

INTERFACIAL COMPOSITION OF MICROEMULSIONS: MODIFIED SCHULMAN-BOWCOTT MODEL

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The interfacial composition of oil-external microemulsions formed with sodium stearate, pentanol, brine and various oils (octane, dodecane and hexadecane) was determined in terms of moles of alcohol per mole of surfactant present at the interface (n_a^i/n_s) using a modified three compartment Schulman-Bowcott model. The modified model takes into account the solubility of pentanol in aqueous and hydrocarbon phases. For a constant brine/surfactant ratio, it was found that the value of n_a^i/n_s was highest for dodecane containing microemulsion which corresponded to the maximum solubilization of brine in this microemulsion at optimal salinity. This behavior is explained on the basis of chain length compatibility in microemulsions. The optimal salinity for solubilization increased with the chainlength of oil.

KEYWORDS Microemulsions Interfacial composition Optimal salinity
Chainlength compatibility Solubilization

INTRODUCTION

Mixtures of oil and water are naturally unstable but can be stabilized by the addition of appropriate surfactants and cosurfactants. In contrast to regular emulsions which are unstable, microemulsions can be thermodynamically stable. They are clear or translucent systems containing microdomains of oil and/or water stabilized by a mixed film of surfactant and cosurfactant. Microemulsions have been studied extensively theoretically as well as experimentally by various investigators.¹⁻¹⁰ The formation and various physicochemical properties of the microemulsions are influenced by the alkyl chain length of surfactant, cosurfactant as well as hydrocarbons. For example the interfacial composition and distribution of alcohol in the oil and aqueous phases are influenced by the alkyl chainlength of alcohol and oil.^{11,12}

Various physicochemical models have been proposed for the formation of microemulsions. Ruckenstein and coworkers^{13,14} have done extensive work and have been successful in modeling the formation of microemulsions based on thermodynamics. In one of the models,¹³ they assumed that solubilized phase was dispersed as globules in the continuous phase with the droplets surrounded by adsorbed surfactant. The conclusion was that the single nonionic surfactants possessing the usual range of heats of adsorption and with the head group area less than 100 angstroms per surfactant

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molecule are not likely to generate microemulsions. In a subsequent paper¹⁴ they described the domain of existence of microemulsions. One of the earliest models was that by Bowcott and Schulman.¹⁵ They attributed the formation of microemulsions to the molecular interactions taking place at the interface. The interface was seen as a third phase in equilibrium with the oil and the aqueous phases. Using the model involving the distribution of alcohol in various phases and assuming that solubility of alcohol was negligible in water and that all the surfactant molecules partitioned in the interphase, the alcohol to surfactant ratio at the interface was determined.¹⁵

The assumption that all surfactant is present at the interface may be satisfactory in the case of oil-external microemulsions if high volume fraction of the dispersed phase (water) is present in the system. However, the assumption that the alcohol does not partition in the aqueous phase may be questionable particularly in case of butanol and pentanol. In the present paper we have modified the Schulman-Bowcott method to predict the ratio of alcohol to surfactant at the interface taking into account the solubility of alcohol in aqueous phase and the oil phase for sodium stearate system. The aqueous phase used was brine and oils used were straight chain hydrocarbons. The brine solubilization capacity and optimal salinity of these microemulsions were determined experimentally. Dilution of these microemulsions with brine as well as oil provided necessary information to determine the molecular ratio of alcohol to surfactant at the interface.

EXPERIMENTAL STUDY

Materials

Sodium stearate of 99% purity from Matheson, Coleman and Bell, Inc. was used for preparing microemulsions. Pentanol and oils were purchased from Chemical Samples Company and were of 99% purity or greater. Double-distilled water was used in making all the microemulsions.

Brine Solubilization Limit

The microemulsions were prepared by mixing surfactant (1 gm), alcohol (4 ml), oil (10 ml) and brine of different concentrations to get a clear solution. The brine solubilization limit was determined by mixing additional brine slowly from a graduated 1-ml pipette to the microemulsion, until turbidity was observed and two-phase formation occurred. In all cases, the end point was sharp (within 0.1 ml of added brine). At the endpoint the systems were initially turbid, but after a few minutes of standing two clear phases formed.

RESULTS AND DISCUSSION

The brine solubilization capacity of sodium stearate microemulsions as a function of brine concentration for different oils is shown in Figure 1. As the electrolyte concentration is increased, the solubilization limit increases, passes through a

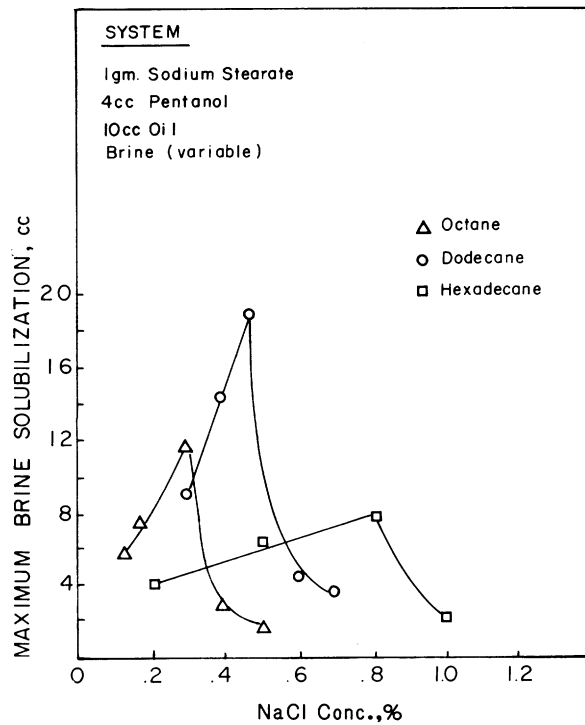


FIGURE 1 Brine solubilization capacity of sodium stearate-pentanol microemulsions in presence of different oils.

maximum then decreases. Upon addition of brine, a new microemulsion phase forms whose structure has to be determined by the phase behavior and other physicochemical measurements. Upto a certain extent, the alcohol from the oil phase can partition into the interface to stabilize the additional interfacial area. However, as the alcohol in the oil phase is depleted further growth of water droplets would increase the interfacial tension at the oil/water interface due to an increase in the area per molecule and thus destabilize the microemulsion, and hence prevent further solubilization of brine.

The solubilization of brine is maximum at a specific NaCl concentration for each oil. It has been shown^{16,17} that the salinity at which the highest amount of brine is solubilized in oil corresponds to the optimal salinity of the microemulsions. The optimal salinity of the surfactant formulation is defined as the salinity at which the middle phase microemulsion solubilizes equal volume of oil and brine.¹⁸ It is seen that as the alkyl chain length of oil increases, the optimal salinity also increases as shown in Figure 1. This observation is in agreement with the study carried out using petroleum sulfonates.^{16,19} The concept of optimal salinity and solubilization capacity of microemulsions is very important in enhanced oil recovery processes by surfactant flooding.²⁰⁻²²

There is a preferred chain length of oil which can solubilize the highest amount of brine (dodecane as shown in Figure 1). This can be explained on the basis of chain length compatibility effect observed in microemulsions^{12,23} as well as in other

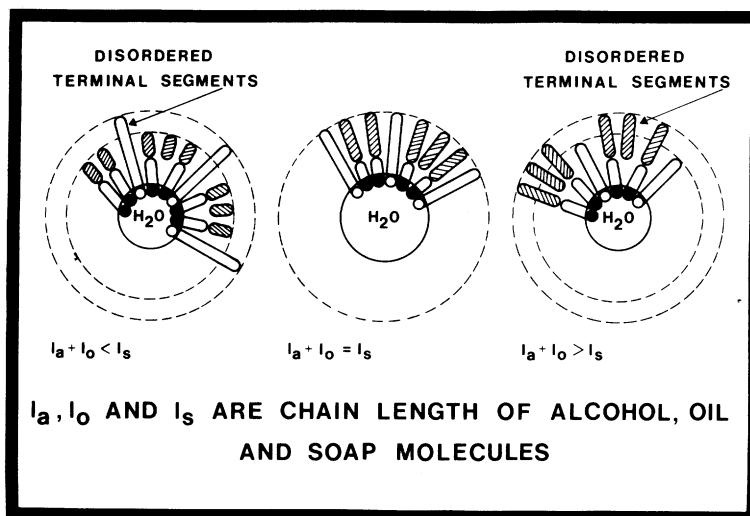


FIGURE 2 A schematic illustration of the disordering effect of the terminal segment of alkyl chain protruding out of the interfacial film and the solubilization capacity of microemulsions. l_a , l_o and l_s are the chain length of alcohol, oil and surfactant molecules, respectively.

system.²⁴⁻²⁶ When $l_a + l_o = l_s$, where l_a is chain length of alcohol, l_o , chain length of oil and l_s , chain length of surfactant, there will not be a region of disordered hydrocarbon chains near methyl groups around the droplet as shown in Figure 2. Using mixed monolayer we have shown that the thermal motion of the terminal segment produces a disruptive effect on the packing of surface active molecules and increases the area per molecule at the interface.²⁷ It was further shown²⁸ that this disruptive effect causes an increase of 0.05 angstrom in the intermolecular distance between surfactant molecules at the interface. When dodecane was used as an oil for making the microemulsion, the relation $l_a + l_o = l_s$ was satisfied (approximately, but much better than either with octane or hexadecane), the amount of brine that the microemulsion could solubilize was the highest due to maximum cohesive interaction between hydrocarbon chains or in other words, due to minimum disruptive effect in the interfacial region under these conditions.

At optimal salinity not only the molecular packing is the highest but also the molecular ratio of alcohol to surfactant is maximum at the interface. The following section describes the determination of this ratio at the interface using extended Schulman-Bowcott model.

SCHULMAN-BOWCOTT MODEL

Bowcott and Schulman¹⁵ attributed the formation of microemulsion to the molecular interactions taking place at the interface. The interface was seen as the third phase in equilibrium with the oil and the aqueous phase as shown in Figure 3. They assumed that all surfactant was present in the interphase. This assumption holds good if there is

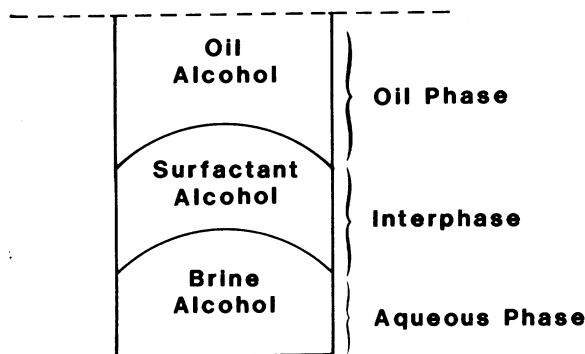


FIGURE 3 Three compartment model of microemulsions.

a high volume fraction of water to provide a large area for the soap to be at the interface for oil-external microemulsions. To dilute the system with oil, it is necessary to maintain a constant alcohol to oil ratio in the continuous phase i.e.

$$n_a^o/n_o = K_1 \quad (1)$$

where n_a^o is the number of moles of alcohol in the oil phase and n_o is the moles of oil. If n_a^i is the moles of alcohol present at the interphase and n_a^{aq} is the moles of alcohol in the aqueous phase, the total alcohol n_a in the microemulsion can be represented as

$$n_a = n_a^o + n_a^i + n_a^{aq} \quad (2)$$

Substituting Eq. (2) in (1) and dividing the whole expression by the number of surfactant moles n_s present in the system

$$n_a/n_s = \frac{n_a^i}{n_s} + \frac{n_a^{aq}}{n_s} + \frac{K_1 n_o}{n_s} \quad (3)$$

The dilution of microemulsion by oil makes the system turbid. This turbid emulsion is titrated with alcohol until it becomes clear. By plotting this molar ratio of alcohol to surfactant *vs.* the ratio of oil to surfactant, a straight line may be obtained if the formation of the microemulsion obeys Schulman–Bowcott model. The intercept of this line on *y*-axis is $n_a^i/n_s + n_a^{aq}/n_s$ from Eq. (3). For a long chain alcohol, the solubility of alcohol in aqueous phase is negligible and hence the intercept of the line gives the alcohol to surfactant ratio at the interface.

MODIFICATION

The precise calculation of interfacial alcohol concentration is not possible using the Schulman–Bowcott model especially when a short chain alcohol is used for the preparation of microemulsion because of the increased solubility of the alcohol in aqueous phase. However, using similar arguments of Schulman–Bowcott model, the molar ratio of alcohol to surfactant can be determined accurately by extending this model further. For a microemulsion (say w/o) if the volume fraction of dispersed phase

is increased, it is necessary to maintain a certain ratio of alcohol to water in the aqueous phase for the formation of microemulsion and hence,

$$n_a^{aq}/n_{aq} = K_2 \quad (4)$$

where n_a^{aq} is the number of alcohol moles in the aqueous phase and n_{aq} is the moles of brine in the microemulsion. Substituting Eq. (4) in (2) and dividing by the moles of surfactant, n_s ,

$$\frac{n_a}{n_s} = \frac{n_a^o}{n_s} + \frac{n_a^i}{n_s} + \frac{K_2 n_{aq}}{n_s} \quad (5)$$

Combining Eqs. (1) and (5) yields,

$$n_a/n_s = n_a^i/n_s + K_1 n_o/n_s + K_2 n_{aq}/n_s \quad (6)$$

As described earlier, the dilution of microemulsion with oil can give the value of K_1 and the intercept which includes n_a^i/n_s . If the microemulsion is concentrated with the dispersed phase (increasing the amount of brine in the system) the system becomes turbid. This turbid emulsion is titrated with alcohol until it becomes clear. This method is repeated and the data are plotted as n_a/n_s vs. n_{aq}/n_s and if the formation of microemulsion obeys the extended Schulman–Bowcott method, a straight line may be obtained according to Eq. (6) with a slope K_2 and a y -intercept $n_a^i/n_s + K_1 n_o/n_s$ for a fixed value of n_o/n_s . The value of K_1 is known from the oil dilution experiment and hence the value of molar alcohol to surfactant ratio at the interface can be obtained from this intercept. A check of this value could also be provided if the oil dilution results are expressed in the form of Eq. (6).

EXPERIMENTAL VERIFICATION

Following approach was taken to check the validity of this modified model. Microemulsions were prepared using sodium stearate, pentanol, various straight chain hydrocarbons and brine as an aqueous phase. The clear microemulsion was diluted with oil or concentrated with brine until it became turbid. The turbid macroemulsion was then titrated with pentanol until it became clear. For brine dilution experiments, the initial microemulsion contained surfactant (1 gm), oil (10 ml), and a small amount of brine. This mixture was titrated with pentanol until it became clear. For oil dilution experiments, the initial microemulsion contained surfactant (1 gm), brine (amount selected based on solubilization limit at high salinity for each oil), and a small amount of oil. This mixture was titrated with pentanol until it became clear. The dilution data were plotted in the form of Eq. (6) for all the systems. Figure 4 shows the variation of total alcohol in the system per mole of surfactant as a function of moles of octane present in the microemulsion per mole of surfactant at fixed brine to surfactant ratio. The brine concentrations were below, at, and above optimal salinity for each oil. As mentioned before, the n_{aq}/n_s molar ratio was fixed for each oil. The specific value of n_{aq}/n_s was based on solubilization limit at high salinities. Whereas Figure 5 shows the moles of alcohol per mole of surfactant as a function of the moles of brine per mole of surfactant at fixed octane to surfactant ratio for different concentrations of brine. It is

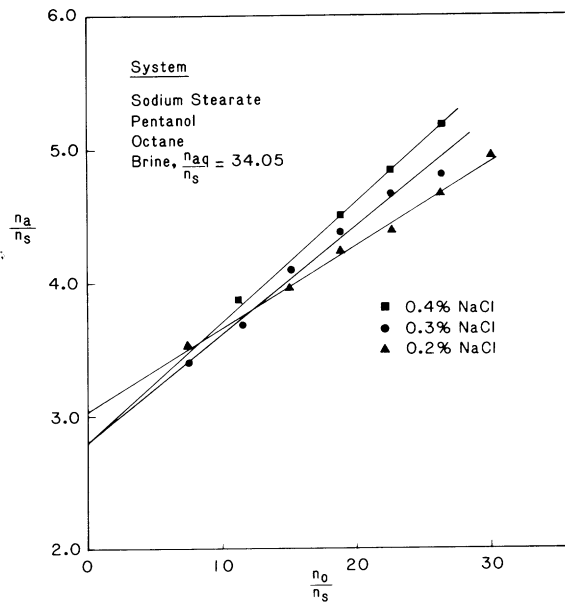


FIGURE 4 Effect of brine concentration on octane/alcohol titration plots of microemulsions. n_a , n_s , n_{aq} and n_o are the numbers of moles alcohol, surfactant, water and oil present in the microemulsion respectively.

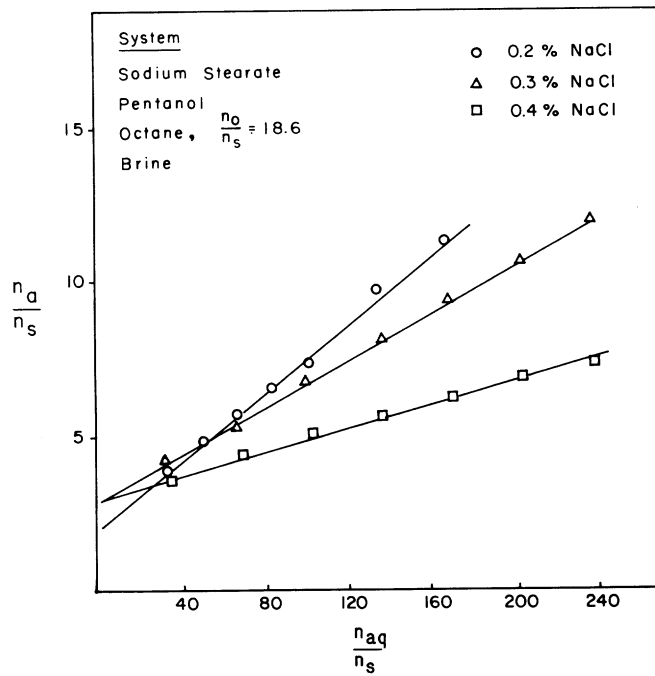


FIGURE 5 Effect of brine concentration on brine/alcohol titration plots of microemulsions, n_a , n_s , n_{aq} and n_o are the numbers of moles of alcohol, surfactant, water and oil present in the microemulsion respectively.

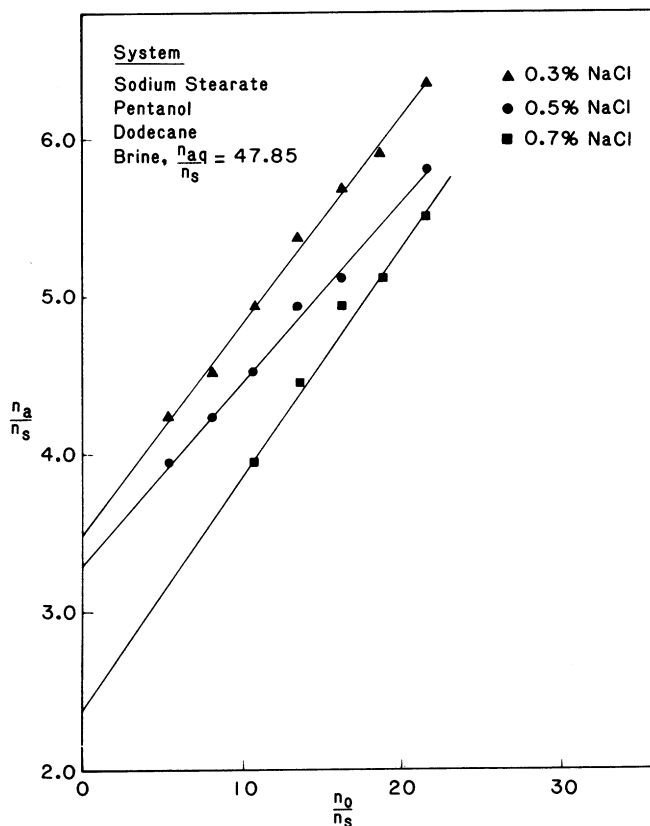


FIGURE 6 Effect of brine concentration on dodecane/alcohol titration plots of microemulsions. n_a , n_s , n_{aq} and n_o are the numbers of moles of alcohol, surfactant, water and oil moles present in the microemulsions respectively.

seen that the dilution data are well represented by a straight line for all brine salinities. The intercept of these lines according to Eq. (6) gives two values of n_a^i/n_s . These values agree within 20%. The dilution data for dodecane containing microemulsions are shown in Figures 6 and 7. It is seen that these data lie on a straight line for oil dilution (Figure 6). However, when the microemulsion was diluted with other than optimal salinity brine, some deviation was observed for high values of n_{aq}/n_s (Figure 7). This deviation was positive when the dilution was done with the lower than optimal salinity brine while negative deviation was found for higher than optimal salinity brine. The values of molar alcohol to surfactant ratio at the interface was obtained using the straight line portion of the brine dilution data. These values agree well within 20%. Figures 8 and 9 represent the results of microemulsions prepared using hexadecane. For all three salinities the data lie on a straight line. The value of n_a^i/n_s calculated from Eq. (6) agree well within 10%.

The average values of the molar alcohol to surfactant ratio at the interface is shown in Figure 10 as a function of brine concentration for octane, dodecane and hexadecane

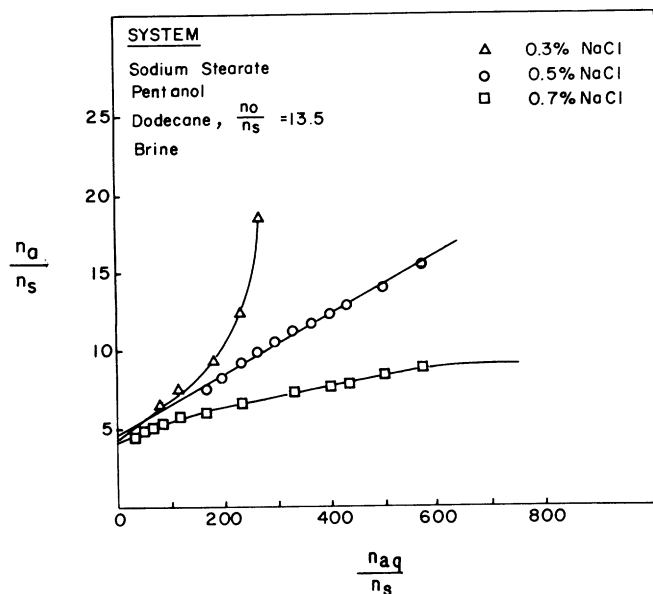


FIGURE 7 Effect of brine concentration on brine/alcohol titration plots of microemulsions. n_a, n_s, n_{aq} and n_o are the numbers of moles of alcohol, surfactant, water and oil present in the microemulsion respectively.

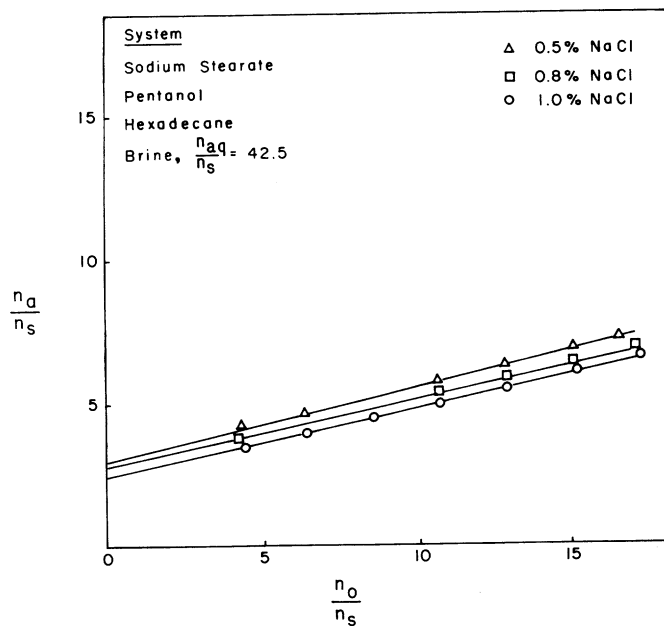


FIGURE 8 Effect of brine concentration on hexadecane/alcohol titration plots of microemulsions. n_a, n_s, n_{aq} and n_o are numbers of moles of alcohol, surfactant, water and oil present in the microemulsion respectively.

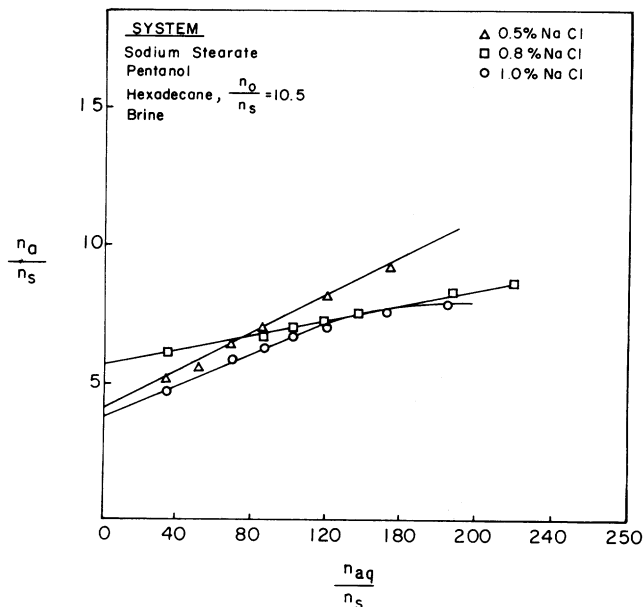


FIGURE 9 Effect of brine concentration on brine/alcohol titration plots of microemulsions. n_a, n_s, n_{aq} and n_o are the numbers of moles of alcohol, surfactant, water and oil present in the microemulsion respectively.

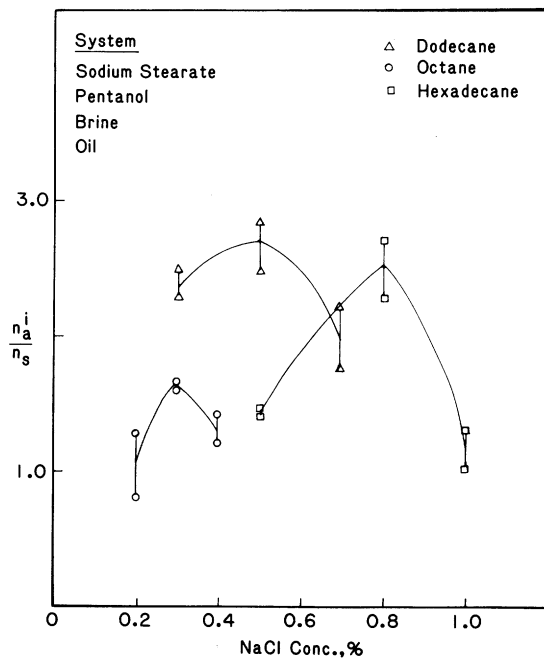


FIGURE 10 Effect of oil chain length on the ratio of alcohol to surfactant moles at the interface (n_a^i/n_s) at various brine concentrations.

containing microemulsions. It is seen that at a particular salinity this ratio is maximum for each oil and this brine concentration corresponds to the optimal salinity of the system. Further, the dodecane containing microemulsion has the highest alcohol to surfactant ratio at the interface. This is a supporting evidence for the highest brine solubilization capacity of the dodecane containing microemulsion at its optimal salinity.

CONCLUSIONS

1. Optimal salinity increases as chain length of oil increases for sodium stearate/pentanol/oil/brine system.
2. There is a preferred chain length of oil (dodecane) where the microemulsion can solubilize maximum amount of brine. This can be explained on the basis of chain length compatibility in microemulsions.
3. The molar ratio of alcohol to surfactant can be determined using the extended Schulman–Bowcott model.
4. At optimal salinity, the alcohol to surfactant ratio (molar) is maximum for the systems studied.

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NOMENCLATURE

l_a	chain length of alcohol
l_o	chain length of oil
l_s	chain length of surfactant
n_a^{aq}	number of moles of alcohol in aqueous phase
n_a^i	number of moles of alcohol in the interphase
n_a^o	number of moles of alcohol in oil phase
n_{aq}	number of moles of water
n_o	number of moles of oil
n_s	number of moles of surfactant

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