Microcalorimetry of Surfactant Adsorption onto Sandstone

NJM. van Os G, Haandrikman
Shell Research Laboratories
Amsterdam, Netherlands
TA Instruments, 109 Lukens Drive, New Castle, DE 19720, USA

ABSTRACT

Surfactants are used in the chemical flooding of oil reservoirs in order to enhance oil recovery. However, surfactant adsorption onto reservoir minerals occurs, resulting in the waste of expensive materials and more importantly it can render the process ineffective. It would therefore be useful to gain a scientific understanding of the relationship between the chemical structure of the surfactants and their relative adsorptive properties. These include the amount of surfactant adsorbed and also the value of the Gibbs free energy of adsorption. In the past, microcalorimelry techniques have been used successfully to determine the enthalpy of displacements of solvent molecules from the surface of the adsorbent by solute molecules. The enthalpy of adsorption can be obtained only if the number of solvent molecules displaced by one solute molecule is known. In previous studies, using the batch or the immersion method, it was only possible to determine the amount adsorbed, in a separate experiment. Clearly it would be advantageous to measure simultaneously the enthalpy displacement and the adsorption isotherm. The Thermal Activity Monitor together with a liquid a liquid flow adsorption cell and a U.V. spectrophotometer has been developed for this purpose. The advantages offered by this technique include:

1. It allows the study of surfactant desorptiou from solid/liquid interfaces.
2. It enables the conditions which control adsorption and desorption, such as surfactant concentration, temperature, salinity, pH and the presence of oil and sacrificial agents, to be varied during the course of the experiment.

In this experiment the adsorption of sodium p-(2-decyl) benzene sulphonate from aqueous solution onto crushed Bentheun sandstone at 30°C is investigated.

EXPERIMENTAL

The 2277 Thermal Activity Monitor (TAM) microcalorimeter was used, and all measurements were made at 30°C, According to the specification, the thermostat bath temperature constancy was 0.0002°C. The adsorbent Bentheim sandstone (specific area of 0.35 m^2/g) was crushed and packed into a specially manufactured microcore (Fig 1) which was then inserted directly into the measuring cell of the Thermal Activity Monitor.

The microcore contained two stainless steel filters to hold the sandstone in position and could be disassembled easily for inspection and cleaning. A Waters LC spectrophotometer, model 481, was connected to the outlet of the microcore to monitor the optical density of the surfactant solution passing away from the cell. An LKB 2150 HPLC pump was used to pump water through the flow cell at a rate of 0.02 ml/min for 15 hours. After this time the baseline was stable and a noise of 0.1 microwatt was obtained. The heat of displacement was determined with solutions containing increasing concentrations of sodium p-(2-decyl) benzenesulphonate. Each new sample was injected after the exothermic curve from the previous injection had returned to the baseline. Glass beads were used as core packing in control experiments in order to determine the (endothermic) heat of dilution.

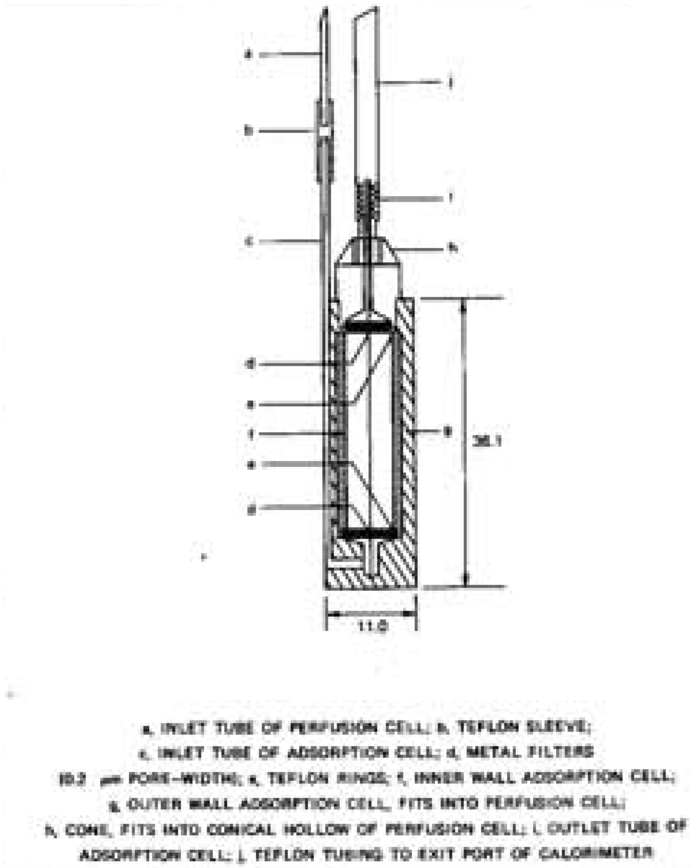

Fig 1. Section through stainless steel adsorption cell, with principal dimensions shown (mm).

RESULTS

The results of these dynamic adsorption studies are shown in Fig 2. The bottom curve indicates how the integral enthalpy of displacement changes with the equilibrium surfactant concentration. It is interesting to note that the curve attains a constant value beyond the critical micelle concentration.

The enthalpy of displacement, disH, can be obtained from Q(2) as follows:

$$disH = Q(2)-dilH$$

where dilH includes all enthalpy changes taking place in solution during dilution. The magnitude of dilH determined in the blank experiments indicated that these effects were in¬significant in the adsorption process. Similar values of dilH were obtained by Berg et al who also employed liquid-flow microcalorimetry to study surfactant adsorption from solution onto a solid surface.

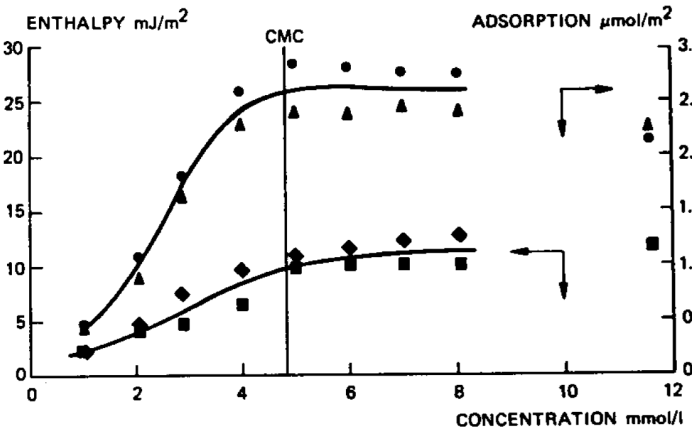

Fig 2. Enthalpy of Displacement and Amount of Surfactant Adsorbed as a Function of Bulk Surfactant Concentration.

The amount adsorbed is obtained from the LC spectroscopic data according to the method used by Noll and others. The results are shown in the top curve of Fig 2. The solid curve drawn through the experimental points is termed the adsorption isotherm and has the same sigmoidal shape as the enthalpy curve: again levelling off at a concentration similar to the CMC of the surfactant. Since the adsorption density for a close packet monolayer is estimated at 0.3 nm, it is clear that a monolayer is not formed in this experiment. From the data in Fig 2, the enthalpy of adsorption is estimated to be of the order of -5 kj/mol. This low heat effect points to the weak physisorption of the surfactant molecule on the sandstone surface.

CONCLUSION

The results indicate that:

1. The exothermic heat effect associated with the adsorption process could be observed without difficulty.
2. The enthalpy of displacement and the adsorption isotherm were determined simultaneously.

Therefore, the combination of liquid flow microcalorimetry together with a suitable system of analysis is a valuable additional tool for the future study of the adsorption process.

REFERENCES

1. Berg R L ACS Symposium Ser. **1979**, 91 p87-102
2. Noll L A US Department of Energy Report
   Dof/BETC/Rl-82/7 (DE82015392)

This Application Note has been produced by kind permission of N.M. van Os and G. Haandrikman and is based on an original entitled "Liquid-Flow Microlcalorimetry of Surfactant Adsorption onto Sandstone. 1. Experimental Method and Initial Results." Ref: Langmuir, 3,1051-1056,1987