Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials

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A B S T R A C T

Adsorption of cationic and anionic surfactants on carbonate materials is investigated in this study. Cetyl-pyridinium chloride (CPC) and sodium dodecyl sulfate (SDS) are chosen as typical cationic and anionic surfactants, respectively. It is found that the cationic CPC exhibits negligible adsorption on synthetic calcite in deionized water compared with the adsorption of the anionic SDS. However, a substantial amount of adsorption of CPC is observed on natural carbonates, such as dolomite and limestone. X-ray photoelectron spectroscopy (XPS) reveals that that a substantial amount of silicon and aluminum exists in natural dolomite and limestone but not in synthetic calcite. The adsorption plateau of CPC on carbonates highly depends on the silicon composition in the carbonate samples due to the strong electrostatic interaction between CPC and negative binding sites in silica and/or clay. The adsorption of CPC on natural carbonates is reduced in the presence of 1 atm CO_2 compared with the case under 1 atm air, while SDS precipitates out of the solution under 1 atm CO_2 due to its intolerance to divalent ions released from the carbonate surface as a result of CO_2 acidification.

1. Introduction

Surfactants are commonly used in enhanced oil recovery (EOR) processes for various purposes, including reduction of oil/water interfacial tension, wettability alteration, and foam generation [1]. Examples of these processes were reported in the literature such as high-temperature, high-salinity surfactant flooding [2,3], alkaline/surfactant/polymer (ASP) flooding [4–6] and foam mobility control [7–12]. Different EOR processes require different strategies to optimize the surfactant selection, and the choice of surfactants highly depends on the conditions of oil reservoirs. Among all different surfactant-based EOR processes at various conditions, a critical requirement for surfactants is that adsorption on reservoir formation be low to ensure effective propagation of the surfactants in porous media. High adsorption on reservoir formation leads to chromatographic retardation of the surfactants when they transport through a reservoir, making the designed EOR processes inefficient and economically unfeasible.

Oil reservoirs are generally divided into two categories based on the formation rocks: sandstone and carbonate. In sandstone reservoirs, anionic surfactants are usually preferentially employed due to the relatively low adsorption compared with other types of surfactants (cationics, nonionics and zwitterionics) [13–16]. Typical sandstone contains large amount of quartz (silica, SiO_2) and small amount of carbonate and silicate minerals [14,17], and the composition depends on the sedimentology of the reservoir formation. Electrostatic interactions play a governing role over other forces in surfactant adsorption in systems where both the surfactants and the solid surface are charged [18]. Silica bears negative charge over a large range of pH (the isoelectric point (IEP) of silica is 1.7–3.5 [19]) and the electrostatic repulsion between the formation and the anionic surfactants inhibits the adsorption [20]. However, some clay minerals (mainly kaolinite and illite) in sandstone may cause certain amount of adsorption of anionic surfactants [17,21] because of the heterogeneous surface charge in clay [22,23]. In this case, the adsorption is dependent on how the clay minerals spread over the surface of sandstone.

In carbonate reservoirs, the surface chemistry of carbonates in aqueous solutions has an important influence on surfactant adsorption. Complex dissolution behavior was found in the salt-like minerals in carbonate formations, such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) or magnesite ($MgCO_3$) [24–27]. The electrokinetic data of the IEPs of calcite were summarized by Wolthers et al., which ranged from 7.8 to 10.6, and were even undetermined (always positive or negative charged) in some cases within this range of pH [27]. The value of the IEP of calcite depends on the sources of materials, the equilibrium time, and the ionic strength in aqueous solutions. Given the same ionic strength (10^{-3} mol dm^{-3} NaCl) in the pH range of 7–11, it was found that the natural calcite (Polcarb, ECC International) was more negatively charged than the synthetic calcite (Socal-U1, Solvay, UK) [28]. It

was thought that a very small amount of impurities (clay and/or silica) possibly led to significant changes of the zeta potential of calcite in aqueous solution [29].

The complication of surface charge on carbonates makes it challenging to determine whether anionic or cationic surfactants should be used to minimize electrostatic interactions between the surfactants and the formation surfaces. Tabatabai et al. [30] performed static adsorption experiments to compare the adsorption of anionic and cationic surfactants on carbonates. An anionic surfactant, sodium dodecyl sulfate (SDS), and two cationic surfactants, cetylpyridinium chloride (CPC) and dodecylpyridinium chloride (DPC), were evaluated on natural dolomite (Ward Scientific, Salasvann, Norway) and synthetic calcite (Aesar, Johnson Matthey Inc., USA) powder. Their results showed that CPC/DPC exhibited significantly less adsorption on both dolomite and calcite than that exhibited by SDS without adjusting pH in the solutions. It was also shown that divalent ions, such as Ca^{2+} and Mg^{2+}, can reduce the adsorption of CPC/DPC on carbonates. In their study, CPC showed negligible adsorption on synthetic calcite powder compared with SDS, and the presence of 0.05 M $CaCl_2$ or $MgCl_2$ turned the adsorption of CPC on calcite to be negative. The presence of divalent ions makes the surface of carbonates more positively charged, and the coulombic interactions repelled CPC from the interfacial region. However, negative adsorption was not observed in the case of DPC on either dolomite or calcite.

Other researchers, however, did not show the advantage of low adsorption on carbonates using cationic surfactants instead of anionic surfactants. For example, on an ordinary garden grade limestone, the adsorption plateaus of the cationic surfactants decyltrimethylammonium bromide (C_{12}TAB) and tetradecyltrimethylammonium bromide (C_{14}TAB) were 5.70×10^{-7} mol/g and 8.25×10^{-7} mol/g, respectively; while the adsorption plateaus of the anionic surfactants monosodium monodecyldiphenylether monosulfonate (MAMS) and disodium didecyldiphenylether disulfonate (DADS) were 1.07×10^{-6} mol/g and 5.12×10^{-7} mol/g, respectively [31]. In their work, it was also shown that the molar adsorption on limestone of the cationic gemini surfactants was much larger than that of their corresponding conventional surfactants due to the increased hydrophobic interaction between the hydrophobic chains of the surfactants. Another work showed an adsorption plateau of 6.9×10^{-6} mol/m^2 (2.51 mg/m^2) for the cationic cetyltrimethylammonium bromide (C_{16}TAB) on limestone (containing 99% calcium carbonate) in deionized water [32]. This value was a substantial amount of adsorption, which was higher than the adsorption of some ethoxylated anionic surfactants on synthetic calcite, such as alkyl aryl ethoxylated sulfonated phenol (Oil Chem 4-22, adsorption plateau 0.9 mg/m^2) and alkyl aryl ethoxylated sulfonate (Oil Chem SS6566, adsorption plateau 1.3 mg/m^2) [33]. A recent study showed higher adsorption of C_{16}TAB than SDS on either natural magnesite (magnesite mine Grochow, lower Silesia, Poland) or natural dolomite (old quarry Kletno, lower Silesia, Poland) in a low-salinity solution containing 10^{-4} M NaCl [34]. Based on the isotherms reported in their study, the adsorption plateaus of C_{16}TAB were 6.9 and 5.8 mg/m^2 on magnesite (pH = 8.5) and dolomite (pH = 10.4), respectively; while the adsorption plateaus of SDS were 1.1 and 2.2 mg/m^2 on magnesite and dolomite, respectively. Chemical analysis showed that the magnesite and dolomite used in their work contained 88% and 98% of carbonates, respectively.

These puzzling results indicate that the source of carbonate materials can have an important impact on ionic surfactant adsorption, and cationic surfactants may not have low adsorption if the material is not pure carbonate. For example, higher adsorption of octadecyltrimethylammonium bromide (ODTMA) (cationic) is observed compared with that of SDS (anionic) on various clay minerals such as montmorillonite and illite [35]. If abundant silica

and/or clay exist in carbonate formation, a substantial amount of adsorption of cationic surfactants may be expected. To understand the mechanism of surfactant adsorption on carbonates and guide the selection of surfactants for EOR processes in carbonate reservoirs, we investigate the adsorption of cationic and anionic surfactants with various carbonate materials, including natural and synthetic carbonate. Possible impurities in natural carbonate, such as silica and clay, are also investigated in this study. The surface charge and the surface chemistry are characterized in various materials to identify the binding sites for cationic and anionic surfactants.

2. Materials and methods

2.1. Materials

Hexadecylpyridinium chloride monohydrate [$C_{21}H_{38}ClN \cdot H_2O$] (CPC) and sodium dodecyl sulfate [$CH_3(CH_2)_{11}OSO_3Na$] (SDS) are supplied by Sigma–Aldrich. CPC is a cationic surfactant and SDS is an anionic surfactant.

Four natural carbonate materials, including dolomite and limestone, are used in this work. The particle size in terms of the diameter, surface area, ζ-potential and source of these materials are listed in Table 1. The particle size is obtained from either sieve sizing in the laboratory (for dolomite and limestone) or the material safety data sheet provided by the manufacturer (for calcite, silica and kaolin). To distinguish different sources of the carbonate samples, the dolomite samples supplied by Vital Earth/Carl Pool and Sciencelab.com, Inc are referred as dolomite (Carl Pool) and dolomite (Sciencelab.com), respectively. The limestone samples supplied by Franklin Minerals and Carthage Crushed Limestone are referred as limestone (Franklin) and limestone (Carthage), respectively.

Chemical-grade synthetic calcium carbonate (99.5% metals basis) powder supplied by Alfa Aesar is used a standard calcite sample. According to the manufacture, this calcite sample has a uniform size of 5 μm. Fine round silica flour (MIN-U-SIL10, U.S. Silica Company) is used as a representative silica [SiO_2] material. In order to remove Fe_2O_3 and other metal oxides in the original sample, the silica flour is washed with 1 mol/L HCl, 0.01 mol/L $NaHCO_3$ solution and deionized water sequentially and is dried in a convection oven at 80 °C overnight prior to use. Kaolin [$Al_2Si_2O_5(OH)_4$] powder (Sigma–Aldrich) is used as a typical clay material in this study.

The BET (Brunauer–Emmett–Teller) surface areas of the samples are measured using a Quantachrome Autosorb-3b BET Surface Analyzer. This instrument utilizes multipoint BET to fit experimentally measured data (11 data points for each sample) using nitrogen as the adsorbate gas. The correlation coefficients for the fit to all samples are larger than 0.999. The results are shown in Table 1.

2.2. Static adsorption experiments

CPC and SDS are dissolved in deionized water at various concentrations to serve as initial surfactant solutions, respectively. The adsorbent material is mixed with surfactant solution in 50-mL centrifuge tubes at various weight/volume ratios to obtain different data points on the adsorption isotherm. For the experiments in the presence of 1 atm CO_2, CO_2 is loaded to the system by repeatedly applying CO_2 above the surface of the solution in the centrifuge tube at a gauge pressure of 3.4 kPa for one minute to remove residual air in the gas phase and shaking the tube for five seconds after the cap of the centrifuge tube is closed. The chemical equilibrium with 1 atm CO_2 is approached by repeatedly performing this CO_2-displacement and tube-shaking procedure until a sta-