ISSN 1110-0354
Bull. Nat. Inst. of Oceanogr. & Fish., A.R.E., 1997. Vol. (23): 103-110

ANIONIC DETERGENTS ADSORPTION ON THE SURFACE OF CALCIUM CARBONATE CRYSTALS (CALCITE)

BY

S. K. HAMDONA* AND TH. H. MAHMOUD

*National Institute of Oceanography & Fisheries, Alexandria, Egypt.

Key Words: Anionic Detergents, Adsorption, Calcium Carbonate

ABSTRACT

Anionic detergents adsorption on the surface of calcium carbonate crystals has been investigated as a function of concentration of detergents, amount of calcium carbonate crystals, time of adsorption and temperature. The experimental data has been interpreted according to Langmuir adsorption isotherm.

INTRODUCTION

Formation of calcium carbonate scales in water purification, energy production technology, water and waste water pipes is a persistent problem (Nancollas and Sawada, 1982; Weijnene, *et al.* 1983). In many cases, formation of hard crystalline deposits limits the efficiency of a particular process or plant design. Whenever crystals grow; the rate of growth may be strongly affected by the presence of non-constituent ions or molecules. The reduction in the growth rate may be interpreted by the adsorption of the non-constituent at the active sites on the crystal surface (Hamza and Nancollas, 1985; Hamdona and Khader, 1993, Hamza and Hamdona, 1992).

Detergents are synthetic surface-active compounds which inter the water with municipal and industrial effluents. Commercial products contain active compounds in the form of surfactants and aids. The cationic detergents, on the other hand, are mainly found in the industrial wastes. The active substances present in the majority of synthetic detergents consist of a series of alkyl benzene sulphonate (ABS), some of which are resistant to oxidation and treatment (Cosovic ***et al.***, 1979).

The main hazards in the marine environment presented by detergents contained in domestic sewage are the effects on several living species and larvae. This harmful effect of detergents may result from their general impact on the biogeochemical cycles of other pollutants and biogenic elements. Detergents affect markedly the solubility and the physicochemical state as well as the accumulation of heavy metals, hydrocarbons and other microconstituents.

With regard to the Egyptian coastal areas, the anionic detergent content in the Alexandria coastal waters is relatively high. Detergents ranges in Abu Qir Bay (0.0-4.71 mg eq. LAS l^{-1}) and Eastern Harbour (0.05-3.06 mg eq. LAS l^{-1}) is much higher than obtained in Lake Borollos (0.0-0.89 mg eq LAS l^{-1}) and El-Mex Bay (0.08-1.70 mg eq LAS l^{-1}) Mahmoud and Beltagy (1988) and Mahmoud (1989, 1990, 1991).

In the present work, the adsorption of anionic detergents on the surface of calcium carbonate crystals have been studied. The effect of time, amount of crystals, concentration of detergents and temperature has been investigated.

EXPERIMENTAL

Adsorbent:

Calcium carbonate crystals were prepared by a method similar to that used by Reddy and Nancollas, (1973). The crystals were aged at least one month before being filtered to obtain the dry crystals that were used in the adsorption experiments. The crystals were confirmed as calcite by X-ray powder diffraction (Shimadzu XD-3 diffractometer). The specific surface area (SSA) of crystals, measured using a single point nitrogen adsorption apparatus, was 0.63 ± 0.01 m^2 g^{-1}.

Adsorbate:

Solutions of anionic detergent were prepared using triply distilled, deionized water. Solutions were carefully filtered through Millipore (maximum) pore size

100 nm filter and diluted as required. Concentrations of anionic detergents were determined using methylene blue method as described by Standard Method for the Examination of water and waste water (1981).

Adsorption Experiments :

Accurately weighted samples of the calcite crystals were placed in tightly stoppered bottles containing a given volume of saturated calcium carbonate solutions. The suspensions were dispersed, by shaking for 30 min before a measured volume of the adsorbate solution was added. The amounts adsorbed were taken as the differences between the initial and final concentrations. With each bath of equilibrating samples; controls without adsorbent were included. In no case adsorption onto the bottle was detected.

Analytical Methods :

The solutions were filtered through 0.22 μm Millipore filter, which had been prewashed in order to remove any residual wetting agents or surfactants. Then, they were analyzed by using methylene blue method.

RESULTS AND DISCUSSION

Experiments to study adsorption of anionic detergent on the surface of calcite crystals suspended in saturated calcium carbonate solution have been performed at 25°C. The time allowed for adsorption varied between 5 min and 24 h, but it was confirmed that adsorption was effectively completed within 15 min as shown in Fig.1, which shows the adsorption of anionic detergent on the surface of calcite crystals until 35 min only. All experiments in this work were performed at constant time 30 min.

Experiments for studying the influences of the amount of seed on the adsorption of anionic detergent on the surface of calcite crystals at different concentrations from detergent solutions has been given as shown in Fig.2. It was found that as the amount of seeds adsorbed increase, the amount of anionic detergent increase. This may be due to the increases of the active sites on the surface of the crystals.

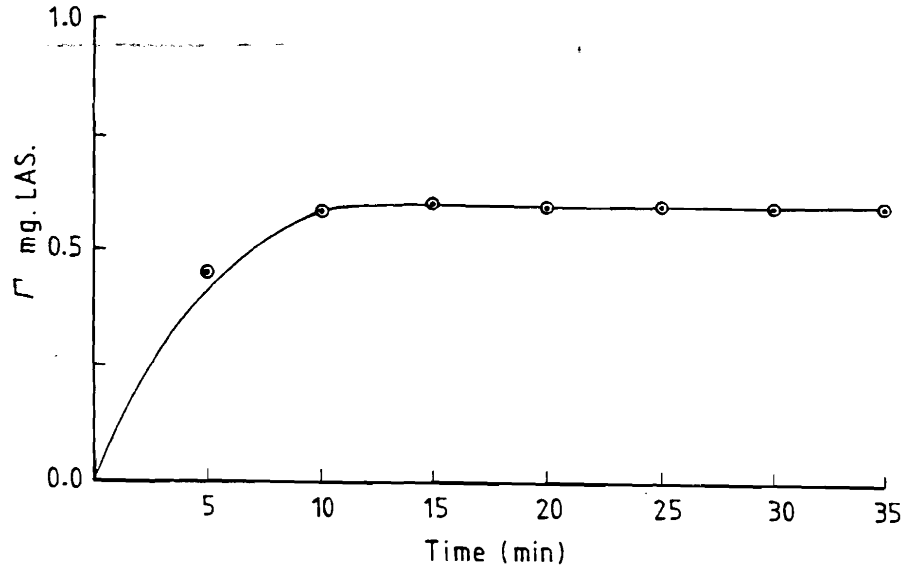

Fig. (1). Adsorption isotherm of anionic detergents onto calcite crystals at equilibrium. Plots Γ against (time).

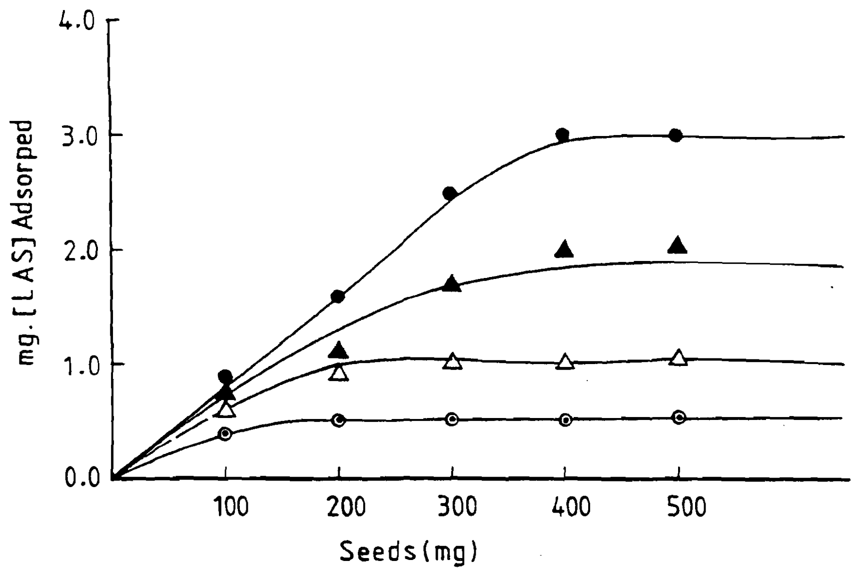

Fig. (2). Adsorption isotherm of anionic detergents onto calcite crystals at equilibrium. Plots Γ against amount of seeds (mg). 50 μg (⊙), 100 μg (△), 200 μg (▲) and 400 μg (●).

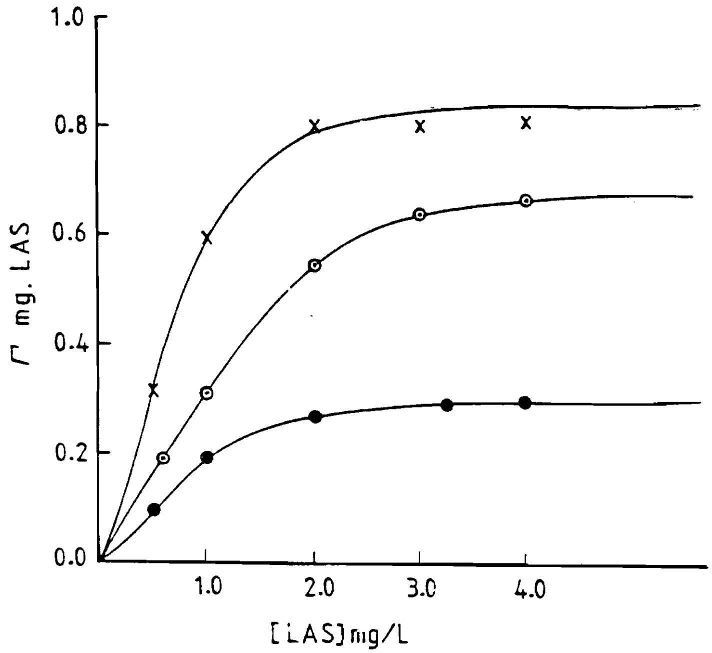

Fig. (3). Adsorption isotherm of anionic detergents onto calcite crystals at different temperture. Plots of Γ against [LAS] at 25°C (x), 35°C (⊙) and 50°C (•).

Effect of temperature on the adsorption of detergent on the surface of calcium carbonate has been performed at constant amount of seed (100 mg) and 30 min as shown in Fig.3. It can be seen that increase in the temperature decreases the adsorption of detergent on the crystal surfaces of calcium carbonate.

In all cases it was confirmed that the experimental isotherms correspond to the Langmuir-type model. The Langmuir isotherm can be derived from either kinetic or equilibrium arguments (Harkins and Wampler, 1931; Harkins and Alexander, 1959) and is most commonly applied to the chemisorption of gases. The appropriate form of the isotherm as applied to solutions may be given by:

$$\theta = KC / 1+KC \qquad (1)$$

where θ is the fraction of the solid surface covered by adsorbed molecules and K is a constant at constant temperature. Where, $\theta = N/N_m$, N is the number of moles adsorbed per gram of solid at an equilibrium solute concentration C and N_m is the number of moles per gram required to form a monolayer. Making this substitution and rearranging Eq.(1), we obtain:

$$C/N = 1/KN_m + C/N_m \qquad (2)$$

Plot of C/N versus C will yield a straight line from which K and N_m can be obtained from the slope and intercept, respectively.

It was found that the linearity of all of the plots of experimental data according to equation (2) given in Fig.4, indicates, therefore, that the adsorption model is quite adequate for the treatment of adsorption with the present detergent on calcium carbonate crystals. The adsorption parameters of anionic detergent under study were obtained from linear regression of data such as shown in Fig.4. The numerical values of these parameters are given in Table 1. It can be seen that the affinity constant K increases with decreasing the temperature, which reflects the higher adsorption at low temperatures.

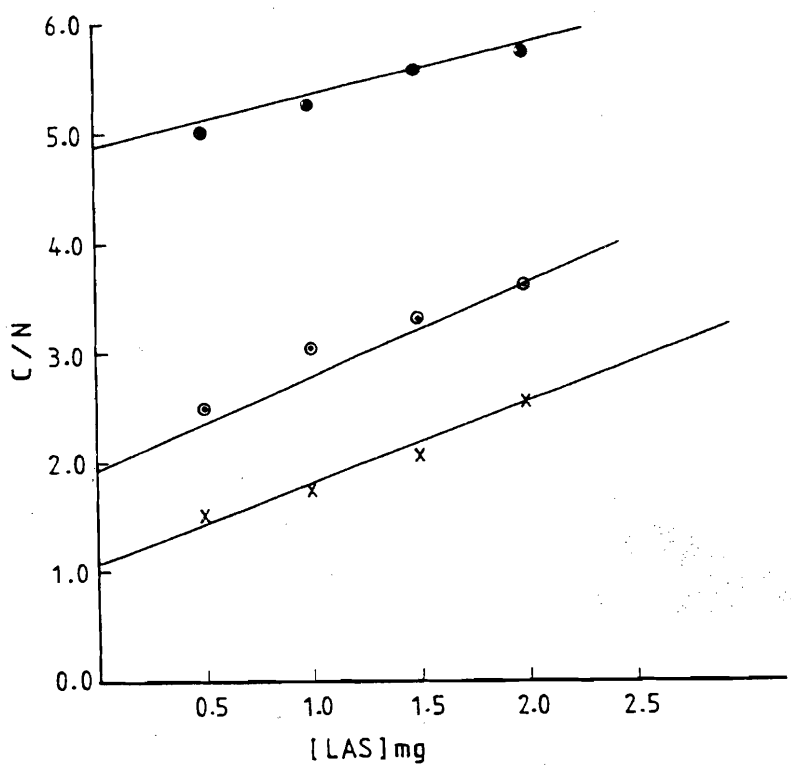

Fig.(4). Adsorption isotherm of detergents at different temperture. onto calcite crystals at equilibrium. Plots C / N against [LAS] at 25°C (x), 35°C (⊙) and 50°C (●).

Table (1): Adsorpation parameter of detergent onto calcite crystals at 25°C, 35°C and 50°C.

T	N_m 10^5. mol. gm^{-1}	K 10^5. mol^{-1}
298	1.3	6.80
308	1.4	3.73
323	2.0	1.02

REFERENCES

Cosovic, B., Zutic, V., Kozarac, Z., Vojvodic, V. and Novokovic, T., 1979. Investigation of surfactants in the period of 1974 to 1978. Evaluation of natural variations and pollution effects. Rapp. Comm. Int. Mer Medit; 25/26, 9: 55-60.

Hamdona, S.K. and Khader, A.M., 1993. Influence of some metals ions on the spontaneous precipitation on calcite crystals. Afinidad L1, 450, 117-121.

Hamza, S.M. and Nancollas, G.H., 1985. Constant composition study of the kinetic of the dissolution of strontium fluoride in aqueous solution, J. Chem. Soc., Faraday Trans., 1. 81, 1833.

Hamza, S.M. and Hamdona, S.K., 1992. Dossolution of calcium carbonate crystals: A constant composition kinetic study. J. Chem., Soc., Faraday Trans., 88 (18), 2713-2716.

Harkins, W.D. and Alexander, A.E., 1959. Determination of surface and Interfacial Tension, in A. Weissberger (ed.), "Technique of Organic Chemistry" 3rd ed., Vol.I, Part 1, Chap. XIV, Interscience, New York.

Harkins, W.D. and Wampler, R.W., 1931. The activity coefficients and the adsorption of organic solutes: I- Normal Butyl alcohol in aqueous solutions by the freezing point method. J. Amer. Chem. Soc., 53, 850.

Mahmoud, Th.H. and Beltagy, A.I., 1988. Detergents in Lake Borollos. Rapp. Comm. Int. Mer Medit, CIESM, 31 (2) 72.