# JOURNAL OF CHEMICAL & ENGINEERING DATA

# Water Solubilization Capacity and Conductance Behaviors of Anionic and Cationic Microemulsion Systems

Achinta Bera, Ajay Mandal,\* Keka Ojha, and T. Kumar

Department of Petroleum Engineering, Indian School of Mines, Dhanbad-826004, India

**ABSTRACT:** One of the most important tools in enhanced oil recovery (EOR) is microemulsion flooding to recover residual oil trapped in the reservoir after water flooding. The solubilization and phase equilibria of oil—water microemulsion have been studied with special attention on the role of alkane carbon number (ACN) of hydrocarbon, surfactant, and cosurfactant concentration on the formation of microemulsion. The ability of anionic and cationic microemulsion systems to solubilize alcohol has been investigated for different hydrocarbons. The effect of additives (NaCl salt with different concentrations) on electrical conductivity was studied by dropwise addition of brine in different concentrations to justify percolation of the microemulsion systems. The temperature effect on conductivity of microemulsions was also studied. Different aliphatic hydrocarbons ( $C_6$  to  $C_{12}$ ) and aromatic hydrocarbons such as benzene and toluene were used as synthetic oils. For the preparation of microemulsions, propan-2-ol and 3-methyl-1-butanol were selected as cosurfactants. The dependence of concentrations of the cosurfactant and surfactant on the boundary phase separation was also investigated.

# INTRODUCTION

Microemulsion in enhanced oil recovery (EOR) is an efficient tool because of its high level of extraction efficiency.<sup>1</sup> The formation and stability of a microemulsion are driven by a very low water—oil interfacial tension to compensate for the large increase in the dispersion entropy.<sup>2</sup> In this process, a microemulsion containing surfactant, alcohol, oil, and brine is used as injection fluid. The interfacial tension between the microemulsion and the reservoir oil or brine is as low as  $10^{-3}$  mN·m<sup>-1</sup> or less, which increases the displacement efficiency.<sup>3</sup> Under suitable conditions, a microemulsion slug is miscible with both oil and brine.<sup>4</sup> However, depending on the salinity, the microemulsion slug may partitions into three phases, namely, a surfactant rich middle phase microemulsion, surfactant lean brine, and oil phase.<sup>5,6</sup> Complete studies on phase behavior, interfacial tension, rheological properties, and solubilization are the primary determinants of the potential success of a microemulsion flooding for EOR.

In the past several years, it has been shown that the phase behavior of a surfactant-oil-brine/water system is of immense importance in the interpretation and forecasting the scopes of applications in the field of EOR<sup>7</sup> Microemulsion flooding has been gaining its importance in the various projects on EOR because of the ability of microemulsion to solubilize oil and water simultaneously which in turn reduces the interfacial tensions between oil and water significantly.<sup>8</sup> In this connection, the phase behavior of oil-water-surfactant-cosurfactant systems plays an important role in the subject of intensive studies.<sup>9–12</sup> At present, it is common that the formulation of surfactant-brine-oil systems that exhibit desirable phase behavior is an important stage in optimizing performance of microemulsion systems for EOR<sup>13,14</sup> Microemulsions are transparent and translucent homogeneous mixtures of hydrocarbons and water with large amounts of surfactants.<sup>15,16</sup> Alkanols (medium chain alcohols) are generally used as cosurfactants for the preparation of microemulsions. The solubility of alkanols in water depends on the alcohol chain length.

Short chain alcohols such as methanol, ethanol, and propanol are able to undergo miscibility process with water. On the other hand, long chain alcohols (from butanol) show a lower solubility in water. Microemulsions actually contain a cosurfactant such as a medium chain alcohol (viz., propan-2-ol, butanol, 3-methyl-1butanol, etc.) in combination with a primary surfactant.<sup>17,18</sup> The water solubilization capacity of microemulsions decreases with increasing chain length of the alkane, and it decreases with the increase of temperature. The water solubilization capacity and phase equilibria of microemulsion systems are determined by two phenomenological parameters such as the spontaneous curvature and the elasticity of the interfacial film.<sup>19</sup> The addition of electrolytes can enhance the water solubilization capacity of microemulsions, and the solubilization limit reaches to a maximum by changing the electrolytes.<sup>20,21</sup> The measurement of electrical conductivity of ionic microemulsions has become a standard technique for percolation study.<sup>22-24</sup> In ionic microemulsions the formation of a system-spanning (or "infinite") cluster can be noticed by a sharp increase of the conductivity. The increase in conductivity of the microemulsion system is due to "Stoke Process" in which the hopping of charged surfactants from one droplet of cluster to another takes place.<sup>25</sup> When middlephase microemulsions equilibrate with excess water and oil phase, then the maximum solubilization power of mixed surfactant is obtained.<sup>7,26,27</sup> In the case of middle-phase microemulsions (three-phase system), ultralow interfacial tensions are attained, and microemulsions are changed from Winsor type I to Winsor type II through Winsor type III phase behavior.<sup>7,28</sup> In general the middle-phase microemulsion system has a bicontinuous structure

Special Issue: Kenneth N. Marsh Festschrift

Received:	March 25, 2011
Accepted:	April 22, 2011
Published:	May 10, 2011

made by an equal mixture of water-in-oil and oil-in-water type microemulsions.<sup>15,16</sup> Glover et al.<sup>29</sup> demonstrated that the distorted phase boundaries are formed with the variation of alcohol concentration when the concentration of total surfactant is varied and because of the direction that the phase boundaries twist or deform is totally controlled by the nature of the alcohol used.

In the present study, experiments have been carried out to verify and illustrate the proposed theory of chain length compatibility of oil and interfacial film phenomena. The solubilization behavior is discussed in terms of partitioning of alcohol among oil, water, and the interface depending upon the nature of alcohol and chain length of hydrocarbon, as well as in terms of molecular packing at the interface in relation to the disorder produced by the chain length compatibility effects. The ability of anionic and cationic microemulsion systems to solubilize alcohol was investigated for different hydrocarbons. The influence of the hydrocarbon chain length on the molecular structure of the water-oil microemulsions was also discussed. Moreover, the solubilization of water in microemulsions was studied in detail as a function of alkane carbon number (ACN) of hydrocarbon as well as cosurfactants. The effect of alcohol concentration and nature of alcohol on the phase boundaries has been studied. Besides, the effect of salinity in the formation of microemulsions was also discussed. Along with these, the effect of salt concentration on electrical conductivity was studied by dropwise addition of brine in different concentrations to justify percolation of the microemulsion systems. The temperature effect on conductivity of microemulsions was also studied.

## EXPERIMENTAL SECTION

Materials. Sodium dodecyl sulfate (SDS) (0.96 mole fraction) procured from Fisher Scientific, India and cetyl trimethylammonium bromide (CTAB) of mole fraction purity 0.98 procured from Merck, India were used as anionic and cationic surfactants in the present study. Different alkanes and aromatic compounds were used as synthetic oils. Two lower alkanes, namely, hexane (0.98 mole fraction) and heptane (0.98 mole fraction), were purchased from Loba Chemie Pvt. Ltd., India. Other alkanes such as octane, decane, and dodecane with a mole fraction purity 0.99 each were analytical reagent grade products of Otto-Kemi Pvt. Ltd., India. The aromatic compounds benzene and toluene (0.98 mole fraction) were purchased from Nice Chemical Pvt. Ltd., India. 3-Methyl-1-butanol and propan-2-ol with 0.98 mole fraction each (CDH Pvt. Ltd., India) were used as the cosurfactant. Sodium chloride (NaCl) (0.98 mole fraction), procured from Qualigens Fine Chemicals, India, was used for brine. Reverse osmosis water from Millipore water system (Millipore SA, 67120 Molshein, France) was used for the preparation of solutions.

**Methods.** Conductivity Measurements. For the preparation of microemulsions, oil  $(5 \cdot 10^{-3} \text{ kg} \text{ heptane})$  was added in the mixture SDS  $(0.5 \cdot 10^{-3} \text{ kg})$  and propan-2-ol  $(2 \cdot 10^{-3} \text{ kg})$ , followed by the addition of brine with different concentrations at 298 K until just turbid or phase separation takes place. The conductivity of microemulsion was measured by using a digital conductometer (Biocraft Scientific Systems (P) Ltd.; model no. CEI-13). In all cases measurements were made after homogeneous mixing by magnetic stirrer. The conductivity of the selected microemulsions was measured as a function of weight fraction of water. The error limit of conductance measurements was  $\pm 1$  %.

Measurement of Alcohol Solubilization Capacity. Typical microemulsions were made by mixing  $0.8 \cdot 10^{-3}$  kg surfactant (SDS or CTAB separately), desired amount of alcohol (3-methyl-1-butanol), oil (different hydrocarbons), and water. The mixture obtained was clear and transparent. After reaching equilibrium (room temperature, 298 K), alcohol solubilization capacity was measured by further addition of alcohol until a turbid, cloudy solution results.

Measurement of Water Solubilization Capacity. The solubilization of water in the microemulsion region was determined by a conventional titration method of microemulsion with brine or water under satisfied conditions until the opaqueness of the microemulsions was obtained. Here the opaqueness is especially defined as the turbid, densed milky appearance of that system through which nothing can be seen. For different cases a different colored translucent mixture was not considered the required opaqueness of the system. However, the end point of the titration was considered the actual transition point of the clear, transparent, and isotropic microemulsions to a birefringent phase where the boundary was determined as the onset of the cloudiness due to a lack of a strong turbidity. For the determination of the effect of surfactant concentration on the solubilization of water in microemulsion, a different amount of surfactant was added in the microemulsion systems and then titrated with water until the turbidity appeared. In all cases, more than three successive measurements were carried out, and the standard deviation did not exceed  $\pm 0.1 \cdot 10^{-3}$  kg. All of the experiments were performed at 298 K.

*Phase Behavior.* During the water solubilization study, the phase behavior of the system SDS/propan-2-ol/hydrocarbons/ water or brine was investigated as function of ACN, amount of propan-2-ol, and salinity. For the determination of phase boundaries, a mixture of SDS/hydrocarbons/propan-2-ol system was titrated with water and brine for different studies. Phase behavior of different systems were drawn by visual observation of phase changes and corresponding readings.

#### RESULTS AND DISCUSSION

Conductivity Behavior of Microemulsion Systems. The structure of oil-water microemulsion can be characterized by conductivity measurements (Liu et al., 1998). The conductivity of a microemulsion is a strong function of its water content, salt concentration, molar ratio of water to surfactant (W), and temperature. Figure 1 shows the variation of conductivity as a function of W for different systems with varying NaCl concentration. The conductivity behavior of surfactant-rich microemulsion is due to the presence of Na<sup>+</sup> ions released from SDS. In all cases, conductivity increases with an increase in molar ratio of water to surfactant. The rate of increase is vary fast up to a certain values of W and then varies asymtodically on further increase of W with constant SDS in the solution. This is due to the fact that when water content increases there would exist a more open structure, which could cause less hindrance to the mobility of the Na<sup>+</sup> ions. At higher W when practically there is no hindrance the conductivity remains almost constant. NaCl is a strong electrolyte, which can contribute conductivity in its aqueous solution. It may also be found from the figure that conductivity increases with an increase in concentration of NaCl in the microemulsion as expected. The conductance changes due to interdroplet interaction leading to the transfer of the charge carriers from one droplet to another. However, it has been found that the



**Figure 1.** Dependence of conductivity (*k*/S ⋅ m<sup>-1</sup>) on the molar ratio of water to surfactant (*W*) in microemulsion systems containing  $5 \cdot 10^{-3}$  kg of heptane,  $0.5 \cdot 10^{-3}$  kg of SDS, and  $2 \cdot 10^{-3}$  kg of propan-2-ol. Symbols: **■**, 0.0 mass fraction of NaCl; **●**, 0.005 mass fraction of NaCl; **●**, 0.01 mass fraction of NaCl; **●**, 0.015 mass fraction of NaCl; **●**, 0.02 mass fraction of NaCl; left-pointing triangle, 0.025 mass fraction of NaCl; right-pointing triangle, 0.03 mass fraction of NaCl.



**Figure 2.** Effect of temperature (T/K) on conductivity  $(k/S \cdot m^{-1})$  of microemulsion systems containing  $5 \cdot 10^{-3}$  kg of heptane,  $0.5 \cdot 10^{-3}$  kg of SDS, and  $2 \cdot 10^{-3}$  kg of propan-2-ol. Symbols: ■, 0.0 mass fraction of NaCl; ●, 0.005 mass fraction of NaCl; ▲, 0.01 mass fraction of NaCl; ▼, 0.015 mass fraction of NaCl; ◆, 0.02 mass fraction of NaCl; left-pointing triangle, 0.025 mass fraction of NaCl; right-pointing triangle, 0.03 mass fraction of NaCl.

relative changes in conductivity gradually decreases with increase in NaCl concentration. This phenomenon is due to the fact that NaCl diminishes the effective polar area of SDS and decreases the attraction between the droplets, which leads to the very small increase in conductance of the systems.<sup>30–32</sup>

Effect of Temperature on Conductivity of Microemulsion Systems. The influence of temperature on the conductivity of microemulsion systems at different salinity is plotted in Figure 2. The conductivity of water/oil microemulsions was found to

Table 1. Activation Energy  $(E/kJ \cdot mol^{-1})$  and Correction Factor (*r*) Determined from the Arrhenius Type Equation (eq 4) by Plotting ln *k* vs 1/T for the SDS Microemulsion Systems at Different Mass Fractions of NaCl ( $M_f$ )

$M_{ m f}$	$E/kJ \cdot mol^{-1}$	r
0.0	13.172	0.987
0.005	13.689	0.986
0.01	14.182	0.998
0.015	15.427	0.998
0.02	14.825	0.999
0.025	13.668	0.996
0.03	11.821	0.997

increase with the increase in temperature of the system. The interaction of microemulsion droplets during the percolation<sup>33–36</sup> process is sometimes very specifically described by the "transient fusion-mass transfer-fission" process.<sup>37–39</sup> During the percolation process Na<sup>+</sup> ions transfer through the interfacial membrane. The activation energy associated with this process may be the sum of energies required for the mass transfer of Na<sup>+</sup> ions and that required for separating the droplets in the "transient fusion-mass transfer-fission" process. Its value can be estimated by using Einstein's law and self-diffusion coefficient, we get the following relationships:

$$k = ne\mu = ne^2 D/k_{\rm B}T \tag{1}$$

$$D = 4l^2 k_{\rm B} T / h \exp(-E/RT)$$
<sup>(2)</sup>

where k is the conductivity  $(S \cdot m^{-1})$ ; n is the number of the charge carriers per unit volume  $(m^{-3})$ ; e is the elementary charge or electronic charge (C);  $\mu$  is the mobility  $(m^2 \cdot V^{-1} \cdot s^{-1})$ ; D is the self-diffusion coefficient  $(m^2 \cdot s^{-1})$ ; l is the thickness of the surfactant monolayer (m); T is the temperature (K);  $k_B$  is the Boltzmann constant  $(J \cdot K^{-1})$ ; E is the activation energy  $(J \cdot mol^{-1})$ ; R is the gas constant  $(J \cdot K^{-1} \cdot mol^{-1})$ ; and h is the Planck's constant  $(J \cdot s)$ . The combination of eqs 1 and 2 yields

$$k = 4ne^2l^2/h\exp(-E/RT)$$
(3)

$$k = A \exp(-E/RT) \tag{4}$$

where  $A = 4ne^2 l^2/h$ . Equation 4 seems to be the Arrhenius equation. Now eq 4 can be written as:

$$\ln k = \ln A - E/RT \tag{5}$$

The activation energies can be estimated by plotting  $\ln k \text{ vs } 1/T$  and are listed in Table 1.

From Table 1 it is observed that the estimated activation energies of the systems do not follow any general trends. This can be described on the basis of optimum salinity. The optimum salinity decreases with increasing temperature, due to lower hydrophilicity of surfactant system, until an equilibrium value is reached.<sup>41</sup> It is very common that at optimum salinity an equal volume of oil and water undergo solubilization. So solubilization of both oil and water does not take place at higher salinity equally. That is why activation energy is high at a particular salinity; rather, it does not obey the increasing salinity trend.

**Alcohol Solubilization.** The presence of alcohol and surfactant at the interface influence the solubilization behavior of



**Figure 3.** Plot of wt ratio of cosurfactant (3-methyl-1-butanol) to surfactant  $(W_{cs}/W_s)$  vs wt ratio of oil to surfactant  $(W_o/W_s)$  for SDS microemulsion systems. Symbols:  $\blacksquare$ , hexane;  $\bullet$ , heptane;  $\blacktriangle$ , decane;  $\checkmark$ , dodecane.



**Figure 4.** Plot of wt. ratio of cosurfactant (3-methyl-1-butanol) to surfactant  $(W_{cs}/W_s)$  vs wt ratio of oil to surfactant  $(W_o/W_s)$  for CTAB microemulsion systems. Symbols:  $\blacksquare$ , hexane;  $\bullet$ , heptane;  $\blacktriangle$ , decane;  $\blacktriangledown$ , dodecane.

microemulsions significantly. The higher the amount of surfactant and alcohol at the interface, the higher the solubilization capacity of microemulsion.<sup>42</sup> The solubilization of alcohol (3methyl-1-butanol) was studied by the titration method for different hydrocarbon—water—SDS and hydrocarbon—water— CTAB systems separately. The weight ratio of alcohol (cosurfactant) to surfactant and oil to surfactant for the formation of microemulsion have been plotted in Figures 3 and 4 for two different surfactants, respectively. The data for a particular system are fitted in a straight line. The slope of the line represents the number of mole of alcohol per mole of oil in the continuous phase. The amount of alcohol required for the formation of microemulsion increases with the increase in chain length of

Table 2. Values of Slopes (for SDS,  $m_s$  and for CTAB,  $m_c$ ), Intercepts (for SDS,  $c_s$  and for CTAB,  $c_c$ ), and Correction Factors (for SDS,  $r_s$  and for CTAB,  $r_c$ ) in Microemulsion Systems with Different Hydrocarbons (HC) (Hexane, C<sub>6</sub>; Heptane, C<sub>7</sub>; Decane, C<sub>10</sub>; Dodecane, C<sub>12</sub>)

HC	ms	c <sub>s</sub>	r <sub>s</sub>	$m_{\rm c}$	$c_{\rm c}$	r <sub>c</sub>
C <sub>6</sub>	0.378	5.632	0.997	0.203	2.143	0.997
C <sub>7</sub>	0.445	5.812	0.999	0.232	2.327	0.984
C <sub>10</sub>	0.462	5.969	0.997	0.263	2.497	0.998
C <sub>12</sub>	0.464	6.199	0.996	0.326	2.530	0.985



**Figure 5.** Solubilization of the amount of water  $(W_w/\text{kg})$  as a function of ACN of oil in the microemulsion. Symbols:  $\blacksquare$ , containing  $5 \cdot 10^{-3}$  kg of oil,  $0.7 \cdot 10^{-3}$  kg of SDS, and  $4 \cdot 10^{-3}$  kg of propan-2-ol;  $\clubsuit$ , containing  $5 \cdot 10^{-3}$  kg of oil,  $0.7 \cdot 10^{-3}$  kg of SDS, and  $2 \cdot 10^{-3}$  kg of propan-2-ol.

hydrocarbons. On the other hand, the intercept which represents the molar ratio of alcohol to surfactant at the interface<sup>43</sup> increased as the oil chain length increased. The values of slope (m) and intercept (c) were calculated and shown in Table 2. The values of slope and intercept for SDS-based microemulsion system are higher than those of CTAB because of higher hydrophobicity of CTAB with higher chain length.

Water Solubilization and Phase Behavior Study. Effect of Alkane Carbon Number (ACN) of Oil. The solubilization of water in oil-water microemulsions depends upon oil chain length or ACN of oil. The effects of ACN on the water solubilization in SDS-based microemulsion systems have been shown for two different systems with different alcohol concentrations in Figure 5. When  $4 \cdot 10^{-3}$  kg of alcohol was used as cosurfactant, the amount of water solubilized in the microemulsions increases with increasing ACN of oils up to octane and then decreases upon further increasing the oil chain length. But when  $2 \cdot 10^{-3}$  kg of alcohol was used as the cosurfactant, water solubilization increased up to decane and then decreased for higher chain alkanes. Similar variations were also observed in other studies with different surfactants and cosurfactants.<sup>42,44</sup> Thus, the phase separation of microemulsions has been found to be a strong function of oil chain length. Birefringent liquid crystalline phases<sup>44</sup> were observed in both cases of different alcohol concentration. In case of higher alcohol concentration, the birefringent phase "b" was observed for



**Figure 6.** Solubilization of an amount of water  $(W_w/kg)$  as a function of propan-2-ol concentration  $(W_{cs}/W_s)$  in the microemulsion consisting of  $0.8 \cdot 10^{-3}$  kg. SDS,  $8 \cdot 10^{-3}$  kg oil (hexane, heptane, octane, and dodecane separately) and propan-2-ol. Symbols:  $\blacksquare$ , hexane;  $\blacklozenge$ , heptane;  $\bigstar$ , octane;  $\blacktriangledown$ , dodecane.

oils with chain length up to octane. Beyond the C<sub>8</sub> hydrocarbon, the Winsor type-II phase was obtained and designated as "eo" in the figure, whereas in case of lower alcohol concentration, the birefringent liquid crystalline phases were observed up to dodecane. The decrease in water solubilization in microemulsions with increasing ACN of oil after a critical chain length of hydrocarbon is due to the enhanced interdroplet attraction.<sup>45–47</sup> Water solubilization in microemulsions regarding the chain length compatibility can be considered a result of counterbalanced effects of interdroplet interactions.<sup>48</sup>

Effect of Cosurfactant Concentration. Cosurfactants play a significant role on solubilization of water in microemulsions by promoting the interfacial fluidity. The water solubilization as a function of propan-2-ol concentration for two different systems have been shown in Figure 6 and 7, respectively. The solubilization curves pass through a maxima for all hydrocarbons, though the maxima is more prominent for octane and dodecane due to the chain length compatibility effect.<sup>42</sup> For aliphatic hydrocarbons, the solubilization of water increases with increasing alcohol concentration up to a certain limit showing the birefringent phase "b". This is due to increased concentration of alcohol, which can increase the alcohol partitioning at the interface that leads to the enhanced interfacial area for the solubilization of water. At sufficiently high concentrations, the fluidity of the interface increases<sup>49,50</sup> to the extent that attractive interdroplet interaction starts dominating the system, and hence the solubilization of water decreases. For high concentrations of alcohol, a gel-like state of microemulsion "g" was observed for aliphatic hydrocarbons. From Figure 7, it is clear that aromatic hydrocarbons (benzene and toluene) do not exhibit birefringent phase at any concentration of alcohol; rather, the end point shows a gel-like state of microemulsion "g" as shown in the figure. This probably due to the fact that aromatic hydrocarbon has an electron cloud around the nucleus, and hence the alcohol does not penetrate into the interfacial film effectively. Water-oil microemulsions consisting of aromatic hydrocarbons generally show less tendency of water solubilization than that of aliphatic hydrocarbons.<sup>51–53</sup> It has also been found that water solubilization



**Figure 7.** Solubilization of amount of water  $(W_w/\text{kg})$  as a function of propan-2-ol concentration  $(W_{cs}/W_s)$  in the microemulsion. Symbols:  $\blacksquare$ , consisting of  $0.2 \cdot 10^{-3}$  of kg SDS,  $8 \cdot 10^{-3}$  kg of benzene and propan-2-ol;  $\bullet$ , consisting of  $0.2 \cdot 10^{-3}$  kg of SDS,  $8 \cdot 10^{-3}$  kg of toluene and propan-2-ol.

for both the systems pass through a maxima around  $W_{cs}/W_s$  equals 40. The maximum water solubilization for benzene is greater than toluene. It was early stated that the water solubilization of nonpolar alkanes microemulsion is larger than polar aromatic hydrocarbon. Since benzene is considered to be nonpolar (dipole moment = 0 Cm) and toluene is polar (dipole moment = 0.4 Cm), then maximum water solubilization for benzene is higher than toluene at any concentration of cosurfactant.

Effect of Surfactant Concentration on Solubilization of Water. The dependency of water solubilization in microemulsion on surfactant concentration has been shown in Figure 8 for two different weight percentages of cosurfactant in the system. From the figure it has been found that solubilization of water in microemulsion steadily increases with increase in concentration of surfactant. Water solubilization is also enhanced with higher cosurfactant concentration because of increasing interfacial fluidity. The plots can provide the information about solubilization efficiency from the slope and the amount of surfactant not partitioning at the interface from the intercept on the surfactant concentration axis.<sup>54–56</sup>

Effect of Salinity on Solubilization of Water in Water-Oil Microemulsion. Water solubilization in microemulsions also depends on salinity of the system. Typical plots of water solubilization as a function of NaCl mass fraction in the microemulsions consisting heptane and SDS along with propan-2-ol and 3-methyl-1-butanol are shown in Figure 9. In case of propan-2-ol maximum brine solubilization was observed at NaCl mass fraction of 0.015, whereas for the 3-methyl-1-butanol it was 0.01. These salinities are generally referred as "optimal salinity" for microemulsion systems.<sup>57</sup> So optimal salinity for microemulsion systems containing alcohol increases as alcohol chain length decreases. At optimum salinity the middle-phase microemulsion has the ability to solubilize equal amounts of oil and brine.5,58 After optimum salinity the water solubilization decreases with the increase in concentration of brine. As salinity increases, the microemulsion phase changes from Winsor type-I (designated as "eo") to Winsor type-II (designated as "ew"). These phenomena can be illustrated on the basis of attractive



**Figure 8.** Solubilization of amount of water  $(W_w/\text{kg})$  as a function of amount of SDS  $(W_s/\text{kg})$  concentration  $(W_s)$  in the microemulsions containing of  $5 \cdot 10^{-3}$  kg of heptane and different amount of propan-2-ol and SDS. Symbols:  $\bullet$ ,  $2 \cdot 10^{-3}$  kg of propan-2-ol;  $\blacktriangle$ ,  $4 \cdot 10^{-3}$  kg of propan-2-ol.

![](_page_5_Figure_4.jpeg)

**Figure 9.** Brine solubilization  $(W_b/\text{kg})$  as a function of NaCl mass fraction  $(M_f)$  in the microemulsions. Symbols: **I**, containing of  $5 \cdot 10^{-3}$  kg of heptane,  $0.5 \cdot 10^{-3}$  kg of SDS, and  $2 \cdot 10^{-3}$  kg of propan-2-ol; **•**, containing of  $5 \cdot 10^{-3}$  kg of heptane,  $0.5 \cdot 10^{-3}$  kg of SDS, and  $2 \cdot 10^{-3}$  kg of 3-methyl-1-butanol.

interdroplet interaction and interfacial bending stress. The decreasing solubilization of brine with increasing salinity caused by an increase in interfacial rigidity. At the low salinity region alcohol can partition at the interface so the solubilization of brine was large.

### CONCLUSIONS

The structure of oil—water microemulsion has been characterized by conductivity measurements. The conductivity of a microemulsion was found to be a strong function of its water content, salt concentration, molar ratio of water to surfactant, and temperature. The presence of alcohol and surfactant at the interface influence the solubilization behavior of microemulsions. The amount of alcohol required for formation of microemulsion increases with an increase in chain length of hydrocarbons. Water solubilization in microemulsion depends upon oil chain length. The phase behavior studies show that a birefringent liquid crystalline phase boundary up to a certain chain length of hydrocarbon which subsequently forms a Winsor type-II phase for a higher hydrocarbon chain. The presence of alcohol as cosurfactant plays a significant role on water solubilization in microemulsion for aliphatic and aromatic hydrocarbons. With the increase in alcohol concentration the phase boundary passes through birefringent phase to a gel-like microemulsion for aliphatic hydrocarbons. Surprisingly the aromatic hydrocarbon shows only a phase boundary for gel-like microemulsion without any birefringent phase. The solubilization of water in microemulsion was found to increase steadily with the increase in concentration of surfactant. The water solubilization shows a maxima at a particular salinity known as "optimum salinity". At optimal salinity the middle-phase microemulsion has the ability to solubilize equal amounts of oil and brine.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: mandal ajay@hotmail.com.

#### Funding Sources

The authors gratefully acknowledge for the financial assistance provided by University Grant Commission [F. No. 37-203/2009 (SR)] to Department of Petroleum Engineering, Indian School of Mines, Dhanbad, India.

#### ACKNOWLEDGMENT

We are grateful to all individuals associated with the project.

#### REFERENCES

(1) Santanna, V. C.; Curbelo, F. D. S.; Castro Dantas, T. N.; Dantas Neto, A. A.; Albuquerque, H. S.; Garnica, A. I. C. Microemulsion flooding for enhanced oil recovery. *J. Pet. Sci. Eng.* **2009**, *66*, 117–120.

(2) Bumajdad, A.; Eastoe, J. Conductivity of mixed surfactant waterin-oil microemulsions. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1597–1602.

(3) Kowk, W.; Hayes, R. E.; Nasr-El-Din, H. A. Modelling Dynamic Adsorption of an anionic Surfactant on Berea Sandstone with Radial Flow. *Chem. Eng. Sci.* **1995**, *50*, 769–783.

(4) Hsieh, W. C.; Shah, D. O. The Effect of Chain Length of Oil and Alcohol As Well as Surfactant to Alcohol Ratio on the Solubilization, Phase Behavior and Interfacial Tension of Oil/Brine/Surfactant/Alcohol Systems . *Soc. Per. Eng. AIME* **1976**, paper 6594.

(5) Healy, R. N.; Read, R. L.; Stenmark, D. G. Multiphase Microemulsion System. Soc. Per. Eng. J. 1976, 261, 147–160.

(6) Reed, R. L.; Healy, R. N. In Improved Oil Recovery by Surfactants and Polymer Flooding; Shah, D. O., Schechter, R. S., Eds.; Academic Press, Inc.: New York, 1977; pp 383–437.

(7) Shah, D. O.; Schechter, R. S. Improved Oil Recovery by Surfactant and Polymer Flooding; Academic Press: New York, 1977.

(8) Bellocq, A. M.; Biais, J.; Clin, B.; Gelot, A.; Lalanne, P.; Lemanceau, B. Three Dimensional Phase Diagram of the Brine-Toluene-Butanol-Sodium Dodecyl Sulfate System. *J. Colloid Interface Sci.* **1980**, 74, 311–321.

(9) Bellocq, A. M.; Biais, J.; Bothorel, P.; Clin, B.; Fourche, G.; Lalanne, P.; Lemaire, B.; Lemanceau, B.; Roux, D. Microemulsions. *Adv. Colloid Interface Sci.* **1984**, 20, 167–278.

(10) Xu, J.; Li, G.; Zhang, Z.; Zhou, G.; Ji, K. A study of the microstructure of CTAB/1-butanol/octane/water system by PGSE-NMR, conductivity and cryo-TEM. *Colloids Surf*, A **2001**, *191*, 269–278.

(11) Kegel, W. K.; Lekkerkerker, H. N. W. Phase behaviour of an ionic microemulsion system as a function of the cosurfactant chain length. *Colloids Surf.*, A **1993**, *76*, 241–248.

(12) Biais, J.; Bothorel, P.; Clin, B.; Lalanne, R. Theoretical behavior of microemulsions: geometrical aspects and dilution properties. *J. Colloid Interface Sci.* **1981**, *80*, 136–145.

(13) Healy, R. N.; Reed, R. L. Physicochemical Aspects of Microemulsion Flooding. *Soc. Pet. Eng. J.* **1974**, No. Oct., 491–501.

(14) Healy, R. N.; Reed, R. L.; Carpenter, C. W. A Laboratory Study of Microemulsion Flooding. *Soc. Pet. Eng. J.* **1975**, *259*, 87–100.

(15) Schulman, J. H.; Stoeckenius, W.; Prince, L. M. Mechanism of Formation and Structure of Micro Emulsions by Electron Microscopy. *J. Phys. Chem.* **1959**, *63*, 1677–1680.

(16) Stoeckenius, W.; Schulman, J. H.; Prince, L. M. The structure of myelin figures and microemulsions as observed with the electron microscope. *Kolloid Z.* **1960**, *169*, 170.

(17) Barakat, Y.; Fortney, L. N.; Schechter, R. S.; Wade, W. H.; Yiv, S.; Graciaa, A. Criteria for structuring surfactants to maximize solubilization of oil and water: II. Alkyl benzene sodium sulfonates. *J. Colloid Interface Sci.* **1983**, *92*, 561–574.

(18) Lalanne-Cassou, C.; Carmone, I.; Fortney, L. N.; Samii, A.; Schechter, R. S.; Wade, W. H.; Weerasoooriya, U.; Weerasoooriya, V.; Yiv, S. Minimizing Cosolvent Requirements for Microemulsion Formed With Binary Surfactant Mixtures. *J. Dispersion Sci. Technol.* **1983**, *8*, 137–156.

(19) Liu, D. J.; Ma, J. M.; Cheng, H. M.; Zhao, Z. G. Solubilization behavior of mixed reverse micelles: effect of surfactant component, electrolyte concentration and solvent. *Colloids Surf.*, A **1998**, *143*, 59–68.

(20) Kunieda, H.; Shinoda, K. Solution behavior of aerosol ot/ water/oil system. J. Colloid Interface Sci. 1979, 70, 577–583.

(21) Kunieda, H.; Shinoda, K. Solution behavior and hydrophilelipophile balance temperature in the aerosol OT-isooctane-brine system: Correlation between microemulsions and ultralow interfacial tensions. J. Colloid Interface Sci. **1980**, 75, 601–606.

(22) Lagues, M. Electrical conductivity of microemulsions: a case of stirred percolation. J. Phys. Lett. **1979**, 40, 331–333.

(23) Bhattacharya, S.; Stokes, J. P.; Kim, M. W.; Huang, J. S. Percolation in an Oil-Continuous Microemulsion. *Phys. Rev. Lett.* **1985**, *55*, 1884–1887.

(24) Clarkson, M. T.; Smedley, S. I. Electrical conductivity and permittivity measurements near the percolation transition in a microemulsion: I. Experiment. *Phys. Rev. A* **1988**, *37*, 2070–2078.

(25) Vollmer, D.; Vollmer, J.; Eicke, H.-F. Droplet Cluster vs. Bicontinuous Structures in Percolating Water-in-Oil Microemulsions. *Europhys. Lett.* **1994**, *26*, 389.

(26) Kunieda, H.; Shinoda, K. Solution Behavior and Hydrophile-Lipophile-Balance-Temperature in Ionic Surfactant/Cosurfactant/ Brine/Oil System-Estimation of Hydrophile-Lipophile-Balance of Ionic Surfactant. J. Jpn. Oil Chem. Soc (Yukagaku) **1980**, *29*, 676–682.

(27) Kunieda, H.; Shinoda, K. Phase Behavior and Tricritical Phenomena in a Bile Salt System. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 980–984.

(28) Kunieda, H. Phase behavior and ultralow interfacial tensions around a tricritical point in a sodium taurocholate system. *J. Colloid Interface Sci.* **1987**, *116*, 224–229.

(29) Glover, C. J.; Puerto, M. C.; Maeker, J. M.; Sandvik, E. L. Surfactant Phase Behavior and Retention in Porous Media. *Soc. Pet. Eng. J.* **1979**, 183–193.

(30) Ray, S.; Bisal, S. R.; Moulik, S. P. Structure and dynamics of microemulsions. I: effect of additives on percolation of conductance and energetics of clustering in water—AOT—heptanes microemulsions. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 3277–3282.

(31) García-Río, L.; Leis, J. R.; Mejuto, J. C.; Peña, M. E.; Iglesias, E. Effects of Additives on the Internal Dynamics and Properties of Water/AOT/Isooctane Microemulsions. *Langmuir* **1994**, *10*, 1676–1683.

(32) García-Río, L.; Hervés, P.; Mejuto, J. C.; Pérez-Juste, J.; Rodriguez-Dafonte, P. Effects of Alkylamines on the Percolation Phenomena in Water/AOT/Isooctane Microemulsions. *J. Colloid Interface Sci.* **2000**, 225, 259–264. (34) Hait, S. K.; Moulik, S. P.; Rodgers, M. P.; Burke, S. E.; Pulepu, R. Physicochemical Studies on Microemulsions. 7. Dynamics of Percolation and Energetics of Clustering in Water/AOT/Isooctane and Water/AOT/Decane w/o Microemulsions in Presence of Hydrotopes (Sodium Salicylate,  $\alpha$ -Naphthol,  $\beta$ -Naphthol, Resorcinol, Catechol, Hydroquinone, Pyrogallol and Urea) and Bile Salt (Sodium Cholate). *J. Phys. Chem. B* **2001**, *105*, 7145–7154.

(35) Dogra, A.; Rakshit, A. K. Phase Behavior and Percolation Studies on Microemulsion System Water/SDS + Myrj45/Cyclohexane in the Presence of Various Alcohols as Cosurfactants. *J. Phys. Chem. B* **2004**, *108*, 10053–10061.

(36) Wines, T. H.; Somasundaran, P. Effects of Adsorbed Block Copolymer and Comb-like Amphiphilic Polymers in Solution on the Electrical Percolation and Light Scattering Behavior of Reverse Microemulsions of Heptane/Water/AOT. J. Colloid Interface Sci. 2002, 256, 183–189.

(37) Zhang, X. G.; Dong, J. F.; Zhang, G. Y.; Hong, X. L.; Li, X. F. The effect of additives on the water solubilization capacity and conductivity in n-pentanol microemulsions. *J. Colloid Interface Sci.* **2005**, 285, 336–341.

(38) Paul, B. K.; Mitra, R. K. Percolation phenomenon in mixed reverse micelles: The effect of additives. *J. Colloid Interface Sci.* 2006, 295, 230–242.

(39) Fu, X.; Pan, Y.; Hu., Z. S.; Ma., Z. F. Conductivity study on the w/o microemulsion of a saponified mono(2-ethylhexyl) phosphoric acid extractant system. *Colloids Surf.*, A **1996**, *110*, 55–61.

(40) Mathew, C.; Patanjali, P. K.; Nabi, A.; Maitra, A. On the concept of percolative conduction in water-in-oil microemulsions. *Colloids Surf.* **1988**, *30*, 253–263.

(41) John, A. C.; Rakshit, A. K. Phase Behavior and Properties of a Microemulsion in the Presence of NaCl. *Langmuir* 1994, 10, 2084–2087.

(42) Bansal, V. K.; Shah, D. O.; O'Connell, J. P. Influence of alkyl chain length compatibility on microemulsion structure and solubilization. *J. Colloid Interface Sci.* **1980**, *75*, 462–475.

(43) Kumar, S.; Singh, H. N. Influence of alkyl chain branching of cosurfactant on the water solubilizating capacity of a water-in-oil microemulsion. *Colloids Surf.* **1990**, *44*, 17–27.

(44) Leung, R.; Shah, D. O. Solubilization and Phase Equilibria of Water-in Oil Microemulsions II. Effects of Alcohols, Oils, and Salinity on Single-Chain Surfactant systems. *J. Colloid Interface Sci.* **1987**, *120*, 330–344.

(45) Huang, J. S. Critical phenomena in Microemulsions. Tutorial Lecture in 189th ACS National Meeting, Division of Colloid and Surface Chemistry, Miami, FL, April 28–May 3, 1985, paper no. 81.

(46) Robinson, B. H.; Fletcher, P. D. I.; McDonald, J. A.; Galal, M. F. Neutron and Light Scattering Studies in *189th ACS National Meeting*, *Division of Colloid and Surface Chemistry*, Miami, FL, April 28–May 3, 1985.

(47) Atik, S. S.; Thomas, J. K. Transport of ions between water pools in alkanes. *Chem. Phys. Lett.* **1981**, *79*, 351–354.

(48) Friberg, S. E.; Burasczenska, I. Microemulsions in the waterpotassium oleate-benzene system. *Prog. Colloid Polym. Sci.* **1978**, *63*, 1–9.

(49) Di Meglio, J. M.; Dvolaitzky, M.; Taupin, C. Determination of the rigidity constant of the amphiphilic film in "birefringent microemulsions"; the role of the cosurfactant. *J. Phys. Chem.* **1985**, *89*, 871–878.

(50) Lufimpadio, N.; Negy, J. B.; Derouane, E. G. Surfactants in Solution; Mittal, K. L., Lindeman, B., Eds.; Plenum: New York, 1984; Vol. 3, p 1483.

(51) Magid, L. J.; Martin, C. A. In *Reverse Micelles: Biological and Technological Relevance of Amphiphilic Structures in Apolar Media*; Luisi, P. L., Straub, B. E., Eds.; Plenum: New York, 1984; p 181.

(52) Peri, J. B. The state of solution of aerosol OT in nonaqueous solvents. *J. Colloid Interface Sci.* **1969**, *29*, 6–15.

(53) Keh, E.; Valeur, B. Investigation of water-containing inverted micelles by fluorescence polarization. Determination of size and internal fluidity. *J. Colloid Interface Sci.* **1981**, *79*, 465–478.

(54) Bansal, V. K.; Chinnaswamy, K.; Ramachandran, C.; Shah, D. O. Structural aspects of microemulsions using dielectric relaxation and spin label techniques. *J. Colloid Interface Sci.* **1979**, *72*, 524–537.

(55) Pithapurwala, Y. K. Interfacial Properties of Microemulsions in Relation to Enhanced Oil Recovery Systems. Ph.D. thesis. University of Florida, Lake City, FL, 1984.

(56) Johnson, K. A.; Shah, D. O. In *Surfactant in Solution*; Mittal, K. L., Bothorel, P., Eds.; Plenum: New York, 1986; Vol. 6, p 1441.

(57) Pithapurwala, Y. K.; Shah, D. O. Interfacial Composition of Microemulsions: Modified Schulman-Bowcott Model. *Chem. Eng. Commun.* **1984**, 29, 101–112.

(58) Chan, K. S.; Shah, D. O. The Effect of Surfactant Partitioning on the Phase Behavior and Phase Inversion of the Middle Phase Microemulsions. SPE 7896-MS, presented at *SPE-AIME Internation Symposian on Oil-field and Geothermal Chemistry Meeting*, Houston, TX, 1979.