The Effect of Divalent Cations (Ca^{++} and Mg^{++}) on the Optimal Salinity and Salt Tolerance of Petroleum Sulfonate and Ethoxylated Sulfonate Mixtures in Relation to Improved Oil Recovery

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ABSTRACT

It was demonstrated that a surfactant formulation consisting of a petroleum sulfonate and an ethoxylated sulfonate can tolerate a large amount of CaCl$_2$ and MgCl$_2$ in solution without any precipitation or phase-separation. The stability of this surfactant formulation was not influenced significantly by the presence of divalent cations. The maximum salt concentration permissible for a stable formulation depended primarily on the ionic strength of the salt solution and not on the relative proportions of the divalent and monovalent cations. It was also observed that though the optimal salinity (Sγ) decreased upon increasing the amount of divalent cations, the interfacial tension at optimal salinity was always in the millidyne ($\simeq 10^{-3}$ dynes/cm) range. This study has a practical application in designing the surfactant formulations for tertiary oil recovery process for reservoirs consisting of high concentrations of mono- and divalent cataions.

INTRODUCTION

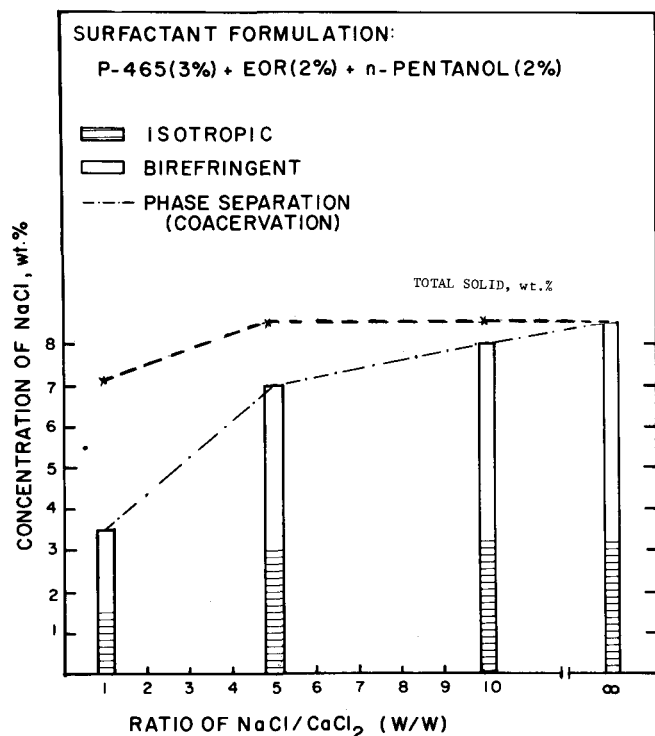The use of the surfactants for improved oil recovery was

FIG. 1. The effect of NaCl/CaCl$_2$ ratio on the optical appearance of surfactant formulation.

recognized by De Groot (1) as early as 1930. Later, a number of patents (2-5) were issued on the use of surfactants for improved oil recovery either in the form of microemulsions or in micellar solutions. In recent years, review articles (6-8) on the status of surfactants for improved oil recovery have been published. It has been established (9) that for an efficient improved oil recovery process, the capillary number (i.e., the ratio of viscous to interfacial forces) should be in the region of 10^{-2}. In practice, this can be accomplished by reducing the interfacial tension to a very low value ($\simeq 10^{-3}$ dynes/cm) at the oil/brine interface. Recent studies (10,11) on aqueous solutions of petroleum sulfonate demonstrate that such low tensions can be achieved with a proper choice of type and concentration of surfactant and alcohol as well as salt concentration.

The solubilization, phase behavior, and interfacial tension of petroleum sulfonate solutions have been studied by various workers (12-18). When the surfactant formulation consisting of petroleum sulfonate and alcohol is equilibrated with the oil, a surfactant-rich middle phase is formed within a particular salinity range. This surfactant-rich middle phase was termed as the middle phase microemulsion by Healy and Reed (15). This middle phase microemulsion consists of solubilized oil, water, surfactant, and alcohol. If the volume of solubilized oil in the middle phase is V$_o$, the volume of solubilized water V$_w$, and the volume of surfactant V$_s$, the solubilization parameter V$_o$/V$_s$ or V$_w$/V$_s$ indicates the solubilized volume of either oil or water per unit volume of surfactant in the microemulsion phase. The value of the solubilization parameter V$_o$/V$_s$ increases as salinity increases, while V$_w$/V$_s$ decreases upon increasing salinity. The intersection point of V$_o$/V$_s$ and V$_w$/V$_s$ is defined as the optimal salinity for phase behavior (S$_\phi$), i.e., equal volume of oil and water is solubilized in the middle phase microemulsion.

It was also found by Healy and Reed (15) that the interfacial tension between middle phase microemulsion and oil (γ_{mo}) decreases as the salinity increases, while brine-microemulsion phase interfacial tension (γ_{mw}) increases with increasing salinity. The intersection point between γ_{mo} and γ_{mw} was defined as the optimal salinity for interfacial tension behavior (Sγ). It was also observed by Reed and Healy that values of S$_\phi$ and Sγ are very close to each

TABLE I

The Effect of NaCl/CaCl$_2$ Ratio on the Maximum Salt Concentration Required for the Stable Surfactant Formulation (Petrostep-465, 3% + EOR-200, 2% + n-Pentanol, 2%)

NaCl/CaCl$_2$ ratio (w/w)	Total dissolved solids at maximum salt concentration, wt %	Ionic strength at maximum salt concentration ($I = 1/2 \ \Sigma \ c_i z_i^2$)
∞ (no CaCl$_2$)	8.5	1.45
10	8.8	1.58
5	8.7	1.57
1	7.0	1.54
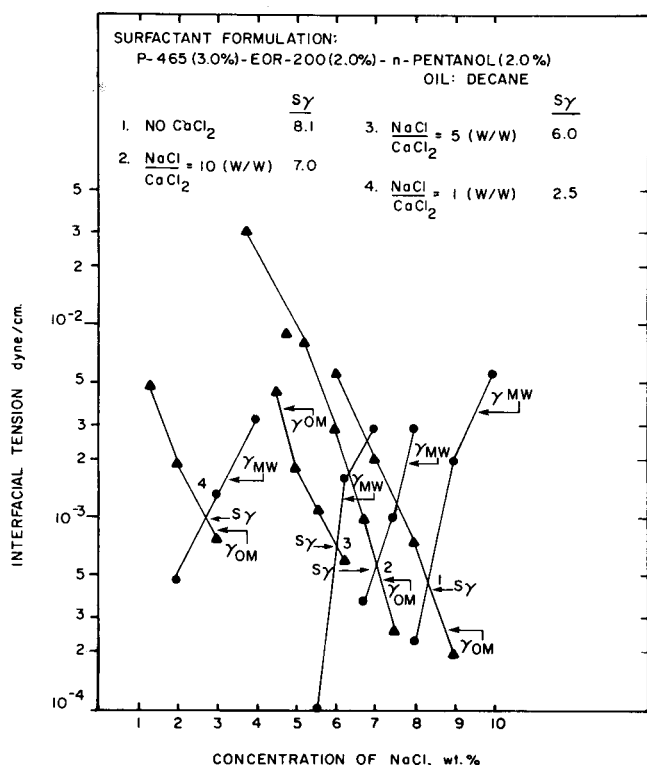
FIG. 2. The effect of $NaCl/CaCl_2$ ratio on interfacial tension and optimal salinity (S_γ).

FIG. 3. The effect of $NaCl/CaCl_2$ ratio on solubilization parameters and optimal salinity (S_ϕ).

other. Also, when the surfactant solution was injected at its optimal salinity, maximum oil recovery occurred (16,19,20).

From the existing literature on petroleum sulfonates, it appears that the surfactant formulations consisting of petroleum sulfonates exhibit low salt tolerance and optimal salinity (1-2% NaCl), and the presence of Ca^{++} ions decreases the optimal salinity value of surfactant formulations (16). It was reported (21) that the presence of an ethoxylated alcohol in a surfactant formulation increases the temperature stability and salt tolerance of the formulation. Recently, we have found (22,23) that the addition of an ethoxylated sulfonate (EOR-200) in petroleum sulfonate solutions increases the salt tolerance and optimal salinity of the solutions. Also, the stability of surfactant formulation could be increased up to 24% NaCl concentration with the addition of EOR-200 in the surfactant formulation.

This paper reports the effect of Ca^{++} and Mg^{++} on the salt tolerance and optimal salinity of the surfactant formulation consisting of petrostep 465 (3%) + EOR-200 (2%) + n-pentanol (2%). This system we chose because of its high salt tolerance (8.5% NaCl) and a high optimal salinity (8.1% NaCl). This allowed us to study the effect of higher ratios of $CaCl_2/NaCl$ on optimal salinity behavior. This study has a practical application in formulating the surfac-
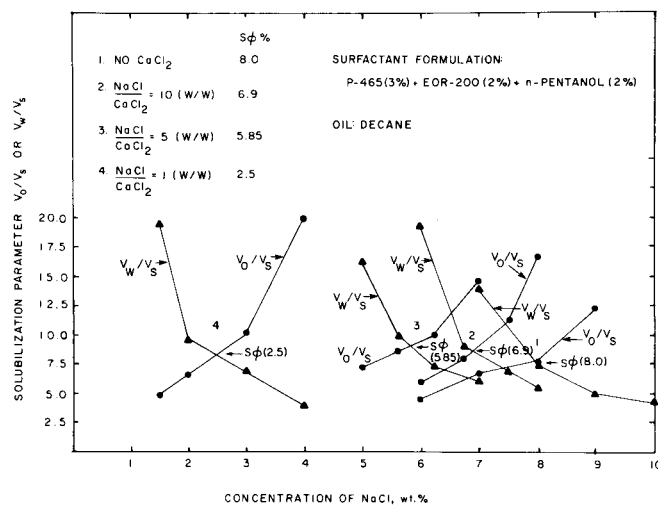
tant formulation for tertiary oil recovery for reservoir brines consisting of high concentrations of mono-, di-, and trivalent cations.

MATERIALS AND METHODS

Petroleum sulfonate (Petrostep-465) and ethoxylated sulfonate (EOR-200) were supplied by Stepan Chemicals and Ethyl Corporation respectively. Paraffinic oil (n-decane) as well as n-pentanol of 99% purity was purchased from Chemical Samples Company.

Aqueous solutions consisting of petrostep-465 (3%), EOR-200 (2%), and n-pentanol (2%) were prepared at various salt concentrations. The effect of Ca^{++} on optimal salinity was studied at three different ratios ($NaCl/CaCl_2$ = 1,5,10, w/w) and the effect of Mg^{++} was studied at $NaCl/MgCl_2$ ratios of 5 and 10 (w/w). The optimal salinity values were obtained by the approach described by Healy and Reed (14). The density of different phases were measured with a 5 ml density bottle. The interfacial tension was measured with the spinning drop tensiometer developed by the University of Texas. The phase volume and interfacial tension data were obtained at room temperature.

RESULTS AND DISCUSSION

The increasing salt concentration caused unusual effects on the surfactant formulation reported here. The surfactant formulation passes through different regions, namely, isotropic clear, birefringent, and then phase separation, upon increasing the salt concentration. At low concentration of salt, the surfactant solution is isotropic and clear; with further increase in salt concentration, a stable birefringent phase forms. However, upon further increase in salt concentration, the birefringent phase is destroyed and a non-

TABLE II

The Effect of $NaCl/CaCl_2$ Ratio on the Optimal Salinity, the Interfacial Tension, and Solubilization Parameter at Optimal Salinity of the Surfactant Formulation (Petrostep-465, 3%, EOR-200, 2% n-pentanol, 2%)

$NaCl/CaCl_2$ ratio (w/w)	Optimal salinity (S_γ) wt % NaCl	Total dissolved solids	Ionic strength (I^a)	IFT (γ_{om} or γ_{mw}) at optimal salinity	Solubilization parameter (V_o/V_s or V_w/V_s) at optimal salinity
∞	8.1	8.1	1.38	5×10^{-4}	7.5
10	7.0	7.7	1.38	5.8×10^{-4}	8.7
5	6.0	7.2	1.35	7×10^{-4}	9.0
1	2.5	5.0	1.1	10^{-3}	8.7

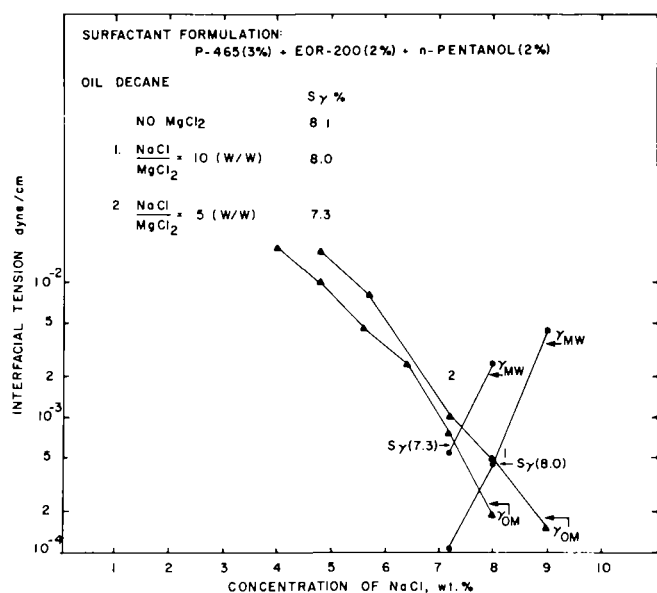$a_I = \frac{1}{2} \Sigma C_i Z_i^2$.

FIG. 4. The effect of $NaCl/MgCl_2$ ratio on interfacial tension and optimal salinity (S_γ).

birefringent surfactant phase separates out. The upper limit of birefringent region which remains stable, is taken as a salt tolerance limit for the surfactant formulation. The upper limit of the birefringent region (salt tolerance limit) for the surfactant formulation was found to be 8.5 wt % NaCl and for isotropic clear region was ca. 3.5% NaCl. The effect of $NaCl/CaCl_2$ ratio on the optical appearance and on the stability of the surfactant formulation is shown in Figure 1.

The stability range in terms of NaCl concentration of the surfactant formulation decreases upon increasing the amount of $CaCl_2$ in the surfactant formulation (8.5% to 3.5%). Though the initial effect of $CaCl_2$ on the stability range of surfactant formulation is not significant, the salt tolerance (total dissolved solids, wt %) decreased from 8.5% to 7.0% when $NaCl/CaCl_2$ ratio decreases from ∞ to 1 (Fig. 1). If we consider the stability of the surfactant formulation in terms of total dissolved solid, it is evident that this type of surfactant formulation is not sensitive to the presence of divalent cations as shown in Table I. The percentage of total dissolved solid in the stable surfactant formulation decreases only to 7% when NaCl to $CaCl_2$ ratio increases to 1. Table I shows that the maximum salt concentration which can be tolerated by surfactant formulation depends primarily upon the ionic strength of salt solutions and not on the relative proportion of the divalent to monovalent cations.

From this observation it is evident that the surfactant formulation consisting of a petroleum sulfonate and an ethoxylated sulfonate is capable of tolerating high concentration of $CaCl_2$ without any precipitation or phase separation up to 3.5% NaCl (or 7.0% wt total solid).

Figure 2 shows the effect of $NaCl/CaCl_2$ ratio on the interfacial tension and interfacial optimal salinity (S_γ) of the surfactant formulation. Figure 3 shows the effect of $NaCl/CaCl_2$ ratio on the phase behavior optimal salinity (S_ϕ). It is evident from Figures 2 and 3, that upon increasing the amount of $CaCl_2$ in the surfactant formulation, the optimal salinity (S_ϕ or S_γ) decreases. The optimal salinity, S_γ, at different ratios of $NaCl/CaCl_2$ and the corresponding ionic strength are given in Table II.

From the calculated ionic strength (Table II) it is evident that though the optimal salinity decreases drastically from 8.1 to 2.5 upon increasing the ratio of NaCl to $CaCl_2$ to 1 in the surfactant formulation, the decrease in ionic strength
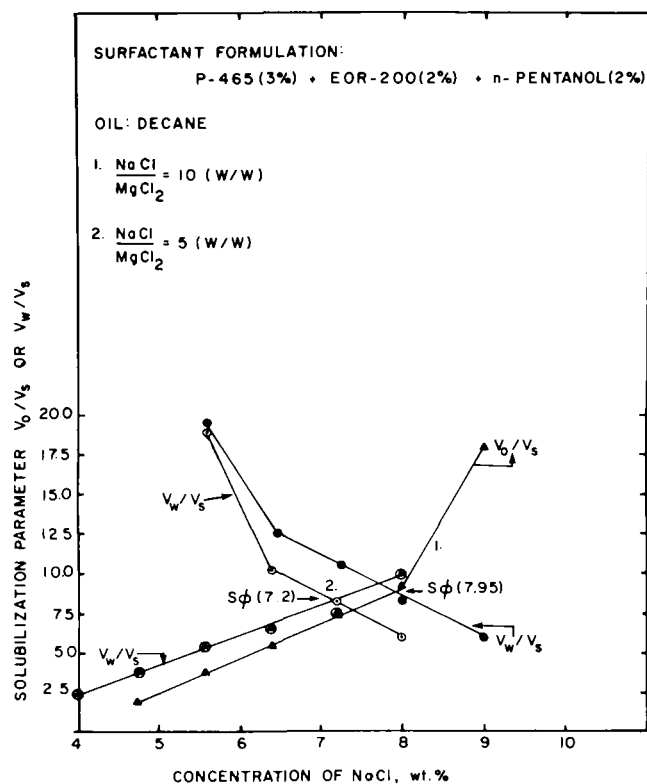

FIG. 5. The effect of $NaCl/MgCl_2$ ratio on solubilization parameters and optimal salinity (S_ϕ).

value is not very much (1.38 to 1.1). It is also evident from Figures 2 and 3 that these surfactant formulations are capable of producing very low interfacial tension at optimal salinity (in the range of millidyne) value in the presence of high concentration of divalent ions. The interfacial tension and solubilization parameter (V_o/V_s or V_w/V_s) are not much affected by the presence of divalent ions at the optimal salinity value. Though there is a slight increase in the solubilization parameter and the interfacial tension upon increasing the amount of $CaCl_2$ in the formulation, the interfacial tension was still in the millidyne range.

Figures 4 and 5 show the effect of $NaCl/MgCl_2$ ratio on the interfacial tension and phase behavior of the surfactant formulation. It is evident that the optimal salinity value decreases upon increasing the amount of $MgCl_2$ in the surfactant formulation. The decrease in optimal salinity values by $MgCl_2$ is much less as compared to that by $CaCl_2$. From the comparison of the two systems, Ca^{++} ions are more effective in lowering optimal salinity as compared to Mg^{++} ions. From Figures 2 and 3 or 4 and 5, optimal salinity values obtained by interfacial tension measurements (S_γ) are very close to phase behavior optimal salinity value (S_ϕ) as obtained by Healy and Reed (14,15).

From the results presented here, the surfactant formulation consisting of petroleum sulfonate and ethoxylated sulfonate can tolerate a large amount of $CaCl_2$ and $MgCl_2$ in the surfactant formulation without any precipitation or phase separation. Moreover, these surfactant formulations still produce very low interfacial tension (in the range of millidyne) even in the presence of high concentration of divalent cations (Table II), though there is a slight increase in interfacial tension upon increasing the amount of divalent cations in the surfactant formulations. We believe that appropriate mixtures of petroleum sulfonate and ethoxylated sulfonate are very promising for tertiary oil recovery because of their improved salt tolerance and ability to produce ultra-low interfacial tension in the presence of rela-

tively high concentrations of mono- and divalent cations.

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[Received September 1, 1977]