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An Electrokinetic Study of the Adsorption of Dodecyl Ammonium Amine Surfactants at the Muscovite Mica–Water Interface

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The adsorption of dodecyl single chain surfactants with primary, secondary, tertiary, and quaternary ammonium headgroups at the muscovite mica basal plane–water interface has been investigated using a flat plate streaming potential apparatus and atomic force microscopy (AFM). Both a hemi-micelle concentration (HMC) and a point of zeta potential reversal (PZR) were observed as the surfactant adsorbed at the muscovite mica–water interface. The HMC and PZR were shifted to higher surfactant concentration as the headgroup was changed from the primary to the quaternary ammonium group. AFM images of surfactant patches adsorbed at the mica–water interface indicate that the surfactant patch size becomes smaller and distributes more uniformly with change from the primary to quaternary ammonium headgroups. The hydrophobic force contribution of the hydrocarbon chain to the adsorption of the C₁₂ surfactant, estimated by subtracting other contributions from the total adsorption free energy, was calculated to decrease as the headgroup was changed from the primary to the quaternary amine.

Introduction

The adsorption of ionic surfactants at the solid–solution interface has been extensively investigated and the technological importance of the area is unquestioned. A large proportion of the work has examined the effects of hydrocarbon chain length,^{1–6} the effect of aromatic groups,^{7,8} the affinity of the surfactant for the solid–liquid interface^{4,8–12} and the variation in electrical double layer properties of the interface as affected by electrolyte concentration and/or pH.^{13–19} However, the role of the geometry of a surfactant molecule in the adsorption process

has only been sparsely examined although it is well accepted that adsorption will be highly sensitive to the type of molecule. The lack of quantitative studies of surfactant headgroup geometry is due to a difficulty in defining the exact role of the headgroup in the adsorption process. This is because adsorption simultaneously involves a variety of physical and chemical contributions which cannot be easily separated.²⁰ Because of this, an understanding of the role of the headgroup of a surfactant in the adsorption process has focused on chemical interactions, for instance, xanthate on sulfides^{21–24} and oleate on oxides and salt-type minerals.^{25–35}

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Ottewill and Rastogi³⁶ attempted to explain the effect of headgroup size in the adsorption of surfactants with cationic headgroups such as ammonium, tri-methylammonium, pyridinium, and quinolinium by examining the adsorption of these surfactants onto negatively charged AgI. Keizer and Lyklema³⁷ investigated the adsorption of tetra-alkylammonium ions onto AgI sols as a function of the number of CH₂ groups in the alkyl chain. The common observation between these works was that the point of zeta potential (ζ) reversal or PZR shifted to higher concentration with an increase in the headgroup size or length of the hydrocarbon chain. Therefore, the hydrophobic interaction between headgroups and the AgI surface was assumed to dominate the adsorption process with an increase in the size of the headgroup. On this basis, extraction of quantitative information as to the effect of headgroup geometry was deemed too complicated. Smith³⁸ investigated the effect of dodecyl primary, secondary, tertiary, and quaternary ammonium chlorides on flotation response and discussed the pH-response of flotation and air–water contact angles in relation to the solubility and ionization of the amine surfactants in bulk aqueous solution. However, very few studies on the effect of the variation in the headgroup of a surfactant on the adsorption to hydrophilic surfaces have been presented.

In this study, we report the effect of the geometry of the headgroup of molecules on the adsorption of surfactants at the muscovite mica basal plane–water interface. The mica basal plane can be regarded as a hydrophilic oxide surface in aqueous electrolyte solutions and the mica basal plane–cationic surfactant system has been utilized in a number of surface force apparatus investigations. Most of the surface force work was directed at understanding the long-range attractive interaction between surfactant coated surfaces.^{39–45} The latter area of study is made viable by the atomically smooth nature of the cleaved muscovite mica surface.

Experimental Section

Materials. Sheets of mica used in this study were green muscovite mica (Mica Supplies Ltd., England) and were kindly supplied by Dr. P. Kekicheff, formerly of the Australian National University. All chemicals and electrolytes were analytical grade. Water used in all experiments was prepared in a Milli-Q system. The final conductivity of the water was less than $1 \times 10^{-6} \text{ S cm}^{-1}$. KBr was used as background electrolyte.

Dodecylamine hydrobromide (DAB), dodecylmethylamine hydrobromide (DMAB), dodecyl dimethylamine hydrobromide (DDMAB), and dodecyltrimethylammonium bromide (DTAB) were used. DAB, DMAB, DDMAB, and DTAB were obtained from the Aldrich Chemical Co., the K&K laboratory Division of ICN Biomedicals Inc., Tokyo Kasei Kogyo, and Eastman Kodak, respectively. The amines other than DTAB were prepared and purified as follows. The surfactants were dissolved in acetone

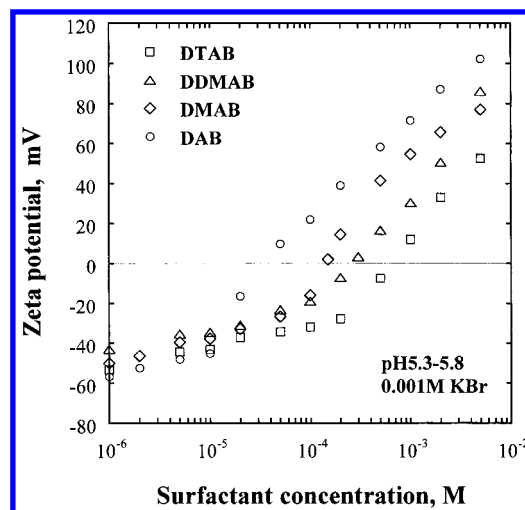


Figure 1. Zeta potentials of muscovite mica as a function of the concentration of single dodecyl chain surfactants with primary, secondary, tertiary, and quaternary ammonium headgroups in the presence of 0.001 M KBr at pH 5.3–5.8.

and then amine hydrobromides were precipitated by adding an equivalent molar mass of hydrobromic acid. After filtering and drying, the precipitated amine hydrobromides were recrystallized 3–4 times from a mixture of acetone and ethanol. DTAB was also recrystallized in the same manner as the other surfactants. They were freeze-dried after filtering and stored in a desiccator. Chemical analysis showed high purity of all these surfactants.

Methods. Electrokinetic measurements were conducted using a flat plate streaming potential apparatus⁴⁶ at a temperature of 25 °C. A rectangular capillary was formed between two mica sheets separated by a Teflon gasket. Streaming potentials were recorded for flow in both directions and the zeta potential (ζ) was calculated using the Helmholtz–Smoluchowski equation.⁴⁷ Mica sheets were glued to glass microscope slides with a low melting point (80 °C) inert wax (Shell-Epicote Resin 1002). The mica was cleaved to produce a fresh surface prior to each streaming potential measurement.

Critical micelle concentrations (cmc) for each of the surfactants were estimated by the DuNouy ring method using a platinum ring at a temperature of 25 °C, without background electrolyte.

Imaging of the surfactants on the mica surface was performed using an Atomic Force Microscope (Digital Instruments, NanoScope III). At low concentrations, the surfaces were imaged with a very low force in contact mode. Double layer imaging was not employed due to a weak repulsion, or at some points, weak attraction between the surface/surfactant layer and the tip. The resolution for contact imaging for adsorbed surfactants is poor but surfactant coated areas of the mica could still be clearly defined.

Results

The zeta potential of mica as a function of surfactant concentration in the presence of 0.001M KBr as background electrolyte at pH 5.3–5.8 is shown in Figure 1. In each ζ curve, a reduction in the magnitude of ζ clearly occurs at a critical concentration which is referred to as the hemi-micelle concentration (HMC) and ζ becomes zero at a concentration defined as the point of ζ reversal or PZR. For surfactant concentrations greater than the PZR, ζ is reversed in sign. The HMC and PZR are uniformly shifted to higher concentrations in the order DAB, DMAB, DDMAB, and DTAB (i.e., as the headgroup size and hydrophobicity is increased). It should be noted at this point that the pK_a of the surfactants with primary to tertiary headgroups ranges from 9.7 to 11.0³⁸ and DTAB does not yield a neutral amine.⁵⁰ On this basis, the presence

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and coadsorption of neutral amine molecules can be ignored in this pH 5.3–5.8 study.

A number of force studies showing the PZR of amine surfactants are reported in the literature and a comparison to the work of Herder⁴³ on DAC (dodecylamine hydrochloride) to the present work for DAB is appropriate. The PZR for DAB on mica is observed to be at a higher concentration than DAC. The bromide ion is more strongly bound to the ammonium headgroup than chloride⁵¹ suggesting that the PZR of a surfactant with a counterion more strongly bound to a headgroup should shift to higher concentrations.

Counterion binding studies of the higher order amines in micelles^{52,53} shows that the counterion of the quaternary ammonium headgroup is less bound than its primary ammonium equivalent under common conditions. However, the ζ data presented in Figure 1 shows DTAB to have a PZR of higher concentration than DAB. This indicates that the effect of counterion binding is not sufficient to explain the trends in the data with surfactant headgroup observed in Figure 1.

Ottewill and Rastogi³⁶ examined the adsorption of surfactants with ammonium, tri-methylammonium, pyridinium, and quinolinium headgroups onto AgI. It was observed that the PZR for these surfactants shifted to higher concentration on decreasing the size of the headgroup. For example, the PZR of DTAB occurred at a concentration of 10^{-5} mol dm⁻³ whereas the PZR for DAC was 10^{-4} mol dm⁻³. It is interesting to note that their results show the complete opposite trend in the effect of headgroup to that shown in the present study. The observation reflects a significant difference in the affinity of these same surfactants for AgI and mica.

In the case of hydrophobic AgI sols, the removal of hydrocarbon chains of the surfactant from solution into the hydrophobic surface region may dominate the adsorption, as distinct from the hydrophobic association of hydrocarbon chains on the interface, especially in the initial stages of adsorption (i.e., at concentrations between the HMC and the PZR). It is expected that the surfactant will adopt a horizontal orientation at these concentrations.⁵⁴ Under such conditions, DTAB adsorption would be favored relative to DAB since DTAB has a more hydrophobic headgroup. On the other hand, hydrophobic interactions between the mica surface and hydrophobic moiety of the surfactant (the CH₃ groups of the headgroup and/or a long hydrocarbon chain) could be neglected since highly charged layer silicate minerals such as mica are unlikely to favor such interaction. In this instance, adsorption of ionic surfactants should be well defined by Coulombic and lateral hydrophobic interactions. In this respect, the mica–water interface can be regarded as an ideal system in which to quantify the contributions of the headgroup to adsorption without the complication of the interaction of the hydrocarbon component of the molecule with the surface.

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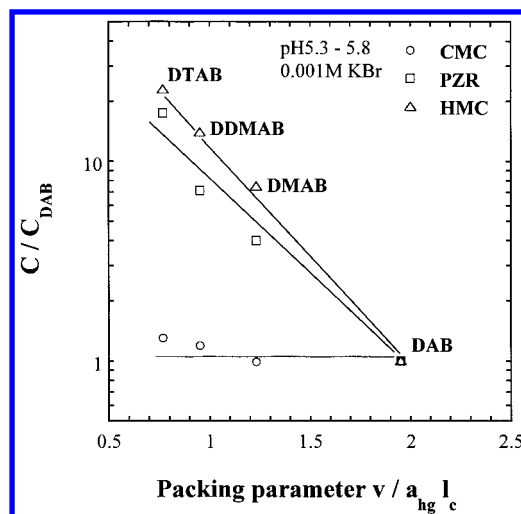


Figure 2. Critical micelle concentration (cmc), hemi-micelle concentration (HMC), and point of zeta potential reversal (PZR) as a function of the geometric packing parameter at pH 5.3–5.8. Each value has been normalized to the DAB case.

Table 1. The CMC and Effective Head Group Radius of the Amine Surfactants used in This Work

surfactant	cmc $\times 10^2$, M	head group radius, Å
dodecyl amine hydrobromide (DAB)	1.12	1.85
dodecyl methylamine hydrobromide (DMAB)	1.10	2.33
dodecyl dimethylamine hydrobromide (DDMAB)	1.34	2.65
dodecyl trimethylammonium bromide (DTAB)	1.46	2.95

^a The cmc's shown in Table 1 compare well to the values presented in a previous study.⁵¹ The effective radius of the asymmetric headgroups of DMAB and DDMAB were estimated from the known value for the radius of DAB and DTAB⁵² and the volume ratio of headgroups between DMAB (or DDMAB) and DAB (or DTAB). The headgroup volumes were calculated using a molecular modeling program.

In Figure 2 the cmc, PZR, and HMC are plotted against the geometric packing parameter of each of the surfactants. The values are normalized to the DAB case. The geometric packing parameter was introduced by Israelachvili et al. to argue the expected self-assembly structures of hydrocarbon amphiphiles based on both geometric and free energy constraints.^{55,56} They postulated that this geometric parameter was a suitable predictor for the expected type of self-assembly structure for amphiphilic molecules in bulk solution. The parameter is defined as $v/a_{hg} l_c$, where v is the volume of hydrocarbon chain of the surfactant, l_c is the optimum chain length corresponding to the fully extended molecular length of the hydrocarbon, and a_{hg} is the optimum headgroup area. This latter parameter was calculated in this study using the value of the effective headgroup radius presented in Table 1.

A marked dependence of both the PZR and HMC is observed (see Figure 2) on the packing parameter while a cmc dependence is absent. This implies that the driving force for self-assembly to produce a micelle could be different from that to produce adsorption layers at the solid–liquid interface. Tanford⁵⁷ discussed the dependence

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of micelle aggregation number and the value of the cmc on salt concentration between DAC and DTAC according to the results presented by Kushner et al.⁵⁸ and Emerson et al.⁵⁹ The aggregation number for DAC increased significantly with increasing salt concentration where little response was observed for DTAB. The cmc's of the two molecules also showed a slight salt dependence in the concentration regime of interest.

Geer⁵³ reported a decrease in aggregation number of micelles with a change from the primary to quaternary ammonium headgroup. It was concluded on this basis that even a small variation in the headgroup structure affects the size and structure of micelles whereas the cmc is relatively insensitive to such changes. This observation is also supported by the difference in shape of micelles between DAC and DTAC presented by Debye et al.⁶⁰ and Anacker,⁶¹ where DAC forms prolate ellipsoidal micelles and DTAC micelles are spherical. The cmc of these two surfactants is similar. The result in Figure 2 reflects the fact that the adsorption of surfactants at the solid–liquid interface is best reflected as a two-dimensional micellar aggregate structure.

Discussion

The adsorption of ionic surfactants at the solid–water interface has been intensively discussed in terms of the Stern–Graham(SG) style of isotherm,²⁰ such that

$$\Gamma = 2rC \exp\left(\frac{-\Delta G_{\text{ads}}^0}{kT}\right) \quad (1)$$

where Γ is adsorption density, r is the ionic radius of the headgroup, C is the equilibrium concentration and ΔG_{ads}^0 is the free energy of adsorption. This type of isotherm is appropriate for extremely low coverage of surfactant or comparison between different surfactants at identical, preferably low, coverage. Within these limitations, eq 1 provides at best, a semiquantitative description of the adsorption mechanism. Somasundaran et al.^{3,54} divided the adsorption free energy, ΔG_{ads}^0 , into a number of separate contributions

$$\Delta G_{\text{ads}}^0 = ze\Psi_i + n_{\text{eff}}\theta_{\text{cc}} + \theta_{\text{hg}} \quad (2)$$

where $ze\Psi_i$ is a Coulombic interaction term including z , the valency of the headgroup, e , the electronic charge, and Ψ_i , the potential at the inner Helmholtz plane. $n_{\text{eff}}\theta_{\text{cc}}$ is a hydrophobic interaction term which consists of the effective number, n_{eff} , of CH_2 groups removed from water into the adsorbed layer or structure and a contribution of each of the CH_2 groups, θ_{cc} . θ_{hg} is the contribution of the headgroup. The contribution of the headgroup to the hydrophobic interaction term in the adsorption energy is neglected in the case of a hydrophilic surface like mica in aqueous electrolyte solution where the electrostatic contribution is expected to be the most significant parameter.

The Coulombic energy was calculated assuming $\Psi_i \approx \zeta$ at the HMC and neglected at the PZR. The approximation of $\Psi_i \approx \zeta$ almost certainly underestimates the magnitude of Ψ_i but the trends in the data are unlikely to be altered. To calculate a value of ΔG_{ads}^0 , the adsorption density was first estimated using atomic force microscopy data (AFM).

Table 2. Values of the Adsorption Density of each of the Surfactants at the HMC and PZR Estimated from AFM Data^a

surfactant	HMC (mol cm ⁻²) × 10 ¹¹	PZR (mol cm ⁻²) × 10 ¹¹
dodecylamine hydrobromide (DAB)	1.6	29.9
dodecylmethylamine hydrobromide (DMAB)	2.7	28.1
dodecyltrimethylamine hydrobromide (DDMAB)	3.2	27.8
dodecyl trimethylammonium bromide (DTAB)	4.7	27.5

^a The data are for 0.001 M KBr background electrolyte at pH 5.3–5.8.

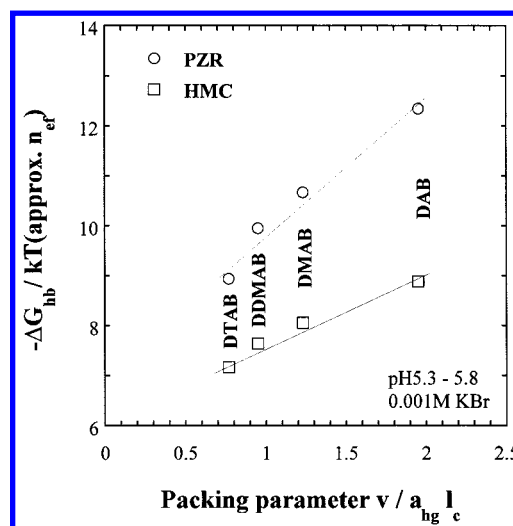


Figure 3. Lateral hydrophobic interaction energy normalized by kT ($\Delta G_{\text{hb}}^0 = n_{\text{eff}}\theta_{\text{cc}}/kT$) as a function of the geometric packing parameter at pH 5.3–5.8.

The details of the AFM imaging of mica in surfactant solutions are published elsewhere.⁶² Briefly, to obtain an adsorption density, the surface area of mica covered with surfactants was calculated using image-analysis. The area covered by surfactant could be clearly distinguished from the bare mica surface. Table 2 shows the adsorption density values for the surfactants utilized in this work at both the HMC and PZR. The adsorption density at the HMC was in the order DTAB > DMAB > DDMAB > DAB. The adsorption density at the PZR was similar in each case. Although the values at the PZR (shown in Table 2) are slightly lower than the value expected from complete neutralization of the lattice charge of mica, the value for DAB is in reasonable agreement with that for DAC obtained from an ESCA study.⁶³ The discrepancy is most probably due to competitive adsorption of K^+ and in particular, H^+ ions onto the lattice charge which reduces the lattice charge available for surfactant adsorption.

Figure 3 shows the lateral hydrophobic interaction energy ($\Delta G_{\text{hb}}^0 = n_{\text{eff}}\theta_{\text{cc}}$) as a function of the packing parameter. The value of ΔG_{hb}^0 is normalized by kT . The magnitude of ΔG_{hb}^0 is calculated to be significantly larger at the PZR relative to the HMC. Since only minor surfactant association is expected at the HMC, the trend seems reasonable. However, it is of greater interest to note that the magnitude of ΔG_{hb}^0 increases with an increase in the packing parameter (or decrease in the

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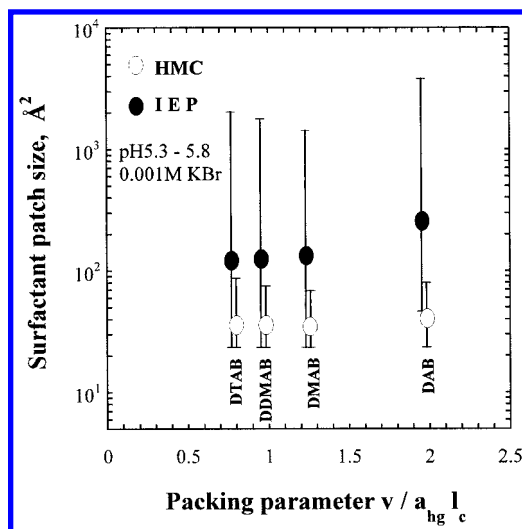


Figure 4. Average patch size of each of the cationic surfactants adsorbed at the mica-water interface as a function of the geometric packing parameter at pH 5.3–5.8.

headgroup size) at the PZR. The adsorption density is similar for all surfactants at this reference point.

Previous work on the adsorption of ionic surfactants onto hydrophilic oxide surfaces suggests that θ_{cc} should have a value in the range from 0.7 to 1.0 kT .^{64,65} Accordingly, the change in the $-\Delta G_{hb}^0/kT$ values shown in Figure 3 correspond to changes in n_{eff} , the effective number of CH_2 groups per molecule removed from water into a more hydrophobic environment within the interface. The value of n_{eff} also increases with an increase in the packing parameter. For example, in the DAB case at the PZR, the value of n_{eff} was approximately 12 but in the DTAB case, a value of less than 9 is calculated. This suggests the entire hydrocarbon chain of DAB is surrounded by other surfactant molecules and that aggregation in the adsorbed layer is more extensive as the packing parameter increases (i.e., as the headgroup size decreases).

The average patch size of the surfactants adsorbed at the mica–water interface as a function of the packing parameter is shown in Figure 4. The patch size or aggregate size was calculated from image analysis of AFM data. The patch size clearly increases with an increase in the surfactant concentration from the HMC to the PZR. The bars in the figure reflect the range of patches encountered in the analysis and are not actually a reflection of errors. Furthermore, the patch size shows a tendency to increase in moving from the quaternary to the primary ammonium headgroup. Since the surface coverage of the ammonium surfactants is similar at the PZR, the population of patches decreases with an increase in the packing parameter. Based on these observations, a schematic diagram for the adsorption layer of DAB and DTAB at concentrations close to the PZR is presented in Figure 5. For DAB, the adsorption is more localized and forms larger surfactant islands or aggregates than for DTAB. It supports the contention that the surfactant adsorbs to produce a more hydrophobic environment with less chain contact with water as the packing parameter increases or the headgroup size decreases. That the smaller headgroups show a greater tendency to hydration possibilities on the bulk water side of aggregates is also not unreasonable.

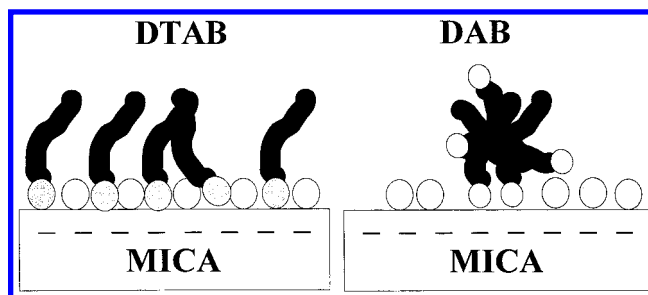


Figure 5. Schematic overview of the adsorption of DAB and DTAB at concentrations close to the PZR at pH 5.3–5.8.

Recent AFM imaging of cationic surfactants adsorbed to various substrates at concentrations in excess of the PZR clearly shows that the surfactants form micellar or hemi-micellar adsorbed aggregate structures, sometimes with a cylindrical conformation showing macroscopic continuity across the surface.^{66,67} These studies also strongly support the contention that the adsorbed layer is aggregating and that the structure and amount of adsorbed material at the surface is controlled by both the association of the hydrophobic moiety of the surfactant with the surface and by the structure of the headgroup.

Conclusion

The adsorption of single dodecyl chain surfactants with primary, secondary, tertiary, and quaternary ammonium headgroups at the muscovite mica basal plane–water interface has been investigated using a flat plate streaming potential apparatus and an atomic force microscope. It was observed that both the HMC and the PZR shifted to higher concentration in the headgroup order, quaternary > tertiary > secondary > primary. The effective number of CH_2 groups per molecule in the hydrocarbon moiety of the chain contributing to the hydrophobic effect has been estimated using the Stern–Graham (SG) isotherm equation. This effective number of CH_2 groups increased with an increase in the surfactant packing parameter. The analysis of AFM images of the mica–solution interfaces in the presence of surfactant indicated that the patch size showed a tendency to increase with an increase in the packing parameter but the number of patches decreased. For DAB, the adsorption seemed to be more localized and formed larger surfactant islands than for DTAB. These observations support the contention that it is both the nature of the initial interaction of the surfactant with the surface and the tendency of the surfactant to form aggregates that determine the adsorption profile and in the case of hydrophilic surfaces.

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