Optimal Phase Diagrams and the Effect of Salt Anion Composition in a Model Surfactant System for Improved Oil Recovery

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Optimal phase behaviour of a multicomponent surfactant, brine, oil, and alcohol system can be reduced to a meaningful pseudo-ternary representation when the equivalence of two anions in the brine has been obtained.

Surfactants are of interest because they can improve the recovery of oil from reservoirs.[1] For good performance it is necessary to achieve optimal phase behaviour in which three phases are produced.[2] This means that the factors affecting the phase behaviour must be understood. As part of this objective a representative model surfactant system containing sodium dodecylbenzenesulphonate, butan-1-ol, decane, and brine is being studied. The work reported here is part of a programme aimed at constructing a phase diagram from which phase compositions and phase masses can be predicted for any overall composition. This contrasts with other work on a similar system where phase maps have been produced which do not allow such predictions to be made.[3] Three phases need to be considered and so it follows from Gibbs' phase rule that a minimum of three pseudo-components are required to represent the phase behaviour. In this work the optimal plane is described using a pseudo-ternary representation. The composition and concentration of the brine has an important influence on phase behaviour.[4] This necessitated an investigation of salt partitioning[5] and the equivalence of salt anions because sulphonate surfactants often contain sulphate ions as an impurity.

Mixtures of the components in the model system have been prepared in phase tubes and allowed to equilibrate into separate phases while held at 25 °C. Optimal systems, in which equal volumes of decane and water are solubilised into the surfactant rich middle phase, have been determined. All phases in optimal systems have been analysed for water, decane and alcohol by gas chromatography, surfactant by a two phase titration method,[6] NaCl by a conductometric titration[7] and Na_2SO_4 by a potentiometric titration using a lead selective electrode.[8] The phase compositions measured for an optimal system using a sulphate brine are shown in Table 1.

Two important observations were made. While the excess aqueous and oleic phases were found to contain some butan-1-ol, most of the alcohol partitioned with the surfactant, and salt concentrations in the middle phases were less than those in the corresponding aqueous phases.

The pseudo components for the sulphate brine are also shown in Table 1, where the pseudo brine and pseudo oil correspond to the lower and upper phases. The water associated with the pseudo surfactant was necessary to represent the salt partitioning effect.

The equivalence of mixed brines containing both Na_2SO_4 and NaCl was considered. Optimal systems were identified by salinity scans using added brines ranging from those containing only Na_2SO_4 to those containing only NaCl. These results are shown in Figure 1. It may be seen that on a weight basis the chloride is 1.7 times as effective as the sulphate (0.70 times on a molar basis). Also the ratios of anions in corresponding lower and middle phases are nearly constant as indicated by the dotted tie lines.

The salinity of the system corresponding to a pseudo ternary plane is defined as the equivalent sodium chloride concentration in the brine pseudo component. The salt equivalence diagram allows the prediction of other optimal combinations of salt components.

Electrochemical theory has been applied to these results in an attempt to model the observed equivalence between chloride and sulphate. It was assumed that the micellar phase has a lamellar structure at optimal conditions.[9] The Poisson–Boltzman equation for the electric potential between the surfactant layers was solved numerically to determine the anion distribution in the surfactant-rich phase in equilibrium with a given anion composition in the brine phase. The lower salt concentrations in the micellar phase arise because anions

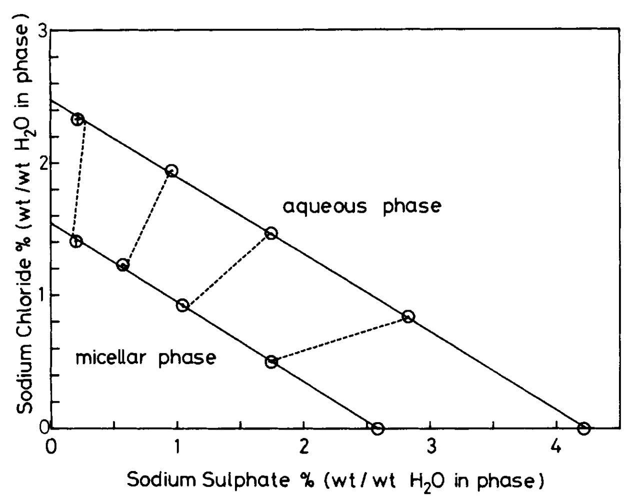

Figure 1. Optimal salinity equivalence diagram.

Table 1. Compositions of optimal phases and ternary pseudo-components. All weight percent.

	Phase composition			Ternary pseudo-components		
Components	Aqueous	Micellar	Oleic	Brine	Surfactant	Oil
Decane	0	32.1	92.3(6)	0	0	92.3(6)
Water	92.5	43.9	0.1(4)	92.5	47.0	0.1(4)
Na_2SO_4	3.90	1.13(5)	0	3.90	0	0
Surfactant	0	9.21	0	0	25.5	0
Butanol	3.63	13.6	7.51	3.63	27.5	7.51

are excluded from the negatively charged surfactant layers by electric forces. The theoretical model has also successfully predicted the salt composition in the micellar phase based on the experimental brine phase curve.

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References

1 M. C. Puerto and W. W. Gale, *Soc. Pet. Eng. J.*, 1977, 193.
2 R. N. Healy and L. R. Read, 'Improved oil recovery by surfactant and polymer flooding,' ed. D. O. Shah and R. S. Schecter Academic Press, New York, 1977, 383.
3 A. M. Bellocq, D. Bourbon, and B. Lemanceau, *J. Colloid Interface Sci.*, 1981, **79**, 419.
4 J. Biais, M. Barthe, M. Bourrel, B. Clin, and P. Lalanne, *J. Colloid Interface Sci.*, 1986, **109**, 576.
5 J. Sjoblom, C. Blom, and P. Stenius, *Acta Chem. Scand.*, 1986, 306.
6 R. W. S. Foulser, S. G. Goodyear, and R. J. Sims, ACS Symposium Series, Toronto 1988, to be published.
7 G. H. Castellan, 'Physical Chemistry,' second edition, Addison-Wesley, 728.
8 A. Hulanicki, R. Lewandowski, and A. Lewenstam, *Analyst*, 1976, **101**, 939.
9 Y. Talmon and S. Prager, *J. Chem. Phys.*, 1978, **69**, 2984.