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Original Scientific Paper

Interactions of Sodium Dodecylbenzenesulfonate and Calcite in 0.55 M NaCl Solution*

Damir Krznarić,[a] *Nada Filipović-Vincekovié,*[b] *Vesna Babić-Ivančić,*[b]
and Halka Bilinski[b]

[a]*Ruđer Bošković Institute, Center for Marine Research,*
P.O.B. 1016, 10001 Zagreb, Croatia

[b]*Ruđer Bošković Institute, Department of Chemistry,*
P.O.B. 1016, 10001 Zagreb, Croatia

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Complex mutual interactions of calcite and sodium dodecylbenzene sulfonate (NaDBS) were studied in 0.55 M NaCl solution, using several complementary techniques.

Adsorption of NaDBS on calcite could be resolved from other processes such as adsorption onto the reaction vessel and/or formation of solid crystalline phase, when a special a.c. voltammetric procedure was used below the critical micelle concentration (c.m.c. = $= 9 \times 10^{-5}$ mol/L). A two-plateau type isotherm was obtained. Initial adsorption of NaDBS occurs at Ca^{2+} ions on the calcite/solution interface through electrostatic interactions. The second stage of adsorption was described as hydrophobic interaction between hydrocarbon chains from bulk solution and those electrostatically adsorbed on calcite, forming surface aggregates.

The results of adsorption were analyzed by a two-step adsorption model. The equilibrium constants k_1 and k_2 for the first and second adsorption step, the surface aggregation number, n, the amount of adsorbed monomer, Γ_1, the saturated adsorption, Γ_∞, and the standard free energy of surface aggregate formation for one mole of surfactant, ΔG^0_{hm}, were calculated.

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* Dedicated to Marko Branica on the occasion of his 65th birthday.

INTRODUCTION

The present work is complementary to the one dealing with calcite, sodium dodecylbenzene sulfonate, Pb (II) and Cd(II) interactions in seawater medium, using surfactant concentrations above the c.m.c. value.[1] The idea of measuring adsorption isotherms for some alkylbenzene sulfonates on different adsorbents is not new. However, previous measurements have been performed in distilled water,[2] with reported,[3] c.m.c. = 1.7×10^{-3} mol/L and also in 0.01 M NaCl solution,[4] with c.m.c. = 2×10^{-4} mol/L. The adsorbents used were alumina and kaolinite. To our knowledge adsorption of NaDBS on calcite has not been previously studied. The goal of our present work was to develop such an experimental procedure that will make it possible to measure NaDBS adsorption below the c.m.c. at an ionic strength close to that of seawater. Such a procedure was used to obtain and quantify the adsorption isotherm of NaDBS on calcite.

EXPERIMENTAL

Materials

Sodium dodecylbenzenesulfonate, NaDBS (n-$C_{12}H_{25}$-Ph-SO_3Na), a BDH (England) product, was used as received. It was of chemical reagent grade; all of the other reagents were analytical grade (Merck, Darmstadt, Germany). Twice distilled water was used as the solvent. Electrolyte solution contained 0.55 M NaCl, to which 0.03 M $NaHCO_3$ solution was added to regulate pH close to that in seawater. $CaCO_3$, used as a model adsorbent with a surface area[5] of 0.55 m^2 g^{-1}, was identified with calcite as the only component.[6]

Instruments

The critical micelle concentration (c.m.c.) was determined in 0.55 M NaCl from the surface tension – log C(NaDBS) curve by Interfacial Tensiometer K8, Krüss, Hamburg.

The activity of calcium ions in reference samples containing 0.5 g $CaCO_3$ and the electrolyte solution was determined after 24 hours of equilibration, being $C(Ca^{2+}) = (6.8 \pm 0.1) \times 10^{-6}$ mol/L. A PVC matrix calcium ion selective electrode (the body purchased from W. Moeller, Zürich) and a Ag/AgCl/KCl reference electrode were used for measurement with the Orion microprocessor pH/millivolt meter.

The electrophoretic mobility of particles was determined using an automated electrophoretic instrument (type S 3000, Pen Kem). Turbidity measurements were performed with a Hach turbidimeter (Model 2100 A). Turbidity is expressed in Nephelometric Turbidity Units (NTU). Optical micrographs were obtained by using an Orthoplan Leitz microscope with polarizing equipment.

Electrochemical measurements were performed in systems containing solid particles, using a multimode polarographic analyzer PAR 170 for phase selective alternating current voltammetric measurements (ACV). A Metrohm cell of 50 mL with a three electrode system was used. The working electrode was a Metrohm hanging mercury drop electrode (HMDE) with a surface area of 0.022 cm^2. A saturated calomel electrode (SCE) served as the reference electrode with a platinum auxiliary electrode. Deoxygenation of solution was not necessary, since at the a.c. frequency (300 Hz) used, the oxygen reduction current is depressed. An a.c. amplitude of 10 mV was used and the a.c. phase angle was 90° out of phase for all measurements.

All measurements were performed at 298 K in the presence of atmospheric carbon dioxide.

Phase Selective Alternating Current Voltammetric (ACV) Measurements

NaDBS adsorbs on the mercury electrode surface from about –0.2 to –1.3 V *vs.* S.C.E. In Figure 1A, ACV curves for several concentrations of NaDBS below the c.m.c. are given. The adsorption of NaDBS on the mercury electrode surface results in depression of the capacitive component of the current (i_c). At more negative potentials than –0.9 V, different peaks are observed. The origin of those peaks is discussed in the

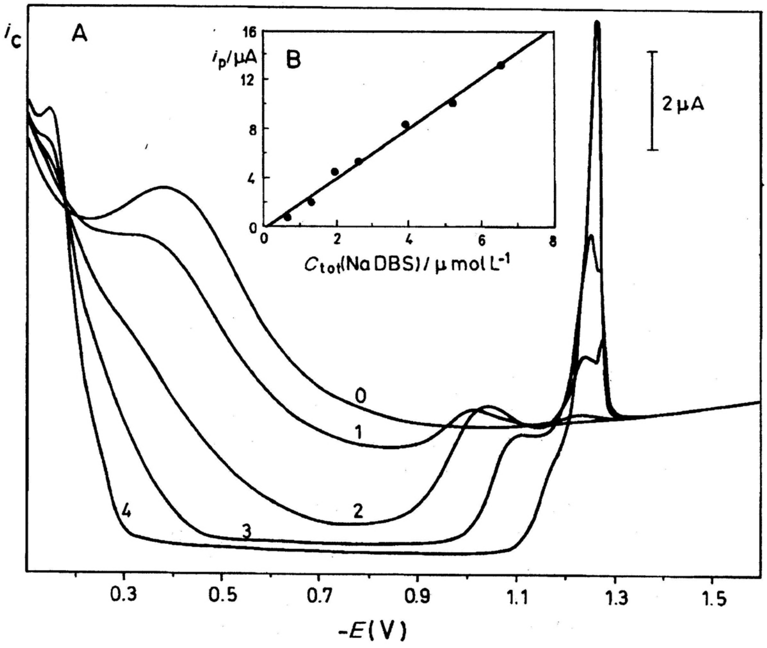

Figure 1. (A) A.c. voltammetric curves for selected concentrations of NaDBS in 0.55 M NaCl. Scan was started from –0.1 V without prior accumulation. Scan rate was 10 mV s^{-1} and phase angle 90°. Used concentrations of NaDBS in mol/L are: (0) 0, (1) 7.72×10^{-6}, (2) 1.93×10^{-5}, (3) 3.07×10^{-5}, (4) 5.34×10^{-5}.
(B) Calibration line showing the concentration dependence of peak current i_p at $E \approx -1.25$ V *vs.* C_{tot}(NaDBS). Deposition time, t_D = 1 min under stirring. Deposition potential, E_D = –0.6 V. Scan rate was 10 mV s^{-1} and phase angle 90°. For each point the cell was pretreated with the solution of the given NaDBS concentration.

context of reported literature.[7–10] The most pronounced sharp desorption peak at about –1.25 V was chosen for analytical determination of the NaDBS concentration. The peak height is proportional to the amount of NaDBS adsorbed on the electrode surface and thus also to the dissolved concentration of surfactant. The NaDBS concentration in solution was determined by accumulation at the electrode surface at –0.6 V for 60 s while stirring the solution. Subsequently, NaDBS was stripped from the electrode by scanning the potential towards the negative values. The dependence of the NaDBS desorption current (i_p) on the NaDBS solution concentration is shown in Figure 1B. In order to minimize errors due to the adsorption of NaDBS on cell walls, the cell was pretreated for each sample with a solution containing the same amount of NaDBS expected in the experimental sample.

The calcite-NaDBS-electrolyte systems studied were equilibrated by stirring for 15 min with a Teflon stirrer and were allowed to stand 24 hours before measurements. No visible change in the electrochemical response could be observed after this period. A blank solution without calcite was prepared and carried through all the experiments in parallel. After 24 hours of equilibration with calcite, an aliquot of solution above the sedimented calcite was analyzed for NaDBS. NaDBS was removed from the solution due to the adsorption on calcite particles, adsorption on the electrochemical cell or flask walls as well as due to the possible precipitation of solid or liquid crystals. The value of the amount of NaDBS removed from the blank solution was subtracted from the value removed from the suspension containing calcite. In this way, the loss of NaDBS by processes other than adsorption on calcite was accounted for.

RESULTS AND DISCUSSION

Properties of the Subsystem NaDBS-Electrolyte

To be able to differentiate the several processes occurring when calcite is dispersed in surfactant-electrolyte mixtures it is necessary to take into account interactions between the surfactant and electrolyte. Data for the surface tension, turbidity and electrophoretic mobility measurements, performed with increasing surfactant concentration for the NaDBS-electrolyte system are summerized in Figure 2. The critical micelle concentration (c.m.c.) was estimated to be 9×10^{-5} mol/L (Figure 2a). The c.m.c. is shifted to very low *C*(NaDBS) with electrolyte addition when compared with the value in distilled water.[3] Immediately above the c.m.c., mixtures became increasingly turbid with increasing surfactant concentration (Figure 2b). Electrophoretic mobility presented in Figure 2c shows increasing negative charge of particles with increasing *C*(NaDBS).

Microscopic inspection of the subsystem, illustrated in Figures 3a–d, exhibited the formation of lamellar dispersion. The number and size of lamellar droplets increased with increasing *C*(NaDBS). The size of the spherical lamellar units ranged from the lower limit of observation of the optical microscope (0.5 μm) to 15 μm (Figure 3a). When their size is large enough, the

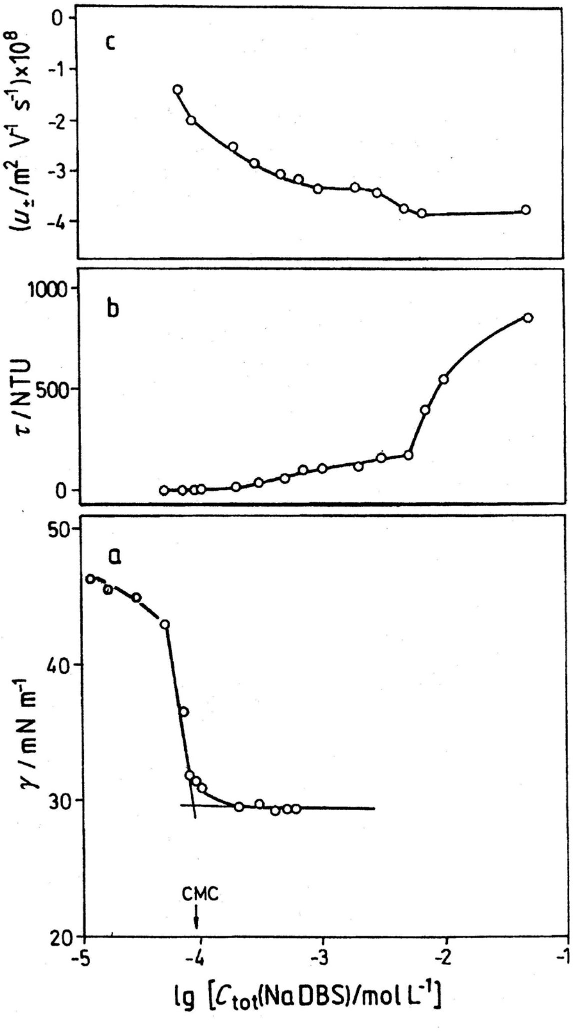

Figure 2. Some properties of the subsystem NaDBS-electrolyte: (a) surface tension, γ/mN m^{-1}; (b) turbidity, τ/NTU; (c) electrophoretic mobility, epm/ m^{-2} V^{-1} s^{-1} plotted *vs.* log C_{tot}(NaDBS). Electrolyte is 0.55 M NaCl solution, containing 0.03 M $NaHCO_3$ to maintain pH in the range 8.2–8.5.

Maltese crosses are viewed under crossed polarizers[11] (see Figure 3b), indicating radial symmetry. At *C*(NaDBS) > 0.003 mol/L, the droplets were strongly flocculated (Figure 3c). At *C*(NaDBS) = 0.01 mol/L, the lamellar phase with streaky appearance coexisted with small lamellar droplets (Figure 3d).

The narrow micellar range and transition to liquid crystalline (LC) phase at relatively low surfactant concentration is in accord with the observed salt-induced phase transition from an isotropic micellar solution into a lamellar liquid crystalline phase in dilute NaDBS aqueous solutions.[12]

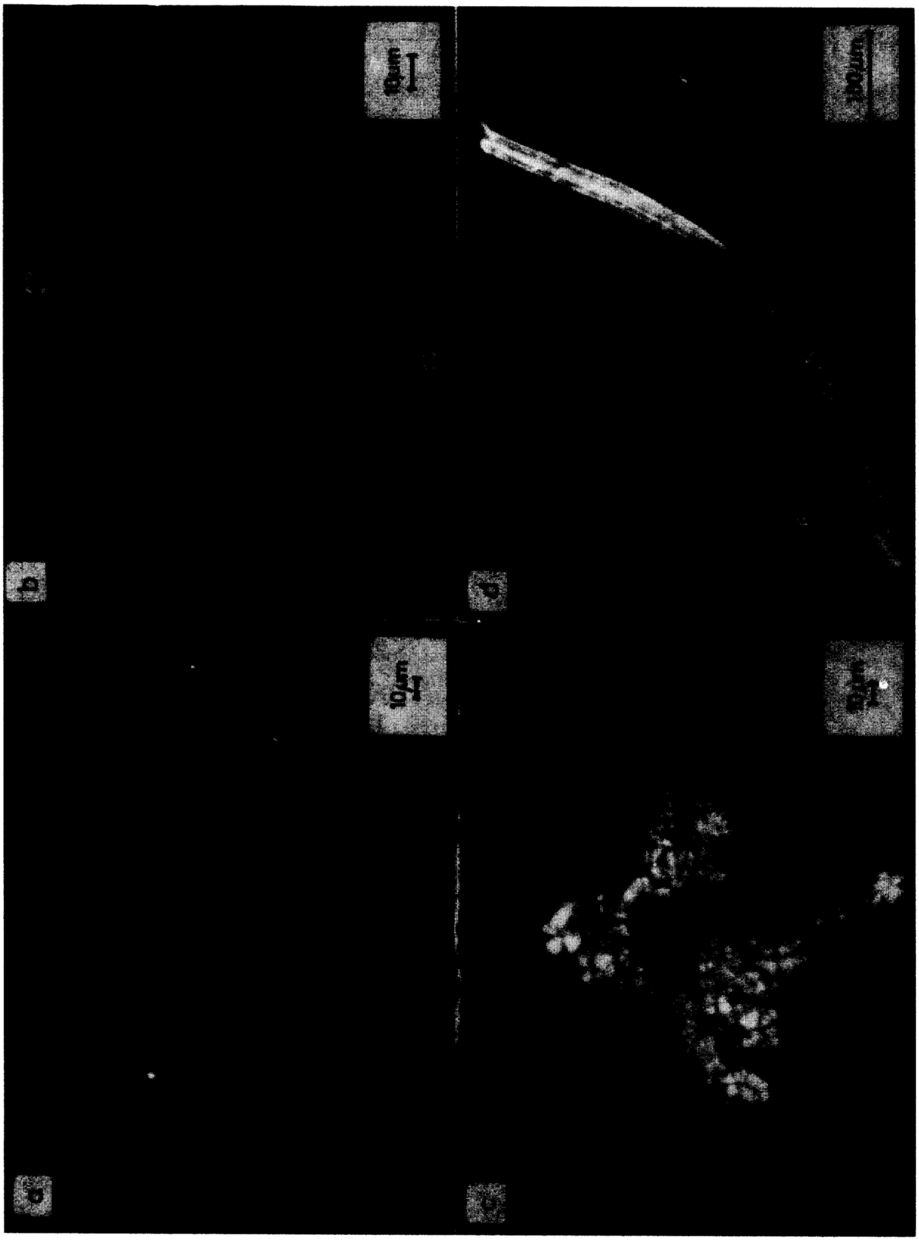

Figure 3. Microscopic observation of phases formed in the subsystem NaDBS-electrolyte. (a) lamellar dispersion formed at C_{tot}(NaDBS) = 0.0003 mol/L; (b) lamellar droplets with typical Maltese crosses formed at C_{tot}(NaDBS) = 0.001 mol/L; (c) flocculated lamellar droplets from the system C_{tot}(NaDBS) =.0005 mol/L(d) streaky lamellar phase with small lamellar droplets formed at C_{tot}(NaDBS) = 0.01 mol/L. (crossed polarizers).

Properties of the System Calcite-NaDBS-Electrolyte

Calcite particles in contact with an electrolyte solution will undergo partial dissolution, its extent depending on solution conditions (pH, ionic strength, temperature and other chemical species present). Under our experimental conditions, the prevailing species of dissolved calcium is Ca^{+2}. Therefore one might expect NaDBS loss due to $Ca(DBS)_2$ precipitation. However, the data do not support $Ca(DBS)_2(s)$ precipitation. On the contrary, when different concentrations of soluble $CaCl_2$ were added to the NaDBS solution (C(NaDBS) = 3×10^{-5} mol/L) and were equilibrated in the usual manner for 24 hours, no change in the concentration of soluble NaDBS was observed (Figure 4).

Figure 5a shows microscopic examination of aggregated calcite particles in the absence of NaDBS. Thin platelike transparent solid crystals (SC) appearing in systems prepared below the c.m.c. can be seen in Figure 5b. At concentrations above the c.m.c., mixtures of calcite and the liquid crystalline phase coexisted. Lamellar droplets of varying size are shown in Figure 5c. With increasing C(NaDBS), calcite particles were more aggregated and located around streaky networks of the liquid crystalline phase, as shown for C(NaDBS) = 10^{-2} mol/L in Figure 5d.

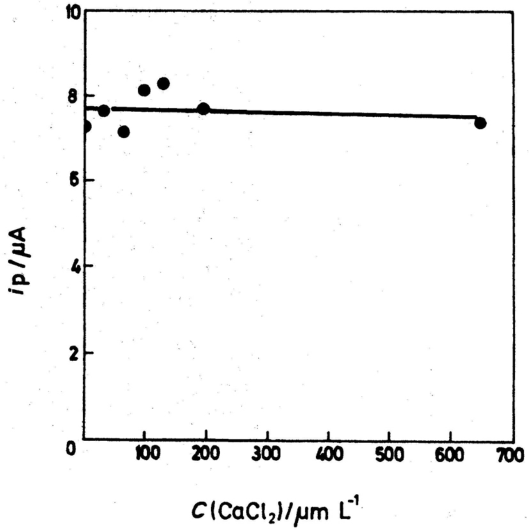

Figure 4. NaDBS ACV peak current vs. the concentration of $CaCl_2$ added to the solution of 3×10^{-5} M NaDBS, 0.55 M NaCl and 0.03 M $NaHCO_3$. t_D 1 min diffusion; E_D −0.6 V; phase angle 90°; scan rate 10 mV s^{-1}. Each solution was equilibrated for 24 hours.

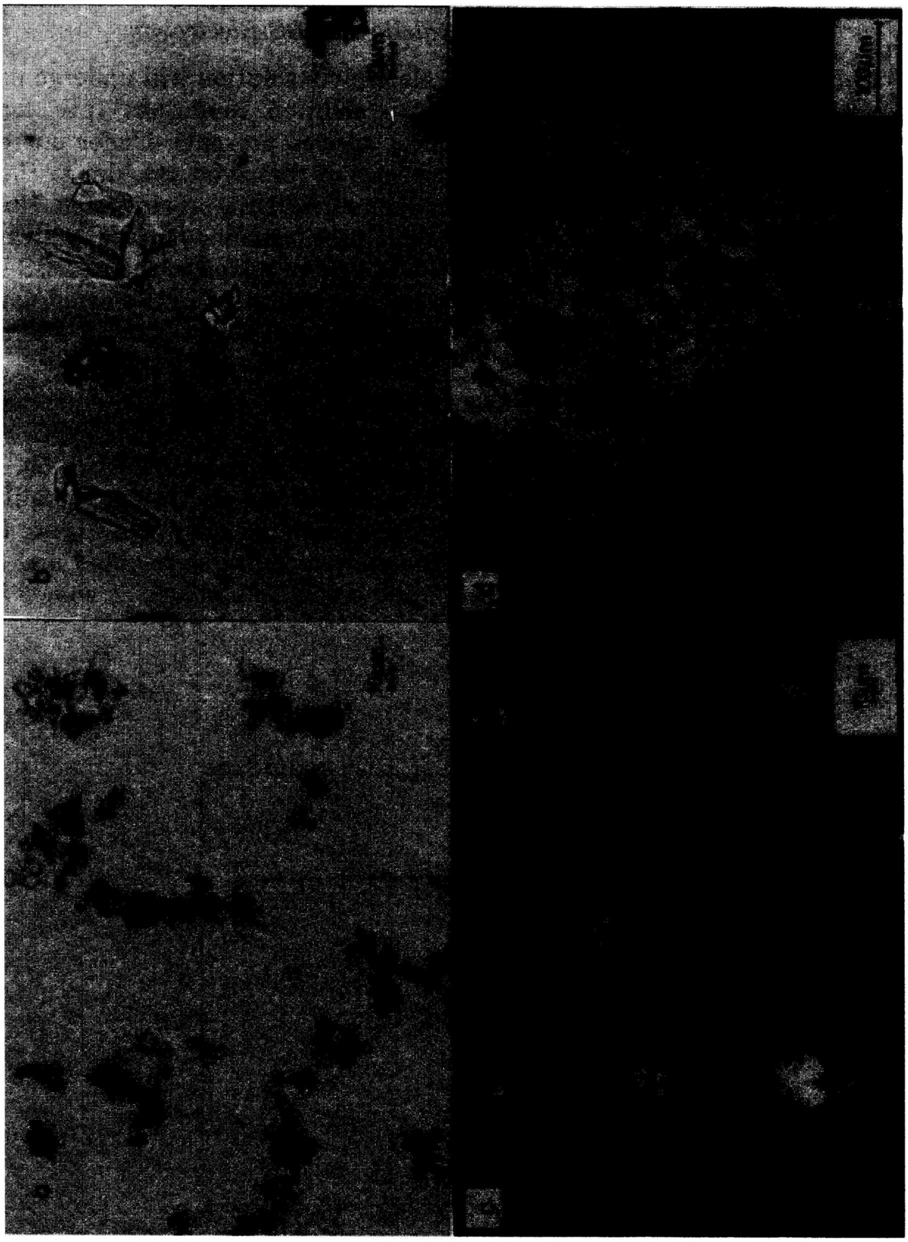

Figure 5. Microscopic observation of phase formed in the system calcite-NaDBS-electrolyte: a) calcite crystals in the absence of NaDBS.; b) mixture of aggregated calcite and thin platelike solid crystals formed at C_{tot}(NaDBS) = 0.00001 mol/L; c) mixture of calcite and lamellar droplet formed at C_{tot}(NaDBS) = 0.0005 mol/L (crossed polarizers); d) oily streak network of liquid crystalline phase with incorporated calcite crystals formed at C_{tot}(NaDBS) = 0.01 mol/L (crossed polarizers).

The sample with the highest NaDBS concentration was centrifuged, dried and studied by X-ray powder diffraction (XRD). The resulting XRD spectrum is presented in Figure 6a. Besides the calcite pattern (Ref. No. 5–0586),[6] an additional crystalline phase X is observed. This phase is different from NaDBS (Figure 6b) and from $Ca(DBS)_2$ (Figure 6c). At present, we do not know with certainty its composition but one may conclude that the liquid crystalline phase with bound sodium and calcium ions as counterions are formed. The mechanism of counterion binding is not well understood in the liquid crystalline state but it has been shown that the properties of the lamellar phase will be strongly changed when divalent ions are added.[13]

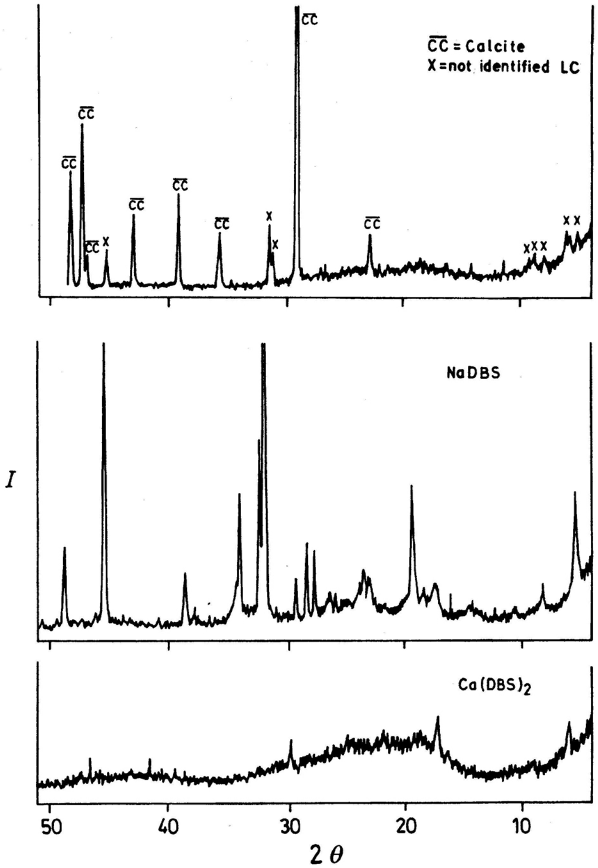

Figure 6. X-ray diffraction of powder of: a) solid found after filtration of sample containing calcite and C_{tot}(NaDBS) = 0.01 mol/L in the electrolyte; b) of NaDBS solid crystals; c) of $Ca(DBS)_2$ solid crystals.

Special precaution should be taken when interpreting adsorption of NaDBS on calcite. Namely, several processes occur simultaneously such as adsorption of surfactant onto calcite surface, adsorption on the surface of the reaction vessel, precipitation of SC below the c.m.c. and formation of the LC phase above the c.m.c.

The total amount of NaDBS removed, C_{adtot}(NaDBS), (including all processes) *vs.* total NaDBS concentration added, C_{tot}(NaDBS), is presented in Figure 7. C_{adtot}(NaDBS) can be expressed as

$$C_{\mathrm{adtot}}(\mathrm{NaDBS}) = C_{\mathrm{tot}}(\mathrm{NaDBS}) - C_{\mathrm{eq}}(\mathrm{NaDBS})$$

where C_{eq}(NaDBS) is the concentration of NaDBS in bulk solution in equilibrium with NaDBS adsorbed on calcite and vessel, and with precipitated SC and LC. Crosses represent spectrophotometric data and dots a.c. voltammetric data. The two experiments were performed with 0.5 g/L and 1.0 g/L of calcite respectively. The samples were centrifuged prior to spectrophotometric measurements, while for ACV measurements the solution above the precipitate was taken without prior centrifugation. At concentrations of NaDBS higher than c.m.c., the values for the two methods coincide although performed with two different amounts of calcite. It indicates that NaDBS is removed from the solution mainly due to the coprecipitation process rather than due to adsorption on calcite. Discrepancies between spectrophotometric

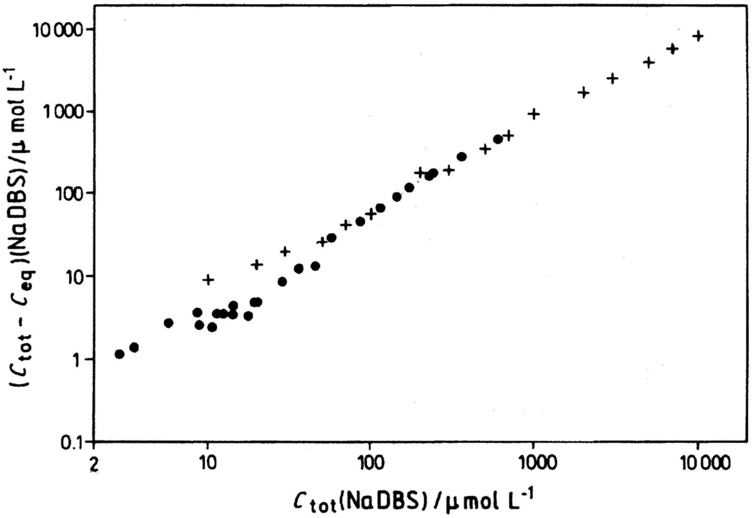

Figure 7. Totally removed ($C_{\mathrm{tot}} - C_{\mathrm{eq}}$) NaDBS from electrolyte solution plotted *vs.* added NaDBS, C_{tot}(NaDBS). (+) spectrophotometric, (•) ACV measurements.

and ACV measurements at NaDBS concentrations below c.m.c. can be explained by adsorption losses during the process of centrifugation, necessary for spectrophotometric measurements.

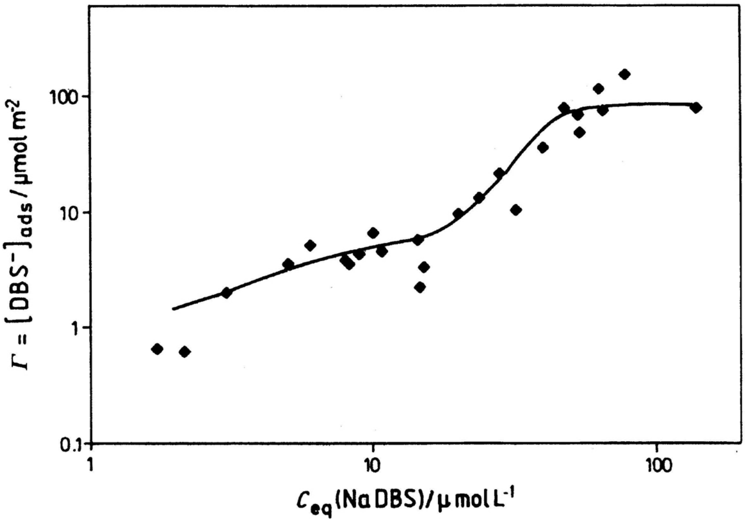

Figure 8. Adsorption isotherm of NaDBS on calcite in 0.55 M NaCl (presented in logarithmic scale in order to include all experimental data). The amount of calcite was 1 g/L. Equilibration of solution was 15 min stirring and 24 hours quiet. Before a.c. voltammetric measurements, each solution was if necessary diluted to be in the measurable range.

The adsorption isotherm of NaDBS on calcite is given in Figure 8. A typical two-step isotherm is observed (Figure 8), the first region showing a low increase in adsorption with increasing NaDBS concentration and the second region an abrupt increase in the slope. This is characteristic of a two-stage process with a monolayer and subsequent surface aggregate formation.[15] In the first step, the surfactant ions are adsorbed through interactions with the solid phase. There are two possible explanations for anionic surfactant adsorption on the surface which is negatively charged (in the electrolyte studied calcite is found on average to be negatively charged, with a zeta potential of −10.9 mV). One is chemical and/or hydrophobic interactions and the other alternative is electrostatic interaction due to heterogeneous distribution of charge on the calcite surfaces (the presence of both positively and negatively charged patches on the surfaces). In the second step, the surfactant monomers are adsorbed through hydrophobic interaction. The first step provides possible active centres for surface aggregates called hemimicelles.

Based on the two-step adsorption model and mass action treatment, a general adsorption isotherm equation is given by[15]

$$\Gamma = \frac{\Gamma_{\infty} k_1 C \left(\frac{1}{n} + k_2 C^{n-1} \right)}{1 + k_1 C \left(k_2 C^{n-1} \right)}$$

where Γ is the adsorbed amount, C is the equilibrium concentration, Γ_{∞} is the saturated adsorption obtained from adsorption data at high concentrations, n is the surface aggregation number (of surface micelle or hemimicelle), k_1 and k_2 are equilibrium constants for the first and second step respectively.

The value of k_1 was calculated from adsorption data at lowest concentrations using a limiting Langmuir type equation and the plot $1/\Gamma$ *vs.* $1/C$.

The values obtained are: $k_1 = 7.45 \times 10^4$ with a first plateau value $\Gamma_1 = 7.3 \times 10^{-6}$ mol/m^2. This value corresponds to approximately 23 Å^2 of calcite surface occupied by one molecule of NaDBS. It corresponds to the calcite surface occupied by Ca^{2+} surface ions[16] implying the electrostatic interaction between anionic surfactant monomers and Ca^{2+} ions on the calcite/solution interface. The distribution of the electrophoretic mobility spectrum (epm) for the control system (calcite-electrolyte), showing the presence of some positive and prevailing negative charge on calcite particles, provides additional confirmation.

The value $\Gamma_{\infty} = 8 \times 10^{-5}$ mol/m^2 was obtained directly from the second plateau at concentrations near the c.m.c. Using a trial and error method, the best values were obtained for the remaining unknowns k_2 and n: $k_2 = 4 \times 10^{26}$ and $n = 7$.

Using the data of the adsorption isotherm in Figure 8 and Eq. (22) from the reported paper,[15]

$$\text{h.m.c.} = \left[\frac{3(n-2) - \{3n(n-2)\}^{1/2}}{3(n-2) - \{3n(n-2)\}^{1/2}} \cdot \frac{1}{k_2} \right]^{\frac{1}{n-1}}$$

the hemimicellization concentration (h.m.c.) was calculated to be 3×10^{-5}. mol/L. According to the same reference, the standard free energy of hemimicellization for one mole of surfactant can be calculated as $\Delta G^0_{\text{hm}} = -21.3$ kJ/mol using the equation

$$\Delta G^0_{\text{hm}} = \frac{1}{n} RT \ln k_2 .$$

It might be of some interest to mention that the same type of isotherm was obtained for NaDBS on kaolinite.[4] The values for k_1 in our work (7.5×10^4)

and in Ref. 4 (3.4×10^4) are in relatively good agreement at similar pH. Since k_1 characterizes the first part of the »two plateaus« (LS-type) isotherm, *i.e.* the part corresponding to the adsorption of monomers, it seems that NaDBS single molecules adsorb on calcite and kaolinite in a relatively similar manner. It is most likely that in both cases the monolayer coverage is attained through attachment of NaDBS molecules to the positive charges of the heterogeneously charged surface of calcite or kaolinite. Of course, the densities of those charges are different on calcite and kaolinite which results in different monolayer coverages by NaDBS.

At first sight, k_2 in our case (4×10^{26}) and in Ref. 4 (1.2×10^{11}) seem to be in considerable disagreement. Since constant k_2 describes the second step of the isotherm or the aggregate formation stage, it is to be expected that it should depend mostly on the nature of the adsorbed molecule and the nature and concentration of the counter ions. The type of mineral should influence k_2 to a lesser degree. Therefore, the most probable source of disagreement in k_2 values between our work and Ref. 4 should be sought in the concentration of counterions. The concentration of NaCl in our experiment was 0.55 mol/L and in Ref. 4 it was 0.01 mol/L resulting in c.m.c. of 9×10^{-5} mol/L and 2.1×10^{-4} mol/L, respectively. Using Eq. (22) from Ref. 15, the hemimicellization concentration (h.m.c.) was calculated to be 3×10^{-5} mol/L and 9.5×10^{-5} mol/L for this work and Ref. 4, respectively. Comparing the shift of h.m.c. values with the shift for c.m.c., it seems reasonable to conclude that the cause of the different values of k_2 is the concentration of NaCl. Such a conclusion is in accordance with the well known fact that the primary forces involved in the formation of ionic surface aggregates are the same as those involved in micelle formation, including the importance of counterions. The degree of counterion binding on adsorbed surfactant aggregates appears to be significantly higher than binding on micelles. The increase of counterion concentration induces surface aggregate formation.[17]

CONCLUSIONS

The complex interaction of NaDBS and calcite in 0.55 M NaCl was studied in detail by several complementary techniques.

A special a.c. voltammetric procedure was developed in order to get adsorption of NaDBS on calcite resolved from other processes occurring simultaneously.

A general two-step adsorption model has been applied successfully. It was suggested that in the first step the surfactant monomer is adsorbed through electrostatic interaction *via* Ca^{2+} existing as a surface calcite ion. In the second step adsorption increases dramatically due to the surface aggregate formation through hydrophobic forces.

Comparison with the literature[4] indicates that the NaDBS adsorption behaviour is similar on calcite and kaolinite.

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SAŽETAK

Interakcija natrijeva dodecilbenzensulfonata i kalcita u 0,55 M otopini NaCl

Damir Krznarić, Nada Filipović-Vinceković, Vesna Babić-Ivančić, i Halka Bilinski

Složeno međudjelovanje kalcita i natrijeva dodecilbenzensulfonata (NaDBS) proučavano je u otopini NaCl (0,55 mol/L) s pomoću eksperimentalnih metoda.

Upotrebom posebnog postupka fazno osjetljive voltametrije s izmjeničnom strujom, razlučena je adsorpcija NaDBS na kalcitu od drugih procesa poput adsorpcije na reakcijsku ćeliju i(ili) nastajanja krute kristalne faze. Taj je postupak primijenjen za mjerenja pri koncentracijama NaDBS nižim od kritične micelarne koncentracije (k.m.c. = 9×10^{-5} mol/L.). Dobivena je adsorpcijska izoterma s dva platoa. Početna adsorpcija NaDBS zbiva se na Ca^{2+} ionima u međufazi kalcit/otopina uslijed elektrostatskih međudjelovanja. Drugi stupanj adsorpcije pripisan je hidrofobnom međudjelovanju ugljivodičnih lanaca iz otopine i onih elektrostatski adsorbiranih na kalcitu, što rezultira nastajanjem površinskih agregata.

Rezultati adsorpcije analizirani su adsorpcijskim modelom s dva stupnja. Izračunane su ravnotežne adsorpcijske konstante k_1 i k_2 za prvi i drugi adsorpcijski stupanj, površinski agregacijski broj, n, količina adsorbiranog monomera, Γ_1, maksimalna adsorpcija, Γ_∞, te standardna promjena Gibbsove energije površinskih agregata po molekuli površinski aktivne tvari, ΔG^0_{hm}.