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Bozenna Kawalec-pietrenko[a]; Anatol Selecki[b]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, TECHNICAL UNIVERSITY, GDANSK, POLAND [b] INSTITUTE OF CHEMICAL ENGINEERING, TECHNICAL UNIVERSITY, WARSAW, POLAND

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Investigations of Kinetics of Removal of Trivalent Chromium Salts from Aqueous Solutions Using Ion and Precipitate Flotation Methods

BOŻENNA KAWALEC-PIETRENKO

DEPARTMENT OF CHEMICAL ENGINEERING
TECHNICAL UNIVERSITY
GDAŃSK, POLAND

ANATOL SELECKI

INSTITUTE OF CHEMICAL ENGINEERING
TECHNICAL UNIVERSITY
WARSAW, POLAND

Abstract

Trivalent chromium salt solutions were flotated using cationic and anionic surfactants. The results indicate that the course of ion and precipitate flotation in the range of parameters investigated can be described by an equation analogous to a first-order rate equation. In the region of precipitate flotation the flotation rate constant reaches a maximum at a definite pH value. Increases in the surfactant concentration result in decreases in the flotation rate. Flotation of chromium at higher surfactant concentrations results in a delay effect which increases with the concentration of the surface-active agent. Increases in the flotation gas flow rate result in increases in the rates of ion and precipitate flotation.

INTRODUCTION

Trivalent chromium salts are common components of sewage from many chemical plants. Their removal from sewage and possible recycling may frequently be essential due to environmental and economic considerations. In cases of large volumes of sewage containing low concentrations of chromium salts, ion and precipitate flotation processes may be of importance.

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Ion flotation is based upon the separation of surface-inactive ions from aqueous solutions by means of surfactants. The ions form insoluble compounds with oppositely charged functional groups of the surface-active agent on the surface of gas bubbles. Particles of the compound are transported to the foam overlying the solution.

In precipitate flotation an insoluble product is formed as a result of electrostatic interaction between the surface charge of the colloid or precipitate and oppositely charged functional groups of a surfactant. Due to long hydrocarbon chains which are directed outward, the surface of the product is hydrophobic and the particle formed can firmly adhere to the surface of a gas bubble rising in the liquid phase.

Practical application of ion and precipitate flotation for sewage purification requires knowledge of the kinetics of both processes. The present article is an attempt to present some such information. Joint discussion of both types of flotation results from the properties of solutions of trivalent chromium salts.

APPARATUS AND PROCEDURE

The measurements were carried out in the experimental arrangement schematically presented in Fig. 1. The main part of the apparatus consists of a glass column (4). The column is constructed of a 60-mm i.d. glass pipe with a G-5 glass frit mounted at the bottom. The column height from the glass frit to the foam recovery point (6) is 900 mm. The flotation gas (nitrogen) is passed from a tank to a manostat (1) and through water scrubbers (3) to the flotation column. Foam formed in the process is recovered in a tank (7) from which the foam condensate passes to a

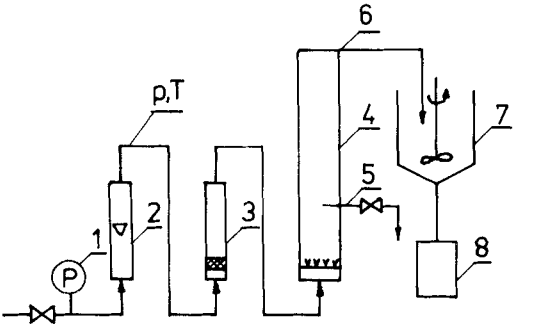

FIG. 1. Experimental system.

container (8). Tubing (5) with a valve placed in the axis of the column at a height of 300 mm from the bottom is used for sampling the residue.

Solutions of chromium salt were prepared by dissolving $Cr_2(SO_4)_3 \cdot 6H_2O$ in distilled water. Freshly prepared surfactant solution was added to this solution. Anionic Nekal BX (sodium diisobutylnaphtylsulfonate) and cationic CTMA-Br (cetyl-trimethylammonium bromide) were employed as surface-active agents. The pH was adjusted by means of sulfuric acid or sodium hydroxide. 1820 cm^3 of the mixture was poured into the column. The experiments were carried out at 293–295 K.

The concentration of chromium in the residue was determined colorimetrically by employing the reaction with diphenylcarbazide (*1*). CTMA-Br and Nekal BX were determined by means of two-layer titrations with sodium tetraphenylborate (*2*) and bromophenyl blue (*3*), respectively. The accuracy of the analytical techniques was about 5%. All the experiments were repeated at least two times.

The results of the investigations are described by means of the final flotation recovery

$$R_f = 100 \frac{c_i - c_r}{c_i} \tag{1}$$

and relative flotation recovery

$$R = 100 \frac{c_i - c}{c_i - c_r} \tag{2}$$

where c = concentration of chromium in liquid in the column
c_i = concentration of chromium in the initial solution
c_r = concentration of chromium in residue

Assuming that the kinetics of ion and precipitate flotation can be described by the equation

$$-dc/dt = k(c - c_r) \tag{3}$$

the results of the kinetic studies are in the form of the relationship

$$\ln (100 - R) = F(t) \tag{4}$$

correlated by the method of least squares as

$$\ln (100 - R) = -kt + m \tag{5}$$

The effect of pH on the final flotation recovery and the effects of pH, concentration of surfactant, and the flotation gas flow rate on the rate constant k in Eq. (5) were studied for initial concentrations of chromium equal to 2.72, 48.3, and 225.0 mg/dm^3.

RESULTS AND DISCUSSION

Effect of pH on the Final Flotation Recovery

The dependence of the final flotation recovery on pH is shown in Figs. 2, 3, and 4. The curves are of a characteristic shape, exhibiting broad, flat maxima. The shape of the curves can be explained by examining the solubility diagram (Fig. 5) of hydrated chromic hydroxide (*4*). The area of the diagram can be divided into three regions. In the first and third regions the soluble ionic forms exist: Cr^{3+}, $CrOH^{2+}$, and $Cr(OH)_2^+$ in the first, and CrO_2^- in the third. In the middle region an insoluble colloidal precipitate of the type $Cr(OH)_3 \cdot nH_2O$ predominates. Thus, ion flotation occurs mainly in Regions I and III, whereas in region II precipitate flotation prevails. It follows from the solubility data that ion flotation occurs for pH < 6.2 and pH > 10.9; pH < 5.5 and pH > 12.2, and pH < 5.2 and pH > 12.8 for concentrations of chromium equal to 2.72, 48.3, and 225.0 mg/dm^3,

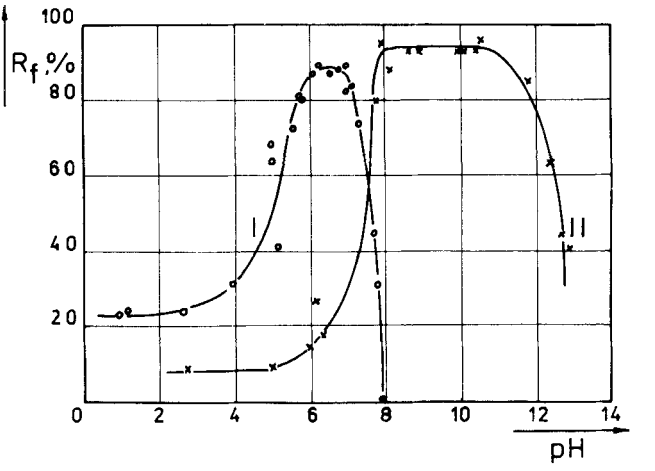

FIG. 2. Relation between chromium final flotation recovery and pH. c_i = 2.72 mg/dm^3, I = Nekal BX; c_{ic} = 250 mg/dm^3, II = CTMA-Br; c_{ic} = 36.4 mg/dm^3, V_{N_2} = 12 dm^3/h.

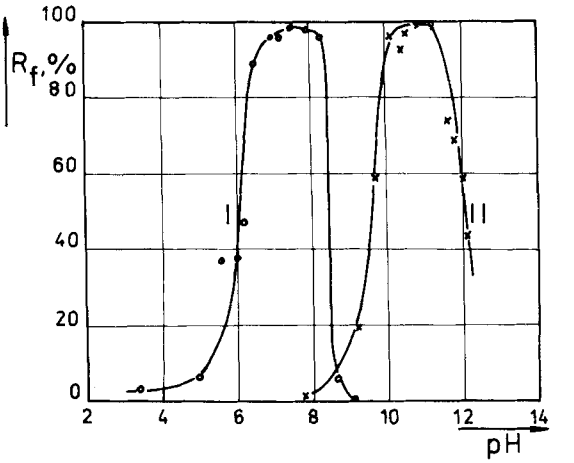

FIG. 3. Relation between chromium final flotation recovery and pH. c_i = 48.3 mg/dm^3, I = Nekal BX; c_{ic} = 34.2 mg/dm^3, II = CTMA-Br; c_{ic} = 36.4 mg/dm^3, V_{N_2} = 12 dm^3/h.

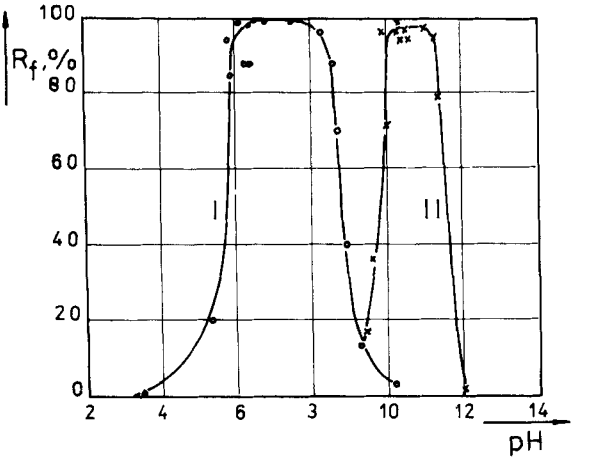

FIG. 4. Relation between chromium final flotation recovery and pH. c_i = 225 mg/dm^3, I = Nekal BX; c_{ic} = 75 mg/dm^3, II = CTMA-Br; c_{ic} = 85 mg/dm^3, V_{N_2} = 12 dm^3/h.

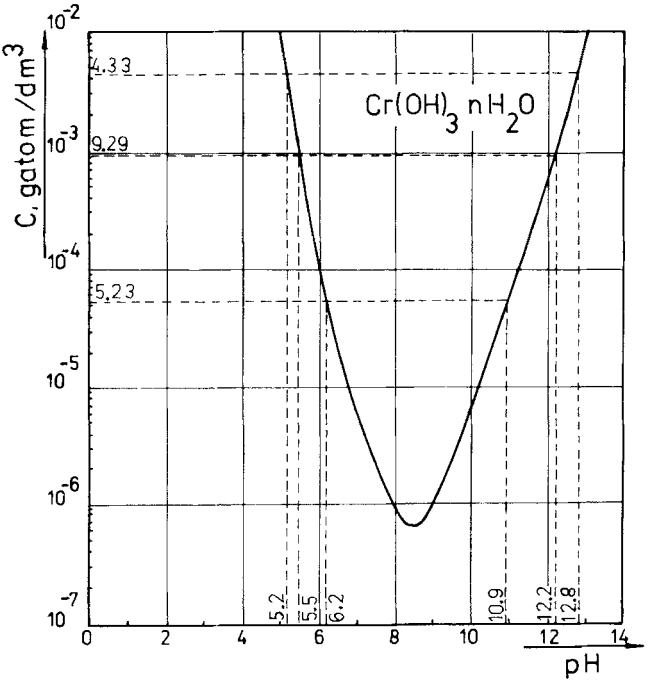

FIG. 5. Solubility diagram of chromic hydroxide. $T = 293$ K (*4*).

respectively. The results obtained show that there is a coincidence between the pH range of maximum flotation recovery (Figs. 2, 3, and 4) and that of insoluble $Cr(OH)_3 \cdot nH_2O$ in the solubility diagram (Fig. 5). This indicates that higher flotation recovery is obtained for precipitate flotation.

As shown in Figs. 2, 3, and 4, there are two different flotation maxima for anionic and cationic surfactants. The charge and sign of the surface charge of the Cr(III) hydroxide is produced as a result of the adsorption of products of $Cr(OH)_3 \cdot nH_2O$ dissociation. The concentration of $Cr(OH)_2^+$ ions at pH 8.48 is equal to the concentration of CrO_2^- ions (*4*). Parks (*5*) reports the zero point of charge of Cr(III) hydroxide for pH 8.2–9.3. The sign of the surface charge changes from positive at lower pH values to negative at higher pH values. This fact is reflected in the sharp decrease of both curves for CTMA-Br and Nekal BX within the range between both maxima.

It should be pointed that similar results for 48.3 mg/dm^3 chromium solutions were obtained by Bhattacharyya et al. (*6*) using sodium laurylsulfonate.

Effect of pH on the Flotation Rate

The results of studies of the flotation kinetics were plotted in a semilogarithmic coordinate system according to the equation(5).An exemplary plot of this relationship for chromium salt solutions containing 2.72 mg/dm^3 of Cr^{3+} and Nekal BX is shown in Fig. 6. The correlation coefficients for linear regression curves range from −0.99 to −0.95. Similar values of correlation coefficients were obtained for all other cases investigated. This confirms the assumption that ion and precipitate flotation may be first-order processes, and permits the use of the rate

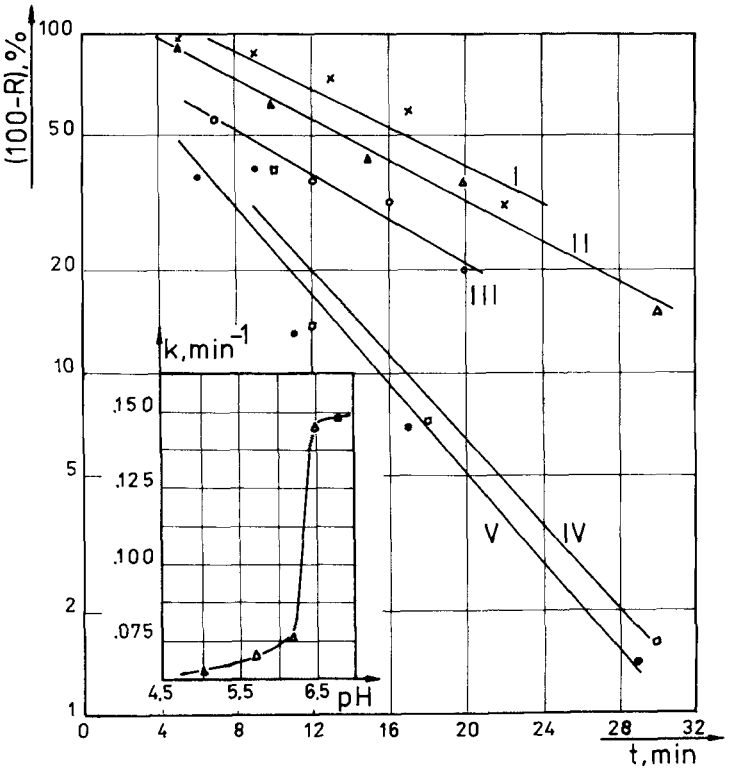

FIG. 6. Ion and precipitate flotation rate constant as a function of pH. c_i = 2.72 mg/dm^3, V_{N_2} = 12 dm^3/h, I = pH = 5.0, $y = 5.000 - 0.064t$; II = pH = 5.7, $y = 4.849 - 0.070t$; III = pH = 6.2, $y = 4.550 - 0.075t$; IV = pH = 6.5, $y = 4.726 - 0.145t$; V = pH = 6.8, $y = 4.621 - 0.149t$.

constant k (Eq. 5) determined experimentally for characterization of the kinetics of the processes.

The effect of pH on the rate constant k can also be discussed on the basis of Fig. 6. Small values of k are observed for pH < 6.2. According to the solubility data and the above discussion, this is due to ion flotation. For pH > 6.2 the k value increase rapidly, which results from a change in the mechanism of the process from ion flotation to precipitate flotation. In the latter process the product transported by gas bubbles is formed as a result of electrostatic interactions between the surface charge of the precipitate (the sign of which depends on the pH) and the oppositely charged ions of the surfactant. The quantitative composition of the product is not exactly defined, but aggregates formed from molecules of the surface-active agent and micelles of Cr(III) hydroxide contain considerably more chromium atoms than follows from the stoichiometry of compounds formed in the process of ion flotation. Hence, the flotation rate of chromium during precipitate flotation is higher than during ion flotation.

Plots of the flotation rate constant as a function of the pH (Figs. 7 and 8) exhibit maxima in the region corresponding to insoluble chromic hydroxide.

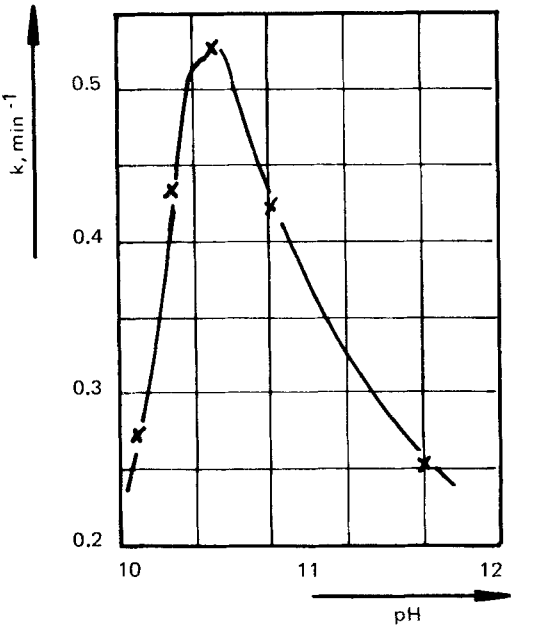

FIG. 7. Precipitate flotation rate constant as a function of pH. c_i = 48.3 mg/dm^3, V_{N_2} = 12 dm^3/h, c_{ic} = 36.4 mg/dm^3.

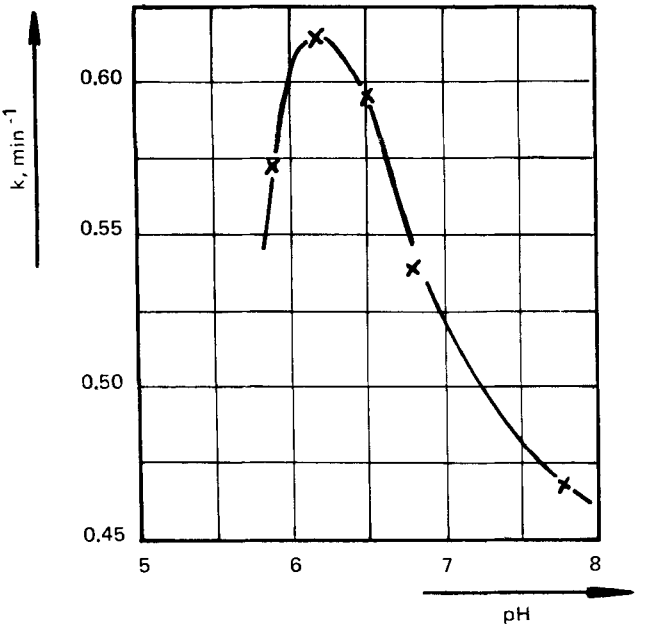

FIG. 8. Precipitate flotation rate constant as a function of pH. c_i = 225 mg/dm^3, V_{N_2} = 12 dm^3/h, c_{ic} = 75 mg/dm^3.

These maxima occur in the region of maximum dependence of final flotation recovery on pH (Figs. 3 and 4). The lower values of the flotation rate constant can be explained by a transition from colloidal solution to ordinary solution and are associated with a simultaneous increase in the slower process of ion flotation; this phenomenon occurs at low pH values for Nekal BX and at high pH values for CTMA-Br. The second, decreasing portion of the curve can be interpretated in terms of a transition from a positively charged colloid to a negatively charged colloid. This is known to occur at the point of zero charge (*7*).

Effect of the Surfactant Concentration on the Flotation Rate

The effect of the surfactant concentration on the flotation rate was studied in the pH region in which, according to the solubility diagram (Fig. 5), precipitate flotation should occur. The solutions containing 48.3 and 225.0 mg/dm^3 of chromium were investigated for CTMA-Br concentrations varying from 36.4 to 145.6 mg/dm^3 and from 85.0 to 170.0 mg/dm^3,

respectively. The results are presented in Table 1. For comparison purposes, data concerning the rate of flotation of the surfactant occurring simultaneously with flotation of the chromium are also included. As can be seen from the data in Table 1, increases in concentration of the surfactant result in decreases in the rate constants for the flotation of both chromium and collector.

Additionally, at higher concentrations of the surfactant, the process proceeds in two stages. In the first stage CTMA-Br is floated without visible flotation of chromium; in the second stage the precipitate flotation of chromium compounds occurs. Visual observations also confirm the fact that the flotation process at higher concentrations of the surfactant is stepwise. A characteristic green color of the foam is observed after a certain period of time from the beginning of the experiment. The delay in precipitate flotation of chromium compounds increases with the concentration of CTMA-Br. These facts are confirmed by the value of the intercept of the linear regression lines for chromium and collector (Table 1). Thus, for the collector the intercept was close to ln 100 (within experimental error) whereas for chromium the intercept exceeded ln 100 and increased with the surfactant concentration.

Two phenomena require elucidation at this point: the decrease in the precipitate flotation rate with an increase in the surfactant concentration, and the fact that the process occurs in two stages at higher surfactant concentrations.

TABLE 1
Effect of Concentration of CTMA-Br on the Flotation Rate and Delay Time

c_i (mg/dm^3)	pH	V_{N_2} (dm^3/h)	c_{ic} (mg/dm^3)	Parameters in Eq. (5) for chromium		Parameters in Eq. (5) for CTMA-Br		t_0 (min)
				k	m	k	m	
48.3	10.8	12.0	36.4	0.409	3.916	0.098	4.494	0
			72.8	0.296	3.909	0.089	4.553	0
			91.0	0.239	5.429	0.060	4.497	3.1
			145.6	0.239	7.050	0.041	4.604	10.2
225.0	10.3	12.0	85.0	0.233	4.526	0.106	4.575	0
			95.0	0.229	4.613	0.131	4.582	0
			125.0	0.106	4.689	0.087	4.920	2.2
			170.0	0.062	5.973	0.031	4.575	22.1

Both phenomena can be explained, assuming that in the system consisting of negatively charged (pH = 10.3–10.8) colloidal micelles of Cr(III) hydroxide, molecules of CTMA-Br and the products of their interaction exist in equilibrium as described in Fig. 9. At low concentrations of CTMA-Br the equilibrium is shifted to the left and the solution contains particles A and B as well as molecules of CTMA-Br. In the flotation process the molecules of CTMA-Br and particles B adsorbed on the surface of bubbles due to their hydrophobic properties are removed from the solution, both processes being competitive. The larger the excess of CTMA-Br, the larger the fraction of the bubble surface occupied by these molecules. Hence, the possibility of micelles B adhering to the bubble surface and, consequently, the flotation rate of the chromium compound are smaller.

Two mechanisms can be responsible for the delay effect. At sufficiently high concentration of CTMA-Br the equilibrium is shifted to the right and the system under consideration will consist of micelles C and molecules of CTMA-Br. Type C micelles are not adsorbed at the gas–liquid interface due to their hydrophilic properties. In such a case only molecules of the surfactant are transported with the gas bubbles. This leads to a decrease in concentration of the surfactant and shifts the equilibrium to the left. The micelles of the C type are converted into the B type, their surfrace becomes hydrophobic, and the particles can be removed by the gas bubbles. However, the fact that the free surfactant competes for the limited bubble area better than the adsorbed surfactant, could be the next reason for the delay effect. The delay effect is defined as the period from the beginning of flotation to the start of flotation of Cr(III) hydroxide, and increases with surfactant concentration. The values of the delay effect extrapolated from the linear regression curves for $R = 0$ are listed in Table 1.

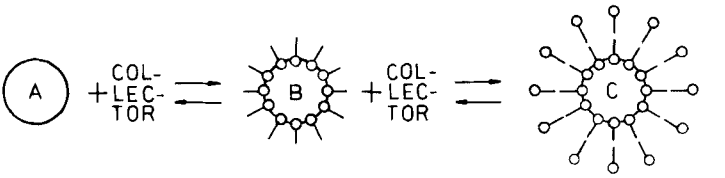

FIG. 9. Equilibrium in the flotation system. A, a micelle of chromium compound; B, a micelle of chromium compound covered with a monomolecular layer of CTMA-Br with chains directed toward liquid, having hydrophobic properties; C, micelle in which the outer layer of ionic functional groups of CTMA-Br results in hydrophilic properties.

Effect of the Gas Flow Rate on the Flotation Rate

The effect of the gas flow rate on the flotation rate represented by the rate constant k is shown in Fig. 10. It is apparent that the rate constant k at constant temperature should depend, although evidently not exclusively, on the gas–liquid interface at which the particles of the product (chromium ion, surfactant ion, and molecules of surfactant) are adsorbed. The specific interfacial area can be calculated from the mean diameter of the bubbles and the mean value of gas holdup in the bubble column:

$$a = 6\varepsilon/d_{32} \tag{6}$$

It was shown (7) that the mean Sauter diameter d_{32} of the gas bubbles is proportional to $V_G^{0.2}$ and the gas holdup is proportional to $V_G^{0.64}$. This means the specific interfacial area is proportional to $V_G^{0.44}$. The curves in Fig. 10 show that the flotation rate constant becomes more dependent on the gas

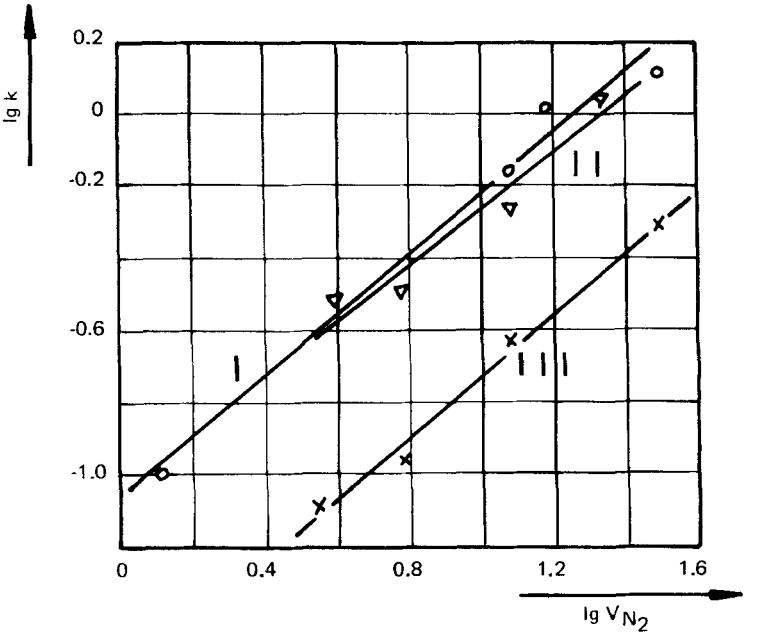

FIG. 10. Precipitate flotation rate constant as a function of gas flow rate. I = c_i = 48.3 mg/dm^3, c_{ic} = 34.2 mg/dm^3, pH = 7.5, log k = 0.847 log V_{N_2} − 1.083; II = c_i = 225 mg/dm^3, c_{ic} = 75 mg/dm^3, pH = 6.8, log k = 0.776 log V_{N_2} − 1.042; III = c_i = 225 mg/dm^3, c_{ic} = 85 mg/dm^3, pH = 10.3, log k = 0.856 log V_{N_2} − 1.582.

flow rate with increases in the latter. The flotation rate constant is proportional to the gas flow rate to about the 0.8 power. It is supposed that this phenomenon is due to additional factors, e.g., turbulence in the bubble column. Elucidation of this problem requires, however, more comprehensive investigations.

CONCLUSIONS

The course of ion and precipitate flotation of trivalent chromium salts in the investigated range of parameters can be described with sufficient accuracy by the equation

$$-dc/dt = k(c - c_r)$$

Precipitate flotation is a considerably more rapid process than ion flotation.

In the region of precipitate flotation of trivalent chromium salts, the flotation rate constant reaches a maximum for definite pH values corresponding to regions of the occurrence of maxima for the dependence of final flotation recovery on pH.

Increases in the surfactant concentration result in decreases in the flotation rate.

Flotation of chromium at higher surfactant concentrations results in a delay effect which increases with the concentration of the surface-active agents.

Increases in the flotation gas flow rate lead to increases in the rates of flotation.

SYMBOLS

a	specific area gas–liquid (m^2/m^3)
c	concentration of chromium in liquid in the column (mg/dm^3)
c_i	concentration of chromium in the initial solution (mg/dm^3)
c_{ic}	concentration of surface active agents in the initial solution (mg/dm^3)
c_r	concentration of chromium in residue (mg/dm^3)
d_{32}	Sauter mean diameter of bubbles (m)
k	flotation rate constant (min^{-1})
m	parameter in Eq. (5)
R_f	final flotation recovery (%)
R	relative flotation recovery (%)

t time of flotation (min)
t_0 delay time (min)
V_{N_2} flotating gas flow rate (dm^3/h)
ε gas hold-up in the bubble column

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