Adsorption of mixtures of nonionic sugar-based surfactants with other surfactants at solid/liquid interfaces
II. Adsorption of *n*-dodecyl-β-D-maltoside with a cationic surfactant and a nonionic ethoxylated surfactant on solids

Lei Zhang, Rui Zhang, P. Somasundaran *

NSF Industry/University Cooperative Research Center (I/UCRC) for Advanced Studies on Novel Surfactant, School of Engineering and Applied Sciences, Columbia University, New York, NY 10027, USA

Abstract

Synergy and antagonism between sugar-based surfactants, a group of environmentally benign surfactants, and cationic surfactants and nonionic ethoxylated surfactants have been investigated in this study with solids which adsorbs only one or other when presented alone. Sugar-based *n*-dodecyl-β-D-maltoside (DM) does not adsorb on silica by itself. However, in mixtures with cationic dodecyltrimethylammonium bromide (DTAB) and nonionic nonylphenol ethoxylated decyl ether (NP-10), DM adsorbs on silica through hydrophobic interactions. In contrast, although DM does adsorb on alumina, the presence of NP-10 reduces the adsorption of DM as well as that of the total surfactant adsorption. Such synergistic/antagonistic effects of sugar-based *n*-dodecyl-β-D-maltoside (DM) in mixtures with other surfactants at solid/liquid interfaces were systematically investigated and some general rules on synergy/antagonism in mixed surfactant systems are identified. These results have implications for designing surfactant combinations for controlled adsorption or prevention of adsorption.
© 2006 Elsevier Inc. All rights reserved.

Keywords: Adsorption; Surfactant mixtures; Sugar-based surfactants; *n*-Dodecyl-*β*-D-maltoside; Solid/liquid interfaces

1. Introduction

Sugar-based surfactants, as a group of environmentally benign surfactants, have shown some unique interfacial behavior [1]. In our previous studies [2], adsorption behavior of sugar-based *n*-dodecyl-β-D-maltoside has been investigated in mixtures with anionic sodium dodecylsulfate at the solid/liquid interface. It was found that synergy or antagonism between these two surfactants at solid/liquid interface can change dramatically just by changing the solution pH.

To further explore the interfacial behavior of mixed surfactant systems, nonionic sugar-based *n*-dodecyl-β-D-maltoside (DM) was studied in mixtures with cationic dodecyltrimethyl-ammonium bromide (DTAB) and nonionic ethoxylated surfactant, nonylphenol ethoxylated decyl ether (NP-10) at the solid/liquid interfaces to explore possible synergism or antagonism between these surfactants. Various interactions between solid substrates and cationic–nonionic or nonionic–nonionic surfactant systems have been reported [3–8].

Although both *n*-dodecyl-β-D-maltoside and nonylphenol ethoxylated decyl ether are nonionic surfactants, they have drastically different behavior at solid/liquid interfaces. Sugar-based surfactants have been reported to adsorb strongly on alumina, hematite and titania, but weakly on silica [1]. In contrast, ethoxylated surfactants are known to adsorb strongly on silica, but weakly on alumina [9,10]. Study of the mixture of these two types of surfactants at silica and alumina surface will be of great interest in understanding surfactant interactions at solid/liquid interface and optimizing such interactions.

---

* Corresponding author.
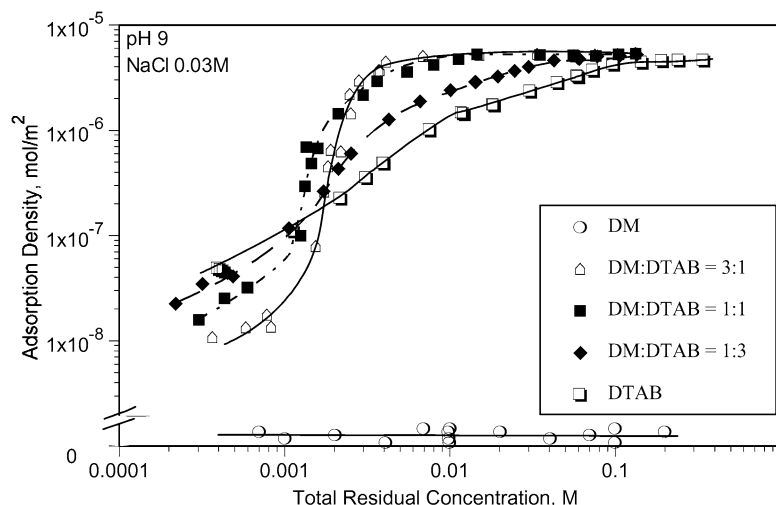*E-mail address:* ps24@columbia.edu (P. Somasundaran).

Fig. 1. Adsorption of DM, DTAB and their mixtures on silica.

2. Materials and methods

2.1. Surfactants

Nonionic sugar-based surfactant, n-dodecyl-β-D-maltoside (DM) from Calbiochem, cationic dodecyltrimethylammonium bromide (DTAB) from TCI Chemicals, Japan, and nonionic nonylphenol ethoxylated decyl ether (NP-10) from Nikko Chemicals, Japan were used as received.

2.2. Solids

Alumina AKP-50 obtained from Sumitomo had a mean diameter of 0.2 μm and specific surface area of 10.8 m^2/g and an isoelectric point (iep) of 8.9. Silica from Geltech had a mean diameter of 0.3 μm and surface area of 12.2 m^2/g. The iep of silica was 2.

2.3. Adsorption

The adsorption process was discussed in part I of this paper [2]. Dodecyltrimethylammonium bromide (DTAB) concentration was determined by complexing the surfactant with excess SDS and measuring the noncomplexed SDS using the two-phase titration. nonylphenol ethoxylated decyl ether (NP-10) concentration was determined using UV spectroscopy and sugar-based surfactant concentration determined by measuring the total organic carbon (TOC) in the sample using a Shimazu Total Organic Carbon Analyzer, or by colorimetric method through phenol–sulfuric acid reaction. In the case of surfactant mixtures, the total surfactant concentration was measured by TOC method, while the individual surfactant was monitored by combination of two-phase titration, UV and colorimetric methods.

3. Results and discussion

3.1. Adsorption of n-dodecyl-β-D-maltoside/dodecyltrimethyl-ammonium chloride mixtures on silica

The adsorption of nonionic–cationic mixtures of n-dodecyl-β-D-maltoside/dodecyltrimethylammonium chloride (DM/

DTAB) on silica was studied as a function of their total concentrations. N-dodecyl-β-D-maltoside does not adsorb on silica at the tested pH, whereas the cationic DTAB adsorbs strongly on silica under the same conditions. The adsorption isotherms of 3:1, 1:1 and 1:3 DM/DTAB mixtures on silica at pH 9 is shown in Fig. 1, together with those of for the single surfactants. The adsorption of DM alone on silica is very low; this is in accord with our previously reported finding that DM adsorbs strongly on alumina but very weakly on silica. DTAB, on the other hand, exhibits strong adsorption on the negatively charged silica due to electrostatic attractions.

The adsorption of the mixtures is lower than that of DTAB at low concentrations because at these concentrations DM does not adsorb on silica. The isotherms show a sharp increase at 0.1–0.2 mM, indicating the onset of the region where hydrophobic chain–chain interaction begins to dominate the adsorption process. In this region, the adsorption of the mixtures is higher than that of DM or DTAB alone. Two factors contribute to this increase. Firstly, the highly surface active DM reduces the critical micelle concentration of the surfactant mixture and for the same reason the hemimicelle concentration, leads to high adsorption at low concentrations. Secondly, DM can co-adsorb with DTAB on silica due to hydrophobic chain–chain interactions. Thus there exists strong synergistic effect between dodecylmaltoside and dodecyltrimethylammonium bromide, especially in the sharp rising portion of the isotherms.

To elucidate the behavior of each surfactant component in the mixture, the adsorption densities of dodecyltrimethylammonium bromide alone and from the DM/DTAB mixtures on silica are plotted in Fig. 2 as a function of residual DTAB concentration. Clearly the presence of DM promotes DTAB adsorption and the adsorption of DTAB from the mixtures is higher than that of DTAB from its single component solutions. The more the percentage of DM in the mixture, the higher is the adsorption of DTAB in regions below the plateau. In the plateau region, the surface is saturated with surfactants and under these conditions the adsorption of dodecyltrimethylammonium bromide (DTAB) is less than that when it is present alone due to the
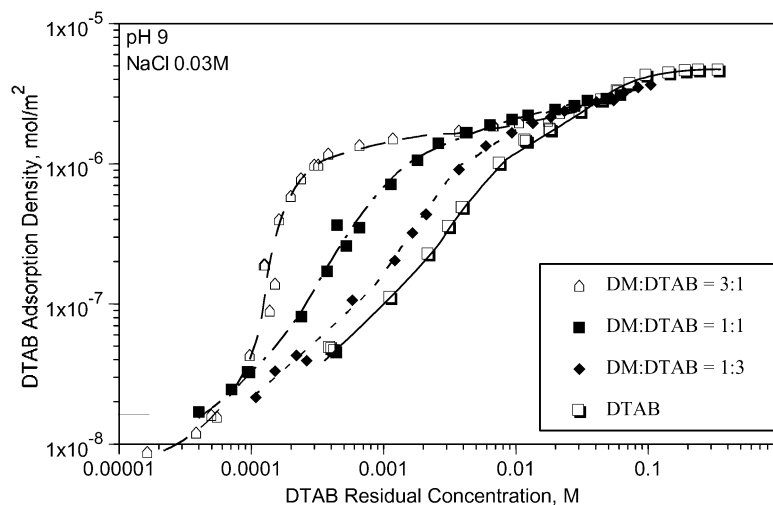
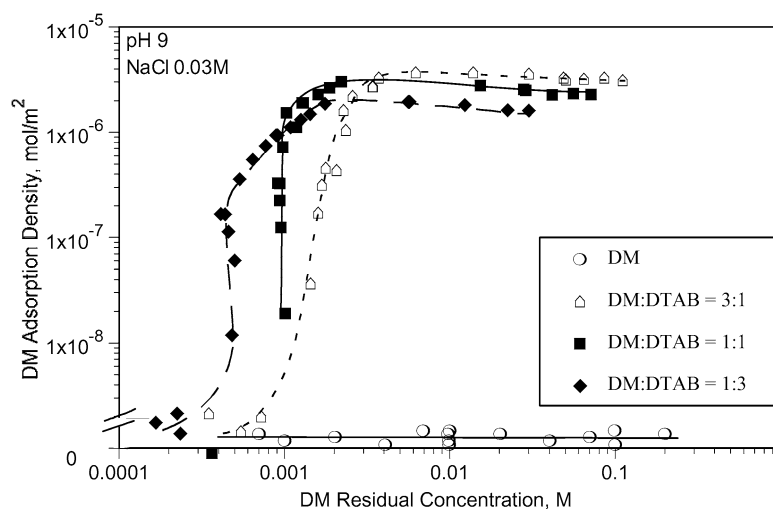Fig. 2. Adsorption of DTAB on silica: adsorption alone and from DM/DTAB mixtures.

Fig. 3. Adsorption of DM on silica: adsorption alone and from DM/DTAB mixtures.

competition from dodecylmaltoside (DM) for adsorption sites on the solid.

Similarly, to identify the behavior of dodecylmaltoside in the mixture, adsorption of DM from the DM/DTAB mixtures is given in Fig. 3 along with that from DM alone. It can be seen that while DM does not adsorb at all on silica by itself, its adsorption is facilitated greatly by the presence of DTAB. The adsorption in mixtures is proposed to be due to the hydrophobic chain–chain interactions between DM and DTAB. The DTAB in the hemimicelles that form at the solid/liquid interface acts as anchor species for the DM molecules.

Thus, it can be concluded that sugar-based dodecylmaltoside, which does not adsorb on silica by itself, can adsorb in the presence of DTAB. In the mixed system, DTAB also adsorbs more from the mixture than it does alone, due to the reduction of critical micelle concentration by DM and hence the increase in the monomer activity. In a similar study, Huang et al. has reported that in the case of adsorption of the cationic tetradecyl-trimethylammonium chloride/nonionic pentadecylethoxylated nonylphenol mixtures at the negatively charged alumina/liquid

interface, presence of tetradecyltrimethylammonium chloride in the system leads to adsorption of pentadecylethoxylated nonylphenol on alumina, where the latter does not normally adsorb by itself [3].

The interaction between the two surfactants is clearly seen by plotting the adsorption of the mixtures together with DM:DTAB ratios in the adsorbed layer. The DM/DTAB ratio for the 1:1 mixture is shown in Fig. 4. At low concentrations (<0.15 mM), DM shows a low ratio due to lack of specific chain–chain interactions between it and the solid. Adsorption is mostly due to the adsorption of DTAB through electrostatic interactions. At about 0.15 mM residual concentration, the adsorption of the mixture rises sharply due to hydrophobic chain–chain interactions. The DM/DTAB ratio also increases rapidly at this concentration, suggesting strong hydrophobic chain–chain interactions to cause more DM to co-adsorb on the surface. In a certain concentration range, the DM/DTAB ratio is more than 1, DM adsorbs more than DTAB itself, although it is co-adsorbing through DTAB. The DM/DTAB ratio reaches a maximum and then decreases. The decrease is attributed to the
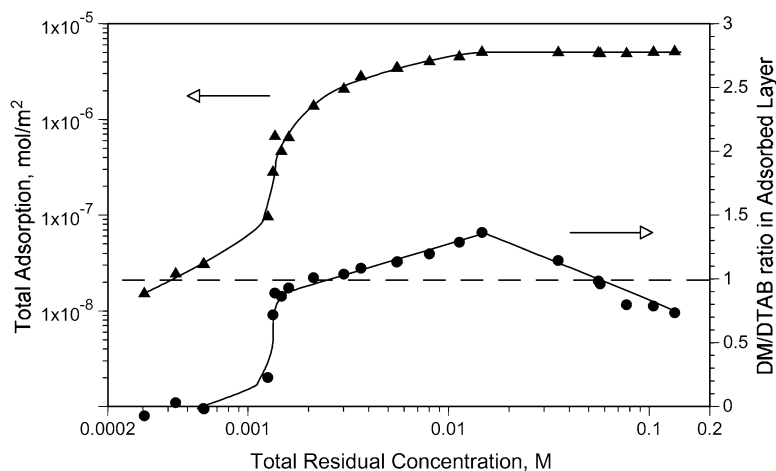
Fig. 4. Adsorption of DM/DTAB mixtures and the DM/DTAB ratios on silica. (a) 1:1 mix; (b) 3:1 mix; (c) 1:3 mix.
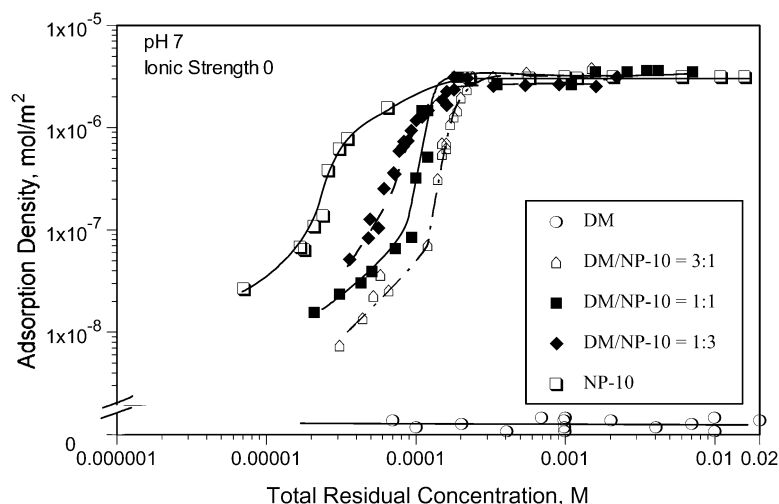

Fig. 5. Adsorption of DM, NP-10 and their mixtures on silica.

competition between the micelles in solution and the hemimicelles at the solid/liquid interface for the more surface active DM. Interestingly, the maximum ratio corresponds to the onset of the plateau region. Thus interactions between the surfactants in solutions and at solid/liquid interfaces are dominated by different forces in different regions.

Similar trends are found for the DM/DTAB ratios in 3:1 and 1:3 mixtures. For both mixtures, the DM/DTAB ratio is low at low concentrations, increases rapidly at the concentration where hydrophobic chain–chain interaction dominates the adsorption process, reaches a maximum at the onset of the plateau region, and then decreases. Since composition of the adsorbed layer will determine to a large extent the interfacial behavior of the particles such as wettability and dispersion, the practical application of the above finding is to be noted.

3.2. Adsorption of n-dodecyl-β-D-maltoside/nonylphenol ethoxylated decyl ether mixtures on silica

The adsorption of *n*-dodecyl-β-D-maltoside (DM) and nonylphenol ethoxylated decyl ether (NP-10) mixtures on silica

was investigated next. Interestingly, although both surfactants are nonionic and their liquid/air interfacial behaviors are similar, they behave quite differently at solid/liquid interfaces. Sugar-based surfactants adsorb on alumina but not on silica, whereas ethoxylated nonionic surfactants exhibit an opposite behavior. The behavior of mixtures of the two at solid/liquid interfaces is examined further below.

The adsorption isotherms of *n*-dodecyl-β-D-maltoside (DM), nonylphenol ethoxylated decyl ether (NP-10), and their mixtures on silica are shown in Fig. 5. NP-10 adsorbs on silica strongly due to hydrogen bonding, while DM does not. Their mixtures adsorb less than that of NP-10 alone at low concentrations and approximately the same as that of NP-10 alone at higher concentrations. This is different from that of DM/DTAB mixtures, where the adsorption densities of the mixture are higher than those of either DM or DTAB in the region where hydrophobic interactions dominate the adsorption process. This can be explained by the fact that NP-10 is more surface active than DM, and DM plays a minor role in the mixtures.

Similar to that in the case of DM/DTAB mixtures where DM promotes DTAB adsorption in mixtures, it was found that DM
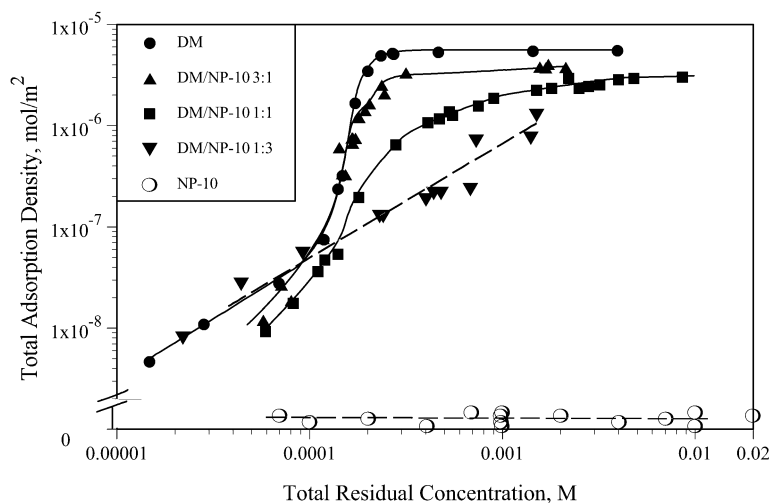
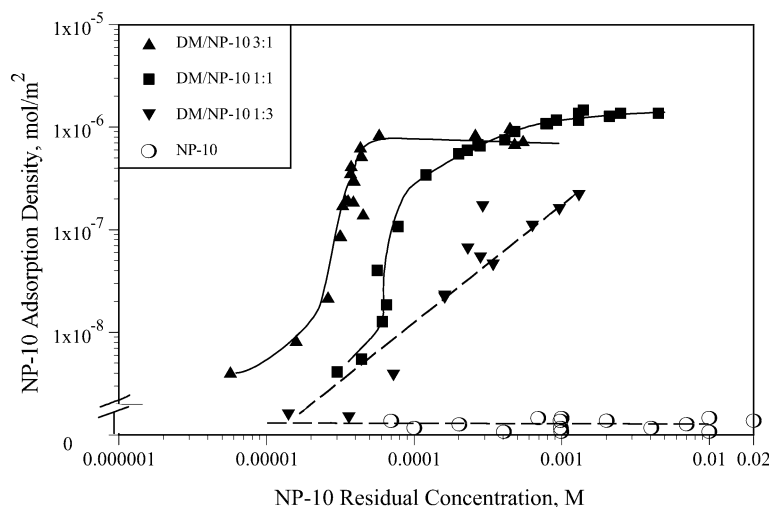Fig. 6. Adsorption of DM, NP-10 and their mixtures on alumina.

Fig. 7. Adsorption of NP-10 on alumina: adsorption alone and from mixtures

increases the adsorption of NP-10, especially at low concentrations. The dodecylmaltoside in the DM/NP-10 mixture, on the other hand, adsorbs much more on the surface than DM alone as a result of the hydrophobic chain–chain interactions. This phenomenon again is very similar to that in the case of DM adsorption from DM/DTAB mixtures. The variation of DM/NP-10 ratio in the adsorbed layer as a function of adsorption was found to be very similar to those of DM/DTAB mixtures as well.

3.3. Adsorption of n-dodecyl-β-D-maltoside/nonylphenol ethoxylated decyl ether mixtures on alumina

The adsorption isotherms of *n*-dodecyl-β-D-maltoside (DM), nonylphenol ethoxylated decyl ether (NP-10), and their mixtures on alumina are shown in Fig. 6. In this case, DM adsorbs strongly on alumina and NP-10 does not adsorb. At all mixing ratios, the adsorption of the mixtures is considerably lower than that of DM alone. The adsorption density data shows that the surface is not fully covered by the surfactant.

The presence of NP-10 in the systems reduces the adsorption of the sugar-based DM, suggesting that there exist antagonistic interactions between the two surfactants at the alumina–water interfaces.

The adsorption of NP-10 from solutions with and without DM on alumina is plotted in Fig. 7 as a function of residual NP-10 concentration. Adsorption of NP from the mixtures is facilitated by the presence of DM. This is proposed to be due to the adsorbed DM functioning as anchor molecules for NP-10 through hydrophobic chain–chain interactions. Thus, for NP-10, there are clear synergistic effects when mixed with DM.

In contrast to the above, from Fig. 8 it can be seen that the DM adsorption is depressed by NP-10 in the plateau region. From Fig. 6 it can be seen that the total adsorption of DM + NP-10 is much less than that of DM alone. It can be stated that in this system, as a whole there are mainly antagonist effects between DM and NP-10. This is very similar to the adsorption of *n*-dodecyl-β-D-maltoside/sodium dodecylsulfate on negatively charged alumina [2].
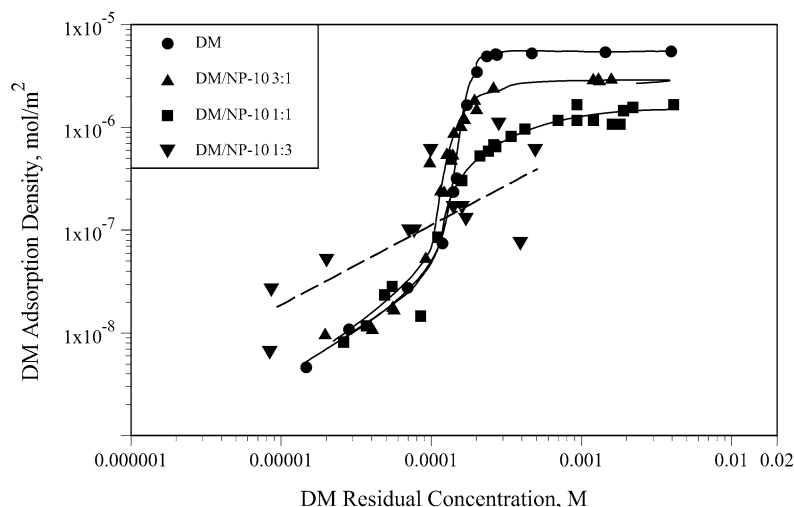
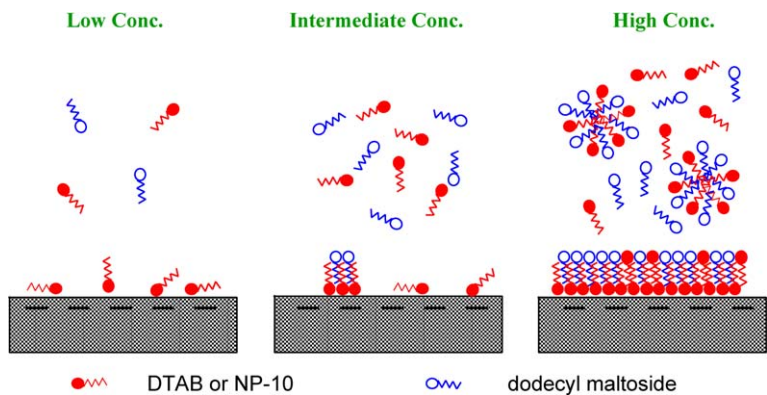Fig. 8. Adsorption of DM on alumina: adsorption alone and from mixtures.

Fig. 9. Adsorption models for DM/DTAB and DM/NP-10 mixtures on silica.

4. Summary and conclusions

In the case nonionic–cationic mixtures of *n*-dodecyl-β-D-maltoside (DM) and dodecyltrimethylammonium bromide (DTAB) on silica, DM does not adsorb on the silica by itself. However, in the mixtures, DM can adsorb on silica through hydrophobic chain–chain interactions with the adsorbed DTAB species. The DM adsorption is characterized by a sharp increase in density at a given concentration.

In these mixed systems, DTAB acts as anchor for DM. Its adsorption is markedly affected by the presence of DM. As long as the surface is not saturated, DTAB adsorbs more because of the presence of DM. When the surface is saturated, DTAB adsorption is reduced due to competition from DM for adsorption sites. The ratio of DM/DTAB in the adsorbed layer is a function of the adsorption density. The ratio starts as a small value at low concentrations, increases rapidly in regions where chain–chain interactions dominate, reaches a maximum at the onset of plateau region, and then decreases. The synergistic interaction between DM and DTAB in this system is obvious.

The adsorption of nonionic–nonionic mixtures of *n*-dodecyl-β-D-maltoside (DM) and nonylphenol ethoxylated decyl ether (NP-10) on silica is very similar to that of DM/DTAB system:

Table 1

Adsorption and synergistic/antagonistic interactions of various surfactants in mixtures with sugar-based DM

Surfactants	Anionic SDS		Cationic DTAB	Nonionic NP-10	
Solid substrates	Alumina at pH 6	Alumina at pH 11	Silica at pH 9	Silica at pH 7	Alumina at pH 7
DM adsorbs on substrate?	Yes	Yes	No	No	Yes
Surfactant adsorbs on substrate?	Yes	No	Yes	Yes	No
Synergism/ antagonism	Synergism	Antagonism	Synergism	Synergism	Antagonism

DM adsorbs on silica through hydrophobic chain–chain interactions with the adsorbed NP-10 which acts as an anchor for DM, while NP-10 adsorption is influenced by the presence of DM. The ratios of DM/NP-10 in the adsorbed layer are also similar to those of DM/DTAB systems, suggesting that similar interactions are responsible for the co-adsorption of DM on silica. A schematic diagram is proposed to describe the adsorption of DM./DTAB and DM/NP-10 on silica (Fig. 9).

In the case of alumina, where DM adsorbs and NP-10 does not, the adsorption of the mixtures is considerably lower than

that of DM alone. Although NP-10 adsorption on alumina does increase due to hydrophobic chain–chain interactions with adsorbed DM, similar to the case of DM/NP-10 on silica, the DM adsorption is reduced. For the DM/NP-10 mixtures, at high concentrations, the surface is not even fully covered by the surfactants. The presence of NP-10 in the system reduces the adsorption of the DM and the total adsorption. There are thus antagonistic interactions between the two surfactants in this case.

Synergistic/antagonistic effects of sugar-based *n*-dodecyl-β-D-maltoside (DM) in mixtures with other surfactants at solid/liquid interfaces are summarized in Table 1. Some general trends can be observed:

(1) When the other surfactant adsorbs on the solid by itself, no matter whether DM adsorbs on the solid or not, the mixture of the two usually shows synergy. The two surfactants assist each other in adsorption. They compete when the surface is saturated with surfactants.
(2) When the other surfactant does not adsorb on the solid by itself, and DM adsorbs, the mixture of two usually show antagonism. The other surfactant prevents DM adsorption, resulting in low total adsorption.

The various synergistic/antagonistic interactions between sugar-based surfactant and other surfactant have implications for designing surfactant combinations for controlled adsorption to optimize their performance.

References

[1] L. Zhang, P. Somasundaran, C. Maltesh, J. Colloid Interface Sci. 191 (1997) 202.
[2] L. Zhang, P. Somasundaran, J. Colloid Interface Sci. (2006), in press (this issue).
[3] L. Huang, C. Maltesh, P. Somasundaran, J. Colloid Interface Sci. 177 (1996) 222.
[4] F. Portet, P.L. Desbene, C. Treiner, J. Colloid Interface Sci. 184 (1) (1996) 216–226.
[5] Z. Huang, Z. Yan, T. Gu, Colloids Surf. 36 (1989) 353.
[6] J.D. Hines, G. Fragneto, R.K. Thomas, P.R. Garrett, G.K. Rennie, A.R. Rennie, J. Colloid Interface Sci. 189 (1997) 259.
[7] K. Boschkova, J.J.R. Stalgren, Langmuir 18 (2002) 6802.
[8] J. Penfold, E.J. Staples, I. Tucker, R.K. Thomas, Langmuir 16 (2000) 8879.
[9] P. Somasundaran, E.D. Snell, Q. Xu, J. Colloid Interface Sci. 144 (1991) 165.
[10] S.A. Lawrence, J.A. Pilc, J.R. Readman, P.A. Sermon, J. Chem. Soc. Chem. Commun. 1035 (1987).