

Reservoir resilience of viscoelastic surfactants

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Abstract Viscoelastic solutions are notoriously sensitive to temperature and ionic strength. In order to be applicable for use in oil reservoirs, they need to be resilient to higher temperatures as well as to saline content. We define the essential characteristics required. Refractory properties obtained under Couette testing do not necessarily provide the same performance under pressure-driven flow. Nonetheless, it is possible to formulate solutions which clearly indicate that subsurface application is practicable. We show examples where salinity enables significantly enhanced viscoelasticity above ambient temperatures.

Keywords Viscoelastic surfactants (VES) · Shear-induced structures (SIS) · Water floods · Oil recovery · Porous media · Channel flow · Temperature resistance · Salinity resilience

Abbreviations

RF	Retardation factor
SIS	Shear-induced structure
SRF	Size selective retardation factor
VCR	Viscosity contrast ratio
VES	Viscoelastic surfactant
VR	Velocity retardation

List of symbols

L	Fracture length
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p	Pressure
Q	Fluid flow
RF	Resistance factor
T	Temperature
u	Darcy velocity
W	Parameter of the fracture width (i.e. smallest wall to wall distance)

Greek symbols

$\dot{\gamma}$	Shear rate
κ	Permeability
μ	Shear viscosity from rheometer

Subscripts

a	Additive
app	Apparent
bf	Base fluid
c	Critical
m	Maximum
l	Large
s	Small
w	Wall
0	Zero shear

Introduction

The principle technology for extracting oil from a reservoir is water injection to replace the depleted original natural pressure (Dowd 1974). Fluids generally follow the path of least resistance. The resulting uneven advance of the displacing water limits efficient recovery. The different fluid resistance zones in the reservoir are due to different permeability zones and fractures. Water displaces oil mostly from the permeable matrix in the reservoir. Fractures direct water away from these regions since they offer lower-resistance

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pathways to the producer well. This is a major cause of high water cuts in produced oil whose recovery is less efficient.

A possible solution is to create a more uniform flow front to overcome the effect of spatially varying flow resistance in the reservoir. Viscoelastic surfactant (VES) solutions in water are promising candidates for the control of water flow in oil reservoirs. Unlike the better known viscoelastic polymers which are shear thinning, VES can be used to selectively slow down the fluid velocity in low-resistance zones. VES solutions slow down more in highly permeable cores than in low permeability ones (van Santvoort and Golombok 2015a). The same effects have been shown in capillaries and conduits (van der Plas and Golombok 2015a, b), i.e. more fluid retardation can be obtained in a larger aperture compared to a smaller aperture capillary or conduit. This results in much improved and faster oil recovery (van Santvoort and Golombok 2015b).

Temperatures and salt concentrations affect the rheological behaviour of VES fluids. The VES solutions for reservoir fluid flow control should be resilient to these factors because reservoirs have temperatures of around 60 °C and injection fluids have salt concentrations of 3–20 wt% (covering the range from sea water to the saturated brines found in aquifers). This represents a well-known challenge to the application of novel chemical additives for fluid property modification in oil recovery. Surfactant and viscosity effects, particularly the non-Newtonian ones which we are seeking to exploit here, are notoriously fickle when it comes to application at higher temperatures or salinity. Previous work was concentrated on room temperature measurements, usually in VES solutions in distilled water. Our aim in this work is (1) to extend applicability to reservoir temperatures, i.e. to 60 °C and (2) enable operation in higher salinity brines.

Most parametrisation work has been reported in Couette cells. However, our previous work has shown that these are not a good predictor of pressure-driven flow behaviour so that the latter are also performed in this study. The background is summarised in “Background” section where reservoir conditions and the VES solutions will be described. “Experimental setup” section gives a survey of the experimental setups and the solutions we have tested. In “Results and discussion” section, Couette and pressure-driven flow results are presented. Different channels represent small and large fractures in an oil reservoir for the purposes of studying selective retardation.

Background

The VES solutions consist of low concentrations of a surfactant and a co-solute in base fluid such as water or brine. Depending on the concentration and ratio of the

components, spherical or worm-like micelles can be formed (Ezrahi et al. 2006). The formation of the latter can be enhanced by an increase in shear. The micelles become entangled, increasing the viscosity of the fluid even more at higher shear rates. Due to relatively weak bonds, the formations start to break apart beyond a certain shear rate and the fluid viscosity decreases again. This is the mechanism behind the typical shear rate–viscosity response of Fig. 1 (Cressely and Hartmann 1998). The novel fluid rheology shows a non-monotonic viscosity versus shear rate response. There are three regimes. The first regime starts at zero shear rate and ends at the critical shear rate ($\dot{\gamma}_c$) where the fluid starts to thicken. The viscosity–shear rate response over this low shear rate regime is often (Cressely and Hartmann 1998) but not always constant and is characterised by the gradient given by:

$$m_0 = \frac{\mu(\dot{\gamma}_c) - \mu_0}{\dot{\gamma}_c - \dot{\gamma}_0} \quad (1)$$

At the critical shear rate $\dot{\gamma}_c$, the fluid thickens to maximum viscosity (μ_{\max}) and then shear thins. This regime is called the shear-induced structure (SIS) regime. The final regime, the high shear-regime, starts from the shear rates where a near constant viscosity is restored.

The viscosity is thus low at small and high shear rates. In the intermediate regime, viscosity is higher and reaches a maximum. The viscosity contrast ratio (VCR) represents the ratio between the maximum viscosity (μ_{\max}) and the viscosity at the critical shear rate [$\mu_c = \mu(\dot{\gamma}_c)$].

$$\text{VCR} = \frac{\mu_{\max}}{\mu_c} \quad (2)$$

This represents the maximum range of exploitable viscosity contrast. For example, a large viscosity contrast ratio results in more flow resistance in larger fractures compared to small fractures (van der Plas and Golombok 2015b). This is only for the case of

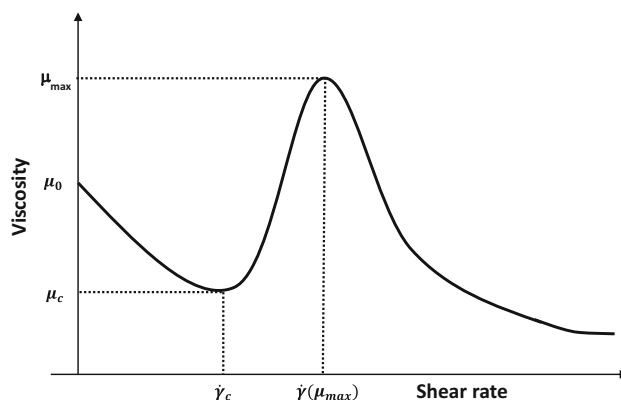


Fig. 1 A general viscosity–shear rate response for VES fluid. Where μ_0 is the zero shear viscosity, $\dot{\gamma}_c$ the critical shear rate. At shear rate, $\dot{\gamma}(\mu_{\max})$ the maximum (peak) viscosity μ_{\max} is reached

pressure-driven flow where the path through different parallel fractures or conduits all have the same pressure gradient. In that case, the shear $\dot{\gamma}_c$ is directly proportional to the width of the conduit as discussed in the results section below. [This has to be contrasted with the case of identical flow velocities in which case the relationship is inverted (van der Plas and Golombok 2015b).]

Standard Couette cell measurements can be used to characterise the VES fluid rheology in shear driven flow. However, oil recovery operations are pressure driven and the direct link between shear and pressure-driven flow is not straightforward for non-Newtonian fluids (Ferguson and Kembłowski 1991). Previous studies (van der Plas and Golombok 2015a, b) characterised pressure-driven VES fluid flow in a fracture using an average Darcy velocity (u) between the base fluid (bf) (i.e. the water or brine into which VES is later mixed) and the VES solution itself (VES), with a retardation factor

$$RF = \frac{u_{bf}}{u_{VES}} \Big|_{\Delta p/L} \tag{3}$$

Note that for fixed widths and pressure drops, this RF can also be interpreted as a non-dimensionalised viscosity (i.e. $RF = \mu_{ves}/\mu_{bf}$) where the viscosity of the VES fluid is an average bulk viscosity across the aperture (also called “apparent” viscosity) (Gonzalez et al. 2005; Rojas et al. 2008). The retardation factor depends on the fracture aperture size and is higher in larger fractures.

For oil recovery operations, the reservoir temperature is typically 60 °C and injection fluids typically have salinities of between 3 and 20% w/w. These are the givens for trying to obtain viscoelastic effects for improved volumetric sweep and indicate the regime on which to focus for injection fluid at reservoir conditions.

The viscosity depends on the temperature and the concentration of sodium chloride (Hartmann and Cressely 1997a). Previous literature only analyses changes based on Couette cell measurements, which are poor predictions for pressure-driven flow. Increase in temperature of VES fluid resulted in an increase in the critical shear rate $\dot{\gamma}_c$ and a decrease in the zero shear viscosity μ_0 (Hartmann and Cressely 1997b). Above a temperature of 30 °C, the shear thickening effect was no longer observed. Similarly adding salt to the VES solutions increases the critical shear rate $\dot{\gamma}_c$ and the zero shear viscosity μ_0 . At quite low concentrations (<1%), the shear thickening “hump” disappears (Fig. 1). However, it has previously been shown that even solutions without the Couette non-monotonic response still show a selective aperture size effect (van der Plas and Golombok 2015a). This is because of the viscoelastic effect which is dependent on the time scale of deformation (van der Plas and Golombok 2015b). This has also been observed in

porous media flows where there is a constantly changing aperture size which can add to the effective resistance to the fluid in highly permeable zones (van Santvoort and Golombok 2015b).

Experimental setup

Viscosity as a function of shear rate is measured with an Anton Paar MCR 302 double gap rotational Couette rheometer. The sample fluid is held between a rotating part (rotor) and a cup. A constant temperature of the fluid is ensured by a Peltier system and a heating bath. Due to formation and relaxation times of the VES fluid, we pre-shear for each shear rate measurement point until a constant viscosity is reached. The VES fluid response has a time-dependent component which can lead to induced viscosity (van der Plas and Golombok 2015b). A pre-shear time ranging up to 300 s is sufficient to reach a steady state prior to the measurement itself.

A slit rheometer measures the effective bulk properties of flowing VES fluids in a rectangular conduit. A schematic overview of the experimental setup is given in Fig. 2. A digitally controlled Quizix QX6000 dual syringe pump (2) feeds the system with a pulse-less flow. The volume flow is measured at the pump outlet and has an accuracy of 0.1% of set flow rate between 0.06 and 3000 ml/h. The rectangular channel (3) is made of two stainless steel holder plates which are bolted to each other with a stainless steel spacer plate clamped in between them to form the aperture (0.5–5 mm). A flow distributor, placed in a milled opening directly after the inlet of the slit, ensures distributed laminar flow. A pressure transducer (4) is connected to the two pressure measurements holes 10 cm downstream from the upstream inlet and 10 cm upstream from the downstream outlet. The pressure drop over the conduit is measured by a

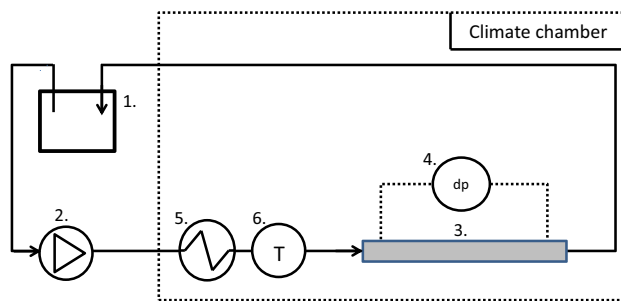


Fig. 2 Diagram of the experimental setup. The injection fluid in the intake container (1) is pumped by a Quizix QX6000 dual syringe pump (2) through the conduit (3). The pressure drop over the conduit is measured by a differential pressure transducer (4). The fluid gets the climate chamber temperature in the heat exchanger (5), which is checked with the temperature sensor (6)

Rosemount 3051CD2 transducer with a maximum static pressure of 460 mbar and an accuracy of 0.02 mbar.

The unit is placed in a Memmert IPP750+ constant climate chamber and a heat exchanger (see Fig. 2). The climate chamber allows temperature control with a temperature range of 0–70 °C. In the heat exchanger, the fluid is heated to a constant temperature. Before the fluid flows in the slit, the temperature is measured by a type K (chromel–alumel) thermocouple. To ensure that gas is excluded, the system is first filled first with CO₂, secondly with water and finally with VES test fluid. The base fluid was deionised water to which salt was added. As mentioned above, 3% w/w salt solution approximately represents sea water and 20% w/w a saturated brine in the field. The VES materials consisted of a surfactant/co-solute pair. The surfactant was cetyl trimethyl ammonium bromide (CTAB). The co-solute was sodium salicylate (NaSal). These were dissolved in the base fluids and mixed for a couple of hours until dissolved. We denote the concentrations as [CTAB]/[NaSal] where [CTAB] and [NaSal] are the concentrations of CTAB and NaSal in mmol/l (=mM). A range of concentrations and resultant ratios were chosen. Previous work has shown that the best effects are obtained around a ratio of 3/2 (Golombok et al. 2008) although this has not been confirmed for other salinities and temperatures so were subject to variation in this study.

A typical Darcy velocity in the permeable matrix in oil reservoirs is 1 ft/day (3 μm/s). At this velocity, a reservoir with a permeability of 100 mD leads to a reservoir pressure drop gradient of 300 mbar/m. Supposing mid-reservoir conditions where the Darcy velocity is constant, a fracture of 0.1 mm [equivalent to 10,000 mD (Aguilera 1995)] has a pressure drop gradient which is 100 times less than over the porous matrix. Thus, the fracture pressure drop gradient is 3 mbar/m. The same arguments for highly permeable matrix ($\kappa = 5000$ mD) in the mid-reservoir can be used and lead to a pressure drop gradient of 6 mbar/m. These examples give an indication of relevant ranges for our experimental measurements.

Results and discussion

Rheometer

The viscosity–shear rate response in a Couette cell for 12/8 VES dissolved in deionised water is shown in Fig. 3a for different temperatures (21, 40 and 60 °C). At 40 °C, the “hump” shifts to higher shear rates. At 60 °C, it is gone and the viscosity is that of water at the same temperature. (The slightly increased viscosity measured at shear rates $\dot{\gamma} > 500$ s⁻¹ is due to flow instabilities and turbulent effects

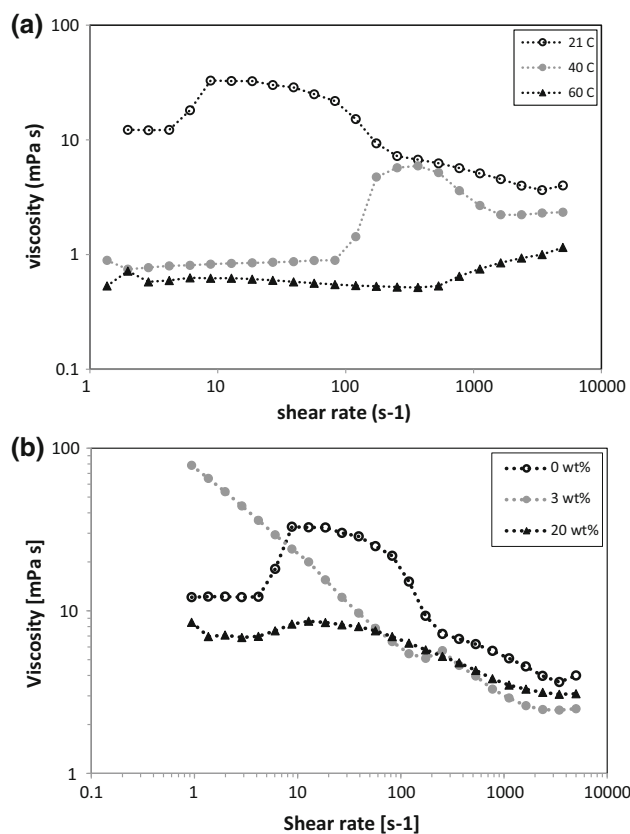


Fig. 3 Couette viscosities showing 7.5/5 mM VES solutions **a** measured at 21, 40 and 60 °C. **b** In 0, 3, 20 wt% sodium chloride at a temperature of 21 °C

which are also observed for water.) The SIS-regime Couette “hump” decreases when salt is added (Fig. 3b). We recall that such a Couette “hump” is not necessarily needed for size selective retardation when we consider the effects in “real life”, i.e. in a porous matrix or fracture flow where the constantly changing aperture size ensures that extra fluid resistance arises from the viscoelastic effects (van der Plas and Golombok 2015b). The Couette “hump” is, however, essential if we wish to have enhanced selective retardation in smooth channel conduits—which have previously been the basis for experimental comparison. The primary lever for controlling viscosity is the concentration of the viscosifying components as well as the ratio of the components. For example, measurements show that solutions of 1.5/4.5 mM/mM have better saline resistance—i.e. the non-monotonic “hump” is preserved with increasing salt concentration.

Slit experiments

A typical VES flow response is shown in Fig. 4a. In this figure, the average velocity–pressure gradient dependence for 6/4 VES fluid is shown for 2 conduits—respectively,

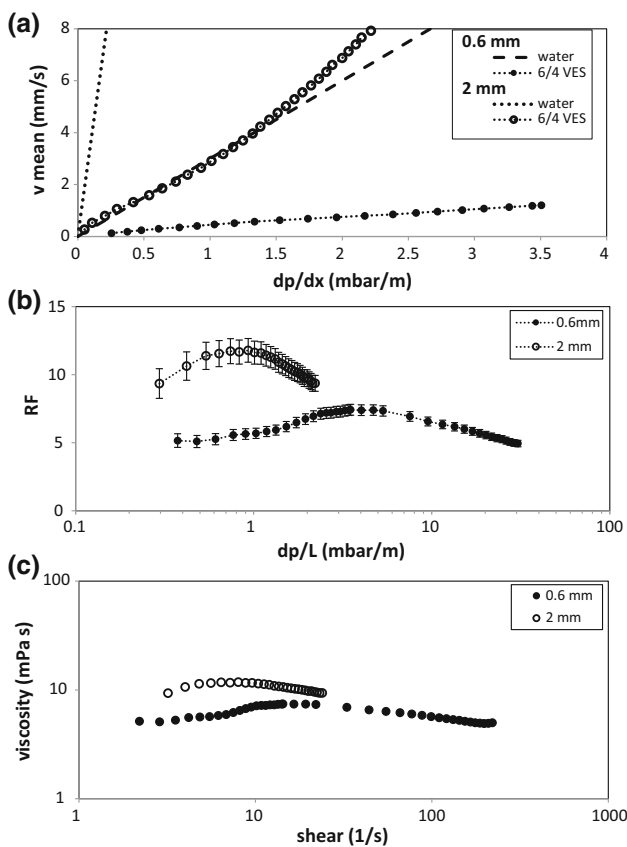


Fig. 4 **a** Average velocity as a function of the pressure gradient for 6/4 VES and water at 21 °C. **b** Retardation factor (RF) as a function of the pressure drop gradient for 6/4 VES at 21 °C. **c** Data of (b) transformed to viscosity versus shear

the dependent and independent observable variables in this experiment. Water is indicated for comparison. To do a comparison with Couette behaviour, we calculate the viscosity from the slope in Fig. 4a. The permeability in Darcy’s law is given by

$$\kappa = \frac{w^2}{12} \tag{4}$$

which for the slits indeed yields the expected calibration value of around 1 mPa s for water. In the 2 mm conduit, the fluid appears to have a more visible nonlinear dependence than in the 0.6-mm conduit. Figure 4a also shows that the velocity differences between water and 6/4 VES are higher in the 2-mm conduit than in the 0.6-mm conduit. Thus, there is higher fluid velocity retardation in the larger conduit. This can be quantified by comparison with the base fluid, using the retardation factor which we recall (Eq. 3) actually measures the apparent pressure-driven flow viscosity. Figure 4b shows this non-linear and non-monotonic behaviour of the VES fluid for both conduits. The RF (i.e. apparent viscosity as discussed above) is higher in the larger conduit than in the smaller conduit. We

observe a maximum of RF = 12 in the large slit and only RF = 7 in the smaller 0.6-mm conduit. The peaks are at different pressure gradients. For this particular 6/4 concentration ratio, the maximum contrast between the two conduits is obtained at a point where the retardation factor is still low in the small conduit, but near the maximum in the larger conduit. This is at $dp/L = 0.6$ mbar/m.

As mentioned above, the retardation factor RF can be equated to an apparent viscosity normalised to that of the base fluid. (Very roughly, assuming the base fluid is water, the scale in this case can be read as an equivalent viscosity in mPa s.) Figure 4b is thus a pressure flow analogue to the Couette plots shown in Fig. 1. However, two problems emerge in trying to do a comparison between the Couette results in the preceding discussion, and the pressure-driven flow in these capillaries. First of all there is the nonlinearity of the response—particularly in the larger capillary. Secondly, it is not possible to directly convert the independent variable in the pressure-driven flow case (i.e. the pressure gradient) into a single shear value.

In Couette flow, there is an applied single shear whereas for the former pressure-driven flow, we only have an applied pressure gradient as our controlling independent variable. In pressure-driven flow, there is a distribution of shear in the conduit—it is zero in the centre and maximum γ_w at the wall with a distribution at positions in between. The maximum value at the wall for a Newtonian fluid is given by

$$\gamma_w = \frac{w \Delta p}{2\mu L} \tag{5}$$

Figure 4c shows the data transformed for comparison with the Couette data in Fig. 3. The values are consistent although the points above need to be noted, i.e. in Couette flow, the viscosity is identical at every point, and in pressure-driven flow of VES materials it is not, as has been previously demonstrated (van der Plas and Golombok 2016).

Returning to Fig. 4b, the relative slowing down in the large fracture compared to the small fracture can be parametrized by the ratio of retardation factors:

$$S = \frac{RF_l}{RF_s} \tag{4}$$

This parameter tells us whether the solution viscosity is sufficient to selectively slow down flow in the larger conduit with respect to the smaller one. If u_{VES} and u_{bf} are the Darcy velocities of VES solution and base fluid, respectively, then the desired result for flow in the large (l) and small (s) conduits is that the relative flow velocities should be more closely matched for the same pressure. For water, the relative flow is u_{bf}/u_{sbf0} . With VES, this ratio should decrease i.e.

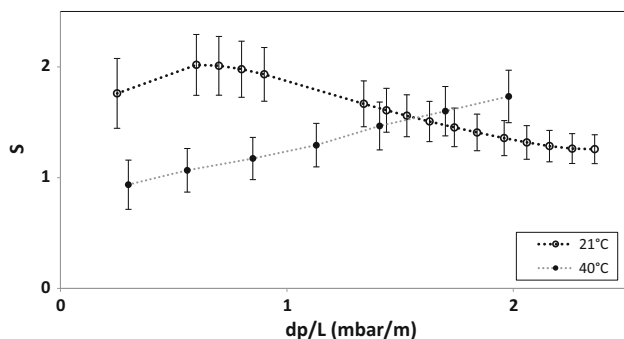


Fig. 5 Size selective retardation factor S measure the relative slowing down of flow in the larger fracture (2 mm) compared to the smaller fracture (0.6 mm) normalised to water. The solution was 6/4 VES at two temperatures

$$\frac{u_{\text{VES}}}{u_{\text{sVES}}} < \frac{u_{\text{bf}}}{u_{\text{sbf}}}$$

Using Eq. 3 this become

$$RF_s < RF_1$$

which means (using the definition of Eq. 4) that to reduce flow in the larger conduit we need to have the condition $S > 1$. If we carry out this comparison for the two slit systems discussed above, for one solution at 21 °C, then we see in Fig. 5a change in response on going to a higher temperature (40 °C). The selective retardation response actually increases with higher pressure drop at the higher temperature. Classical viscosity–temperature responses might indicate that selective retardation is not possible at higher temperatures; however, Fig. 5 indicates that the use of VES materials is not ruled out on temperature response considerations.

To achieve an elevated viscosity at 60 °C, higher VES concentrations are needed. Figure 6 shows the Couette zero shear viscosity μ_0 as a function of the NaSal concentration (C_{CO}) at 60 °C for a fixed CTAB concentration (C_{VES}) dissolved in deionised water and 3% NaCl (i.e. similar to sea water). The figure shows elevated viscosities for

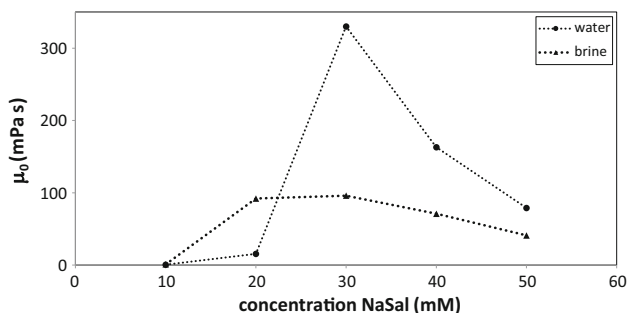


Fig. 6 Zero shear viscosity as function of NaSal concentration (C_{CO}) for viscoelastic surfactant (CTAB) concentration of 30 mM at 60 °C in DI water and 3 wt% brine

concentrations of $C_{\text{CO}} \geq 20$ mM with maxima at equimolar concentrations. Hence, it is possible at 60 °C to form micelles which increase the viscosity of the base fluid. This proves the importance of the concentration ratio, i.e. an increase in concentration of CTAB alone does thus not necessarily lead to an increased viscosity at 60 °C. The zero shear viscosity decreases when sodium chloride is added although the viscosity remains enhanced compared to water.

Conclusions

Flow-induced viscosities can be generated in brine solutions at elevated temperatures. VES fluid viscosity overall decreases for higher temperatures, but this does not always mean that the non-monotonic behaviour disappears. Up to 40 °C, it has been shown that it can be maintained or even increased, shifting to higher shear rates when the temperature increases. While most VES solutions show a negative gradient in the low Couette shear-regime, this can become flat for increasing temperatures or sodium chloride concentration. Adding salt does not necessarily lead to a change in the zero shear viscosity μ_0 . (e.g. can be much higher in 3% salt solution than in either 0 or 20%.)

Size selective retardation in slits was shown for temperatures up to 40 °C at mid-reservoir pressure drop gradients. The “hump” observed in Couette tests is only a prerequisite if we have shear-induced effects under steady flow in smooth channels. Real fractures have continuously varying apertures where flow is continuously redeveloping. Increasing the salinity often causes better temperature stability. Elevated viscosities and shear thickening at 60 °C have been shown at equimolar surfactant and co-solute concentrations in excess of 20 mM.

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