

A model study of enhanced oil recovery by flooding with aqueous solutions of different surfactants: how the surface chemical properties of the surfactants relate to the amount of oil recovered.

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ABSTRACT

The main aim of this work is to establish how the fraction of oil recovered from an oil-filled calcite powder packed column by injection of aqueous surfactant solution depends on the phase behaviour and surface chemical properties of the surfactant system. We have measured the phase behaviour, the adsorption of surfactant to the oil-water, calcite-water and calcite-oil interfaces, tensions and contact angles for anionic, cationic and non-ionic surfactant/oil/aqueous phase systems. We show how the measured surface chemical properties can be used to approximately predict the fraction of oil recovered as a function of the volume and concentration of the surfactant solutions injected into the column. Measured and calculated plots of %oil recovery versus surfactant concentration show reasonably good agreement for the different surfactant systems. The experimentally-validated model for oil recovery provides a sound basis for the rational selection of surfactant type and concentration to achieve maximum oil recovery based on laboratory measurements of the surface chemical properties of candidate surfactants.

INTRODUCTION

In primary oil recovery, oil is released from the reservoir as a result of the high initial pressure in the reservoir. Further oil is released in secondary recovery by increasing the reservoir pressure by injection of water. Following these processes, it is common for more than 50% of the total oil in the reservoir to remain unrecovered. The residual oil is hard to remove since it is held within the porous reservoir rock by capillary forces. Further increasing the reservoir pressure by water injection does not remove this capillary trapped oil, mainly because of flow bypassing due to heterogeneous permeability within the porous reservoir rock structure. A range of tertiary recovery methods can be used to release additional fractions of the residual oil trapped by capillary forces; in this work we focus on enhanced oil recovery (EOR) by injection of aqueous surfactant solution into a reservoir with a porous rock structure containing capillary-trapped oil. Previous studies of surfactant EOR include reviews and comparisons of the EOR performance of different surfactant formulations¹⁻⁹, how pore structures may be partially wetted by both oil and water following primary and secondary recovery processes and how subsequent surfactant addition can alter the complex wettability state of the reservoir¹⁰⁻¹⁴, visualisation of complex, multiphase flow in pore networks¹⁵⁻¹⁸ and the development of models to enable prediction of how EOR effectiveness depends on the pore network structure and wettability state of the reservoir, relative oil and water permeabilities, flow rates and other conditions¹⁹⁻²⁶.

Generally, the main focus of these previous studies has mostly been on the reservoir engineering aspects of surfactant EOR; there is a lack of systematic and complete information on the surface chemical properties of the rock + oil + aqueous surfactant solution phase and their explicit relation to surfactant EOR. The key surface chemical properties relevant to surfactant EOR include: (i) how the rock-oil-water contact angle varies with surfactant concentration and (ii) how this relates to surfactant adsorption at the rock-oil, oil-water and rock-water interfaces; (iii) how surfactant adsorption causes its depletion in the injected aqueous surfactant solution; and (iv) how measurements of these properties can be used to predict the fraction of oil recovered for different volumes and concentrations of an injected surfactant solution. In a recent previous paper,²⁷ we tackled this problem by investigating how aqueous solutions of the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) removes *n*-decane oil from porous rock networks consisting of columns packed with calcium carbonate calcite particles. Following development of suitable models, experimental results for %oil recovery as a function of surfactant concentration were successfully compared with model predictions based on the surface chemical properties measured for this AOT + calcite + decane system. Although ref. 27 represents an important first step, establishing the fundamental basis for the rational choice of a surfactant species from the thousands of possible candidates and its optimum concentration required to maximise oil removal under particular oil field conditions using measured values of key surface chemical properties of the candidate surfactant systems is currently not fully resolved. The main aim of the present paper is to establish this fundamental basis by applying the combination of experimental and theoretical methodologies developed previously²⁷ to a range of different surfactant systems. In addition to data for the anionic surfactant AOT with decane as oil, we discuss results for the cationic surfactant benzyldimethyltetradecylammonium chloride (C14BDMAC) with toluene as oil and the non-ionic surfactant bis-2-hydroxyethyl alkyl acetamide (CW-100) with heptane as oil. The different charge types of the surfactants, the oils and the electrolyte compositions of the aqueous phases used were selected to cover a large range of surface chemical properties. We seek to establish how these wide variations in system properties affect the %oil recovery from calcite powder packed columns and whether the behaviour of all the different surfactant systems can be successfully predicted using the theoretical model developed in ref. 27.

This paper is structured as described below. We first summarise experimental details of the materials and methods used and then briefly outline the theoretical model for the prediction of how %oil recovery varies with surfactant concentration which was developed previously²⁷. In the results and discussion section, we first describe and compare the phase behaviour of each surfactant; both in the relevant aqueous phases alone and in the aqueous phases when in equilibrium with the relevant oil phases. Second, we present and compare the adsorption isotherms for surfactant adsorption to the oil-water, calcite-water and (for the non-ionic surfactant)) calcite-oil interfaces. We show how adsorption causes depletion of the aqueous phase concentration of non-adsorbed surfactant to different extents for the different surfactants. Third, we compare measured values of the calcite/water/oil contact angle (through water) as function of surfactant concentration with values derived from the measured adsorption isotherms. Then, we compare plots of the measured values of %oil recovery as a function of the aqueous phase, non-adsorbed surfactant concentrations with values calculated using the theoretical model developed in ref. ²⁷. Finally, to conclude, we summarise the main properties which a surfactant system must have to achieve efficient EOR.

EXPERIMENTAL

Materials.

Calcium carbonate powder (type FC10 of FordaCal product range) was obtained from Minelco UK and consists of natural ground calcium carbonate particles with average radius 1.4 μm . SI Figure 1 shows an SEM image of the powder where it can be seen that the individual particles are irregularly-shaped and polydisperse in size. The figure caption details the key relevant properties of the particles and the column packed with these particles. X-ray diffraction measurements confirmed that the FC10 powder consists exclusively of the calcite polymorph of calcium carbonate. The specific surface area derived from nitrogen adsorption isotherm measurements ($8.6 \text{ m}^2 \text{ g}^{-1}$) is approximately 10-fold larger than the value calculated for non-porous spheres having the same mean particle radius ($0.8 \text{ m}^2 \text{ g}^{-1}$). This result indicates that the calcite specific surface area is dominated by the internal porosity of the particles. The particle internal pores have a volume fraction of 0.08 with an average diameter of 110 nm.

Calcite crystals for contact angle measurements (obtained from John Brommeland, Norway) were cut to size and the upper surface was polished using abrasive paper with a particle size of 4.5 μm .

The pure anionic and cationic surfactants, (sodium bis(2-ethylhexyl) sulfosuccinate, abbreviated as AOT, Sigma-Aldrich, 98%) and (benzyltrimethyltetradecylammonium chloride, abbreviated as C14BDMAC, Fluka Analytical $> 99\%$ pure) were used as received. The non-ionic surfactant is a commercial grade surfactant (Pilot Chemical Company, trade name Calamide CW-100, abbreviated here as CW-100) which consists of a mixture of the non-ionic surfactant bis-2-hydroxyethyl alkyl acetamide and diethanolamine (DEA) in an approximate mass ratio of 8:2. The surfactant mixture has a distribution of hydrophobic alkyl chain lengths of approximately 12-14 carbons²⁸. An average chain length of 13 carbons was assumed here in order to estimate the average relative molar mass of this surfactant and hence enable estimation of the approximate surfactant molar concentration instead of weight percent. As noted above, the CW-100 as used here contained 20 wt% DEA which corresponds to a DEA: surfactant mole ratio of approx. 1.3:1. Because DEA is a very hydrophilic species and therefore unlikely to be surface active, all further discussions of CW-100 and calculations of its molar concentration refer to only the non-ionic surfactant component(s); the DEA component is disregarded. Use of this consistent concentration scale enables easier comparison between the behaviours of the three different surfactants.

Water was purified by reverse osmosis (Elgastat Prima) followed by treatment using a Millipore Milli-Q reagent water system. The purified water had an electrical resistivity of 16 M Ω cm and its surface tension was 71.9 mN m⁻¹ at 25°C, in good agreement with best literature values. The oils *n*-decane (Sigma, >99%), *n*-heptane (Fisher, 99% pure) and toluene (Fisher, Analytical reagent grade); the salts NaCl (Fisher, 99.9%) and Na₂CO₃ (Fisher, 99%) and reagents used in the titrations to determine surfactant concentrations, Hyamine 1622 (Fluka, 98%), dimidium bromide (Sigma, 95%), disulfine blue (Sigma, 50% dye content) and chloroform (Fisher, analytical reagent grade), were all used as received.

Methods.

The experimental setup used to investigate oil removal for calcite powder packed columns is shown in SI Figure 2 and fully detailed in ref. 27. Briefly, the column (a stainless steel cylinder of internal diameter 10 mm and internal length 50 mm, supplied by Kinesis, UK) is first sealed at one end with a frit (mean pore diameter 2 μ m, thickness 1 mm supplied by Kinesis) and end connector. The calcite powder is then added and the column sealed with a second frit and end connector. Mass measurements of the column before and after filling were used to determine the final mass of powder in the packed column. Oil was injected using a syringe pump (WPI model sp100i) operating at a volumetric flow rate of 8.3 μ l min⁻¹ for approximately 5 pore volumes. Again, mass measurements before and after oil filling were used to determine the mass of oil in the packed column prior to injection of surfactant solution and to check that the filled column contained no trapped air. The oil-filled, FC10 calcite packed columns prepared in this way were found to be reproducible and to contain a volume fraction of oil-filled pores $\phi_{\text{pore}} = 0.45$. The average, effective pore radius $r_{\text{pore}} = 0.16$ μ m and was determined as described in ref. 27 (SI Figure 1). Aqueous surfactant solution was pumped into the column using an HPLC pump (Jasco PU-1580 or PU-980 Intelligent HPLC Pump) at a set volumetric flow rate of 0.005 cm³ min⁻¹. To determine the amount of oil removed from the column, the pump was stopped and the column was removed and weighed at the required time intervals. Since the densities of the oils used are smaller than the densities of the aqueous surfactant solutions, the mass of the column increases as oil is displaced from the column by the aqueous solutions. The measured mass differences were used to derive the percentage of the original oil in place recovered (%oil recovery). From repeated measurements, we estimate the uncertainty in the final value of %oil recovered to be $\pm 2\%$. The required oil and aqueous solution densities determined using an Anton Paar DMA 35N density meter.

Concentrations of anionic AOT solutions were measured by titration with the cationic surfactant Hyamine 1622 using the two-phase Epton titration with a mixed, acidified indicator system²⁹. Cationic C14BDMAC concentrations were determined by titration with the anionic surfactant sodium dodecyl sulphate (SDS) using the same titration method. Concentrations of the non-ionic CW-100 surfactant were determined by UV spectrophotometry using a Perkin Elmer Lambda 25 instrument. UV spectra of solutions containing CW-100 and the DEA contaminant (for which correction was made) are shown in SI Figure 3 along with the final calibration plots for both water and heptane as solvent.

The equilibrium partitioning of the surfactants between oil and water were determined as follows. 30 cm³ of the aqueous phase containing the required initial surfactant concentration was added to 30 cm³ of the oil phase in a screw top glass jar fitted with a magnetic stir bar. The samples, held within a thermostat bath on top of a magnetic stirrer, were stirred at a speed sufficiently slow to avoid emulsification. The aqueous phase was sampled and analysed as described above to obtain the equilibrium aqueous phase concentration. The equilibrium oil phase concentration was derived using mass balance. Repeat measurements were made at different equilibration times (between 1 and 14 days) to ensure the final values corresponded to the equilibrium partitioning.

The adsorption isotherms were measured by addition of a known mass of calcium carbonate powder to 20 ml of the required concentration of surfactant solution in a 60 ml glass jar fitted with screw top lid and a magnetic stirrer bar. The samples were held in thermostat bath and equilibrated by stirring at 700 rpm for over 6 hours. Using repeat measurements with different equilibration times, this time was found to be sufficient to ensure equilibrium was reached. When adsorption equilibration was achieved, the calcium carbonate particles were removed by centrifugation at 6000 rpm for 5 minutes using a Baird & Tatlock Mk IV Auto Bench Centrifuge and the supernatant was analysed as described above. The measured concentrations of non-adsorbed surfactant were then used to derive the adsorption isotherm was derived.

Aqueous solution-air and oil-water interfacial tensions larger than 5 mN m^{-1} were measured using the static, maximum pull method using a Krüss K12 instrument with a du Noüy ring. Oil-water tensions less than 5 mN m^{-1} , including ultralow values, were measured using a Krüss SITE 04 spinning drop tensiometer.

Static, advanced oil-water-calcite contact angles of drops of aqueous solution on calcite crystals under oil were measured by first cleaning calcite crystals (9 mm x 9 mm x 9 mm) with the relevant oil and drying using compressed air. The crystal was placed in a glass 10 mm path length cuvette which was then filled with the oil and placed in the thermostatted cell of a Krüss DSA 10 instrument. A drop (0.2-0.5 μl) of the aqueous solution was carefully injected on to the calcite surface and imaged using a horizontal microscope (Navitar 1-60350 zoom system with a Mitutoyo M Plan Apo 5 objective lens and a QImaging QICam digital camera). The contact angle was measured with an on-screen protractor using Iconico software (New York, Version 4.0). Drops for which the oil-water interfacial tension is ultra-low have a very small capillary length and thus require small drop volumes and high magnification to determine the contact angle reliably. For AOT and C14BDMAC solutions, the contact angles reached their final, static values within 1 minute or so and did not change significantly over periods of up to several hours. For CW-100, the contact angle was found to take several hours to achieve the final, static value in some cases. This effect may be a consequence of the fact that CW-100 partitions significantly to the oil phase and also adsorbs relatively strongly to the calcite.

All measurements were made at a temperature of 25°C , except for a few measurements at other temperatures noted in the text. The pH of the aqueous solutions were all the range 9.0 to 10.8; for selected systems, it was checked that changing the pH from 9.0 to 10.8 produced no significant differences.

MODELLING OIL RECOVERY

In this study we attempt to relate the surface chemical properties (phase behaviour, adsorption at the different, relevant surfaces, interfacial tensions and contact angles) of various surfactant/aqueous phase/oil systems to the amount of oil recovered when pumping aqueous surfactant solutions of different concentrations into a column packed with calcite particles where the interstices have been filled with oil. It is important to note two points about the systems discussed here. Firstly, upon initial injection into the oil-filled calcite column, the surfactant solution has not been in contact with the oil phase. Hence, the initial state of the surfactant aqueous phase corresponds to its equilibrium state in the aqueous phase alone. The equilibrium state of the surfactant in multi-phase systems containing both water and oil phases is generally different from that of the aqueous phase alone. Hence, during injection, the surfactant system will generally fully or partially transform from its initial state (aqueous phase equilibrium) to its equilibrium state in an

oil-water multiphase system. For this reason, the phase behaviour and properties of the surfactant/aqueous phase system both in the absence and presence of oil are relevant in attempting to model the oil recovery.

Secondly, in the oil recovery experiments described and modelled here, the aqueous solution is pumped into the packed column at a constant volumetric flow rate with a variable applied pumping pressure drop. The volumetric flow rate used here ($0.005 \text{ cm}^3 \text{ min}^{-1}$) corresponds to an average linear velocity of approximately $2.5 \times 10^{-6} \text{ m s}^{-1}$ (equal to 0.7 feet per day) which is similar in magnitude to the flow velocities used in oil field conditions⁴. Whether or not capillary-trapped oil is mobilised depends on the balance between viscous forces (dependent on flow rate) and pore-scale capillary forces (dependent on, *inter alia*, pore dimensions, wettability and interfacial tension). This interplay of viscous and capillary forces acting on a fluid element is normally discussed in terms of the capillary number Ca taken to be equal to $v\mu/\gamma$ (where v is the fluid velocity at a characteristic length scale, μ is the dynamic viscosity and γ is the interfacial tension). Although the calculation of Ca is controversial due to the uncertainty of the appropriate “characteristic length scale”³⁰, it is expected that when Ca is less than a threshold value (dependent on the choice of length scale adopted), flow is dominated by capillary effects and oil is trapped in the porous network. Oil is mobilised when Ca is greater than the threshold value and the flow is dominated by viscous effects. In principle, one could engineer different Ca values by *either* variation of flow conditions for systems with constant capillary forces *or* by using constant flow conditions and changing system conditions to obtain varying capillary forces. In the study described in ref. 27, the effects of both varying flow rates and variation of capillary forces (by changing the surfactant concentration) were investigated. In the present work, we use a constant imposed flow rate of $0.005 \text{ cm}^3 \text{ min}^{-1}$ and vary only the capillary forces through changes in the surfactant system. As demonstrated qualitatively in ref. 27 for this constant flow rate, systems with low surfactant concentrations and high oil-water tensions lie within the low- Ca regime in which oil trapping is expected. Systems with high surfactant concentrations and low oil-water tensions lie within the high- Ca regime for which oil mobilisation is expected.

The theoretical model used to estimate %oil recovery as a function of surfactant concentration from the measured values of the relevant surface chemical properties of the surfactant systems is fully described, in ref. 27. Briefly, the model consists of three main parts which are inter-linked. In the first part, we consider aqueous phase solutions of surfactant at concentrations less than the critical aggregation concentration (cac) such that the solutions only contain surfactant *monomer*. In general, the surfactant monomers can partition from the water to the oil phases and adsorb at the oil-water, calcite-water and calcite oil phases. The net result of these processes is that the calcite-oil-water contact angle θ (measured through the water phase) changes with surfactant concentration. Using the idealised packed-column internal geometry consisting of monodisperse, cubic packed calcite spheres shown in SI Fig 4, we have postulated that the non-recovered oil is trapped in the form of oil liquid bridges located at each particle-particle contact point (red profile) and the aqueous solution flows through channels located centrally between the particle contact points (green profile). Using the geometry shown in SI Fig 4, the profiles and Laplace pressures ΔP_{bridge} of liquid oil bridges of different volumes can be calculated for any input value of the contact angle θ and oil-water interfacial tension $\gamma_{\text{oil-water}}$. In order to achieve water flow through the circular channels of effective radius r_{chan} , the driving pressure must exceed the capillary entry pressure which is $\Delta P_{\text{chan}} = 2\gamma_{\text{oil-water}}/r_{\text{chan}}$. For fixed contact angle θ and oil-water tension $\gamma_{\text{oil-water}}$, the incoming aqueous phase can either bulge and break through small pores (i.e. low values of r_{chan} , leaving correspondingly large liquid bridges and thereby giving a low % oil recovery) or bulge and break through in large flow channels and leave correspondingly small liquid bridges. We take the effective radius of these flow channels r_{chan} to be equal to the radius of the circle which has an area equal to the area of the particle

interstice minus the areas of the four liquid bridges in contact with it. We also assume that r_{chan} cannot exceed the radius of the circle circumscribed by the particles ($= r_{\text{chan,max}}$). The model postulates that r_{chan} is determined by the condition that $\Delta P_{\text{bridge}} = \Delta P_{\text{chan}}$ for $r_{\text{chan}} < r_{\text{chan,max}}$ and that $r_{\text{chan}} = r_{\text{chan,max}}$ otherwise. For the idealised geometry of SI Fig 4 and surfactant solutions containing only surfactant monomer, the %oil recovery is a *universal function of θ alone* as shown in Figure 1. It does not depend on the calcite particle size, the oil-water interfacial tension or any other parameter specific to a particular system. Additionally, it is predicted that the final value of %oil recovery is achieved when the aqueous phase front has reached the end of the packed column, i.e. after approximately 1 pv of surfactant has been pumped. Continued pumping of surfactant solution at the same concentration is not expected to change θ and the %oil recovery further.

The second part of the model concerns how the %oil recovery changes with surfactant concentration at concentrations greater than the critical aggregation concentration (cac). In this concentration regime, the surfactant forms aggregates which co-exist in equilibrium with the monomers that are present at a concentration equal to the cac. The *surfactant aggregates* may be capable of solubilising the oil. Since only surfactant monomers adsorb at the oil-water interface and they are present at the maximum possible concentration (equal to the cac), the oil-water tension achieves which is the lowest possible value under the prevailing conditions and is independent surfactant concentration. The small magnitude of the oil-water tension causes the capillary number Ca to be greater than the appropriate threshold value and thus conditions favour oil release by emulsification. In addition, the aggregated surfactant present forms a “reservoir” of surfactant capable of releasing surfactant monomers to adsorb on the newly-formed oil drop surfaces released from the trapped oil bridges. Because new emulsion drops cannot be formed unless there is sufficient surfactant to stabilise them, the extent of emulsification is limited by the amount of this “reservoir” of aggregated surfactant. Thus, surfactant concentrations in excess of the cac can increase the %oil recovery above that determined solely by the contact angle θ by two additional mechanisms: solubilisation and emulsification. We assume that the total %oil recovery for [surfactant] > cac is the sum of three contributions

$$\%oil = \%oil_{\theta, \text{cac}} + \%oil_{\text{sol}} + \%oil_{\text{em}} \quad (1)$$

where $\%oil_{\theta, \text{cac}}$ is the %oil recovery resulting from the contact angle when [surfactant] = cac and $\%oil_{\text{sol}}$ and $\%oil_{\text{em}}$ are the contributions to the total %oil recovery resulting from solubilisation and emulsification respectively. In microemulsion systems, the amount of solubilisation is proportional to the amount of aggregated surfactant²⁷. Hence, each mole of aggregated surfactant solubilises R_{sol} moles of oil and the %oil recovered by solubilisation due to the injection of n pore volumes of aqueous surfactant solution is given by

$$\%oil_{\text{sol}} = 100 n MV_{\text{oil}} R_{\text{sol}} ([\text{surfactant}] - \text{cac}) \quad (2)$$

where MV_{oil} is the molar volume of the oil. As discussed above, emulsification is limited by the “reservoir” of aggregated surfactant in excess of the cac and so we assume here that R_{em} moles of oil are emulsified per mole of aggregated surfactant in excess of the cac. Hence, the %oil recovered by solubilisation plus emulsification using n pore volumes of aqueous phase is given by

$$\%oil_{\text{sol}} + \%oil_{\text{em}} = 100 n MV_{\text{oil}} (R_{\text{sol}} + R_{\text{em}}) ([\text{surfactant}] - \text{cac}) \quad (3)$$

In contrast to $\%oil_{\theta}$, for which the final value is achieved after the injection of 1 pv and does not change with further volume injected, $\%oil_{\text{sol}}$ and $\%oil_{\text{em}}$ are predicted to increase progressively with the number n of pore volumes of surfactant solution injected.

The final part of the model accounts for the fact that, due to adsorption, the concentration of non-adsorbed surfactant $[\text{surf}]_{\text{free}}$ in the aqueous phase of the packed column is generally significantly less than the known initial value $[\text{surf}]_{\text{init}}$. In general, this difference is due to depletion by adsorption at the calcite-water, calcite-oil and the oil-water interfaces and also loss by partitioning of the surfactant to the oil phase. However, because the amount of trapped oil-water interface is relatively small and the partitioning to oil is slow, the main contribution to depletion is adsorption from the aqueous phase to the calcite-water interface. Neglecting all other contributions to depletion, consideration of the surfactant mass balance in a system comprising the packed column following injection of n pore volumes of aqueous solution leads to the following approximate relationship between $[\text{surf}]_{\text{init}}$ and $[\text{surf}]_{\text{free}}$.

$$[\text{surf}]_{\text{init}} \approx \frac{\{n\phi_{\text{pore}}[\text{surf}]_{\text{free}} + (1 - \phi_{\text{pore}}) \cdot f \cdot A_{\text{particle}} \rho \cdot \Gamma / N_{\text{Av}}\}}{n\phi_{\text{pore}}} \quad (4)$$

where Γ is the surface concentration of surfactant adsorbed at the calcite-water surface, A_{particle} is the surface area per mass of calcite particles, ρ is the particle density and f is the fraction of the total particle surface area which is in contact with the aqueous solution. The fraction f is less than 1 since some of the particle surface area is covered with oil. The concentration of non-adsorbed surfactant $[\text{surf}]_{\text{free}}$ and adsorbed surface concentration Γ are related by the adsorption isotherm, A_{particle} and ϕ_{pore} are separately measured (Table 1), the calcite density is 2.71 g cm^{-3} and so the only unknown parameter is f . The model of SI Figure 4 enables the calculation of f as a function of %oil recovery and is estimated to be in the range 0.3 – 0.6 for the range %oil recovery values measured here. To simplify the calculations, a mean value of $f = 0.4$ was used to convert the values of $[\text{surf}]_{\text{init}}$ to $[\text{surf}]_{\text{free}}$ on the plots of %oil recovery versus surfactant concentration. This transformation of the surfactant concentration scales enables the values of %oil recovery to be linked directly with the interfacial tensions and contact angles at the same value of $[\text{surf}]_{\text{free}}$ and the critical aggregation concentrations. Additionally, the difference ($[\text{surf}]_{\text{init}} - [\text{surf}]_{\text{free}}$) gives a measure of the amount of surfactant which is “wasted” by its retention on the packed column under different conditions. The ability to estimate the total amount of surfactant needed to achieve different amounts of oil recovery is important to assess the economic viability of the oil-recovery process.

The model outlined above provides a theoretical framework which explicitly relates the surface chemical properties of a surfactant system to its oil-recovery effectiveness as a function of surfactant concentration. Despite the simplifications and approximations involved, we have shown previously that the model successfully captures the main features of %oil recovery versus surfactant concentration for the anionic surfactant AOT²⁷. Illustrative calculations are shown in Figure 1. The upper plot shows the prediction of %oil recovery versus contact angle θ which is applicable to all surfactant systems at concentrations below their cac. This plot is approximate since it is based on the idealised packed particle geometry shown in SI Figure 4. The extent to which it predicts the %oil recovery for packed columns of real, irregularly-shaped, polydisperse particles is shown later. The lower plot shows %oil recovery versus free surfactant concentration for a hypothetical system having the contact angle variation shown plus the additional input parameters listed in the legend. This illustrative calculation serves to show how the %oil recovery is independent of the amount of solution injected for concentrations below the cac (following correction for the difference between initial and free surfactant concentrations) but depends on the number of pore volumes injected for concentrations greater than the cac when the solubilisation and emulsification mechanisms operate.

RESULTS AND DISCUSSION

Equilibrium phase behaviour of the surfactant systems.

In general, aqueous surfactant solutions without added oil contain only monomers at concentrations below a critical aggregation concentration (cac). At higher concentrations, the surfactant present in excess of the cac exists as aggregates present in dynamic equilibrium with the monomers present at a concentration approximately equal to the cac. Depending on the surfactant structure and the prevailing conditions (e.g. temperature, salt concentration), the aggregates formed are commonly micelles but other possibilities include dispersed fragments of lamellar phase which may be in the form of vesicles. Thus, the cac may correspond to the critical *micelle* concentration cmc or the critical *vesicle* concentration cvc. In addition, at temperatures below the Krafft temperature of the particular system, increasing the surfactant concentration above the cac leads to precipitation of a solid surfactant phase and thus the cac corresponds to the surfactant *solubility* in that case.

As discussed in refs. 31, 32, the cac for the anionic surfactant AOT aqueous phases in the absence of oil corresponds to either the cmc (at low salt concentrations) or cvc (at higher salt concentrations). For the cationic surfactant C14BDMAC aqueous phases used here, the Krafft temperature is 26.5°C (see SI Figure 5), slightly higher than the experimental temperature of 25°C and thus precipitation of a solid phase of C14BDMAC is expected. However, it is observed here that initially fully dissolved solutions of C14BDMAC held at 25°C show no signs of precipitation when held at 25°C for periods of up to 1 hour but visible precipitation is observed after 6 hours or so. Precipitation is very slow and the solutions are metastable. As seen in SI Figure 6, measurement of the solution-air tension as a function of surfactant concentration show that the cac of C14BDMAC, which corresponds to either the cmc in a metastable state or the solubility, is 0.065 mM. The non-ionic surfactant CW-100 is a commercial product which contains a distribution of alkyl chain lengths and some unreacted DEA used in its synthesis. Because the different alkyl chain length species present will all have different cmc values, the solution-air tension plot in SI Figure 6 does not show a single break point in the curve. Aggregation of the range of CW-100 species into micelles commences at 0.0063 mM and is complete by 0.033 mM.

The equilibrium phase behaviour of surfactants in systems containing oil and water phases has been extensively discussed³³⁻³⁵. At concentrations less than the critical aggregation concentration, the surfactant is present only as monomers which can distribute between the aqueous and oil phases with an equilibrium partition coefficient defined as

$$P = [\text{surf}]_{\text{oil}}/[\text{surf}]_{\text{water}} \quad (5)$$

As the overall surfactant concentration is increased, the equilibrium concentrations $[\text{surf}]_{\text{oil}}$ and $[\text{surf}]_{\text{water}}$ increase together maintaining the ratio equal to P . For a two phase system with an oil-phase volume fraction ϕ_{oil} and water phase volume fraction ϕ_{water} , the overall surfactant monomer concentration and the individual concentrations in each phase are related according to

$$[\text{surf}]_{\text{overall}} = \phi_{\text{oil}}[\text{surf}]_{\text{oil}} + \phi_{\text{water}}[\text{surf}]_{\text{water}} \quad (6)$$

Above a critical aggregation concentration, the excess surfactant forms one of three types of aggregates: either oil-in-water (o/w) microemulsion aggregates located exclusively in the aqueous phase in equilibrium with an excess oil phase (Winsor I system), water-in-oil (w/o) microemulsion aggregates located in the oil phase in equilibrium with the excess water phase (Winsor II system) or the aggregated surfactant forms a bicontinuous microemulsion phase in equilibrium with both excess

oil and water phases (Winsor III system). The type of microemulsion aggregate and multiphase system (Winsor I, III or II) formed depends on the surfactant structure and prevailing conditions such as temperature and salt concentration. For a particular surfactant, these variables can be used to “tune” the equilibrium microemulsion phase behaviour and thereby control the post-cac oil-water interfacial tension which is minimum (and commonly ultralow) at the particular condition corresponding to the middle of the Winsor III range³⁶⁻³⁹. Whichever type of aggregate is formed, the aggregates are located exclusively in the phase noted above and exist in equilibrium with surfactant monomer concentrations in the aqueous and oil phases. These monomer concentrations are equal to the critical *microemulsion* concentrations; $c_{\mu C_{\text{water}}}$ in the aqueous phase and $c_{\mu C_{\text{oil}}}$ in the oil phase. The aqueous and oil phase monomer concentrations are related according to $P = c_{\mu C_{\text{oil}}}/c_{\mu C_{\text{water}}}$ and the overall critical microemulsion concentration is $c_{\mu C_{\text{overall}}} = \phi_{\text{oil}}c_{\mu C_{\text{oil}}} + \phi_{\text{water}}c_{\mu C_{\text{water}}}$.

At constant temperature, addition of salt drives microemulsion phase inversion corresponding to the Winsor system phase progression I – III –II. Figure 2 shows the appearance of equilibrated samples containing equal volumes of oil and water, surfactant at a fixed concentration in excess of the overall critical microemulsion concentration, and different NaCl concentrations. The anionic AOT/decane system gives Winsor I systems for [NaCl] = 0-50 mM and Winsor III for 60-80 mM. For the cationic C14BDMAC/toluene system, 0-153 mM NaCl gives Winsor I, 324-666 mM gives Winsor III and 837-1180 mM gives Winsor II. For the non-ionic CW-100/heptane system, Winsor I is found for zero salt and 170-1700 mM gives Winsor III. As summarised in Table 1, systems containing AOT with 0, 40 and 75 mM NaCl (giving Winsor I, I and III systems respectively), C14BDMAC with 150 mM NaCl (Winsor I) and CW-100 with pure water (Winsor I) were selected for the detailed studies shown below.

As discussed in ref. 27, anionic AOT monomers do not partition significantly to decane for any of the three salt concentrations investigated. Figure 3 shows the oil-water partitioning behaviour of the C14BDMAC and CW-100 monomers in the cationic and nonionic surfactant/oil systems. In aqueous phases containing 10 mM Na_2CO_3 + 150 mM NaCl, C14BDMAC monomers partition to toluene with $P = 0.43$ with critical microemulsion concentrations $c_{\mu C_{\text{water}}} = 0.040$ and $c_{\mu C_{\text{oil}}} = 0.017$ mM. At higher concentrations, all additional surfactant (corresponding to the aggregates formed), remains exclusively in the aqueous phase, confirming that this composition forms a Winsor I system. These partitioning and $c_{\mu C}$ values for C14BDMAC are in line with measurements from Alaei et al.⁴⁰ for a range of closely related benzyldimethylalkylammonium systems. The non-ionic CW-100 in mixtures of pure water with heptane shows slightly greater monomer partitioning to the oil ($P = 0.82$), higher $c_{\mu C}$ values ($c_{\mu C_{\text{water}}} = 0.17$ and $c_{\mu C_{\text{oil}}} = 0.14$ mM) and Winsor I behaviour. The key properties of the different surfactant plus aqueous phases with and without oil are summarised in Table 1. It can be seen that the $c_{\mu C_{\text{water}}}$ values for the ionic surfactants are similar in magnitude to the cac values in the aqueous phases in the absence of oil. This is not the case for CW-100 which contains a distribution of alkyl chain length species. In the absence of oil, the cac covers the range 0.0063-0.033 mM since the higher chain length species aggregate in water at lower concentrations. In the presence of oil, the $c_{\mu C_{\text{water}}}$ is considerably higher at 0.17 mM, presumably due to loss of the more hydrophobic species from water by partitioning to the oil phase.

Adsorption properties of the three surfactants.

We first consider surfactant adsorption from the aqueous phase to the oil-water surface. Figure 4 shows the variation of the oil-water tension with surfactant concentration from zero to above $c_{\mu C_{\text{water}}}$ for the different systems. For C14BDMAC and CW-100, which partition to the oil phases, the oil-water tension was measured with oil phases containing the correct equilibrium

concentration of surfactant. Since only the surfactant monomers adsorb, the tension reduces with increasing surfactant concentration up to $c_{\mu C_{\text{water}}}$ and thereafter remains virtually constant. Values of $c_{\mu C_{\text{water}}}$ from the break points in the oil-water tension plots were in good agreement with those taken from the surfactant partitioning plots. For the AOT/decane system, the plots at different salt concentrations illustrate how (i) $c_{\mu C_{\text{water}}}$ decreases with salt addition and (ii) that the post- $c_{\mu C_{\text{water}}}$ tension reduces from 0.33 mN m^{-1} in the Winsor I system with 0 mM NaCl to an ultralow value of 0.0079 mN m^{-1} in the Winsor III system with 75 mM NaCl. The pure surfactants AOT and C14BDMAC show clear break-point behaviour, whereas the CW-100 (containing a distribution of species) shows a more complex behaviour that is also seen for the solution-air tension plot (SI Figure 6).

In the plots of Figure 4, the solid lines are fits to equation 7, derived by combining the Langmuir adsorption isotherm and the Gibbs adsorption equation.

$$\gamma = \gamma_0 - kT\Gamma_{\text{max}} \ln(1 + K[\text{surf}]_{\text{free}}) \quad (7)$$

where γ is the oil-water tension at surfactant concentration $[\text{surf}]_{\text{free}}$, γ_0 is the oil-water in the absence of surfactant, Γ_{max} is the maximum surface concentration, K is a constant in the Langmuir adsorption isotherm equation, k is the Boltzmann constant and T is the absolute temperature. The tension γ_0 was measured independently and so the best-fit lines were obtained by adjustment of Γ_{max} and K for $[\text{surf}]_{\text{free}} = 0$ to $c_{\mu C_{\text{water}}}$. The fits are reasonably good for AOT and C14BDMAC but poor for CW-100 due to the distribution of surfactant species present. The best-fit parameters are summarised in Table 2.

We next consider surfactant adsorption to the calcite powder as shown in Figure 5. Comparing the water to calcite-water isotherms, it can be seen that the adsorption of the anionic AOT and non-ionic CW-100 are broadly similar; the adsorption increases sharply in a highly cooperative adsorption at a surfactant concentration around or slightly below the $c_{\mu C_{\text{water}}}$ and is approximately constant at higher concentrations. Adsorption of the cationic C14BDMAC is relatively very low, which meant that the full adsorption isotherm could not be measured. For the limited concentration range measured, the adsorption again appears to increase with concentration up to $c_{\mu C_{\text{water}}}$. However, the plateau value reached at higher concentrations ($\Gamma_{\text{max}} = 0.027 \text{ molecule nm}^{-2}$) is two orders of magnitude lower than Γ_{max} values for AOT and CW-100.

The anionic surfactant AOT does not partition significantly into the oil phase and so adsorption can only occur from the aqueous phase to the calcite-water interface. C14BDMAC and CW-100 monomers both partition to the oil phase and so, in principle, adsorption can occur *both* from water to the calcite-water interface and from oil to the calcite-oil interface. As seen in Figure 5, both isotherms were measured for CW-100; however, the oil to calcite-oil isotherm was not measured for C14BDMAC because the titration method used for this surfactant was not reliable with oil as solvent. For CW-100, adsorption from heptane to the calcite-heptane occurs at lower concentrations but with a smaller Γ_{max} than the water to calcite-water adsorption.

All the calcite adsorption isotherms were fitted to a Langmuir-type isotherm modified to take account of cooperative adsorption through the parameter β (equation 8)⁴¹.

$$[\text{surf}]_{\text{free}} = \frac{(\Gamma / \Gamma_{\text{max}})}{(1 - (\Gamma / \Gamma_{\text{max}})) \cdot K \cdot e^{-\beta \Gamma / \Gamma_{\text{max}}}} \quad (8)$$

where Γ is the surface concentration of adsorbed surfactant, $\Gamma_{\max}$ is the maximum surface concentration, K is the Langmuir isotherm constant reflecting the strength of adsorption and β is a co-operativity parameter. The isotherm reduces to the Langmuir isotherm when the cooperativity β is zero, $\beta > 0$ corresponds to anti-co-operative adsorption and $\beta < 0$ corresponds to co-operative adsorption. In all cases, the fits, corresponding to the solid lines in Figure 5 with best-fit parameters summarised in Table 3, are reasonably good. Anionic AOT and non-ionic CW-100 adsorb highly co-operatively from the aqueous phases with high $\Gamma_{\max}$ values of 2 – 3.5 molecules nm^{-2} . The limited concentration range of the isotherm for C14BDMAC does not allow reliable estimation of the β parameter; the overall adsorption is very low with $\Gamma_{\max} = 0.027$ molecules nm^{-2} . The iso-electric point of the calcite-water surface is approximately pH 9.5⁴²⁻⁴⁷, close to the solution pH used here, and so the calcite-water interface is expected to be only weakly charged. The strong adsorption of the anionic AOT compared to the weak adsorption of the cationic C14BDMAC suggests that the calcite is positively charged under the conditions used here. The AOT isotherms measured here are similar to those reported previously⁴⁸. In relation to the relative adsorptions of the anionic and cationic surfactants seen here, Ma et al.⁴⁹ report similarly strong cooperative adsorption for an anionic surfactant (sodium dodecyl sulphate) and relatively low adsorption of a cationic surfactant (cetylpyridinium chloride) on to calcite at pH 10.8 at 25 °C. Kuno et al.⁵⁰⁻⁵³ report adsorption isotherms for the nonionic surfactant polyoxethylene nonylphenol (C_9PhE_x with $x = 1-10$) on to polar and non-polar surfaces from either polar or non-polar solvents. For adsorption to calcite from non-polar solvents, they observe that the adsorption is non-cooperative and does not exceed monolayer coverage whereas the isotherms for adsorption from polar solvents indicate multilayer adsorption. In line with this observation, $\Gamma_{\max}$ for CW-100 adsorption at the water-calcite is high (3.5 molecules nm^{-2}) whereas $\Gamma_{\max}$ for adsorption to the heptane-calcite interfaces is low (1.0 molecules nm^{-2}). These values are similar to $\Gamma_{\max}$ for adsorption of C_9PhE_6 at the water-calcium carbonate and cyclohexane-calcium carbonate interfaces (4.8 and 1.1 molecules nm^{-2} respectively)⁵³.

The surfactant aggregation and adsorption properties discussed so far affect %oil recovery as a function of surfactant concentration in three main ways. Firstly, the magnitude of the oil-water tension is controlled by the oil-water adsorption isotherm and the value of $c_{\text{MC water}}$. Secondly, as discussed in detail below, the variation of calcite-oil-water contact angle with surfactant concentration is determined by the extents of surfactant adsorption at the oil-water, calcite-water and calcite-oil interfaces. Thirdly, when a surfactant solution is injected into a calcite-powder packed column, the initial aqueous-phase surfactant concentration is reduced due to its adsorption to the various interfaces and possible loss by partitioning into the oil phase. Injection of 1 pore volume of aqueous solution for the systems investigated here results in recovery of most of the oil initially present. Hence, because the amount of residual oil is low, the main contribution to the depletion of the surfactant is loss by adsorption to the calcite-water interface. With the assumption that this is the only significant depletion mechanism, the measured calcite-water adsorption isotherms can be used in conjunction with equation 4 and the measured properties of the calcite packed column to estimate how $[\text{surf}]_{\text{free}}$ is reduced from $[\text{surf}]_{\text{init}}$ as functions of both the surfactant concentration and number of pore volumes injected. Figure 6 shows the calculated plots for the three surfactant systems. AOT and CW-100 adsorb to similar extents and thus show similar plots. The depletion is greatest at initial surfactant concentrations around values of approximately $20/K$ (where K is the Langmuir adsorption isotherm constant equal to $1/(\text{conc at which } \Gamma = \Gamma_{\max}/2)$), i.e. around 70 mM for AOT and CW-100. The depletion is greatest at 1 pv; continued injection of additional surfactant solution reduces the depletion as expected. For the C14BDMAC system, the adsorption to the calcite-water interface is relatively low ($\Gamma_{\max} = 0.027$ molecule nm^{-2} with $K = 1000 \text{ mM}^{-1}$) and depletion is significant only for initial surfactant concentrations less than about 0.2 mM. The importance of these plots is that they reveal how adsorption determines the initial surfactant concentrations which must be injected to

achieve a particular value of $[\text{surf}]_{\text{free}}$ required for a target value of %oil recovery. Obviously, systems with high depletion which require high initial surfactant concentrations to be injected are less economically favourable for EOR.

Contact angles for the three surfactant systems.

Measured values of the static, advanced calcite-water-oil contact angle θ (though the water phase) as a function of the aqueous phase surfactant concentration are shown in Figure 7. For the anionic AOT and non-ionic CW-100 surfactants, θ increases to a slight maximum at concentrations slightly below $c\mu c_{\text{water}}$ and then decreases sharply to a constant value of approximately 30° . The cationic C14BDMAC system shows different behaviour; θ is approximately 120° for $[\text{surf}]_{\text{free}} < c\mu c_{\text{water}}$ and then rises to 180° for $[\text{surf}]_{\text{free}} > c\mu c_{\text{water}}$.

As indicated by the solid lines in the plots of Figure 7, the different contact angle plots are approximately consistent with the tensions and surfactant adsorption properties at the different interfaces. The calcite-water-oil contact angle θ through the aqueous phase is determined by the relative magnitudes of the calcite-water, oil-water and calcite-oil interfacial tensions according to Young's equation.

$$\cos \theta = \frac{\gamma_{\text{calcite-oil}} - \gamma_{\text{calcite-water}}}{\gamma_{\text{water-oil}}} \quad (9)$$

The three interfacial tensions in the absence of surfactant can be estimated from the polar and dispersion force contributions to the excess surface energies (equal to the surface tension) of each component⁵⁴. The interfacial surface energy of a substance x against air ($\gamma_{\text{x-air}}$) is the sum of the contributions arising from the polar and dispersion forces.

$$\gamma_{\text{x-air}} = \gamma_{\text{x-air}}^p + \gamma_{\text{x-air}}^d \quad (10)$$

If the polar and dispersion surface energies of two components x and y against air are known, the x-y interfacial tension of the x-y interface can be calculated using:

$$\gamma_{\text{x-y}} = \gamma_{\text{x-air}} + \gamma_{\text{y-air}} - 2\sqrt{\gamma_{\text{x-air}}^p \gamma_{\text{y-air}}^p} - 2\sqrt{\gamma_{\text{x-air}}^d \gamma_{\text{y-air}}^d} \quad (11)$$

Equations 9-11 and literature values of the relevant polar and dispersion surface energy contributions⁵⁴⁻⁵⁹ enable the estimation of the three interfacial tensions and θ for systems in the absence of surfactant. Table 4 lists the excess surface energy components together with the measured and calculated contact angles for the three oils in the absence of surfactant which are in reasonable agreement.

In the presence of surfactant, the tensions of the three interfaces are decreased by adsorption of surfactant according to the Gibbs adsorption equation.

$$\gamma = \gamma_0 - kT \int_0^C \frac{\Gamma(C)}{C} dC \quad (12)$$

where γ is the tension in the presence of surfactant with non-adsorbed concentration C, γ_0 is the tension in the absence of surfactant, k is Boltzmann's constant, T is the absolute temperature and

$\Gamma(C)$ is the surface concentration of adsorbed surfactant as a function of C . Using the calculated values of γ_0 and the measured surfactant adsorption isotherms then enables calculation of the three interfacial tensions and θ as a function of the surfactant concentration. The anionic surfactant AOT does not partition to the oil and so does not adsorb from oil to the calcite-oil interface: hence $\gamma_{\text{calcite-oil}}$ is taken to remain constant and equal to the value $\gamma_{\text{calcite-oil},0}$. Both C14BDMAC and CW-100 partition to the oil and hence can adsorb from oil to the calcite-oil interface. For CW-100, the measured calcite-oil adsorption isotherm was used in the calculations. For C14BDMAC, the calcite-oil isotherm could not be measured. However, C14BDMAC adsorption from water to the calcite-water interface is very low and it is assumed here that C14BDMAC adsorption from oil to the calcite-oil interface is negligible.

Both the calculated and measured values of contact angle have fairly high uncertainties. Despite this, the calculated lines of Figure 7 successfully capture the main features of the variation of θ with concentration of the different surfactants. From the form of Young's equation, θ is $>90^\circ$ when $(\gamma_{\text{calcite-oil}} - \gamma_{\text{calcite-water}}) < 0$ and vice versa. Hence, strong surfactant adsorption to the calcite-water interface causes θ to decrease. When the surfactant concentration is greater than $c_{\mu C_{\text{water}}}$, $\gamma_{\text{water-oil}}$ is small and hence, depending on whether $(\gamma_{\text{calcite-oil}} - \gamma_{\text{calcite-water}})$ is positive or negative, θ is predicted to be either 0 or 180° when $[\text{surf}] > c_{\mu C_{\text{water}}}$. Surfactants such as AOT and CW-100, which show strong adsorption to the calcite-water surface, therefore give $\theta = 0^\circ$. The cationic C14BDMAC shows low adsorption and $\theta = 180^\circ$ at high surfactant concentrations. Thus, despite the large uncertainties, the analysis here serves to reveal that the variation of θ with surfactant concentration is generally expected to follow one of these two broad patterns of behaviour.

Oil removal as a function of surfactant concentration for the three systems.

Using the column packed with FC10 calcite particles, we have measured %oil recovery as function of the initial surfactant concentration. The measurements were made at a fixed volumetric flow rate of $0.005 \text{ cm}^3 \text{ min}^{-1}$ with the pressure drop across the column adjusting to maintain the fixed flow rate. As discussed in ref. 27, the measured pressure drops during surfactant solution injection are found to be reasonably consistent with predictions based on the model discussed here. The packed column is fitted with porous frits in order to maintain the uniformity of the moving water-oil front across the diameter of the column. The %oil recovery was measured over the range of 0 to not less than 4 packed column pore volumes (pv) of injected surfactant solution.

In order to relate the %oil recovery to the surface chemical properties of the surfactant systems, the initial aqueous phase surfactants concentrations were converted to $[\text{surf}]_{\text{free}}$ values using equation 4. For C14BDMAC and CW-100 which can partition to the oil phase at equilibrium, it is assumed here that, although *localised* partitioning to the oil at the oil-water front can occur and affect the contact angle, partitioning to the bulk oil is slow and therefore negligible during oil recovery. For $[\text{surf}]_{\text{free}} < c_{\mu C_{\text{water}}}$, the %oil recovery is predicted to depend only on contact angle θ and not to increase with volume of solution injected above 1 pv. For $[\text{surf}]_{\text{free}} > c_{\mu C_{\text{water}}}$, the %oil recovery is predicted to increase with increasing surfactant concentration due to solubilisation and emulsification according to equation 3. As shown in the illustrative calculated plot of Figure 1, in this regime the %oil recovery is predicted to increase progressively with the number of pore volumes of surfactant solution injected. For the calculation of %oil recovery versus $[\text{surf}]_{\text{free}}$, the values of all required input parameters have been determined from independent measurements except for $(R_{\text{sol}} + R_{\text{em}})$, which was estimated by fitting to the experimental measurements of %oil recovery.

Comparison of calculated and measured plots of %oil recovery after 4 pv versus $[\text{surf}]_{\text{free}}$ are shown in Figure 8 for the different surfactant/aqueous phase/oil systems. For anionic AOT in systems with 75 mM NaCl, surfactant adsorption to the calcite surface is high and so θ decreases sharply at $c_{\mu\text{C}_{\text{water}}}$; the post- $c_{\mu\text{C}_{\text{water}}}$ tension is ultralow and so high solubilisation/emulsification of the oil is expected. As a result, %oil recovery increases slightly as $[\text{AOT}]_{\text{free}}$ increases from 0 to $c_{\mu\text{C}_{\text{water}}}$, decreases sharply and then increases due to solubilisation/emulsification. The predicted %oil recovery using a fitted value of $(R_{\text{sol}} + R_{\text{em}}) = 600$ is in reasonable agreement with the measured values. In addition, the switch in oil recovery mechanisms at surfactant concentrations below and above $c_{\mu\text{C}_{\text{water}}}$ from being constant with the number of pv injected to having an additional contribution dependent on the number of pv injected is clearly observed in Figure 9. The nonionic CW-100 has qualitatively similar adsorption and contact angle properties and hence the %oil recovery behaviour is qualitatively similar to that for AOT. The post- $c_{\mu\text{C}_{\text{water}}}$ oil-water tension for CW-100 is higher than for AOT with 75 mM NaCl; correspondingly, the value of $(R_{\text{sol}} + R_{\text{em}})$ of 150 is lower. The behavior of the cationic C14BDMAC is rather different: adsorption to calcite is low and so θ is high and reaches a constant value close to 180° when $[\text{surf}]_{\text{free}} > c_{\mu\text{C}_{\text{water}}}$. Because of this high θ / low adsorption, there is no decrease in %oil recovery at $c_{\mu\text{C}_{\text{water}}}$. In addition, it is observed that C14BDMAC gives zero solubilisation/emulsification for $[\text{surf}]_{\text{free}} > c_{\mu\text{C}_{\text{water}}}$ at 25°C . The low solubilisation is likely to be a consequence of the the low Krafft temperature of this surfactant so all surfactant in excess of $c_{\mu\text{C}_{\text{water}}}$ is expected to precipitate as solid rather than being available for emulsification/solubilisation. The middle plots of Figures 8 and 9 show that the solubilisation/emulsification by C14BDMAC is increased slightly when the temperature is increased to 30°C .

When $[\text{surf}]_{\text{free}} < c_{\mu\text{C}_{\text{water}}}$, the %oil recovery is determined solely by θ and is unaffected by the oil-water tension. For $[\text{surf}]_{\text{free}} > c_{\mu\text{C}_{\text{water}}}$, the extent of solubilisation/emulsification is expected to correlate with the post- $c_{\mu\text{C}_{\text{water}}}$ oil-water tension. In equilibrium oil/water/surfactant systems, the extent of solubilisation is maximum at microemulsion phase inversion when the post- $c_{\mu\text{C}_{\text{water}}}$ oil-water tension is minimum. However, the maximum values of R_{sol} for the solubilisation of oil in oil-in-water microemulsion phases in equilibrium Winsor I systems are generally in the range 2-20^{35,60}. The values of $(R_{\text{sol}} + R_{\text{em}})$ observed here are much greater than this range and hence %oil recovery in this regime is consistent with emulsification as the dominant mechanism, rather than solubilisation. As discussed earlier, oil trapped within the porous calcite will be increasingly mobilised by emulsification when the capillary number Ca increases above 1 which, at constant rate flow rate, is favoured by decreasing the oil-water tension. Figure 10 shows the correlation between the values of $(R_{\text{sol}} + R_{\text{em}})$ obtained by fitting the %oil recovery plots and the value of the post- $c_{\mu\text{C}_{\text{water}}}$ oil-water tension for the different surfactant systems. It can be seen that the AOT systems with different $[\text{NaCl}]$ in the aqueous phase and the CW-100 system show the expected correlation of increased emulsification as the post- $c_{\mu\text{C}_{\text{water}}}$ tension decreases. The data for C14BDMAC deviates from the plot, probably as a consequence of surfactant precipitation ($T < T_{\text{Krafft}}$).

CONCLUSIONS

This study elucidates how the inter-related phase behaviour, adsorption, contact angle and tension properties of different surfactant/oil/aqueous phase systems determine %oil recovery as functions of the concentration and the volume of surfactant solution injected. Although the work does not address many of the complicating factors present in oilfield EOR (e.g. the complex composition of crude oil containing indigenous surface active components and fissures and other non-uniformities in the porous rock that give rise to non-uniform permeabilities), it does reveal explicitly which surfactant properties are key for efficient oil recovery from a well-defined,

uniformly-permeable porous medium. To achieve high oil recovery at low surfactant concentration, the surfactant/oil/aqueous phase system should have (i) a low value of $c_{\mu C_{\text{water}}}$; (ii) low adsorption from water to the rock surface to give high contact angle and low depletion of the surfactant; (iii) the surfactant should aggregate rather than precipitate at high concentrations (i.e. the solutions should be used above the Krafft temperature) and (iv) give an ultralow post- $c_{\mu C_{\text{water}}}$ oil-water tension in order to maximise Ca and hence maximise emulsification. Hence, the key impact of this work is that it provides an experimentally-validated, theoretical framework whereby the choice of surfactant and the optimum injection concentration can be rationally optimised for particular field conditions (oil and rock types, temperature, pressure and electrolyte concentrations) using well-established surfactant science techniques and laboratory experiments in advance of expensive field trials. In addition to EOR applications, the results of this work are also applicable to surfactant enhanced soil remediation processes in which liquid oil pollutants are removed from polluted sites by injection of aqueous solutions⁶¹.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

- SI Figure 1.** SEM image of the FC10 calcium carbonate powder used here (scale bar represents a length of 2 μm) and key properties of the powder and packed columns containing it. The average particle radius corresponds to the average of the radii at 50% of the cumulative distribution from sieving analysis and the mean radii derived from SEM images.
- SI Figure 2.** Schematic of the packed powder column flood setup.
- SI Figure 3.** UV spectra (10 mm path length, versus solvent as reference) of 0.006 wt.% CW-100 (containing 0.15 mM surfactant plus 0.11 mM DEA) and 0.125 mM pure DEA in water (upper plot). Calibration plots for CW-100 in water (middle plot) and heptane (lower plot).
- SI Figure 4.** Geometry of cubic close packed calcite particles (black), oil liquid bridge with $\theta = 28^\circ$ (red) and resultant calculated water flow channel (green).
- SI Figure 5.** Solutions of 10 mM C14BDMAC in water containing 150 mM NaCl and 10 mM Na_2CO_3 . The samples were left at 15 $^\circ\text{C}$ for 1 hour, then the temperature increased to the values shown for 30 minutes (upper image). The lower image shows an optical micrograph of the crystals formed from the precipitation of C14BDMAC from an aqueous solution of 5 mM C14BDMAC, 150 mM NaCl and 10 mM Na_2CO_3 left at room temperature (approximately 22 $^\circ\text{C}$) for 12 hours. The scale bar represents 500 μm .

SI Figure 6. Solution-air surface tension versus surfactant concentration for C14BDMAC/ water with 10 mM Na₂CO₃ + 150 mM NaCl (upper plot) and CW100/water (lower plot). The horizontal dotted lines correspond to the tension in the absence of surfactant. The dashed lines are guides for the eye indicating the break points in the plots. For the C14BDMAC system, the cmc (or solubility limit) = 0.065 mM. For the CW-100 system, there are two break points at 0.0063 and 0.033 mM.

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Table 1. Properties of the different surfactant/oil/aqueous phase systems.

Surfactant system	cmc/mM	$c\mu_{\text{water}}/\text{mM}$ (from oil-water tensions and partitioning)	$c\mu_{\text{oil}}/\text{mM}$ (from partitioning)	monomer $P_{\text{oil-water}}$	Winsor type	Post- $c\mu_{\text{oil-water}}$ tension / mN m^{-1}
AOT decane 10 mM Na_2CO_3 0 mM NaCl	0.92 (a)	1.0	0	0	I	0.33
AOT decane 10 mM Na_2CO_3 40 mM NaCl	0.46 (a)	0.60	0	0	I	0.028
AOT decane 10 mM Na_2CO_3 75 mM NaCl	0.33 (a)	0.50	0	0	III	0.0079
C14BDMAC toluene 10 mM Na_2CO_3 150 mM NaCl	0.065	0.040	0.018	0.43	I	0.015
CW-100 heptane water	0.0063 to 0.033	0.17 to 1.0	0.14	0.82	I	0.09

(a) Interpolated from values in B.P. Binks PhD thesis, University of Hull, 1986.

Table 2. Best-fit parameters for the Langmuir isotherm for surfactant adsorption to the oil-aqueous phase interface from the aqueous phase.

Surfactant system	$\Gamma_{\max}$/molecules nm⁻²	K/mM⁻¹
AOT decane 10 mM Na ₂ CO ₃ 0 mM NaCl	1.3	5000
AOT decane 10 mM Na ₂ CO ₃ 40 mM NaCl	1.3	10000
AOT decane 10 mM Na ₂ CO ₃ 75 mM NaCl	1.2	10000
C14BDMAC toluene 10 mM Na ₂ CO ₃ 150 mM NaCl	1.4	7800
CW-100 heptane water	2.0	1800

Table 3. Best-fit parameters for the cooperative Langmuir-type isotherm for surfactant adsorption to the calcite-aqueous phase interface from the aqueous phase (or to the calcite-oil interface from the oil phase when noted).

Surfactant system	$\Gamma_{\max}$/molecules nm⁻²	K/mM⁻¹	β
AOT 10 mM Na ₂ CO ₃ 0 mM NaCl	2.3	0.15	-3.5
AOT 10 mM Na ₂ CO ₃ 40 mM NaCl	2.0	0.30	-3.5
AOT 10 mM Na ₂ CO ₃ 75 mM NaCl	2.2	0.35	-3.5
C14BDMAC 10 mM Na ₂ CO ₃ 150 mM NaCl	0.027	1000	0
CW-100 water	3.5 (1.0 to calcite-heptane from heptane)	0.30 (200 to calcite-heptane from heptane)	-4.0 (0.0 to calcite-heptane from heptane)

Table 4. Values of the polar and dispersion excess surface energy components of the different component-air surfaces used in the calculation of calcite-water-oil contact angles. Calculated and measured calcite-aqueous phase-oil contact angles θ (through the aqueous phase) are compared for the three oils used.

Component	$\gamma^p/\text{mN m}^{-1}$	$\gamma^d/\text{mN m}^{-1}$	Refs.	Calculated $\theta/^\circ$	Measured $\theta/^\circ$
calcite	10.2	22.9	55-59 (value for strongly hydrated calcite)	-	-
Water	50.4	21.5	54	-	-
decane	0	23.8	54	96 $\pm$ 20	120 $\pm$ 10
toluene	2.3	28.5	54	92 $\pm$ 20	121 $\pm$ 10
heptane	0	20.1	54	96 $\pm$ 20	103 $\pm$ 10

Figure 1. Upper plot: %oil recovery as a function of calcite-water-oil contact angle θ measured through the water phase. The curve, calculated as described in the text, applies to all particle/surfactant/oil/water systems. Lower plots: Illustrative calculations of %oil recovery versus aqueous phase surfactant concentration for a hypothetical surfactant/water/oil with the contact angles shown in the middle plot, $c_{ac} = 0.2$ mM, $MV_{oil} = 1.5 \times 10^{-4} \text{ dm}^3 \text{ mmol}^{-1}$ and $(R_{sol} + R_{em}) = 100$. The multiple lines correspond to different numbers of pore volumes n of aqueous solution injected (shown in the figure legend).

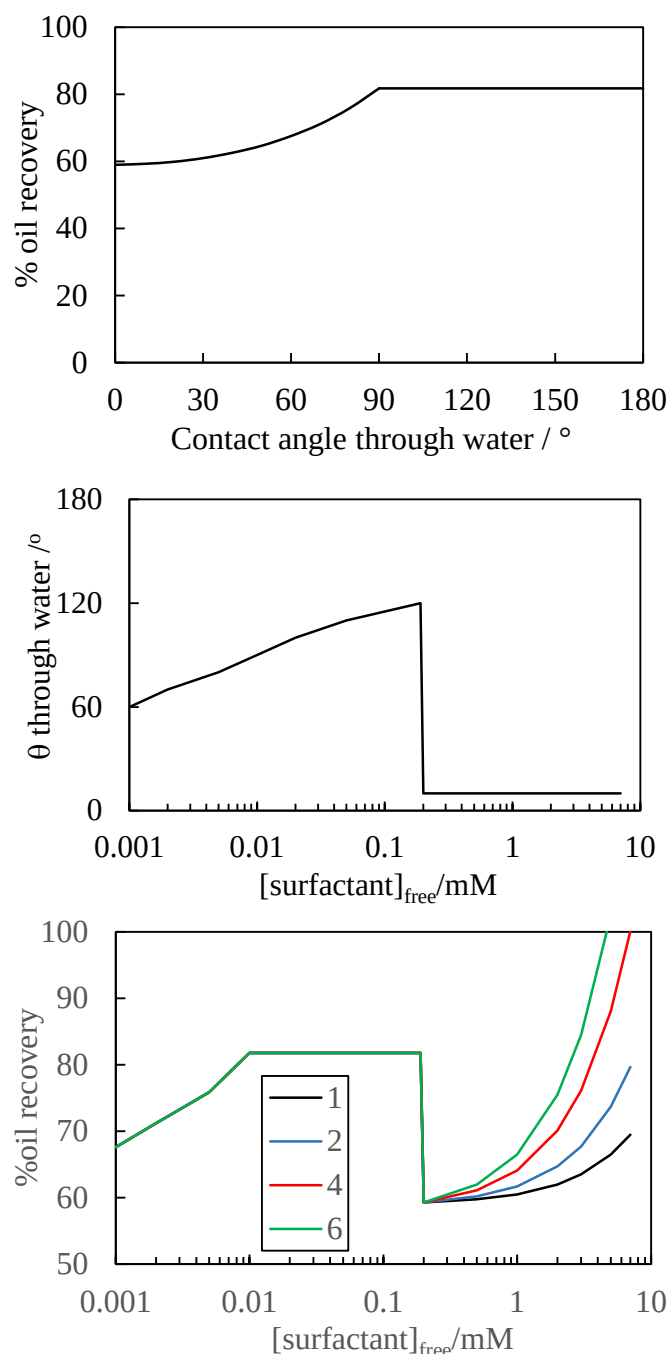


Figure 2. Microemulsion phase tubes for: 5 mM AOT/decane/water with 10 mM Na_2CO_3 plus NaCl concentrations after 15 hours equilibration (upper image); 5 mM C14BDMAC/toluene/water with 10 mM Na_2CO_3 plus NaCl concentrations after 3 days equilibration (middle image); and 25 mM CW-100/heptane/water with the NaCl concentrations after 2 days equilibration (lower image).

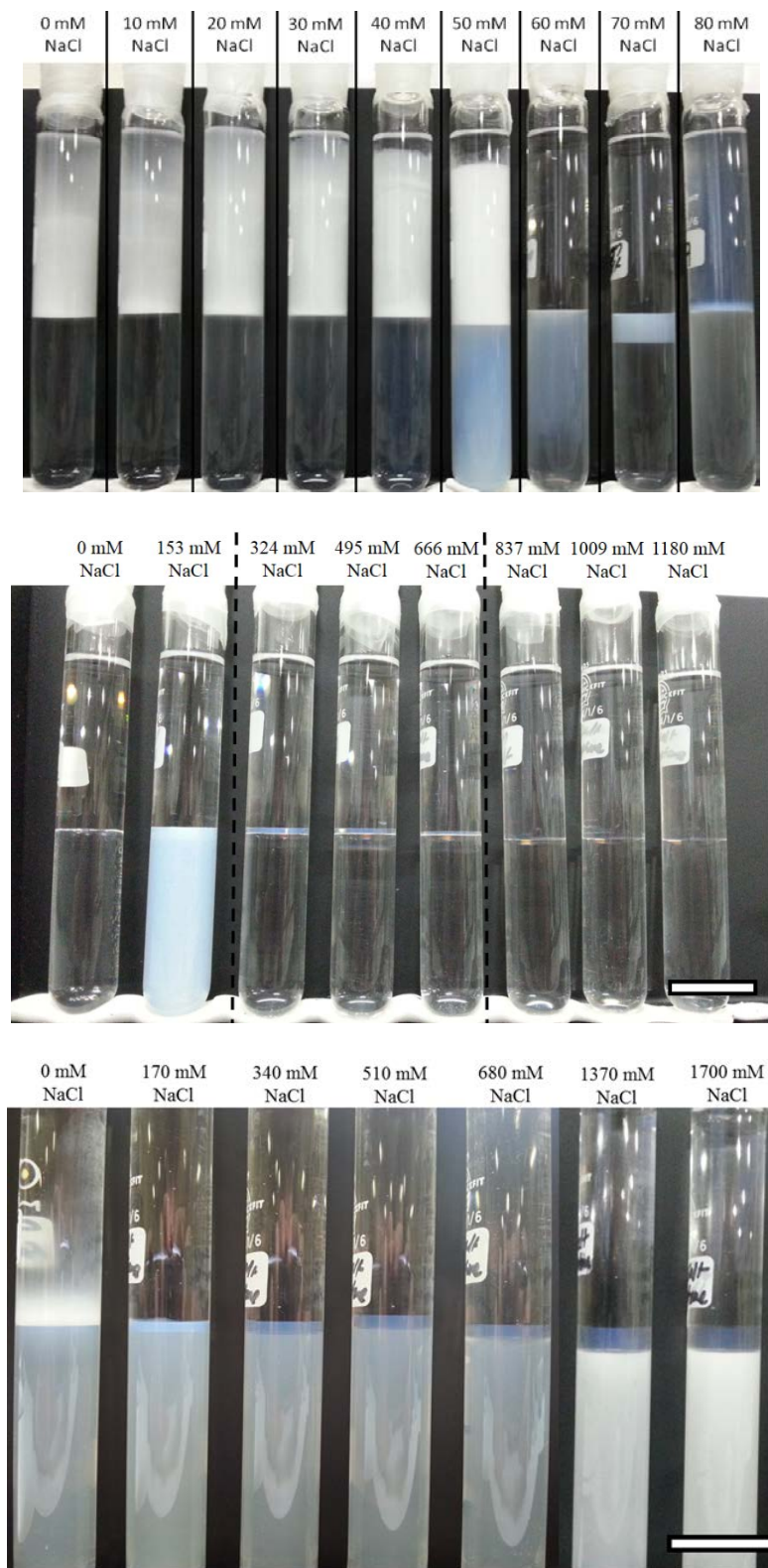


Figure 3. Measured (data points) and fitted (solid lines) equilibrium oil-water partitioning behaviour of C14BDMAC/toluene/ water with 10 mM Na₂CO₃ + 150 mM NaCl (upper plot) and CW100/heptane/water (lower plot). For the C14BDMAC system, the fitted solid lines correspond to $c\mu_{\text{water}} = 0.040$ mM, $c\mu_{\text{oil}} = 0.017$ mM and $P_{\text{oil-water}} = 0.43$. For the CW-100 system, the solid lines correspond to $c\mu_{\text{water}} = 0.17$ mM, $c\mu_{\text{oil}} = 0.14$ mM and $P_{\text{oil-water}} = 0.82$.

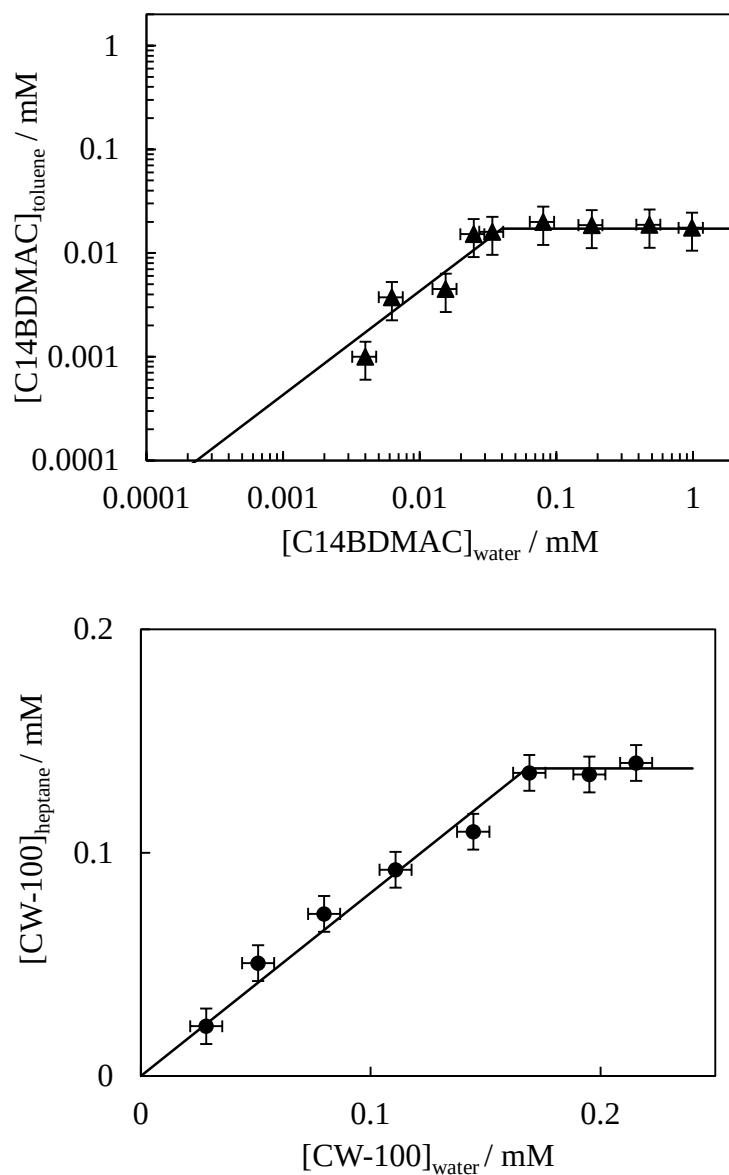


Figure 4. Measured (data points) and fitted curves showing the variation of oil-water tension with aqueous phase surfactant concentration for AOT/decane/water with 10 mM Na_2CO_3 + NaCl aqueous solution interface (upper plot), C14BDMAC/toluene/ water with 10 mM Na_2CO_3 + 150 mM NaCl (middle plot) and CW100/heptane/water (lower plot). The solid lines show the fits to the Langmuir adsorption isotherm with parameters given in Table 2.

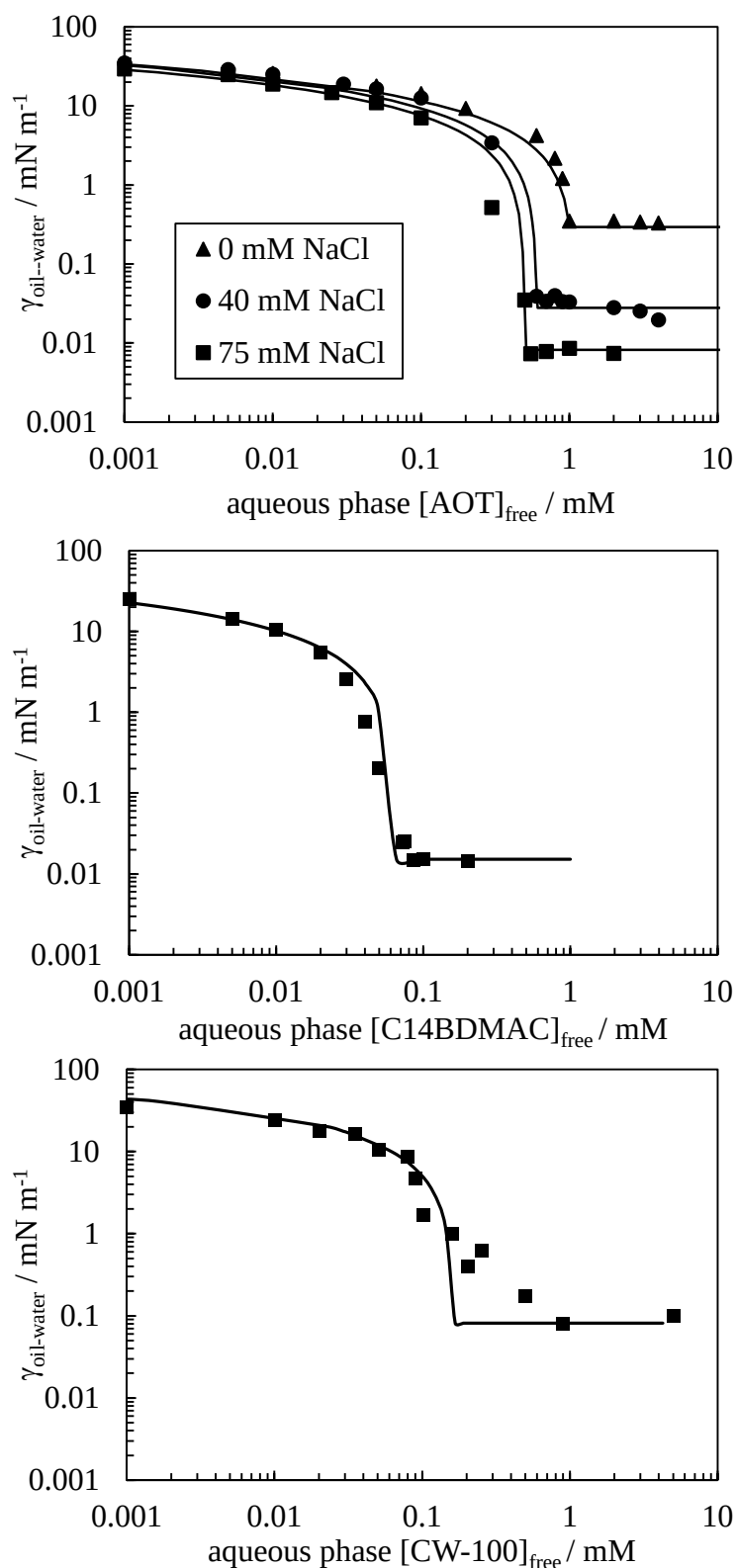


Figure 5. Measured (data points) and fitted calcite adsorption isotherms for AOT/water with 10 mM Na_2CO_3 + NaCl (upper plot), C14BDMAC/ water with 10 mM Na_2CO_3 + 150 mM NaCl (middle plot), and CW-100/water and CW-100/heptane (lower plot). The lines show the fits to cooperative Langmuir-type adsorption isotherm with parameters given in Table 3.

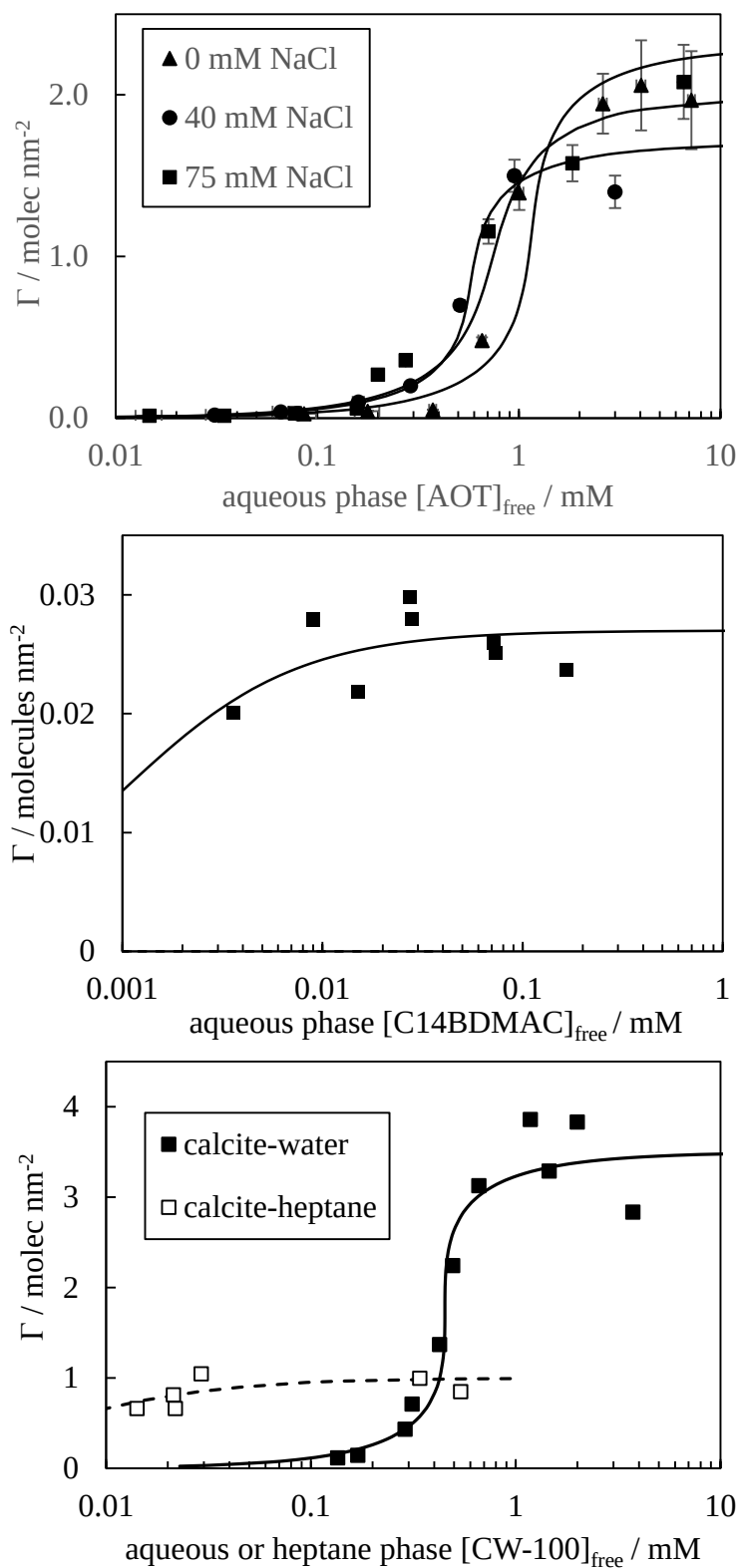


Figure 6. Derived “free” versus initial aqueous phase surfactant concentrations for AOT/water with 10 mM Na_2CO_3 + 75 mM NaCl (upper plot), C14BDMAC/toluene/ water with 10 mM Na_2CO_3 +150 mM NaCl (middle plot) and CW100/heptane/water (lower plot) for different numbers of pore volumes pumped. It is assumed that no significant amount of surfactant transfers from the aqueous to oil phase. The dashed lines correspond to zero depletion.

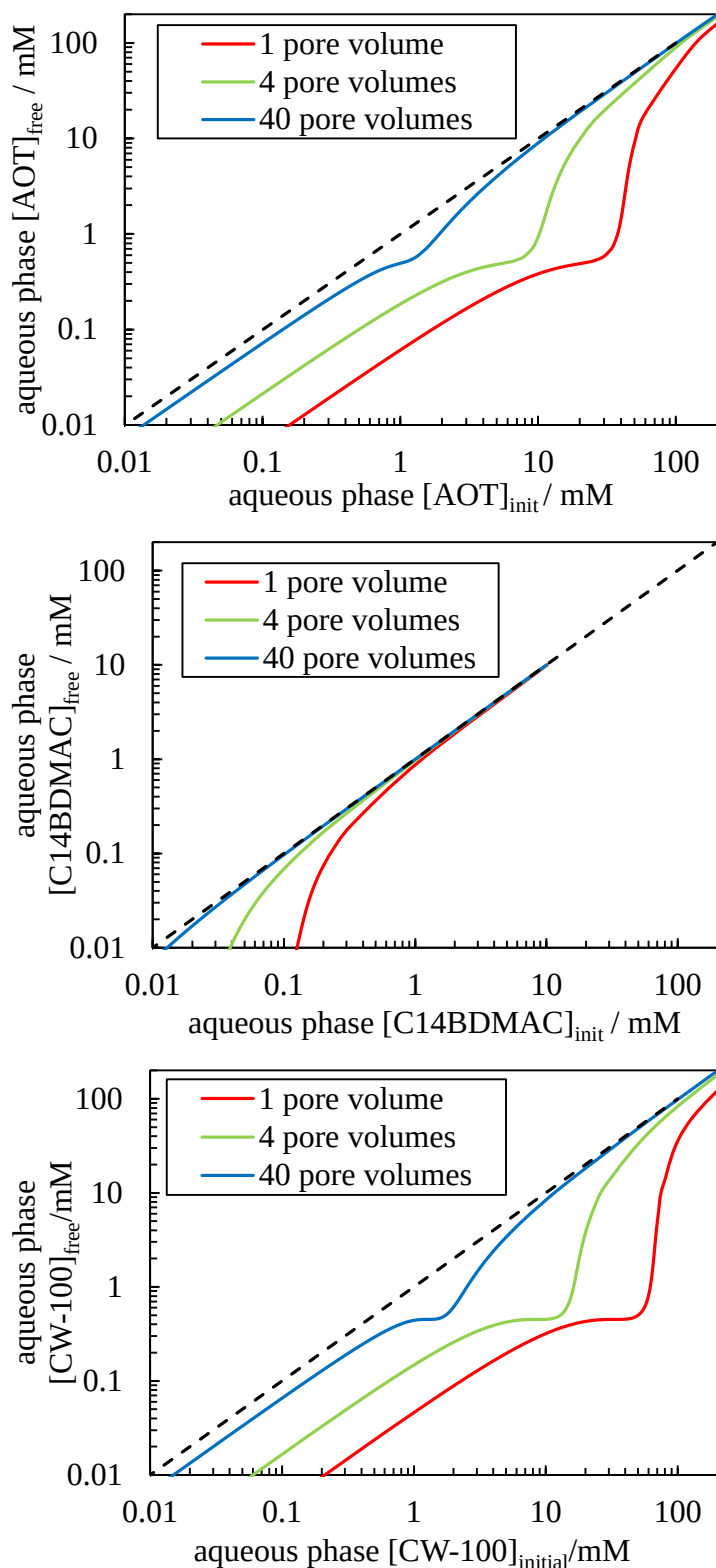


Figure 7. Measured (data points) and calculated (lines) oil-water-calcite contact angles (static, advanced) versus “free” aqueous phase surfactant concentrations for AOT/water with 10 mM Na_2CO_3 + mM NaCl (upper plot), C14BDMAC/toluene/water with 10 mM Na_2CO_3 +150 mM NaCl (middle plot), and CW100/heptane/water (lower plot). For each data set, the lines show the calculated variation of contact angle based on the calcite surface energy components, oil-water tensions and the calcite-water adsorption isotherms.

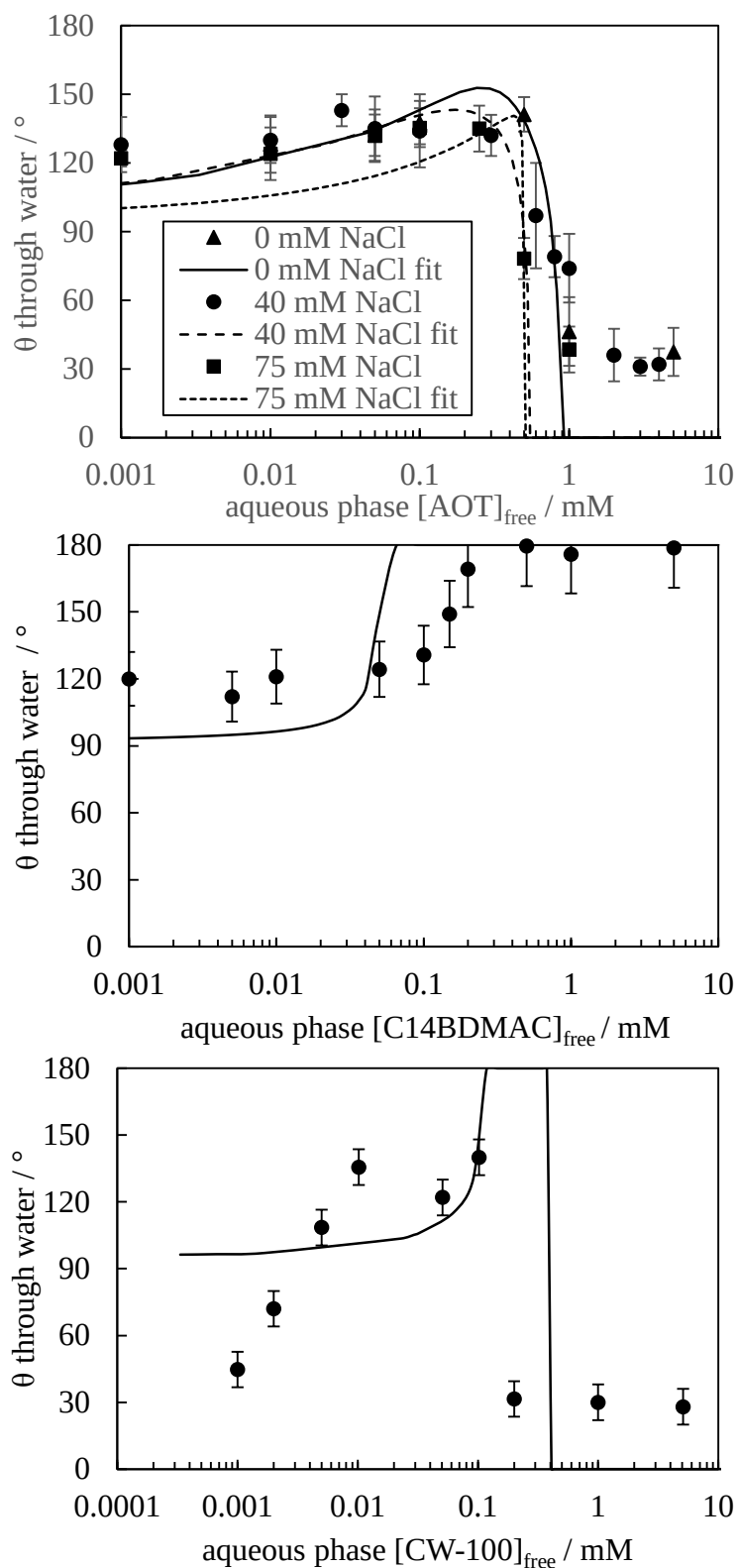


Figure 8. Measured (data points) and calculated (solid lines) plots of %oil recovery versus $[\text{surf}]_{\text{free}}$ for AOT/water with 10 mM Na_2CO_3 + 75 mM NaCl (upper plot), C14BDMAC/toluene/ water with 10 mM Na_2CO_3 +150 mM NaCl (middle plot) and CW100/heptane/water (lower plot). The horizontal dashed lines shows the measured %oil recovery in the absence of surfactant. The vertical dashed lines indicate $c_{\mu\text{C}_{\text{water}}}$. The solid lines shows the predicted recovery according to the model described in the text.

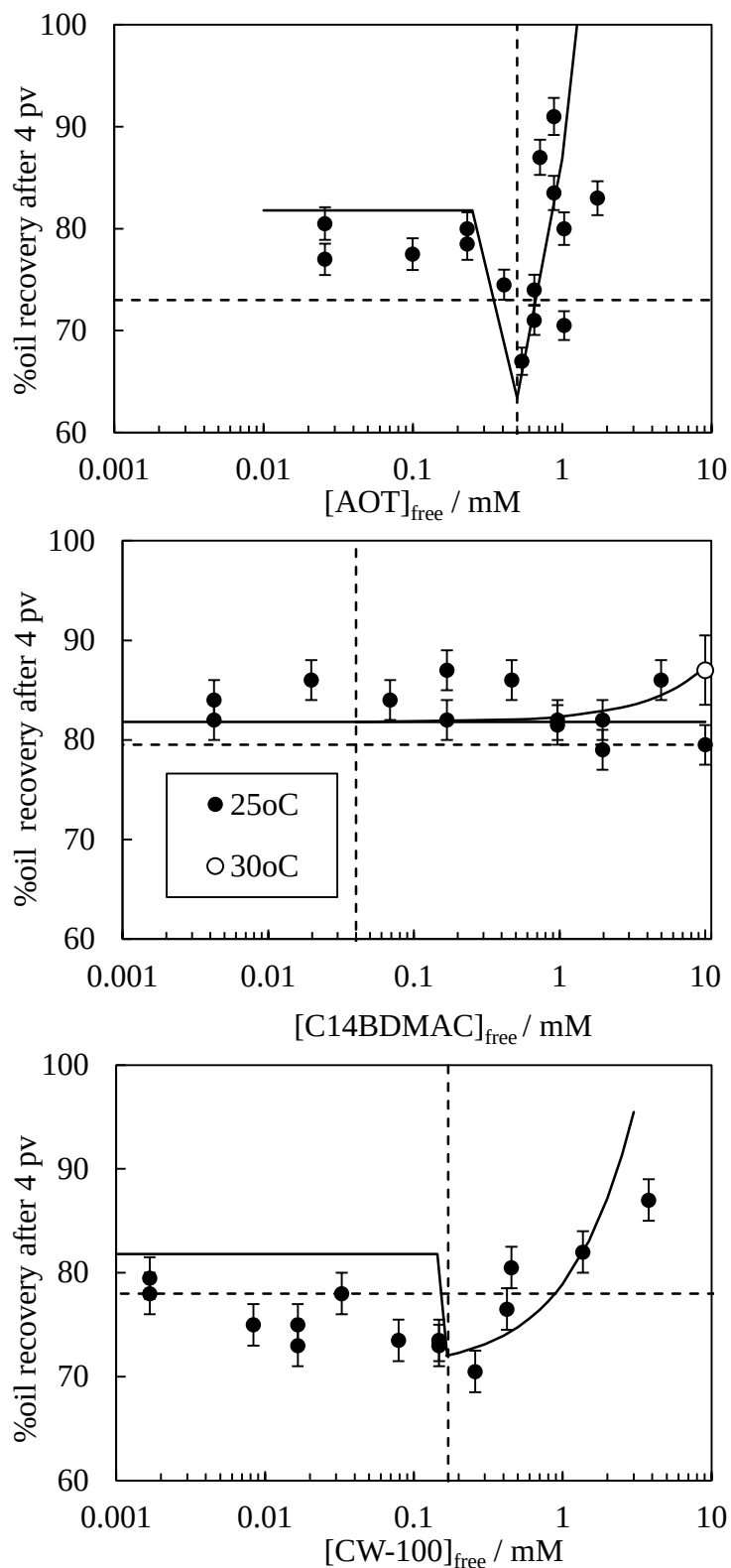


Figure 9. Measured change in %oil recovery between 1 and 4 pv versus aqueous phase $[\text{surf}]_{\text{free}}$ for AOT/water with 10 mM Na_2CO_3 + 75 mM NaCl (upper plot), C14BDMAC/toluene/ water with 10 mM Na_2CO_3 +150 mM NaCl (middle plot) and CW100/heptane/water (lower plot). The horizontal dashed lines show the measured value in the absence of surfactant. The vertical dashed lines indicate $c_{\mu\text{Cwater}}$.

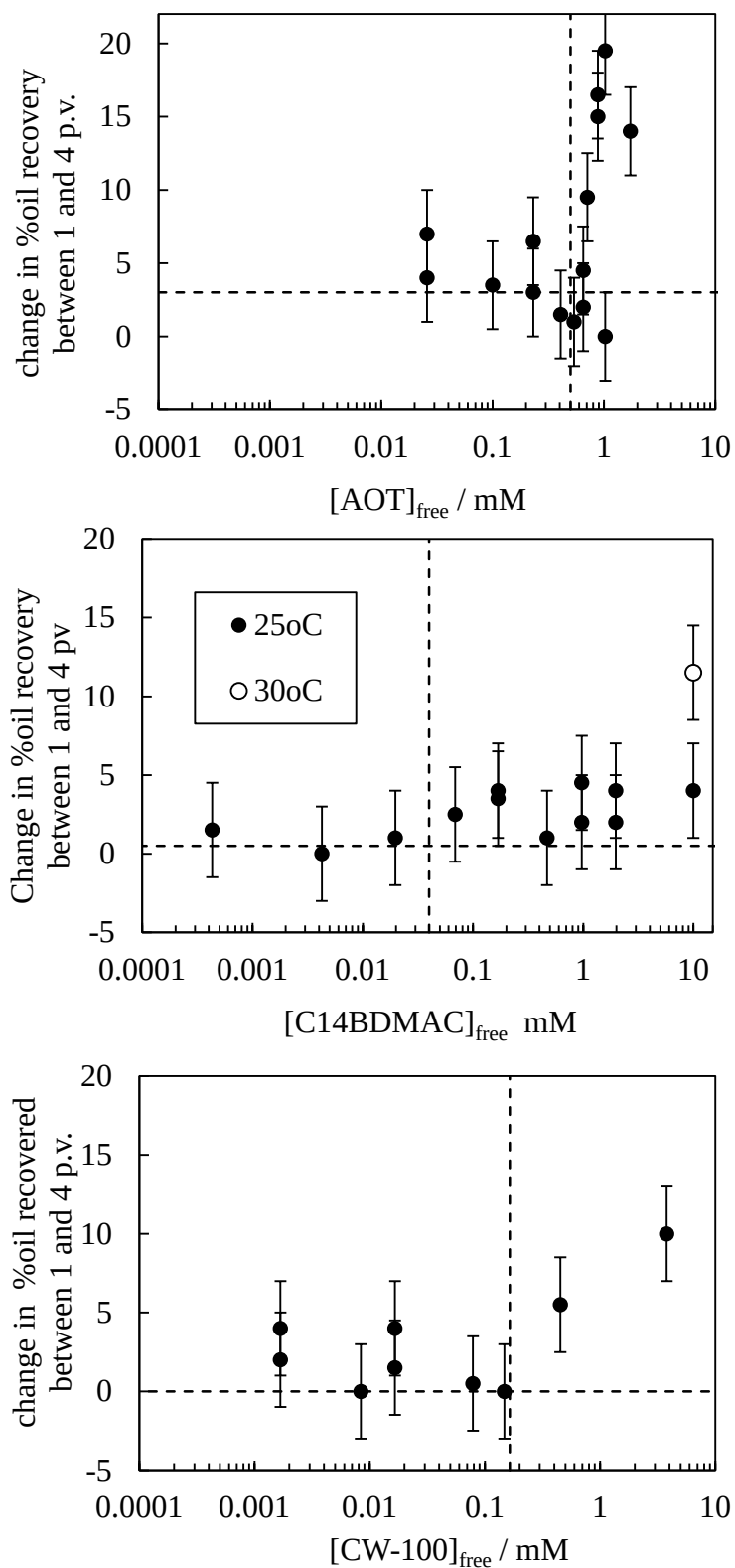


Figure 10. Variation of $(R_{sol} + R_{em})$ with post-cmc oil-water interfacial tension for the different systems.

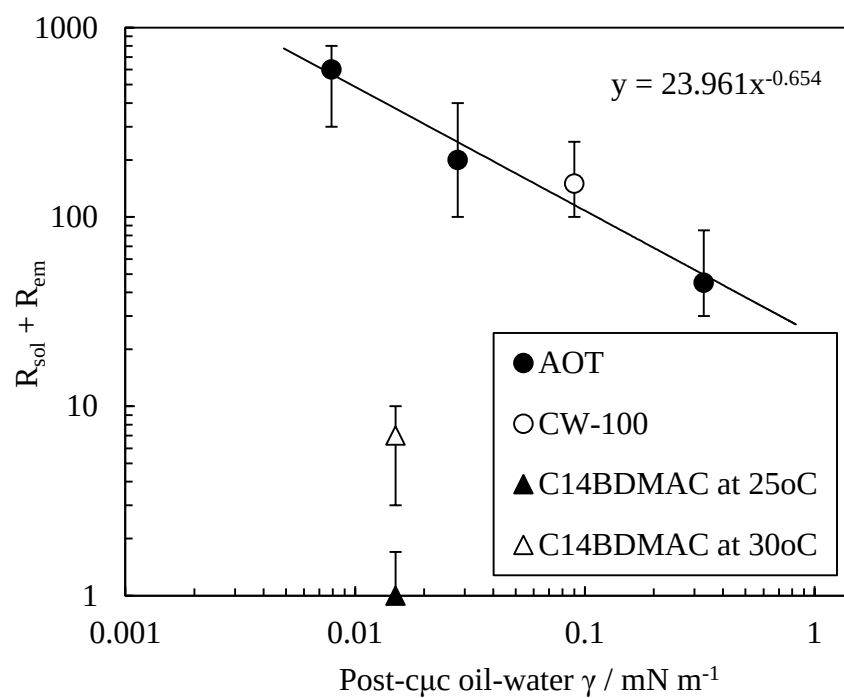


Table of Contents Graphic

Using measured surface chemical properties, we have successfully modelled how recovery varies with surfactant concentration for different surfactant systems.

