Colloids and Surfaces A 535 (2017) 75–82

Contents lists available at ScienceDirect

Colloids and Surfaces A

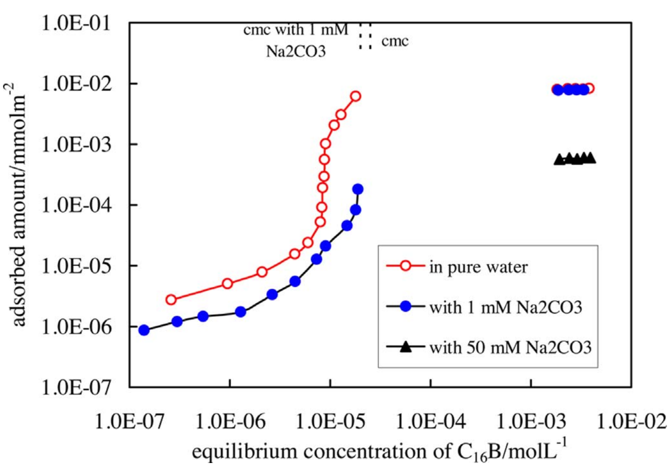
journal homepage: www.elsevier.com/locate/colsurfa

Inhibiting hydrophobization of sandstones via adsorption of alkyl carboxyl betaines in SP flooding by using gentle alkali

Xin Hu, Dan Qi, Limin Yan, Zhenggang Cui*, Binglei Song, Xiaomei Pei, Jianzhong Jiang

The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi, Jiangsu 214122, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Enhanced oil recovery
Inhibiting hydrophobization
Carboxyl betaine surfactants
Adsorption
Wettability
Sandstone

ABSTRACT

Alkyl carboxyl betaines are good surfactants for reducing crude oil/connate water interfacial tension but may turn negatively charged sandstone surfaces to oil-wet at low concentration via in situ hydrophobization. This effect can be inhibited by adding trace amount of gentle alkali such as Na_2CO_3 into surfactant solution, where the OH^- ions shield the positive charges in alkyl carboxyl betaine molecules and thus reduce their adsorption at sandstone/water interface via electrostatic interaction with head-on orientation. The mechanisms relative were revealed by measuring adsorption isotherms of the surfactants and contact angles of water/oil on the negatively charged surfaces.

1. Introduction

It is well known that enhanced oil recovery has been a sustained subject worldwide, especially in China [1–4], where more than 60% of the crude oils consumed are imported and the outputs of the local giant oil fields show a naturally decreasing tendency [5]. On the other hand there remains large amount crude oil (~60% OOIP) underground after water flooding, which are trapped in porous rocks as oil droplets by capillary force. [4,6,7]. An effective method to recover these oils is to use surfactants to reduce crude oil/water interfacial tension (IFT) to

* Corresponding author.
E-mail address: cuizhenggang@hotmail.com (Z. Cui).

http://dx.doi.org/10.1016/j.colsurfa.2017.09.021
Received 22 July 2017; Received in revised form 12 September 2017; Accepted 14 September 2017
Available online 15 September 2017

ultra low (< 0.01mN/m) so that the oil can mobilize towards production well under water flooding pressure [4,8]. Among various surfactant flooding protocols including microemulsion flooding [9–11], alkali flooding [4], alkali-surfactant flooding and alkali-surfactant-polymer (ASP) flooding [3,4,8,12–14], the ASP flooding has been paid more attention due to its technical and economical efficiencies [4,8], where a low surfactant concentration (< 0.5 wt.%) is sufficient thanks to the synergisms between surfactants, alkali, and polymers [4,15,16].

Nevertheless some side effects of using caustic alkali in ASP flooding [4,17] has been revealed in pilot tests, such as scaling and corrosion of equipment and pipelines, as well as reduction of core permeability, due to formation of insoluble substances by reaction of the caustic alkali with components in rocks and connate water. [8] Using weak or organic alkalis to replace caustic alkalis [4,8,17–19] or using SP flooding free of alkali [4,8,17,20–29] have been suggested. It has also been noticed that in absence of alkali the surfactants should have higher hydrophobicity than those used in ASP flooding to compensate the decrease of ionic strength in aqueous phase [30] and lack of the synergism between alkali and surfactants. For this purpose the hydrophobic surfactants with either a branched hydrocarbon chain or double long hydrocarbon chains are effective, [20,23,24,29,31–34], and the zwitterionic surfactants, both alkyl carboxyl betaines and alkyl sulfobetaines, are superior to anionic and nonionic surfactants in reducing crude oil/connate water IFT thanks to their high adsorption at oil/water interface [29,31–38].

In SP flooding, however, the high adsorption of surfactants at oil/water interface and the achieving of ultra low IFT can not ensure a high recovery. The adsorption retention of surfactants and its effect on the wettability of the sandstone surfaces are also crucial [39]. The adsorption especially selective adsorption of mixed surfactants by sandstone results in not only a loss of surfactants and chromatographic separation of mixed surfactants, but also a possible alternation of the wettability of the sandstone surfaces, depending on the orientation of the surfactant molecules at sandstone/water interface. In case of head-on orientation, the sandstone surfaces may be turned to hydrophobic due to the hydrophobization [40] which is unfavorable for obtaining a high oil recovery [39,40].

Studies [41–46] have indicated that the adsorption of surfactants at various solid/water interfaces may be driven by electrostatic attraction, ion-exchange, covalent bonding, chain–chain interaction, hydrogen bonding, hydrophobic bonding, as well as solvation of various species [45,46]. Specifically in case of Daqing sandstone, which is composed of various rocks (90%) and clays (10%) and is negatively charged in aqueous phase [40], the cationic surfactants are not suitable due to their high adsorption retention and *in situ* hydrophobization [40,47]. Although the anionic and nonionic surfactants show lower adsorption retention and no hydrophobization, they behave poor in reducing crude oil/connate water IFT in absence of alkali. On the other hand the carboxyl betaine surfactants behave much better in reducing crude oil/connate water IFT [29,37], but show high adsorption and hydrophobization at low concentration (< cmc) similar to cationic surfactants even in neutral aqueous media [40]. Although the surfactant concentration practically used is far higher than cmc, the hydrophobization will eventually occur due to the depletion of surfactants by sandstone adsorption. To take advantage of the alkyl carboxyl betaines in reducing IFT in SP flooding, it is quite crucial to inhibit their adsorption at sandstone/water interface and the hydrophobization to the sandstone surfaces. In a previous study we have found that by adding a poly alkyl ammonium bromides, $N^1,N^{1'}$-(propane-1,3-diyl) bis (N^1,N^1,N^3,N^3,N^3- pentamethylpropane-1,3- diaminium) bromide, abbreviated as tetra-N(3)-Br, the adsorption of the alkyl carboxyl betaines at the sandstone/water interface and the corresponding hydrophobization to the sandstone surfaces can be significantly inhibited. In the present study we report that similar inhibiting effect can be achieved by adding trace amount of gentle or weak alkali such as Na_2CO_3 into the aqueous solution, where the positive charges in carboxyl betaine molecules are shielded by OH^- and thereby reduction of the electrostatic interaction between the positive charges and the negative charges on sandstone surfaces, whereas the IFT is not significantly affected. The use of trace amount of gentle alkalis in SP flooding is therefore beneficial for achieving a high oil recovery [4,8,17–19].

2. Experimental

2.1. Materials

Mono-alkyl dimethyl carboxyl betaines (C_nB, n = 12–18) were supplied by Solvay (Zhangjiagang) Specialty Chemicals Co. Ltd. as aqueous pastes with an active matter content between 30 wt.% and 20 wt.%. Didodecyl methyl carboxyl betaine ($diC_{12}B$) was synthesized by carboxymethylation [29] of the corresponding tertiary amines from Solvay (Zhangjiagang) Specialty Chemicals Co. Ltd. as an aqueous paste with an active matter content of 50 wt.%. These alkyl carboxyl betaines were purified by removing salts and un-reacted tertiary amines as described elsewhere [29,40] and collected as solid powders with a purity higher than 98%. The molecular structure of these surfactants is given in Table S1 in supporting information. Sodium dodecyl sulfate (SDS) and Hyamine 1622 (both 99% purity, for two-phase titration) were purchased from Sigma and used as received. *n*-Decane with a purity of 98% was purchased from Aladdin, China. Other chemicals such as Na_2CO_3, NaOH, and NaCl, as well as various solvents, are all analytical pure and were from various sources.

Glass slides of 25 × 75 mm was purchased from Sinopharm Chemical Reagent Co. Silica nanoparticles, HL-200, with a purity > 99.8% and a BET surface area of 200 ± 20 m^2/g was provided by Wuxi Jinding Longhua Chemical Co., China. Micro-sized silica particles of 99.9% purity with a primary diameter 10 μm and a BET surface area of 0.807 m^2/g was purchased from Aladdin, China. Natural core discs with a diameter of 25 mm and a thickness between 8–10 mm were cut from a cylindrical natural core (after water flooding) from Daqing oil field. Sandstone powders with a size of 65–100 mesh, which are composed of approximately 90% rocks and 10% clays [40], were obtained by crushing the nature cores followed by washing with benzene–ethanol (3:1) mixture, drying, milling, and sifting. They together with the crude oil and connate water were provided by the Laboratory of Oil Recovery, Institute of Petroleum Exploring and Development of Daqing, China.

2.2. Methods

2.2.1. Contact angle measurement

The contact angle of water or aqueous solution on negatively charged surfaces adsorbed carboxyl betaine surfactants was measured by captured oil drop method using glass slides and core discs as solids. The glass slides were cut to pieces of 25 × 15 mm, which were immersed in 30 wt.% NaOH aqueous solution for 24 h, followed by rinsing with pure water and drying naturally. Then a piece of the glass slide or part of a core disc (cut from a core disc) was put in a glass cell (35 mm (L) × 25 mm(D) × 15 mm(H)) supported by a pair of glass trestle at two ends, and the cell was filled with aqueous solution of a surfactant until the slide piece/core disc was immersed. After 24 h (for reaching adsorption equilibrium) an oil (*n*-decane) drop was released from a U-shaped needle, which was captured by the solid to form an inverted sessile drop. The image of the drop was recorded and the contact angle of the aqueous phase was calculated using software. For each solution at least three angles were measured and their average was taken as the result. The glass cell together with the apparatus was set in a plastic box with the temperature inside controlled at 25 °C/45 °C by an Air-them heater (World Precision Instrument).

2.2.2. Adsorption isotherm of surfactants at particle/water interface

Surface tension method/silica nanoparticles and two phase-titration