

## THE ROLE OF IONOMOLECULAR SURFACTANT COMPLEXES IN FLOTATION

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### ABSTRACT

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The formation of highly surface-active ionomolecular\* complexes has been suggested recently to be a phenomenon that governs the pH-dependence of hematite flotation using oleate. The differential thermogravimetric work reported in the literature on alkylamine—alkylamine hydrochloride mixtures shows complete complexing of them when present in equimolar amounts. The pH dependence of quartz flotation using amine, speculated in the past to be due to various mechanisms, is discussed in the light of these results. The additional correlation obtained for flotation with surfactant complex formation suggests the role of such complexes in froth flotation to be of wide application.

### INTRODUCTION

The governing role of oleic acid-oleate complex in determining the pH dependence of hematite flotation using oleate has been discussed in a recent paper (Kulkarni and Somasundaran, 1974). In that study, the pH of maximum flotation response was found to be identical to the pH of maximum concentration of acid-soap complex. The fact that maximum in both surface tension decay rate as well as surface tension lowering was obtained for oleate solutions at the same pH suggested the higher surface activity of the acid-soap complex compared to that of the acid or the soap to be one major reason for the observed pH effect on flotation response.

In this note, the generality of the above observation on the role of surfactant complexes in flotation is examined in the light of positive results obtained for the existence of stable complexes by Kung and Goddard (1969b) during their differential thermogravimetric work with alkylamine—alkylamine hydrochloride mixtures. Maximum flotation of quartz obtained in the alkaline pH range using amine has often been attributed in the past to the adsorption of the neutral amine molecules along with the ions (Aplan and Fuerstenau, 1962; Smith, 1963; Schubert, 1965; Somasundaran, 1968). Even though one can

\*The term ionomolecular is used here to describe the complex formed between the ionic and molecular forms of surfactant species.

attribute the increased surface activity at the liquid/air interface in the same pH range to such coadsorption, surface pressure work by various workers including Schulman and Rideal (1937), Schulman and Stenhagen (1938), Goddard and Schulman (1953), Bowcott and Schulman (1955), Kung and Goddard (1963, 1965, 1967, 1969a), Goddard et al. (1968), Shah and Dysleski (1969) and Shah (1971), gives strong evidence for the formation of complexes between various long chain carboxylic salt species and long chain alcohols. The role of similar complexes has been discussed by Finch and Smith (1973) as well as Kulkarni and Somasundaran (1974). However, there was no experimental evidence presented to distinguish between the two possibilities. Here the flotation behavior of quartz using amine is reviewed along with the differential thermogravimetric results of amine-salt mixtures and adhesion and surface tension properties of amine solutions. The possible relevance of this phenomenon to the use of extender oils in flotation might be noted.

## RESULTS AND DISCUSSION

The data for the flotation of 48 X 65 mesh Brazilian quartz (cleaned with conc. HCl and washed free of acid) with dodecylammonium acetate as collector at a nitrogen flowrate of 36 ml/min for five and ten sec as a function of solution pH is given in Fig. 1. It can be seen that maximum flotation response is obtained above about pH 10. Previous data (Somasundaran, 1968) for the adhesion tension of glass/dodecylammonium acetate solution/air is reproduced in Fig. 2. Maximum lowering in adhesion tension occurs in the region of pH 9.5–11.5. Surface tension data obtained by R.W. Smith (pers. comm., 1967) for  $4 \cdot 10^{-4}$  mole/l dodecylamine solution is given in Fig. 3. This plot, which contains sufficient experimental points in the region of

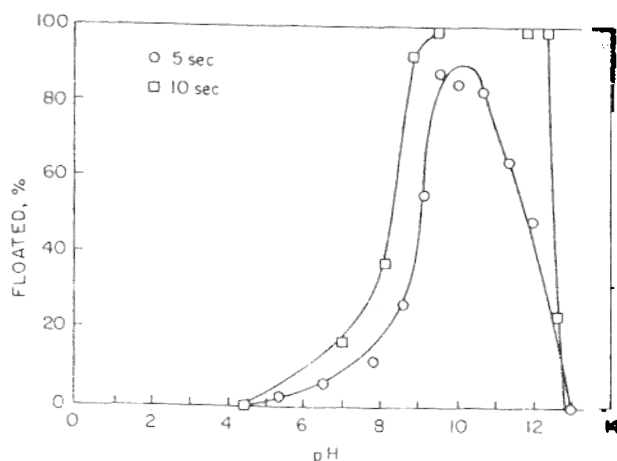


Fig. 1. Flotation recovery of quartz as a function of solution pH using dodecylammonium acetate as collector for flotation duration 5 and 10 sec.

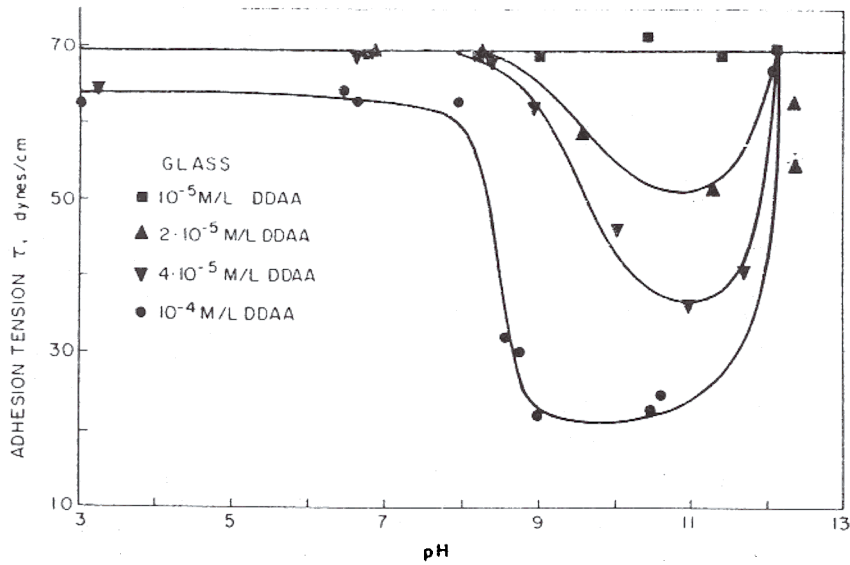


Fig. 2. Adhesion tension of dodecylammonium chloride solution of various concentrations as a function of solution pH. (After Somasundaran, 1968)

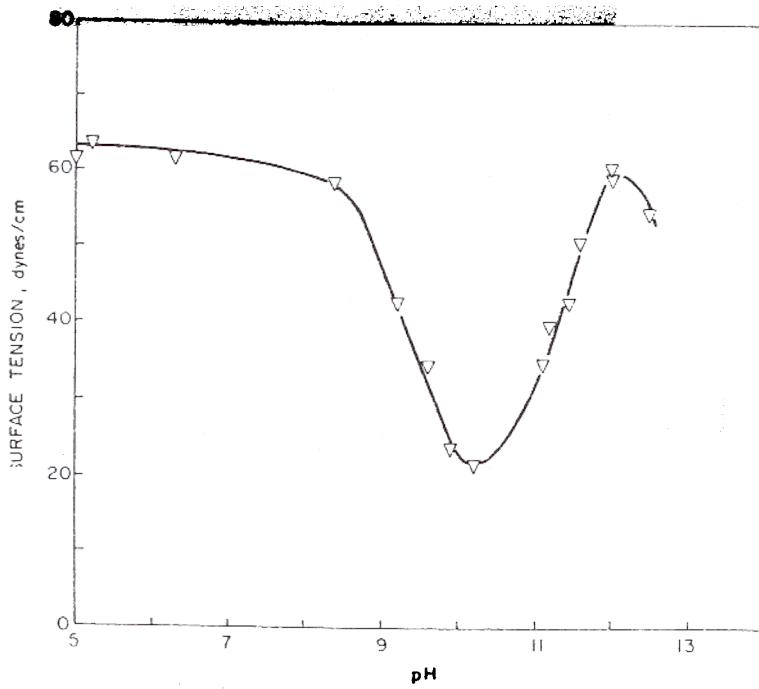


Fig. 3. Surface tension of  $4 \cdot 10^{-4}$  dodecylamine hydrochloride solution as a function of pH determined by pendant drop method, measured 15 seconds after forming drop. (After R.W. Smith, pers. comm., 1967)

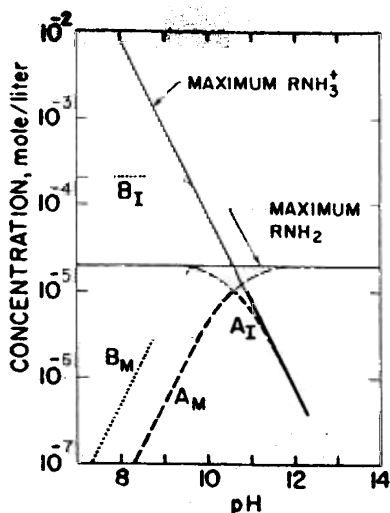


Fig. 4. Concentration of neutral molecules (M) and Ion (I) in  $2 \cdot 10^{-5}$  mole/l (A) and  $2 \cdot 10^{-4}$  mole/l (B) dodecylammonium chloride solution as a function of pH. Solid lines indicate maximum solubility. (After Gaudin, 1957)

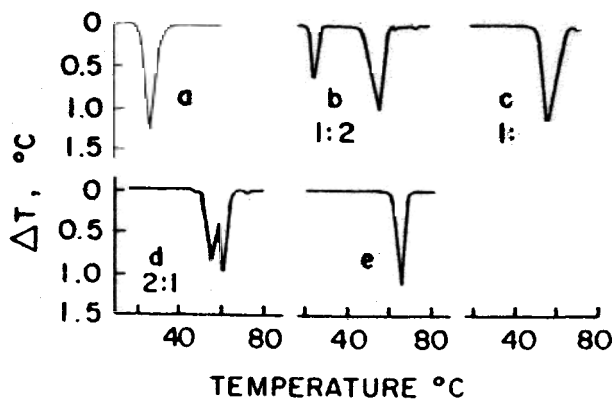


Fig. 5. Differential thermograms of dodecylamine (DDA)—dodecylamine hydrochloride (DDAHCl) system. (a) DDA (b) 62.6% DDA and 37.4% DDAHCl, (c) 45.5% DDA and 54.5% DDAHCl, (d) 29.5% DDA and 70.5% DDAHCl and (e) DDAHCl. (After Kung and Goddard, 1969b)

interest, shows a maximum surface tension lowering at about pH 10.2. These results, suggesting the formation of highly surface-active species around pH 10.2, are in general agreement with those obtained in the past (Fuerstenau, 1957; Gaudin, 1957). Using the data available in the literature for the dissociation constant of dodecylamine, one obtains the distribution given in Fig. 4 for amine and aminium ion as a function of pH at two total surfactant concentrations of  $2 \cdot 10^{-4}$  and  $2 \cdot 10^{-5}$  mole/l (Gaudin, 1957). It can be seen that amine and aminium ions exist in equal amounts at about pH 10.5 in this

case. Kung and Goddard (1969b) have recently shown using differential thermal analysis technique that a 1:1 amine—aminium complex that is highly stable does form and that the conversion of individual species to complex form is complete when equimolar amounts of surfactant molecules and ions are mixed together. Differential thermograms obtained by Kung and Goddard for the dodecylamine (DDA)—dodecylamine hydrochloride (DDAHCl) system are shown in Fig. 5. Amine and amine hydrochloride have peaks at 26°C and 67°C respectively. The 1:2 and 2:1 amine—amine hydrochloride thermograms have double peaks, for the former at 56°C and 27°C and for the latter at 56°C and 61°C. The thermogram of the 1:1 mixture is characterized by a single peak attributed to the complex at 56°C. The disappearance of the amine peak and the hydrochloride peak in the latter case is evidence for a nearly total conversion of the two species into a single species. Similar results suggesting the formation of ionomolecular complex in bulk have been obtained by these authors also for the octadecylamine—octadecylamine hydrochloride system.

The above results support the hypothesis of the formation of stable complexes between neutral surfactant molecules and corresponding ions and their governing role in determining the observed flotation dependence on pH. Additional work on other mineral/collector systems is needed to test it further.

While the mechanism of adsorption of the complexes on quartz is yet to be studied, it is reasonable to assume it to be similar to that proposed in the past for the adsorption of aminium ions on quartz, namely, electrostatic adsorption of cationic surfactant on the negatively charged mineral surface. Thus, the role of pH in determining the surface charge of the mineral and thereby the selective surfactant adsorption and consequent flotation is not suggested here to be any less important. On the other hand, it is to be noted that the higher surface activity of the complexes does depend upon factors other than the surface charge of the mineral, since surface tension data discussed above was indeed obtained in the absence of any mineral particle. *The role of complex formation is simply to increase the flotation due to the significantly higher surface activity of the complexes than that of the complexing species.* In fact, complex formation might be viewed as a process that increases the effective size of the hydrocarbon chain which in turn can be expected to increase flotation.

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