Adsorption of mixtures of nonionic sugar-based surfactants with other surfactants at solid/liquid interfaces
I. Adsorption of n-dodecyl-β-D-maltoside with anionic sodium dodecyl sulfate on alumina

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Abstract

Sugar-based surfactants can be synthesized from renewable materials and are environmentally benign. They have some unique solution and interfacial properties and have potential applications in a wide variety of processes, and there is a need for corresponding information on their behavior at various interfaces. In this study, co-adsorption of nonionic sugar-based n-dodecyl-β-D-maltoside (DM) and anionic sodium dodecyl sulfate (SDS) on alumina was studied as a function of mixing ratios and solution pHs. It is found that at solid–liquid interface, depending on the solid type and the solution conditions, there are various interactions that dictate synergy or antagonism. At pH 6 where alumina is positively charged, marked synergistic effects between DM and SDS were observed, while at pH 11 where alumina is negatively charged, SDS shows antagonistic adsorption effects with DM. The ratios of surfactant components on solids change as a function of surfactant structure and concentrations as well, indicating various interactions at solid/liquid interface under different conditions that can be utilized for many industrial processes.
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Keywords: Adsorption; Surfactant mixtures; Sugar-based surfactants; n-Dodecyl-β-D-maltoside; Solid/liquid interface

1. Introduction

Sugar-based surfactants such as alkyl glucosides can be made from renewable material and are biodegradable. They can be used in many applications as substitutes for other surfactants that are not environmentally sound [1–4]. In addition, sugar-based surfactants exhibit some unusual properties. As nonionic surfactants, their solubility comes from the hydroxyl groups and not the ether oxygens (as in alkyl polyethyleneglycol ethers) (C_iE_j). They do not show the inverse solubility vs temperature, unlike nonionic alkyl polyethyleneglycol ethers which are temperature sensitive. At solid/liquid interfaces, sugar-based surfactant adsorbs on alumina, hematite and titania, but very little on silica [5]. This behavior is opposite to that of the nonionic alkyl polyethyleneglycol ethers, which adsorb strongly on sil-

ica but weakly on alumina and hematite [6,7]. Hydrogen bond has been proposed to be the driving force for adsorption of both types of surfactants on solids [8–10], despite the drastic differences in structure and compositions of their headgroups.

Sugar-based surfactants have been studied as mixtures with other surfactants to explore possible synergism or antagonism between them under various conditions. In solutions, sugar-based surfactants show synergy with cationic and anionic surfactants, the magnitude of such interactions generally follows the order anionic/nonionic > cationic/nonionic > nonionic/nonionic [11].

Adsorption of surfactants at solid–liquid interfaces plays a critical role in many important industrial processes. Significant progress has been made in understanding the adsorption/desorption behavior of single surfactants on solids [12–15]. Also, many studies cover the solid/liquid interfacial behavior of surfactant mixtures as it is important for the theoretical understanding and practical applications of surfactants [16–23].

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In this study the adsorption of nonionic sugar-based surfactant, *n*-dodecyl-β-D-maltoside, in mixtures with anionic sodium dodecyl sulfate on alumina was studied at pH 6 where alumina is positively charged, and pH 11 where alumina is negatively charged. Sugar-based surfactant adsorbs on alumina at both pHs, whereas SDS adsorbs on alumina only at pH 6. It was the aim of this work to study the adsorption behavior of their mixtures in terms of the properties of the surfactant components, the solid substrates, solution pH, and mixing ratios, etc. and to explore possible synergism or antagonism between the two surfactants.

2. Materials and methods

2.1. Surfactants

Nonionic sugar-based surfactant, *n*-dodecyl-β-D-maltoside (DM) was obtained from Calbiochem and was used as received. The purity determined using TLC analysis was reported to be of >98%. Anionic sodium dodecyl sulfate (SDS) of greater than 99% purity purchased from Fluka chemicals was also used as received.

2.2. Solids

Alumina AKP-50 obtained from Sumitomo had a mean diameter of 0.2 μm. The BET specific surface area measured using nitrogen with a Quantasorb system was 10.8 m^2/g and the isoelectric point (iep) was 8.9.

2.3. Other chemicals

HCl and NaOH, used for pH adjusting, were of A.C.S. grade certified (purity >99.9%) and from Fisher Scientific Co. Water used in all the experiments was triple distilled, with a specific conductivity of less than 1.5 μΩ^{-1} and tested for the absence of organics using surface tension measurements.

2.4. Adsorption

Adsorption experiments were conducted in capped 20 ml scintillation vials. Solid samples of 2 g were mixed with 10 ml of triple distilled water for 2 h at room temperature. The pH was adjusted as desired and then 10 ml of the surfactant solution was added and equilibrated further for 16 h with pH adjustment. The suspensions were then centrifuged at 3000–4000 rpm for 30 min and the supernatant analyzed for the residual concentration. Adsorption was calculated based upon surfactant depletion from the solutions.

Sodium dodecyl sulfate (SDS) concentration was determined using a two-phase titration method [24]. Sugar-based surfactant concentration after adsorption was 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 [25]. In the case of surfactant mixtures, the total surfactant concentration was measured by TOC method, while the SDS concentration was
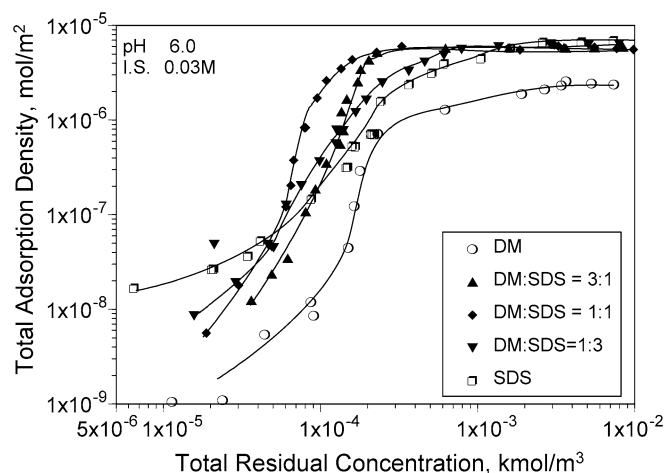

Fig. 1. Adsorption of DM, SDS and DM/SDS mixtures on alumina.

measured by the two-phase titration and sugar-based surfactant by the colorimetric method.

3. Results and discussion

3.1. Adsorption of n-dodecyl-β-D-maltoside/sodium dodecyl sulfate mixtures at pH 6

The isoelectric point of alumina used in this study is 8.9. At pH 6, alumina is positively charged. Anionic sodium dodecyl sulfate (SDS) by itself can adsorb on alumina due to electrostatic interaction. Nonionic *n*-dodecyl-β-D-maltoside (DM) can also adsorb on alumina through hydrogen bonding [8]. The adsorption isotherms of DM/SDS 3:1, 1:1 and 1:3 mixtures on alumina at pH 6 are shown in Fig. 1, together with those of dodecyl-β-D-maltoside and sodium dodecyl sulfate alone. The adsorption of the mixtures is higher than that of either of the components in the sharp rising part of the isotherm, showing strong synergy between DM and SDS. This is the region where hydrophobic chain–chain interaction dominates the adsorption process, with the surface not yet saturated with the surfactants. At lower surfactant concentrations, SDS adsorbs more than DM, as the electrostatic interaction is stronger compared with hydrogen bonding. In this region, adsorption takes place mainly due to electrostatic attraction between the negatively charged dodecyl sulfate and positively charged alumina. Some adsorption of the sugar-based surfactant is evidently due to hydrogen bonding. At higher concentrations, the adsorbed SDS forms mixed aggregates with DM through hydrophobic chain-chain interactions and promotes the DM adsorption. The low critical micellar concentration of DM causes the aggregates to form at lower concentrations and this promotes total adsorption as well. In the plateau region, the adsorption density of the mixture is slightly less than that of SDS. At this stage the surface is saturated with surfactants. Since the sugar-based surfactant has larger head group, the total adsorbed amount is less in molar term.

To better understand the adsorption process and behavior of individual surfactant in the mixtures at the solid/liquid interface, the adsorption densities of sodium dodecyl sulfate alone
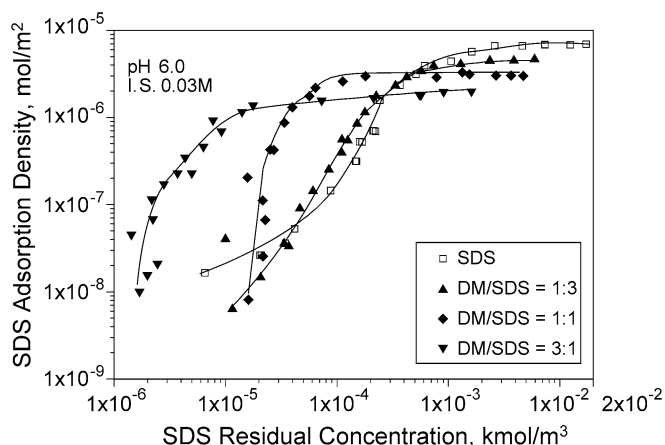
Fig. 2. Adsorption of SDS on alumina: adsorption for SDS alone and from DM/SDS 3:1, 1:1 and 1:3 mixtures.
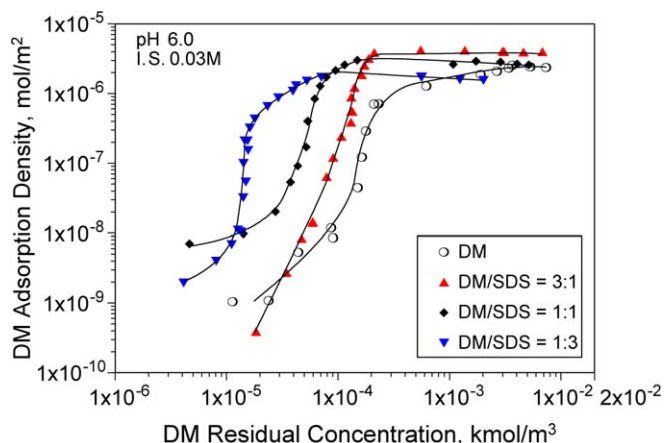

Fig. 3. Adsorption of DM on alumina: adsorption for DM alone and from DM/SDS 3:1, 1:1 and 1:3 mixtures.

concentration, suggesting that the presence of DM facilitates SDS adsorption. As mentioned above, in the plateau region, the surface is saturated with the surfactant, and under these conditions the adsorption of SDS is lower than that when it is present alone due to competition from DM in the system. The higher the DM in the mixing ratio, the lower is the adsorption of SDS, suggesting that more SDS is replaced by DM at the solid/liquid interface.

Similar results for DM adsorption from the DM/SDS mixtures and that from DM alone is given in Fig. 3. It can be seen that the adsorption of DM is enhanced by the SDS as well in this case in the entire concentration range. Interestingly, the more the SDS in the system, the higher is the adsorption of DM in the rising part, suggesting synergistic effects of SDS on DM adsorption.

Based on these results, a schematic diagram is proposed in Fig. 4 for the adsorption of *n*-dodecyl-β-D-maltoside/sodium dodecyl sulfate on alumina at pH 6. At lower concentrations, both surfactants adsorb on the solid surface by themselves due to either electrostatic interaction or hydrogen bonding. At still higher concentrations, interactions between hydrophobic chains of the surfactants take place leading to a rapid rise in adsorption. The mixed aggregates start to form at solid/liquid interface. Above the c.m.c. of the surfactant mixtures, the adsorption reaches a plateau. At this stage, there are mixed aggregates both in solution and at solid/liquid interface.

3.2. Adsorption of n-dodecyl-β-D-maltoside/sodium dodecyl sulfate mixtures at pH 11

At pH 11, alumina is negatively charged. *n*-Dodecyl-β-D-maltoside can adsorb on alumina at this condition, while sodium dodecyl sulfate will not due to its anionic nature. The adsorption of *n*-dodecyl-β-D-maltoside (DM), sodium dodecyl sulfate (SDS) and their 3:1, 1:1 and 1:3 mixtures is illustrated in Fig. 5. At this pH, adsorption of negatively charged SDS on the similarly charged alumina is very low, while adsorption of DM is similar to that at pH 6. Surprisingly, the adsorption of the mixtures under these conditions is between those of DM and SDS. The total adsorption reaches a plateau even when the

and from the DM/SDS mixtures on alumina are plotted in Fig. 2 as a function of the residual SDS concentration. Clearly the adsorption of SDS from the mixtures is higher than that of SDS from its single component solutions in the sharp rising part of the isotherm. The more DM in the system (the higher the DM/SDS ratio), the higher is the adsorption density at a given
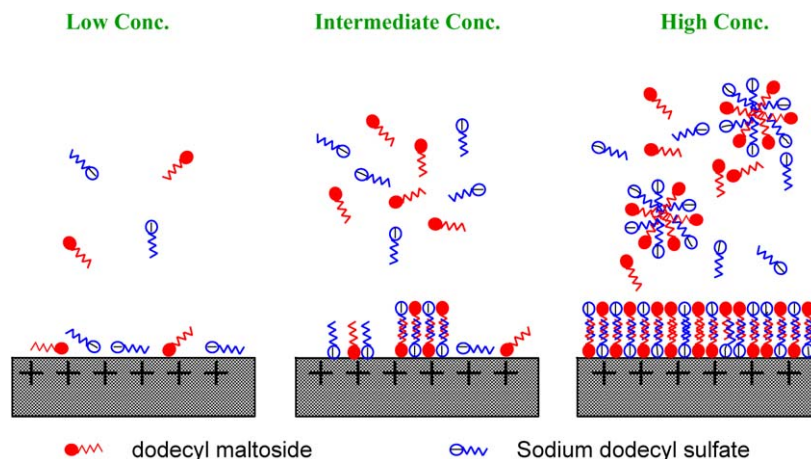

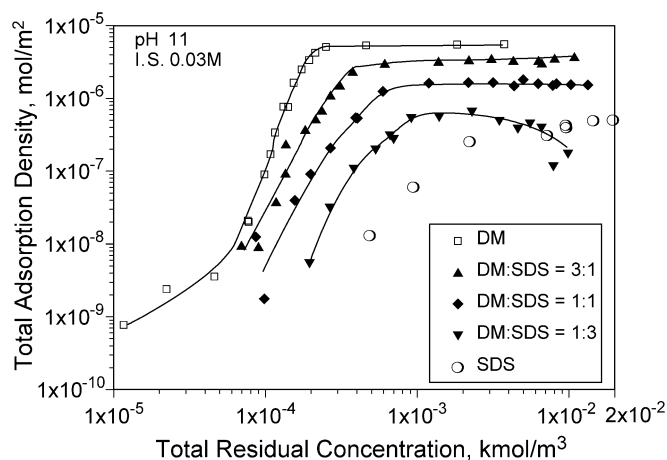Fig. 4. Adsorption models for DM/SDS mixtures on positively charged alumina.

Fig. 5. Adsorption of DM, SDS and their 3:1, 1:1 and 1:3 mixtures on alumina at pH 11.

Fig. 7. Adsorption of DM on alumina at pH 11: adsorption for DM alone and from DM/SDS 3:1, 1:1 and 1:3 mixtures.
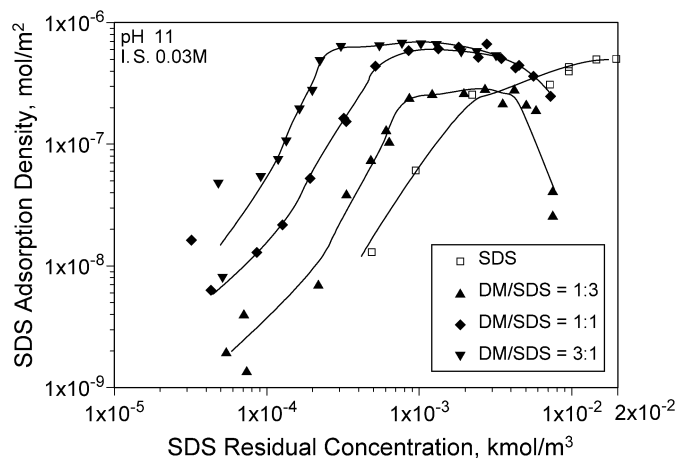

Fig. 6. Adsorption of SDS on alumina at pH 11: adsorption for SDS alone and from DM/SDS 3:1, 1:1 and 1:3 mixtures.

surface is not fully covered by the surfactants, although there is enough DM in the system to adsorb. The more SDS in the system, the lower is the total adsorption density of the surface mixtures. The presence of SDS in the system reduces the adsorption of the sugar-based surfactants under these conditions. Thus, there are antagonistic or competitive effects between SDS and DM under these conditions.

To explore adsorption behavior of individual surfactant in the mixtures at the solid/liquid interface, the adsorption of sodium dodecyl sulfate from SDS solution and from the DM/SDS mixtures on alumina is plotted in Fig. 6 as a function of the residual SDS concentration. Adsorption of SDS from the mixtures is enhanced by the presence of DM except in the very high concentration regions. This is proposed to be due to the adsorbed DM functioning as anchor molecules for the SDS through hydrophobic chain–chain interactions. Thus at least for SDS, there are some synergistic effects in the surfactant mixtures with DM.

In contrast to the above, it can be seen from Fig. 7 that the DM adsorption is enhanced by SDS only in the rising part but depressed in the plateau region. It can be seen from Fig. 5 that the total adsorption of DM + SDS is decreased as SDS in the
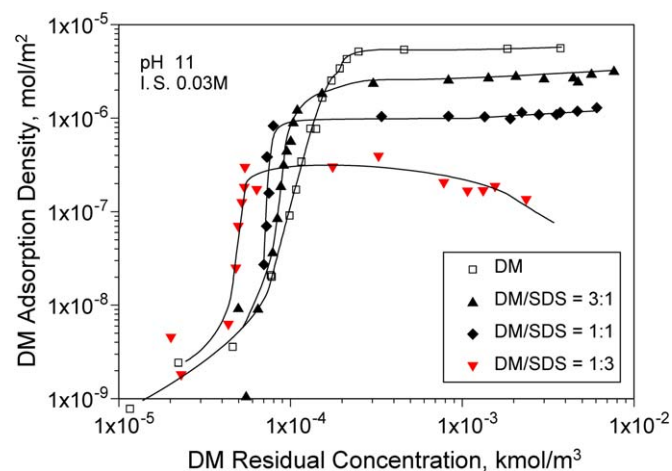
mixture increased. Thus it can be concluded that in this system at pH 11, as a whole there are mainly antagonist effects between DM and SDS, because the adsorption of the mixtures of DM/SDS is markedly lower than that of DM alone.

A schematic diagram is proposed for the adsorption of *n*-dodecyl-β-D-maltoside/sodium dodecyl sulfate on alumina at pH 11 (Fig. 8). At lower concentrations, SDS does not adsorb on alumina, only DM adsorbs on the solid surface through hydrogen bonding. At still higher concentrations, SDS adsorbs at the solid/liquid interface through hydrophobic interactions between surfactant chains of DM and SDS, forming mixed aggregates. Above the cmc, the adsorption reaches a plateau, even though the surface is not fully covered. Under this conditions, there are mixed aggregates both in solution and at solid/liquid interface. It is postulated that since the DM/SDS mixed micelles are DM rich [11], most DM in the systems is consumed by the mixed micelles in solution, leading to lower adsorption of DM at the solid–liquid interface. This phenomenon has implications in applications that warrant lower adsorption of surfactants, as in enhanced oil recovery.

4. Summary and conclusions

In summary, co-adsorption of *n*-dodecyl-β-D-maltoside (DM) with sodium dodecyl sulfate (SDS) on alumina was studied at pH 6 and 11. At pH 6, where alumina is positively charged, marked synergistic effects between DM and SDS were observed, especially in the region where hydrophobic chain–chain interaction dominates the adsorption process as long as the surface is not saturated. In the plateau region, clearly there is competition for adsorption sites. At this pH, SDS and DM promote the adsorption of each other and there exists mainly synergism. The strongest synergism was found when the DM:SDS was 1:1 due to possible 1:1 complex formation and/or better packing.

At pH 11 where alumina is negatively charged, the adsorption of DM/SDS mixtures is less than that of DM alone. The presence of SDS in the systems reduces the sugar-based surfactant adsorption except in the rising part of the isotherm,
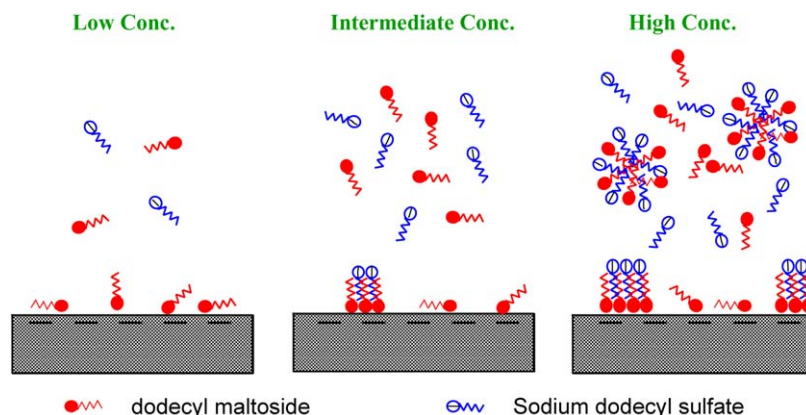
Fig. 8. Adsorption models for DM/SDS mixtures on negatively charged alumina.

although the SDS adsorption is increased due to hydrophobic interaction with the sugar-based surfactants. In general there are mainly antagonistic effects between n-dodecyl-β-D-maltoside and sodium dodecyl sulfate (SDS) at this pH.

These results have implications for many industrial processes that need synergy and antagonism to control the adsorption process. For example, in enhanced oil recovery (EOR), to reduce the surfactant loss due to adsorption on reservoir rock, weak adsorption of the surfactants is one of the important factors to keep the process cost-effective.

Acknowledgments

References

[1] K. Hill, W. von Rybinski, G. Stoll (Eds.), Alkyl Polyglycosides, Technology, Properties and Application, VCH Publishers, New York, 1997.
[2] W. von Rybinski, K. Hill, Angew. Chem. Int. Ed. 37 (1998) 1328.
[3] D. Balzer, Tenside Surf. Det. 28 (1991) 419.
[4] C. Stubenrauch, Curr. Opin. Colloid Interface Sci. 6 (2001) 160.
[5] L. Zhang, P. Somasundaran, C. Maltesh, J. Colloid Interface Sci. 191 (1997) 202.
[6] P. Somasundaran, E.D. Snell, Q. Xu, J. Colloid Interface Sci. 144 (1991) 165.
[7] S.A. Lawrence, J.A. Pilc, J.R. Readman, P.A. Sermon, J. Chem. Soc. Chem. Commun. (1987) 1035.
[8] L. Zhang, P. Somasundaran, J. Mielczarski, E. Mielczarski, J. Colloid Interface Sci. 256 (2002) 16.
[9] G.A. Smith, A.L. Zulli, M.D. Grieser, M.C. Counts, Colloids Surf. 88 (1994) 67.
[10] A. Doren, D. Vargas, J. Goldfrab, Inst. Min. Metall. Trans. Sect. C 84 (1975) 34.
[11] R. Zhang, L. Zhang, P. Somasundaran, J. Colloid Interface Sci. 278 (2004) 453.
[12] P. Somasundaran, D.W. Fuerstenau, J. Phys. Chem. 70 (1966) 90.
[13] P. Somasundaran, H.S. Hanna, Soc. Pet. Eng. J. 19 (1979) 221.
[14] P. Somasundaran, S. Krishnakumar, Colloids Surf. A 123 (1997) 491.
[15] P. Somasundaran, L. Huang, Adv. Colloid Interface Sci. 88 (2000) 179.
[16] E.D. Snell, E. Fu, Q. Xu, P. Somasundaran, Colloids Surf. 63 (1992) 49.
[17] P. Somasundaran, L. Huang, Adv. Colloid Interface Sci. 88 (2000) 179.
[18] A. Thibaut, A.M. Misselyn-Bauduin, J. Grandjean, G. Broze, R. Jerome, Langmuir 16 (2000) 9192.
[19] F. Porter-Koltalo, P.L. Desbene, C. Treiner, Langmuir 17 (2001) 3858.
[20] Z. Huang, Z. Yan, T. Gu, Colloids Surf. 36 (1989) 353.
[21] W.J. Lokar, W.A. Ducker, Langmuir 20 (2004) 4553.
[22] J. Brinck, F. Tiberg, Langmuir 12 (1996) 5042.
[23] L. Huang, P. Somasundaran, Langmuir 13 (1997) 6683.
[24] Z. Li, M.J. Rosen, Anal. Chem. 53 (1516) 1981.
[25] M. Dubois, K.A. Gilles, J.K. Hamilton, P.A. Rebers, F. Smith, Anal. Chem. 28 (1956) 350.