PHASE BEHAVIOUR OF PH DEPENDENT MICROEMULSIONS AT HIGH TEMPERATURES AND HIGH SALINITIES

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This paper describes the formulation principal for a model microemulsion system which exhibits pH dependent phase behaviour. The system investigated consists of octane, brine, alkyl ether carboxylic acid surfactants and short chain alcohols. The CMCs of these surfactants were lower in acid form of the surfactant (COOH) than for the salt form (COO-), also the micelles formed in acid solutions were smaller than for the salt. Furthermore the surface and interfacial tensions were found to increase with increasing pH. Increasing pH ionises the carboxylic acid head group thereby making the surfactant more hydrophilic. The effect of an increase in pH can be counterbalanced by increasing the electrolyte concentration. Measurements of ultralow interfacial tensions at different salinities and temperatures have been made using a spinning drop apparatus. Three phase microemulsion systems were studied as a function of temperature and pH. It was observed that the presence of ethylene oxide (EO) moiety in the surfactant molecule made the surfactants less sensitive to salinity than anionic surfactants. In addition, the carboxylic ionic head group made the surfactant more stable to temperature than simple EO nonionic surfactants. Thus these surfactants are more robust than either simple anionic or nonionic surfactants and thus these materials have potential in the field of surfactant flooding for tertiary oil recovery.

INTRODUCTION

Low interfacial tension, high solubilization and acceptable adsorption are considered to be the important design parameters in optimising microemulsion systems for recovering trapped oil from the petroleum reservoirs [1]. Huh [2]

empirically established a correlation between the solubilisation parameter and interfacial tension. It has been established that the interfacial tensions required to mobilise oil ganglia and to obtain sufficient oil recovery fall in the range of 10^{-2} to 10^{-4} mN/m [3]. Evidence shows [2] that the best conditions to generate such low interfacial tensions occur when a carefully designed surfactant rich phase (Winsor's type-III) exists in equilibrium with excess oil and water phases. The optimum middle phase, as defined by Huh [2] and Bourrel *et al*. [4], is the one in which the equal volumes of oil and water are solubilised.

Many oil reservoirs targeted for surfactant flooding contain a medium to high salinity brine especially in the North Sea [5]. Previously, ethoxylated petroleum sulfonates were used in order to overcome the high salinity problems [6]. These surfactants are expensive, unavailable on a commercial basis and some exhibit hydrolytic decomposition at medium to high temperatures [7]. Therefore the aim of this work is to look for the surfactants which are not only commercially available but also sustain effectivness at high temperature and high salinity and show good recovery capability for improved oil recovery.

Recently, ethoxylated carboxylated surfactants have received much attention because of their chemical and thermal stability, a good tolerance to mono and divalent ions, low losses in the medium through retention in the pores of the reservoir rocks [7] and [8]. As primary surfactants, alkyl carboxylated surfactants have exhibited moderate potential for use in enhanced oil recovery [9]. Another advantage is that the oil recovered by using these surfactants are free of emulsion [10]. At low degree of ethoxylation, these surfactants have demonstrated the formation of microemulsion in the absence of co-surfactants [11].

In this work, we have investigated a homologous series of commercially available surfactants, alkyl ether carboxylic

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acids, containing a mixture of C_{13} to C_{15} as a straight alkyl chain with different numbers of oxyethylene units. It has been shown [12] that these surfactants are very sensitive to pH and the hydrophilicity of the surfactant increases with the increase of the degree of ionisation. The critical micelle concentration is higher for the salts than for the acids. The surfactant micelles formed in the acid aqueous solution are smaller than for the salts. The purpose of this paper is to investigate the effect of pH on the micelle (aggregate) size, and hence on the phase behaviour of alkyl ether carboxylic acids in oil and water systems.

1 MATERIALS

The Alkyl Ether Carboxylic Acid (AECA) surfactants were the Atlas G series, supplied by *ICI Surfactants,* Wilton, UK and largely consisted of an anionic surfactant ($C_{13}H_{27}$-$C_{15}H_{31}$-O-$(CH_2CH_2O)_n$-COOH) with a small amount of unconverted nonionic surfactant. In these structures n = 2.5, 4, and 7. The hydrocarbon (octane) was supplied by the *Fluka Chemicals (UK) Ltd* and its purity was > 96%. Sodium chloride and sodium hydroxide used were analytical quality materials, supplied by *BDH*. The short chain alcohols studied were isobutanol and n-pentanol.

2 EXPERIMENTAL PROCEDURE

All pH measurements were made using the commercially available pH meter, Model 3020, produced by *Jenway England*. The dilute surfactant solutions of known concentration was titrated against strong base solution of NaOH to obtained the required pH. The surfactant aggregate size was measured using a Malvern 4700 PCS apparatus (supplied by *Malvern Instruments Ltd, UK)*. Surface tensions measurements were performed using a KRÜSS Digital Tensiometer K10, with a Platinum Wilhelmy plate. A spinning drop interfacial tensiometer (SITE 04, *KRÜSS GmbH, FRG)* was used for the interfacial tension (IFT) measurements.

The surfactant solutions were mixed with oil by water-to-oil ratio equal to one in glass tubes. The tubes were then hand shaken and allowed to equilibrate at constant temperature over a period of 3-4 days. The mixture separated into distinct phases with phase transition of Winsor's Type-I to Type-III to Type-II microemulsions and the phase volumes of all the phases were recorded as a function of temperature.

3 RESULTS AND DISCUSSION

The pK_a values of all the three surfactant solutions were determined by potentiometeric titration and are given in Table 1. It is found that the pK_a values decreased with the

increase of degree of ethoxylation. Thus it appears that the ethylene oxide chain in the molecule increases the acidity of the carboxylic group. A similar trend was observed by Binana *et al*. [13]. Table 1 also lists the CMC values for the three surfactants for the acid and salt solutions. The measurements show that the CMC values increase with the degree of ionisation and they are higher for salts than for the acids. It is also clear that the CMC values increase with increasing number of ethylene oxide units (EON) in the surfactant molecule.

TABLE 1

CMCs and pK_a values of the surfactants investigated

Surfactants	EON	CMCs (g/100 ml)		pK_a
		Acid	Salt	
Atlas G-5086	2.5	0.00242	0.00260	5.9
Atlas G-5760	4	0.00382	0.00465	5.25
Atlas G-5411	7	0.00788	0.01200	5.2

Increasing the pH increases the degree of ionisation of the carboxylic head group, which in turn increases solubility of surfactant in the water [9]. The weakly ionised surfactant molecule retains the best properties of nonionic surfactants [14]. With low EO units, EO = 2.5 and EO = 4, the surfactant molecules are close to, or above the cloud point and hence the aggregate size is large for acid solution as shown in Figure 1.
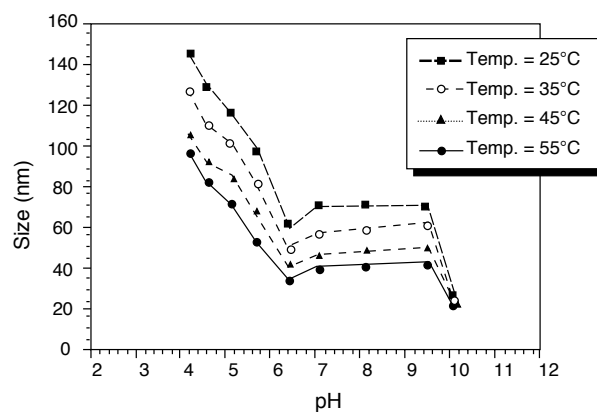

Figure 1

Effect of pH and temperature on the size of aggregate of AEC + EO4 (conc. = 0.05 g/100 ml).

Nakagawa and Tori [15] have found a large increase in the aggregate weight for nonionic surfactants near the cloud point. Increasing the pH will increase the salt to acid ratio and hence the charged molecules dissociate thereby decreasing the average size of the aggregates. When the pH

of surfactant solution increases the pK_a value (pH ≥ 6), more than half of the surfactant is now ionised and aggregates constituted mostly by the ionised surfactant molecules dominate in size. The micelle size increases with increase of pH until the whole of the surfactant solution is completely ionised. Binana *et al*. [13] have found that for ethoxylated carboxylate surfactants, the aggregation number increases with the increase of temperature only if the surfactant concentration is above than CMC. It is observed that if the pH is further increased (> 10), the double layer starts compressing and the micelles and the aggregate size decreases, Figure 1.

Figure 2 shows that the aggregate size decreases with increasing temperature. However, the effect of temperature on the aggregate size is greater for acid solution than for the salt. When the pH of the solution becomes equal to 10, the influence of temperature on the aggregate size becomes negligible.
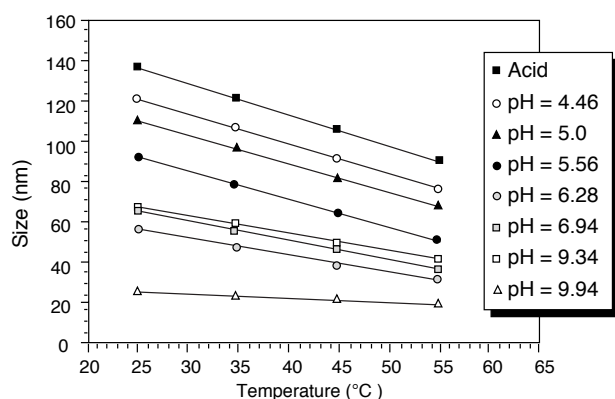
Figure 2

Effect of temperature on size of aggregates of AEC + EO4 (conc. = 0.05 g/100 ml).

For the surfactant in acid form in aqueous solution, the micelles formed are neutral aggregates and micellisation occurs at the same concentration as with the nonionic surfactants [14]. However, increasing the pH of the acid solution will increase the degree of ionisation thereby making the surfactant more hydrophilic [12]. The micelles formed under these conditions are aggregates of ionised head groups and critical aggregation occurs at concentration higher than that for unionised surfactant. Therefore the surface or interfacial tension is generally lowest at an acidic pH and it gradually increases with the increase of ionisation of the carboxylic head group as shown in Figure 3. Increasing the EO units in the surfactant molecules inhance the effect of the degree of ionisation and hence the surfactant molecules become more hydrophilic. Therefore the surface and interfacial tensions will increase with the increase of EO units in the surfactant molecule.
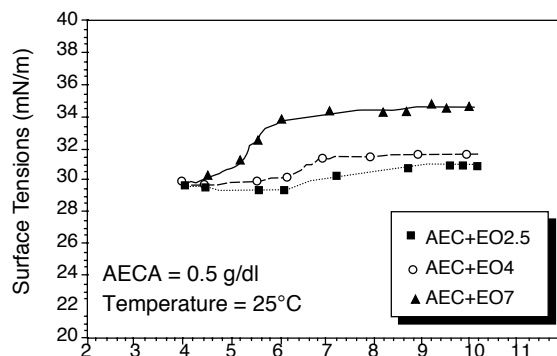
Figure 3

Influence of pH on surface tension of ether carboxylic acids.

The phase behaviour of pH dependant ether carboxylic acid system depends on salinity in the same way as in ethoxylated sulfonates [9]. In this study, we have observed that the middle phase microemulsion is formed at low to high pH as a function of temperature at constant salinity as shown in Figure 4. This figure also indicates that the three phase region moves towards higher temperature as the pH of the surfactant solution is increased. It is observed that the solubility of oil and water in the middle phase increases with the increase of pH. This is because all the surfactant is completely ionzed at this pH.
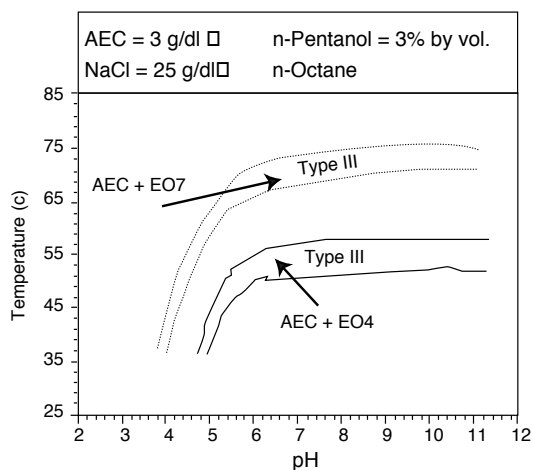
Figure 4

The effect of pH as a function of temperature on the phase behaviour of surfactants AEC + EO4 and AEC + EO7.

It observed that for a fixed alkyl group, the middle phase region is large for EO = 4 than EO = 2.5 and EO = 7. However, the three phase region is observed at low salinity and low temperature at constant pH, for EO = 2.5 and are observed at high temperatures and at high salinity for EO = 4 and EO = 7 as shown in Figure 5.
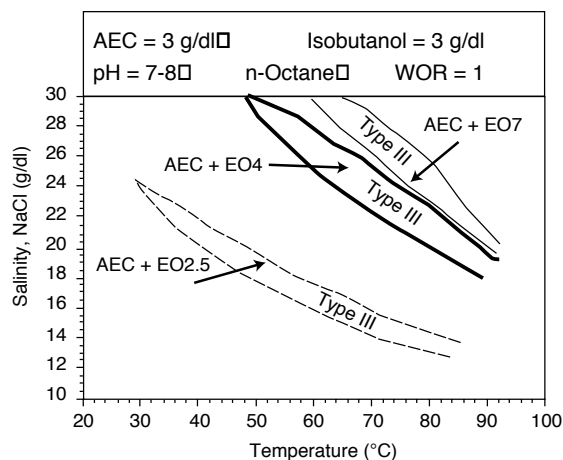
Figure 5

Effect of temperature with salinity on three phase region (Type-III microemulsion) of alkyl ether carboxylic acids at constant pH (7-8).

The most important parameter in the design of enhanced oil recovery systems employing surfactants is the reduction of interfacial tension at the water/oil interface. Low interfacial tensions has been reported with surfactants having carboxylate head groups [2] and [7]. Figure 6 shows the interfacial tension as a function of temperature at constant pH = 6.3 for two different salinities. It is interesting to see that the minima occurs at temperature 35°C for salinity 20 g/dl. It is found that minima in IFT at different pH can be optimised with changing the salinity and temperature. The maximum decrease in low IFT was observed in the region for
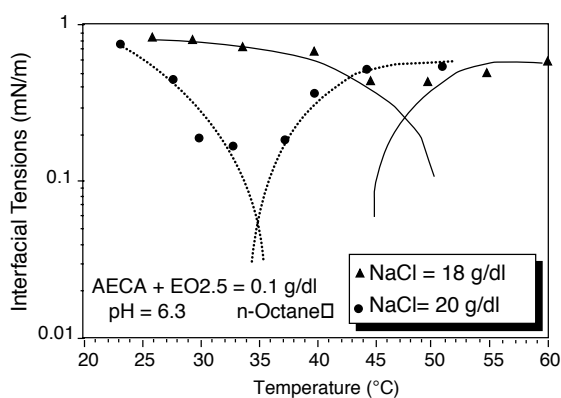

Figure 6

Interfacial tension versus temperature of aqueous solution and octane for AEC + EO4 at constant pH (6.3) and salinities (18 g/dl and 20 g/dl).

pH range of 6-10 where the maximum solubility of oil and water in the middle phase was observed.

CONCLUSIONS

For commercial surfactants, alkyl ether carboxylic acids, containing an average oxyethylene units of 2.5, 4, and 7, it is found that the micelles size increases with increase of pH and decreases with the increase of temperature. The surface and interfacial tensions increases with increasing pH. The effect of salinity on IFT is similar to that observed in ether sulfonates. The size of micelles and hence the solubility of oil and water in the middle phase microemulsion can be adjusted by changing the pH. Increasing the EO units in the surfactant molecules make the surfactant molecule more hydrophilic and hence high salinity and temperature are required to achieve optimum region.

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