Study on the Floatability of Mineral Particles in the Presence of Surface Active Agents. I. Relation between Adsorption of the Collector Ion and the Electrokinetic Potential in Flotation

By

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The electro-osmotic velocity, the adsorption density and the floatability of mineral particles were measured for the following systems: fluorite-sodium dodecyl benzene sulphonate, quartz-sodium dodecyl benzene sulphonate, quartzoctadecyl dimethyl benzyl ammonium chloride, scheelite-octadecyl dimethyl benzyl ammonium chloride and quartz-dodecyl ammonium acetate.

The relations among the differences in the zeta-potential, the adsorption density and the floatability are discussed.

As a result of this research, it was found that the difference in the zetapotential of the mineral can be correlated with the adsorption density of the collector on the mineral surface, and that, therefore, the floatability of the mineral can be correlated with the difference in the zeta-potential.

1. Introduction

The electrokinetic potential (zeta-potential) of minerals may be varied by the adsorption of collector ions (or molecules) on the mineral surface. It is, therefore, important to clarify the relation between the adsorption of the collector ion and the change of the zeta-potential of minerals.

A. M. Gaudin and S. C. Sun¹) have pointed out the correlation between mineral behavior in cataphoresis and in flotation, and they have found experimentally that the ζ -coefficient and the floatability were correlative. It was also reported by one of the authers²) that the difference in the zeta-potential correlated closely with the floatability. A. M. Gaudin and J. G. Morrow³) measured the adsorption of dodecyl ammonium acetate on hematite and discussed the relation between the adsorption density and

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the surface charge. Recently, it was reported by D. W. Fuerstenau⁴) that there was excellent experimental correlation between the contact angles, adsorption density, zeta-potentials, and flotation rate of the system quartz-dodecyl ammonium acetate.

This investigation was carried out to clarify mainly the relation between the adsorption of collector ions and the change of zeta-potential of a mineral in a flotation process for the following systems; (i) fluorite-sodium dodecyl benzene sulphonate, (ii) quartz-sodium dodecyl benzene sulphonate, (iii) quartz-octadecyl dimethyl benzyl ammonium chloride, (iv) scheelite-octadecyl dimethyl benzyl ammonium chloride and (v) quartz-dodecyl ammonium acetate.

2. Preparation of the Minerals

The quartz, scheelite and fluorite used in the present investigation came from the Otani mine (Kyoto prefecture), the Kaneuchi mine (Kyoto prefecture) and South Korea, respectively. The high grade coarse pieces of these minerals were crushed, and the pure particles (about 2-3 mm. in diameter) of each mineral were picked up, and then each product was ground in an agate mortar.

The samples for the flotation, electro-osmosis, and adsorption tests were 48–100 mesh, 80–100 mesh and minus 270 mesh materials, respectively. Particles smaller than 10μ in diameter were discarded from the samples used in these experiments.

The surface areas of the samples for adsorption, as measured by the nitrogen gas adsorption method, were $1550 \text{ cm}^2/\text{g}$ for quartz, $1880 \text{ cm}^2/\text{g}$ for scheelite and $1570 \text{ cm}^2/\text{g}$ for fluorite.

The qualitative analysis of the mineral samples was done with a Quartz medium spectrograph. In Table I are shown the results of spectro chemical analysis of the mineral samples. These samples were excited by a 110 V. D.C. arc using carbon electrodes.

Elements Kind of sample	Ca	Si	w	Fe	Al	Mg	Mn	Ti	Cu	Cd	Pb	Other elements
Fluorite	+ + + + +	tr.		min. tr.	min. tr.	min. tr.	min. tr.	min. tr.	±	±	土	none
Quartz	min. tr.	++- +-+-+	—	min. tr.	min. tr.	min. tr.			min. tr.	_		none
Scheelite	- 1	min. tr.	++	min. tr.	tr.	tr.	tr.	_	min. tr.		+	none

Table I. Spectro chemical analysis of mineral samples.

Sign: (+)…present, (-)…no detected, tr.…trace, min. tr.…minute trace, (±)…barely visible.

From the results of Table I, it may be said that each mineral sample is pure for the purpose of this study.

3. Collectors

The sodium dodecyl benzene sulphonate (the active ingredient is 97.7% pure) and the octadecyl dimethyl benzyl ammonium chloride (the active ingredient is 97.5% pure) were produced by the Kaō Soap Co. Ltd., and the dodecyl ammonium acetate was prepared from dodecyl amine and acetic acid glacial (chemical extra pure) in auther's own laboratory.

4. Experimental methods

4.1 Zeta-potential measurements

The zeta-potential of the mineral-solution interface was evaluated from the electro-

osmotic velocity. The electro-osmotic apparatus is shown in Phot. 1. The details of the apparatus, the experimental technique, and the evaluation of the zeta-potential have been described in a previous $paper^{5}$.

Fig. 1 shows examples of electroosmotic velocity data obtained with quartz or fluorite in distilled water. The figure indicates that the electroosmotic velocity is proportional to the potential difference across the plug within the margin of experimental error.

The distilled water used in this experiment had a specific conductance less than 2×10^{-6} ohm⁻¹ cm⁻¹.

4.2 Adsorption test

1) Quartz or scheelite-octadecyl dimethyl benzyl ammonium chloride

For each test, a weighed amount of quartz or scheelite, 1 g. and 20 or 25 ml of freshly prepared starting solution containing measured amounts of octadecyl dimethyl benzyl ammonium chloride were agitated slowly in a 25 ml glass-stopper cylinder. This cylinder was kept in



Photo. 1. Electro-osmotic apparatus.





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the thermo-stat $(25\pm0.5^{\circ}C)$ for 16 hrs. (In preliminary tests, it was established that the adsorption equilibrium was reached within 16 hrs.). Then the solution in the cylinder was separated from the solids using a centrifuge. The pH was measured, and the collector concentrations of the initial and final solutions were determined spectrophotometrically. The amount of collector adsorbed was evaluated from the decrease in the collector concentration in the solution during the test. Blank tests were carried out at the same time to conpensate for the adsorption on the glass wall and the decomposition of the solutes. Fig. 2 shows the spectrum of the solution of octadecyl dimethyl benzyl ammonium chloride.

The peak at $210 \,\mathrm{m}\mu$ wavelength provided a suitable basis for quantitative analysis. Fig. 3 shows a plot of the height of the peak at $210 \,\mathrm{m}\mu$ vs the concentration of octadecyl dimethyl benzyl ammonium chloride in solution. Close correlation results.



The optical density was measured with a Beckman DU type quartz spectrophotometer.





Fig. 2. Spectrum of solution of octadecyl dimethyl benzyl ammonium chloride.

Fig. 3. Concentration of octadecyl dimethyl benzyl ammonium chloride vs optical density at 210 m μ .

2) Fluorite or quartz-sodium dodecyl benzene sulphonate

The amount of collector adsorbed was determined spectrophotometrically. The details of the adsorption tests and the results obtained have been described in a previous paper⁶.

3) Quartz-dodecyl ammonium acetate.

The adsorption isotherm with this system was quoted from de Bruyn's and F. Schulz's $paper^{7,8}$.

4.3 Flotation tests

The floatability of mineral particles was measured by using a modified Hallimond tube⁶).

4.4 Conductivity measurements of aqueous collector solution

The electrical conductivity measurements were carried out by using a pyrex glass cell ($18 \text{ mm}\phi \times 36 \text{ mm}$, platinum electrodes: $14 \text{ mm}\phi \times 2$, electrode distance: 15 mm, cell constant: 0.7631), a modified kohlrausch bridge arrangement and a 1000 cycle A.C. oscillator. The cell was thermostated and measurements were made at $25\pm0.5^{\circ}$ C.

5. Experimental results

5.1 Change of zeta-potential of the minerals

The results obtained are shown in Fig. 4, 5, 6, 7 and 8, which record the zetapotential of each mineral as a function of the molar concentration of solutions for each collector.

(1) Fluorite-sodium dodecyl benzene sulphonate

The electro-osmotic measurements show that the zeta-potential of fluorite in distilled water is positive. This is in agreement with the result obtained by A. M. Gaudin and S. C. Sun¹).

As can be seen from Fig. 4, in aqueous solutions of sodium dodecyl benzene





sulphonate, the zeta-potential of fluorite decreases abruptly at concentrations exceeding $1.5 \times 10^{-5} \text{ mol}/l$ and changes its sign from positive to negative at a solution concentration of about $2 \times 10^{-5} \text{ mol}/l$. That is, the zeta-potential of fluorite varies remarkably upon increasing the solution concentration from 1.5×10^{-5} to $4 \times 10^{-5} \text{ mol}/l$.

(2) Quartz-sodium dodecyl benzene sulphonate

Fig. 5 shows that in aqueous solutions of sodium dodecyl benzene sulphonate the zeta-potential of quartz scarcely increases in absolute value for solution concentrations up to about 5×10^{-4} mol/l and for higher concentrations it decreases very slightly in absolute value.

Comparing Fig. 5 with Fig. 4 in the solution concentration of $1.5 \times 10^{-5} \sim 4 \times 10^{-5}$ mol/*l*, it is found that the zeta-potential of flourite varies very



considerably but that of quartz varies very slightly. This suggests that the dodecyl benzene sulphonate ions adsorb strongly for fluorite and scarcely for quartz. Also, this is in agreement with the adsorption results described in a previous $paper^{6}$.

(3) Quartz-octadecyl dimethyl benzyl ammonium chloride

Fig. 6 illustrates the variation of zeta-potential of quartz with the concentration of octadecyl dimethyl benzyl ammonium chloride. The zeta-potential of quartz de-









Fig. 7. Zeta-potential of scheelite in solutions of octadecyl dimethyl benzyl ammonium chloride at pH 5.6~5.8.

creases in absolute value with increasing the solution concentration and changes its sign from negative to positive at a solution concentration of about $2 \times 10^{-6} \text{ mol/}l$. That is, the zeta-potential of quartz markedly varies upon increasing the solution concentration from 2×10^{-7} to $6 \times 10^{-6} \text{ mol/}l$.

(4) Scheelite-octadecyl dimethyl benzyl ammonium chloride

Fig. 7 shows that in aqueous solutions of octadecyl dimethyl benzyl ammonium chloride, the zeta-potential of scheelite decreases in absolute value upon increasing the solution concentration and changes its sign from negative to positive at a solution concentration of about 4×10^{-6} mol/*l*. That is, the zeta-potential of scheelite varies remarkably upon increasing the solution concentration from 6×10^{-7} to 6×10^{-6} mol/*l*.

(5) Quartz-dodecyl ammonium acetate

As can be seen from Fig. 8 in aqueous solutions of dodecyl ammonium acetate,





the zeta-potential of quartz decreases abruptly for concentrations exceeding 4×10^{-5} mol/*l* and changes its sign from negative to positive at a solution concentration of about 2×10^{-4} mol/*l*. That is, the zeta-potential of quartz varies considerably upon increasing the solution concentration from 4×10^{-5} to 2.5×10^{-4} mol/*l*. This is in agreement with the results obtained by A. M. Gaudin and D. W. Fuerstenau⁹ approximately.

5.2 Results of adsorption

(1) Quartz-octadecyl dimethyl benzyl ammonium chloride

Fig. 9 shows the variation of the amount adsorbed with the solution concentration. The amount of collector adsorbed increases with the starting concentrations or the equilibrium concentrations. This isotherm is of the Freundlich type, because the $\log \Gamma$ (the adsorption density) is approximately proportional to $\log C$ (the equilibrium concentration) as will be discussed later.

(2) Scheelite-octadecyl dimethyl benzyl ammonium chloride

Fig. 10 illustrates the variation of the amount adsorbed with the solution concentration.

5.3 Results of floatability

The results obtained are summarized in Fig. 11 and 12, which record the floatability of each mineral particle as a function of the molar concentration of each collector solution. As can be seen from Fig. 11 and 12, the floatability



Fig. 9. Adsorption isotherm of octadecyl dimethyl benzyl ammonium chloride on quartz from solutions of pH 5.75~6.0.





of mineral particles in each system, except the quartz-sodium dodecyl benzene sulphonate system, increases with the solution concentration. In the quartz-sodium dodecyl benzene sulphonate system, however, the floatability of quartz is extremely low even with increased solution concentrations.

5.4 Results of electrical conductivity measurements

Most of the properties of the surface active agent, such as its electrical conductivity, viscosity, density, scattering of light, etc. vary remarkably at the critical micelle concentration. The critical micelle concentration is influenced by the presence





of impurities in the solution. Accordingly, it is necessary to determine the critical micelle concentration for each collector used in this study. They were determined by measuring the electrical conductivity of each collector solution. The results obtained are shown in Fig. 13, 14 and 15. From Fig. 13, 14 and 15, the critical micelle concentration of sodium dodecyl benzene sulphonate, octadecyl dimethyl benzyl ammonium chloride and dodecyl ammonium acetate are about 2.5×10^{-3} , 2×10^{-4} and 1.5×10^{-2} mol/*l*, respectivily.

The highest concentration of each collector used in the zeta-potential measurement, and the adsorption and flotation tests is still below the critical micelle concentration. Accordingly, it may be said that each collector in the bulk solution is almost completely ionized.



Fig. 13. Variation of equivalent conductivity with concentration of sodium dodecyl benzene sulphonate.



0.02

0.03

0.04



Fig. 15. Variation of equivalent conductivity with concentration of dodecyl ammonium acetate.

6. Consideration of experimental results

6.1 Relation between the difference of zeta-potential and floatability

0.01

The relations between the difference of zeta-potential and the floatability of mineral particles are summarized in Fig. 16, 17, 18 and 19. The difference of zeta-potential means the difference between the magnitude of the zeta-potential of the mineral in distilled water and that of the same mineral in an aqueous solution of the collector at the same pH.



Fig. 16. Relation between floatability and difference of zeta-potential in system fluorite-sodium dedecyl benzene sulphonate,

100

Equivalent conductivity & 00 08

20

0

In the system fluorite-sodium dodecyl benzene sulphonate, both the floatability and the difference of zeta-potential of the fluorite increase remarkably upon increasing the solution concentration from 1.5×10^{-5} to $4 \times 10^{-5} \text{ mol/}l$. In the solution concentration range of $4 \times 10^{-5} \sim 1.4 \times 10^{-4} \text{ mol/}l$, the difference of zeta-potential hardly increases at all and the floatability of the fluorite is about constant, nearly 100%.

In the system quartz or scheelite-octadecyl dimethyl benzyl ammonium chloride, the floatability of each mineral increases with the difference of zeta-potential in the solution concentration range of $1.2 \times 10^{-6} \sim 5.7 \times 10^{-6} \text{ mol}/l$. At concentrations exceeding $5.7 \times 10^{-6} \text{ mol}/l$, the difference of zeta-potential in each system increases gradually



Fig. 17. Relation between floatability and difference of zeta-potential in system quartz-octadecyl dimethyl benzyl ammonium chloride.



Fig. 18. Relation between floatability and difference of zeta-potential in system scheelite-octadecyl dimethyl benzyl ammonium chloride,

and the floatability of each mineral is approximately constant, nearly 100%.

In the system quartz-dodecyl ammonium acetate, the floatability of quartz increases with the difference of zeta-potential in the solution concentration range of 4×10^{-5} $\sim 1.6 \times 10^{-4}$ mol/l. At concentrations exceeding 2×10^{-4} mol/l, the difference of zeta-potential increases slightly, and the floatability of quartz is constant, nearly 100%.

On the other hand, in the system quartz-sodium dodecyl ben-



Fig. 19. Relation between floatability and difference of zeta-potential in system quartz-dodecyl ammonium acetate.

zene sulphonate a difference of zeta-potential is scarcely detected and the floatability of quartz does not change.

From the above results it is found that the floatability of mineral particles correlates with the difference of zeta-potential. This is in agreement with the view suggested by A. M. Gaudin and S. C. Sun¹). As will be discussed later in this paper, this may be based on the fact that the change of zeta-potential is in close relation to



Fig. 20. Relation between difference of zeta-potential and adsorption density in system fluorite-sodium dodecyl benzerne sulphonate.

the adsorption of collector ion on the mineral surface.

6.2 Relation between difference of zeta-potential and adsorption density

Fig. 20, 21, 22 and 23 show the relation between the difference of zeta-potential and the adsorption density of the mineral particles.

The adsorption density in very dilute solutions could not be plotted in the above figure, because the measurement of the adsorption in such dilute solutions was beyond the power of the spectrophoto-







Fig. 22. Relation between difference of zeta-potential and adsorption density in system scheelite-octadecyl dimethyl benzyl ammonium chloride.



Fig. 23. Relation between difference of zeta-potential and adsorption density in system quartz-dodecyl ammonium acetate.

metrical method. But if extrapolation of the plots obtained by the experiments is valid, it may be estimated that the difference of zeta-potential in the system fluorite —sodium dodecyl benzene sulphonate and quartz or scheelite—octadecyl dimethyl benzyl ammonium chloride increases with the adsorption density in the solution concentration range of $1.5 \times 10^{-5} \sim 4 \times 10^{-5} \text{ mol}/l$ and $5.7 \times 10^{-7} \sim 5.7 \times 10^{-6} \text{ mol}/l$ respectively.

In the system quartz—dodecyl ammonium acetate, the difference of zeta-potential is approximately proportional to the adsorption density obtained by F. Schulz in the solution concentration range of $1 \times 10^{-4} \sim 2 \times 10^{-4} \text{ mol/l}$. It is similarly recognized that the difference of zeta-potential increases with the adsorption density obtained by de Bruyn in the above concentration range.

From above results, it may be said that the difference of zeta-potential correlates well with the adsorption density.

Now, the relation between the difference of zeta-potential and the adsorption density will be considered theoretically.

According to the concept of the electrical double layer at the solid-liquid interface, the following equations are given.

Here $q_0 =$ surface charge per unit area

- q_1 =adsorbed layer charge per unit area
- q_2 =diffused layer charge per unit area
- δ =distance between solid surface and the outer Helmholz plane
- D =dielectric constant of the liquid medium
- $e_i = \text{charge of electron}$
- T = absolute temperature in degrees Kelvin
- k =Boltzmann's constant
- n =number of ions per unit volume in the bulk solution
- n^* = number of adsorbed ions per unit area of solid surface
- ψ_1 = electrical potential of the outer Helmholz plane relative to the interior of the solution phase
- ψ_0 = electrical potential at the solid surface.

The above quantities are expressed in C.G.S.e.s.u.

If there is electrical neutrality in the system,

$$q_0 + q_1 + q_2 = 0$$
.

Substituting equations (1), (2) and (3) in eq. (4), equation (5) is derived.

If the number of adsorbed ions per unit surface area is n_1^* and n_2^* for solution concentrations of n_1 and n_2 respectively, equation (6) and (7) are obtained from equation (5).

Where, ψ_{1,n_1} and ψ_{1,n_2} represent ψ_1 for solution concentrations n_1 and n_2 , respectively.

If it is assumed that ψ_0 is constant at the same pH, and D and δ in equation (6) and (7) are identical, equation (8) is derived.

$$n_{2}^{*}-n_{1}^{*}=\frac{D}{4\pi\delta e_{i}}(\psi_{1,n_{1}}-\psi_{1,n_{2}})+\sqrt{\frac{D}{2\pi kT}}(\psi_{1,n_{2}}\sqrt{n_{2}}-\psi_{1,n_{1}}\sqrt{n_{1}})\quad \dots\dots\dots(8)$$

If ψ_{1,n_1} and ψ_{1,n_2} are identical with the zeta-potential, ζ_{n_1} and ζ_{n_2} , in solution concentration n_1 and n_2 at the same pH, equation (8) may be written as follows,

This equation represents the relation between the difference of zeta-potential, the concentration in the bulk solution, and the adsorption density.

Assuming the numerical value of D, T, and δ , n^* in equation (9) can be calculated from the difference of zeta-potential obtained in this experiment. Thus, n^* is proportional to the difference of zeta-potential in the proper solution concentration range in each system. But there are some differences between the calculated value of the adsorption, n^* , and the experimental value. This may be due to the fact that the conditions of the experiment of adsorption can not be strictly identical to those of the zeta-potential measurement.

It is, however, believed that the correlations between the difference of zeta-potential and the adsorption density as summarized in Fig. 20, 21, 22 and 23 may be based substantially on equation (5) or (9).

And therefore, it may be said that the floatability of mineral particles correlates with the difference of zeta-potential in these experiments.

Summary

The electro-osmotic velocity, the adsorption density and the floatability of mineral particles were measured on the following systems: (i) fluorite-sodium dodecyl benzene sulphonate, (ii) quartz-sodium dodecyl benzene sulphonate, (iii) quartz-octadecyl dimethyl benzyl ammonium chloride, (iv) scheelite-octadecyl dimethyl benzyl ammonium chloride and (v) quartz-dodecyl ammonium acetate. And the relations between the difference of zeta-potential, the adsorption density and the floatability were discussed.

The results are as follows:

(1) The zeta-potential of the minerals in systems (i), (iii), (iv) and (v) decreases in absolute value upon increasing the solution concentration and changes its sign from positive to negative or from negative to positive at solution concentrations of about 2×10^{-5} , 2×10^{-6} , 4×10^{-6} and $2 \times 10^{-4} \text{ mol}/l$ respectively. In system (ii), however, the zeta-potential of quartz does not change remarkably and it has a negative value in the solution concentration range of $5 \times 10^{-5} \sim 1 \times 10^{-2} \text{ mol}/l$.

(2) The difference of zeta-potential in system (i), (iii), (iv) and (v) increases considerably with increasing solution concentration from 1.5×10^{-5} to 4×10^{-5} mol/l, from 2.3×10^{-7} to 6×10^{-6} mol/l, from 6×10^{-7} to 6×10^{-6} mol/l, and from 4×10^{-5} to 2×10^{-4} mol/l, respectively. On the other hand, the floatability of each mineral in the above systems also increases remarkably in approximately the same concentration range. In system (ii), however, a difference of zeta-potential can be scarcely detected and the floatability of quartz does not change with concentration.

Therefore, it is found that the floatability correlates with the difference of zetapotential.

(3) The adsorption of each collector ion on each mineral in every system except(ii) increases with the solution concentration and it follows the Freundlich isotherm.In system (ii), hardly any adsorption of collector ion on quartz can be found.

Accordingly, it may be said that the difference of zeta-potential correlates with the adsorption density in the proper low solution concentration range.

(4) On the relation between the difference of zeta-potential and the adsorption density, the following equation was derived,

$$n_{2}^{*}-n_{1}^{*}=\frac{D}{4\pi\delta e_{i}}(\zeta_{n_{1}}-\zeta_{n_{2}})+\sqrt{\frac{D}{2\pi kT}}(\zeta_{n_{2}}\sqrt{n_{2}}-\zeta_{n_{1}}\sqrt{n_{1}}).$$

As mentioned above, it may be said that the difference of zeta-potential of the mineral correlates with the adsorption density of collector on the mineral surface, and that therefore the floatability of the mineral correlates with the difference of zeta-potential.

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