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Surface Chemistry of Oil Recovery From Fractured, Oil-Wet, Carbonate Formations

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Abstract

Oil recovery by water flooding in fractured formations is often dependent on spontaneous imbibition. However, spontaneous imbibition is often insignificant in oil-wet, carbonate rocks. Sodium carbonate and anionic surfactant solutions are evaluated for enhancing oil recovery by spontaneous imbibition from oil-wet carbonate rocks. Crude oil samples must be free of surface-active contaminants to be representative of the reservoir. Calcite, which is normally positively charged, can be made negative with sodium carbonate. The ease of wettability alteration is a function of the aging time and temperature and the surfactant formulation.

Introduction

Much oil remains in fractured, carbonate oil reservoirs after waterflooding and in some cases in paleo-transition zones, which result from the

oil/water contact moving upward before discovery.

The high remaining oil saturation is due to a combination of poor sweep in fractured reservoirs and the formation being preferentially oil-wet during imbibition^{1,2}. (*Imbibition* is defined as the process of water displacing oil. *Spontaneous imbibition* is defined as imbibition that takes place by action of capillary pressure and/or buoyancy when a core sample or matrix block is surrounded by brine.) Poor sweep is not an issue in paleo-transition zones but yet the remaining oil saturation may still be significant.

There are several reasons for high remaining oil saturation in fractured, oil-wet, carbonate formations. If the formation is preferentially oil-wet, the matrix will retain oil by capillarity and high oil saturation transition zones will exist where the upward oil film flow path is interrupted by fractures. This is illustrated in Fig. 1, which shows

the oil retained by oil-wet capillaries of different radii. The height of the capillary retained oil column is proportional to the product of interfacial tension and cosine of the contact angle and is inversely proportional to the capillary radius. In oil-wet systems, oil is the phase contacting the rock surfaces, and surface trapping is likely to be particularly important in rocks with highly irregular surfaces and large surface areas¹, Fig. 2.

The objective of this investigation is to develop a process to overcome the mechanisms for oil retention illustrated by Figs. 1 & 2. Oil is retained by wettability and capillarity. Thus by altering the wettability to preferentially water-wet conditions and reducing the interfacial tension to ultra-low values, the forces that retain oil can be overcome. Introducing an injected fluid into the matrix of a fractured formation is challenging because the injected fluid will flow preferentially in the fractures rather than through the matrix. Thus the process must be designed to cause spontaneous imbibition of the injected fluid from the fracture system into the matrix, as illustrated in Fig. 3. Spontaneous imbibition by capillarity may no longer be significant because of low interfacial

tension. However, if wettability is altered to preferentially water-wet conditions and/or capillarity is diminished through ultra-low interfacial tensions, buoyancy will still tend to force oil to flow upward and out of the matrix into the fracture system. The injected fluid in the fractures will replace the displaced oil in the matrix and thus the invasion of the injected fluid into the matrix will continue as long as oil flows out of the matrix.

Spontaneous imbibition by capillarity is an important mechanism in oil recovery from fracture reservoirs. A recent survey by Morrow and Mason reviews the state-of-the-art³. They state that spontaneous imbibition rates with different wettability can be several orders of magnitude slower and displacement efficiencies range from barely measurable to better than very strongly water-wet. The primary driving force for spontaneous imbibition in strongly water-wet conditions is usually the capillary pressure. Reduction of interfacial tension reduces the contribution of capillary imbibition. Buoyancy, as measured by the product of density difference and the acceleration of gravity then becomes the dominant parameter governing the displacement,

even if oil is the wetting phase⁴.

Application of surfactants to alter wettability and thus enhance spontaneous imbibition has been investigated by Austad, et al.⁷⁻¹¹ with chalk and dolomite cores. Chen, et al.¹², investigated enhanced spontaneous imbibition with nonionic surfactants. Spinler, et al.¹³, evaluated 46 surfactants for enhanced spontaneous imbibition in chalk formations. Standnes, et al.¹¹ and Chen, et al.¹² used either nonionic or cationic surfactant with a strategy to alter wettability but avoid ultra-low tensions. The work presented here differs from the previous work in that sodium carbonate and anionic surfactants are used to both alter wettability and reduce interfacial tension to ultra-low values. The primary recovery mechanism in this work is buoyancy or gravity drainage. Wettability alteration and ultra-low interfacial tensions are designed to minimize the oil retention mechanisms.

Crude Oil Samples

It is important to have a representative crude oil sample when designing an EOR process. Since the process is based on surface phenomena, it is important that the crude oil is free of surface-active materials such as emulsion breaker, scale inhibitor,

or rust inhibitor. A simple test for contamination is to measure the interfacial tension (IFT) of the crude oil sample with synthetic brine. Fig. 4 is a plot of the oil/brine IFT of several crude oil samples from the same field. These measurements were made with a pendant drop apparatus with automatic video data acquisition and fit to the Young-Laplace equation. Samples MY1 and MY2 have low initial IFT that further decreases with time. This is an indication that these samples contain a small amount of surface-active material, which slowly diffuses to the interface and reduces the IFT. Samples MY3 – MY6 have a much larger initial IFT. Even though there is some decrease in IFT with time, the IFT remains in the range of 20-30 mN/m. Some early experiments were made with MY1 before we were aware of the contamination but the later experiments were made with MY3.

The properties of the crude oil samples are listed in Table 1. The higher acid number and viscosity for MY1 compared to the other samples suggest that it may be an outlier. The wettability of the oil samples were compared by pressing an oil drop in brine against a calcite (marble) or glass plate for 5-10 minutes, withdrawing the drop, and

measuring the water advancing contact angle after motion has ceased. The water advancing contact angles of MY1 and MY3 against calcite or glass after aging time of 5-10 minutes are compared in Fig. 5. Clearly, MY1 and MY3 crude oils have different wettability properties.

Formation Wettability

Spontaneous imbibition in carbonate formations often does not occur or is slow compared to sandstone formations.¹⁴⁻¹⁹ Treiber, Archer, and Owens¹⁴ measured the equilibrated water advancing contact angles of fifty crude oils. They found that of the carbonate reservoir-crude oil-water systems tested, 8% were water-wet; 8% intermediate; and 84% oil-wet. This is in contrast to 43% water-wet; 7% intermediate-wet; and 50% oil-wet for silicate formation reservoirs.

Freedman, et al.²⁰, evaluated the wettability of Bentheim sandstone, Berea sandstone, and the dolomite formation of the present investigation. A crude oil from the North Sea was used for the evaluation. Water would spontaneously imbibe into the sandstone formation materials but no measurable spontaneous imbibition occurred in the

dolomite samples during 24 hours. The dolomite cores were partially water flooded to an intermediate saturation and the NMR relaxation time distribution of the remaining oil was measured. The relaxation time distributions of the crude oil in the sandstones were identical to that of the bulk oil, indicating that the sandstones were water-wet. However, the relaxation time distribution of the crude oil in the dolomite sample was shortened, indicating surface relaxation of the oil. This occurs due to oil making contact with the pore walls. Thus, this is evidence of oil wetting the pore walls in the dolomite sample.

The wettability of the MY3 crude oil was evaluated by measuring the water advancing contact angle on calcite (marble) plates. The plates were solvent cleaned, polished on a diamond lap to remove the surface layer, aged in 0.1 M NaCl brine overnight, and aged in the crude oil for 24 hours, either at room temperature or 80° C. The reservoir is close to room temperature but elevated temperature aging was used to compensate the short aging time compared to geological time. Photographs of an oil drop in brine on the upper calcite surface after all motion had stopped are

shown in Fig. 6. It is clear that the water advancing contact angle is near 180° , i.e., it is oil-wet. It should be noted that MY3 aged for only 5-10 minutes, shown earlier in Fig. 5, had an advancing contact angle of only 50° . These results demonstrate the importance of aging time on wettability.

One of the most important factors in the determination of the wettability of crude oil-brine-mineral systems is the electrical or zeta potential of the crude oil/brine interface and of the mineral/brine interface²¹⁻²³. The zeta potentials of these interfaces as a function of pH are shown in Fig. 7. The zeta potential of the MY1 crude oil is negative for pH greater than 3. This is due to the dissociation of the naphthenic acids in the crude oil with increasing pH. The surface of calcite²⁴⁻³¹ is positive for pH less than 9 when the only electrolytes are 0.02 M NaCl and NaOH or HCl to adjust pH. The opposite charge between the oil/brine and mineral/brine surfaces results in an electrostatic attraction between the two interfaces, which tend to collapse the brine film and bring the oil in direct contact with the mineral surface. Thus this system can be expected to be non-water-wet around neutral

pH^{32,33}. However, this figure also shows that the zeta potential of calcite is negative even to neutral pH when the brine is 0.1 N $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ plus HCl to adjust pH. This is because the potential determining ions for the calcite surface are Ca^{2+} , CO_3^{2-} and HCO_3^- . An excess of the carbonate/bicarbonate anions makes the surface negatively charged. If both the crude oil/brine and calcite/brine interfaces are negatively charged, there will be an electrical repulsion between the two surfaces, which tends to stabilize a brine film between the two surfaces. Thus a system with brine containing sufficient excess carbonate/bicarbonate ions may be expected to have a preference to be water-wet, compared to in the absence of excess carbonate ions.

Figs. 8 and 9 illustrate the effect of alkaline surfactant solutions on wettability alteration of a calcite (marble) plate that has been aged in crude oil either at room temperature or at 80°C . The oil-wet systems, with brine as the surrounding fluid, Fig. 8(a) and Fig. 9(a) are the same as that shown in Fig. 6(a) and 6(b). The displacement of oil by reduction of the interfacial tension and the alteration of the wettability upon replacement of the brine with

0.05% CS-330 / 0.5 M Na_2CO_3 are shown as a function of time. Both systems showed the oil streaming from the surface at early times as a result of the reduction in interfacial tension, Fig. 8(b) and 9(b). Later, small oil drops remaining on the marble plate are observed with higher magnification and the change in contact angle can be observed, Fig. 8(c)-(f) and 9(c)-(f).

The observation of the oil streaming off the plate as surfactant reduces the interfacial tension and alters the contact angle is explained as follows. An oil drop on the upper surface of a solid immersed in brine is not stable for drop dimensions such that the Bond number, $N_B = \frac{\Delta\rho g L^2}{\sigma}$, is the order of unity or greater. Fig. 10 illustrates possible hydrostatic shapes of axisymmetric oil drops^{34,35}. The length scales are made dimensionless with respect to the capillary constant, $\sqrt{\sigma/(\Delta\rho g)}$. The different curves only have different dimensionless curvature at the apex of the drop. The interface intersects the solid surface at the point where the inclination angle of the interface is equal to the contact angle with the substrate. Suppose the L in the Bond number is the equatorial radius if the

contact angle is 90° or less; and is the radius of the contact line if the contact angle is larger than 90° . The Bond number of a drop in Fig. 10 is then the square of the dimensionless radius to the equator or to the contact line. The maximum hydrostatic Bond number from Fig. 10 ranges from 0.25 for contact angles less than 90° to 10 for contact angles approaching 180° . Thus larger contact angles can have larger hydrostatic drop size, for the same IFT.

The definition of the Bond number implies that the maximum hydrostatic oil drop size is proportional to the square root of the interfacial tension. As the interfacial tension was reduced to ultra-low values, the large oil drop was unstable and small drops streamed off. The observation that the oil drop size became 10^{-2} smaller when brine was replaced by alkaline surfactant solution is consistent with the observation that the IFT was 10^{-4} smaller, i.e., reduced from 30 mN/m to about 3×10^{-3} mN/m. Also, for the same interfacial tension, oil drops with smaller contact angles are smaller than drops with larger contact angles.

Alteration of wettability also contributes to displacement of the oil. Fig. 8(c)-(f) shows the

wettability being altered from strongly oil-wet to preferentially water-wet for the plate that was aged 24 hours in crude oil at room temperature. An oil drop becomes unstable and detaches as the contact angle approaches a small value. Fig. 9(c)-(f) shows that the plate that was aged 24 hours in crude oil at 80° C altered to intermediate wet conditions during the 4- day period of observation. Fig. 9(c)&(d) is one drop and Fig. 9(e)&(f) is another drop. No further change was observed after the first day to the fourth day.

Similar observations were made for systems with TDA-4PO and a blend of CS-330 and TDA-4PO. The sodium carbonate concentrations were near that which gave minimum interfacial tension. Besides initially equilibrating the marble plate in NaCl brine, some experiments had the plate initially equilibrated in sodium carbonate solution or in alkaline surfactant solution. The advancing contact angle at the end of the observation period ranged from preferentially water-wet to intermediate-wet. These variations did not result in a systematic change in wettability compared to the effect of aging time and temperature in crude oil.

Spontaneous Imbibition

Spontaneous imbibition is most commonly associated with counter-current capillary imbibition in systems that are preferentially water-wet³. If the interfacial tension is very low, capillarity becomes less important compared to buoyancy⁴. However, for systems that are preferentially oil-wet, spontaneous imbibition of brine usually does not occur and capillarity is the mechanism that retains oil in the matrix, as illustrated in Fig. 1. The height of an oil column in a preferentially oil-wet capillary is proportional to the product of the interfacial tension and the cosine of the contact angle. Buoyancy is an omnipresent driving force for displacement of oil by water. Reduction of interfacial tension and alteration of wettability inside the matrix will reduce the tendency for capillarity to retain the oil. Thus a low-tension process has the process fluids entering the matrix to replace the oil that is leaving by buoyancy⁴, as illustrated in Fig. 3.

The effect of buoyancy displacing oil from between two parallel surfaces is demonstrated with the system in Fig. 11. A calcite (marble) plate was aged in crude oil at room temperature. It is placed

in an optical cell with a plastic film as a spacer to create a 13 μm gap between the plate and the front wall of the cell. The glass of the front of the cell has been treated with a dilute solution of hexadecyltrimethylammonium bromide to make the glass preferentially oil-wet. Oil in the gap is not displaced when the cell is filled with brine, Fig. 12(a). The buoyancy forces cannot overcome the capillary entry pressure to displace the oil from the gap. However, when the brine is replaced with 0.05% CS-330 / 0.3 M Na_2CO_3 , the displacement of oil is rapid, Fig. 12(b). The alkaline surfactant solution both lowers the interfacial tension and alters the wettability of both the calcite and glass surfaces. Only isolated drops of oil remain after 7 hours.

One qualitative difference between displacement of oil from a gap between parallel surfaces and a porous rock is that the gap has 100% oil saturation while a porous rock has formation brine occupying the pore space along with the oil, Fig. 13. Buoyancy may displace the mobilized oil but the formation brine may form a bank ahead of the alkaline surfactant solution. Dispersive mixing is necessary for the alkaline surfactant solution to

penetrate through the bank of formation brine and contact the trapped oil. Also, the alkaline surfactant solution must remain active as it mixes with the formation brine.

Surfactant Formulations

It was mentioned earlier that nonionic and cationic surfactants have been previously evaluated for wettability alteration in carbonate formations⁵⁻¹³. This investigation focuses on the use of anionic surfactants and sodium carbonate. It builds on the previous understanding developed for alkaline surfactant flooding^{36,37}. Also, this technology has found many applications during the past decade when it was commonly thought that surfactant flooding was not economical because of the expense of the surfactant³⁸⁻⁵³.

There are a number of reasons for choosing sodium carbonate as the alkali. We mentioned earlier that the carbonate/bicarbonate ion is a potential determining ion for carbonate minerals and thus is able to impart a negative zeta potential to the calcite/brine interface, even at neutral pH. A negative zeta potential is expected to promote water-wetness. Other reasons for choosing sodium

carbonate include:

- The moderately high pH generates natural surfactants from the naphthenic acids in the crude oil by in situ saponification;
- Sodium carbonate suppresses calcium ion concentration;
- Sodium carbonate reduces the extent of ion exchange and mineral dissolution (in sandstones) compared with sodium hydroxide^{40, 54};
- Adsorption of anionic surfactants is low with the addition of an alkali, especially with sodium carbonate^{36, 52-56};
- Carbonate precipitates do not adversely affect permeability as compared to hydroxide and silicates⁵⁴;
- Sodium carbonate is an inexpensive alkali since it is mined as the sodium carbonate – bicarbonate mineral, trona.

The phase behavior of MY3 crude oil and different concentrations of sodium carbonate solution is shown in Fig. 14. The aqueous phase is most turbid at a concentration of 0.1 M and

becomes clear at a concentration of 0.2 M. Based on an acid number of 0.2 mg KOH/g, a concentration of 0.003 M Na_2CO_3 is required to neutralize the acid to soap and NaHCO_3 . The pH of the equilibrated solutions exceeds 10 with a Na_2CO_3 concentration of 0.05 M. The clear aqueous phase at a concentration of 0.2 M indicates that a Winsor Type II microemulsion has formed at this concentration. This is an oil-continuous microemulsion, or is commonly called as “over-optimum”. Thus a concentration of alkali large enough to transport through a reservoir is often over-optimum in electrolyte strength. Some crude oil-brine-mica systems, which were water-wet at high pH and low salinity, became oil-wet at high pH and high salinity^{57, 58}. Thus, the over-optimum phase behavior must be avoided if water-wet conditions are desired. Also, over-optimum conditions result in high surfactant retention in conventional surfactant flooding⁵⁹.

The choice of surfactants to use for an alkaline surfactant process for carbonate formation was guided by the experience with sandstone formations but recognizing that adsorption is going to be on the carbonate minerals, calcite and dolomite. Thus

internal olefin sulfonates, which are effective for sandstones³⁷, were not considered since they are very sensitive to calcium ions. Rather, ethoxylated and propoxylated sulfate surfactants were evaluated⁶⁰⁻⁶³ because of their known tolerance to divalent ions. Sulfates rather than sulfonates were evaluated because of their greater availability and because the target application is at a low temperature where the sulfate hydrolysis should not be a problem. The surfactants evaluated are identified in Table 2. CS-330 is similar to NEODOL 25-3S, used previously³⁶. The propoxylated surfactants are calcium tolerant such that CaCl_2 has been used as the electrolyte to achieve optimal salinity⁶³.

The phase behavior of the MY3 crude oil with alkaline surfactant solutions as a function of Na_2CO_3 concentration with 0.05% (active material) surfactant is shown in Figs. 15-18. The systems were shaken for 2 days and allowed to equilibrate for 5-7 days. CS-330 is shown in Fig. 15; C12-3PO in Fig. 16; TDA 4PO in Fig. 17; and ISOFOL14T-4.1PO in Fig. 18. Only Na_2CO_3 was used as the electrolyte rather than a mixture of NaCl and Na_2CO_3 to reduce a degree of freedom in the

comparisons. The spinning-drop interfacial tensions of the equilibrated (5-19 days) oleic and aqueous phases are shown in Fig. 19. All systems have interfacial tension in the range $10^{-3} - 10^{-2}$ mN/m for a range of Na_2CO_3 concentrations. Nelson et al.³⁶ pointed out that the amount of oil relative to the amount of synthetic surfactant is an important parameter since the natural surfactant from the naphthenic acids and the synthetic surfactant have different optimal salinities. This is illustrated by the dependence of the interfacial tension on the water/oil ratio, Fig. 20, since the synthetic surfactant is supplied with the water and the natural surfactant comes from the oil. While each system had ultra-low tension at a water/oil ratio of 1:1, the tension increases with increase in water/oil ratio. This increase is rapid for CS-330 but much less for TDA-4PO. The phase behavior of the systems with increased concentrations of TDA-4PO of 0.2% (active material) and 1% are shown in Figs. 21 and 22. Compared to a concentration of 0.05%, the corresponding phase behavior has moved to higher Na_2CO_3 concentrations. The interfacial tensions, shown in Fig. 23, have optimal conditions at higher Na_2CO_3 concentrations. Also,

the minimum tension is lower with the higher surfactant concentrations. Apparently, the optimal salinity changes to higher electrolyte strength since the ratio of the synthetic surfactant to natural surfactant increases with increasing surfactant concentration. These dependencies must be considered in optimizing a system for oil recovery^{36,62}.

Mixing with formation brine

Mixing with formation brine has always been an important issue with surfactant flooding, but new considerations are needed because of the presence of sodium carbonate. Hard water cannot be used to prepare the solutions for injection because of precipitation of CaCO_3 . Also, premature production of injected fluids should be minimized to avoid production well scaling and produced emulsions. Fig. 13 shows that there will be mixing with the formation brine as the alkaline surfactant solution invades the formation matrix. Besides dilution, alkalinity will be lost due to precipitation of divalent ions in the formation brine. The surfactant formulation should be formulated such that the diluted system is active in altering wettability and lowering IFT at the low concentration “toe⁶²” of the

concentration profile illustrated in Fig. 13. This will require evaluating changes in: electrolyte strength, alkalinity and pH, surfactant concentration, and ratio of synthetic/natural surfactants. The small solubility product of calcium carbonate sequesters calcium ion concentration. A small amount of sodium silicate should be considered in the formulation to sequester the magnesium ion concentration³⁷.

Alkali consumption and surfactant adsorption

Alkali consumption is an important issue in sandstones because of ion exchange with clays, dissolution of silicate minerals, mixing with formation brine, and neutralization of the acids in the crude oil. Soluble calcium minerals such as gypsum or anhydrite can contribute to alkali consumption. However, Cheng⁵⁴, found no significant consumption of Na_2CO_3 on dolomite. Olsen, et al.³⁸, reported 5.8 meq of alkalinity consumed per kg of carbonate rock with an ASP system using Na_2CO_3 and sodium tripolyphosphate. Measurement of alkali consumption of the system of interest is needed to determine how much of the

electrolyte strength can be accomplished with NaCl rather than Na_2CO_3 .

Addition of an alkali significantly reduces surfactant adsorption in sandstones³⁶. Al-Hashim, et al.⁵⁵, showed surfactant adsorption on limestone to be decreased in the presence of 1:1 $\text{NaHCO}_3\text{:Na}_2\text{CO}_3$ for low surfactant concentrations.

Surfactant adsorption on powdered calcite without or with sodium carbonate was determined by potentiometric titration with hyamine. The initial surfactant concentration was fixed at either 0.05% or 0.1% (active material), while calcite powder were added at varied weight ratios. The equilibrium surfactant concentration was determined by titration. The calcite powder surface area was determined by BET adsorption, and surfactant adsorption density was calculated.

The adsorption of a 1:1 blend of CS-330 and TDA-3PO without or with sodium carbonate is shown in Fig. 24. The adsorption isotherm in the absence of sodium carbonate is similar to a Langmuir adsorption isotherm with a plateau adsorption of about 0.002 mmol/m^2 . This corresponds to adsorption of $83 \text{ \AA}^2/\text{molecule}$. This

is about one-fourth of the adsorption density of a close-packed monolayer (of $20 \text{ \AA}^2/\text{molecule}$ for a linear alkane surfactant.). Addition of 0.3 – 0.45 M sodium carbonate reduced the adsorption by a factor of 10 to about $2 \times 10^{-4} \text{ mmol/m}^2$.

The adsorption density without and with sodium carbonate was similar for CS-330. However, the apparent adsorption of TDA-3PO with sodium carbonate had abnormal high values with small addition of calcite, Fig. 25. It was observed that solutions of TDA-4PO and 0.3 M sodium carbonate were turbid and light scattering measurements indicated 200-300 nm aggregates. Apparently the aggregates co-precipitated with the calcite when the latter was separated by centrifugation. The solutions of CS-330 and 1:1 CS-330/TDA-4PO with sodium carbonate were not turbid and did not show abnormal adsorption.

Oil recovery by spontaneous imbibition

Spontaneous imbibition experiments were conducted with formation brine, stock tank oil, MY3, and core samples of the dolomite formation of the reservoir of interest. The properties of the dolomite core samples and experimental conditions

are listed in Table 3. There was no further extraction or cleaning of the cores. The composition of the formation brine is in Table 4. The initial oil saturation was established by flowing oil with the indicated pressure drop. Some samples were aged 24 hours at 80°C. Oil recovery by spontaneous imbibition was measured by placing the oil-saturated cores in imbibition cells filled with either formation brine or alkaline surfactant solution, Fig. 26. Not a single drop of oil was recovered by spontaneous imbibition in formation brine during one to two weeks, Fig 26(a). The formation brine was replaced with alkaline surfactant solution and the enhanced oil recovery by spontaneous imbibition was measured. Small drops of oil on the top end face of the core could be observed accumulating, detaching and being collected in the imbibition cell, Fig. 26(b). The appearance of oil on the top face rather than the sides of the core suggests that the displacement was dominated by buoyancy rather than counter-current capillary imbibition. The oil recovery as a function of time is shown in Fig. 27.

Possible factors affecting the difference in oil recovery in Fig. 27 include permeability, initial

oil saturation, surfactant formulation, and condition of aging. The surfactant formulation and aging conditions are not the dominant parameters since systems with the greatest and least recovery have the same surfactant formulation and the system aged at 80° C has greater recovery than the system aged at room temperature. The effect of difference in permeability can be evaluated by plotting the oil recovery as a function of dimensionless time for gravity dominated recovery.

$$t_{Dg} = \frac{k k_{ro}^o \Delta \rho g t}{(S_{oi} - S_{or}) \phi \mu_o L} \dots\dots\dots(1)$$

The fractional recovery is expressed as a fraction of recoverable oil, assuming that the remaining oil saturation at the last measured point in Fig. 27 is the residual oil saturation. The experimental results are compared to the one dimensional, gravity drainage analytical solution^{64,65} assuming zero capillary pressure and a relative permeability exponent of $n=3$. The analytical solution is as follows.

$$E_R = \frac{S_{oi} - \bar{S}_o}{S_{oi} - S_{or}} \dots\dots\dots(2)$$

$$E_R = \begin{cases} t_{Dg}, & t < t_{BT} \\ 1 - \frac{(1-1/n)}{(nt_{Dg})^{\frac{1}{n-1}}}, & t > t_{BT} \end{cases} \dots\dots\dots(3)$$

$$t_{Dg,BT} = 1/n \quad \dots\dots\dots(4)$$

The fractional recovery is plotted as a function of dimensionless time for gravity drainage and compared with the analytical solution in Fig. 28. The recovery expressed in this way accounts for the difference in permeability. The fractional recovery appears to scale as if the rate of recovery of the mobile oil is due to gravity drainage. However, the remaining oil saturation (ROS) appears to be a function of permeability or initial oil saturation, Table 3. More investigation is needed to determine if permeability or initial oil saturation is indeed the responsible parameter and if so, why. The surfactant and alkali system needs to be optimized to minimize the remaining oil saturation.

The hypothesis that the recovery was dominated by capillary imbibition was examined by plotting the oil recovery as a function of dimensionless time for recovery by spontaneous capillary imbibition⁶⁶ in Fig. 29.

$$t_{D,P_c} = t \sqrt{\frac{k}{\phi}} \frac{\sigma}{\sqrt{\mu_o \mu_w}} \frac{1}{L_c^2} \dots\dots\dots(5)$$

The interfacial tension in the dimensionless time is a value of 10^{-3} mN/m, which was a typical value for

the three systems, Fig. 19. The measured oil recovery occurred faster than that for the very strongly water-wet (VSWW) correlation. This observation implies that either some other mechanism such as gravity was contributing to recovery or capillary imbibition was contributing but the interfacial tensions are different from the assumed value.

If the oil recovery is dominated by buoyancy and each matrix block acts independently, the analytical solution, Eq. (3) can be used to scale-up to different permeability and matrix block size. The time to a given level of recovery will be proportional to the height of the matrix block, L , and inversely proportional to permeability, k . However, the assumption that the matrix blocks act independently is challenged by the possibility of capillary contact between matrix blocks. Capillary contact between matrix blocks and re-entry of oil into matrix blocks will lengthen the time for oil recovery.

Future work

The work to date has been to identify the important factors affecting enhanced recovery with alkaline

surfactant solution rather than to optimize the system. A practical system will have only enough Na_2CO_3 to satisfy the alkali consumption and use NaCl for the remainder of the electrolyte strength. The frontal advance rates of the alkali, surfactant and salinity should be optimized to have maximize the size of the active region. The process should be designed to be robust to tolerate mixing with the formation brine either in the fractures or in the matrix⁶⁷.

The different surfactants need to be systematically characterized. Fundamental questions remain about mixtures of dissimilar surfactants, i.e., naphthenic soap and synthetic surfactant.

Measurement of interfacial tensions between the upper and lower phases is problematic because the microemulsion in a three-phase system is segregating to a very thin middle layer with time. The loss of microemulsion from the measured excess aqueous and oil phases results in increasing interfacial tension values.

One alkaline surfactant system shown here altered a calcite plate that was aged at room

temperature to preferentially water-wet conditions. However, the system that was aged at 80° C only altered to intermediate-wet (~90° contact angle). The mechanisms governing the wettability alteration^{57,68} and methods to make the elevated aging temperature system more water-wet will be sought.

The long-term stability of surfactant formulations at the condition of application should be evaluated. Talley⁶⁹ shows that ethoxylated sulfates, as those shown here are unstable at low pH and high temperatures. They were more stable at neutral and high pH provided a significant concentration of calcium ions was not present. Na_2CO_3 should suppress the calcium ion concentration in the alkaline surfactant systems discussed here.

The spontaneous imbibition experiments shown were in small cores. The controlling displacement mechanism needs to be identified and be scaled to the rate of displacement from matrix blocks of dimensions typical of actual reservoirs.

The scope of the work discussed here is limited to a single matrix block. Sweep efficiency

is an equally important factor in oil recovery, especially in fractured formations. Fracture systems generally have a broad distribution of fracture widths. The wider fractures will act as thief zones for the injected fluid and little of the injected fluid will reach the narrower fractures. Favorable mobility ratio displacement aids in the distribution of injected fluids in heterogeneous systems. Polymer has commonly been used for mobility control of surfactant flooding processes. However, polymer will also retard the invasion of the surfactant solution into the matrix. An alternative process of mobility control for surfactant flooding is foam^{53, 70}. Foam mobility control has been field demonstrated for aquifer remediation^{71, 72} and since then, applied to full-scale expansions.

Conclusions

1. Crude oils used for interfacial research should be screened for contamination. Crude oil/brine interfacial tension less than 10 mN/m is an indication of contamination.
2. Calcite, which is normally positively charged at neutral pH, can be made

negatively charged through the presence of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ in the brine.

3. The wettability of crude oil/brine on a calcite plate is a function of aging time. After 24 hours, the plate was oil-wet regardless of whether the aging in crude oil was at room temperature or 80° C. The degree of wettability alteration with alkaline surfactant systems observed here ranged from preferentially water-wet to intermediate-wet and was a function of the prior aging temperature in crude oil.
4. Oil is retained in oil-wet pores by capillarity. Oil displacement can occur by buoyancy if an alkaline surfactant solution reduces interfacial tension and/or alters wettability to more water-wet conditions. The displacement could also be assisted by capillarity if the contact angle is less than 90°.
5. Oil recovery from oil-wet dolomite cores has been demonstrated by spontaneous imbibition with an alkaline anionic surfactant solution.

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Nomenclature

E_R	=	recovery efficiency
g	=	acceleration of gravity, m/s ²
IFT	=	interfacial tension, mN/m
k	=	permeability, m ² (md)
k_{ro}^o	=	relative permeability
L	=	length, m
n	=	oil relative permeability exponent
N_B	=	Bond number
ROS	=	remaining oil saturation
S_{oi}	=	initial oil saturation
S_{or}	=	residual oil saturation

t	=	time, s
t_{Dg}	=	dimensionless time for gravity drainage
$t_{D, pc}$	=	dimensionless time for capillary imbibition
μ_o	=	oil viscosity, Pa·s (cp)
μ_w	=	water viscosity, Pa·s (cp)
ϕ	=	porosity
σ	=	interfacial tension, N/m
$\Delta\rho$	=	density difference, kg/m ³

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Table 1 Crude oil properties (Jill Buckley, private communication)

Oil ID	°API	RI@20°C	ρ @20°C	Acid# mgKOH /g	Base # mgKOH /g	IEP pH	B/A	Sat. %	Arom. %	Resins %	Asph. %	Visc.(cp)
MY1	27.2	1.4979	0.8887	0.50	1.17	3.2	2.34	64.02	24.59	9.67	1.71	22.6
MY2	28.9	1.4941	0.8789	0.17	1.16	3.7	6.82	62.52	23.72	12.68	1.08	18.1
MY3	28.2	1.4955	0.8830	0.20	1.17	3.3	5.85	61.86	24.83	12.22	1.09	19.1
MY4	28.4	1.4943	0.8818	0.22	1.23	3.4	5.59	65.28	23.69	9.94	1.10	18.8

Table 2 Surfactant identification

Trade name	Structural name
CS-330	Sodium dodecyl 3EO sulfate
C12-3PO	Sodium dodecyl(Guerbet) 3PO sulfate ⁶³
TDA-4PO	Ammonium iso-tridecyl 4PO sulfate ⁶³
ISOVOL14T-4.1PO	Sodium tetradecyl(Guerbet) 4PO sulfate ⁶³

Table 3 Core properties and recovery

Property	Core A	Core B	Core C
Diameter, inch	1.5	1.5	1.5
Length, inch	3.5	3	3
Porosity, %	20	24	24
Permeability, md	90	122	40
Brine*	Brine 1	Brine 2	Brine 2
Crude oil	MY3	MY3	MY3
Pressure drop, psi	250	130	550
Initial oil saturation	0.71	0.68	0.82
Aging	80 °C, 24hr	80 °C, 24hr	None
Time in brine, days	9	8	14
Recovery in brine, %OOIP	0	0	0
Surfactant	TDA-4PO	CS-330+ TDA-4PO	CS-330+ TDA-4PO
Surf. conc., wt%	0.05	0.025 +0.025	0.025 +0.025
Na ₂ CO ₃ , M	0.3	0.3	0.3
Time in surf., days	381	138	132
Recovery in surf, %OOIP	28	44	14
ROS	0.51	0.38	0.70

Table 4 Formation brine composition

Salts	Brine 1, gram/liter	Brine 2, gram/liter
NaCl	24.497	5.815
KCl	0.275	0.000
CaCl ₂ .2H ₂ O	5.502	2.942
MgCl ₂ .6H ₂ O	7.984	2.032
Na ₂ SO ₄	0.606	0.237
Fe(NH ₄) ₂ (SO ₄) ₂ .6H ₂ O	0.000	0.007

Fig. 1 The height of the retained oil in oil-wet matrix pores is a function of the pore radius, interfacial tension, and contact angle.

Fig. 2 Oil is trapped by surface trapping in oil-wet and small pores of oil-wet systems.

Fig. 3 Spontaneous imbibition of surfactant solution from the fracture system into the matrix occurs to replace the oil that flows out of the matrix by buoyancy.

Fig. 4 Crude oil/brine IFT is an indication of whether or not the crude oil is contaminated with surface-active materials.

Fig. 5 Water advancing contact angles of MY1 and MY3 crude oils on calcite and glass with 5-10 minutes aging time.

Fig. 6 Water advancing contact angle of MY3 crude oil in 0.1 M NaCl brine after aging for 24 hours either at room temperature or 80 °C.

Fig. 7 Zeta potential of MY1 crude oil/brine and calcite/brine interfaces in 0.02M NaCl as a function of pH without and with added Na_2CO_3 / NaHCO_3 and pH adjusted with HCl.

Fig. 8 Wettability alteration of calcite plate aged at room temperature with 0.05% CS-330 / 0.5 M Na_2CO_3 .

Fig. 9 Wettability alteration of calcite plate aged at 80 °C with 0.05% CS-330 / 0.5 M Na_2CO_3 . (Two different drops show different wettability.)

Fig. 10 Family of axisymmetric oil interfaces for an oil drop immersed in water. Each curve has a different curvature at the apex of the drop. The distances are normalized by $\sqrt{\sigma/(\Delta\rho g)}$.

Fig. 11 A calcite (marble) plate has two plastic films to create a 13 μm gap between the plate and the front of an optical cell.

Fig. 12 Displacement of crude oil in narrow gap with (a) brine or with (b) alkaline surfactant solution.

Fig. 13 Saturation/concentration profiles in a narrow gap or in a porous rock during displacement of oil by buoyancy.

Fig. 14 Phase behavior of MY3 crude oil and different concentrations of Na_2CO_3 .

Fig. 15 Phase behavior of MY3 crude oil with 0.05% (AM) CS-330.

Fig. 16 Phase behavior of MY3 crude oil with 0.05% (AM) C12-3PO.

Fig. 17 Phase behavior of MY3 crude oil with 0.05% (AM) TDA-4PO.

Fig. 18 Phase behavior of MY3 crude oil with 0.05% (AM) ISOVOL 14T-4.1PO.

Fig. 19 IFT of MY3 crude oil with 0.05% (AM) surfactant solution as a function of Na_2CO_3 concentration. Water/Oil ratio = 1:1

Fig. 20 IFT of MY3 crude oil with 0.05% (AM) surfactant solution as a function of water/oil ratio. WOR=1 is close to optimum Na_2CO_3 concentration.

Fig. 21 Phase behavior of MY3 crude oil with 0.2% (AM) TDA-4PO

Fig. 22 Phase behavior of MY3 crude oil with 1% (AM) TDA-4PO.

Fig. 23 IFT of MY3 crude oil with 0.05%, 0.2%, and 1% (AM) TDA-4PO as a function of Na_2CO_3 concentration. Water/oil ratio = 1:1.

Fig. 24 Adsorption isotherms of 1:1 CS-330 + TDA-4PO without and with sodium carbonate.

Fig. 25 Adsorption isotherms of TDA-4PO without and with sodium carbonate.

Fig. 26 Spontaneous imbibition with (a) brine, or (b) alkaline surfactant solution.

Fig. 27 Oil recovery by spontaneous imbibition.

Fig. 28 Oil recovery by spontaneous imbibition as function of dimensionless time for gravity drainage.

Fig. 29 Oil recovery for spontaneous imbibition as function of dimensionless time for capillary imbibition, assuming IFT of 10^{-3} mN/m.

$$\Delta\rho g h = -\frac{2\sigma \cos\theta}{R}$$

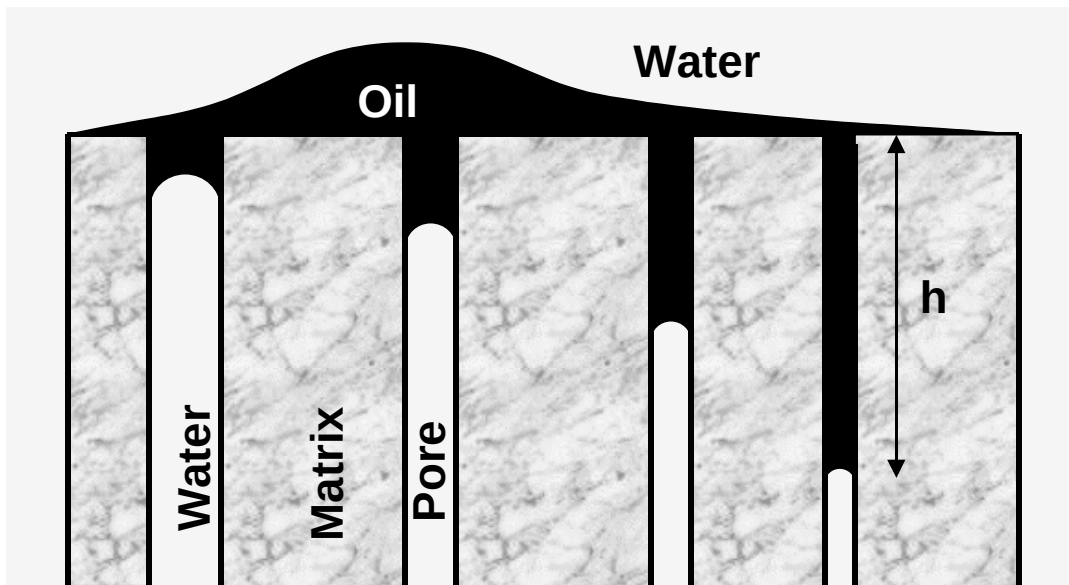


Fig. 1 The height of the retained oil in oil-wet matrix pores is a function of the pore radius, interfacial tension, and contact angle.

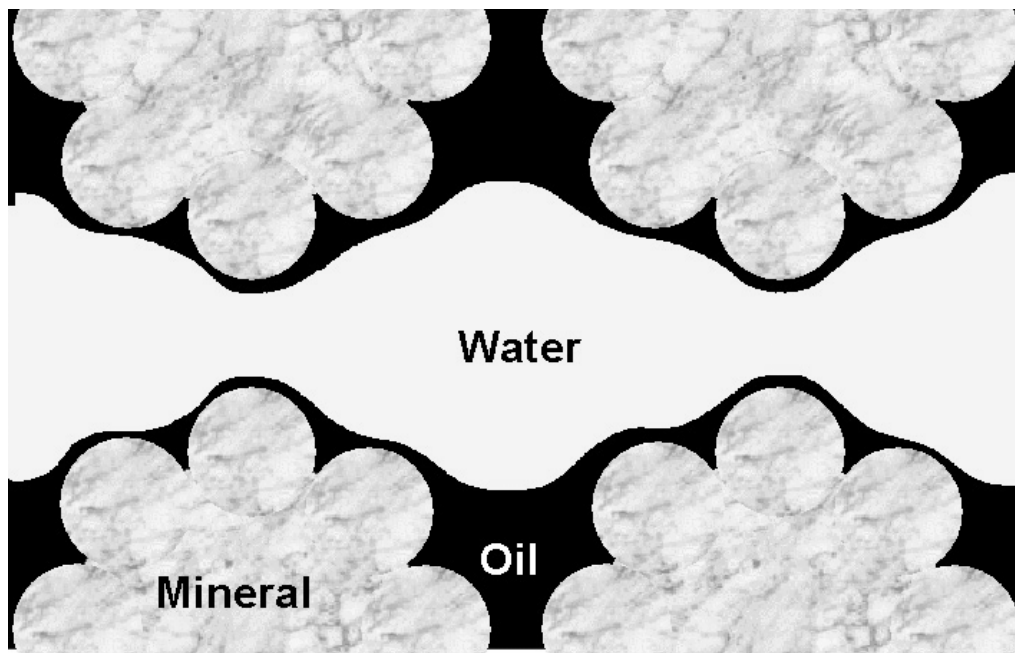


Fig. 2 Oil is trapped by surface trapping in oil-wet and small pores of oil-wet systems.

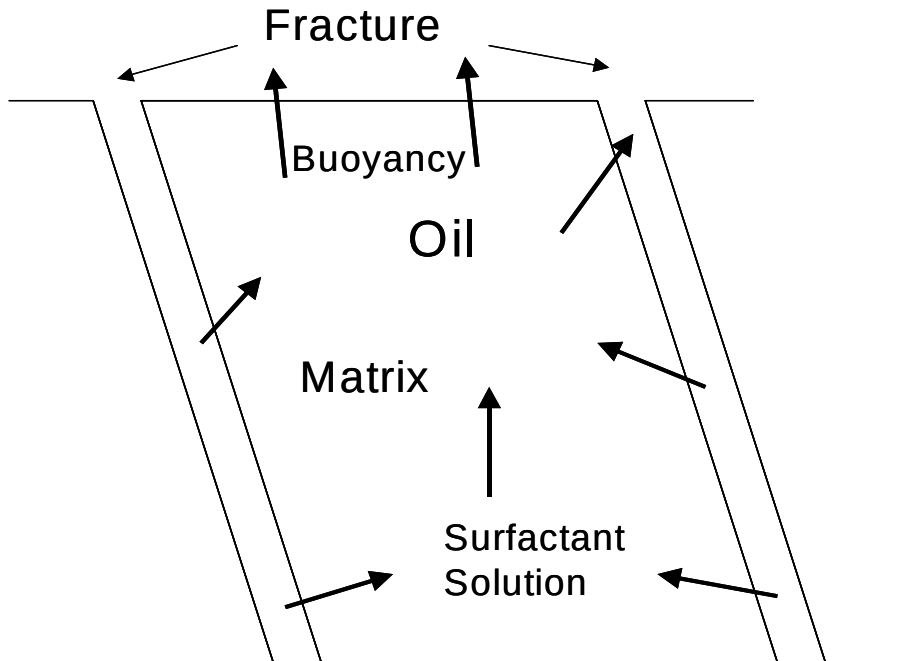


Fig. 3 Spontaneous imbibition of surfactant solution from the fracture system into the matrix occurs to replace the oil that flows out of the matrix by buoyancy.

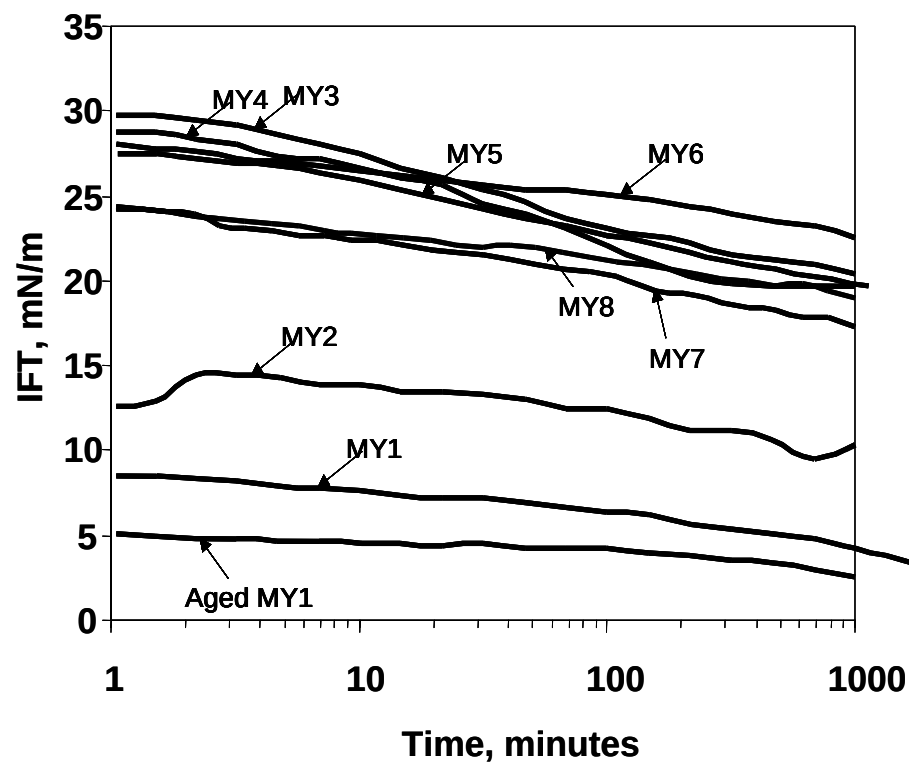


Fig. 4 Crude oil/brine IFT is an indication of whether or not the crude oil is contaminated with surface-active material.

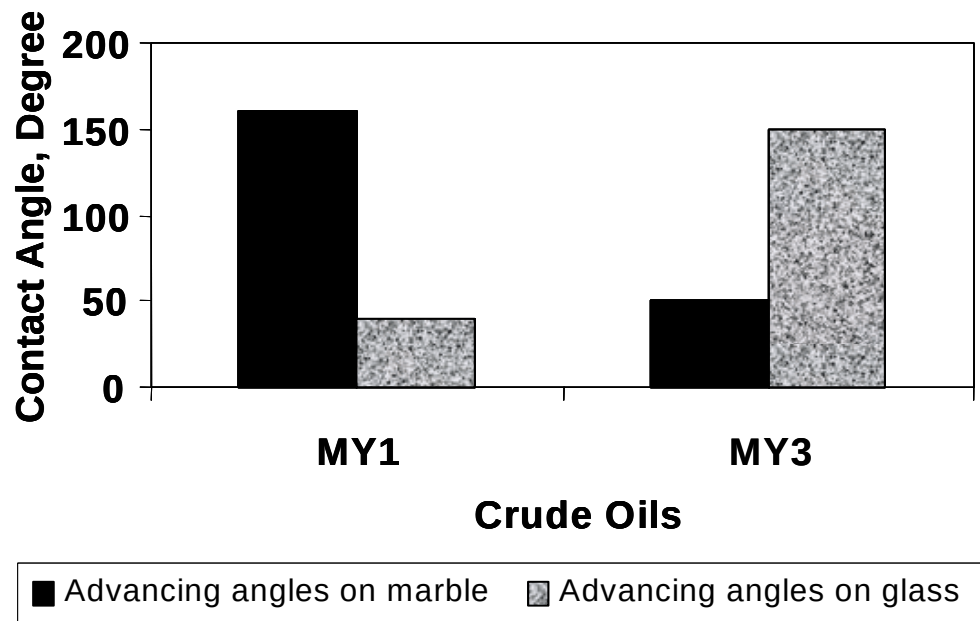
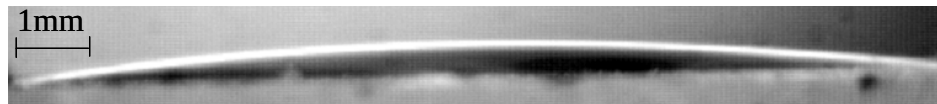


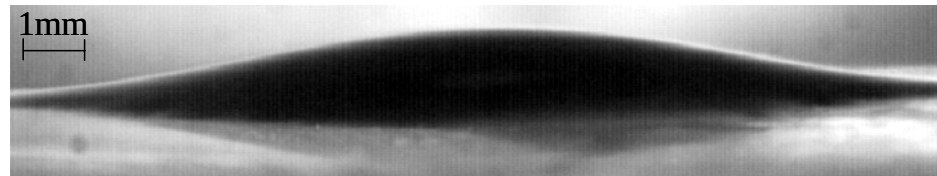
Fig. 5 Water advancing contact angles of MY1 and MY3 crude oils on calcite and glass with 5-10 minutes aging time.

Aged at room temperature



(a)

Aged at 80 °C



(b)

Fig. 6 Water advancing contact angle of MY3 crude oil in 0.1 M NaCl brine after aging for 24 hours either at room temperature or 80 °C.

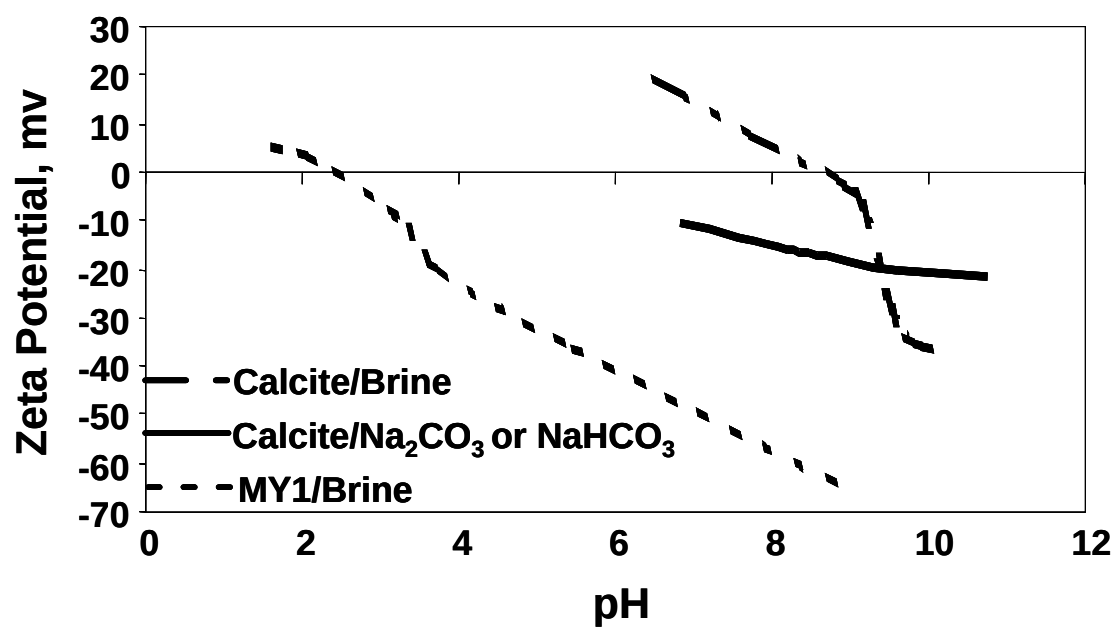
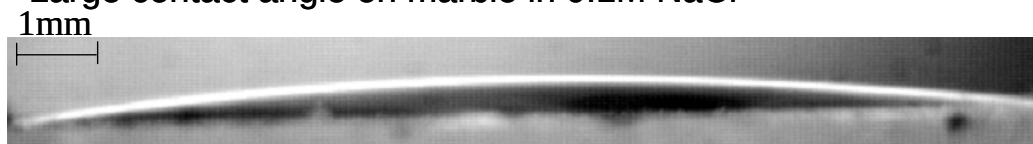


Fig. 7 Zeta potential of MY1 crude oil/brine and calcite/brine interfaces in 0.02M NaCl as a function of pH without and with added Na_2CO_3 / NaHCO_3 and pH adjusted with HCl.

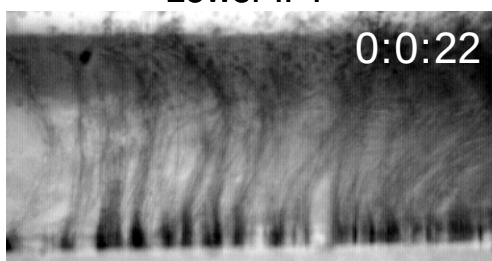
- Large contact angle on marble in 0.1M NaCl



(a)

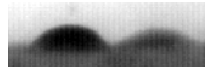
- Effect of 0.05% CS-330/0.5M Na₂CO₃

✓ Lower IFT

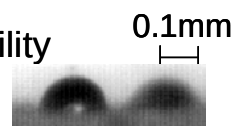


(b)

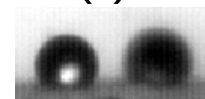
✓ Alter wettability



(c)



(d)



(e)

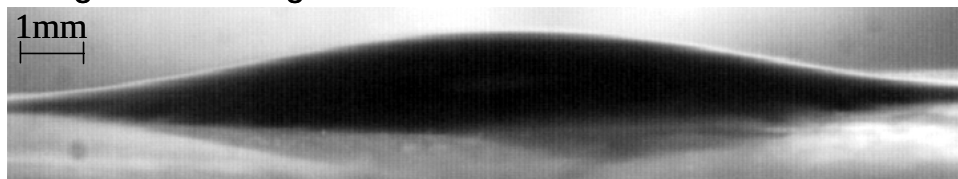


(f)

(Time: [hours: minutes: seconds])

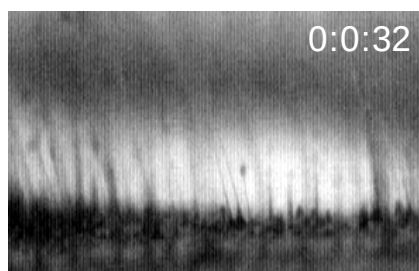
Fig. 8 Wettability alteration of calcite plate aged at room temperature with 0.05% CS-330 / 0.5 M Na₂CO₃.

- Large contact angle on marble in 0.1M NaCl



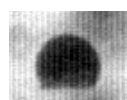
(a)

- Effect of 0.05% CS-330/0.5M Na₂CO₃

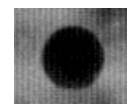


(b)

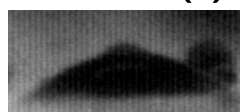
0.1mm



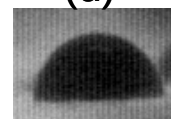
(c)



(d)



(e)



(f)

(Time: [hours: minutes: seconds])

Fig. 9 Wettability alteration of calcite plate aged at 80 °C with 0.05% CS-330 / 0.5 M Na₂CO₃. (Two different droplets show different wettability.)

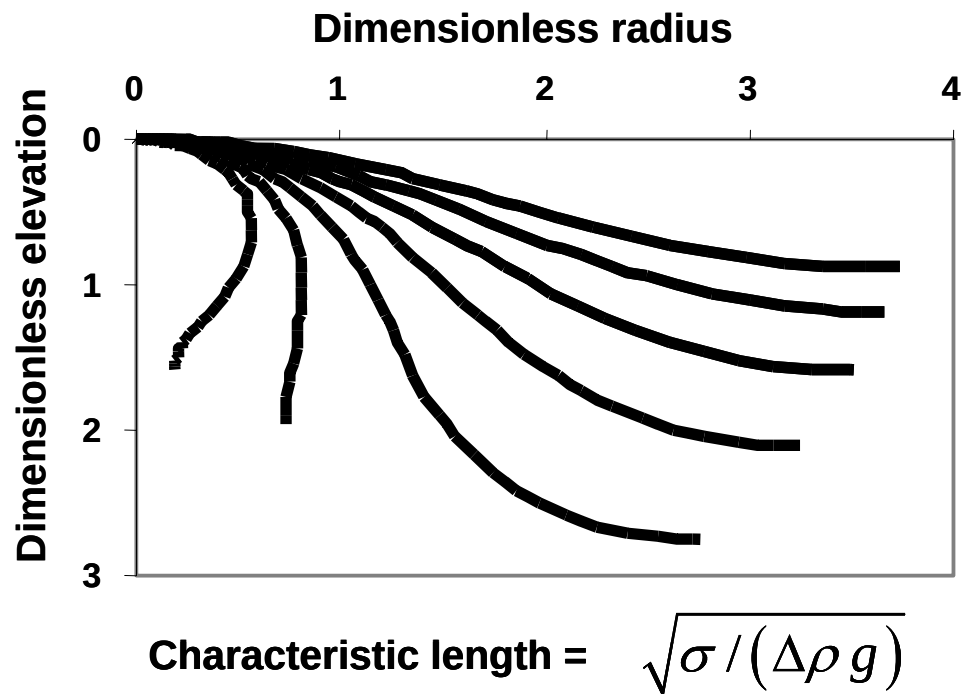


Fig. 10 Family of axisymmetric oil interfaces for an oil drop immersed in water. Each curve has a different curvature at the apex of the drop. The distances are normalized by $\sqrt{\sigma / (\Delta \rho g)}$.

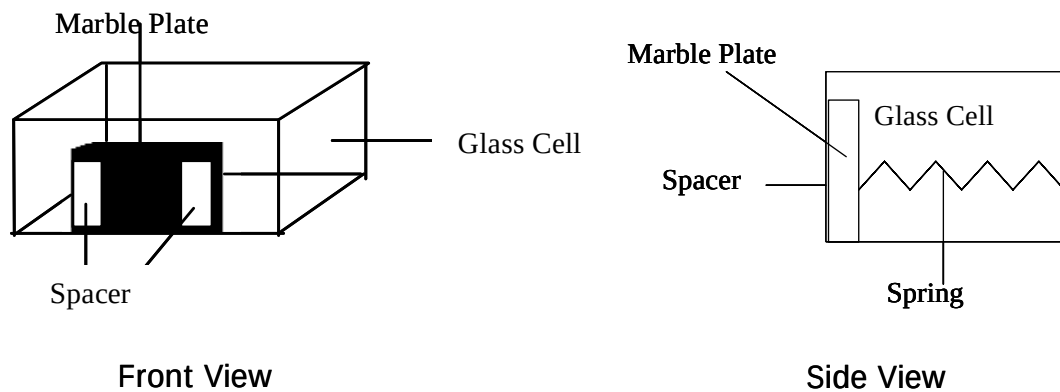
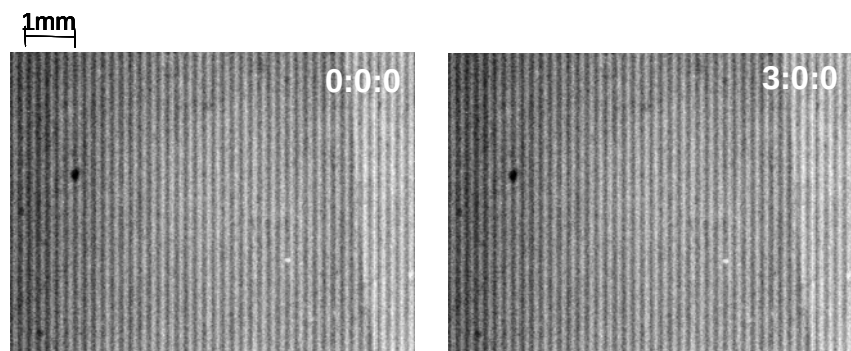
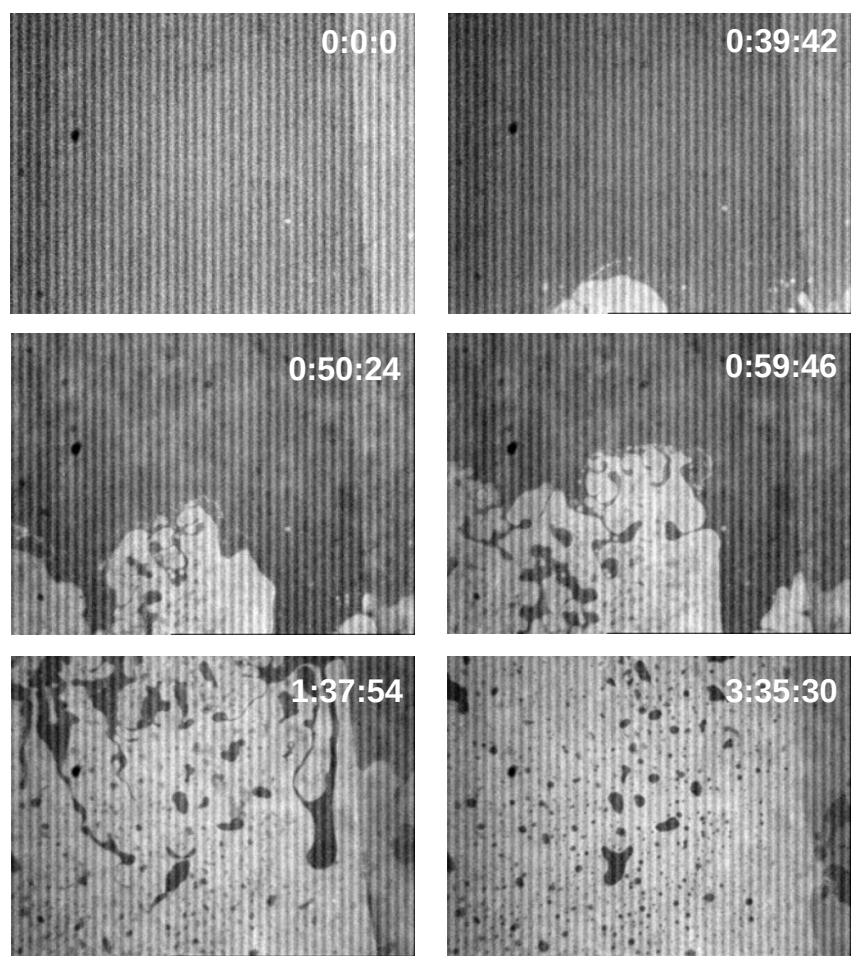


Fig. 11 A calcite (marble) plate has two plastic films to create a 13 μm gap between the plate and the front of an optical cell.



(a)



(b)

Fig. 12 Displacement of crude oil in narrow gap with (a) brine or with (b) alkaline surfactant solution.

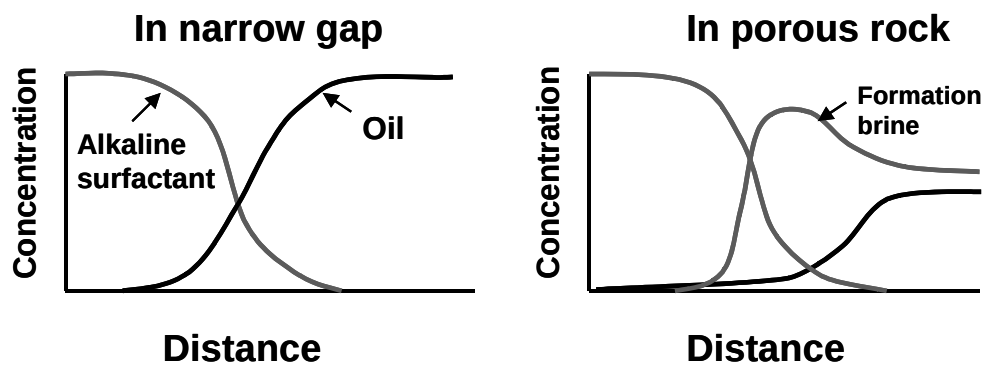


Fig. 13 Saturation/concentration profiles in a narrow gap or in a porous rock during displacement of oil by buoyancy.

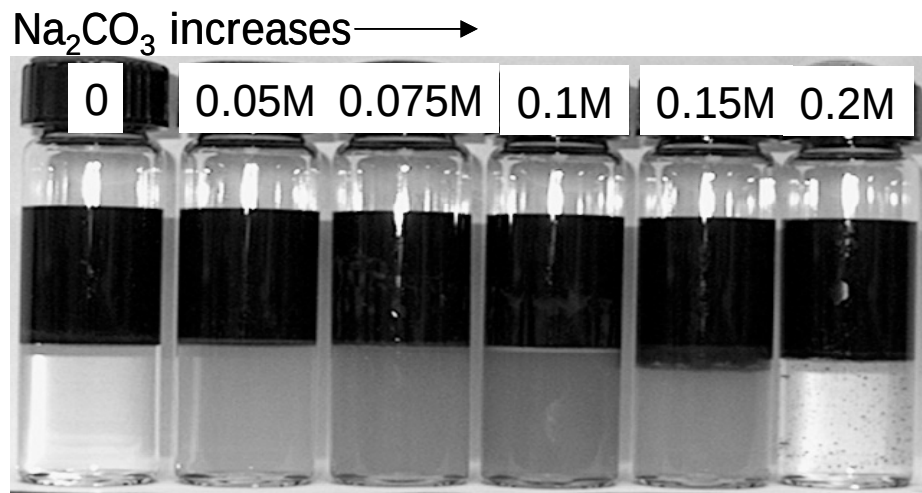
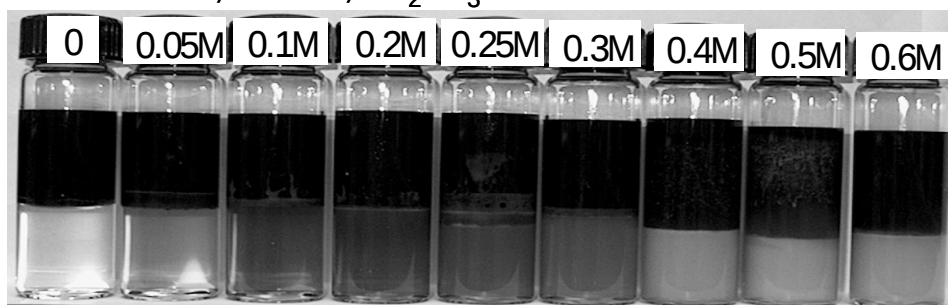


Fig. 14 Phase behavior of MY3 crude oil and different concentrations of Na_2CO_3 .

0.05% CS-330, WOR=1, Na_2CO_3 increases →



0.05% CS-330/ 0.5 M Na_2CO_3 , WOR increases →

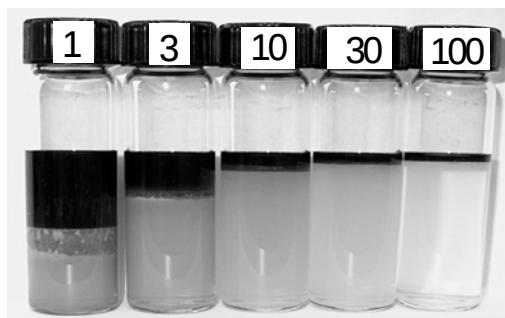
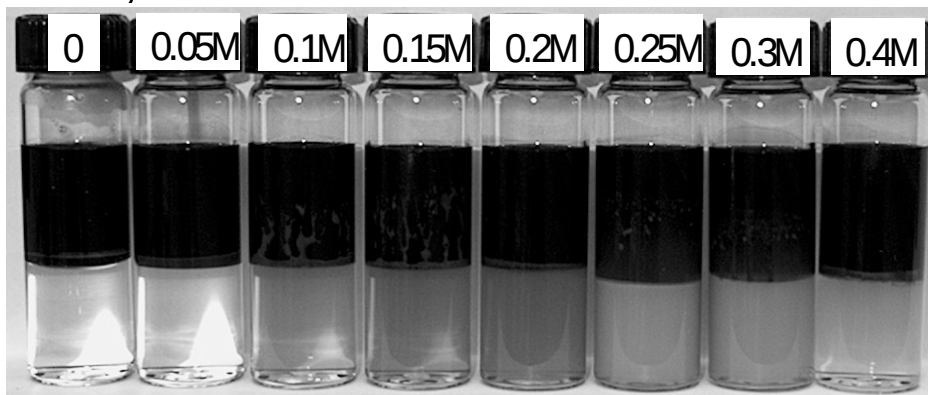


Fig. 15 Phase behavior of MY3 crude oil with 0.05% (AM) CS-330.

WOR=1, Sodium carbonate increases →



0.2M Na_2CO_3 , WOR increases →

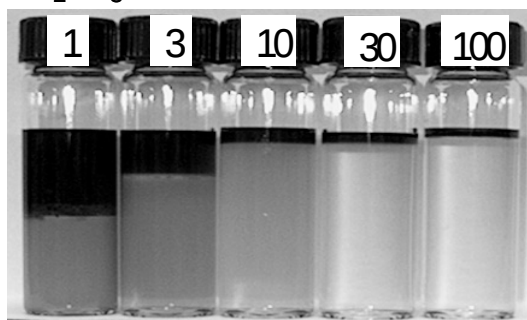
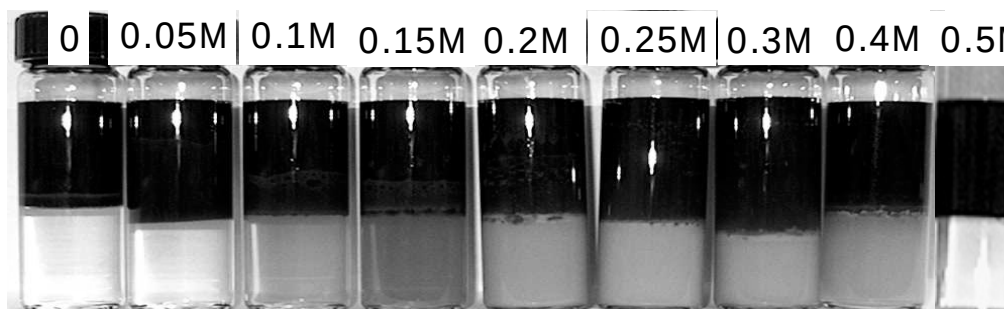


Fig. 16 Phase behavior of MY3 crude oil with 0.05% (AM) C12-3PO.

WOR=1, Sodium carbonate increases →

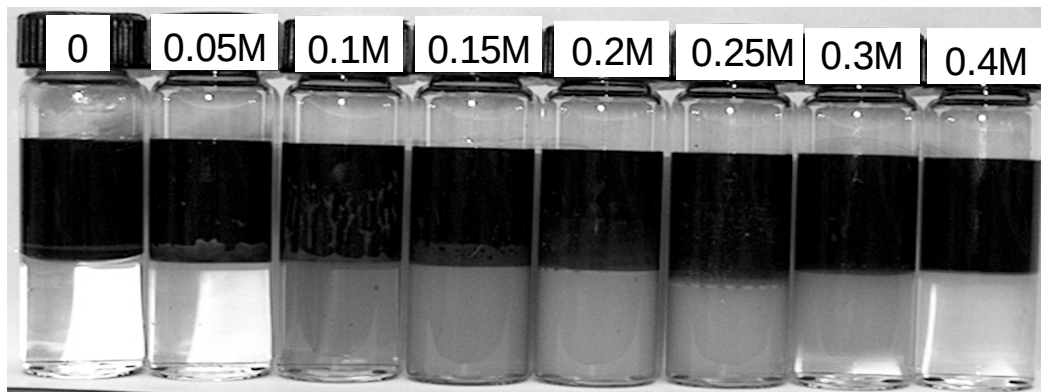


0.3M Na_2CO_3 , WOR increases →



Fig. 17 Phase behavior of MY3 crude oil with 0.05% (AM) TDA-4PO.

WOR=1, Sodium carbonate increases →



0.2M Na_2CO_3 , WOR increases →

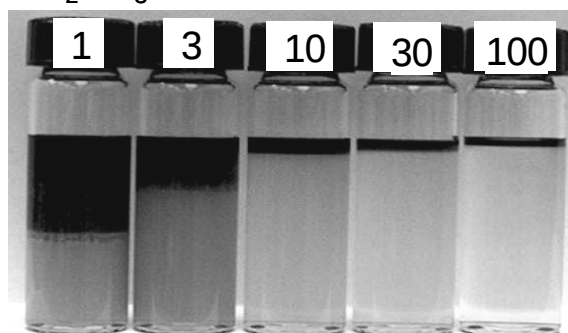


Fig. 18 Phase behavior of MY3 crude oil with 0.05% (AM) ISOFOL 14T-4.1PO.

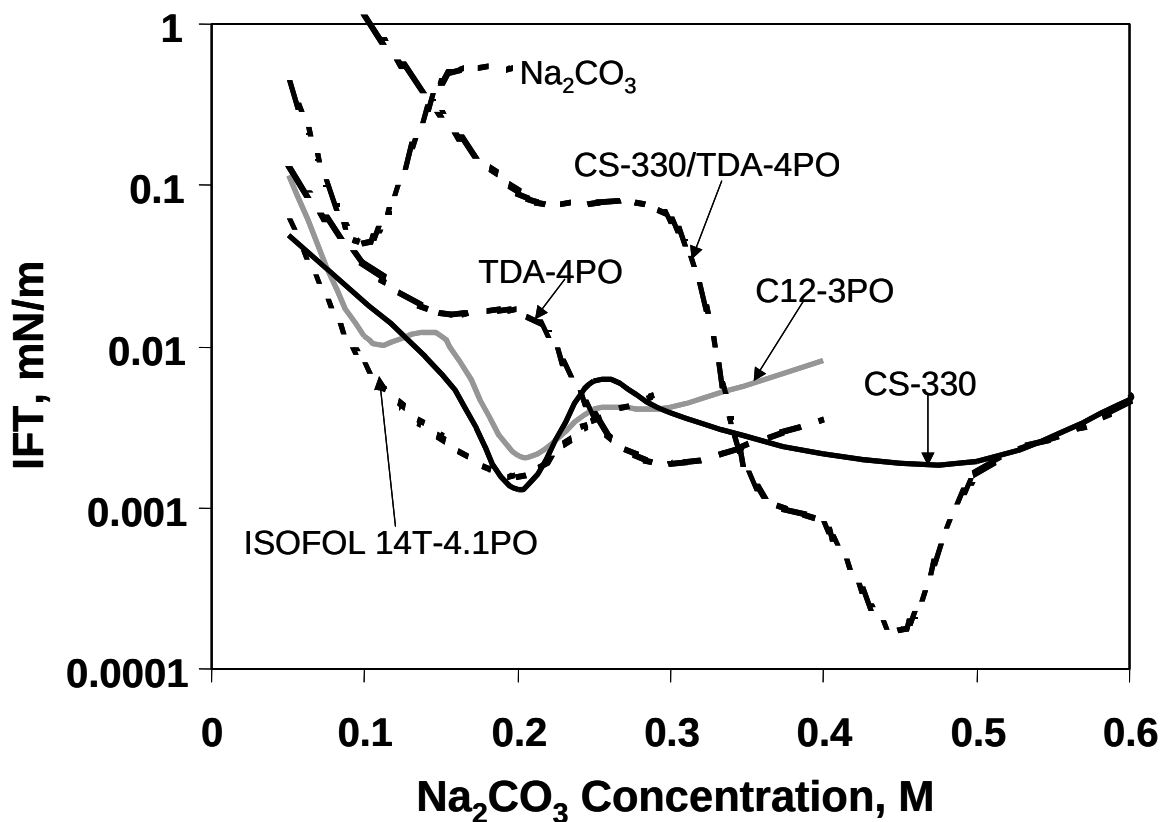


Fig. 19 IFT of MY3 crude oil with 0.05% (AM) surfactant solution as a function of Na_2CO_3 concentration. Water/Oil ratio = 1:1

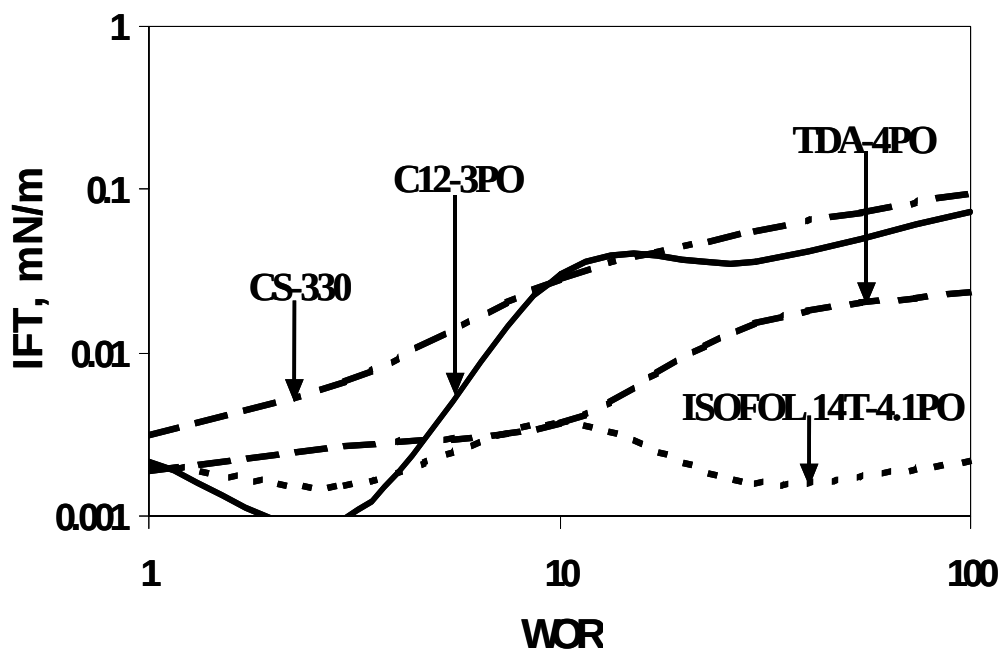
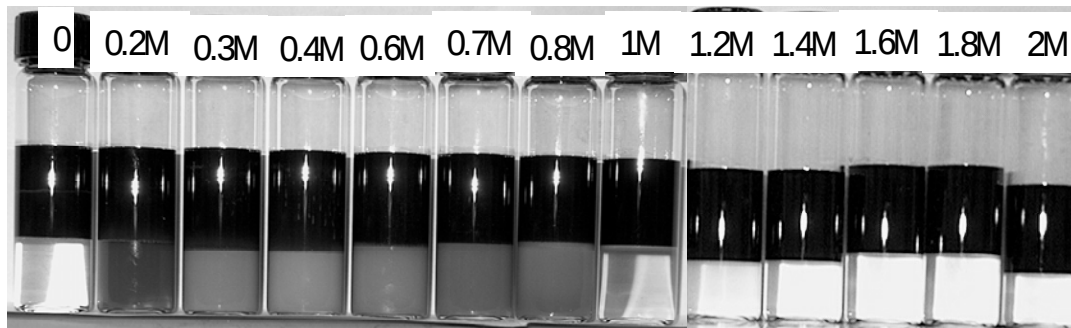


Fig. 20 IFT of MY3 crude oil with 0.05% (AM) surfactant solution as a function of water/oil ratio. WOR=1 is close to the optimal Na_2CO_3 concentration.

WOR=1, Sodium carbonate increases →



0.4M Na₂CO₃, WOR increases →

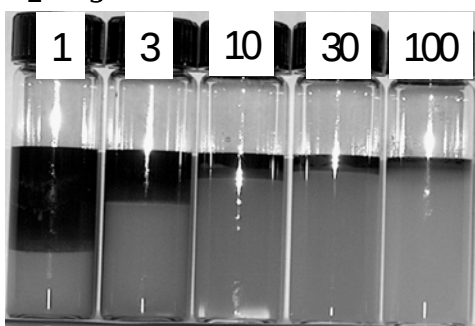
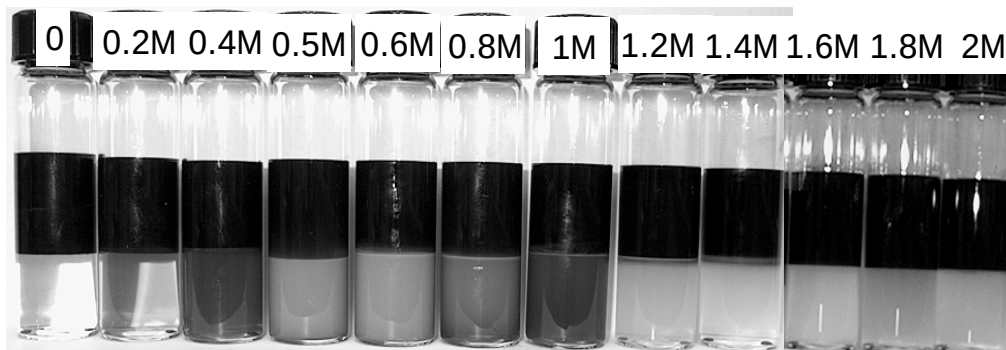


Fig. 21 Phase behavior of MY3 crude oil with 0.2% (AM) TDA-4PO.

WOR=1, Sodium carbonate increases →



1.4M Na₂CO₃, WOR increases →

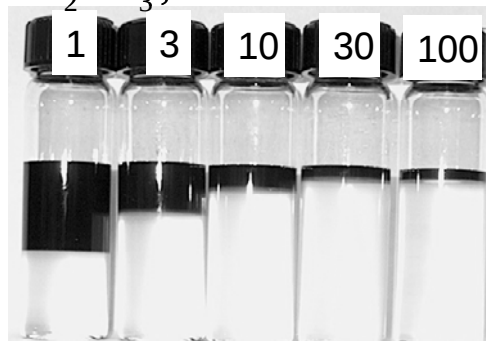


Fig. 22 Phase behavior of MY3 crude oil with 1% (AM) TDA-4PO.

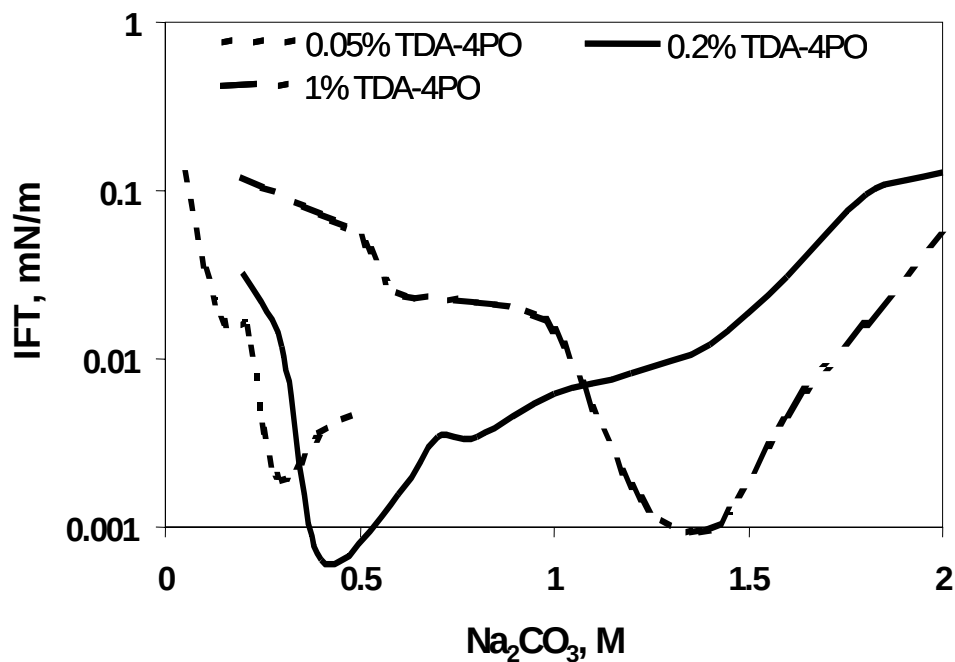


Fig. 23 IFT of MY3 crude oil with 0.05%, 0.2%, and 1% (AM) TDA-4PO as a function of Na_2CO_3 concentration. Water/oil ratio = 1:1.

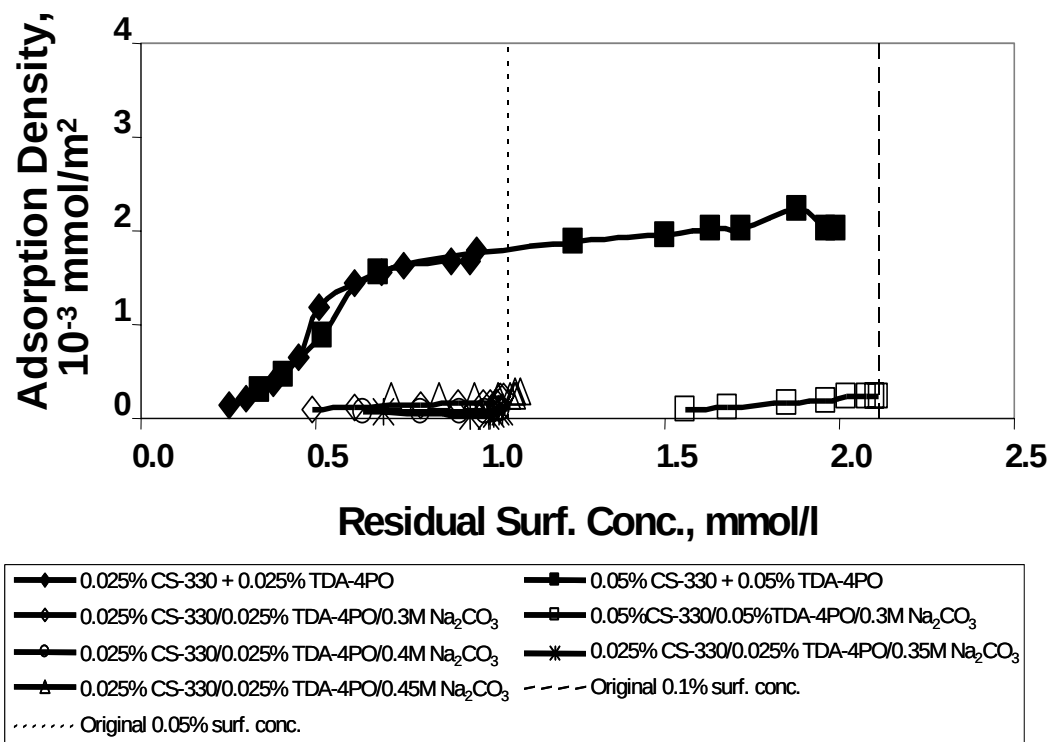


Fig. 24 Adsorption isotherms of CS-330 + TDA-4PO without and with sodium carbonate.

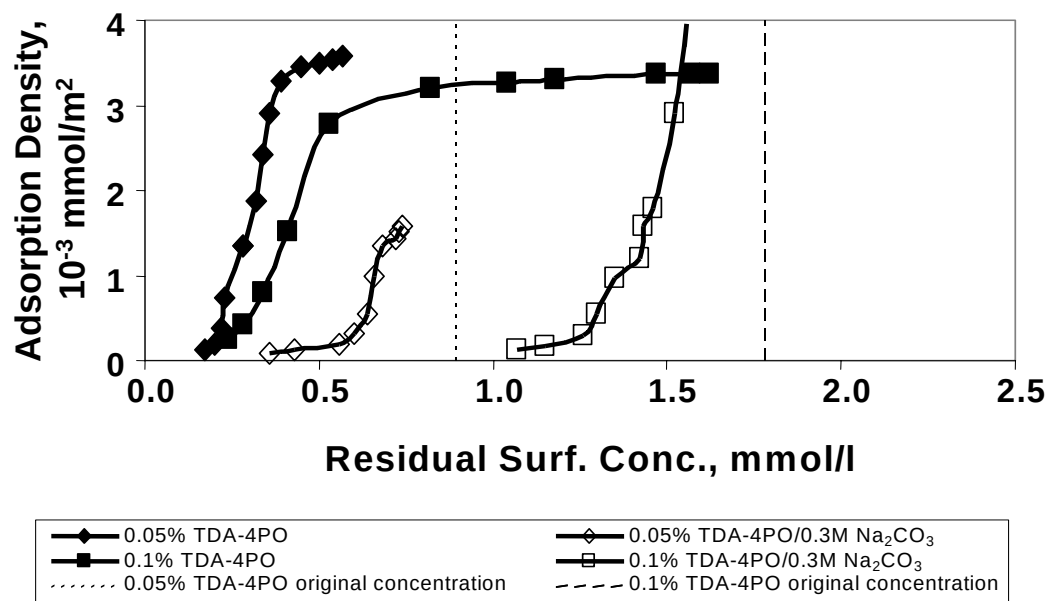


Fig. 25 Adsorption isotherms of TDA-4PO without and with sodium carbonate.



Fig. 26 Spontaneous imbibition with (a) brine, or (b) alkaline surfactant solution.

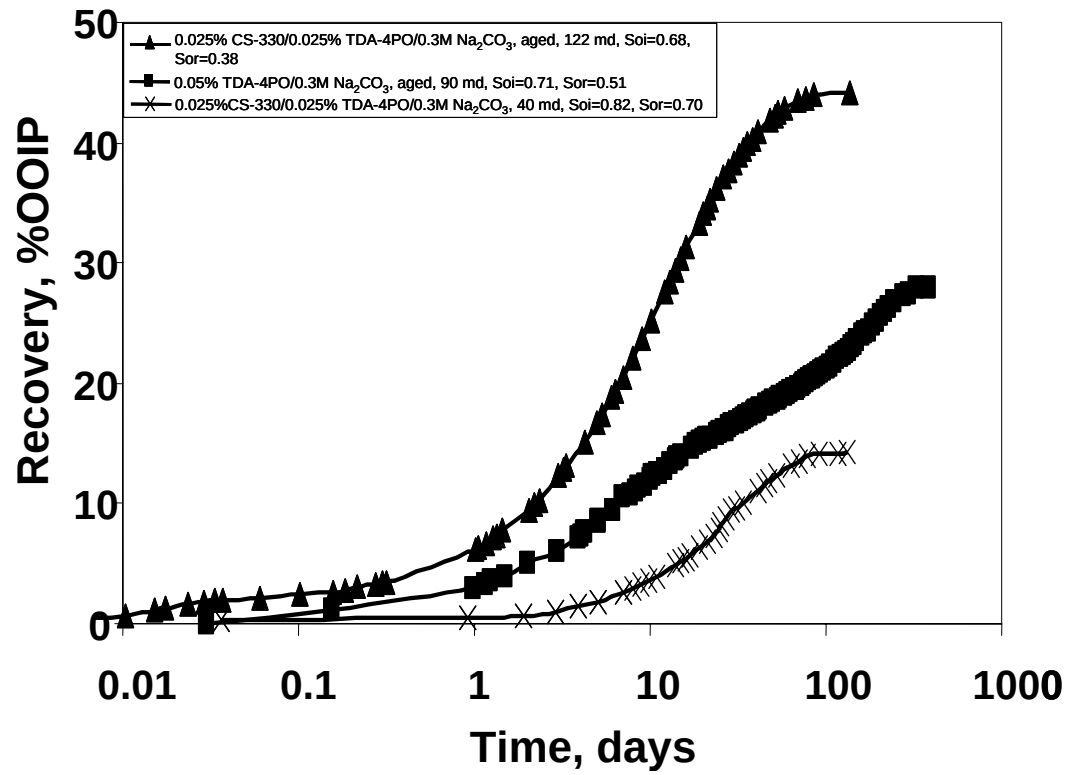


Fig. 27 Oil recovery by spontaneous imbibition.

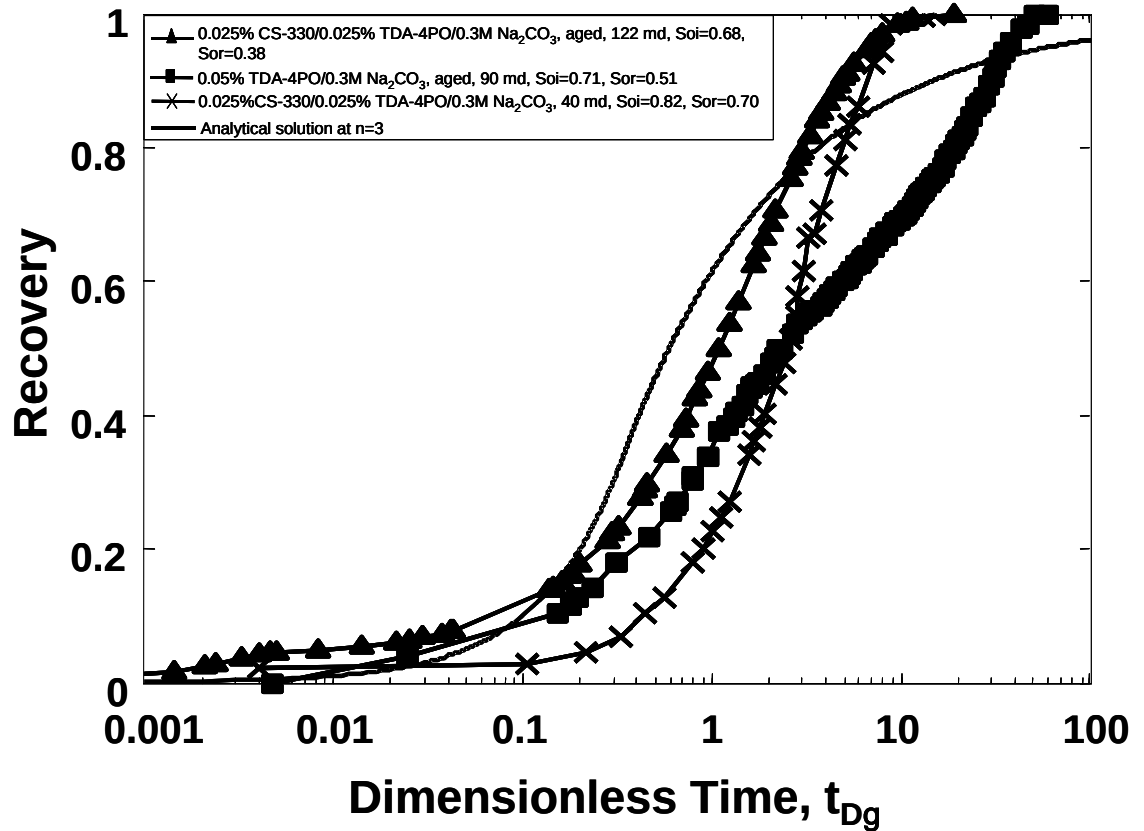


Fig. 28 Oil recovery by spontaneous imbibition as function of dimensionless time for gravity drainage.

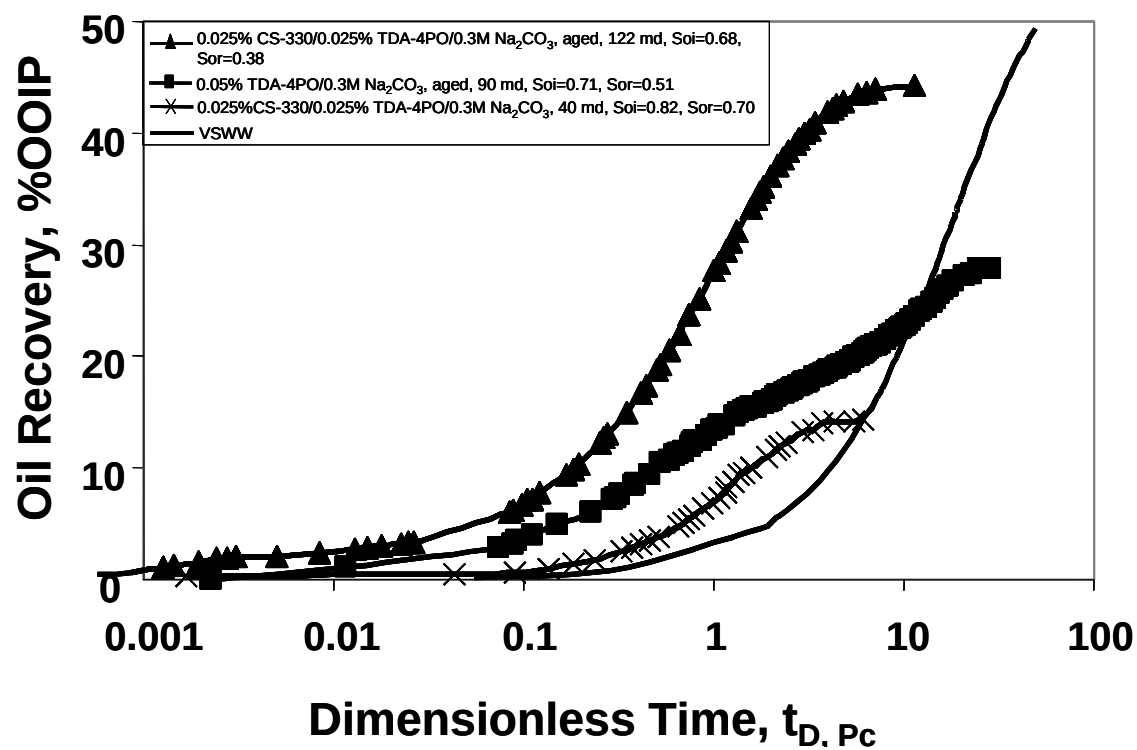


Fig. 29 Oil recovery by spontaneous imbibition as function of dimensionless time for capillary imbibition, assuming IFT of 10^{-3} mN/m