Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Polymer-Surfactant Interactions in Flotation of Quartz

P. Somasundaran[a]; L. T. Lee[a]
[a] HENRY KRUMB SCHOOL OF MINES COLUMBIA UNIVERSITY NEW YORK, NEW YORK

To cite this Article Somasundaran, P. and Lee, L. T.(1981) 'Polymer-Surfactant Interactions in Flotation of Quartz', Separation Science and Technology, 16: 10, 1475 — 1490
To link to this Article: DOI: 10.1080/01496398108058312
URL: http://dx.doi.org/10.1080/01496398108058312

SEPARATION SCIENCE AND TECHNOLOGY, 16(10), pp. 1475-1490, 1981

Polymer-Surfactant Interactions in Flotation of Quartz

P. SOMASUNDARAN and L. T. LEE

HENRY KRUMB SCHOOL OF MINES
COLUMBIA UNIVERSITY
NEW YORK, NEW YORK 10027

ABSTRACT

Separation of minerals currently often involves the use of polymers along with surfactants. Polymer-surfactant interactions in flotation are studied here for quartz, which along with clay is present in coal, oil shale etc., using nonionic, anionic, and cationic surfactants. Polymers are found under most conditions to affect flotation. It can activate or depress flotation markedly depending on the nature of the charge of the reagents. Possible mechanisms by which flotation is affected by the polymers are discussed. Reasons for the observed maximum in flotation vs. amine concentration are also considered here briefly.

INTRODUCTION

Conventional mineral processing techniques become inefficient for the beneficiation of low-quality ores ground to ultrafine size range for the purpose of liberation (1). Techniques that are being developed for the benefication of such ultrafines often involve use of polymers. For example, the selective flocculation technique that has been successfully demonstrated on a commercial scale for the beneficiation of low grade iron ore uses polymeric type reagents (2). Selective flocculation and general flocc-flotation techniques involve use of polymers in addition to surfactants (3), and the success of the process depends to a great extent on the type of interactions between these two types of reagents.

Polymers have also been proposed for reducing energy consumption during grinding, but when used for such a purpose, can enter the flotation stream. Furthermore, polymers used in filtration, effluent treatment or waste disposal can re-enter the process stream through recycled water. Recycled polymers and surfactants can also affect, in addition to flotation, grinding, filtration, pelletizing, and all such upstream and downstream beneficiation techniques. Proper control of the polymer-surfactant interactions is critical for maintaining the required separation efficiency and the integrity of the overall mineral beneficiation process.

Usoni et al (4) have in fact shown that polymers can enhance or depress flotation depending on the nature, concentration, and duration of contact of the polymers with the mineral. For example, the flotation of sphalerite and smithsonite was found to be activated by the addition of Separan and certain Aerofloc and Nalco flocculating agents up to certain concentrations and to be depressed above them. The reasons for this are largely speculative at present. In contrast to the above, Rubio and Kitchener (5) have reported good selective flocculation of certain mineral fines using hydrophobic polymers when the fines are first treated with xanthate surfactants. Ghigi and Botre (6,7) have also reported the use of polymer-surfactant complexes for quartz and magnetite flotation.

It is important to understand the nature of interactions of polymers and surfactants with mineral in order for them to be controlled for optimum mineral separation. While polymer-surfactant interactions in bulk solutions have been studied to some extent in the past (8-18), no major study has been conducted to our knowledge on their interactions at the mineral surface. It is the aim of our work to investigate the effects of polymer-surfactant interactions on solid-liquid and liquid-air, as well as bulk solution properties using various techniques. Availability of data for all these effects for the same mineral/polymer/surfactant system makes it possible to develop information on the mechanisms of interactions. In this paper, we examine specifically the role of polymer-surfactant interactions on flotation of quartz using both anionic and cationic surfactants and polymers. Quartz, clay and other silicate type mineral are almost always present with energy minerals such as coal and shale, and it is considered important to understand the behavior of these minerals. Also, it is the quartz-hematite system that has been subjected to selective flocculation on a commercial scale and successful extension of it to other ores pivots on a complete understanding of the basic interactions involved in this mineral system.

EXPERIMENTAL

Materials

Quartz: Brazilian quartz was purchased from Wards Natural Science Establishment, and the mineral samples were crushed using a roll crusher and sized by sieving in a "Rotap". The -28 +65 mesh portion was collected and passed through a magnetic separator several times to remove any iron contamination. The mineral was then leached with warm nitric acid for 15 minutes. This was followed by several washings with triple distilled water until the natural pH (~5.7) was obtained and then stored in triple distilled water in a polypropylene bottle.

Chemicals

(i) Surfactants: Dodecylamine hydrochloride and sodium dodecylsulfonate were purchased from Eastman Kodak Co. and Aldrich Chemical Co. respectively and were used as received.

(ii) Polymers: Acrylamide (AM) monomer was purchased from Eastman Kodak Co. in powder form, and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) co-monomer was obtained from Lubrizol Chemical Corporation. The cationic co-monomer, methacrylamido propyltrimethyl ammonium chloride (MAPTAC) was purchased from Jefferson Chemical Co. as a stabilized liquid. The inhibitor, hydroquinone, was removed before use by passing the liquid through an activated carbon column.

Polymer Synthesis

All the polymers were synthesized at Columbia University using a radiation induced heterogeneous polymerization technique with ^{60}Co source. The MW of all the polymers were greater that 1 million. The charge densities of the anionic and cationic polymers were estimated to be 3 mol% and 10 mol% respectively.

Solution Preparation

All solutions were prepared with triple distilled water of specific conductivity of $\sim 10^{-6}$ μmho.

Polymer stock solution was prepared by stirring the required amount of solid polymer in triple distilled water using a teflon coated stirring bar in a volumetric flask until all the solid had dissolved. The polymer solution was sealed with teflon tape and stored in the refrigerator till use. All polymer solutions used were less than 10 days old.

Surfactant stock solution was prepared by dissolving the solid in triple distilled water, warming when necessary.

For the preparation of the polymer-surfactant mixture, the required volume of the polymer stock solution was added to triple distilled water in a flask followed by the surfactant stock solution. The mixture was shaken on a wrist-action shaker for 2 hours.

Techniques

Flotation: One gram of the mineral sample was conditioned with the surfactant in a 100cm^3 volumetric flask by tumbling at 16 r.p.m. for 10 minutes and then transferred to a modified Hallimond cell for flotation (19). Flotation was conducted for 15 seconds using nitrogen at a flow-rate of 36cm^3/min. pH of the solution was measured before and after flotation, but no change was observed during flotation for the present system.

Surface Tension: Surface tension measurements were made using the Wilhelmy Plate method (20). The sensor used was a sandblasted platinum plate of known dimensions. Care was taken to ensure proper wetting of the sensor by the solution and readings were taken at equilibrium.

ABBREVIATIONS FOR REAGENTS

For convenient reference of reagents, the following abbreviations are adopted here:

DDA-HCl = Dodecylamine hydrochloride
NaDDS = Sodium dodecylsulfonate
PAM = Polyacrylamide (nonionic)
PAMS = Co-polymer of acrylamide and AMPS (anionic)
PAMD = Co-polymer of acrylamide and MAPTAC (cationic)

RESULTS AND DISCUSSIONS

Dodecylamine

Flotation of quartz at pH 6.5 is given in Figure 1 as a function of dodecylamine hydrochloride concentration. It is seen that amine causes flotation but interestingly, use of excess amine causes a depression. The flotation obtained at lower concentration is in agreement with the expected electrostatic adsorption of the cationic amine surfactant on the quartz particles that are negatively charged at pH 6.5 (21). The decrease in flotation at higher amine concentrations can be attributed to the following major reasons:

(i) Reverse adsorption of surfactants: Hydrophobicity of the particles and the resultant flotation is attributed to the adsorption of the surfactant with the hydrophobic part oriented towards the bulk solution. Surfactants that adsorb initially due to electrostatic forces can often continue to adsorb even after the mineral charge has been completely neutralized by adsorption owing to lateral interaction between the hydrocarbon chains to form two di-

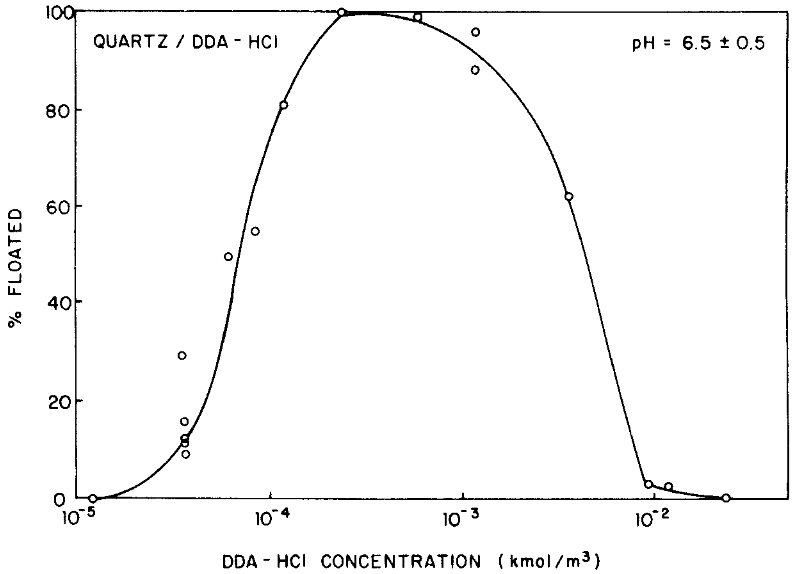

Fig. 1. Flotation of quartz as a function of docecylaminehydrochloride concentration.

mensional aggregates called hemi-micelles. This type of adsorption has been shown for the case of alumina/dodecylsulfonate system (22), and has been suggested above the charge neutralization point to take place with a reverse orientation (23). Such an adsorption with the ionic part of the surfactant turned towards the bulk solution is energetically favored but also depresses the hydrophobicity of the mineral and thereby flotation.

(ii) Armoring of bubbles: Complete coverage of the bubble surface with surfactants can hinder particle-bubble attachment in some cases. A layer of ionic groups around the bubble can unfavorably alter the disjoining pressure in the film between the bubble and the particle both by reducing the Van der Waals attractive forces and by increasing the electrostatic repulsive forces between them if there is reverse adsorption of surfactants on the mineral.

(iii) Decrease in levitation force: If the gas pressure for production of bubbles is maintained constant, as the surfactant concentration is increased, according to Laplace capillary pressure equation, bubble size should decrease with decrease in surface tension. In practice, bubbles were observed to be smaller in concentrated surfactant solutions. Such decrease in bubble size will naturally decrease the levitating ability of the bubble and hence flotation.

All the above three factors can individually or in combination cause a decrease in flotation at high surfactant concentrations. It will be most interesting to investigate how the flotation decrease is also affected by polymer additions to the system.

Polyacrylamide and Dodecylamine

The effect of addition of polyacrylamide (PAM), a nonionic polymer, on quartz flotation at pH 6.5 using amine is illustrated in Figure 2. At 3.6×10^{-5} k mol/m^3 amine, PAM, which does not adsorb on quartz (24) and does not by itself cause flotation of it, has no measurable effect on the amine flotation in the neutral pH range. At 6×10^{-5} k mol/m^3 amine, flotation is, however, slightly increased by the addition of polymer. This is attributed to the uptake of water molecules by the polymer for hydration, causing effectively an increase in the concentration of the surfactant (in the free water). The effect of this "salting-out" type phenomenon is evident at 6×10^{-5} k mol/m^3 amine concentration since, as can be seen from Figure 1, it is in this concentration range that a small increase in amine concentration produces a measurable increase in flotation.

Sulfonated Polyacrylamide and Dodecylamine

The effect of addition of the anionic PAMS on amine flotation of quartz is illustrated in Figure 3. It can be seen that PAMS does increase flotation. Anionic PAMS is not expected to adsorb on the negatively charged quartz particles. Direct activation of amine adsorption is therefore not expected. Evidently, "salting-out" of amine is again responsible for the enhancement of flotation. Furthermore, the extent of "salting-out" by PAMS is significantly higher than that by PAM due to the greater hydration tendency of

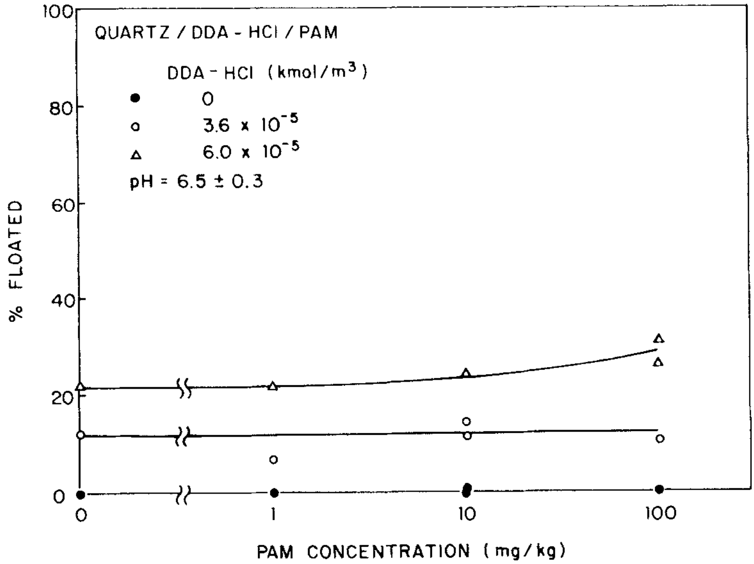

Fig. 2. Diagram illustrating the effect of the nonionic polymer, PAM, on the flotation of quartz using dodecylaminehydrochloride.

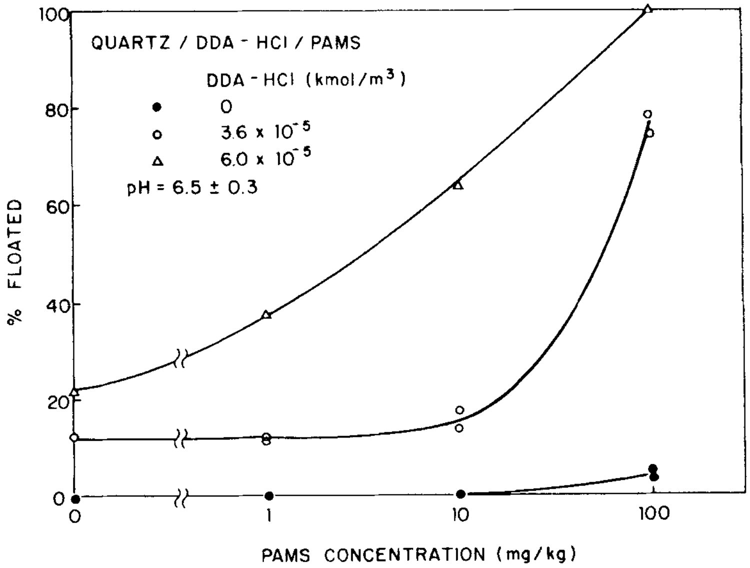

Fig. 3. Diagram illustrating the effect of the anionic polymer, PAMS, on the flotation of quartz using dodecylaminehydrochloride.

the former than that of the latter. A comparison of the amount of polymer required to increase the flotation, for example, from 22% to 29% at 6.0×10^{-5} k mol/m^3 in fact suggests the hydration of PAMS to be about 250 times that of PAM. It is such a strong hydration that is able to produce an effect on flotation even at the lower amine concentration of 3.6×10^{-5} k mol/m^3.

In addition to the hydration effect, there can be direct polymer-surfactant electrostatic interaction leading to the formation of complexes with high collecting property. It has been reported that such complexes can possess higher collector properties than the corresponding surfactant components (6,7). Any surfactant-polymer complex formation can also lead to a reduction in the depression of flotation due to armoring of bubbles. The anionic polymer molecules can essentially bridge the adsorbed amine on the quartz particles to the amine on the bubble surface and can thus in fact, even enhance flotation under saturated adsorption conditions (Figure 4).

Cationic Polyacrylamide and Dodecylamine

Flotation obtained in solutions containing the amine and a similarly charged polymer is illustrated in Figure 5. It is clear that a cationic polymer can completely depress the flotation of quartz using a cationic surfactant. The depression might partly be due to the competitive interaction between the polymer and amine at the adsorption sites on the mineral. PAMD is known to adsorb well on quartz and even cause flocculation of it even though the flocs are redispersed easily during stirring in the flotation cell.

It is to be noted that the co-adsorbed polymer itself does not contribute to any flotation. Flotation in the absence of amine is zero at all polymer concentrations since adsorbed polymer exposes essentially a hydrophilic surface to the bulk solution. The flotation reduction obtained particularly above the concentration corresponding to the maximum is attributed to this hydrophilic nature of the co-adsorbed polymer. Reduction in

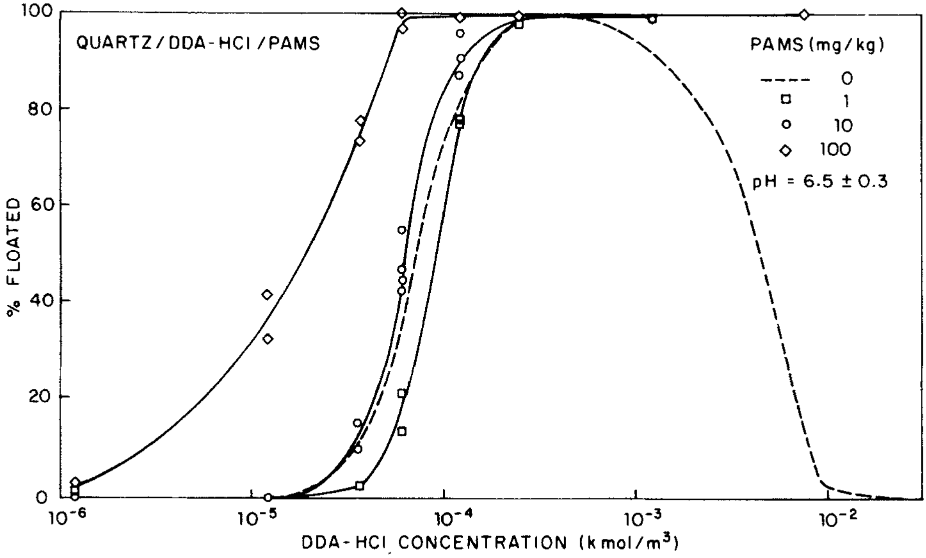

Fig. 4. Diagram illustrating the effect of the anionic polymer, PAMS, on the flotation of quartz using dodecylaminehydrochloride.

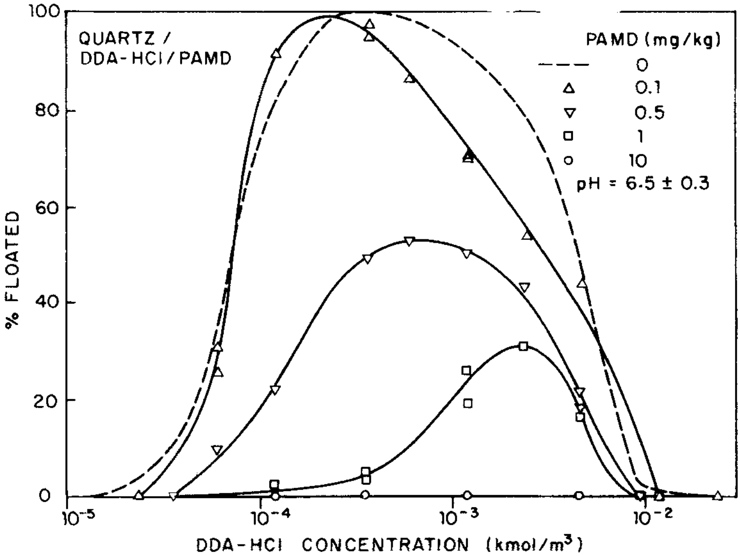

Fig. 5. Diagram illustrating the effect of the cationic polymer, PAMD, on the flotation of quartz using dodecylaminehydrochloride.

flotation obtained under these concentration conditions is not as severe as that obtained at lower amine concentrations since in this range any reduction in amine adsorption itself is not expected to lead to any decrease in flotation. Mainly, the decrease in flotation is considered to be due to the masking of the adsorbed amine by the massive polymer species (25). Furthermore, any reduction in adsorption due to electrostatic repulsion between the unadsorbed polymer loops and the surfactant will also contribute towards flotation depression. However, such reduction in adsorption has not yet been observed experimentally.

Polymer-surfactant complexation will be insignificant in this case due to charge repulsion between the species. Thus even with the "salting-out" effect, interaction between the adsorbed PAMD and amine in combination with the above factors operates to depress the quartz flotation.

Cationic Polyacrylamide and Dodecylsulfonate

If the cationic polymer can depress flotation of quartz with a similarly charged surfactant, it can be expected to possibly activate flotation with a negatively charged surfactant. This effect is in fact observed when the PAMD is added along with dodecylsulfonate for the flotation of quartz (see Figure 6). While no flotation is obtained with sulfonate alone, complete flotation results with the addition of PAMD. Sulfonate does not float quartz because of electrostatic repulsion between the anionic head and the negatively charged quartz which prevents surfactant from adsorbing on the mineral. PAMD, on the other hand, adsorbs electrostatically, and even though it does not cause flotation, it activates flotation with sulfonate. This activation is mainly the result of PAMD providing adsorption sites for the sulfonate.

As in the case of PAMS-amine system, PAMD can complex with the sulfonate electrostatically in the bulk solution. The complex itself, if only partially neutralized by the surfactant, can adsorb on the quartz and produce flotation. Clearly, partial neutralization can be expected at high polymer-surfactant concentration ratios. It

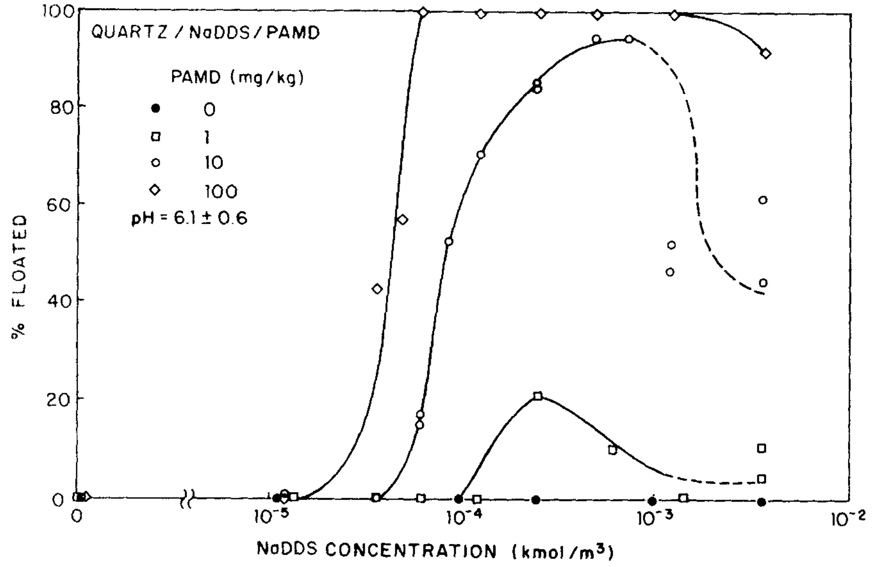

Fig. 6. Diagram illustrating the effect of the cationic polymer, PAMD, on the flotation of quartz using sodium dodecylsulfonate.

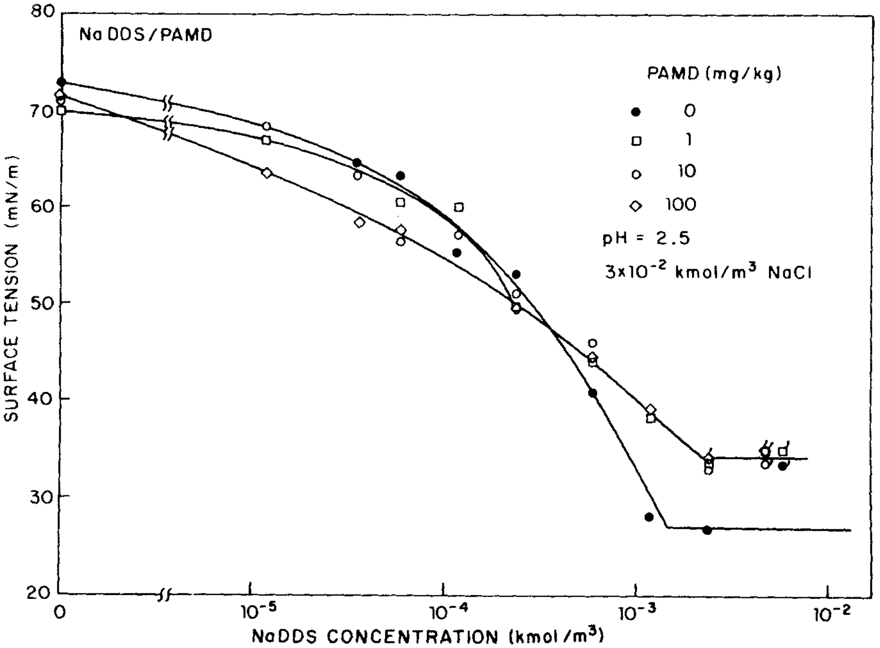

Fig. 7. Surface tension of sodium dodecylsulfonate/cationic polymer (PAMD) solutions. Points marked (,) indicate solutions that were warmed to dissolve precipitates that were formed under these conditions.

can be seen from Figure 6 that flotation is in fact activated at such concentration ratios.

In all the above cases, "salting-out" of the surfactant by the polymer can be expected to produce an increase in surface activity and thereby adsorption and flotation. Evidence for the increase in surface activity is obtained from an analysis of the data for the dependence of surface tension of the surfactant solution on polymer addition (see Figure 7). It can be seen that polymer addition does cause a decrease in surface tension at low surfactant concentration. At higher surfactant concentrations, however, complexation of the surfactant with the polymer leads to a reduction in the surfactant monomer activity and thereby an increase in surface tension.

SUMMARY

1. Quartz flotation using amine is found to exhibit a maximum as a function of amine concentration. The decrease in flotation at high amine concentration is attributed to reverse adsorption (with the ionic head turned towards the bulk solution), armoring of the bubbles and decrease in bubble size.

2. Flotation of quartz is affected by all the polymers tested in this study.

3. The nonionic polyacrylamide increases flotation slightly but only at high polymer and amine concentrations. The observed increase is considered to be the result of "salting-out" of the surfactant by the polymer.

4. The anionic polymer, PAMS, enhances flotation markedly under all conditions. The larger effect of PAMS results from the greater tendency of PAMS to hydrate and thereby salt-out the amine. PAMS-amine complex is also expected to contribute towards flotation.

5. The cationic polymer, PAMD, depresses flotation of quartz using amine. This is ascribed to competitive interactions between PAMD and amine on the mineral surface and masking of the adsorbed amine by the bulky polymeric species.

6. The cationic polymer is found to activate flotation of quartz using the anionic sulfonate. Neither the polymer not the

sulfonate causes flotation when present alone. The combined action is considered to be the result of co-adsorption of negatively charged sulfonate on the cationic polymeric species adsorbed on the mineral partice. PAMD-sulfonate complex can also act as collector for quartz.

7. Surface tension data obtained for solutions containing polymers and surfactants is indicative of "salting-out" of the surfactant as well as polymer-surfactant complex formation.

ACKNOWLEDGEMENTS

The support of the National Science Foundation (DAR-79-09295) is greatly acknowledged.

REFERENCES

1. P. Somasundaran, "Fine Particles Treatment", Research Needs in Mineral Processing, (P. Somasundaran and D.W. Fuerstenau, eds.), Columbia University, New York, 1976, p. 125.
2. J.W. Villar and G.A. Dawe, "The Tilden Mine - A New Processing Technique for Iron Ore", Miner. Congr. J., October, 1975, p.40.
3. P. Somasundaran, "Principles of Flocculation, Dispersion, and Selective Flocculation", Fine Particles Processing, (P. Somasundaran, ed.), AIME, New York, 1980, Vol. 2, p.946.
4. L. Usoni, G. Rinelli, A.M. Marabini and G. Ghigi, "Selective Properties of Flocculants and Possibilities of Their Use in Flotation of Fine Minerals", VIIIth Int. Miner. Process. Congr., Leningrad, 1968, paper D-13.
5. J. Rubio and J.A. Kitchener, "New Basis for Selective Flocculation of Mineral Slimes", Trans. Inst. Min. Met., London, 86, p. C97, (1977).
6. G. Ghigi and C. Botre, "Polymer Compexes as New Collectors and Their Use in Flotation", Trans, Inst, Min, Met., London, 75, p. 240, (1966).

7. G. Ghigi, "Flotation of Quartz with Some Polymer Complex Collectors", Trans, Inst, Min, Met., London, 78 p. C212, (1978).

8. S. Saito and Y. Mizuta, "Solubilization of Polymers in Aqueous Cationic Surfactants". J. Colloid Interface Sci., 23, p. 604, (1967).

9. M.J. Schwuger, "Mechanism of Interaction between Ionic Surfactants and Polyglycol Ethers in Water", J. Colloid Interface Sci., 43, p. 491, (1973).

10. E.D. Goddard and R.B. Hannan, "Anionic Surfactant Complexes with Charged and Uncharged Cellulose Ethers", Micellization, Solubilization and Microemulsion, (K.C. Mittal, ed.) Plenum, 1977, p. 835.

11. M.N. Jones, "The Interaction of Sodium Dodecylsulfate with Polyethylene Oxide", J. Colloid Interface Sci., 23, p. 36, (1967).

12. H. Arai, M. Mukata and K. Shinoda, "The Interaction between Polymer and Surfactant: The Composition of the Complex between Polyvinylpyrrolidone and Sodium Alkyl Sulfate as Revealed by Surface Tension, Dialysis and Solubilization", J. Colloid Interface Sci., 37, p. 223, (1971).

13. E.D. Goddard and R.B. Hannan, "Polymer/Surfactant Interactions", J. Amer, Oil Chem, Soc., 54, p. 561, (1977).

14. E.D. Goddard and R.B. Hannan, "Cationic Polymer/Anionic Surfactant Interactions", J. Colloid Interface Sci., 55, p. 73, (1976).

15. K.E. Lewis and C.P. Robinson, "The Interaction of Sodium Dodecylsulfate with Methyl Cellulose and Polyvinyl Alcohol", J. Colloid Interface Sci., 32, p. 539, (1970).

16. S. Saito, "Solubilization Properties of Polymer-Surfactant Complexes", J. Colloid Interface Sci., 24, p. 227, (1967).

17. B. Cabane, "Structure of Some Polymer-Detergent Aggregates in Water", J. Phys. Chem., 81, p. 1639, (1977).

18. B. Kalpakci and R. Nagarajan, "Surfactant Binding to Polymer and Phase Separation in Aqueous Surfactant-Polymer Solutions", presented at AIChE Meeting, Houston, April, 1981.

19. P. Somasundaran, "Foam Separation Methods", Separation and Purification Methods, 1, p. 117, (1972).

20. R.D. Kulkarni and P. Somasundaran, "Kinetics of Oleate Adsorption at the Liquid/Air Interface and its Role in Hematite Flotation", AIChE Symposium Series, 71, No. 150, p. 124, (1975).

21. D.W. Fuerstenau, T.W. Healy and P. Somasundaran, "The Role of the Hydrocarbon Chain of Alkyl Collectors in Flotation", Trans. AIME, 229, p. 321, (1964).

22. P. Somasundaran and D.W. Fuerstenau, "Mechanisms of Alkylsulfonate Adsorption at the Alumina - Water Interface", J. Phys. Chem., 70, p. 90, (1966).

23. M. Celik and P. Somasundaran, "Wettability of Reservoir Materials by Flotation and Correlation with Surfactant Adsorption", SPE Paper 9002, presented at Oilfield and Geothermal Chemistry Symposium, May, 1980.

24. J. Cleverdon and P. Somasundaran, Unpublished Results.

25. P. Somasundaran, "Adsorption of Starch and Oleate and Interaction between Them on Calcite in Aqueous Solutions", J. Colloid Interface Sci., 31, p. 559, (1969).