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著者	USUI Shinnosuke
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The Effect of Potassium Dodecyl Xanthate on the Stability of Sphalerite Suspensions*

Shinnosuke USUI

The Research Institute of Mineral Dressing and Metallurgy

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Synopsis

The effect of potassium dodecyl xanthate (KDX) on the coagulation, dispersion and flotation recovery of sphalerite in aqueous suspensions is investigated by means of adsorption isotherm, electrokinetic measurement and pneumatic flotation test. The degree of coagulation and the flotation recovery increase with increasing KDX concentration, approaching a maximum at the coverage corresponding approximately to a close-packed monolayer of KDX on the surface of sphalerite, and then decrease as the adsorption of KDX proceeds to the bimolecular layer. The coagulation mentioned above is interpreted not by the decrease of the electrical repulsion between particles caused by the lowering of the ζ -potential, but by the hydrophobic modification of the surface of sphalerite due to the oriented adsorption of KDX. The dispersion may be due to the hydrated surface caused by the double adsorbed layer with polar groups directed towards the solution and the increase of the ζ -potential of particles. The KDX concentration at which the dispersion occurs is correlated to the cmc of KDX. The relation between the stability of suspensions and the hydrophobic or hydrophilic nature of particles is discussed on the basis of the Hamaker-Vold theory concerning the van der Waals' forces between colloid particles.

I. Introduction

To control the stability of sphalerite suspensions is of great significance in metallurgical and chemical applications, such as flotation, coating of fluorescent paints, etc. It has widely been accepted that the stability of aqueous suspensions depends upon the electrical repulsion between particles, while their stability is also closely related to the hydrophobic or hydrophilic nature of particles. The purpose of the present paper is to study the effect of potassium xanthate bearing long chain alkyl radical, potassium dodecyl xanthate (KDX), on the coagulation or dispersion of sphalerite and the floatability of the sample by means of the adsorption isotherm and electrokinetic measurement.

II. Experimental

II-1. Samples

Natural sphalerite obtained from Budo mine was carefully selected by hand and ground by a porcelain mortar for about 40 hours. The ground sphalerite was washed with distilled water three times by centrifugation, and the sediment was dried in vacuum. The analysis of the sample showed Zn: 62.4% (Calculated

* The 140th report of the Research Institute of Mineral Dressing and Metallurgy.

for ZnS, Zn: 67%) Fe: 1.0%, Cu: tr. For comparison, an artificial zinc sulfide (Dainihon Toryo Co., purest grade class A) was also used in adsorption experiments. The specific surface area of the samples by B.E.T. method utilizing CO_2 gas adsorption was $5.5 \times 10^4 \text{ cm}^2/\text{g}$ for natural sphalerite and $14.7 \times 10^4 \text{ cm}^2/\text{g}$ for artificial zinc sulfide respectively. KDX was prepared by the reaction between potassium alcoholate led from dodecyl alcohol and metallic potassium and carbon disulfide, and recrystallized twice from ethyl alcohol.

II-2. Experimental procedure

2 grams of sphalerite was suspended into 20 ml. of aqueous solution and the suspension was placed into 25 ml. graduated glass cylinder and shaken gently. After it was allowed to stand for 25 minutes, the degree of coagulation or dispersion

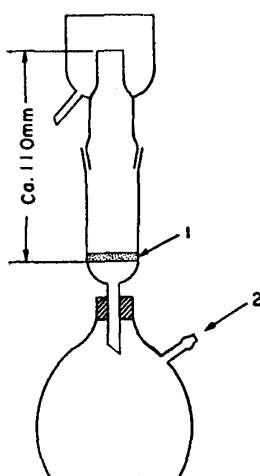


Fig. 1. Flotation cell.

1: Glass filter (28 mm ϕ). 2: Inlet of compressed air.

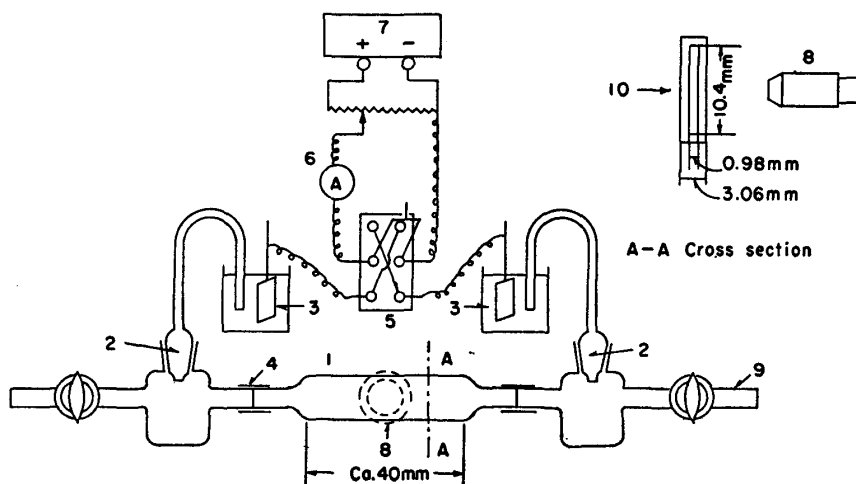


Fig. 2. Apparatus for observation of electrophoresis.

1: Measuring cell made by quartz	2: Salt bridge (KCl-agar)
3: Cu-CuSO ₄ electrode	4: Vinyl tube band
5: Polarity exchanger	6: Microammeter
7: DC135 V stabilized source	8: Microscope
9: 7 mm glass tube	10: Light source

was evaluated by measuring the sedimentation volume and the transparency of the supernatant liquid of the suspension. The measurements of transparency were made in a Hitachi EPO-B photoelectric photometer*¹ and the adsorption experiments, flotation tests and ζ -potential measurements were carried out under the same conditions as those of the coagulation experiments. The amount of KDX adsorbed on sphalerite particles was calculated by the difference in the concentration of KDX in the solution before and after adsorption. The analysis of KDX was performed in a Hitachi EPB-U spectrophotometer by applying the absorption band at $300\text{m}\mu$ which is characteristic of xanthogenates. All measurements were conducted at $30^\circ \pm 1^\circ\text{C}$. As shown in Fig. 1, the flotation test was performed in a glass cell of pneumatic type having the capacity of about 40 ml, and pure terpeneol was used as a frother in the concentration of 300 mg/l. The pressure and discharge of air were 13 cm Hg and 36 ml/min./cm² respectively. The ζ -potential of sphalerite particles was measured in a microscopic electrophoresis cell (Fig. 2) and was calculated by means of Smoluchowski's equation (1)

$$\zeta = \frac{4\pi\eta u}{\varepsilon H} \quad (1)$$

where η is viscosity of the solution, u , electrophoretic mobility, ε , dielectric constant of the solution and H , gradient of the applied potential. From the relation $H=i/\lambda s$ (i is electric current passed, λ , specific conductivity of the solution, and s , cross sectional area of the cell), equation (1) can be transformed into equation (2) at 30°C on an assumption $\varepsilon=80$ and $\eta=0.008$ as follows:

$$\zeta = 1.15 \times 10^6 \frac{\lambda}{i} u \text{ mV} \quad (2)$$

where λ is $\Omega^{-1}\text{cm}^{-1}$, i , μA , and u , $\mu. \text{sec}^{-1}$

The specific conductivity of the solution was measured in a Kohrlausch bridge utilizing a.c. 1 kc.

III. Results

III-1. The effect of KDX on the coagulation and dispersion of the aqueous suspension of sphalerite

Table 1 shows the transparency of the supernatant liquid of the suspensions, sedimentation volume and pH of the solutions with respect to the initial concentration of KDX. It is well known that the sedimentation volume is a measure of the coagulation; the coagulation (dispersion) causes an increase (decrease) in sedimentation volume.⁽¹⁾ The values of the sedimentation volume and transparency in Table 1 indicate that the coagulation of suspensions becomes stronger

* 1 No filter is used.

(1) H.R. Kruyt, *Colloid Science*, 1 (1952), 86.

Table 1. Results of the coagulation experiment for aqueous suspensions of sphalerite.

No.	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Initial concentration of KDX (moles/l)	0	7.9×10^{-5}	4.1×10^{-4}	7.8×10^{-4}	4.3×10^{-3}	7.8×10^{-3}	1.6×10^{-2}
Sedimentation volume (cc/g)	1.10	1.15	1.30	1.30	1.80	1.50	0.55
Transparency of supernatant liquid*	89	89	92	96	95	18	4
pH of solution	6.20	6.91	7.40	7.39	8.95	10.19	10.83

* Relative value to distilled water.

with an increase in concentration of KDX and reaches a maximum at the concentration of 4.3×10^{-3} moles/l of KDX, and the coagulation is weakened and the dispersion takes place if KDX is added over this concentration. The increase of the pH values of the solutions with the concentration of KDX may be due to the hydrolysis of KDX. It is still ambiguous whether the dispersion mentioned above is caused by the increase in the concentration of KDX or by the increase of the pH of the solution, since there is often the case where the stability of suspensions is closely related to the pH of the solution. Therefore, the effect of the pH on the coagulation of aqueous suspensions of sphalerite was tested. The pH of the solution was adjusted with KOH or HCl. The suspension exhibited the coagulation even at the pH 10.18, whereas the suspension containing KDX was dispersed at that pH, (No. 6 in Table 1) and furthermore, the suspension having the pH 10.19 (No. 6 in Table 1) remained in the state of dispersion even at the pH below 8.0. These observations indicate that the dispersion of suspensions in the range of high concentration of KDX cannot be ascribed only to the effect of the increase of pH values. However, the dispersion of the suspension at the concentration of 1.6×10^{-2} moles/l of KDX (No. 7 in Table 1) might be due to the incorporation of the effect of KDX and that of the increase of the concentration of OH ion, because when the pH is controlled to 10.83 by the addition of KOH alone, the suspension is dispersed.

III-2. Floatability of sphalerite particles with KDX

The results of flotation tests of sphalerite particles are illustrated in Fig. 3. The ordinate shows the flotation recovery and the abscissa is the initial concentration of KDX. The numbers in Fig. 3 correspond to those of Table 1. Fig. 3 indicates that the flotation recovery increases with the increase in the concentration of KDX and reaches a maximum, and then rapidly decreases with the excess of concentration of KDX. The floatability completely disappears when the concentration of KDX reaches 1.6×10^{-2} moles/l. The results in Fig. 3 may be correlated to those in Table 1; the best coagulation corresponds to the maximum recovery and the dispersion does to the poor flotation results.

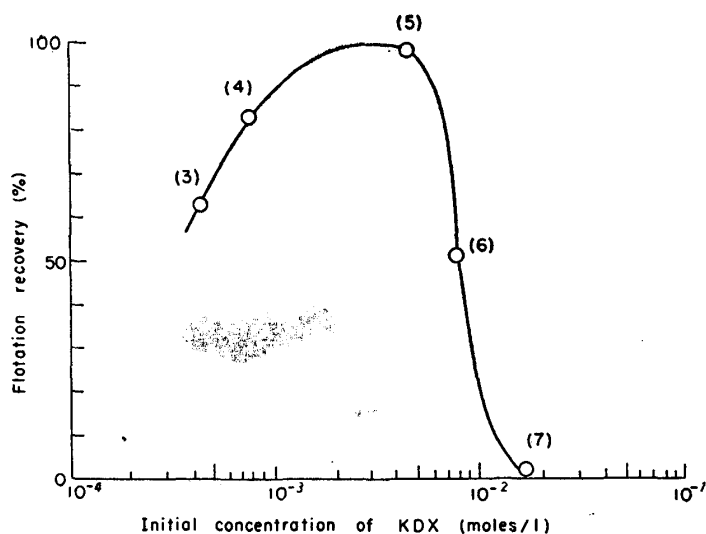


Fig. 3. Flotation recovery of sphalerite as a function of the initial concentration of KDX.

III-3. Adsorption of KDX on sphalerite

The amount of KDX adsorbed on sphalerite particles is shown in Fig. 4 as a function of the equilibrium concentration of KDX. The adsorption time including centrifugation is 40 minutes. The number of moles of KDX necessary to complete the close-packed monolayer was found to be 4.6×10^{-5} moles/g of sphalerite

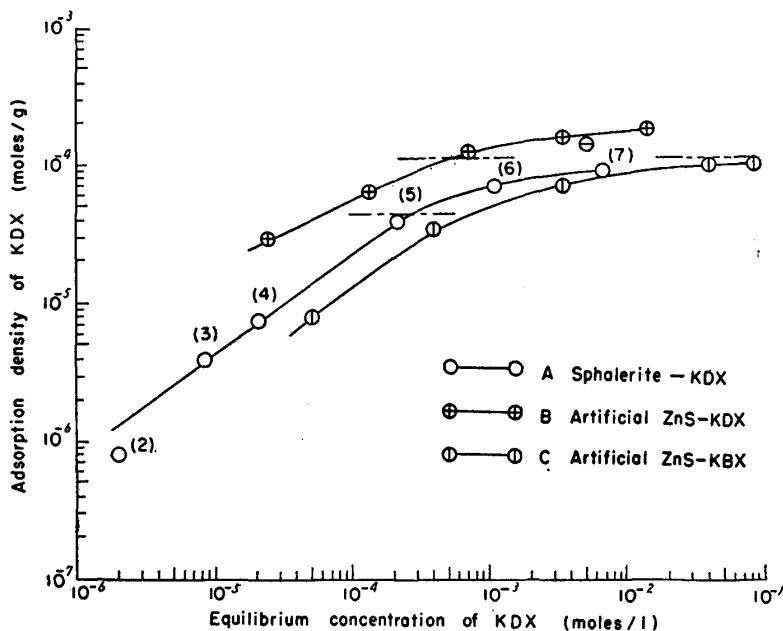


Fig. 4. Adsorption isotherms of KDX on sphalerite or artificial zinc sulfide.

particles if the cross sectional area of dodecyl xanthate molecule is assumed to be identical with that of ethyl xanthate molecule, namely, $20A^{(2)}$. This value is indicated by a horizontal dotted line in Fig. 4. From Fig. 4 (A) it can be seen

(2) J. Shimoizaka, Nippon Kogyo Kai-shi, **72** (1956), 13.

that the adsorption of KDX exceeds the amount corresponding to the monolayer coating and approaches the amount corresponding to bimolecular adsorption, namely, 9.2×10^{-5} moles/g of sphalerite. Curves (B) and (C) are adsorption isotherms of KDX and potassium butyl xanthate (KBX) for artificial zinc sulfide respectively. For the artificial samples, the amount of monolayer adsorption of xanthate is found to be 1.2×10^{-4} moles/g of zinc sulfide. From adsorption isotherms (B) and (C), it can easily be shown that KDX is adsorbed on the artificial zinc sulfide exceeding the monolayer, whereas the adsorption of KBX is limited to the monolayer coating. Similar to the case where sphalerite was used, the dispersion of suspensions of artificial zinc sulfide containing KDX gave the phenomena similar to those of natural sphalerite; the dispersion was brought about when the adsorption of KDX exceeded the monolayer coating. With suspensions containing KBX, no dispersion was caused in the range of the concentration tested.

Thus, from the results shown in Table 1, Fig. 3 and Fig. 4, the following conclusion might be reached that the coagulation and flotation recovery approach a maximum at the point where the coverage of KDX on the surface of sphalerite reaches a close-packed monolayer and that the dispersion and the depression of floatability occur as the adsorption of KDX exceeds the monolayer one.

Similar phenomena have been reported by Shimoizaka⁽³⁾ on the aqueous suspension of magnetite containing sodium oleate. The flotation recovery of magnetite decreases as the adsorption of sodium oleate reaches a bimolecular layer on the surface of magnetite, and a complete disappearance of floatability was observed at the concentration approximately corresponding to cmc of sodium oleate. He ascribed this feature to the bimolecular adsorption on the magnetite surface where the polar group of sodium oleate was oriented towards the solution. Analogous

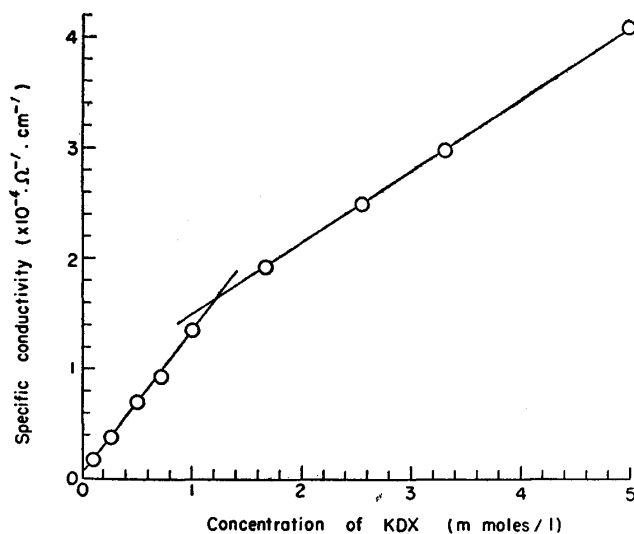


Fig. 5. Specific conductivity of solution as a function of the concentration of KDX.

(3) J. Shimoizaka, Tohoku Kozan, 6. No. 3 (1959) 15.

conception would be applicable to the interpretation of the dispersion phenomena observed in the present work. Fig. 5 shows the specific conductivity of the solution of KDX as a function of the concentration. Measurements of the specific conductivity of the solution were carried out in the coexistence of potassium hydroxide at the concentration of 5% equivalent to KDX and the temperature was kept at 50°C. Furthermore, care was taken to finish one run of the measurement within 20 minutes to avoid the decomposition of KDX as small as possible in the course of the experiment.*2. From this figure we find that the cmc of KDX, intersection of two straight lines to be about 1 m mole/l. The value of cmc thus obtained seems to correspond to the equilibrium concentration of KDX at which the dispersion appears.

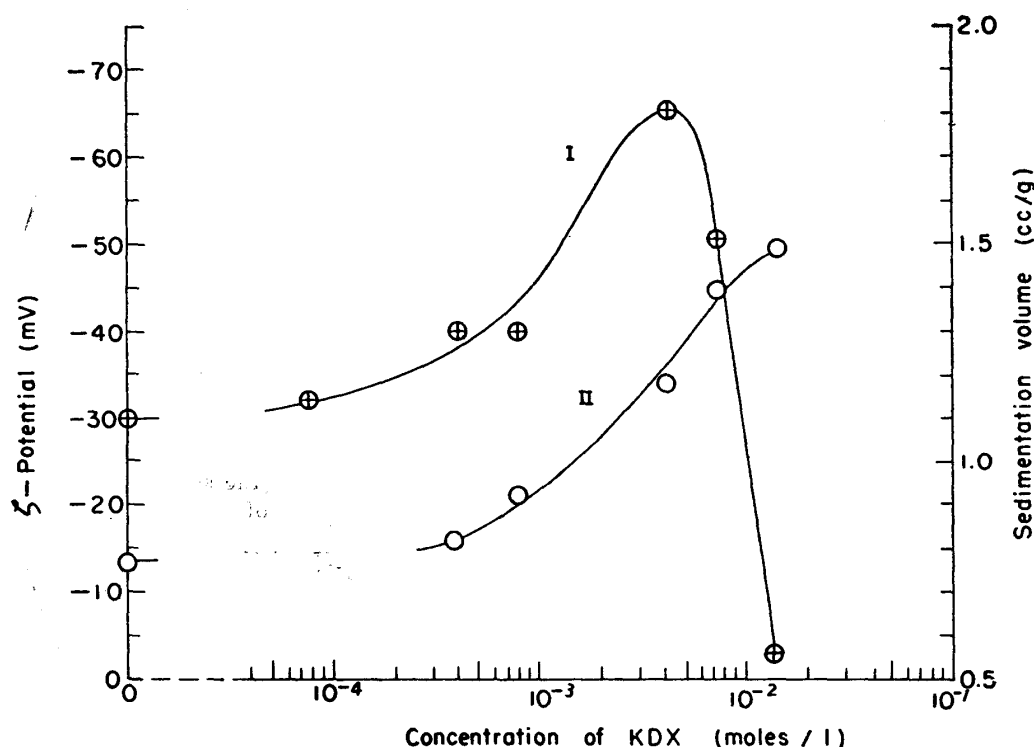


Fig. 6. ζ -potential of sphalerite as a function of the initial concentration of KDX.

I: Sedimentation volume

II: ζ -potential

III-4. ζ -potential of sphalerite

ζ -potentials of sphalerite in the solution are illustrated in Fig. 6 as a function of the initial concentration of KDX. Values of the sedimentation volume cited in Table 1 are also included in the same figure. It is seen that ζ -potentials of sphalerite increase steadily with the rise in the concentration of KDX, while the sedimentation volumes show a maximum at the concentration of 4.3×10^{-3} moles/l of KDX. This fact seems to indicate that the maximum coagulation mentioned above cannot be interpreted in terms of the decrease of the electrical

*2 The preliminary test showed that the decomposition of KDX was less than 3% under the condition adopted.

repulsion between particles which is caused by the lowering of the ζ -potential of particles. It is still unclear, however, whether the increase of the ζ -potential of sphalerite is produced by the effect of KDX or the increase of pH which was led from the hydrolysis of KDX. It is desirable, therefore, to survey the effect of pH on the ζ -potential of sphalerite in the solution containing KOH alone. The result is given in Fig. 7. In this figure the ζ -potential data rear-

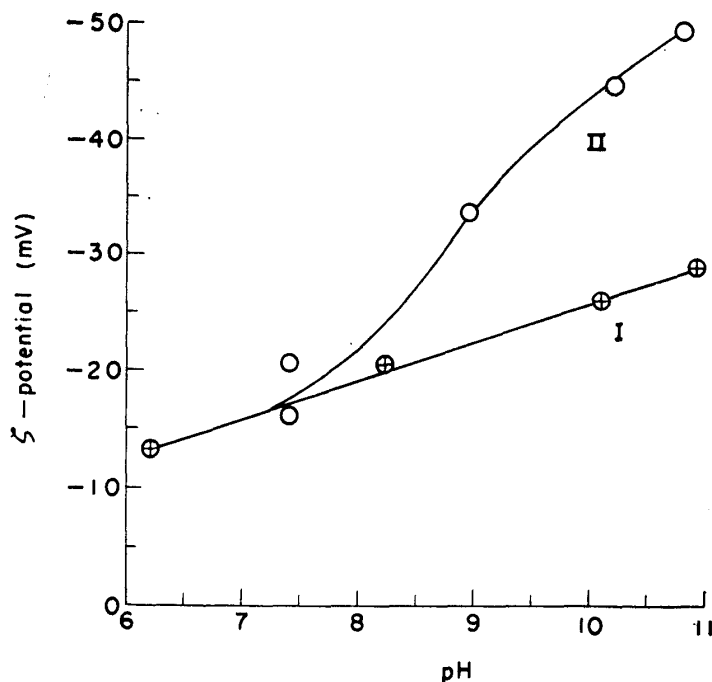


Fig. 7. ζ -potential of sphalerite as a function of pH of the solution.
I. In the absence of KDX. II. In the presence of KDX.

ranged from Fig. 6 are included as a function of the pH of the solution. The ζ -potential of sphalerite in the solution containing KOH alone is found to be analogous to that reported by Gaudin and Sun⁽⁴⁾. With the ζ -potential of sphalerite in the solution containing KDX, on the other hand, rapid rise of the negative value is seen when the pH exceeds over 9. It is known from the Table 1 and Fig. 4 that the pH 9 (more exactly 8.95) corresponds to the pH value of the solution having the initial concentration of KDX 4.3×10^{-3} moles/l at which the approximate monolayer adsorption of KDX is achieved on the surface of sphalerite. It is difficult to discuss quantitatively, in the present stage of this study, the relation between the ζ -potential and the surface coverage of KDX. However, from the results of Fig. 7, it might be pointed out qualitatively that the ζ -potential increases its negative value rapidly when the KDX exceeds the concentration at which the close-packed monolayer of KDX is attained on the surface of sphalerite. This observation, which indicates the fact that "the xanthate ion" is adsorbed on the surface of sphalerite over the monolayer adsorption, would be correlated to the adsorption isotherm shown in Fig. 4.

(4) A.M. Gaudin and S.C. Sun, Min. Tech. Tech. Publ. (1946), 2005.

IV. Discussion

The stability of lyophobic colloids or suspensions depends upon the energy of interaction between particles. According to the Verwey-Overbeek theory,⁽⁵⁾ the energy is composed of electrical repulsion and long range London-van der Waals' attraction. For a given suspension London-van der Waals' attraction is assumed to be constant, while the repulsion changes with the electrolyte content of the system and electrokinetic potential of particles. However, it is difficult to interpret the coagulation of the sphalerite suspension observed at the initial concentration of 4.3×10^{-3} moles/l of KDX in terms of the decrease of the electrical repulsion, since the ζ -potential of sphalerite increased rather than decreased under coagulation.

The stability of aqueous suspensions, on the other hand, depends upon the hydrophobic or hydrophilic nature of particles; the hydrophobic (hydrophilic) nature leads the suspensions to coagulation (dispersion). This has been studied by several investigators⁽⁶⁾⁽⁷⁾⁽⁸⁾ for system in which particle surfaces are modified into hydrophobic or hydrophilic nature by the adsorption of surface active agents. By considering the correlation between the flotation recovery and the coagulation of suspension with the aid of the adsorption isotherm, it would be apparent that the coagulation observed in the present study is due to hydrophobic modification of particles caused by the oriented adsorption of KDX with hydrocarbon chain directed towards the solution, and that the dispersion is due to the hydrophilic modification brought about by the double adsorbed layer with polar groups directed towards the solution.

As described above, the force responsible for particle association is London-van der Waals' forces. According to Hamaker,⁽⁹⁾ the energy of London-van der Waals' interaction between particles of identical composition is given by equations (3) and (4) as follows:

$$E = \frac{-A}{12} H(d, R_1, R_2) \quad (3)$$

$$A = A_{M-M} + A_{P-P} - 2A_{M-P} \quad (4)$$

where, H is a function of the radii of particles (R_1 and R_2) and distance of separation between particles (d) and is always positive. A is London-van der Waals' constant, A_{M-M} , A_{P-P} and A_{M-P} are the constant for medium-medium, particle-particle and medium-particle respectively, and they depend upon the composition of the medium and the particle. From the assumption $A_{M-P} =$

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- (5) E.J.W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (1948).
 (6) K. Meguro, *Nippon Kagaku Zasshi*, **77** (1956), 77.
 (7) J.F. Hazel and H.O. Strange, *J. Colloid Sci.*, **12** (1957), 529.
 (8) A. Watanabe, *Bull. Inst. Chem. Res. Kyoto Univ.*, **38** (1960), Nos. 2~3.
 (9) H.C. Hamaker, *Physica*, **4** (1937), 1058.

$\sqrt{A_{M-M} \cdot A_{P-P}}$,⁽¹⁰⁾ equation (3) is transformed into equation (5) as follows:

$$E = \frac{-1}{12} (\sqrt{A_{M-M}} - \sqrt{A_{P-P}})^2 H(d, R_1, R_2) \quad (5)$$

Equation (5) shows that in the suspension composed of particles of identical composition, the resultant London-van der Waals' interaction is always negative (attractive), the magnitude of which is determined by the difference of London-van der Waals' constant between medium-medium and particle-particle. Now, it is of interest to compare the values of $A_{ZnS/W}$ with $A_{HC/W}$ in the suspension in which either ZnS particles or hydrocarbon droplets are dispersed in water respectively. It is difficult, however, to obtain accurate values of A for various materials. Vold⁽¹¹⁾ reported the values of A_{W-W} and A_{HC-HC} as being 4.15×10^{-12} and 2.17×10^{-13} respectively, by correlating London-van der Waals' energy between molecules with the surface tension of liquids. On the other hand, Reerink and Overbeek⁽¹²⁾ estimated the value of $A_{AgI/W}$ at about 5×10^{-13} in their study on the stability factor of AgI suspension. The subscripts W and HC represent water and saturated hydrocarbon respectively. If we assume that the value of $A_{ZnS/W}$ differs little from that of $A_{AgI/W}$, then we can easily derive $A_{ZnS/W} = 5 \times 10^{-13}$ and $A_{HC/W} (= (\sqrt{A_{W-W}} - \sqrt{A_{HC-HC}})^2) = 2.5 \times 10^{-12}$. By comparing these two values a reasonable conclusion might be drawn that in aqueous suspensions, the attractive potential between hydrocarbon droplets is larger than that between sphalerite particles, i.e., hydrocarbon droplets are more strictly coagulated one another than sphalerite particles. Of course, the system in which sphalerite particles covered with oriented hydrocarbon groups are dispersed in water, can hardly be treated on the same basis with the one in which hydrocarbon droplets are dispersed in water. However, the concept that the surface of sphalerite particles covered with close-packed monolayer of KDX can be regarded as the one done with hydrocarbon itself might be accepted with an increase of the length of hydrocarbon chain of adsorbate, and

(10) H.R. Kruyt, *ibid.*, 268.

(11) M.J. Vold, *J. Colloid Sci.*, **16** (1961), 1.

(12) H. Reerink and J. Th. G. Overbeek, *Discussions Faraday Soc.*, No. 18 (1954), 74.

*3 The repulsive energy between particles was calculated on the suspension exhibiting the maximum coagulation (No. 5 in Table 1) from Verwey-Overbeek's equation,⁽⁵⁾ $V_R = 64nKT/\kappa \cdot \gamma^2 \cdot \exp(-2\kappa d)$, where n is the number of ions per cm^3 far from the surface, κ , reciprocal of the thickness of the double layer, e, elementary charge, d, half distance of separation between particles, γ , $\exp(Z/2) - 1 / \exp(Z/2) + 1$, and Z, valency of the counter ion. The value 9.5×10^{-3} ergs/cm² was obtained at the condition $\kappa d = 1$. In the calculation from Fig. 4 and Fig. 6, 2.2×10^{-4} moles/l and -34 mV were used for the concentration of KDX and the ζ -potential respectively. Hence, the magnitude of the attractive energy necessary to compensate the repulsive energy can be calculated from the equation $E = A / 48\pi d^2$ when $A \geq 5.7 \times 10^{-12}$ is satisfied. This value of A is larger than that predicted in the above discussion, i.e., $A_{HC/W} = 2.5 \times 10^{-12}$. However, it will be difficult to discuss this contradiction quantitatively, because of the uncertainty in the evaluation of the correct value of A in addition to the difficulty of measurement by means of which the absolute value of ζ -potential is determined.

consequently, London-van der Waals' constant A_{ZnSIW} increases towards the value of A_{HClW} to enhance the coagulation of sphalerite particles in the aqueous suspension.*³.

When the bimolecular adsorption in which the polar groups are oriented towards the solution is established, London-van der Waal's constant will tend to the value $A=(\sqrt{A_{W-W}}-\sqrt{A_{W-W}})^2=0$, i.e., the disappearance of attraction, as a result of the hydration of polar groups on particle surfaces. Accordingly, the electrical repulsion will predominate over the attraction and the dispersion of suspension may appear. In addition to this hydration effect, the increase of the ζ -potential of sphalerite particles in the range where the adsorption of KDX reaches the bimolecular layer will contribute much to the dispersion of the suspension.

The concept described above can be extended to the system in which particles are dispersed in nonpolar solvents. For example, in the case where particles covered with hydrocarbon are embedded in the liquid hydrocarbon, London-van der Waals' constant will approach the value $(\sqrt{A_{HC-HC}}-\sqrt{A_{HC-HC}})^2=0$ and a possibility of dispersion will be expected. Actually, the stable suspension can be realized when sphalerite particles which have been coagulated previously with close-packed monolayer of KDX in water are re-dispersed into kerosene after they are dried. Akamatsu⁽¹³⁾ pointed that the control of London-van der Waals' forces between particles played an important role in the stability of suspensions containing surface active agents. The reasonable qualitative interpretation of his notes may be given in the preceding discussion.

Thus, the coagulation which has not been well interpreted in terms of the lowering of the electrical repulsion, and dispersion which was caused by the hydrophilic modification may be explained on the basis of the Hamaker-Vold theory.

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(13) H. Akamatsu, *Kagaku*, **13** (1958), 726.