sci. 85, 463 – 478.

Scamehorn, J. F.; Schechter, R. S. and Wade, W. H. (1982b). Adsorption of Surfactants on Mineral Oxide Surfaces from Aqueous Solutions. II. Binary Mixture of Anionic Surfactants, J. Colloid Interface Sci. 85, 479 – 493.

Scott, B. A. (1963). Mechanism of Fatty Soil Removal, J. Appl. Chem. 13, 133 – 144.

Schott, H. (1975). A Kinetic Study of Fabric Detergency, J. Am. Oil Chem. Soc. 52, 225 – 229.

Schott, H. (1976). Limitation in Studying the Kinetics of Fabric Detergency, Textile Res. J. 46, 459 – 462.

Sexsmith, F. H. and White, H. J. (1959a). The Absorption of Cationic Surfactants by Cellulosic Materials I. The Uptake of Cation and Anion by a Variety of Substrates, J. Colloid Sci. 14, 598 – 618.

Sexsmith, F. H. and White, H. J. (1959b). The Absorption of Cationic Surfactants by Cellulosic Materials. III. A Theoretical Model for the Absorption Process and Discussion of Maxima in Absorption Isotherms for Surfactants, J. Colloid Sci. 14, 630 – 639.

Sharma, M. M.; Chamoun, H.; Sarma, D. S. H. S. R. and Schechter, R. S. (1992). Factors Controlling the Hydrodynamic Detachment of Particles from Surfaces, J. Colloid Interface Sci. 149, 121 –134.

Somasundaran, P. and Fuerstenau, D. W. (1966). Mechanisms of Alkyl Sulfonate Adsorption at the Alumina-Water Interface, J. Phy. Chem. 70, 90 – 96.

Somasundaran, P.; Healy, T. W. and Fuerstenau, D. W. (1964). Surfactant Adsorption at the Solid-Liquid Interface-Dependence of Mechanism on Chain Length, J. Phy. Chem. 68, 3562 – 3566.

Trogus, F. J.; Schechter, R. S. and Wade, W. H. (1978). A New Interpretation of Adsorption Maxima and Minima, J. Colloid Interface Sci. 70, 293 – 305.

Vaughn, T. H.; Vittine, A. and Bacon, L. R. (1941). Detergent Action of the System Modified Soda-Soap Water, Ind. Eng. Chem. 33, 1011 – 1019.

Vold, R. D. and Sivaramakrishnan, N. H. (1958). The Origin of the Maximum in the Adsorption Isotherms of Association Colloids, J. Phy. Chem. 62, 984 – 989.

Wang, W. and Kwak, J. C. T. (1999). Adsorption at the Alumina-Water Interface from Mixed Surfactant Solutions, Colloids Surf. A 156, 95 – 110.

Yoneyama, Y. and Ogino, K. (1982). The Behavior of Carbon Black in a Detergent Solution, Bull. Chem. Soc. Jpn. 55, 3079 – 3084.