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Studies of the Removal of Dye Ions by Adsorbing Particle Flotation

Koichi Kobayashi, Nobuhiro Watabe, and Tsunetaka Sasaki
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo 158

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The removal of an anionic dye, Scarlet Red, a zwitterionic dye, Congo Red, and a cationic dye, Crystal Violet, from aqueous solutions was studied by the method of adsorbing particle flotation, using bentonite and benzylhexadecyldimethylammonium chloride as flotation agents. More than 99% of the Crystal Violet and Scarlet Red and 96% of the Congo Red could be floated under optimum conditions. It was found that a larger amount of a cationic surfactant was required for the flotation with an increase in the anionic nature of the dye ions, although the flotation was efficient irrespective of the ionic nature of dyes used. From this fact, the flotations of anionic and cationic dyes were confirmed to differ from each other in that the cationic-dye ions are floated by a direct exchange adsorption on bentonite, while the anionic-dye ions are floated by the adsorption on bentonite through the bimolecular layer of the cationic surfactant. The flotation efficiency of a dye ion, particularly of zwitterionic dye, was confirmed to depend on the pH.

A limited number of studies have been reported of the flotation of dye ions.[1–4] Karger *et al.* examined in detail the solvent sublation process for the removal of two dyes, Methyl Orange and Rhodamine B, using hexadecyltrimethylammonium bromide as the collector and 2-octanol as the immiscible organic liquid layer.[5–7] We ourselves have previously reported that Cu^{2+},Cd^{2+}, and Co^{2+} ions were effectively removed from an aqueous solution by adsorbing particle flotation,[8–10] which is considered to be an effective method of flotation. The process is defined as the removal of the dissolved materials by the flotation of the particle-like bentonite upon which the ions to be removed is adsorbed. So far, however, no application of the adsorbing particle flotation has been made to the removal of dye ions from an aqueous solution. Dye ions are especially suited to the study of flotation since they include various types of ions—namely anions, cations, and zwitterions—and they can be easily detected visually or assayed by colorimetry.

The present paper will describe the applicability of adsorbing particle flotation for the removal of dye ions, such as anionic Scarlet Red, zwitterionic Congo Red, and cationic Crystal Violet, from their aqueous solutions. Here, the effects of the gas-flow time, the pH, the amount of bentonite, the amount of the cationic surfactant, and the nature of the dye ions on the flotation efficiency have been studied.

Experimental

Materials. The benzylhexadecyldimethylammonium chloride (BHDAC) was obtained from the Nippon Oils and Fats Co., Ltd., and was purified by recrystallization from acetone. The bentonite powder(Bt) used as an ion exchanger was obtained from the Wako Pure Chemical Co., Ltd.; the fraction passing through a 350-mesh sieve was collected and dried under reduced pressure. The dyes used included cationic Crystal Violet(CV), anionic Scarlet Red(SR), and zwitterionic Congo Red(CR). These dyes were purified by recrystallization from ethanol and ether. A stock solution of the dye ions of a 1×10^{-4} mol/l concentration was prepared by dissolving these dyes in triply distilled water.

Apparatus and Procedure. The apparatus used for the flotation measurements was the same as has been described in a previous paper.[2] The sample solution of flotation was prepared by introducing 1 ml of a stock solution of the dye ions, and given amounts of Bt and BHDAC into a 10-ml measuring flask, adjusting the pH to a desired value, and diluting the solution to 10 ml with water. Nitrogen gas humidified with water vapor and controlled to a constant rate of gas-flow was bubbled through a glass filter (No. 4) into a flotation cell containing about 10 ml of the sample solution. After the flotation, the underlying liquid was taken out of the flotation cell for the determination of the dye-ion and Bt contents.

For the determination of the dye-ion concentration, the light absorption were measured for the dye ions and the calibration curves were prepared at their maximal absorption wavelengths (500 nm for CR, 580 nm for CV, and 500 nm for SR). The initial concentration of each dye ion of the sample solution was determined by using these calibration curves before the Bt addition. However, the dye-ion concentration after the flotation cannot be determined similarly since the measurement is hindered by the presence of the Bt-particle, which also reduces the light intensity by scattering. The concentration of the dye ions of such a solution was estimated by assuming that the absorbance at the maximal absorption wavelength is the sum of the absorbances of the dye ions and the scattering by Bt, while the absorbance at the minimal absorption wavelength is considered to be mainly due to the scattering by Bt. Then, the calibration curves of Bt without the dyes at the maximal and minimal absorption wavelengths were drawn. The amount of Bt in the sample was determined from the absorbance at the minimal absorption wavelength by applying the calibration curve of Bt at the minimal absorption wavelength; the contribution of the absorbance due to Bt at the maximal wavelength was estimated by applying the calibration curve of Bt at the maximal absorption wavelength. The absorbance due to dye ions alone was obtained by subtracting this contribution from the total absorbance by the sample solution at the maximal absorption wavelength. The concentration of dye ions was determined by using the calibration curve for the dye ions at the maximal absorption wavelength.

The flotation efficiency of the dye ions or Bt is conventionally expressed by:

$$F=\frac{C_i-C_f}{C_i}\times100\%$$

where C_i and C_f are the initial and final concentrations respectively of the dye ions or Bt.

Results and Discussion

Gas-Flow Time, Amount of Bt, and Flotation Efficiency. First, we studied the effects of the amount of added Bt and the gas-flow time on the flotation efficiency for

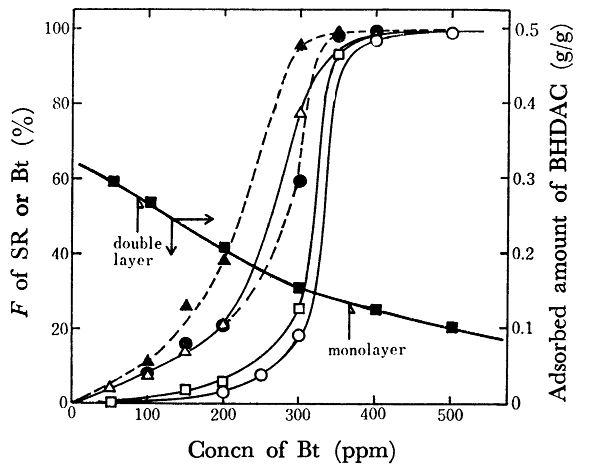

Fig. 1. Effect of gas-flow time on flotation efficiency. SR: 1×10^{-5} mol/l, BHDAC: 50 ppm, gas-flow rate: 5 ml/min, pH: 5.4—5.9, gas-flow time (○, ●: 2 min, □: 5 min, △, ▲: 15 min), ——: *F* of SR, ----: *F* of Bt, ■: adsorbed amount of BHDAC.

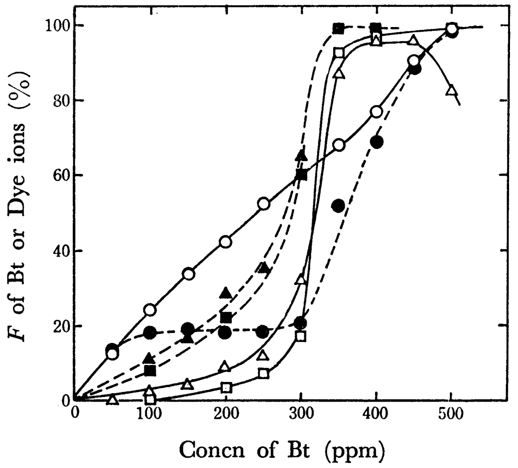

Fig. 2. Effect of ionic nature of dye on flotation efficiency.
Dye ions: 1×10^{-5} mol/l, BHDAC: 50 ppm, gas-flow rate: 5 ml/min, gas-flow time: 2 min, ——: *F* of dye ions (○: CV, △: CR, □: SR), ----: *F* of Bt (●: CV, ▲: CR, ■: SR).

the SR–BHDAC–Bt system, keeping the amount of BHDAC and the gas-flow rate constant. The results are shown in Fig. 1. As may be seen in the figure, flotation efficiencies of SR and Bt increase with the increases in the gas-flow time and in the amount of Bt added. The curves sharply rise in the vicinity of 300 ppm Bt, and nearly 100% flotation efficiencies of SR and Bt are obtained at 400 ppm Bt. In the region of Bt content below 400 ppm, the flotation efficiency of SR is lower than that of Bt. This may suggest the presence of free SR being adsorbed neither on Bt nor on an aqueous surface. Since SR alone and the SR–BHDAC complex are not easy to float, as will be shown later (Fig. 8), the coincidence of the SR and Bt curves near 100% flotation at about 400 ppm may indicate the complete adsorption of SR on Bt. Further, the amount of adsorption of BHDAC on Bt, though not directly measured, was presumed from the adsorption isotherm on Bt of hexadecyltrimethylammonium chloride,[11] which has a molecular structure similar to that of BHDAC. The solid squares in Fig. 1 indicate the amount of the adsorption of BHDAC on Bt on such an assumption. Here, the arrows indicate a monolayer and a bimolecular layer adsorption of BHDAC, as estimated from the base-exchange capacity of Bt.[11] As may be seen in the figure, the flotation efficiency of Bt decreases from 100% to a very low value in the concentration region from the monolayer to the bimolecular layer adsorption. This behavior is similar to those reported in a previous paper.[11] Since an *F* value of 100% was obtained at the gas-flow time of 2 min and above, all the subsequent experiments were carried out under the conditions of 50 ppm BHDAC, 0 to 500 ppm Bt, 1×10^{-5} mol/l dye, pH 5.4 to 5.9, a gas-flow time of 2 min, and a gas-flow rate of 5 ml/min.

Ionic Nature of Dyes and Flotation Efficiency. In order to study the effect of the ionic nature on the flotation efficiency, the flotation experiments were carried out for CR and CV by varying the amount of added Bt under the same conditions as for SR. The results for the flotation efficiency of dye ions and Bt are illustrated by the solid and broken lines respectively in Fig. 2, together with the experimental results for SR shown in Fig. 1. The flotation efficiencies of the dye ions and Bt increase for all the dye–Bt–BHDAC systems with an increase in the amount of added Bt. Here, zwitterionic CR behaves as an anion under experimental condition of a pH value between 5 and 6 since it has an isoelectric point of about 3. Therefore, the *F* curves for CR–BHDAC–Bt and SR–BHDAC–Bt systems are similar in their behavior: the *F* curve of the dye ions is lower than that of Bt, and beyond 400 ppm of Bt addition, *F* increases to 95—97% for both Bt and dye flotation efficiencies. In the case of cationic CV, however, the flotation efficiency of Bt exhibits a low plateau in the region of a small Bt addition: it then increases sharply near the 300 ppm Bt addition, and rise to nearly 100% in the vicinity of 500 ppm Bt. In the case of CV flotation, the flotation efficiency of the dye ions is higher than that of Bt over the whole region of Bt added, while the flotation efficiency of the dye ions is lower than that of Bt in the cases of CR and SR. These discrepancies indicate the existence of free dye ions not adsorbed on Bt; in the case of CV the free ions are adsorbed directly on bubbles and are floated, while CR and SR are not adsorbed and are not floated: this adsorption effect is dominant in the region of smaller amounts of Bt addition and lower *F* values, where there is not much Bt available for CV adsorption. Further, the possibility that CR and SR combine with BHDAC and float is considered. However, such a possibility can not be practically expected considering the flotation data for various anionic dyes by several cationic surfactants[12] and also the results shown in Fig. 8.

The effects of the anionic and cationic dyes on the flotation efficiency of Bt were further studied in detail in relation to the system without any added dye. The results are shown in Fig. 3. As may be seen in the figure, the flotation curves of Bt for the anionic dye–

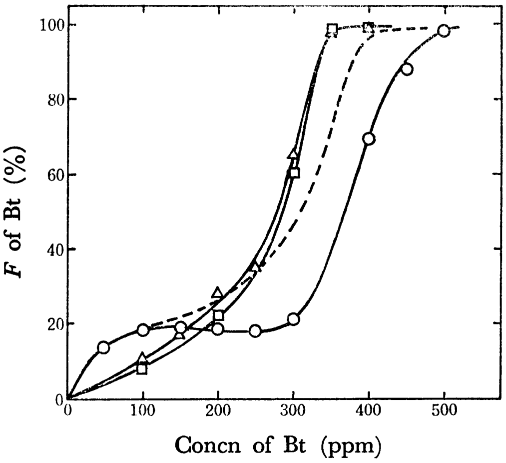

Fig. 3. Effect of dye ions on flotation efficiency of Bt. Dye ions: 1×10^{-5} mol/l, BHDAC: 50 ppm, gas-flow rate: 5 ml/min, gas-flow time: 2 min, ——: *F* of Bt (○: CV, □: SR, △: CR), ----: *F* of Bt for system of no added dyes.

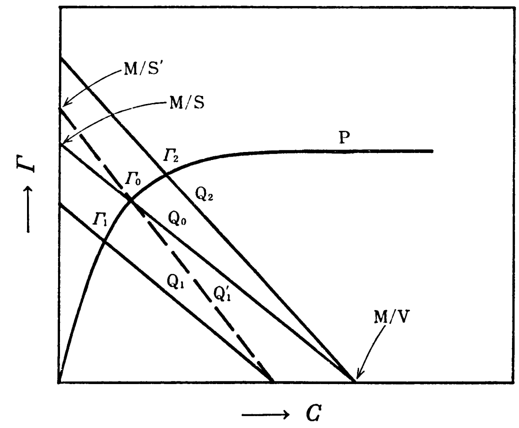

Fig. 4. Relation between amount of adsorption and equilibrium concentration of BHDAC.

BHDAC–Bt and cationic dye–BHDAC–Bt systems shift left and right, respectively, to the curve of the BHDAC–Bt system. These phenomena can be explained from the amount of BHDAC adsorption as follows.

The amount of adsorption of BHDAC on Bt, Γ, can be calculated from the adsorption isotherm;

$$\Gamma = f(C) \tag{1}$$

and

$$S\Gamma + VC = M \tag{2}$$

where V is the volume of solution; C and M, the equilibrium concentration and the total amount of BHDAC respectively, and S, the total amount of Bt added to the system. According to these equations, the value of Γ is graphically obtained to be as is shown in Fig. 4. In this figure, the P and Q lines express Eqs. 1 and 2 respectively, while the point of intersection, Γ, gives the amount of adsorption for a given S, V, and M. Since the intercept of Eq. 2 on the ordinate is M/S, and since that of the abscissa is M/V, Γ is a function of M/S and M/V for a given Eq. 1, that is, for the BHDAC–Bt system. If the straight line, Q_0, expresses Eq. 2 for the system without a dye, the Γ_0 value in Fig. 4 is the amount of adsorption for this system. Now, the amount of effective BHDAC, M, decreases when SR or CR are added because the dye combines with it. Thus, Eq. 2 for the SR system moves from Q_0 to Q_1, and the point of intersection, Γ_1, shifts towards a smaller value. To restore Γ_1 to the original value, Γ_0, for the system without a dye, the value of S should be decreased to S' so as to increase the M/S ,as is shown by the broken line, Q'_1. This means that the same F value can be obtained by a smaller addition of Bt to the SR and CR systems as compared with the system without a dye: this results in a shift of the SR and CR curves in Fig. 3 to the left. In the case of the CV–BHDAC–Bt system, the effective S available for BHDAC adsorption decreases because some of the adsorption sites of Bt are occupied by cationic CV. The decrease in S increases the M/S value, Eq. 2 moves from Q_0 to Q_2 and the Γ_0 value increases to Γ_2. This results in an opposite effect to that in the case of SR and shifts the F curve of CV to the right of that for the system without a dye.

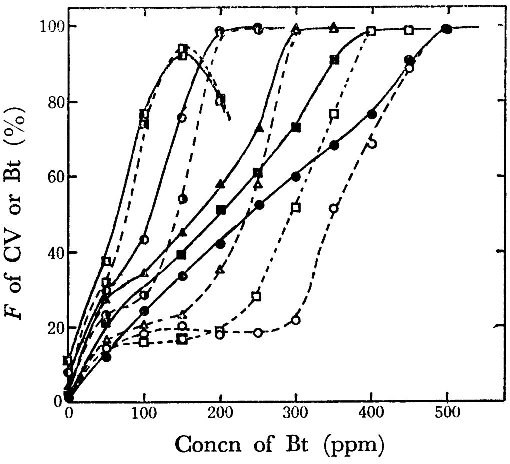

Fig. 5. Effect of BHDAC on flotation efficiency. CV: 1×10^{-5} mol/l, BHDAC (◨, ◧: 10 ppm, ◐, ◑: 20 ppm, △, ▲: 30 ppm, □, ■: 40 ppm, ○, ●: 50 ppm), pH: 5.3—5.9, gas-flow rate: 5 ml/min, gas-flow time: 2 min, ——: *F* of CV, ----: *F* of Bt.

Concentration of BHDAC and Flotation Efficiency. Figure 5 shows the flotation efficiencies of CV and Bt as a function of the amount of Bt for various concentrations of BHDAC. As may be seen in the figure for a given concentration of BHDAC, at a relatively small amount of Bt addition, the F for CV flotation is larger than that for Bt, while both values are close or agree and become 100% at larger amounts of Bt addition, regardless of the concentration of BHDAC. In the case of an BHDAC addition of 10 ppm, however, the flotation efficiency of Bt and CV shows a maximum less than 100% at 150 ppm Bt. This means that the amount of BHDAC adsorbed decreases below the minimum amount of BHDAC adsorption necessary for 100% flotation.

In Fig. 5, the weight ratio of BHDAC/Bt may be observed to be constant to about 1/10 at the shoulder of $F\simeq100\%$, regardless of the amount of BHDAC added. According to the adsorption isotherm of

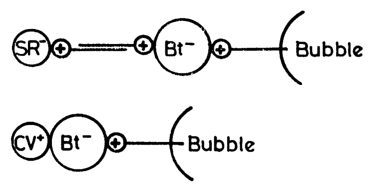

Fig. 6. Comparison of sublate structure of SR–Bt–BHDAC and CV–Bt–BHDAC systems. ⊕——: BHDAC.

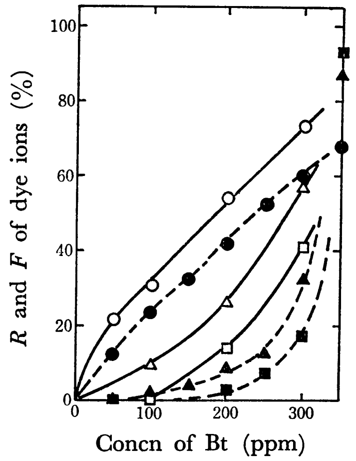

Fig. 7. Effect of dye ions on percent removal of dye ion. Dye ion: 1×10^{-5} mol/l, BHDAC: 50 ppm, gas-flow rate: 5 ml/min, gas-flow time: 2 min, ——: R of dye ions (○: CV, □: CR, △: SR), ----: F of dye ions (●: CV, ■: CR, ▲: SR).

BHDAC on Bt (Fig. 4) this means the constancy of M/S and that Γ is independent of M/V. This can be realized only when the adsorption isotherm (Eq. 1) shows an initial rise very close to the ordinate and exhibits a distinct shoulder, as has previously been reported.[11)] Further, since, in this condition, the dyes and Bt nearly completely float, the above BHDAC/Bt ratio is nearly equal to the composition of the BHDAC–Bt sublate. Thus, when we compare the SR system of 50 ppm BHDAC and 400 ppm Bt in Fig. 1 with the CV system of 40 ppm BHDAC and 400 ppm Bt in Fig. 5, both of them showing a nearly 100% flotation efficiency of the Bt and dye ions, a larger amount of surfactant is required for the sublate of SR than for that of CV. Some tentative models for such systems are shown schematically in Fig. 6. The situation is quite similar to the case of Fe^{3+} and MnO_4^- flotation previously reported.[13)]

Centrifuging. For systems in which the F values of Bt and dye ions are nearly 100%, as is shown in Figs. 1 and 2, the dye ions are considered to be completely adsorbed on Bt and subsequently floated by BHDAC. However, when the F value is less than 100% and when the curves for dye and Bt do not coincide, some dye ions are considered not to be combined with Bt. To confirm such details, the underlying liquid of the system after flotation carried out under the conditions of Fig. 2 was centrifuged for 20 min at 4000 rpm. In Fig. 7, the total percentage of the removal (R) of dye ions centrifuged and floated, namely, the percentage obtained by subtracting the percentage of dye ions remaining after centrifugation from 100%, is plotted against the amount of added Bt as solid lines. The dye flotation curves of Fig. 2 are also drawn for comparison. As may be seen, the total removal curves of CV, SR, and CR are located above the flotation curve. The difference in the ordinate between the two curves gives the amount of dyes combined with Bt and retained in the solution. In Fig. 7, the total percentage of the removal of CV is read as 22% for the system of 50 ppm Bt, where the total percentage of the removal of Bt is found to be 100%. From these data, together with the 14% flotation efficiencies of both Bt and CV at 50 ppm Bt addition (Fig. 2), the following equations are obtained:

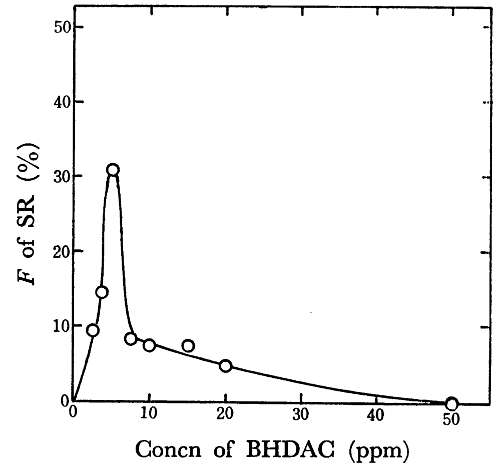

Fig. 8. Flotation efficiency of SR *vs.* BHDAC concentration for SR–BHDAC system. SR: 1×10^{-5} mol/l, gas-flow rate: 5 ml/min, gas-flow time: 2 min.

$$F_0 + F_1 = 14, \quad F_0 + F_1 + S_1 = 22,$$

$$S_1/F_1 = (100-14)/14, \quad S_0 + S_1 + F_0 + F_1 = 100$$

where F_0 is the flotation efficiency of CV ions adsorbed directly on bubbles; F_1, the percentage of CV ions adsorbed on Bt and floated; S_0, the percentage of free CV ions remaining in the solution, and S_1, the percentage of CV ions adsorbed on Bt and remaining in the solution. From the above equations, F_0, F_1, S_0, and S_1 are calculated to be 12.7%, 1.3%, 78.0%, and 8.0%. Thus, we can confirm the amounts of the dye ions in various states in the solution and in the sublate, although this is an instance of rather incomplete flotation, as judged from the position on the curve in Fig. 7.

Flotation of the SR–BHDAC System. Figure 8 shows the flotation efficiency curve for the SR–BHDAC system without Bt. A sharp but small rise in flotation efficiency is seen in the relatively low concentration region. This result shows that the possible formation of the SR–BHDAC complex, if any, does not contribute appreciably to the SR flotation efficiency.[13)] Rather, it decreases the free SR ion and hinders the adsorbing flotation, as has been mentioned above. The experiment also confirms that the addition of Bt is essential for a high flotation efficiency, with the possible sublate structure shown in Fig. 6.

Effect of the pH on the Flotation Efficiency. The

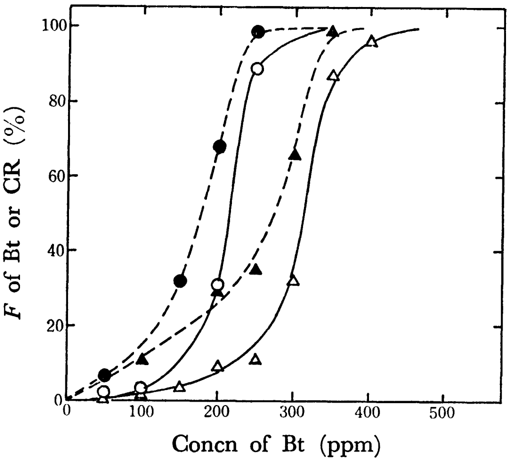

Fig. 9. Effect of pH on flotation efficiencies of CR and Bt. CR: 1×10^{-5} mol/l, BHDAC: 50 ppm, gas-flow rate: 5 ml/min, gas-flow time: 2 min, ——: *F* of CR (○: pH 2, △: pH 5—6), ----: *F* of Bt (●: pH 2, ▲: pH 5—6).

effect of the pH on the ion flotation is usually considered to be important. Figure 9 shows the effect of the pH on the flotation efficiency of the CR and Bt of the CR–BHDAC–Bt system. Here, we used CR as a dye since it is sensitive to the pH because of its zwitterionic nature. The measurements were made at pH 2 and 5, adjusted by the addition of hydrochloric acid. Since the isoelectric point of CR is near 3, CR ions are considered to be in the cationic and anionic forms respectively at the respective pHs. It may be expected, therefore, that the *F* curve of Bt shifts right at pH 2 and left at pH 5 to the *F* curve of Bt without dye addition, as is shown in Fig. 3. The result obtained at pH 5 is in accord with the expectation, while the result at pH 2 is contrary to what is expected: the *F* curve of Bt markedly shifts even left to that of the SR shown in Fig. 2. This can be explained by saying that, since the H$^+$ ion concentration at pH 2 is markedly higher than that of the BHDAC ion (10^{-5} mol/l), the adsorption of the BHDAC cation on Bt is hindered by hydrogen-ion adsorption; the effect is equal to the reduction of the BHDAC concentration as far as the amount of adsorption is concerned. Thus, the shift of the *F* curve for CR at pH 2 is in the same direction as that for SR, as shown in Fig. 3. Here, as the concentration of the hydrogen ion is much larger than that of the SR ions in Fig. 2, the shift for CR is expected to be far greater than that for SR.

Table 1. The optimum conditions of dye-ion flotation

Dye	CV$^+$	CR$^\pm$	SR$^-$
Dye concn. (mol/l)	1×10^{-5}	1×10^{-5}	1×10^{-5}
Surfactant concn. (ppm)	15	50	50
Bt concn. (ppm)	150	400	350
Surfactant/Bt	1/10	1/8	1/7
Gas-flow time (min)	2	2	2
Gas-flow rate (ml/min)	5	5	5
F of dye (%)	98	96	98
Volume of liquid taken (ml)	10	10	10

Optimum Condition of Flotation. The optimum conditions of dye-ion flotation obtained in this study are tabulated in Table 1. In Table 1, the BHDAC/Bt ratio expresses the composition of the solution, which also represents the composition of the sublate for the reasons mentioned already. This table confirms that a larger amount of cationic surfactant is required for the flotation with an increase in the anionic nature of the dye ions; this is in accord with the results obtained for Fe^{3+} and MnO$_4^-$ ion flotation.[12)]

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