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# Mutual Interaction between Collectors and Frothers in Flotation

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## Abstract

The behavior of a frother in flotation was investigated from the viewpoint of the mutual interaction between a collector and a frother. The floatability of galena and the interfacial tensions of the mercury-solution interface were measured using ethyl and amyl xanthates and normal alcohols containing 1~5 carbon atoms. The floatability test showed that butyl and amyl alcohols were favourable as a frother. The interfacial tension measurements verified that alcohol molecules can adsorb on the mercury surface only in coexistence with xanthate molecules in a solution. The degree of the coadsorption of alcohol molecule with xanthate molecule on mercury increases with increasing the number of carbon atoms in the alkyl chain of alcohol. It was clarified from the discussion of the infrared-spectroscopic study for the reagents that the value of  $\ln(\nu-\nu_0)$  based on the shift of  $\text{CH}_3$  stretching vibration was closely related to the degree of the coadsorption of a frother with a collector at the mineral-solution interface. Furthermore, the value of  $\ln(\nu-\nu_0)$  was shown to be one of the measures indicating the choice of their proper combination.

## 1. Introduction

Collecting phenomena in flotation are composed of two major steps, one of them is the reaction between a collector ion and a mineral surface and the other is a process in which a bubble adheres to the hydrophobic surface of mineral. The coverage of a collector on a mineral surface is considered as a measure indicating what degree in water-repellent property the mineral surface changes to. The more closely the collector coverage on a mineral surface approaches unity, namely a complete monolayer, the more the surface increases its hydrophobic property. The collection of mineral particles is, however, not always proportional to the collector coverage. Gaudin and Sun<sup>1)</sup>

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pointed out that the optimal value of the collector coverage to float mineral particles ranged from five to fifteen percent of a monolayer. Leja and Schulman<sup>2)</sup>, who had interest in this phenomenon, concluded in one of their papers that the mutual penetration among collector and frother molecules was possible at the bubble-mineral interface. Many engineers engaged in the mineral flotation practice have known well through their experiences that all substances which make bubbles may not always be frothers suitable in the practical flotation. Although the mutual interaction between a collector and a frother is closely concerned with an optimal collecting condition of mineral particles, only a few pieces of research work on this problem have been published until to-day.

From the above point of view, the floatability of mineral, the interfacial tension at the mercury-liquid interface was measured using a series of homologous xanthates and alcohols as collector and frother, respectively. And then, the mutual interaction between a collector and a frother in flotation was discussed on the basis of the infrared-spectroscopic characteristic, namely the shift of the wave number of the C-H stretching vibration for the xanthates and alcohols used in this study.

## 2. Materials and experimental methods

Galena produced in the Hosokura mine was used in this experiment. The minus 65 plus 100 mesh fraction of the mineral particles was prepared. Potassium ethyl xanthate and potassium amyl xanthate were synthesized in the author's laboratory and purified by the usual method. A series of homologous alcohols was obtained from the Nakarai Chemicals Company, each of them being of extra pure grade. Mercury used in this experiment was purified by the air-oxidation followed by washing with a dilute nitric acid solution for the removal of base metallic impurity and finally by the low pressure evaporation for the removal of noble metallic contamination. A conventional flotator of the M-S type was used to measure the floatability of galena at the natural pH value of the pulp tested.

The drop-weight method<sup>3)</sup> was employed to determine the interfacial tension of the mercury-solution interface, the value of the interfacial tension for the mercury-water interface being 375 dyne/cm as a standard value. The interval of dropping mercury is ranged from 3 to 5 seconds in the scope of the experiment.

### 3. Experimental results and discussions

#### 3-1. Floatability of galena particles using a series of homologous normal alcohols as frothers

The effect of the hydrocarbon chain length of alcohol on the floatability of galena particles is given in Figure 1. The experiments were performed at the natural pH of the pulp by the use of methyl, ethyl, propyl, butyl, and amyl alcohols, 0.01 mol/l, respectively and potassium ethyl xanthate, 1 mg/l, as a collector during all the test. Figure 1 shows that the recovery of galena particles is favourable with such alcohols having a long alkyl group as butyl and amyl alcohols, while it is poor with methyl or ethyl alcohol which has a short hydrocarbon chain. It was especially with amyl alcohol that an excellent recovery of galena particles was obtained. This fact is well coincident with the practical flotation where some higher alcohols are used as frothers.

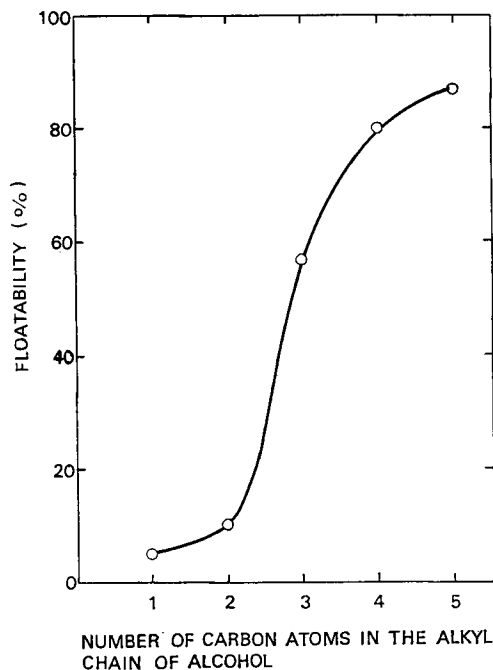


Fig. 1. Relation between floatability of galena and the number of carbon atoms in the alkyl chain of alcohol.

#### 3-2. Mutual interaction between a collector and a frother from the viewpoint of the interfacial tension at the mercury-solution interface

On the interaction of a frother and a collector in flotation, Leja and Schulman stated that collector molecules adsorbed on a mineral surface first as

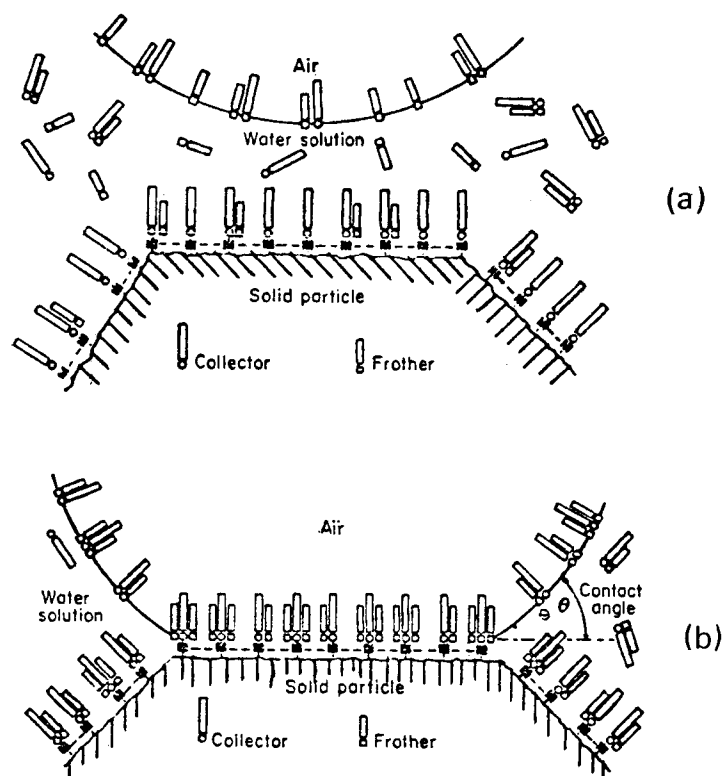


Fig. 2. Schematic representation of the penetration of frother and collector films<sup>2)</sup>.

Table 1. Surface tension of normal alcohols in water (dyne/cm).

	T°C \ %	7.5	10	25	50	60	80	90	100	
Methyl alcohol-water	20	60.90	59.04	46.38	35.31	32.95	27.26	25.36	22.65	
	30	59.23	59.27	45.30	34.52	32.26	26.48	24.42	21.58	
	T°C \ %	5	10	24	34	48	60	72	80	96
Ethyl alcohol-water	20				33.24	30.10	27.56	26.28	24.91	23.04
	40	54.92	48.25	35.50	31.58	28.93	26.18	24.91	23.43	21.38
	T°C \ %	0.1	0.5	1	50	60	80	90		
<i>n</i> -Propyl alcohol-water	25	67.10	56.18	49.30	24.34	24.15	23.66	23.41		
	T°C \ %	0.04	0.41	9.53	80.44	86.05	94.20	97.40		
<i>n</i> -Butyl alcohol-water	30	69.33	60.38	26.97	23.69	23.47	23.29	22.25		

shown in Figure 2(a) and then, when the mineral surface contacts with a bubble, frother and collector molecules coadsorb mutually in proper density

on the mineral surface, as indicated in Figure 2(b), keeping firmly the attachment between the mineral particle and a bubble.

Table 1 is a list of the surface tensions of some normal alcohol aqueous solutions<sup>4)</sup>. It can be seen from Table 1 that the surface tension decreases markedly with increasing the alcohol concentration in every case. This means that any alcohol molecule can adsorb at the water-air interface. On the other hand the results shown in Figure 1 suggest that alcohol molecules behave differently in the flotation phenomena with the alkyl chain length of alcohol. It may be considered that the facts in Figure 1 are mainly due to the difference in the co-adsorption of alcohol and xanthate molecules on the mineral surface, or due to the difference in the penetration of the xanthate film by alcohol molecules.

It can also be considered that the co-adsorption of alcohol and xanthate molecules should occur at the solid-water interface. If this coadsorption phenomenon is admitted, the variation of the interfacial tension at the solid-solution interface can be accepted to occur, too. Therefore, the interfacial tension of the solid-solution interface was measured using mercury in place of a mineral and ethyl alcohol as a lower alcohol and amyl alcohol as a

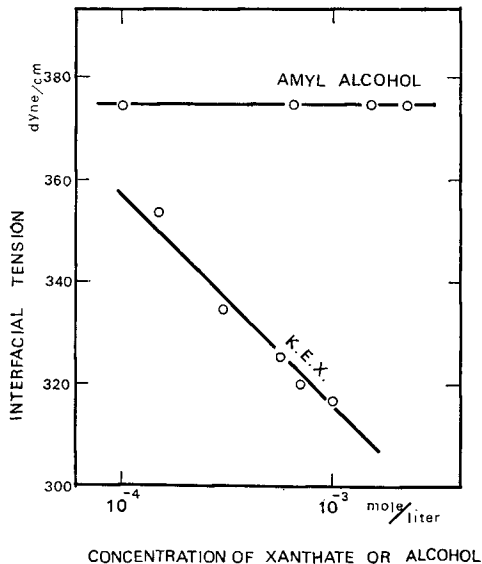


Fig. 3. Variation in the interfacial tension of mercury with xanthate or alcohol concentrations.

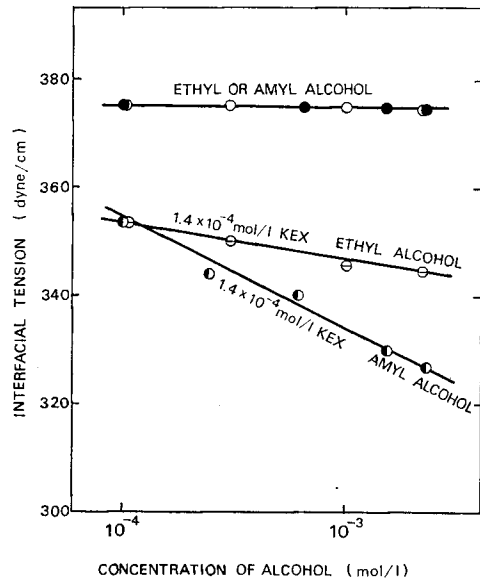


Fig. 4. Effect of alcohol concentrations on the interfacial tension of mercury both at the absent of xanthate and at the present of xanthate,  $1.4 \times 10^{-4}$  mol/l, in solutions.

higher one.

The relation between the interfacial tension of the mercury-solution interface and the concentration of amyl alcohol or of ethyl xanthate is given in Figure 3. Figure 3 shows that in the case of amyl alcohol the interfacial tension does not vary as the alcohol concentration increases, while in the case of ethyl xanthate it decreases as the xanthate concentration increases. This fact suggests that amyl alcohol molecules scarcely adsorb on mercury, but xanthate molecules do so remarkably.

Figure 4 shows the effect of the alcohol concentration on the interfacial tension of mercury at a constant concentration of potassium ethyl xanthate,  $1.4 \times 10^{-4}$  mol/l. It is noted from Figure 4 that for solutions containing ethyl or amyl alcohol alone there is no variation in the interfacial tension of mercury with alcohol concentrations, but the coexistence of xanthate molecules with alcohol molecules in a solution causes notable change in the interfacial tension of mercury with alcohol concentrations. The degree of change in the interfacial tension is greater in amyl alcohol solutions than in ethyl alcohol solutions.

It can be considered that this fact should be due to the coadsorption of alcohol and xanthate molecules on the mercury surface and that the longer the chain length of hydrocarbon in alcohol is, the greater is its effect. Figures 1 and 4 show that the coadsorption of collector and frother on the mineral surface plays an important role in flotation. Therefore, it is very important for engineers to take account of the combination of a frother and a collector in order to get a good recovery in industrial practice.

### **3-3. Mutual interaction between a collector and a frother from the viewpoint of their infrared spectroscopic characteristics**

As mentioned in the introduction, the flotation phenomena are consisted of two processes, namely one is the reaction of a collector onto a mineral surface, and the other the bubble adhesion to the mineral surface covered with a collector film. Furthermore, it is needless to say that the successful separation and recovery of a desired mineral depend on a proper selection for collectors and frothers. Therefore, it is quite useful in the industrial flotation practice to get a standard measure for the choice of a collector or a frother by making use of the physico-chemical properties of both reagents.

According to the fact that the shift of wave number for the C-H stretching vibration of the alkyl group of a reagent occurs as the alkyl chain length of the reagent changes, the correlation of the shift phenomena with the col-

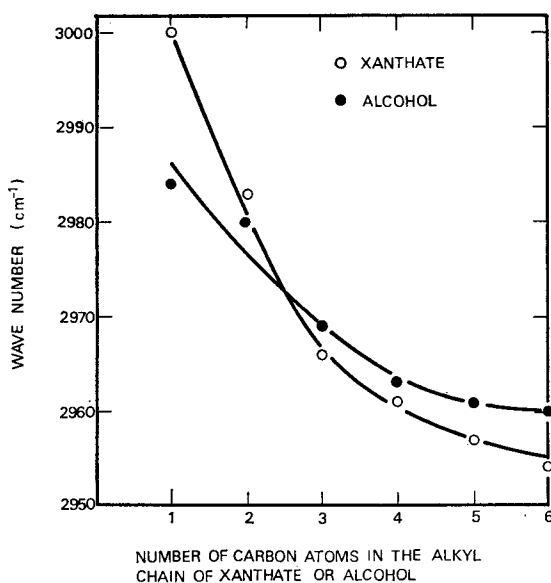


Fig. 5. Relation between the wave number of  $\text{CH}_3$  stretching vibration and the number of carbon atoms in the alkyl chain of xanthate or alcohol.

lector-frother mutual interaction was considered. One of the authors has already published the infrared absorption characteristics of the alkyl xanthates and alcohols<sup>5</sup>. Some of those experimental results for the alkyl xanthates and alcohols are presented in Figure 5, which show the shift in the asymmetric stretching vibration of the  $\text{CH}_3$  group around  $2960 \text{ cm}^{-1}$  as a function of the number of carbon atoms in the alkyl group.

As can be seen from Figure 5, the wave number of the  $\text{CH}_3$  stretching vibration of xanthates and alcohols decreases markedly with increasing the number of carbon atoms in the alkyl group. This shift phenomenon is explained as due to the change in the inductive effect of a polar group on the C-H bond of the  $\text{CH}_3$  group. In the case of normal alkyl group this inductive effect decreases remarkably as the number of carbon increases up to 6 or 7. Therefore, the wave number approaches a limited value, presumably that of the saturated hydrocarbons, as the hydrocarbon chain becomes longer beyond 6 or 7 carbons.

Palit<sup>6</sup> explained qualitatively the relations among the hydrocarbon chain length of alcohols, their affinity to water, and their solubility from the viewpoint of the inductive effect of polar group. It is, therefore, considered that the hydrophobic property of alcohol molecules has a close relation to their adsorption onto a mineral surface covered with a collector film as well as



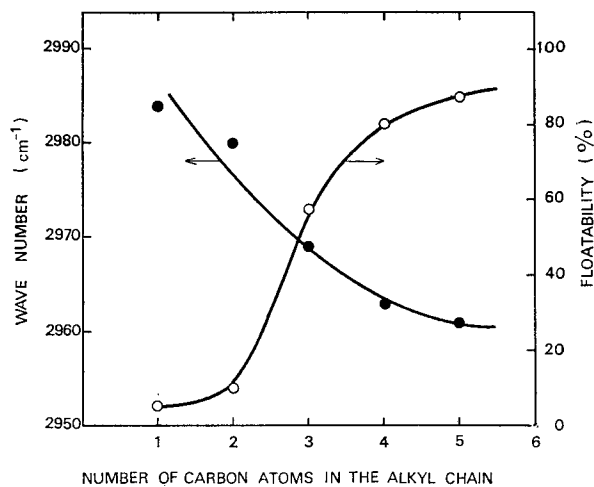


Fig. 6. Comparison of the floatability of galena with the wave number of alcohol.

their adsorption at the gas-liquid interface.

Figure 6 presents the experimental results of the floatability of galena in Figure 1, together with the shifts of the wave number of alcohols in Figure

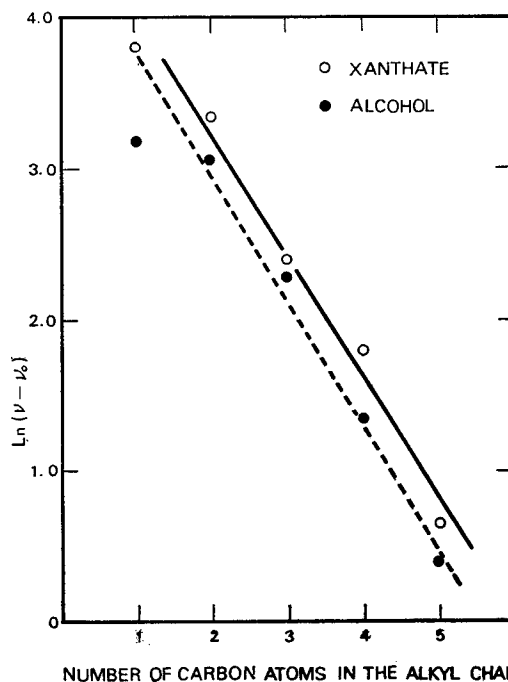


Fig. 7. Values of  $\ln(\nu - \nu_0)$  as the function of the number of carbon atoms in the alkyl chain of xanthate or alcohol.

5. When ethyl xanthate is used as a collector, butyl and amyl alcohols are suitable to get a good recovery of the mineral. To say it in terms of the wave number of the  $\text{CH}_3$  stretching vibration, alcohols having close values to  $2960 \text{ cm}^{-1}$  are favorable as frothers.

Goto and Takenaka<sup>7)</sup> took the value of  $\ln(\nu - \nu_0)$  as one of measures indicating the inductive effect of the polar group, where  $\nu$  represents the wave number of the  $\text{CH}_3$  stretching vibration of substances and  $\nu_0$  that of the saturated hydrocarbon. The correlation between the value of  $\ln(\nu - \nu_0)$  and the number of carbon atoms in the alkyl group is presented in Figure 7, where  $\nu_0$  is taken as  $2959 \text{ cm}^{-1}$  for a series of homologous alcohols and  $2955 \text{ cm}^{-1}$  for xanthates, respectively.

From Figure 7 values of  $\ln(\nu - \nu_0)$  are expressed in very simple figures and probably, are convenient for use in the choice of a collector and a frother. Furthermore, it is verified that the values of  $\ln(\nu - \nu_0)$  are closely related to the degree of the coadsorption of a collector and a frother at the mineral-solution interface.

#### 4. Conclusion

The mutual interaction between a collector and a frother was discussed in order to elucidate how their mutual interaction is relative to the collection phenomena in flotation. The floatability of galena and the interfacial tension of the mercury-solution interface were measured using ethyl and amyl xanthates as a collector and a series of normal alcohols as a frother. Then, the collector-frother interaction was considered from the viewpoint of the shift in the  $\text{CH}_3$  stretching vibration of the reagents by the infrared spectroscopy.

The results obtained are as follows:

(1) In the floatability experiments of galena using ethyl xanthate as a collector and normal alcohols containing 1~5 carbon atoms as a frother, butyl and amyl alcohols, especially amyl alcohol, gave a good recovery in the galena flotation.

(2) The interfacial tension measurements of the mercury contacting with aqueous solutions including a sole alcohol, a sole xanthate, and a mixture, indicated that alcohol molecules did not adsorb on the mercury surface at the absence of xanthate molecules, but could coadsorb on it at the presence of xanthate molecules. The longer the alkyl chain length of the alcohol is, the more its coadsorption with xanthate on the mercury surface becomes. It is, therefore, very important for the stable attachment between a bubble and a mineral particle to choose a proper combination of frother and collector.

(3) As a measure indicating the mutual interaction of a collector and a frother and the choice of their suitable combination, the shift of the wave number in the  $\text{CH}_3$  stretching vibration by the infrared spectroscopy of the reagents is considered. As a result, the value of  $\ln(\nu - \nu_0)$  based on the shift of  $\text{CH}_3$  stretching vibration was closely related to the degree of the coadsorption of a frother with a collector at the mineral-solution interface and was also expected to be one of the measures indicating the choice of their proper combination.

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