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Some Parameters Affecting the Flotation of Cationic Surfactants

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Summary

A study was made of the flotation of very dilute solutions of two cationic collectors, hexadecyltrimethylammonium chloride (HTMAC) and dodecylpyridinium chloride (DPC), in the presence of added electrolytes. The concentration, charge, and nature of these electrolytes were found to have a pronounced effect on the rates of flotation. The determinations were made at two different gas flow-rates; unexpectedly, the ratios of the flotation rates were found to be different to the total surface areas of the bubbles passing.

The discrepancy can be explained on the basis of the repulsions which exist between bubbles due to the charged surfactant species which are adsorbed on them. Small bubbles, which lack kinetic energy, are unable to penetrate the lower reaches of the foam and are swept back into the solution. The latter, therefore, contains too high a proportion of small bubbles which leads to an erroneous estimate of the total surface area available, and casts doubt on the validity of a photographic method which has been used in the past.

The flotation of DPC proved considerably more difficult than that of HTMAC due to the reduced chain-length and lower surface activity of the former.

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INTRODUCTION

To understand the mechanisms of the flotation of precipitates and colloids by surface-active collectors, it has been found necessary to examine the flotation of the collectors themselves. No such investigation using the very small bubbles produced in a flotation cell with a fine porosity frit has been reported previously. Even with larger bubbles, little has been published on the flotation of cationic collectors, although Grieves et al. (*1–4*) have examined some of the parameters. Their studies have been mostly on continuous flow systems and include the effects of surfactant concentration, gas flow-rate, feed rate, foam height, foam column diameter, feed position, and temperature. The interpretation of the data is complicated by the drainage which occurs from the copious foams formed when using large bubbles and high gas flow-rates. An advantage of using small bubbles and low gas flow-rates is that the foams formed are drier and of small volume, and the removal of collector from the solution is therefore more a function of flotation than of drainage from the foam. Under these conditions the kinetics and extent of removal by flotation can be assessed with greater confidence.

The purpose of the work described in the present communication, therefore, was to study the flotation of cationic collectors using small bubbles. Hexadecyltrimethylammonium chloride (HTMAC) and dodecylpyridinium chloride (DPC) were chosen and the most significant parameters were found to be the concentration, charge, and nature of the other ions present in the solution. The effects of gas flow-rate and temperature were also studied.

EXPERIMENTAL

Materials

Dodecylpyridinium chloride was obtained from Hooker Chemical Company, New York, and was recrystallized from ethanol and acetone before use. Hexadecyltrimethylammonium chloride, from Armour & Company, Illinois, and sodium ethylxanthate, from Fisher Chemicals, were used without further purification. Of the radioactive labels used, HTMAC was available directly but DPC had to be prepared by reacting 1-bromododecane with tritiated pyridine under reduced pressure at 100°C for 12 hr. The radioactive HTMAC and pyridine were obtained from The Radiochemical Centre, Amersham, England.

Apparatus

The flotation cell used was about 0.09 m in diameter, of 2 liter capacity, and was constricted at the top to prevent the loss of radioactive material during flotation (cf. Fig. 1). It contained a fine porosity frit, the average pore size of which was 10 μm. A tap in the base of the cell allowed the removal of any radioactive solution that inadvertently leaked through the frit; another tap in the side of the cell was used for the removal of samples of the aqueous solution. Nitrogen was used for the flotations; before flowing into the cell, this gas was passed through a

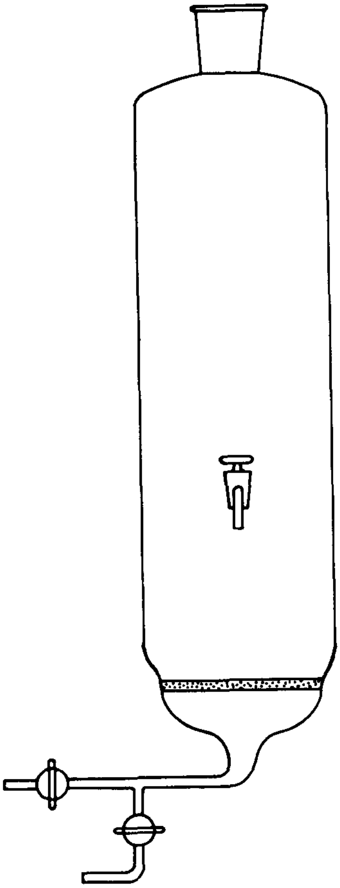

FIG. 1. The flotation cell.

bulb of 2 liter capacity to dampen the effects of unexpected surges, through a flow meter, and finally through a copper, heat-exchanging coil. The apparatus was housed in an enclosed space, the temperature of which was controlled to about 1° by the use of an ice pail or a small electric heater.

Photographs of bubbles in the cell were made by mounting a Nikkor F camera in front of a microscope which was focused in the solution. On the other side of the flotation cell, pointing directly into the microscope, was a Rollei Strobomatic E66 electronic flash unit, covered by a Nikkor R60 red filter. An exposure of 1/60 sec at *f*3.5 was used with a pan F ASA 50 extra fine grain filter. The microscope was fitted with a graticule which was ruled in a pattern of regular squares. The image of this graticule became part of the photograph and afforded a means of estimating the bubble diameters. This was done by photographing a wire of known diameter against the background of the graticule, thereby obtaining a scale factor for converting measurements on a photograph to actual distances.

Procedure

A volume of 1500 ml of the solution to be floated was prepared by adding the requisite amounts of collector, radioactive label, and salt, together with 10 ml of ethanol to reduce the sizes of the gas bubbles. The solution was poured into the cell, about 5 ml was withdrawn through the sampling tap, and 1 ml of this sample was weighed into a container to be used for scintillation counting. The flow of gas was commenced and adjusted as rapidly as possible to a rate of either 2 or 5 l/hr. More samples were taken at predetermined times after the commencement of the run, which lasted 50 to 60 min.

To each sample was added 15 ml of a scintillation solution, made by dissolving 5 g PPO (2,5-diphenyloxazole) and 0.1 g POPOP (1,4-bis-2-(4-methyl-5-phenyloxazolyl)-benzene) in 1 liter of dioxane. The samples were counted on a Packard Tri-carb Scintillation spectrometer. The percentage recoveries were calculated by proportionately comparing the count rate of all samples with that of the initial sample taken before flotation commenced. The flotation curve was then obtained by plotting percentage recovery against time.

The total surface areas of the bubbles in the flotation cell at any time were determined by making photographs by the method described earlier, and measuring the diameter of every distinguishable bubble with venier slide calipers to an accuracy of 0.1 mm. Sixteen such photographs were taken at predetermined intervals in each of two flotations. In both, the gas flow-rate was 2 l/hr and 10^{-3} M of sodium chloride and 10 ml of ethanol were present, but the concentrations of HTMAC were either 10^{-5} or 10^{-4} M. In all, 975 and 699 bubbles were measured in the first and second flotations, respectively.

It was assumed that the bubbles seen in each photograph were representative of the whole assembly, i.e., the ratio of their total surface area to their combined volume was equal to the total surface area moved through the solution during a given period divided by the total volume of gas passed into the cell in that time. The latter volume was the product of the flow rate and the time for which the gas flowed.

The calculations were performed using an IBM 360 Model 50 computer. The surface area to volume ratio was determined for each photograph together with a progressive value of this ratio for increasing numbers of bubbles. The progressive value converged quite rapidly to the over-all ratio obtained for the run, and gave an indication of how many bubbles should be measured in order to estimate the final ratio.

The method of determining surface areas described previously was time-consuming and tedious, and an examination was made of the effect of using less accurate measurements. The full range of actual bubble diameters were subdivided into intervals of 0.01, 0.02, or 0.04 mm (corresponding to 0.6, 1.2, or 2.4 mm on the photographs). The accurately measured bubbles, therefore, were grouped in these classes and the number in each group was recorded. The total surface area and volume for each interval was then calculated using these numbers and the diameters corresponding to the midpoints of the intervals; a value for each photograph, together with a progressive value, was obtained as before. In addition, a histogram of bubble populations in each of the 0.01-mm intervals was printed for each photograph in order to reveal any systematic drift in the sizes of bubbles during a run. (It is worth noting that since this work was completed, image analyzers have become commercially available which enable rapid, automatic measurement of the dimensions of images or photographs to be made.)

To determine the kinetics of the flotation process, the percentage recoveries of collector with time were substituted in several possible integrated rate equations. The best correspondence was found with the equation $M \ln[M/(M - R)] = kt$, in which M and R are the fractions of collector removed at $t = \infty$ and $t = t$, respectively, and k is a constant. The equation is readily derived by assuming that both the flotation process and that which is responsible for the return of collector to the bulk solution, the return process, are of first order. It has been shown by Rubin et al. (*5*) to apply to the flotations of similar systems to those investigated here, and with bubbles of about the same dimensions. The present data also showed good correspondence with the equation

$$\frac{M}{2-M}\ln\frac{M+R-MR}{M-R}=kt$$

which can be derived by assuming that the flotation and return processes are first and second order, respectively. It is not possible from the present results, therefore, to decide on the order of the return process.

The equations were tested by estimating a value of M from the flotation curve, and then substituting the experimental values of R at various values of t. The best straight line which fitted the plotted points was found by polynomial regression, using the method of least squares. The fit of the data to the best straight line was estimated by means of the standard statistical F test. The program (*6*) which fitted the straight line also calculated the value for F, where $F = (Y_d)^2/(Y_d - Y_f)^2$, where Y_d = ordinate of the data point and Y_f = ordinate of the point

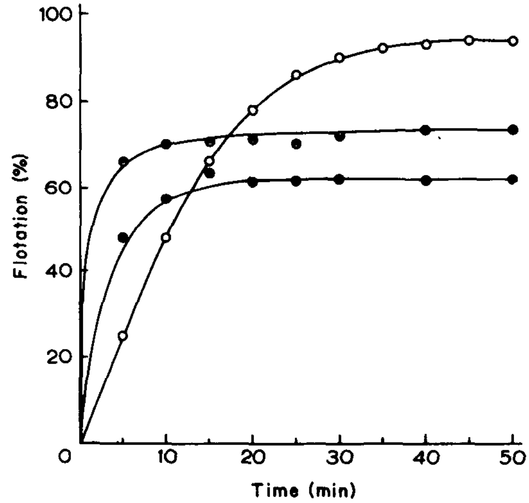

FIG. 2. The effect of NaCl on the flotation of 10^{-5} M HTMAC: (○) 10^{-3} M NaCl, (●) 10^{-2} M NaCl, and (⊖) 10^{-1} M NaCl.

on fitted line. Clearly, the larger the value of F, the more satisfactory was the fit.

Having assumed that first-order kinetics were applicable, an improved estimate of M was then made. Although this was not necessary for curves which had leveled off and for which little further extraction was to be expected, improved estimates were required for other curves in which a gradual increase with time occurred. For each flotation it was considered that the final percentage recovery, M_i, could have any integral value between R_f and 100%, the former being the recovery value for the last sample taken. For each value of M_i, the function $Y_t = M_i \ln [M_i/(M_i - R)]$ was plotted against the values of time t corresponding to the values of R, and the best straight line was fitted in each case. The value of M_i which produced the highest value of F was then taken as the correct value of M. This empirical method was applied to each flotation, whether a reliable estimate of M had been made for it or not. In all cases where the estimate had been made easily, the optimum value of M determined as above was within 2% of the estimate.

RESULTS

Flotation Experiments

The flotations of 10^{-5} and 10^{-4} M solutions of HTMAC at gas flow-rates of 2 and 5 l/hr resulted in very poor recoveries of the collector. It was found, however, that the addition of salts greatly enhanced these recoveries, and all subsequent work was performed in solutions of appreciable ionic strength.

The flotation curves of 10^{-5} and 10^{-4} M solutions of HTMAC in the presence of 10^{-3}, 10^{-2}, and 10^{-1} M sodium chloride were determined at the above gas flow-rates, those for 5 l/hr being shown in Figs. 2 and 3. It is clear that the rates of flotation, i.e., the slopes of the curves in the initial stages, increased with increasing ionic strength and also that the recovery of HTMAC was almost complete from 10^{-4} M solutions but was often lower for the more dilute solutions.

The flotation of HTMAC from any one solution differed at the two flow-rates only in the speeds at which the collector was removed. Rate constants for these processes are shown in Table 1 and are discussed later. Figure 4 is typical of the different rates of removal.

The effects of added salts were even more marked with sodium sulfate for which, at lower concentrations, only about one-tenth to one-hun-

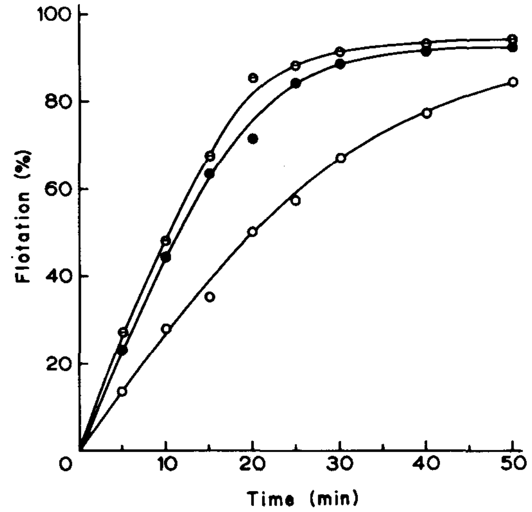

FIG. 3. The effect of NaCl on the flotation of 10^{-4} *M* HTMAC: (○) 10^{-3} *M* NaCl, (●) 10^{-2} *M* NaCl, and (⊖) 10^{-1} *M* NaCl.

dredth as much was required to give the same recoveries as when using sodium chloride (cf. Fig. 5). The behavior was not maintained on raising the sulfate ion concentration, however, as little improvement occurred in recoveries from 10^{-3} to 10^{-2} *M*. The enhanced effect at low concentrations can be attributed to the double charge on the sulfate ion, be-

TABLE 1

Rate Constants for the Flotation of HTMAC

		Rate constants (min^{-1})		
Concn of HTMAC (*M*)	Concn of salt (*M*)	2 l/hr (*M* values in parentheses)	5 l/hr (*M* values in parentheses)	Ratio of rate constants β
10^{-5}	10^{-3} NaCl	0.031 (1.00)	0.099 (0.94)	3.2
10^{-4}	10^{-3} NaCl	0.011 (1.00)	0.042 (0.96)	3.8
	10^{-2}	0.025 (1.00)	0.077 (0.94)	3.1
	10^{-1}	0.048 (1.00)	0.11 (0.94)	2.3
	10^{-4} Na_2SO_4	0.024 (1.00)	0.061 (0.92)	2.5
	10^{-3}	0.037 (1.00)	0.075 (0.91)	2.3

cause similar experiments using strontium chloride as added electrolyte gave results which were little different from those for sodium chloride at comparable concentrations. It is, therefore, the nature of the anion, and not of the cation, which is significant.

The concentration and the charge are not the only features of the anion which influence the flotation of the cationic collector. When, for example, sodium ethylxanthate was used as the added salt, it was found that the flotations were more rapid than in the presence of one hundred times as much sodium chloride (cf. Fig. 6). Both anions are singly-charged but their influences on the flotation of HTMAC are widely different.

A synergistic effect exists for the flotation of ethylxanthate and collector ions in that each floats poorly on its own but very well from a solution of the two together. Similar synergistic behavior exists for the surface tensions of such solutions, and also for the flotation of certain minerals which float well using the combined collectors but poorly with either one alone (7). Such effects indicate that appreciable surface interactions exist between the two species, and how these arise will be considered in the next section.

Regarding the effects of temperature on the flotation of HTMAC, it was found that changes occurred for 10^{-5} *M* solutions, but none for

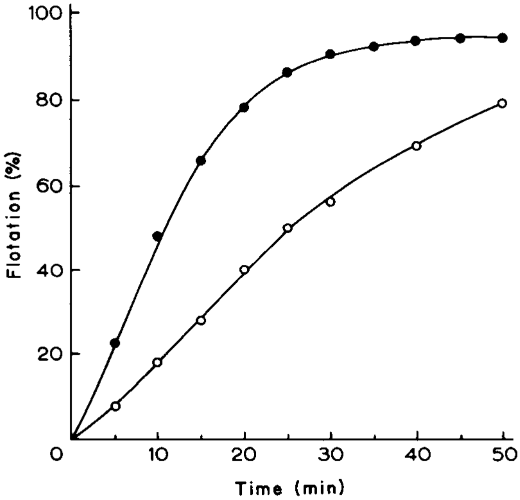

Fig. 4. The effect of gas flow-rate on the flotation of HTMAC: (○) 2 l/hr, and (●) 5 l/hr.

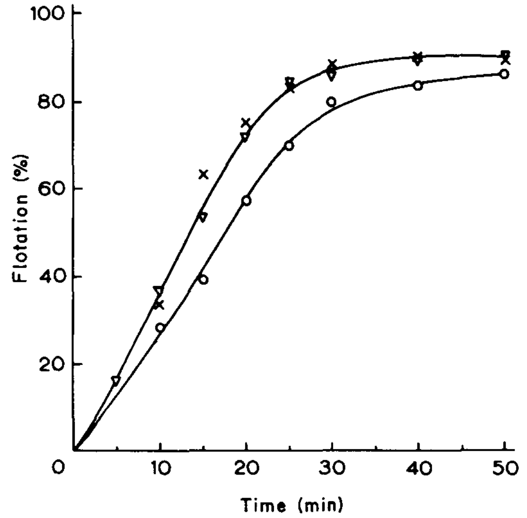

FIG. 5. The effect of Na_2SO_4 on the flotation of 10^{-4} *M* HTMAC: (○) 10^{-4} *M* Na_2SO_4, (▽) 10^{-3} *M* Na_2SO_4, and (×) 10^{-2} *M* Na_2SO_4.

10^{-4} *M* solutions, on raising the temperature. In Fig. 7, for example, the curve at 30°C shows that extraction was delayed in the early stages, after which flotation proceeded normally. This delay coincided with an obvious difficulty, during the first 10 min, in forming a foam.

The removal of DPC from solution by flotation was considerably more difficult (cf. Fig. 8) than for HTMAC. Concentrations of 10^{-1} *M* of sodium chloride, or 10^{-2} *M* of sodium sulfate, were required before any flotation occurred. Further, no foam was observed and very little DPC was removed from solutions of the surfactant that were less concentrated than 10^{-4} *M*.

Surface Area Determinations

From the photographic method described earlier, it was determined that the total surface areas passing through 10^{-5} and 10^{-4} *M* HTMAC solutions at 2 l/hr during 50 min of flotation were 93 and 120 m^2, respectively. The surface area to volume ratios were 56 and 71 m^2/liter and the mean sizes of the bubbles were 0.077 and 0.067 mm, respectively. The number of bubbles passing through each system was about 8 million/min. The distribution of sizes was such that the surface area of the smaller bubbles, which occupied one-third of the total volume of the bubbles photographed, accounted for about one-half of the total surface area present.

The determination of the total surface area by grouping the bubbles into classes of size differing by 0.01, 0.02, and 0.04 mm instead of measuring each bubble as accurately as possible showed that certain approximations could be made with justification. For example, the first two class intervals above gave agreement within 1% and the other interval up to 2.5% of the accurately calculated value. It is concluded, therefore, that in measuring bubbles with actual diameters of about 0.1 mm under a magnification of 50×, they may be grouped into size classes which differ by 1 mm on the photograph. The surface areas and volumes are then calculated from the frequency of the bubbles and the mean diameter of the class interval. Such an approximation greatly facilitates the determination.

A marked difference was evident between the two flotations regarding the number of bubbles to be processed before the progressive totals of the surface area and the volume of the bubbles converged to the values ultimately found for the whole run. Such convergence occurred after measuring 450 and 180 bubbles for the 10^{-5} and 10^{-4} M HTMAC solutions, respectively. There was no significant difference between the

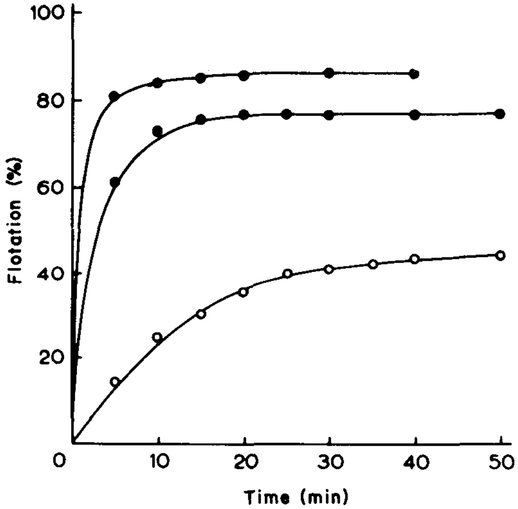

FIG. 6. The effect of sodium ethylxanthate on the flotation of 10^{-5} M HTMAC at 5 l/hr: (○) 10^{-5} M, (●) 10^{-4} M, and (⊖) 10^{-3} M.

rates of convergence of the accurate values of the surface areas and those obtained using class intervals. The limited data above do not allow a conclusion to be made regarding the number of bubbles to be processed but it is clear that this number may vary considerably from one set of conditions to another.

The histogram, prepared from the data obtained from each photograph, showed no systematic drift in the sizes of the bubbles during a run. It must be concluded, therefore, that although the concentration of the surfactant present decreased with time, the average size of the bubbles did not change.

Kinetic Considerations

As explained previously, two rate equations were found to fit the flotation results adequately. Both identified the flotation process as being of first order but the return process could be either first or second order. This uncertainty is not surprising as the return process involves drainage from foams, which is not simple. Only in those cases, therefore, for which *M* was close to 1.0, i.e., those for which the rate constant of the return process was much smaller than that for flotation, have the values of *k* been used in the present discussion. These values for the flotation

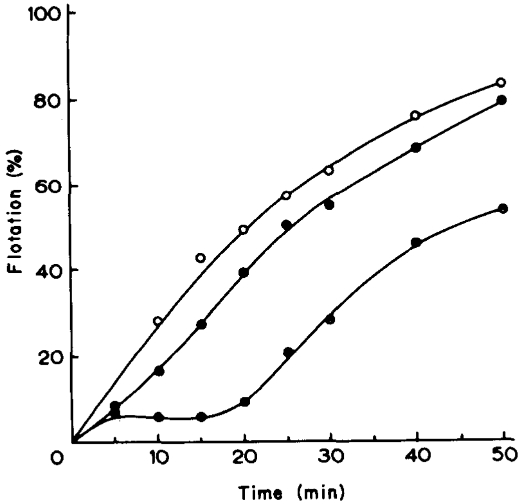

FIG. 7. The effect of temperature on the flotation of 10^{-5} *M* HTMAC in the presence of 10^{-3} *M* NaCl at 2 l/hr: (○) 10°C, (●) 20°C, and (⊖) 30°C.

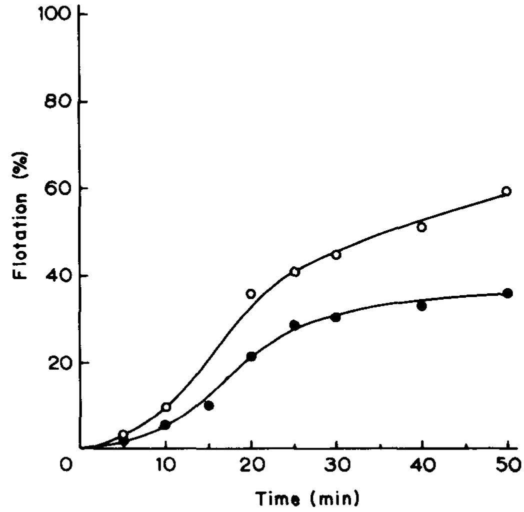

FIG. 8. The flotation of DPC from 10^{-1} *M* NaCl solutions at 5 l/hr: (○) 10^{-5} *M*, and (●) 10^{-4} *M* DPC.

of 10^{-4} *M* HTMAC in the presence of sodium chloride or sodium sulfate at flow rates of 2 and 5 l/hr are given in Table 1. The corresponding values for sodium ethylxanthate as well as all but one of those for 10^{-5} *M* HTMAC solutions are omitted as these flotations were too rapid to provide meaningful results. The values of *M* used in each determination are given in parentheses. The ratio of the rate constants at the two flow rates (β) are also included, as these values will be compared to the ratio of the total surface areas of the bubbles passing at 5 and 2 l/hr.

An estimate of this latter ratio was made from the measurements of Spargo and Pinfold (*8*) who first used the photographic method to estimate the total surface areas available during such flotations. A value of 2.1 was obtained. It is considered significant that the values of β in Table 1 appear to converge to this value, with increasing concentrations of added salts.

DISCUSSION

It is not difficult to understand why the rates of flotation of the HTMAC increase with increasing ionic strength. The collector ions adsorbed on a bubble repel each other because of their like charge, and oppose the adsorption of further collector. The bubbles, therefore, are sparsely laden, and removal by flotation is slow. In addition, the foam formed at the surface of the solution is unstable because of the low concentration of surfactant in the lamellae, and redispersion of the floated material occurs quite readily. On increasing the ionic strength of the solution by the addition of salts, a higher concentration of counterions occurs on the solution side of the double layer, which lowers the mutual repulsions of the adsorbed collector ions and allows an increase in their concentration in the surface. The flotations are consequently more rapid, with the higher charged sulfate ions having a greater influence than chloride ions.

An increase in ionic strength also has an effect on the stability of the foam and hence on the rate at which floated material is redispersed into the solution. As shown in Fig. 2, almost complete recovery of HTMAC is possible from solutions 10^{-3} *M* with respect to sodium chloride. Higher concentrations of the salt lead to more rapid flotations, as witnessed by the increase in the initial slopes of the flotation curves, but the final recoveries are well below 100%. The presence of higher concentrations of electrolyte in the foam reduces the repulsions between the two layers of collector ions on opposite sides of the lamellae, and allows the latter to become very thin. This causes the foam to be unstable, and marked redispersion of the collector occurs. The horizontal portions of the curves in Fig. 2 represent conditions under which the rate of removal of collector by flotation is the same as that of redispersion of collector back into the solution. The latter effect is not as evident in Fig. 3 because the higher concentration of HTMAC used results in more stable foams which are less susceptible to the disruptive effects of added electrolyte.

The marked increases in the rates of flotation which occur in the presence of ethylxanthate ions are the result of their ability to take up positions between the adsorbed collector cations in the interface. The polar heads of the two species are then approximately in the same plane while the hydrophobic parts extend into the gas phase and allow of further attraction between the species by van der Waals forces. The ethylxanthate ions are thus able to neutralize the repulsions between the cations much more effectively than either the sulfate or chloride which cannot approach the interface as closely. The bubbles are consequently more heavily laden with collector and the flotation is more rapid than with sulfate or chloride ions.

The effects of temperature described previously probably arise from two causes. First, adsorption is an exothermic process and therefore decreases with increasing temperature, and second, foams are more stable at lower temperatures because the drainage of entrained liquid is reduced by a higher viscosity. Both effects lead to better recoveries at lower temperatures but are apparent only for the lower HTMAC concentration, where the extent of adsorption is smaller and the foam is less stable.

The difficulty with which DPC floats in comparison to HTMAC can be attributed to the difference in their surface activities. For similar conditions, the bubbles are less laden and the foams are less stable for the former surfactant, leading to poorer recoveries.

Regarding the distribution of bubble sizes and the rate constants for flotation of HTMAC, an explanation is required for the following phenomenon. The average bubble sizes and the rate constants for flotations of 10^{-5} and 10^{-4} M solutions of HTMAC were not the same, and yet after 90% of the collector in the latter solution had been removed the concentration was 10^{-5} M. The state which existed at the beginning of the flotation of a 10^{-5} M solution, therefore, must have been different from that of a solution initially 10^{-4} M but from which 90% of HTMAC had been removed, although the concentration of the collector was the same.

In explanation of the above it is suggested that bubbles which are laden with collector ions repel each other strongly because of the like charge distributed over their surfaces. Such repulsions prevent their coalescence if they are small enough and lack the kinetic energy to overcome such forces. As it is only the larger bubbles which are able to force their way out of the liquid, small bubbles, laden with collector, accumulate in the solution. The material which is floated is carried from the solution by the larger bubbles, not the smaller ones.

It is suggested that the repulsions referred to above are most significant in the lower reaches of the foam where bubbles have gathered but have not yet been incorporated in a foam structure. This layer, which contains a high proportion of water, is really a concentrated air in water emulsion. Bubbles which resist coalescence remain in this region and the probability of them being swept back into the solution by the turbulence is considerably greater than for others that coalesce to form bigger bubbles and move upward.

If this contention is true, no relationship should exist between the total surface area of gas passing through the solution and the rate of flotation, because the former is a summation for bubbles of all sizes while the latter depends only on the larger bubbles. The ratios of the rate constants at two different flow rates should then bear no relationship to the ratios of the total surface areas determined photographically. That this is true is shown in Table 1 where the ratios of the rate constants at 5 and 2 l/hr, β, are markedly different from 2.1, the ratio of the surface areas.

As the ionic strengths of the solutions are raised, the zeta potentials of the bubbles should be reduced and their mutual repulsions lessened. Coalescence should then occur more readily, a larger number of the smaller bubbles should contribute to flotation, and the values of β should approach 2.1, as found in Table 1. That the values are above 2.1 implies that the rate constants at 2 l/hr are smaller than they should be relative to those at 5 l/hr. This is to be expected on the above theory because at the lower flow-rate the smaller bubbles form a greater proportion of the whole than they do at the higher flow-rate where the average size is larger. As small bubbles impede removal by their resistance to coalescence, the rate constants at 2 l/hr are lowered and β is greater than 2.1.

That the flotations follow first-order kinetics is not surprising in that the amount of collector removed depends on the concentration of the latter in the solution and on the total surface area of the bubbles leaving the bulk liquid phase per minute. As the average size of the bubbles does not change noticeably during a run, it is probable that the total surface area of the bubbles leaving the solution in a given time does not change either, and hence the rate of removal of collector depends on its concentration in the solution at that time.

That the rate constants are different from solutions of 10^{-5} and 10^{-4} M HTMAC is explained by the appreciable amounts of collector which are adsorbed on small bubbles, the removal of which is impeded by their mutual repulsions. The quantity of collector which experiences such retarded flotation differs at different initial concentrations. The effect on the rate constant is that while the latter remains the same during a particular run, it differs from one run to another.

That the average size of the bubbles in a run remains constant may also be explained on the basis of repulsions between small bubbles. It might have been expected that with decreases in the collector concentration, and hence increases in the surface tension of the solution, that the average size of the bubbles would increase with time. However, as an appreciable proportion of the population consists of small bubbles which resist coalescence and removal, the small increases which should occur due to higher surface tensions are largely offset.

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