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"THE DIRECT MEASUREMENT OF THE ADSORPTION OF CATIONIC SURFACTANTS ONTO THE SURFACE OF SLURRY SEAL AGGREGATES"

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ABSTRACT

ADSORPTION OF A SURFACTANT ONTO THE SURFACE OF AN AGGREGATE IS ONE OF THE MOST IMPORTANT STEPS IN DETERMINING THE RATE OF BREAK IN A SLURRY SEAL SYSTEM. USING SPECIFIC SURFACTANT ION-SELECTIVE ELECTRODES, IT HAS BEEN POSSIBLE TO DIRECTLY MEASURE THE ADSORPTION ISOTHERMS OF CATIONIC SURFACTANTS ONTO THE SURFACE OF SEVERAL DIFFERENT TYPES OF SLURRY SEAL AGGREGATES. ADSORPTION ISOTHERMS WERE MEASURED UNDER DIFFERENT CONDITIONS, VARYING SIGNIFICANT PARAMETERS LIKE pH, TEMPERATURE, ALUMINIUM SULPHATE CONTENT ETC.

THE RESULTS OBTAINED CORRELATED WELL WITH ACTUAL FIELD OBSERVATIONS OF REAL SLURRY SEAL SYSTEMS AND THEREFORE THE PREDICTION OF THE BEHAVIOUR OF CERTAIN SLURRY SEAL SYSTEMS IS POSSIBLE.

INTRODUCTION

The main characteristic of the use of cationic emulsions in slurry sealing is the quick curing of the mat, which is derived from the rapid coagulation and the coalescence of the emulsion, (binder). There have been many studies of the factors which influence this curing behaviour, such as temperature, aggregate type and emulsifier chemistry, but relatively few have investigated the fundamental processes occurring at a molecular level.

This paper describes the results of a new technique, which uses surfactant-ion selective electrodes to measure the concentration of emulsifiers in model slurry seal systems. These initial studies have been conducted in bitumen free systems using quaternary amine type emulsifiers. The effect of parameters such as temperature, aggregate type, pH and inorganic salts on the extent and rate of adsorption have been determined and related to the actual field observations of slurry sealing.

CATIONIC SURFACTANT ION - SELECTIVE ELECTRODES

A) THEORY

An ion-selective electrode is one which responds in a predictable manner to changes in concentration of the relevant ionic species in aqueous solution. The best known type is the pH meter, which is used to measure the concentration of hydrogen ions in water.

$$\text{pH} = -\log [\text{H}^+]$$

The feature common to most ion selective electrodes is a solid, liquid or polymeric membrane, across which a potential difference is generated in the presence of a concentration gradient of the source ions. A typical electrode system consists of the ionselective electrode and a suitable reference, (eg. calomel electrode), in contact with the aqueous solution under investigation. The electrodes are connected to a high impedance pH meter. As the concentration of the ions, (of interest) in the solution is varied, the e.m.f. measured by the pH meter changes. If the electrode reaction is fully reversible, the response should obey the Nernst equation;

$$\text{e.m.f.} = E^0 + (RT/nF) \ln (\text{Concentration})$$

Where,

E^0	=	Standard Electrode Potential
R	=	Gas Constant
T	=	Absolute Temperature
n	=	Valency of Solute Ion
F	=	Faraday Constant

For a monovalent ion at room temperature, (298K), this equation reduces to:-

$$\text{e.m.f.} = E^0 + 0.059 \log (\text{Concentration})$$

Thus a plot of e.m.f. against \log (concentration) is linear with a slope of 59mV and an intercept at \log (concentration) zero of E^0 .

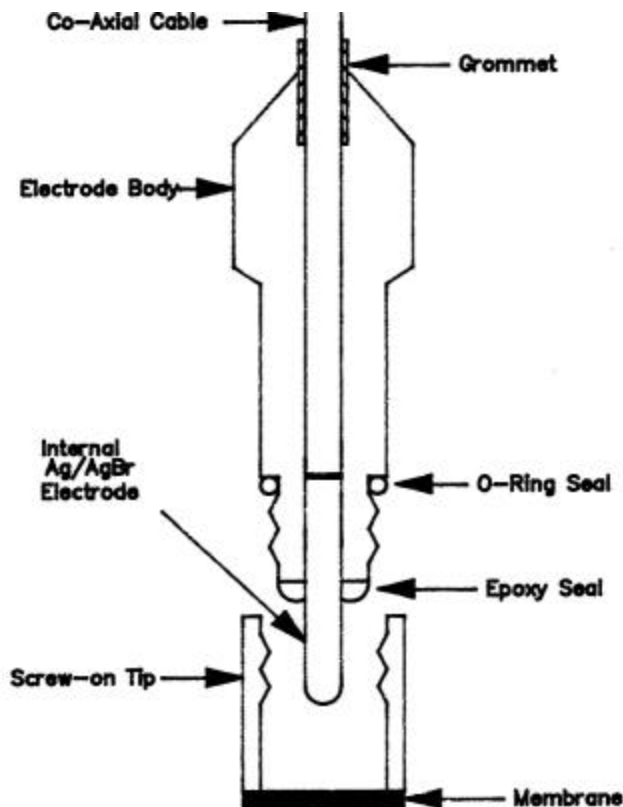
B. PREPARATION

For a cationic surfactant ion-selective electrode responsive to quaternary ammonium compounds, the electrode membrane is manufactured from PVC, which has been prepared using the radical anion $\cdot\text{SO}_3^-$ as the initiator, resulting in terminal negatively charged sulphonate groups on the polymer. The substituted PVC is dissolved in THF and the solution is mixed with an aqueous solution of the quaternary ammonium surfactant. The positively charged surfactant forms a charge complex with the negative groups on the polymer. After precipitation the polymer is washed, dried and cast into a flexible membrane. The electrodes used in these experiments were developed by the University of Salford, United Kingdom and Figure I illustrates the schematic diagram of a cationic surfactant ion-selective electrode. A circular portion of the prepared membrane is attached to the tip of the electrode, which prior to use is filled with an aqueous solution containing one millimolar cationic surfactant.

By applying the calibration equation, the residual concentration of emulsifier in solution can be calculated, and by difference, the amount of adsorbed emulsifier can be determined. An adsorption isotherm shown the variation in amount of bound surfactant against the equilibrium concentration of unadsorped emulsifier in solution may be plotted. However, because the electrodes only respond to surfactant concentrates up to the critical micelle concentration, a few measurements were made at higher concentrations by means of H.p.l.c.

Unless otherwise stated, the standard experimental temperature for the adsorption isotherm measurements was 25C. The normal pH of the system was the natural pH of 9 for both test aggregates. This is in fact the typical pH of slurry seal systems, where in the presence of cement, the complete system quickly reaches a pH of 9 to 10, (Figure II).

FIGURE I
Schematic Diagram of Cationic Surfactant Ion Selective Electrode



EXPERIMENTAL

a) EMULSIFIERS

Quaternary amine surfactants with C_{12} and C_{14} alkyl chains were used as "model emulsifiers".

b) AGGREGATES

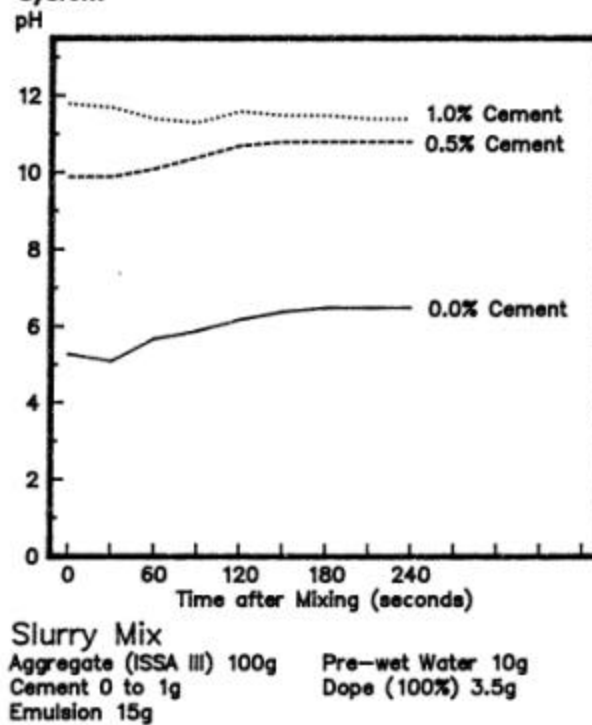
Two slurry seal aggregates were used during these initial studies. A porphyry type aggregate from the Bardon Hill Quarry in the United Kingdom and Moranium type aggregate from West Germany. The Moranium aggregate is known to give problems of application, (poor binder adhesion).

Only the fraction below 1.7mm was used for these experiments. This fraction contributes most of the surface area to the aggregate grading.

c) CELL CONCENTRATION

Adsorption isotherms were measured using a ratio of 6g of aggregate to 30 ml of water, (200g per litre). This ratio is necessary to fully wet the electrode with solution. Although not typical of a real slurry, it is similar to the concentration of just the <1.7mm fraction in certain slurry seal systems.

FIGURE II
Variation of pH within a complete. Slurry Seal System



d) METHOD

Before the electrode system can be used to measure an adsorption isotherm, the system must be calibrated. The concentration of the cationic surfactant in the cell is increased by adding small aliquots of a 0.1 molar solution and recording the corresponding changes in e.m.f. after each addition.

The results are plotted as e.m.f. against log (concentration), and linear regression is performed to formulate the equation of the calibration plot. The electrode only responds to monomeric emulsifier, and micellised emulsifier is not detected.

The titration is repeated but this time 6g of aggregate have been added to the cell, and the e.m.f. is recorded after each aliquot of surfactant. These e.m.f. measurements are lower than in the absence of aggregate and are proportional to the amount of surfactant, which has been adsorbed from solution onto the aggregate.

RESULTS AND DISCUSSION

There are very clear limitations in the results obtained in this paper. The selection of surf actant type and a bitumen free system, coupled to the experimental nature of cationic surfactant-ion selective electrodes could lead to erroneous conclusions. Therefore the observed results can only be considered to be valid for the specific condisions under which the experimental data was collected.

a) EFFECT OF pH

Figure III illustrates the relationship between pH and surfactant adsorption. The expected trend is apparent, where quaternary adsorption increases as the pH rises, ie as the negative charge on the

aggregate becomes correspondingly greater. However, there is an anomaly to this general trend, where the adsorption in 0.1M NaOH is less than that in water. This could be due to partial neutralisation of the negative charge on the aggregate by the adsorption of sodium cations from solution. Although such adsorption takes place in all of the experiments, it is most significant in solutions of high ionic strength.

b) EFFECT OF TEMPERATURE

The effect of temperature can be considered to be one of the most significant factors in determining the performance of a slurry seal system. Therefore, it was surprising to find that the adsorption of surfactant is independent of temperature, (Figure IV) These results are consistent with earlier studies by Akzo of the adsorption of a surfactant onto fumed silica, where again no change in adsorption with temperature was observed.

The electrode has a relatively slow response time (approximately 30 seconds), but it is clear that adsorption is substantially complete after this time, even at 5°C. Thus the slow curing of seals at this temperature is not due to slow emulsifier adsorption, but probably more related to the slow evaporation of water and the viscosity of the binder.

Also this lack of temperature dependence may be an isolated phenomenon, due to the nature of the "model" system.

c) EFFECT OF ELECTROLYTES

Electrolytes can be introduced into slurry sealing in several different ways. They are added via the emulsion for example, as calcium chloride, (added to improve emulsion quality and storage stability); as dopes, eg aluminium chloride or sulphate, to retard the break; and the incorporation of cement in the slurry mix leads to high calcium ion concentrations.

Figure V illustrates the effect of electrolytes on the adsorption isotherms of quaternary ammonium surfactants. The effect of inorganic electrolytes is strongly dependent on the nature of the added cations. A reduction in the level of quaternary adsorption is only achieved after the addition of 0.02M CaCl_2 , whereas adsorption is completely eliminated by the presence of 0.005M $\text{Al}_2(\text{SO}_4)_3$.

The inhibition of quaternary adsorption is probably a result of competitive adsorption of the inorganic cations onto the surface of the aggregate, (c.f. effect of 0.1M NaOH solution). Tripositive aluminium ions have a much greater effect than dipositive calcium ions. The break retarding properties of aluminium ions can be explained and the possible interference of aluminium ions in the adhesion of bitumen to aggregate in a curing seal can be inferred, by the aluminium ions being considered to form a layer or barrier between the bitumen and aggregate.

Cement also has a retarding effect on the break of emulsions stabilised with quaternary amine emulsifiers. As cement dissolves within the system, calcium ions are released and the retarding effect increases.

Figure III
Variation of Surfactant Adsorption with pH

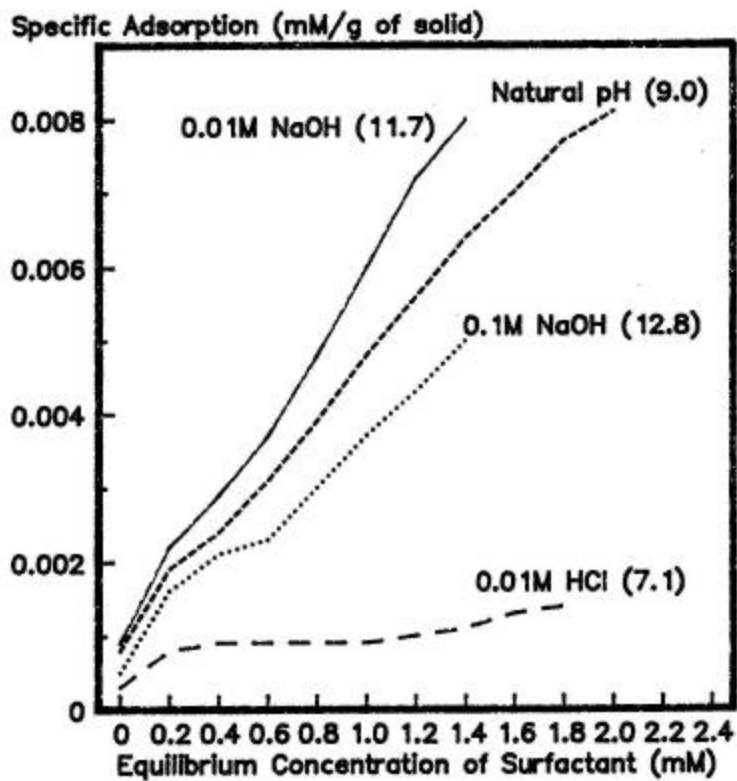


FIGURE IV
Relationship between Surfactant Adsorption and Temperature

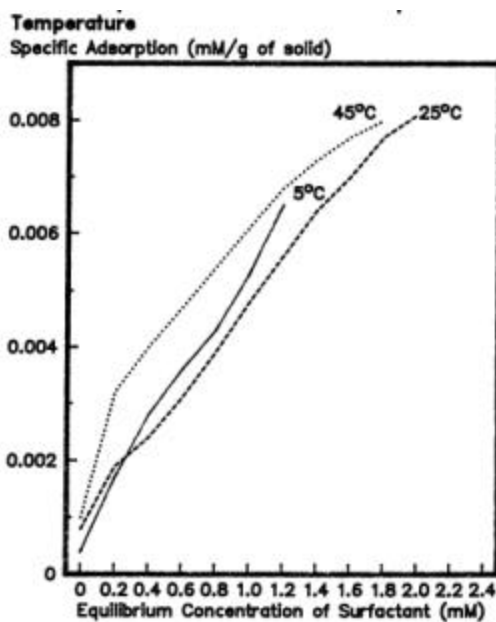
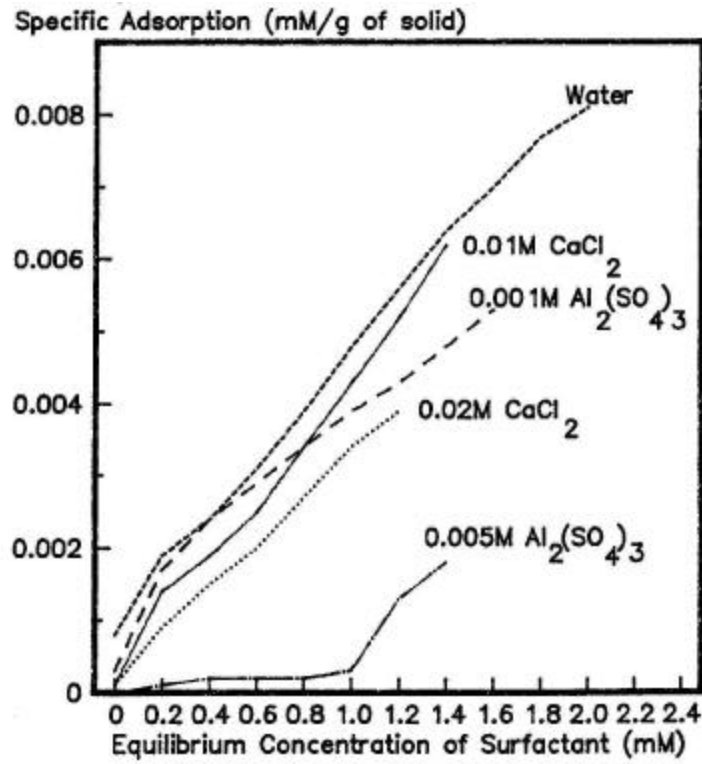


FIGURE V
Relationship between Surfactant Adsorption and Electrolytes



d) EFFECT OF AGGREGATE SURFACE CHEMISTRY ON SURFACTANT ADSORPTION

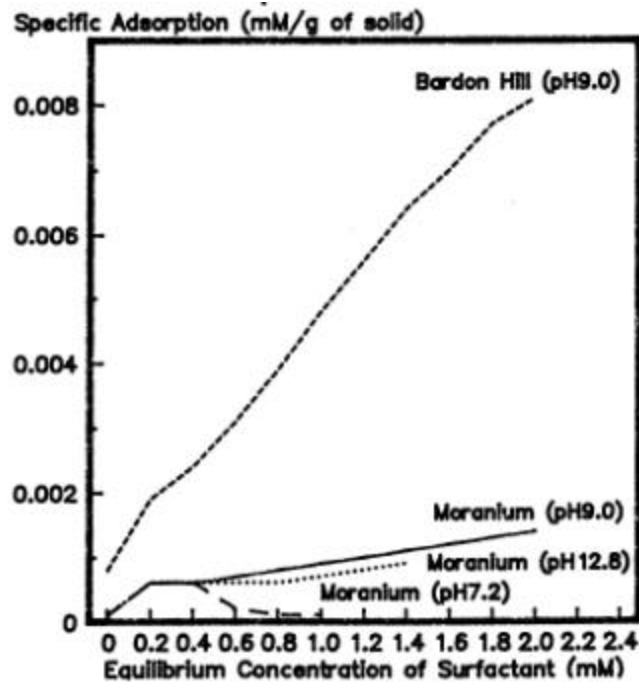
It is well known that the type and source of an aggregate has a very important role in determining the performance of a slurry seal system. Figure VI shows the differences in adsorption behaviour for known "good" and "difficult" aggregates when used in conjunction with model surfactants.

The adsorption of surfactant onto Moranium aggregate is very low at all values of aqueous phase pH, when compared with that onto Bardon Hill aggregate. A possible reason for these adsorption differences are variations in specific surface areas between both aggregates. However, the surface areas of Bardon Hill and Moranium aggregates were found to be 3.3 and 1.5 m²/g respectively₁ (BET N₂ adsorption), and this difference is insufficient to account for the large variation in adsorption behaviour, which must instead be attributed to a contrast in the surface chemistry of the two aggregates.

Both materials are of variable composition, but generally Bardon Hill aggregate is aluminosilicates, whereas Moranium aggregate contains a significant quantity of limestone.

However, the performance behaviour of Moranium aggregate can be dramatically improved by formulating a surfactant system specifically designed to cope with the lower adsorption capacity of Moranium aggregate.

FIGURE VI
Effect of Aggregate Surface Chemistry on Surfactant Adsorption



CONCLUSIONS

Because slurry seal sealing is a multi-component system, actual field application and the chemical interactions within the system are very complicated. Most theories of emulsion breaking can only surmise on the reaction between cationic surfactants and aggregates. The development of cationic surfactant ion - selective electrodes enables the direct monitoring of the physico-chemical reaction between surfactants and aggregate particles. Initial studies have measured the adsorption isotherms of quaternary surfactants, varying significant parameters which are known to influence the break of slurry seal systems.

- i) Considering pK the expected trend was found where surfactant adsorption increases as pK rises.
- ii) Perhaps unexpectedly temperature has no effect on quaternary adsorption. Therefore, other system parameters could be more important ie, water evaporation, binder viscosity etc.
- iii) Positive electrolytes react with negative aggregate sites and therefore limit quaternary adsorption.
- iv) As would be expected the actual surface chemistry of aggregates are very important in determining the adsorption of surfactants.

FUTURE DEVELOPMENTS

Research and Development will eventually allow the technique of ion selective surfactant electrodes to be used routinely as say pH meters. Thus eliminating the estimation of the free surfactant concentration within the system.

For the road industry, this will mean the exact monitoring of the break of emulsions and therefore the corresponding improvement in the quality of road construction maintenance.