

TEMPERATURE DEPENDENCE OF PRECIPITATE REDISSOLUTION: A CALCIUM ADSORPTION MODEL

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ABSTRACT

Long-chain alkyl and alkylaryl sulfonates used in micellar flooding systems were found in previous studies to precipitate upon addition to inorganic electrolytes and in some cases to redissolve and reprecipitate in excess sulfonate solutions. These studies also revealed that the major mechanism responsible for redissolution in micellar solubilization. To further test the validity of this mechanism, data for the dependence of precipitation/redissolution on temperature in the sulfonate/ CaCl_2 system are used to obtain various thermodynamic parameters such as heats of dissolution, micellization, solubilization and calcium adsorption on micelles. Also a sequence of molecular processes leading to precipitate redissolution is proposed and tested using temperature data. The temperature dependence predicted by the model is found to agree with experimental data.

INTRODUCTION

Interaction of long-chain sulfonates with multivalent inorganics, e.g., Ca^{2+} , that are found in petroleum reservoir fluids plays an important role in the displacement of oil in enhanced oil recovery by micellar flooding systems. These interactions were previously found to produce precipitation of sulfonates followed by their redissolution in excess sulfonate concentrations [1,2]. Precipitate redissolution in the sulfonate/calcium system was shown to be caused by micellar solubilization.

To identify the major mechanism governing the system further, a critical parameter, temperature, has been investigated. An understanding of the effect of temperature of the precipitation/redissolution phenomenon is important both from practical and fundamental points of view. Such information can be useful in predicting the precipitation behavior of surfactants in reservoirs of different temperature and even at different locations in the same reservoir. Also, the dependence of precipitation/redissolution on temperature can yield important thermodynamic information on the process. Therefore, the temperature dependence of precipitation/redissolution was investigated for $\text{NaDDBS}/\text{CaCl}_2$ and $\text{NaDDS}/\text{CaCl}_2$ systems. The results

have been analyzed to obtain heats of reaction of various subprocesses involved in precipitation/redissolution.

EXPERIMENTAL

Sodium dodecylbenzenesulfonate (NaDDBS) was purified through de-oiling, recrystallization and desalting techniques. Characterization of this sulfonate using p-NMR and C¹³-NMR indicated the presence of only branched chain impurities. Sodium dodecylsulfonate (NaDDS), specified as > 99% pure, was used without further purification. The critical micelle concentrations (CMCs) of these two sulfonates were found to be 1.5×10^{-4} and 9.8×10^{-3} kmol m⁻³ in agreement with the reported values [3]. Triply distilled water was used in all the experiments.

The turbidity of the solutions was measured with a probe colorimeter. Equal amounts of salt and sulfonate solutions were mixed in test tubes at the desired constant temperature. Turbidity of the solutions was determined from the values for light transmission at $\lambda = 670$ nm, 24 h after mixing.

For the chemical analysis, the precipitate was separated at 17000 rpm. The amount precipitated was determined from the difference between the initial and final sulfonate or electrolyte concentration. The clear supernatant was then analyzed for sulfonate using a two-phase titration technique [4] and for calcium by standard EDTA titration.

CMCs were determined by conductivity, surface tension and dye solubilization techniques. The reason for employing more than one technique to measure CMCs was that no single technique was applicable under all conditions. For example, while surface tension was satisfactory at high salinities, it failed to identify the CMC in precipitating systems. Dye solubilization and conductivity techniques were not feasible at high salinities but the former was found to be adequate in precipitating systems.

The Wilhelmy plate technique using a sandblasted platinum sensor plate was used to measure the surface tension of solutions. Specific conductivity measurements were performed with a linear conductance/resistance meter. The dye solubilization technique is based on the spectral changes of pinacyanol chloride. Details of all the above CMC techniques are given elsewhere [5–7].

RESULTS AND DISCUSSION

The temperature dependence of precipitation of calcium dodecylbenzenesulfonate, Ca(DDBS)₂, and calcium dodecylsulfonate, Ca(DDS)₂, is shown in Figs. 1 and 2 in terms of light transmitted through the solution. The solubilities of Ca(DDBS)₂ and Ca(DDS)₂ are found to increase with increas-

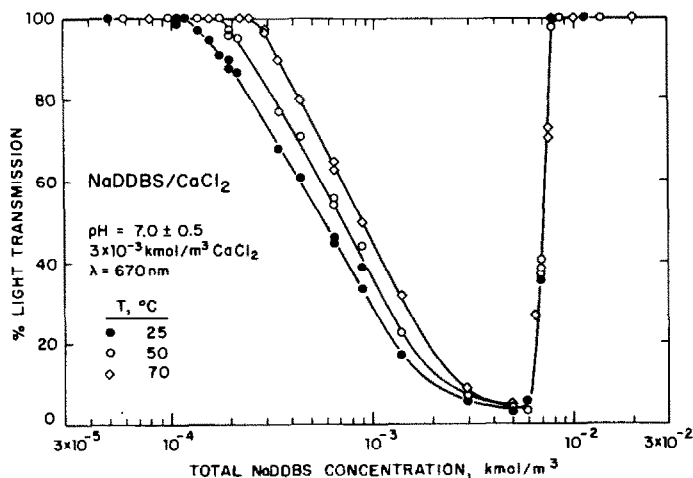


Fig. 1. Effect of temperature on the precipitation/redissolution behavior of the NaDDBS/CaCl₂ system; light transmission of the solutions as a function of sulfonate concentration.

ing temperature. The solubility products of these sulfonates calculated from data for the onset of precipitation are given in Table 1. The solubility product of Ca(DDS)₂ increased by an order of magnitude for a temperature increase from 40 to 70°C. On the other hand, the solubility product of Ca(DDBS)₂ increased only by a factor of 4 over a wider temperature range (25–70°C). Similarly in the redissolution region, Ca(DDS)₂ exhibited a more marked dependence on temperature compared to Ca(DDBS)₂. In all these cases, the onset of redissolution coincided with the CMC of the system, thus,

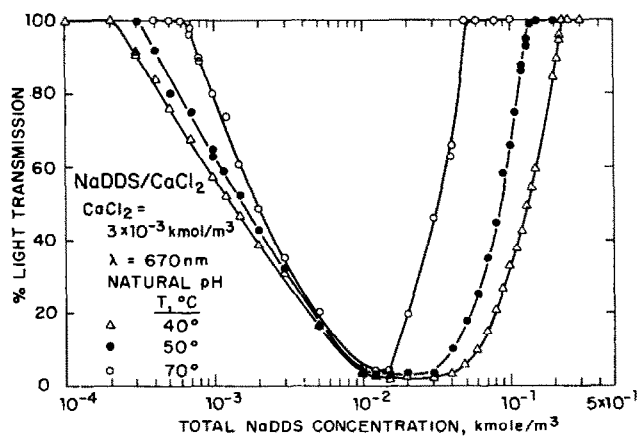


Fig. 2. Effect of temperature on the precipitation/redissolution behavior of the NaDDS/CaCl₂ system; light transmission of the solutions as a function of sulfonate concentration.

TABLE 1

Temperature dependence of solubility product, CMC and solubilization constant of $\text{Ca}(\text{DDBS})_2$ and $\text{Ca}(\text{DDS})_2$

System	T ($^{\circ}\text{C}$)	K_{sp}	CMC (kmol m^{-3})	K_s
$\text{Ca}(\text{DDS})_2$	40	1.2×10^{-10}	8.5×10^{-3}	0.014
	50	2.7×10^{-10}	9.5×10^{-3}	0.023
	70	1.4×10^{-9}	1.1×10^{-2}	0.077
$\text{Ca}(\text{DDBS})_2$	25	4.3×10^{-11}	4.5×10^{-4}	0.37
	50	1.03×10^{-10}	5.3×10^{-4}	0.35
	70	1.88×10^{-10}	5.9×10^{-4}	0.33

once again, confirming the contention that the redissolution of calcium sulfonate precipitate occurs only in the presence of micelles.

Data for the temperature dependence of dissolution can be used as shown below, to determine the heat of dissolution.



$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{R}^-]^2 \quad (2)$$

$$\frac{\partial \ln K_{\text{sp}}}{\partial (1/T)} = \frac{-\Delta H}{RT} \quad (3)$$

$$\ln K_{\text{sp}} = \frac{-\Delta H}{RT} \quad (4)$$

A plot of $\log K_{\text{sp}}$ vs. $1/T$ should yield $-\Delta H/R$ as the slope. The $\log K_{\text{sp}}$ vs. $1/T$ plots are given in Fig. 3 and the values of ΔH_{sp} are:

$$\Delta H_{\text{sp Ca}(\text{DDS})_2} = 18\,500 \text{ cal mol}^{-1}$$

$$\Delta H_{\text{sp Ca}(\text{DDBS})_2} = 6000 \text{ cal mol}^{-1}$$

These values for ΔH_{sp} reflect the earlier conclusion that the temperature dependence of dissolution of $\text{Ca}(\text{DDS})_2$ is stronger than that of $\text{Ca}(\text{DDBS})_2$.

The ΔH_{sp} obtained above corresponds to a process in which calcium sulfonate dissolves in water to give Ca^{2+} and 2R^- ions. Redissolution of the precipitate at higher surfactant concentrations, however, results from the reaction



$$K_s = \frac{(\text{CaR}_2 \cdot \text{micelle})}{(\text{micelle})} \quad (6)$$

$$K_s = \frac{[\text{CaR}_2 (\text{redissolved})]}{c_{\text{R}^-} - \text{CMC}} \quad (7)$$

Thus, the solubilization constant, K_s , defined above is the reaction

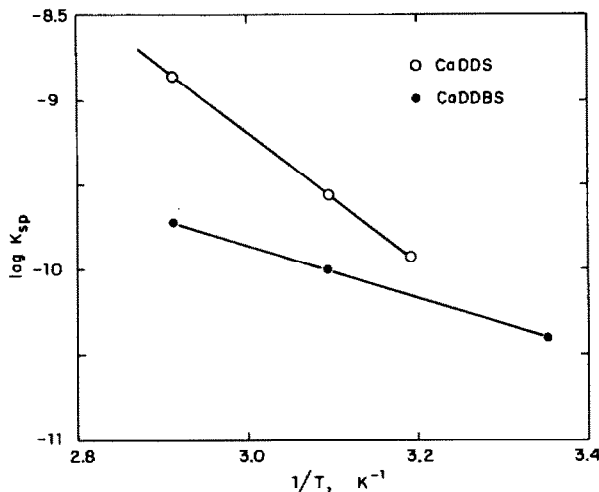


Fig. 3. Solubility product of $\text{Ca}(\text{DDS})_2$ and $\text{Ca}(\text{DDBS})_2$ as a function of the reciprocal of the absolute temperature.

constant for dissolution of the precipitate in the presence of micelles. The temperature dependence of K_s should, therefore, give the enthalpy of dissolution of calcium sulfonate precipitate by micelles.

$$\frac{\partial \ln K_s}{\partial (1/T)} = -\frac{\Delta H}{R} \quad (8)$$

$$\ln K_s = -\frac{\Delta H}{R} + \text{constant} \quad (9)$$

$\ln K_s$ for both NaDDS and NaDDBS was obtained from the precipitation/redissolution curves given in Figs. 1 and 2 (see Table 1). The values of ΔH_s obtained from $\ln K_s$ vs. $1/T$ plots are as follows:

$$\Delta H_{s-\text{Ca}(\text{DDS})_2} = 12\,375 \text{ cal mol}^{-1}$$

$$\Delta H_{s-\text{Ca}(\text{DDBS})_2} = -4 \text{ cal mol}^{-1}$$

It is interesting to note that the heat of redissolution of $\text{Ca}(\text{DDBS})_2$ is almost zero in contrast to the large positive value ($12\,375 \text{ cal mol}^{-1}$) for that of $\text{Ca}(\text{DDS})_2$.

The heat of dissolution obtained from the K_{sp} values, as mentioned earlier, corresponds to the reaction



The heat of dissolution in the presence of micelles, on the other hand, represents the heat involved in the solubilization of CaR_2 by the micelle. This process can be considered to be equivalent to a dissolution reaction given by eqn. (10) and subsequent adsorption of calcium on the micelle

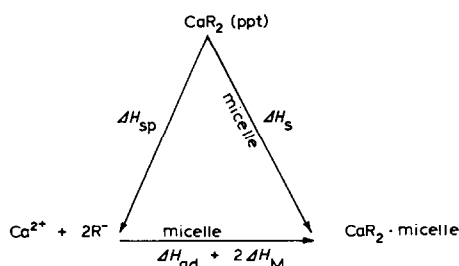
surface followed by the formation of more micelles by the surfactant released. A detailed analysis along these lines to obtain the heat of adsorption of Ca^{2+} on the micelle and a model based upon the temperature dependence data to test the validity of the above proposed molecular mechanism of redissolution are given below.

Heat of adsorption of calcium on micelles

An understanding of the micro-processes involved in the redissolution process now makes it possible to analyze further and to evaluate more thermodynamic information from data for the dependence of precipitation/redissolution on temperature.

Based upon the temperature dependence of K_{sp} and K_s , the heat of reactions, ΔH_{sp} and ΔH_s , were calculated for both NaDDS and NaDDBS in CaCl_2 solutions. While the former, ΔH_{sp} , refers to the dissolution of CaR_2 to yield Ca^{2+} and 2R^- ions, the latter corresponds to the micellar solubilization of the precipitates. Since the available results strongly suggest that redissolution occurs by a process involving adsorption of Ca^{2+} on the micelle and consequent redissolution of CaR_2 , one can obtain the heat of adsorption of calcium on the micelle in the following manner.

As the heat of any reaction is independent of the path taken to achieve the final state, but depends only on the initial and final states (Hess's Law), one can write the schematic diagram given below for the redissolution process.



Since the values of ΔH_{sp} and ΔH_{M} have already been calculated and since ΔH_{M} can be calculated from the dependence of CMC on temperature, one can determine the heat of adsorption of calcium on the micelle.

$$\Delta H_{\text{ad}} = \Delta H_s - \Delta H_{\text{sp}} - 2\Delta H_{\text{M}} \quad (11)$$

The CMC of NaDDS/ CaCl_2 was determined from the conductivity data given in Fig. 4. In the case of the NaDDBS/ CaCl_2 system, CMC was determined in the following manner. The CMC of NaDDBS was determined at different temperatures using the dye technique. Assuming a similar dependence of CMC on temperature for the NaDDBS/ CaCl_2 system, and by knowing the CMC of the latter at 25°C , the remaining values were

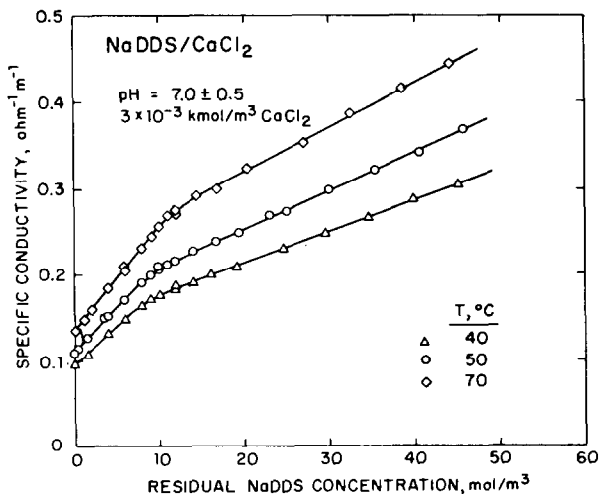


Fig. 4. Residual NaDDS concentration (mol m⁻³).

determined. The heat of micellization itself was obtained using the relation

$$\frac{\partial \ln \text{CMC}}{\partial (1/T)} = \frac{\Delta H_M}{R} \quad (12)$$

$$\ln \text{CMC} = -\frac{\Delta H_M}{RT} + \text{constant} \quad (13)$$

The values of heat of micellization of NaDDS and NaDDBS are, respectively, -1848 and -1210 cal mol⁻¹. These values are in agreement with the reported values of ΔH_M [8].

Using the experimental values of ΔH_s , ΔH_{sp} and ΔH_M in eqn. (11), the heat of adsorption of Ca²⁺ on the micelle was calculated as

$$\Delta H_{\text{ad-Ca}(\text{DDS})_2} = -2429 \text{ cal mol}^{-1}$$

$$\Delta H_{\text{ad-Ca}(\text{DDBS})_2} = -3584 \text{ cal mol}^{-1}$$

The heat of adsorption of calcium on the micelles of NaDDBS and NaDDS is found to be large and negative, the latter value being higher by about 1000 cal mol⁻¹ than the former.

A calcium adsorption model for temperature dependence of redissolution

For the above series of calculations, it was hypothesized that redissolution of the precipitate occurs due to (a) adsorption of calcium by the micelle and (b) dissolution of calcium sulfonate to replenish the solution with calcium according to the solubility product expression, and (c) formation of micelles by the released sulfonate upon dissolution of calcium sulfonate. If the above series of reactions in fact lead to the redissolution of the precipitate, then the

amount of precipitate redissolved should be proportional to the adsorption of calcium on the micelle.

$$K_s(T_i) \propto \Gamma(T_i) \quad (14)$$

where $K_s(T_i)$ is the solubilization constant at temperature T_i and $\Gamma(T_i)$ is the adsorption of calcium on the micelle. For two different temperatures, this can be modified as:

$$\frac{K_s(T_1)}{K_s(T_2)} = \frac{\Gamma(T_1)}{\Gamma(T_2)} \quad (15)$$

Adsorption of calcium can, in turn, be expressed as:

$$\Gamma(T_1) = K_{ad}c_{Ca} \quad (16)$$

where K_{ad} is the adsorption constant and c_{Ca} is the concentration of calcium in the solution. Combining eqns. (15) and (16), we obtain

$$\frac{K_s(T_1)}{K_s(T_2)} = \frac{K_{ad}(T_1)}{K_{ad}(T_2)} \frac{c_{Ca}(T_1)}{c_{Ca}(T_2)} \quad (17)$$

The concentration of calcium in the redissolution region is governed by the solubility product of calcium sulfonate and the CMC of the surfactant, i.e.,

$$c_{Ca} = K_{sp}/(\text{CMC})^2 \quad (18)$$

Also, using the Clausius–Claypeyron Equation for the dependence of K_{ad} and K_{sp} on temperature in the following form and rearranging, one can obtain

$$\frac{\partial \ln K_{ad}}{\partial (1/T)} = - \frac{\Delta H_{ad}}{R} \quad (19)$$

$$\ln \left[\frac{K_{ad}(T_1)}{K_{ad}(T_2)} \right] = - \frac{\Delta H_{ad}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (20)$$

$$\ln \left[\frac{K_{sp}(T_1)}{K_{sp}(T_2)} \right] = - \frac{\Delta H_{sp}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (21)$$

$$\ln \left[\frac{K_{ad}(T_1)}{K_{ad}(T_2)} \right] = \frac{\Delta H_{ad}}{\Delta H_{sp}} \ln \left[\frac{K_{sp}(T_1)}{K_{sp}(T_2)} \right] \quad (22)$$

$$\frac{K_{ad}(T_1)}{K_{ad}(T_2)} = \left[\frac{K_{sp}(T_1)}{K_{sp}(T_2)} \right]^{[\Delta H_{ad}/\Delta H_{sp}]} \quad (23)$$

Substituting for $K_{ad}(T_1)/K_{ad}(T_2)$ and $c_{Ca}(T_1)/c_{Ca}(T_2)$ from eqns. (23) and

(18) in eqn. (17) the final expression can be obtained as:

$$\frac{K_s(T_1)}{K_s(T_2)} = \left[\frac{K_{sp}(T_1)}{K_{sp}(T_2)} \right]^{[1+(\Delta H_{ad}/\Delta H_{sp})]} \left[\frac{CMC(T_2)}{CMC(T_1)} \right]^2 \quad (24)$$

Since all the parameters on the right-hand side of the above expression are known, the $K_s(T_1)/K_s(T_2)$ ratio for $\text{Ca}(\text{DDS})_2$ can be estimated as $K_s(40)/K_s(50) = 0.62$. The experimentally obtained value of $K_s(40)/K_s(50)$ for this system is 0.61, and is in agreement with the predictions. On the other hand the same ratio for $\text{Ca}(\text{DDBS})_2$ is $K_s(25)/K_s(50) = 0.99$. The experimentally obtained value (1.04) is again in agreement with the predicted value based upon the adsorption of calcium on micelle.

CONCLUSIONS

(1) The results for the dependence of precipitation/redissolution on temperature have been used to determine the heat of dissolution of the calcium sulfonate precipitate in water, and in the presence of micelles. Also, the heats of micelles have been estimated.

(2) A model is proposed to check the validity of calcium adsorption for the redissolution process. The experimental results and the model predictions are in agreement with each other, thus indicating that the redissolution process is caused by the uptake of calcium by the micelle.

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