THE ROLE OF THE HYDROCARBON CHAIN OF ALKYL COLLECTORS IN FLOTATION

by D. W. Fuerstenau, T. W. Healy and P. Somasundaran

The flotation behavior of quartz in the presence of alkyl ammonium acetates as a function of alkyl chain length has been interpreted in terms of hemi-micelle formation at the solid-liquid interface. The van der Waals cohesive free energy that is responsible for hemi-micelle formation has been found from these results to be 1.0 kT per CH_2 group. This is in excellent agreement with literature values obtained from research on the properties of micelles in bulk systems.

Collectors of the type $CH_3(CH_2)_{n-2}CH_2$-P, where P is a polar group and n is the number of carbon atoms in the straight alkyl chain, will induce flotation of an appropriate mineral at lower concentrations as n increases. This reduction in collector concentration with increasing n has been reported for such systems as xanthates on sulfides[1,2] and amines on quartz.[3] The effect of chain length of alkyl surfactants on such solution properties as conductivity,[4] surface tension,[5] and solubility[6] and such interfacial properties of solids as contact angle[7] and electrokinetic potential[8] have received considerable attention, but only limited quantitative descriptions of the effects have been given. The electrokinetic studies of alkyl amine salts on quartz indicated that the solution concentration of collector at which the marked change in electrokinetic potential of quartz occurs decreases systematically as the length of the alkyl chain increases.

The aim of the present work was to obtain a quantitative description in terms of current theories of flotation of the effect of the hydrocarbon chain of alkyl ammonium acetates on the flotation behavior of quartz.

BASIC PRINCIPLES

The marked changes in electrokinetic potentials of quartz in dodecylammonium acetate (DAA) solutions were postulated to result from the association of adsorbed collector ions into two-dimensional aggregates, called hemi-micelles.[9] Subsequently, the rapid increase in flotation rate of quartz was shown to coincide with hemi-micelle formation.[10] We would like to discuss briefly the concept of hemi-micelles in terms of recent interpretations of micelles in bulk solution.

Micelle hypothesis: In dilute solutions, alkyl ammonium and related salts behave as ordinary strong electrolytes, but at a certain concentration there is a marked change in physical properties of the solutions, e.g., in equivalent conductance, transport number, freezing point lowering and viscosity. To account for these phenomena, McBain[11] introduced the concept of micelles, which are aggregates of long-chain ions. It is believed that the ionic heads of the constituent ions of the micelle are in contact with water, whereas the nonpolar groups turn away from it and are in contact with each other.

Work must be done to bring these charged polar groups together, but energy is gained (i.e., so called van der Waals cohesive energy) when hydrocarbon chains are expelled from the water and allowed to associate. For a given polar group, the tendency to form micelles will therefore strongly depend on the hydrocarbon chain length. Theoretical treatments of micelle formation by Shinoda[12] and Phillips[13] and others lead to the following expression for the concentration at which micelles form (the critical micelle concentration or cmc) in aqueous solutions of long-chain electrolytes

$$C_M = A \exp\left[(W_e - n\phi')/kT\right] \qquad [1]$$

where C_M is the cmc in mole per liter, A is a constant, W_e is an electrostatic free energy term that describes the process of bringing the polar groups together, and ϕ' is the cohesive free energy per CH_2 group. Stigter and Overbeek[14] have pointed out that ϕ' should be replaced by a term of the form $(\phi'' - TS'')$, where S'' is the entropy per CH_2 group associated with the decrease in the number of free kinetic units upon micelle formation. The quantity ϕ'' is the energy gained by a system when a CH_2 group is removed from an aqueous environment. Values of ϕ' [or better, $(\phi'' - TS'')$] have been found to be in the range 1.0 to 1.1 kT.[12-16]

Since several workers have found that plots of log

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C_M vs n are linear[15,16] the W_e term must have a negligible dependence on n.

Hemi-micelle hypothesis: In dilute solutions DAA and related ions are found to adsorb as individual counter ions in the electrical double layer at the quartz-solution interface.[3,17] As adsorption of the surfactant ions increases, van der Waals cohesive forces between adjacent hydrocarbon chains becomes effective. This interaction effectively increases the number of adsorption sites at the surface over those that would be possible if the adsorption of the collector were limited to electrostatic adsorption as counter ions in the double layer.

Shafrin and Zisman[18] have discussed the association of adsorbed organic molecules in terms of an increase in packing fraction as the adsorbed molecules pack together on the surface. In terms of mechanism, this type of adsorption is more involved and can be interpreted more satisfactorily by the concept of hemi-micelles.

If hemi-micelle formation occurs, ions should be adsorbed individually at low concentrations, but at higher concentrations there should be marked changes in interfacial parameters as the adsorbed collector ions associate into hemi-micelles. Fig. 1 presents a plot of a number of interfacial parameters for the system quartz-dodecylammonium acetate (DAA) at pH 6 to 7 and 20° to 25°C. In Fig. 1, the following parameters are plotted as a function of the concentration of DAA:

1) contact angle (after Morrow[17]), 2) adsorption density (after de Bruyn[3]), 3) zeta potential (after Fuerstenau[6]), and 4) Hallimond tube flotation recovery (present work).

For DAA and quartz at neutral pH, hemi-micelle formation occurs at approximately 10^{-4} M DAA, as shown by the marked changes in the parameters presented in Fig. 1. The expected marked increase in adsorption is accompanied by the concomitant rapid change in the zeta potential. Contact angle and flotation recovery also increase abruptly at the hemi-micelle concentration showing that these phenomena depend primarily on the formation of aggregates of long-chain ions at the solid-liquid interface.

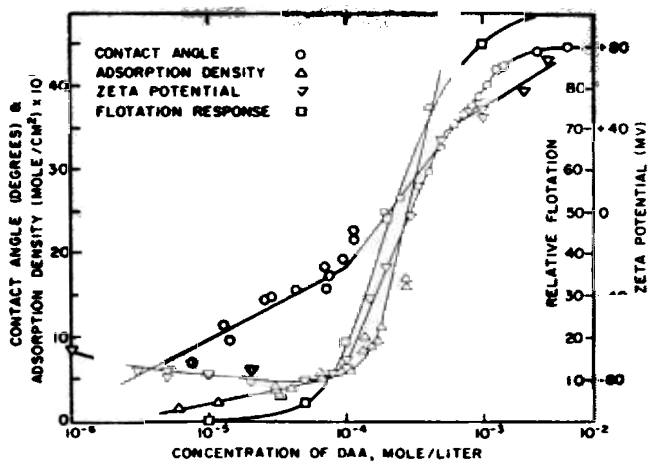

Fig. 1 — Correlation diagram of contact angle, adsorption density, flotation response, and zeta potential for quartz as a function of dodecylammonium acetate concentration at pH 6 to 7, 20 to 25° C.

Experimentally, the Hallimond tube can be operated to yield data that indicate the dependence of the relative rate of flotation on the chemical composition of the aqueous phase.[20] This is accomplished by performing the experiments at some fixed flotation time, aeration rate and agitation degree such that 100% recovery is obtained when the maximum contact angle is reached.[10] In the quartz-DAA system, these particular conditions are approximately achieved with a 5-sec flotation period, and accordingly data for 5-sec flotation recovery are plotted in Fig. 1. Thus, the flotation data in Fig. 1 indicate the flotation response of quartz with DAA as collector at concentrations relative to the concentration at which maximum contact angle is reached.

The correlation diagram (Fig. 1) again emphasizes the fact that surface phenomena which reflect conditions at the solid-liquid interface (adsorption density and zeta potential) can be correlated directly with surface phenomena that reflect conditions at the solid-liquid-gas triple contact (contact angle and flotation experiments). This figure, together with the recent work of Jaycock and Ottewill,[19] certainly must dispel the rather common belief that adsorption and electrokinetic phenomena cannot be correlated directly with flotation because of the different interfaces involved.

The research reported in this paper has been designed to interpret quantitatively flotation in terms of hemi-micelle formation and the van der Waals cohesive energy between hydrocarbon chains.

EXPERIMENTAL MATERIALS AND METHOD

Brazilian quartz (48 × 65 mesh) was used for determination of Hallimond tube flotation recoveries. After the material was leached with concentrated hydrochloric acid, it was washed free of chloride ions and stored in distilled water. The long-chained amines (octyl through octadecyl amine were obtained from Armour and Co., Chicago, Ill., and butyl and hexyl amine were obtained from Matheson Co., Inc., Norwood, O.) were dissolved in anhydrous ether and added to an equimolar quantity of glacial acetic acid. The acetate obtained was recrystallized from anhydrous ether, dried at room temperature in a dessicator, and stored at 0°C. The recovery of quartz by flotation as a function of concentration of various collectors was measured in a modified Hallimond tube using a 1-cm coarse glass frit for gas introduction.[20] About 0.7 g of 48 × 65 mesh quartz was conditioned in a 100 cc volumetric flask for a predetermined time in the absence of air bubbles and then

transferred into the Hallimond tube. The glassware and Hallimond tube were preconditioned with the collector solutions (distilled water plus the aminium acetate at neutral pH) so that none of the collector would be abstracted by these materials from the flotation solution. All flotation experiments were performed under neutral pH conditions at constant agitation and aeration rate (36 ml per min).

RESULTS

Fig. 2 presents the variation of Hallimond tube flotation recovery with concentration of dodecylammonium acetate (DAA) for various flotation times. These curves clearly demonstrate how Hallimond tube flotation tests show relative floatability and that all conditions should be kept as constant as possible. No flotation occurs in solutions containing less than about 4×10^{-6} *M* collector, but above this concentration Hallimond tube flotation response is very time dependent. For long flotation periods, recovery appears to be complete at about 10^{-4} *M*. This same concentration also appears to be important for short flotation periods. The arrow drawn on Fig. 2 indicates that the concentration of collector at which the rapid rise in recovery takes place is shifted with decreasing flotation time into the region of 10^{-4} *M* DAA in the limit of zero time.*

*The collector concentration necessary for rapid increase in Hallimond tube flotation recovery in the limit of zero time appears to be a real situation. Consider a limiting sized column of air bubbles located in the frit and the stirred bed of mineral particles. The limiting (minimum) number of bubbles is determined by the apparatus; namely, by the size of individual bubbles, the mass of mineral to be floated, and the maximum load that a bubble can accommodate but still levitate. Flotation in the limit of zero time corresponds to this limiting sized bubble column being allowed to pass through the stirred bed of mineral. Suppose the limiting column contains *N* bubbles. Then for a collector concentration in the region of the hemi-micelle concentration a column of less than *N* bubbles will give a percentage recovery approaching zero while a column of greater than *N* bubbles will give a percent recovery approaching 100. This concentration to give rapid flotation in the limit of zero time must be the concentration of hemi-micelle formation for the system dodecylammonium acetate-quartz at pH 6 to 7.

The variation of Hallimond tube flotation recovery of quartz with alkyl ammonium acetate concentration

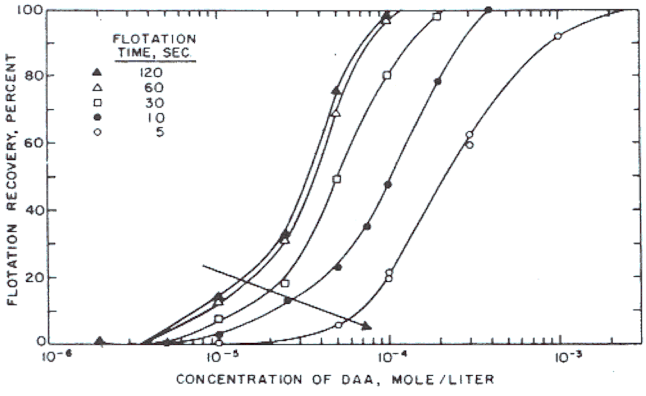

Fig. 2 — The effect of flotation time on the Hallimond tube flotation recovery of quartz as a function of the concentration of dodecylammonium acetate.

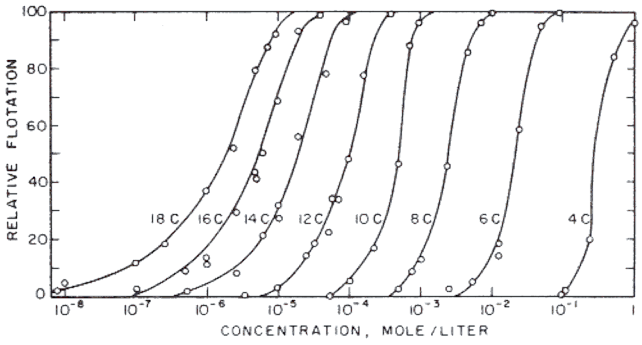

Fig. 3 — The effect of alkyl chain length on the relative flotation response of quartz in the presence of alkyl ammonium acetate solutions.

at pH 6 to 7 for alkyl chain lengths of from 4 to 18 carbon atoms is given in Fig. 3. Note that for this study of the effect of chain length, the more convenient time of 10 sec was arbitrarily selected for the flotation experiments. This is permissible since we are concerned primarily with the relative effect of chain length on flotation. It can be seen that as the chain length increases there is a decrease in the concentration at which a given flotation recovery is obtained. It should be remembered that the solubility of these reagents decreases with increasing chain length and reagents containing more than 16 CH_2 groups may not be completely dissolved.

DISCUSSION

The theory of hemi-micelles can be approached by expressing the adsorption density within the Stern plane of the electrical double layer in the form[21,22]

$$\Gamma_i = 2rC \exp[(-W_e' + n\phi')/kT] \qquad [2]$$

where W_e' and $n\phi'/kT$ are as previously defined, Γ_i is the adsorption density, r is the radius of the organic ion, and C is the equilibrium bulk concentration of the organic ion. If we select the hemi-micelle concentration, that is $C = C_{HM}$, so as to examine the effect of chain length on the system, then rearranging Eq. 2 gives

$$C_{HM} = \left(\frac{\Gamma_i}{2r}\right) \exp[(W_e' - n\phi')/kT]. \qquad [3]$$

Eq. 3 and 1 are of similar form, which strengthens the assumption that hemi-micelle formation at the interface is exactly analogous to micelle formation in the bulk. In the case of hemi-micelles, the aggregates are anchored with the polar head groups oriented toward the surface. Thus, Eq. 1 becomes

$$C_{HM} = A' \exp[(W_e' - n\phi')/kT] \qquad [4]$$

where C_{HM} is the hemi-micelle (bulk) concentration, A' is a constant, W_e' is the electrostatic adsorption energy, and ϕ' (as in Eq. 1) is the van der Waals cohesive free energy per CH_2 group.

Expressing Eq. 3 in terms of natural logarithms

leads to

$$\ln C_{HM} = -(\phi'/kT)n + \ln\left(\frac{\Gamma_i}{2r}\right) + W'_e. \qquad [5]$$

Since hemi-micelle formation depends on the interaction between hydrocarbon chains, the chain length effect is a critical test of the theory. To test this exactly, the region of hemi-micelle formation would have to be found by experiments of extremely short flotation times, that is about 5 sec or even slightly less. But since flotation in a Hallimond tube is a relative phenomenon, the effect of change in concentration observed at the more convenient time of 10 sec should parallel that for 5-sec flotation. For our purposes, a concentration parameter is located by extrapolating the linear steeply rising portion of each curve in Fig. 3 to the concentration axis.*

*The construction is the usual method of analysis of phenomena which give S-shaped curves of the type shown in Fig. 3, for example, determination of coagulation values from light scattering curves.[23]

Eq. 5 suggests that a straight line might be obtained by plotting the logarithm of C_{HM} vs the chain length of the collector. In Fig. 4, the logarithm of the above mentioned parameter (which has been assumed to be proportional to the C_{HM}) is plotted as a function of the number of carbon atoms in the alkyl chain of the collector. Fig. 4 indicates that a linear relation does exist between the logarithm of the concentration parameter and the number of carbon atoms in the collector chain. The slope of this line is 1.0±0.1

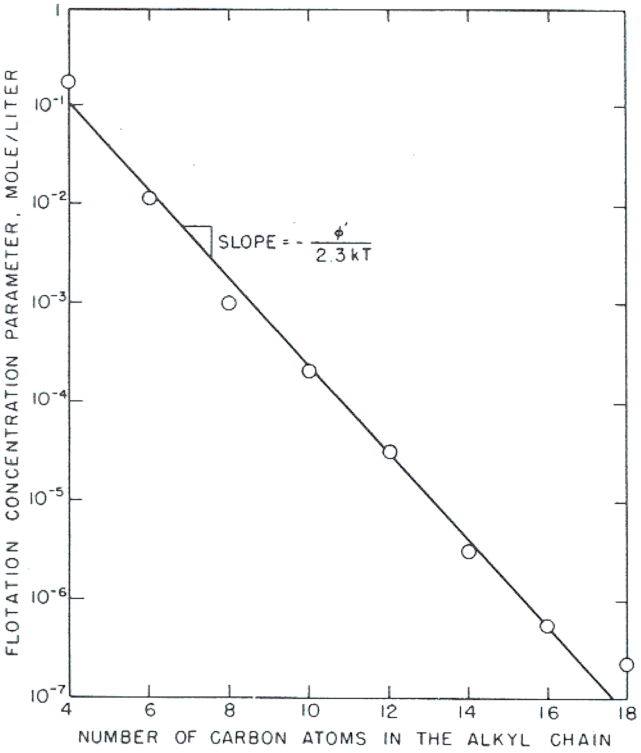

Fig. 4 — The effect of chain length on the concentration parameter for the flotation of quartz with alkyl ammonium acetates.

on a natural logarithm basis. Deviations might be expected for long and short chain lengths. In the case of the C_{18} collector complete dissolution of the collector may not have been attained, while for the C_4 collector there is reason to suspect that for such a short chain micelle formation occurs by a mechanism that involves a negative rather than a positive entropy change upon micellization.[24]

If our concentration parameter is directly proportional to C_{HM}, the ln C_{HM} vs n curve should be a straight line with the same slope as the line in Fig. 4 but would have a different intercept. From the slope of the line in Fig. 4, our value of the van der Waals cohesive free energy per CH_2 group (ϕ') of 1.0±0.1 kT (which is equivalent to 0.6 kcal per mole of CH_2 groups) is in excellent agreement with literature values obtained by studies of micellization. That the accepted value of ϕ' has been obtained is substantial evidence in favor of the concept that the association of hydrocarbon chains occurs in flotation and in support of the use of Hallimond tube techniques in flotation research.

Since lnC_{HM} vs n plots apparently are also linear, then the W'_e term, as in micelle formation, must have a negligible dependence on n. Electrokinetic results for alkyl ammonium acetates on quartz[8] indicate that there is little change in the zeta potential at which hemi-micelles form with change in chain length.

The linearity of the ln C_{HM} vs n plots also means that Γ_i is relatively independent of n. The analogous situation in micelle formation is that although the cmc is changed markedly by change in chain length, the aggregation number or number of single species per micelle is much less affected by change in chain length. This is illustrated by the cmc data of Debye.[16] For the alkyl trimethylammonium bromide surfactants of alkyl chain lengths of 10, 12 and 14 carbons, the cmc values in water in millimoles per liter are 68.0, 15.3 and 3.02, respectively. The corresponding aggregation numbers or units per micelle are 36, 50 and 75, which represent a much less significant change than the corresponding change in cmc.

SUMMARY

New evidence of hemi-micelle formation in flotation systems has been presented. From the variation of Hallimond tube flotation recovery of quartz with chain length of alkyl ammonium acetates, it has been possible to determine the fundamental quantity in hemi-micelle theory, i.e., the van der Waals cohesive free energy (per CH_2 group) between hydrocarbon chains. The present value of 1.0±0.1 kT is in agreement with literature values obtained from research on the properties of micelles.

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