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Application of Ionic Liquid Based Viscoelastic Surfactant in Enhanced Oil Recovery Process

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ABSTRACT

Viscoelastic surfactants have emerged to be a unique class of surfactants that have a surplus property of mobility control other than lowering the interfacial tension. Researchers are now exploring new viscoelastic surfactants which have the potential of recovering residual oil during the enhanced oil recovery processes. In the present study, a viscoelastic surfactant has been prepared using ionic liquid 1-hexadecyl-3-methylimmidazolium bromide, C_{16}mimBr, and a binding agent sodium salicylate (NaSal). The effect of brine concentration on the viscosity of the resulting solution, its interfacial activity with oil and emulsion size distribution has been studied. Though the interfacial activity of the immidazolium ionic liquid diminished, it was found that, the newly formulated viscoelastic surfactant recovered an exceptionally high percentage of oil as compared to the ionic liquid alone during the core flooding experiments.

Keywords

Ionic liquids, Na- salicylate, Interfacial Tension, Viscoelastic surfactants, mobility control

INTRODUCTION

Oil has been a major source of energy today and might remain an important one even further, thus fulfilling the energy requirements of the world. Oil recovery process is classified into primary, secondary and tertiary process. Only one-third of the oil present in a reservoir is recovered by primary and secondary processes [1, 2]. Since a major amount of oil is still left inside the pores of a reservoir, recovering this oil is a major challenge during the tertiary or enhanced oil recovery (EOR) process. Various methods have been used to recover residual oil during an EOR process, viz. thermal and non-thermal methods. Chemical enhanced oil recovery (CEOR) is an important non-thermal method in which foreign chemicals are injected in a reservoir. The injected fluid improves both the displacement efficiency as well as the volumetric sweep efficiency thereby recovering the residual oil. Surfactant flooding is an important CEOR process, in which surfactant solutions capable of reducing interfacial tension (IFT) between oil and the injected fluid to ultralow values are flushed into the reservoir [1-3]. A surfactant selected for surfactant flooding process should have the following properties: good thermal stability (at reservoir temperature), the ability to lower the oil/water IFT to 10^{-3} mN/m, low adsorption on reservoir rock (<1 mg/ (g of rock)), salt tolerance (at reservoir salinity). Before being tested in a particular field, numerous surfactants are screened on the basis of this criteria. The most common surfactants being used during CEOR are petroleum sulfonates. Researchers have also evaluated a number anionic, cationic, nonionic and zwitterionic surfactants for their use in CEOR processes [3]. However most of the surfactants are unstable at high reservoir temperature and salinity thus losing their efficiency in recovering additional oil [1 -3]. Lately, ionic liquid based surfactants have also been evaluated for their potential in recovering oil during a CEOR process.

Ionic liquids (ILs) are also termed as greener solvents due to the novel properties they exhibit. ILs are known for their negligible vapor pressure and non-flammability under ambient conditions, high thermal conductivity, high polarity, low toxicity, low volatility and thermal stability[4]. Many researchers have studied the behaviour of IFT reduction between crude oil/water in the presence of ILs [5 -8]. In a recent study, the effect of different families of ionic liquids (immidazolium and pyridinium) on the IFT between crude oil and water had been studied [5]. The authors have found that found that the immidazolium class of ionic liquids were more effective in reducing IFT than pyridinium type of ionic liquids of same alkyl chain length. It was observed that for both the ILs, IFT between crude oil and IL-brine solution decreased even under high salinity and high temperature conditions [5]. From the above studies it may be concluded that though IL based surfactants lower the IFT between crude oil/water solutions, the obtained IFTs are very high (>1mN/m) and do not fulfil an important criteria of ultra-low values of IFT [5 -8]. This observation is well in accordance with the fact that ionic surfactants having single hydrophobic tail do lower the interfacial tension, but in most cases the critical micelle concentration (CMC) is reached before IFT is close to zero. However addition of an electrolyte or a second surfactant (exhibiting synergistic affect in reducing IFT together with the first surfactnt), lowers IFT further and very small, ultralow values may be reached [9]. Recently it has been observed that, in the presence of added salt, small micellar aggregates of some long-chain cationic surfactants undergo enormous growth and form larger and highly flexible micelles called wormlike micelles [10]. These wormlike micelles have high surface activity and exhibit viscoelastic behavior analogous to a flexible polymer solution. Binding salts, with counterions such as salicylate, tosylate, or chlorobenzoate, tend to induce micellar growth at very low concentrations. M. Awang et al. induced worm like micelles using cationic surfactant Cetyl trimethylammonium bromide (CTAB) and other salts [11]. They observed additional oil recovery due to improved mobility control using worm like micelles. B.Dong et al. found that as in some conventional ionic surfactant/salt aqueous systems, wormlike micelles and network structures could be formed in the 1-hexadecyl-3-methylimmidazolium bromide (C_{16}mimBr) and Sodium Tosylate (NaToS) aqueous solutions [10].

In the present study, the viscoelastic properties of wormlike micelles of surface active IL, C_{16}mimBr, in aqueous solution in the presence of an organic salt, Sodium Salicylate (NaSal), at room temperature (298 K) has been investigated. The effect of increasing salinity on the viscoelasticity of the IL-NaSal based surfactant solution has been studied. In order to investigate the efficiency of the IL-NaSal based surfactant in recovering additional oil during a CEOR process, core flooding experiments has been performed.

MATERIAL AND METHODS

Materials

Paraffin liquid light oil (Finar Chemicals) was used as the oil phase. Sodium chloride (99%), Sodium Salicylate were purchased from Sigma-Aldrich (India). 1-hexadecyl-3-methylimmidazolium bromide, C_{16}mimBr, was prepared and purified as mentioned elsewhere [12]. Aqueous solutions of the ionic liquids were prepared by weighing on an analytical balance with a precision of (0.0001 g (Denver Instrument APX-200)) in degassed Millipore-grade water. Sand (50 mesh size) used in the sand pack column was purchased from Sunrise Glass Factory, India.

Methods

Preparation of the viscoelastic surfactant solution

In this step, an aqueous solution containing 14mM of c16mimBr and 14 mM of NaSal was prepared using a stirrer at a room temperature. The resulting solution was extremely viscous as can be seen in Fig 1. The concentration of the IL and binding salt were held constant thereafter.

Fig 1: Pictorial representation of highly viscous surfactant formulation prepared on mixing of C_{16}mimBr ~ 14 mM and NaSal ~ 14 mM in distilled water.

Viscosity Measurements

Viscosities of the C_{16}mimBr-NaSal at different brine concentrations were measured using an Ostwald viscometer. Brine concentration was varied from 0 – 3 wt%.

Interfacial tension measurements

In the present study interfacial tension between oil phase and aqueous surfactant phase was measured using a KRUSS-T9 Tensiometer (Germany), (Du-Nuoy ring method) under atmospheric pressure. The platinum ring was thoroughly cleaned and flame-dried before each measurement. In all cases, two successive measurements were carried out, and the standard deviation did not exceed ±0.1 mN/m.

Emulsion size distribution analysis

Different ratios of oil and surfactant solutions were homogenized using a strirrer. A sample of the microemulsion phase was then extracted using a micro-pipette. Emulsion size distribution measurements were performed using laser diffraction method of Zetasizer Ver. 6.00 (Malvern Instruments Ltd., Worcestershire, UK). The droplet size distribution of the dispersed particles was obtained by the inbuilt software of the instrument. The software uses a refractive index (RI) of 1.48 (paraffin oil) and a dispersant RI of 1.33 (water) during the measurement. All the experiments were conducted at 298 K.

Core flooding procedure

Sand-packed columns were moduled as reservoir cores and the potential of the two surfactants (C_{16}mimBr and C_{16}mimBr-NaSal) in recovering additional oil during a CEOR process were also investigated. The core flooding setup used in the present study is a vertically placed acrylic column described in the previous work [13]. During the core flooding experiments, the acrylic column was filled with a tightly packed sand-bed. The pore volume and porosity of the sand bed was calculated after saturating it with 3.5 wt % brine. Next, paraffin light oil was injected into the sand-bed until no more water was produced in the effluent stream. After a period of 24 hrs. The artificially moduled core wasthen waterflooded. The amount of oil recovered during waterflooding was noted down. The residual oil was then subjected to CEOR processes. The column was then flooded with surfactant solutions. The effluent was collected in graduated test tubes.

RESULTS AND DISCUSSIONS

Effect of change in brine concentration on viscosity of C_{16}mimBr-NaSal solution

In order to investigate the effect of brine on the viscosity of C_{16}mimBr-NaSal viscous solution, concentration of NaCl in it was varied from 0 – 3 wt%. From visual observation it was clear that as the brine concentration increased the viscosity of C_{16}mimBr-NaSal solution gradually decreased. The viscosity of the solution at different brine concentration was measured using Ostwald Viscometer. The results are shown in Fig 2.

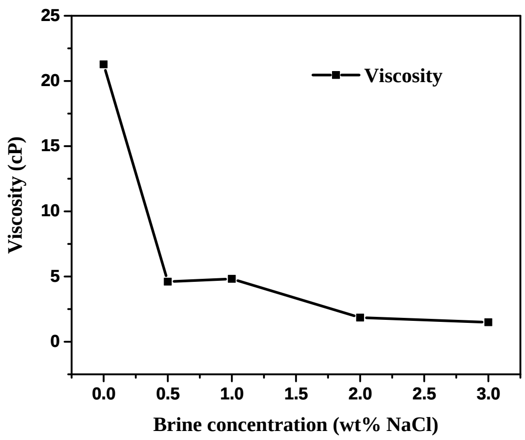

FIG 2: Effect of NaCl concentration on viscosity of the C_{16}mimBr-NaSal solution (14mM each)

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At 0 wt% salinity the solution was extremely viscous as observed in Fig 1. This might be due to formation of worm like micelles. A similar behaviour was reported by B.Dong et al in their study wherein formation of wormlike micelles have been observed in the C_{16}mimBr/NaTos aqueous solutions [10]. S. Kefi et al. in their study about viscoelastic surfactants reported that the worm-like micelles in such surfactants on coming in contact with formation brine and/or hydrocarbons lose their rod like shape and get converted into spherical micelles. The solution thus loses viscosity [14].

Interfacial tension measurements

Fig 3. shows the effect of NaCl concentration on IFT between C_{16}mimBr /oil solution as well as C_{16}mimBr-NaSal/ oil solution. It is clear from the Figure above that surface activity of the IL solution (C_{16}mimBr) has considerably reduced on addition of NaSal. Moreover a reverse effect of increasing salinity has been observed for the two surfactants solutions. In case of C_{16}mimBr solution as salinity increases the IFT between the brine solution and oil phase reduces further. However, for C_{16}mimBr-NaSal solution, with an increase in salinity the IFT between brine phase and oil phase increases. This might be a result of the antagonistic effect in reducing IFT between C_{16}mimBr and the binding salt (NaSal).

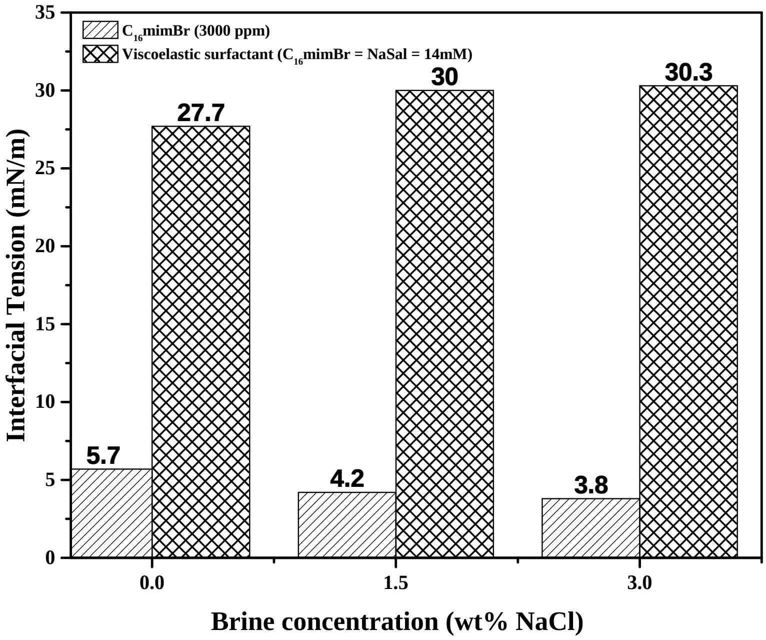

Fig 3: Effect of NaCl concentration on IFT between C_{16}mimBr /oil solution as well as C_{16}mimBr-NaSal/ oil solution.

Emulsion Size distribution

During surfactant flooding, surfactants are expected to lower IFT thus forming emulsions. The smaller the size of emulsions (microemulsions), the more stable they are. Due to this more amount of oil is solubilised leading to increase in oil recovery. In this section the size of emulsion formed when the C_{16}mimBr-NaSal solution and oil are homogenized is determined using dynamic light scattering technique. Emulsion size distribution in the homogenised solution is shown in Fig. 4. The Z –average diameter of dispersed droplet is the mean hydrodynamic diameter and is calculated according to the International Standard of dynamic light scattering ISO13321. The emulsion-size distribution affects emulsion viscosity because it is higher when droplets are smaller. Emulsion viscosity is also higher when the droplet-size distribution is narrow (i.e., droplet size is fairly constant). Emulsions that have smaller size droplets will generally be more stable [15]. The Z-average diameter of dispersed oil droplets formed when the brine concentration is 0 wt % is 14.5 nm. A sharp increase in Z-average diameter (1308 nm) is observed at a salinity of 3 wt % of the C_{16}mimBr-NaSal solution.

Thus we can conclude that, the C_{16}mimBr-NaSal solution show deteriorated interfacial activity in presence of paraffin liquid light oil as compared to C_{16}mimBr solution. Also larger emulsion size indicates that at high brine concentration the oil solubilising capacity of C_{16}mimBr-NaSal solution decreases.

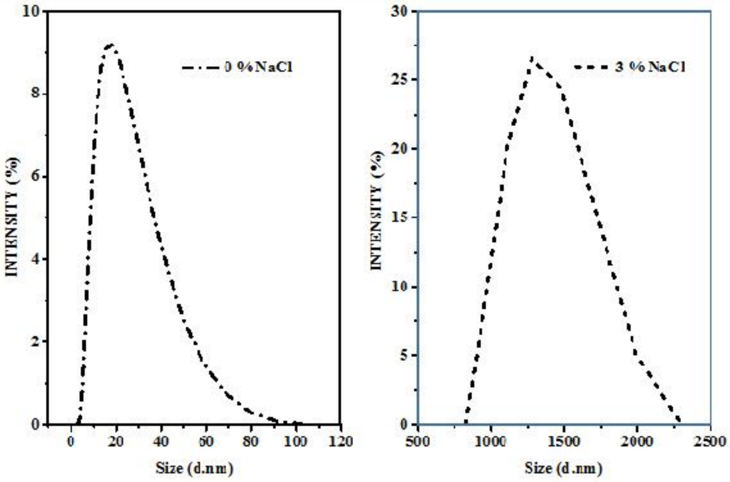

Fig 4: Influence of change in NaCl concentration on the size of emulsion formed in the homogenized solution of C_{16}mimBr-NaSal and oil

Core flooding experiment

In order to investigate the efficiency of C_{16}mimBr-NaSal solution in recovering residual oil during a CEOR process, the C_{16}mimBr-NaSal solution (having 3 wt % salinity) was employed as a surfactant slug during surfactant flooding step. The results were then compared with the oil recovered by surfactant slug -C_{16}mimBr (3000 ppm) solution (having 3 wt % salinity). The results are shown in Fig 5. The core flooding experiments were carried out at room temperature.

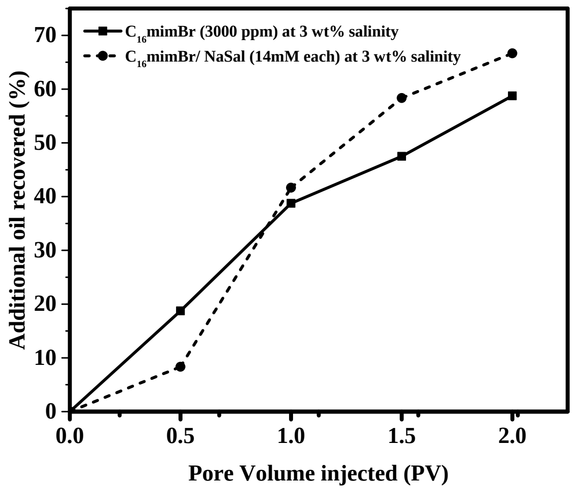

FIG 5: Additional oil recovered during surfactant flooding

From the above figure we see that the C_{16}mimBr-NaSal solution (having 3 wt % salinity) recovers lesser oil as compared to C_{16}mimBr solution initially. However after 0.5 PV being injected there is a steep increase in residual oil recovered (67%). The oil recovered after injection of 2 PV of C_{16}mimBr solution is 58%. Similar results were obtained Awang et al. wherein they attributed the additional oil recovered by viscoelastic surfactants to their efficient mobility control of the displacing phase [11]. The mobility of the slug in relation to the mobility of the oil-water bank enhances the amount of oil recovered during CEOR process.

CONCLUSION

In the present study interfacial activity between an Ionic liquid based surfactant- binding salt solution and oil phase has been investigated. It has been found that not only did the viscosity of the C_{16}mimBr-NaSal solution decrease with increased salinity but also the interfacial activity deteriorated when compared to C_{16}mimBr solution alone at increasing salinities. Core flooding experiments was performed inorder to investigate the potential of C_{16}mimBr-NaSal solution in recovering residual oil. It was found that the residual oil recovered by C_{16}mimBr-NaSal solution was greater as compared to C_{16}mimBr solution. This might be attributed to good mobility control of C_{16}mimBr-NaSal solution during the CEOR process.

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