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Phase Behavior and Physicochemical Properties of (Sodium Dodecyl Sulfate + Brine + Propan-1-ol + Heptane) Microemulsions

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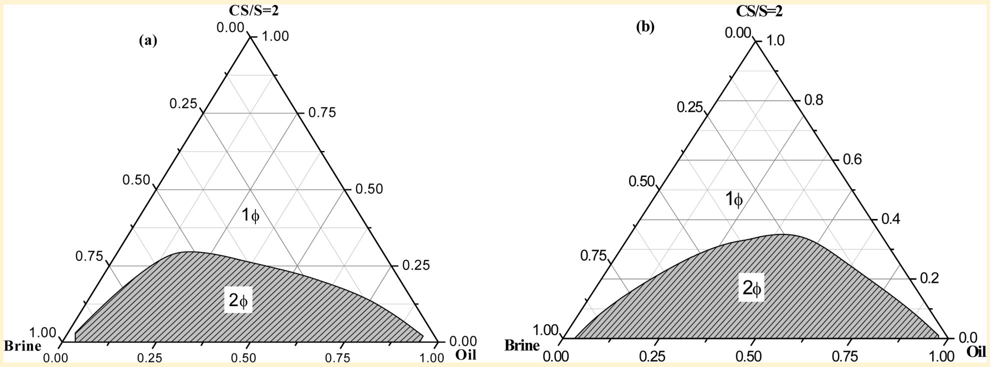

ABSTRACT: Experimental investigations have been made on the phase behavior of the (sodium dodecyl sulfate + brine + propan-1-ol + heptane) microemulsion system and its stability under reservoir conditions for its use in enhanced oil recovery (EOR). An increase in salinity is found to decrease the single-phase microemulsion region as salt interacts with surfactant to reduce its activity. As salinity changes from a low to high value, a phase transition takes place from Winsor I to Winsor II via Winsor III. The temperature also induces a phase transition for low- and high-salinity microemulsion systems. With an increase in temperature, the phase transition takes place from Winsor I to Winsor III for low salinity and Winsor II to Winsor III for high salinity microemulsion systems. The solubilization parameter of oil increases with an increase in salinity, whereas that of water decreases and at optimal salinity both are same. With increasing salinity, interfacial tension (IFT) between oil and microemulsion decreases, whereas that of water and microemulsion increases. At optimal salinity, both IFT values are the same. The optimal salinity increases with increasing temperature. Interestingly the conductivity of the middle-phase microemulsion system showed maxima around optimal salinity.

1. INTRODUCTION

Microemulsion in enhanced oil recovery (EOR) has become more attractive in recent years because of its high level of extraction efficiency.[1−4] Microemulsions are thermodynamically stable, isotropic dispersions of otherwise immiscible oil and water stabilized by surfactants (and/or cosurfactants).[5] Ultra low interfacial tension (IFT) can be obtained by creating a middle phase microemulsion using brine, oil, surfactant, and cosurfactant. The phase behavior of surfactant−brine−alcohol−oil systems is of immense importance for surfactant flooding in EOR due to the well-established relationship between the IFT and microemulsion phase behavior.[6−10] The phase behavior of the surfactant−brine−alcohol−oil system is one of the key factors in interpreting the performance of chemical EOR by the microemulsion process.[11−13]

The phase behavior of aqueous oleic systems is modified drastically upon addition of proper surfactant at a particular pressure and temperature.[14−17] In microemulsion systems, a variety of phases can exist in equilibrium with another phase, with each phase having a different structure. In the case of middle-phase microemulsions (three-phase system) ultralow IFTs ($<10^{-3}$ $\text{mN}\cdot\text{m}^{-1}$) are attained, and microemulsions are changed from Winsor type I to Winsor type II through Winsor type III by systematic variation of salinity at a particular temperature and pressure.[1,18] The commonly observed Winsor-type systems indicate that the microemulsions can remain in equilibrium with excess oil, excess water, or both.[19−21] The factors that affect the phase transition between different types of systems include salinity, temperature, molecular structure, and nature of the surfactant and cosurfactant, nature of the oil, and the water−oil ratio (WOR).[22] Under adequate conditions, the microemulsion system is miscible with both oil and water. The optimum salinity and the amounts of solubilized oil and water contained in a microemulsion play important roles in obtaining low IFTs and higher oil recoveries in chemical EOR. Since IFTs have a minimum value at optimal salinity and solubilization parameters are related to IFT, the estimation of both properties is of great importance in designing economical microemulsion flooding.[23,24] The optimal salinity depends upon many parameters like pressure, temperature, and microemulsion composition, and so forth. The influence of temperature on optimal salinity is quite complex. For the

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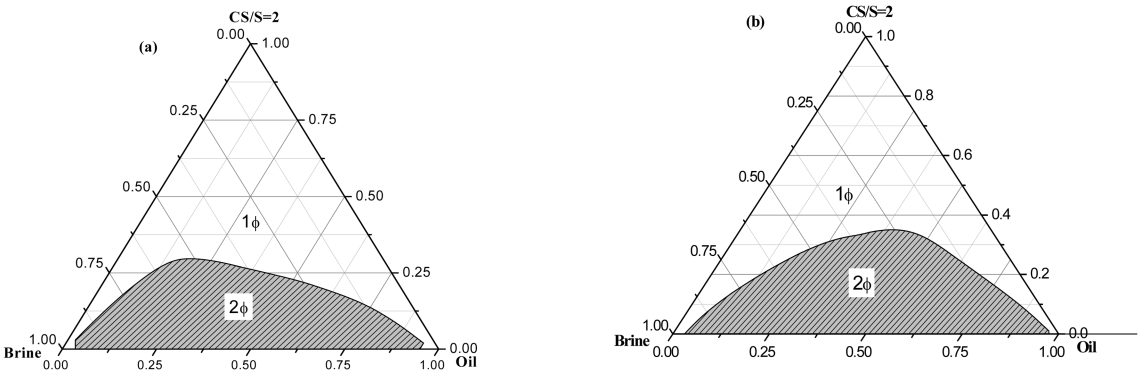

Figure 1. Pseudoternary phase diagram of oil−brine−surfactant−cosurfactant system for (a) low salinity (0.01 mass fraction of NaCl) and (b) high salinity (0.09 mass fraction of NaCl).

anionic microemulsion system, it was observed that optimal salinity increases with an increase in temperature.[25,26] A medium chain alcohol or other amphiphilic cosurfactant must be required for microemulsion formation in the case of anionic and cationic surfactants.[27−29] One reason for the use of cosurfactant that the most commercial surfactants are not balanced with respect to their affinity to water and oil but can be made so by the addition of alcohol. Furthermore, for ionic surfactants the electrostatic interactions have to be screened by salt as a fifth component in the system. The unwanted effects of salt (salting-out) can again be compensated by adjusting the alcohol concentration.[30] The electrical conductivity measurement of microemulsions sometimes helps to obtain information on phase inversion, microstructure of microemulsion, and optimal salinity of the system.[31−33]

The main objectives of the present study are the formation and characterization of microemulsions that are stable at the reservoir temperature. The formation of stable microemulsions using a minimum amount of surfactant is the biggest challenge for its use in EOR. Thus, a complete study on phase behavior and physicochemical properties of microemulsion comprised of sodium dodecyl sulfate (SDS), brine, propan-1-ol, and heptane have been investigated as a function of salinity and temperature. Relative phase volumes (RPVs) of different components in microemulsions are very sensitive to the salinity, temperature, and water content. Therefore, all of these parameters have been studied to perceive their effects on RPVs of the microemulsion systems. Pseudoquaternary phase diagrams have been drawn to identify the microemulsion region. IFTs between oil−microemulsion and water−microemulsion and the conductivity of microemulsion systems have also been studied as a function of salinity.

2. EXPERIMENTAL SECTION

2.1. Materials. The anionic surfactant, sodium dodecyl sulfate (SDS), of mole fraction purity 0.98 was purchased from Fisher Scientific, India. Sodium chloride (NaCl) (0.98 mole fraction) procured from Qualigens Fine Chemicals, India, was used for the preparation of brine. Reverse osmosis water from the Millipore water system (Millipore SA, 67120 Molshein, France) was used for the preparation of solutions. Propan-1-ol with 0.98 mole fraction was used as a cosurfactant. It was supplied by Otto-kemi Pvt. Ltd., India. In this study *n*-heptane (with mole fraction purity >0.99) was used as an oil and purchased from Merck, India. All chemicals were used without further purification.

2.2.1. Experimental Procedures. *Phase Diagram of the Microemulsion System.* The phase diagram has been established by a conventional titration method for the determination of microemulsion region. At a fixed cosurfactant (CS) to surfactant (S) ratio of 2 (CS/S = 2), different amounts of heptane were taken, and the solution was stirred by a Remi magnetic stirrer by the gradual addition of brine solutions (0.01 and 0.09 mass fractions of NaCl for low and high salinity, respectively) from a micropipet until the turbidity appeared. All mixtures were prepared by weight, and compositions are expressed as mass fractions to draw the phase diagram. The experiments have been performed at 302 K, and the data have been reproduced by repeating the experiments.

2.2.2. Determination of the Relative Phase Volume and Solubilization Parameters. Microemulsion phase behavior was determined by equilibrating the surfactant and cosurfactant mixture with equal volumes of oil and brine solution and measuring the volume of the microemulsion phase and excess oil and/or excess brine phase at a constant pressure and temperature. All of the samples were prepared with 0.47, 0.47, 0.04, and 0.02 mass fractions of water, oil, alcohol, and surfactant, respectively. For all systems, a constant water−oil ratio (WOR) was maintained (WOR = 1). The details of the procedure of the experiment were stated in our previous paper.[34] For studying the temperature effect, the prepared samples were heated at different temperature in a thermostat, and the phase volumes were recorded. For a specific salinity (0.05 mass fraction of NaCl) of the microemulsion system, the effect of heating time was also studied. The effect of water content on RPVs have been studied taking different amounts of brine (0.05 mass fraction of NaCl) as rgw aqueous phase following the procedure as stated earlier. The volume of oil and brine that can be solubilized in microemulsion is of interest in characterizing the solubilization capacity of the surfactant (SDS). The volumes of oil and water solubilized per unit volume of surfactant in the microemulsion phase have been considered as solubilization parameters (V_o/V_s and V_w/V_s) of oil and water, respectively. V_s, V_o, and V_w represent the volume of surfactant, oil, and water, respectively, in the microemulsion phase. The solubilization parameters were calculated with the assumption that the total surfactant was contained in the microemulsion phase.[35]

2.2.3. IFT and Electrical Conductivity Measurements of Microemulsion. IFTs of the excess oil−microemulsion system and the excess brine−microemulsion system were measured as a function of salinity. A programmable tensiometer (Kruss GmbH, Germany, model: K20 EasyDyne) was used to measure

IFT. During the measurement, the experimental temperature was maintained at 302 K. In all cases, more than three successive measurements were carried out, and the standard deviation did not exceed ± 0.1 $mN\cdot m^{-1}$.

The conductivity of microemulsion was measured with the variation of salinity by using a digital conductivity meter (Biocraft Scientific Systems (P) Ltd.; model no. CEI-13). The temperature was kept constant at (302 ± 1) K throughout the experiment. In all cases, measurements were made after homogeneous mixing by a magnetic stirrer. The error limit of conductance measurement was ± 1 %.

3. RESULTS AND DISCUSSION

3.1. Phase Diagram of the Microemulsion System. The pseudo ternary phase diagram of (SDS + brine + propan-1-ol + heptane) system has been constructed and shown in Figure 1, where water and NaCl salt considered as a single pseudocomponent and (S + CS) is another single component so that the apexes represent oil, brine, and (S + CS). The importance of the construction of this type of phase diagram is to determine the composition of the microemulsion. Figure 1 depicts the phase diagram of surfactant, cosurfactant, oil, and brine at a constant CS/S ratio of 2. It is also important to prepare microemulsions with low concentrations of surfactant from the economical point of view. In Figure 1a and b, the shaded areas represent the two-phase microemulsion region, and out of the shaded areas imply single-phase microemulsion regions (Winsor IV) for low (0.01 mass fraction of NaCl) and high (0.09 mass fraction of NaCl) salinities, respectively. Salt has a significant effect on the extent of the single-phase microemulsion region. From the figures it is clear that at higher salinity the area of single-phase microemulsion region is slightly smaller than that at low salinity. This is due to fact that salt interacts with surfactant to reduce its activity and changes the phase diagram of the systems. It is also important to note that at low salinity the curve is tilted toward the brine axis and in the case of high salinity the curve is slightly tilted toward the oil axis.

3.2. Relative Phase Volumes. Relative volume fractions of various phases of Winsor I, Winsor III, and Winsor II are plotted in the Figures 2, 3, 4, 5, and 6 as a function of salinity, temperature, and water content, respectively. Experimentally it has been found that the relative phase volumes (RPVs) of the microemulsion system are largely affected by salinity, temperature, and water content.

3.2.1. Effect of Salinity. In Figure 2, RPVs are plotted as a function of salinity. This type of data set is known as a "salinity scan". From Figure 2 it is clear that at a lower salinity region only two phases exist, that is, a water-external microemulsion at the bottom and excess oil phase at the top. This is called Winsor type I phase behavior. With increasing salinity, a bicontinuous microemulsion (B.C.μE) phase is formed. At moderate salinity, three phases coexist simultaneously. This type of phase is considered as Winsor type III. When the salinity further increases, the relative volume of middle phase converted to Winsor type II with oil-external microemulsion at the top and excess water at the bottom. The dependency of phase behavior of the oil–water surfactant system on salts can be explained by interfacial energy. The salting-out phenomenon also plays an important role on the microemulsion phase. As the salt concentration is increased, some of the water molecules are attracted by the salt ions, which decreases the number of water molecules available to interact with the charged part of the surfactant. As a result of the increased demand for solvent molecules, the interactions between the hydrophilic head groups become stronger than the solvent–solute interactions; the surfactant molecules are precipitated by forming hydrophobic interactions with each other. The interfacial film curvature turns from a positive value to zero to a negative one, corresponding to the phase transition from O/W to bicontinuous phase to W/O structure.[36]

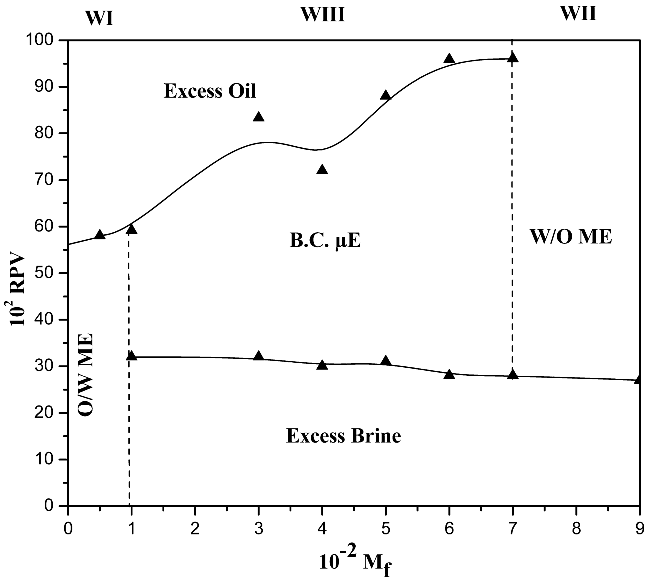

Figure 2. Relative phase volume (RPV) of different layers as a function of mass fraction of NaCl (M_f).

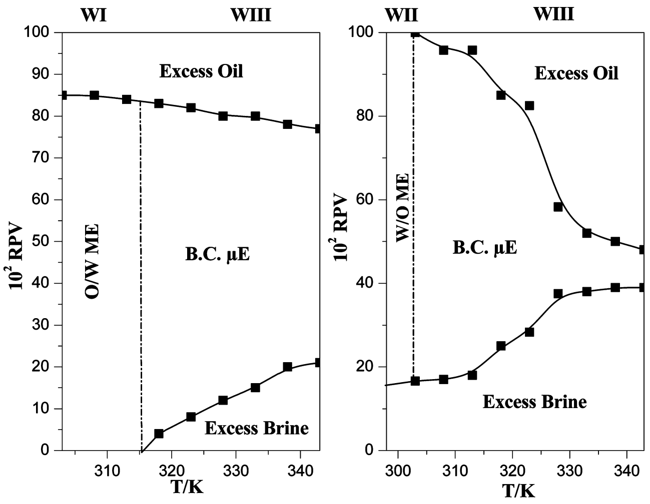

Figure 3. RPV of different layers vs temperature (T/K) at (a) low salinity, 0.01 mass fraction of NaCl and (b) high salinity, 0.09 mass fraction of NaCl.

3.2.2. Effect of Temperature. The dependence of the RPV of the microemulsion system on temperature has been shown in Figures 3 and 4. In the present study, the effect temperature on phase volumes of the microemulsions has been studied for low and high salinities (0.01 and 0.09 mass fraction of NaCl, respectively). The temperature effect on the low salinity microemulsion system has been depicted in Figure 3 a. At low temperature, the system shows the Winsor type I phase behavior, which changes to the Winsor type III microemulsion phase as the temperature increases above 316 K with an

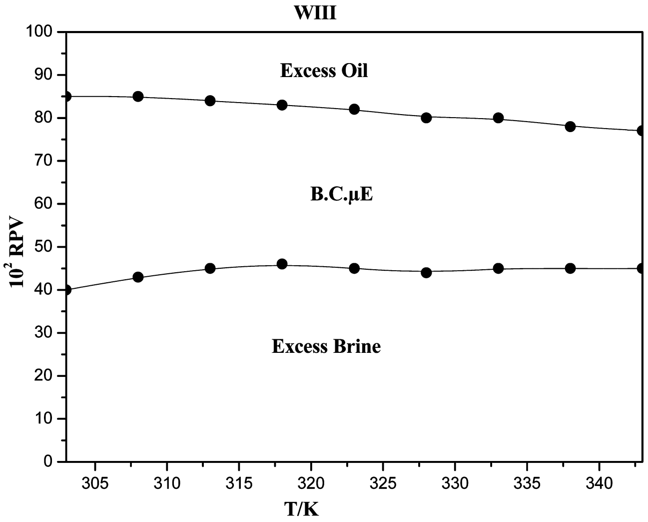

Figure 4. RPV vs temperature (T/K) at moderate salinity, 0.05 mass fraction of NaCl.

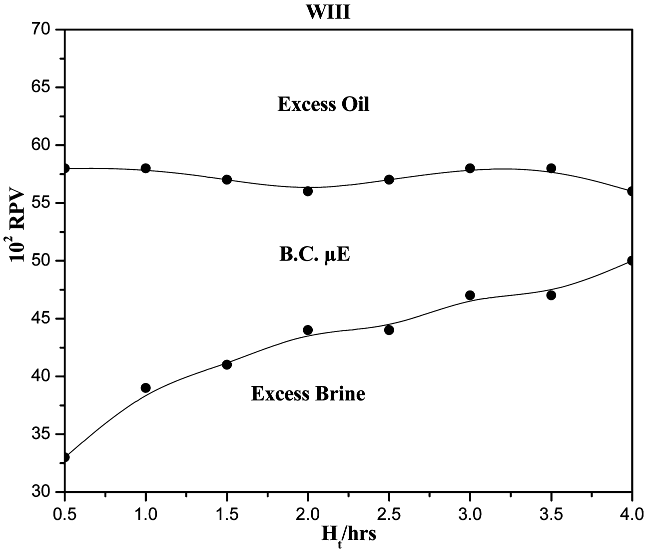

Figure 5. Effect of heating time (H_t/hs) on RPV of 0.05 mass fraction of the NaCl microemulsion system.

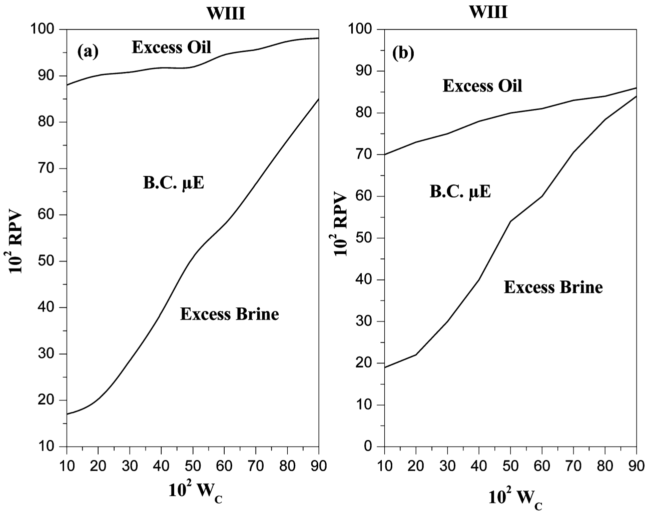

Figure 6. Variation of RPV with water content (W_C) at (a) 303 K and (b) 333 K in a 0.05 mass fraction NaCl solution.

increasing accumulation of the excess brine phase and decreasing volume of the microemulsion phase. In Figure 3b, the temperature effect on the high-salinity microemulsion system has been shown. At low temperature, the system shows Winsor type II phase behavior with upper phase W/O microemulsion and lower phase of excess brine. As temperature increases, the Winsor type III phase starts to form with the release of excess oil. In this case the phase transition from Winsor type II to Winsor type III occurs at 303 K, where the microemulsion phase remains in equilibrium with excess brine and excess oil phase. It may be concluded that the increase of temperature enhances the repulsion between headgroups and spontaneous curvature changes from a negative value to zero to positive for high salinity, and the opposite effect was found in the case of low salinity. At a moderate salinity (0.05 mass fraction of NaCl) which is near to optimal salinity, the middle phase microemulsion is very stable compared to other salinities. In Figure 4, the RPV vs temperature at moderate salinity has been shown. At low temperatures, a large volume of middle phase microemulsion coexists with the excess brine and oil phase. From the figure, it is clear that with increasing temperature the volume of middle phase microemulsion decreases, but the change is not so high. This is due to the high stability of microemulsion around optimal salinity.

The heating time is an important factor for the middle phase microemulsion system. The sample was heated at 333 K for few hours, and data were collected at various time intervals. Figure 5 depicts the effect of heating time on the middle phase microemulsion. For a 0.05 mass fraction of NaCl system, three phases equilibrate and show Winsor type III phase behavior. Initially the volume fraction of middle phase was enough high but decreased significantly as the heating time is increased. This behavior may be due to the breaking of emulsion at high temperatures kept for a long time. Middle phase microemulsions are quite stable up to three hours of heating. Further, it has been observed that after a certain heating time (~ 4.0 h) the phase volume decreases noticeably.

3.2.3. Effect of Water Content. Experimentally it has been found that the size of the microemulsion phase depends on the volume of excess water present in equilibrium with the microemulsion. The RPV of different phases as a function of water content has been shown in Figure 6a. The experiments were conducted at an intermediate salinity where Winsor III type microemulsions were formed. Keeping the salinity constant (0.05 mass fraction of NaCl), it has been found that the volume of middle-phase microemulsion decreases gradually with an increase of water content. This reason behind this decrease of microemulsion is the partitioning of surfactant monomers in the water phase.[37] Similar results are also reported by other researchers[38,39] in different systems. Figure 6b shows the variation of RPV with water content when each tested sample was heated at 333 K for six hours. The objective of the study was to observe the stability of emulsion at high temperature and retention time. It has been found that the size of the microemulsion phase decreases significantly compared to that at room temperature.

3.3. Solubilization Parameters of Oil and Water in Microemulsion. Figure 7 shows the salinity dependence phase behavior of the SDS microemulsion system at (303 and 333) K to characterize the surfactants' solubilization capacities. For the characterization of the surfactants' solubilization capacities, the

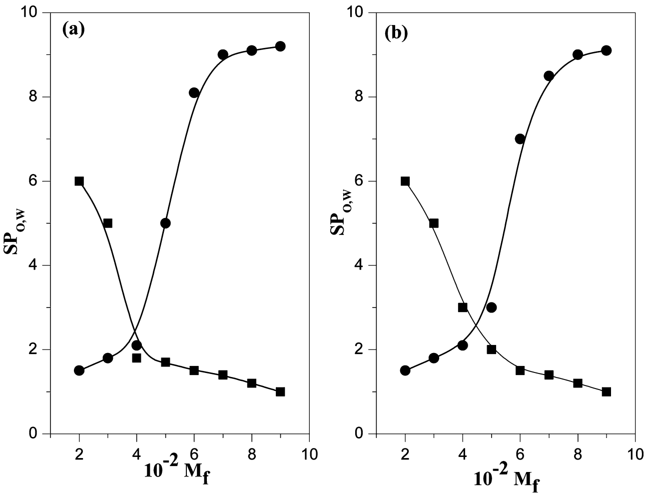

Figure 7. Solubilization parameter for oil ($\mathrm{SP_o} = V_o/V_s$) and water ($\mathrm{SP_w} = V_w/V_s$) as a function of mass fraction of NaCl (M_f) (a) at 303 K and (b) at 333 K. Symbols: ■, solubilization parameter for water ($\mathrm{SP_w}$); ●, solubilization parameter for oil ($\mathrm{SP_o}$).

solubilization parameters (or phase uptakes) are commonly used. Healy and Reed[11] first introduced the terms,

$$\mathrm{SP_i} = V_i/V_s$$

where i refers to water or oil and s refers to the surfactant. Experimental results show that the change of salinity from lower to a higher value leads to the transition of the microemulsion phase from WI to WII via WIII. During the transition, the solubilization parameter for oil ($\mathrm{SP_o}$) increases, while the water solubilization parameter ($\mathrm{SP_w}$) decreases, as shown in Figure 7. The salt concentration corresponding to the situation where both solubilization parameters for oil and water are the same is called the optimal salt concentration or optimal salinity. With an increase in temperature, the optimal salinity increases for the present study as shown in Figure 7, but the solubilization parameter remains more or less constant. In case of the SDS system, the solubilization parameters at optimal salinity are less sensitive to temperature, and with an increase in temperature only a little increase in solubilization parameter at optimal salinity has been observed. The point of optimal salinity has immense importance because several physical properties (e.g., solubilization parameters, IFT, etc.) attain either a maximum or minimum at or near this point.[26]

3.4. Influence of Temperature on Optimal Salinity. Temperature has a significant influence on the optimal salinity of SDS microemulsion systems. The effect of temperature on optimal salinity has been shown in Figure 8. It may be seen from the figure that optimal salinity increases with an increase in temperature. The results are in good agreement with other reported works.[20,25,26] The effect of temperature on optimal salinity may be because of reduced overall component concentration (NaCl salt, cosurfactant, surfactant) and weaker hydrogen bonding and a reduced hydrophobic effect at higher temperatures.[40]

3.5. Effect of Salinity on IFT and Electrical Conductivity of Microemulsion. The behaviors of microemulsions have been characterized by measurements of its IFT of microemulsion–oil and microemulsion–water systems. Figure 9a represents the IFTs of excess oil–microemulsion (O/ME) and excess water–microemulsion (W/ME) systems. With an increase in salinity the IFT between excess oil and microemulsion phase decreases, while that in the water and microemulsion phase increases. Whenever the middle phase microemulsion is present, both values of IFT are low. The curves for both of the measurements were found to intersect usually at low values of IFT, and the salinity corresponding to this point is termed as the optimal salinity for the surfactant system. The values of optimal salinity obtained from the IFT measurements are well-supported by a phase behavior study.

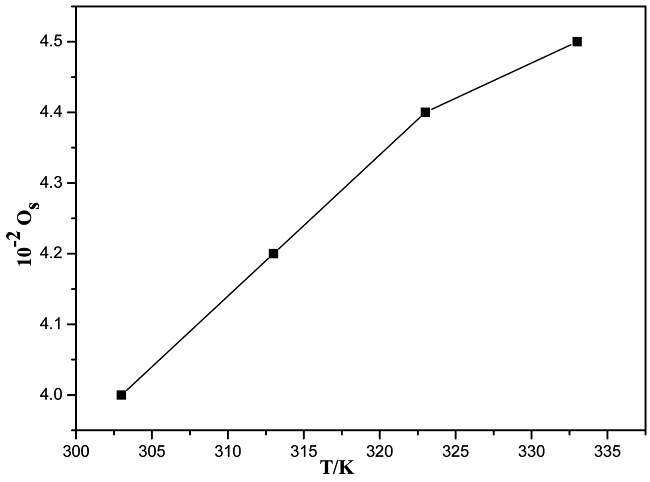

Figure 8. Optimal salinity (O_s) as a function of temperature (T/K) for a NaCl salt and SDS microemulsion system.

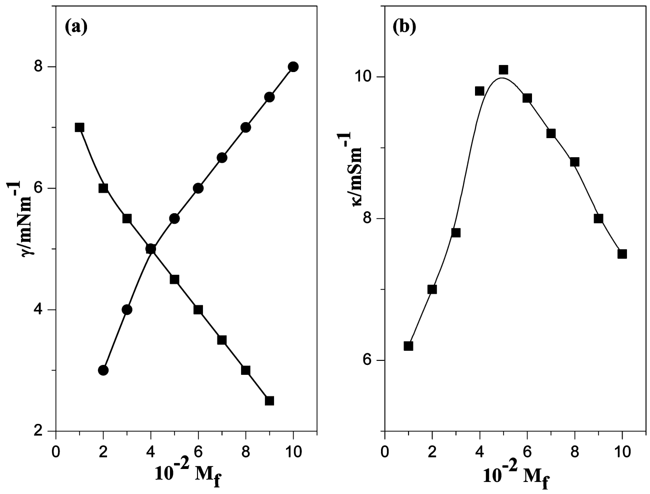

Figure 9. (a) IFTs (γ/mN·m^{-1}) of excess brine–microemulsion and excess oil–microemulsion for the SDS microemulsion system as a function of NaCl mass fraction (M_f). Symbols: ■, excess oil–microemulsion; ●, excess brine–microemulsion. (b) Electrical conductivity (κ/mS·m^{-1}) in the (SDS + heptane + propan-1-ol + brine) system as a function of NaCl mass fraction (M_f) at 302 K.

The electrical conductivity of middle phase microemulsion shows an interesting result with the variation of salinity. Initially the electrical conductivity increases with an increase in salinity up to a certain salinity and then decreases with increasing salinity after passing through maxima as shown in Figure 9b. The observed effects may be described by phase inversion phenomena. The microstructure and salinity have different effects on the conductivity of the microemulsion. At low salinity, the water-rich microemulsions remain in equilibrium with the excess oil. Under this condition, the salts remain fully solubilized in the continuous water phase of microemulsion with a linear relationship between conductivity and salinity. With increases in salinity, the water solubilization in microemulsion decreases, and oil solubilization increases; this leads to a decrease in conductivity of the microemulsion. On the other hand, an increase in the concentration of salt tends to increase the conductivity. The latter effect dominates over the first at a lower concentration range, and reverse behavior was observed at a higher concentration range. Thus, the conductivity versus salinity curve passes through maxima. Surprisingly it has been found that the salinity corresponding to maximum conductivity is very much close to the optimal salinity obtained in phase behavior and IFT studies.

4. CONCLUSIONS

Phase behavior and physicochemical properties of microemulsions comprised of (SDS + brine + propan-1-ol + heptane) and its structural changes with the salinity, temperature, and (surfactant + cosurfactant) concentration have been investigated for the application of microemulsion in EOR. Salinity and temperature play important roles on the RPV and solubilization parameters in microemulsions. Pseudoternary phase diagrams show that with an increase in salinity the single-phase microemulsion region decreases. Similar trends have also been reported by other authors[29,41] for different surfactants. The properties of microemulsions change significantly due to phase inversion as salinity changes.[17,36,42] The results of the present study show that, as salinity changes from low to high, a phase transition takes place from Winsor I to Winsor II via Winsor III. With increasing salinity, the IFT between oil and microemulsion decreases, whereas that of the water and microemulsion increases. It is interesting to note that a microemulsion prepared at optimal salinity shows its highest stability. With an increase in temperature, the volume of middle phase microemulsion decreases, but the rate of decrease is a strong function of salinity and prominent at high salinity. At optimal salinity, the IFT between microemulsion and oil is at a minimum, and solubilizations of oil and water are the same in the microemulsion phase. The optimal salinity increases with an increase in temperature due to weaker hydrogen bonding and a reduced hydrophobic effect. The electrical conductivity of the middle-phase microemulsion system shows maxima around optimum salinity; then it reduces because of phase inversion.

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Notes

The authors declare no competing financial interest.

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