Inhibitor effect of selected anionic surfactants on the dissolution of calcium sulfate in aqueous brines

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Leaching of halite from mineral deposits by solution mining is a technology with worldwide application. For the salt industry, only the valuable components in the mineral deposit must be dissolved and removed to the surface for further processing. Inevitably, several minor impurities, such as calcium sulfate minerals, are also leached and the out-coming contaminated brine must be subject to costly purification treatments. Therefore, the inhibition of the dissolution of calcium minerals is a subject with scientific interest and potential economic impact. The dissolution of anhydrite in saturated brines of sodium chloride may be inhibited by the presence of water-soluble macromolecules, being the effectiveness of the inhibitor evaluated from the degree of coverage of the target surface and the desorption resistance. The ideal macromolecule, besides being selective towards anhydrite, should not harm the morphologic characteristics of the main salt in downstream crystallizations.

In this study, the influence of some selected anionic surfactants on the solubility of gypsum, anhydrite and anhydrite-rich sediments in concentrated brines was investigated.

Introduction

Although the prevention of calcium sulfate scale formation has received a lot of attention from industry and research, studies concerning the inhibition of dissolution of calcium minerals in aqueous brines are scarce. Effective inhibitors are usually good sequestering agents for the lattice cations and it is generally accepted that they exert their action through adsorption at cationic sites on the solid surfaces. Additives may also adsorb upon crystal faces, reducing the rate of dissolution. Since the molecular interactions at the inorganic/organic interfaces depend on the size, ionic charge and structure of the admixture, Nancollas and Zawacki (1984), small molecules with high charge density will interact with charged solids. The concentration and size of the inhibitor molecule are important parameters because the inhibition of dissolution requires a considerable coverage of the surfaces. Anionic surfactants with negative charged head groups seem to have a strong blocking effect upon the dissolution of calcium minerals, according to Mahmoud et al. (2004). The effectiveness of adsorption is inversely proportional to the minimum area demand per molecule, thus making of single-chained surfactants potential good inhibitors. It is not clear, however, to what extent the salts present in the solution affect the inhibitor performance.

Within the scope of this study, the effect of some selected anionic benzene sulfonate surfactants on the dissolution of different forms of calcium sulfate are here reported. Because the length of the chain determines the physicochemical behavior of surfactants in solution, representatives of C_8, C_{12} and C_{12}/C_{13} anionic surfactants were studied. Both the acid and the sodium salt forms of the polar head group were considered for some of these surfactants.

Materials and methods

Three different forms of calcium sulfate were used in the study. The samples of anhydrite-rich sediments, $CaSO_4 \geq 42\%$ (w/w), from three salt dissolution caverns under leaching,

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belonging to the Porto de Mós diapir (Hetangian formation), were kindly provided by REN, Portugal. Gypsum and anhydrite were commercial products with particle mean size < 10 μm and BET surface area of 1.9 and 1.7 m^2/g, respectively. Four anionic surfactants with hydrophilic head group of the benzene sulfonate (BS) type were used. OBS (Na, octyl BS), DBS (Na, dodecyl-BS) and ADBS (dodecyl-BS acid) were purchased from Sigma-Aldrich. A commercial acid surfactant, a mixture of branched and straight chained alkyl, mainly C_{12} and C_{13}, here referred to as D550, was kindly supplied by InChemica, Portugal. Analytical grade sodium chloride, Riedel-de Haën (> 99.8 %), and deionized water were used to prepare the brines by mass to ± 0.01 g. The maximum overall uncertainty in the concentration of the surfactants' stock solutions was ± 0.3 mg L^{-1}.

Anhydrite-rich sediments from 3 different salt caverns under leaching, hereafter referred to as S1, S2, and S3, were used in the experiments. Prior to use the sediments were air-dried, homogenized and sieved. The mean superficial diameter of the solids, calculated from the size distributions, was 52 μm for S1 and S3, and 74 μm for S2, being the BET surface areas 0.4 and 0.2 m^2/g, respectively. Zeta potential measurements showed that all the sediments are negatively charged, ca. – 11 mV.

The mineralogical composition of the sediments was confirmed by X-ray diffraction and FTIR spectroscopy (4000-400 cm^{-1}) and stereo and polarizing microscopy showing the presence of halite, anhydrite, low quartz, carbonate minerals (dolomite, ankerite) and minor contents of clay (clinochlore), organic and inorganic carbon, gypsum, muscovite and pyrite.

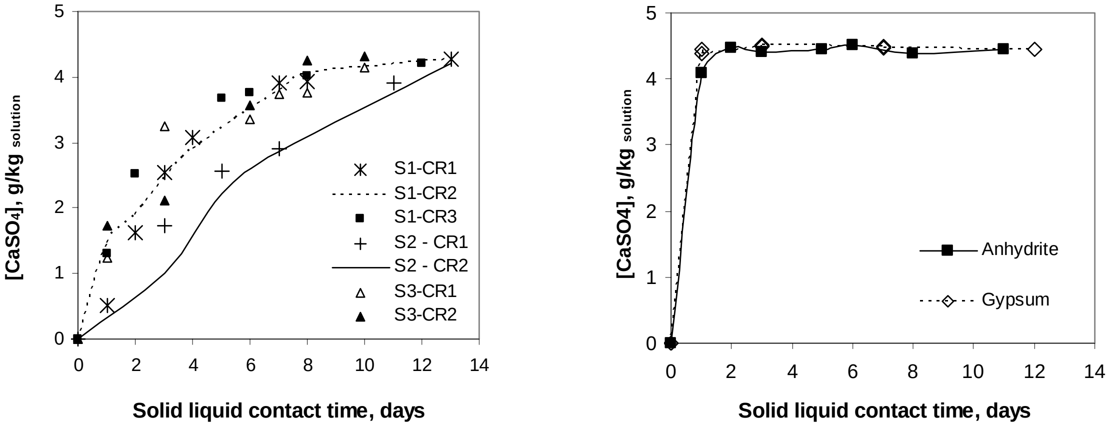
Samples of about 6 to 17 g/L of three forms of solid calcium sulfate, gypsum, anhydrite and anhydrite-rich sediments, together with sodium chloride were equilibrated in aqueous solutions with a surfactant concentration ranging from 0 to 73 mg/kg of saturated brine. Although an excess of solid halite was used in most of the runs to mimic the salt caverns environment, the influence of the degree of saturation of the leaching agent was also evaluated. The plastic flasks were shaken for 7 to 14 days in an orbital shaker, at room temperature. Periodically, the solutions were sampled for analysis. After a settling period of about 3 h, liquid samples were collected with a syringe, equipped with a 0.45-μm filter, and aliquots of the liquid were analyzed for calcium content (S.M. 3500-Ca B. "EDTA Titrimetric Method"). The reported concentrations are the mean values of duplicate analyses on each sample. The content of sulfate ion in the samples was also regularly determined (S.M. 4500 SO42- E. "Turbidimetric Method"), as a cross check for the calcium analysis. At the end of each run, the slurry was filtered and the solids air-dried and weighed. The residual solutions and solids were subsequently analyzed for the content of surfactants (MBAS standard method). Blank runs were carried out to account for the natural variability of sediments composition and for the dependence of calcium sulfate solubility on temperature and NaCl content in the brines. In each series of experiments the effect of the surfactants on the dissolution of the calcium salt was assessed against the corresponding control run.

In order to interpret the behavior of the selected surfactants the surface tension of concentrated NaCl brines (300 g/kg_{water}), with and without admixtures, was determined with a Du-Noüy tensiometer equipped with a Pt ring. All measurements were performed after a 30-min period of equilibration at constant temperature. The tensiometer was previously calibrated against water and NaCl solutions (up to ≈ 6 m), at 298 K.

Results and Discussion

Figure 1 presents the change of calcium sulfate concentration in saturated brines as a function of time, for the three forms of salt studied. The reported rates of dissolution, measured in the presence of solid halite, represent the average values of at least duplicate measurements.

For sediments S1 and S3, Figure 1a, the saturation concentration was reached after one week, whereas for the pure forms of calcium sulfate, Figure 1b, this value was attained in about 24 h. Sediments S2, the coarser of the solids tested, were the slower to dissolve. The results show that both the availability of the calcium salt in the solid and the size of the particles play an important role on rate of dissolution of the calcium mineral.



(a) (b)

Figure 1- Rate of dissolution of different forms of calcium sulfate in saturated brines

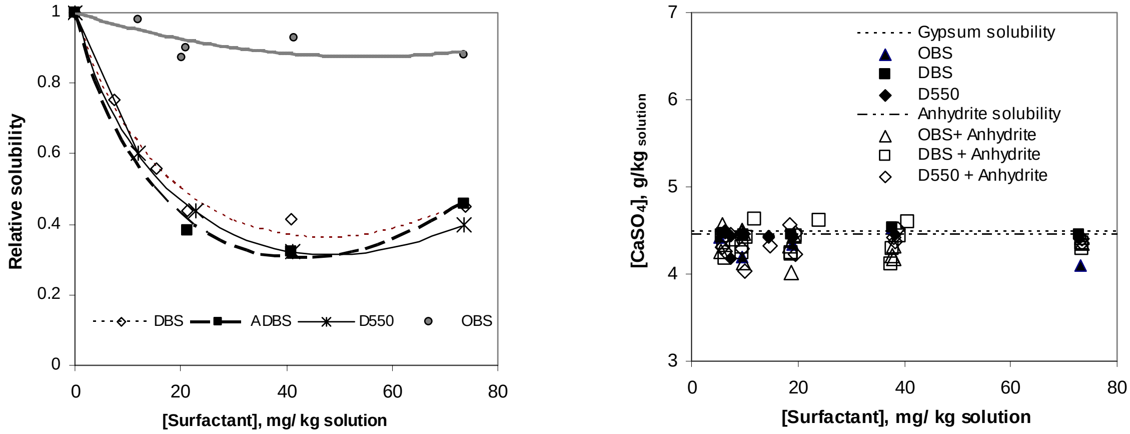
In order to determine how the selected C_8, C_{12} and C_{12}/C_{13} anionic benzene sulfonate surfactants influence the dissolution of calcium sulfate, a total of 76 independent runs were carried out. The decrease of the content of calcium sulfate in solution was evaluated by the relative solubility calculated, for each data point, as the ratio of calcium content in the solution and in the parallel blank run.

Figure 2a illustrates the effect of the type and concentration of the selected anionic surfactants on the calcium sulfate content, after 14 days of curing in slurries of sediments and halite. The chain's length of the organic molecule clearly determines the admixture effectiveness, as a dissolution inhibitor for the calcium mineral, being the effect of the C_8 surfactant, OBS, almost negligible. The type of the head group of the linear C_{12}-BS surfactants (acid for ADBS and sodium salt for DBS) had no significant influence on the solubility reduction. The curves also indicate that, independent of the C_{12}-surfactant type, the maximum reduction in dissolution (≅ 70%) was obtained in slurries containing an initial concentration of about 40 mg/kg$_{\text{solution}}$ of the admixtures. For higher contents, the blocking effect of the surfactants decreases. Oppositely, Figure 2b shows that the tested surfactants had no effect whatsoever on the dissolution of either the hydrate or the non-hydrate calcium sulfate. This behavior stems most probably from a very different order of magnitude between the rates of dissolution and of solid shielding by the surfactants.

The inhibitor effect of the C_{12} and C_{12}/C_{13} surfactants becomes more apparent as the residence time increases, as shown in Figure 3 for DBS and D550. The dissolution of calcium sulfate in the blank run continues up to saturation, whereas in the presence of the surfactants the process is effectively blocked, resulting in a decrease of the relative solubility.

The rate of leaching of the salt caverns determines the concentration of the out- coming brine. The injected water containing the added admixtures is gradually enriched in sodium chloride as the residence time increases, becoming saturated if enough time is allowed. Therefore, to examine the influence of the NaCl content in the admixed solutions upon the rate of the dissolution of the sediments, a series of experiments was carried out using as leaching agents aqueous solutions of DBS and near-saturated NaCl brines (350 g/kg water) containing the same surfactant or its acid form (ADBS).

The results thus obtained are compared in Figure 4 with the relative solubility of calcium sulfate measured in the presence of solid halite. It is clear that the leaching agent, water+surfactant, does no hinder de dissolution of the anhydrite-rich sediments before it becomes enriched in sodium chloride. In near-saturated brines even small concentrations of the admixtures are effective in blocking the dissolution of anhydrite, the equilibrium calcium content in the solution representing 20 to 30% of the blank run concentration. However, it is worth noting that in the presence of solid halite - a more realistic approach to a salt cavern environment - the hindering effect is less pronounced, a fact that might be explained by the existence of a much larger solid surface area to which the organic molecules will indistinctly adhere.



(a) Sediments

(b) Gypsum and anhydrite

Figure 2 - Effect of the type and concentration of OBS, DBS, ADBS and D550 on the dissolution of calcium sulfate after 14 days of curing

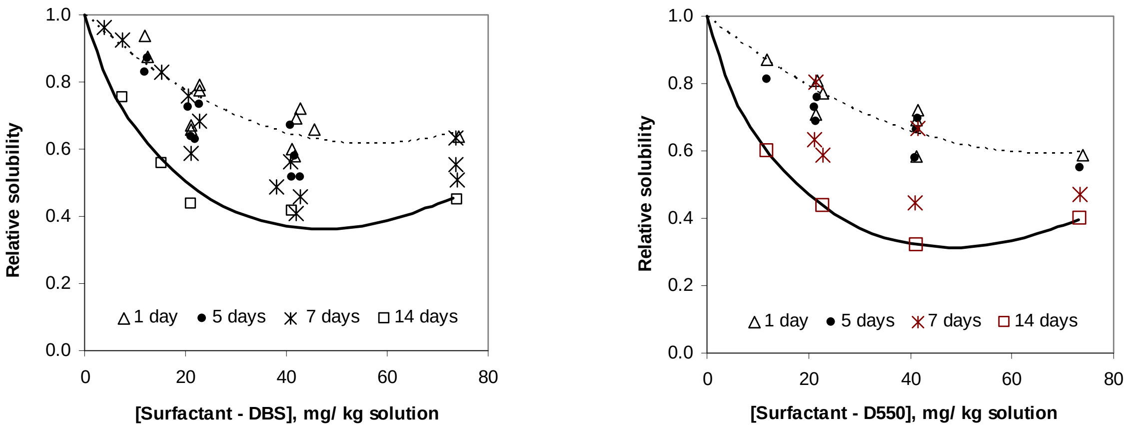


Figure 3 – Influence of the solid-liquid contact time on the dissolution of sediments S3 for several initial contents of two C_{12}BS surfactants

In order to get a better understanding of the observed phenomena, the surface tension of the near-saturated brines containing the studied surfactants was measured at 298 K. Minute amounts of the admixtures originated a sharp reduction in the solution surface tension, but beyond a limiting concentration, which coincided with the appearance of solution opalescence, no further change in this quantity was detected. This surge of turbidity, which represents the onset of a macroscopic phase separation, occurred at concentrations of 0.9, 0.8, 1.4 and 2.3 mg/L for OBS, D550, ADBS and DBS, respectively. It can, therefore, be inferred from these results that during the equilibration of the sediments+halite solid mixtures in the leaching solutions a phase separation will occur, as soon as a high ionic strength is reached. As a consequence of the rejection of the organic phase, the content of the monomers in the leaching solution will remain nearly identical to the clouding concentrations measured. The rejected phase will tend to adhere to the solid surfaces existing in the slurries, thus acting as an organic barrier to the solids' dissolution.

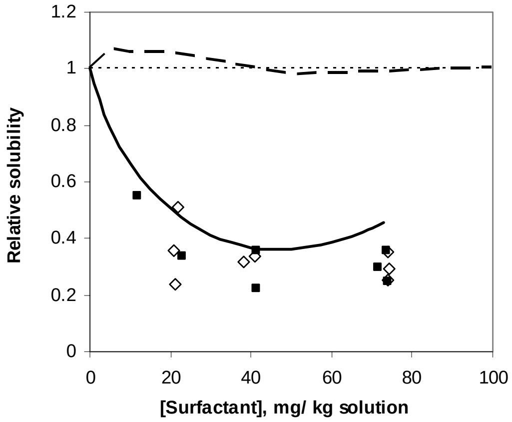
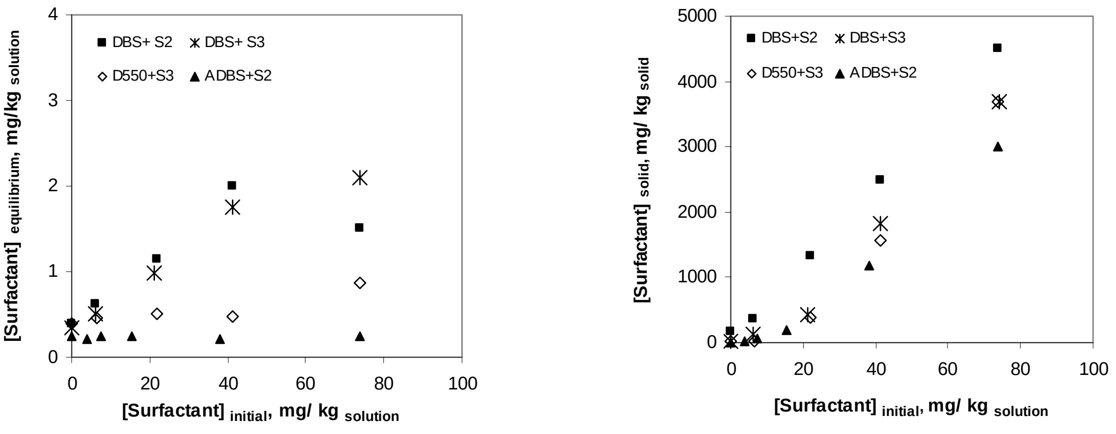


Figure 4- Influence of salt concentration on the solubility reduction of calcium sulfate after 14 days of contact. Lines: broken - DBS in water. Solid - DBS in brines with solid halite. Symbols. Surfactants In near-saturated brines: ■ ADBS; ◇ DBS.

The surfactant contents in the saturated solutions equilibrated during 7 days with anhydrite-rich sediments, shown in Figure 5a, were found to be slightly lower than the corresponding clouding concentrations measured in pure NaCl solutions. These results may indicate that some precipitation of calcium or sodium salts of the benzene sulfonate detergents occurred in the saturated brines. The amount of additives adhering to the anhydrite-rich sediments, Figure 5b, was nearly independent of the type of C_{12}BS surfactants, as well as of the substrata. Due to the negative charge of sediments, electrostatic interactions between the negatively charged head groups and the solid surfaces were ruled out as a possible explanation for the high contents of the admixtures adhering to the sediments.



(a) (b)

Figure 5 – Surfactants concentrations in the (a) liquid and (b) solid phases at equilibrium after 7 days of curing.

The surfactants are also retained by the halite crystals, Figure 6, although in a much lesser extent than by the sediments. The coverage of the salt, and the consequent decrease in its equilibrium concentration, may help explaining the apparent loss of effectiveness of the surfactants for a content of 73 mg/kg$_{solution}$. Because the equilibrium concentration of calcium sulfate varies inversely with the content of sodium chloride at elevated concentrations of the latter, the relative solubility for $CaSO_4$, used as the evaluation tool for the surfactant performance, will increase only because the reference blank run is not affected by the same phenomenon.

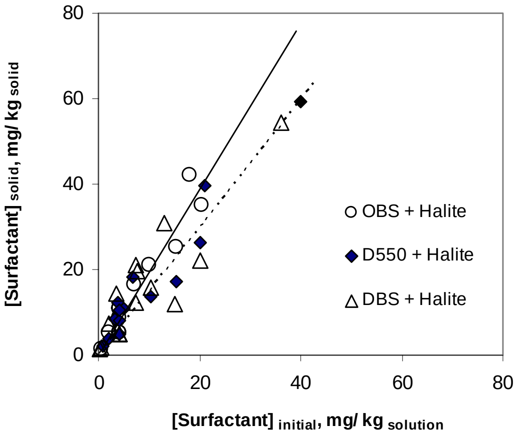


Figure 6 – Surfactants retention in halite crystals after 7 days of solid-liquid contact

Conclusions

Leaching of anhydrite-rich sediments with aqueous solutions of anionic C_{12}-benzene sulfonate surfactants reduces significantly the solubility of calcium sulfate. A maximum reduction of ≅70% was observed in the presence of halite, using brines containing about 40 mg/kg solution of the additives. The type of the surfactant head group (acid or sodium salt) does not influence the detergent performance, but the chain's length of the organic molecule is of importance to the hindering of calcium sulfate dissolution. The availability of the calcium salt in the solid, as well as the size of the "insoluble" debris within the cavern, play an important role on rate of dissolution of the calcium mineral and, therefore, on the contamination of the outcoming brine.

The reduction of the calcium sulfate equilibrium concentration from the negatively charged sediments cannot be attributed to electrostatic interactions between the solid surfaces and the charged head groups of the anionic surfactants. However, the behavior of the C_{12}BS surfactants may be interpreted in terms of the balance between the electrostatic repulsive forces of polar head groups and the attractive forces due to hydrophobic interaction. Aggregation of surface-active molecules stems from the insolubility of the non-polar moiety of the surfactant in the solution. The opposing hydrophilic interactions between polar head groups must be strong enough to ensure the self-assembly of the amphiphile. However, above a certain ionic strength threshold, the hydrophilic interactions are shielded, the driving force to expel the hydrophobic groups from solution augments and macroscopic phase separation occurs, Jönsson et al (1998). It can, therefore, be inferred from the results here obtained that for the examined surfactants a phase separation occurred in the saturated brines. The expelled organic phase, by adhering to the solid surfaces in the slurries, acts as a barrier to the dissolution of the mineral impurities.

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