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PHYSICAL CHEMISTRY

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Abstract

Full Text

PHYSICAL CHEMISTRY

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DEPENDENCE OF THE FLOATABILITY OF ANTIMONITE ON THE MAGNITUDE OF THE ZETA POTENTIAL

The “elementary act” of flotation—the adhesion of a mineral particle to an air bubble—may be regarded as a process consisting of three stages: 1) the approach of the mineral particle to the bubble, during which a wetting film is formed, subjected to the action of surface forces; 2) thinning of the wetting film until it reaches an unstable state; 3) rupture of the wetting film and formation of a wetting perimeter and a contact angle, ensuring firm attachment of the particle to the surface of the bubble.

The relation between the contact angle of wetting and floatability has been studied by both Soviet (1, 2) and foreign (3) investigators. The role of the stage preceding the formation of the contact angle in the flotation process was first noted by A. N. Frumkin (4), who pointed out the importance of studying the process of thinning of the wetting film.

The third stage is the most decisive, since cases are possible in which the wetting film is incapable of rupturing and flotation is impossible. We shall confine ourselves to considering the criterion for the possibility of easy rupture of the wetting film as the principal criterion of effective floatability.

As a result of investigations carried out in this field, it has been established that the stability of the wetting film is determined mainly by forces of two kinds, van der Waals and electrostatic (5-8). These same forces formed the basis of the physical theory of interaction of particles and coagulation of hydrophobic sols and suspensions, both weakly charged (9) and strongly charged (10), as well as of the theory of heterocoagulation, interaction, and adhesion of dissimilar particles in electrolyte solutions (11). The principal propositions and conclusions of the theory of heterocoagulation may also be applied to explaining the adhesion of mineral particles to air bubbles during flotation.

Differences in the nature of the adhering particles may substantially change the character of both the van der Waals and the electrostatic interaction as compared with the case of particles of homogeneous nature. Thus, when homogeneous particles approach one another, the total result of the van der Waals

interactions, taking into account the participation in them of molecules of the dispersion medium, always corresponds to a resultant attraction; whereas for dissimilar particles in a given medium, on the contrary, a resultant repulsion may arise. Such repulsion may, for example, appear when a bulk-hydrophilic mineral particle approaches a bubble.

It follows from the theory of heterocoagulation that repulsion of particles charged to potentials of the same sign but unequal magnitude, upon overlap of their ionic atmospheres, can be observed only at sufficiently large distances. As such particles approach one another, the magnitude of the repulsive forces must have a maximum and then decrease, turning at sufficiently small distances into attraction. In the case where the potentials of both surfaces are opposite in sign or the potential of one of them is equal to zero, attrac-

...should be observed at all distances. This peculiarity of the interaction of dissimilar surfaces leads to a quantitative modification of the stability criteria in comparison with systems containing identical particles. In the general case the modified criterion contains the potentials of both surfaces and has a rather complicated form.

The form of the criterion will be substantially simplified in the case when, owing to the low adsorption of ions on the solution-air interface, the charge of this surface may be taken as zero, and the potential as not rigidly specified. This case was considered by Frumkin and Langmuir in calculating the repulsive forces in a thin wetting film between a solid surface charged to a definite potential Ψ_1 , and the surface of a bubble, whose charge in solutions not containing capillary-active electrolytes is so small that it may be taken, to a good approximation, as equal to zero. It was shown in this connection ⁽¹²⁾ that the repulsive force opposing the thinning of the film will be the same as in the case of a film of twice the thickness between two surfaces charged to the same potential Ψ_1 .

This force, equal to the electrostatic component of the disjoining pressure, was derived earlier by B. V. Derjaguin ⁽⁷⁾ and, for the case of a small potential ψ_1 , is equal to

$$P = \frac{\varepsilon}{8\pi} \frac{\psi_1^2}{d^2 \operatorname{ch}^2(x_0/d)} = \frac{\varepsilon}{8\pi} \frac{\psi_1^2}{d^2 \left[\frac{1}{2}(e^{x_0/d} + e^{-x_0/d})\right]^2}, \quad (1)$$

where ε is the dielectric permittivity of water; d is the thickness of the ionic atmosphere; x_0 is one-half the thickness of the liquid interlayer.

Adding the van der Waals component of the disjoining pressure of the wetting film, we obtain, for the resultant disjoining pressure, the value

$$P = \frac{\varepsilon}{8\pi} \frac{\psi_1^2}{d^2 \operatorname{ch}^2(h_0/d)} + \frac{(A_{12} - A_{11})}{6\pi h^3}, \quad (2)$$

where now h_0 is the thickness of the wetting film; A_{12} and A_{11} are the van der Waals attraction constants of water, respectively, to the mineral particle and to itself.

For volumetrically hydrophobic minerals

$$A_{12} < A_{11}, \quad (3)$$

and their difference is equal to a certain positive constant

$$A = A_{11} - A_{12}. \quad (4)$$

According to fairly rough estimates ⁽¹⁵⁾, for water $A_{11} = 6 \cdot 10^{-13}$ erg. For volumetrically hydrophobic minerals, according to (3), $0 < A_{12}/A_{11} < 1$. Not knowing the true value of A_{12} , it is reasonable to take for it the value $A_{12} = 3 \cdot 10^{-13}$ erg, corresponding to the “average” value $A_{12}/A_{11} = 0.5$.

The condition for the disappearance of the force barrier, dependent on the disjoining pressure $P(h)$, will be (cf. ^(10,11))

$$P = \frac{\varepsilon}{8\pi} \frac{\Psi_1^2}{d^2 \operatorname{ch}^2(h_0/d)} - \frac{A}{6\pi h^3} = 0, \quad \frac{\partial P}{\partial h} = 0. \quad (5)$$

Eliminating A from equations (5), we obtain, for determining the ratio

$$z \equiv 2h_c/d, \quad (6)$$

where h_c is the film thickness corresponding to the disappearance of the force barrier, the equation

$$\frac{z(e^z - e^{-z})}{e^z + 2 + e^{-z}} = 3. \quad (7)$$

The root of this equation is $z \simeq 3.2 \dots$. Substituting this value of z for $2h/d$ in the first equation (5), we find the condition for the disappearance of the force barrier preventing the rupture of the wetting film, i.e., the condition of unhindered floatability:

$$m \equiv dD\psi_1^2/A < 3, \dots \quad (8)$$

In the case of sufficiently dilute electrolyte solutions and small values of the surface potential, it appears possible to identify the surface potential ψ_1 with the ζ -potential. Then the floatability criterion will have the form

$$m \equiv dD\zeta^2/A < C, \quad (9)$$

where C is a constant close to 3.

The criterion given makes it possible to determine at what value of the ζ -potential of particles of a given mineral the fullest possible recovery of it into the froth product can be achieved. The present investigation was carried out in order to establish the relationship, following from the theory, between the magnitude of the ζ -potential and the floatability of antimonite, as well as the possibility of floating it from antimony and antimony-arsenic ores with a single frother.

Table 1

Mineral	pH	Specific electrical conductivity $\chi \cdot 10^8, \text{ ohm}^{-1} \cdot \text{cm}^{-1}$	Electrolyte conc. $C \cdot 10^5, \text{ mol/l}$	Debye thickness of the ionic atmosphere $d \cdot 10^6, \text{ cm}$	Electrokinetic potential $\zeta, \text{ mV}$	$\frac{dD\zeta^2}{A} \equiv m$	Recovery of antimonite into froth prod., %
Antimonite, Zopkhito deposit	3	0,92	0,92	0,45	-13,2	0,21	93
Antimonite, Zopkhito deposit	4	0,63	0,63	0,54	-36,3	1,9	92
Antimonite, Zopkhito deposit	5	0,42	0,42	0,66	-40,3	2,8	91
Antimonite, Zopkhito deposit	6	0,25	0,25	0,86	-42,0	4,1	64

Mineral	pH	Specific electrical conductivity $\chi \cdot 10^8, \text{ohm}^{-1} \cdot \text{cm}^{-1}$	Electrolyte conc. $C \cdot 10^5, \text{mol/l}$	Debye thickness of the ionic atmosphere $d \cdot 10^6, \text{cm}$	Electrokinetic potential ζ, mV	$\frac{dD\zeta^2}{A} \equiv m$	Recovery of antimonite into froth prod., %
Antimonite, Zopkhito deposit	9	0,37	0,37	0,71	-53,3	5,3	38
Antimonite, Marguzor deposit	3	1,7	1,7	0,33	-16,3	0,23	93
Antimonite, Marguzor deposit	4	1,14	1,14	0,36	-32,8	1,1	92
Antimonite, Marguzor deposit	5	0,63	0,63	0,54	-42,2	2,6	90
Antimonite, Marguzor deposit	6	0,36	0,36	0,72	-46,6	4,2	72
Antimonite, Marguzor deposit	9	0,44	0,44	0,65	-52,9	4,9	25
Antimonite, Kadam-Dzhai deposit	3	1,67	1,67	0,33	-17,2	0,27	92

Mineral	pH	Specific electrical conductivity $\chi \cdot 10^8$, $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	Electrolyte conc. $C \cdot 10^5$, mol/l	Debye thickness of the ionic atmosphere $d \cdot 10^6$, cm	Electrokinetic potential ζ , mV	$\frac{dD\zeta^2}{A} \equiv m$	Recovery of antimonite into froth prod., %
Antimonite, Kadam-Dzhai deposit	4	1,35	1,35	0,37	-38,9	1,47	92
Antimonite, Kadam-Dzhai deposit	5	0,57	0,57	0,57	-41,0	2,6	88
Antimonite, Kadam-Dzhai deposit	6	0,26	0,26	0,85	-48,4	5,2	70
Antimonite, Kadam-Dzhai deposit	9	0,33	0,33	0,75	-51,5	5,4	20

Antimonite from the Zopkhito deposits, Georgian SSR, Marguzor, Tajik SSR, and Kadam-Dzhai, Kirghiz SSR, with a particle size of $0,15 \div 0,043$ mm, was studied in media with pH 3, 4, 5, 6, and 9, produced by additions of sulfuric acid and caustic soda. The electrokinetic potential was determined by the electroosmosis method, for which an apparatus described by V. M. Gortikov⁽¹⁴⁾ was used. The electrical conductivity of the solutions was determined by means of a bridge made on a rheochord 10 m long and a KMS-6 resistance box. The bridge was powered from an audio generator with current at a frequency of 1000 Hz. A telephone served as the null indicator. The vessel constant was established using a KCl solution.

The electrokinetic potential was calculated by the formula $\zeta = 2,4 \cdot 10^6 \frac{Vl}{I} \chi$ mV, where $2,4 \cdot 10^6$ is a constant combining several constants and coefficients used for conversion from absolute quantities to those indicated above; χ is the

specific electrical conductivity in $\text{ohm}^{-1} \cdot \text{cm}^{-1}$; V is the flow rate of the liquid transported through the capillary, in ml/min; I is the current strength in mA.

When calculating the constant C from formula (9), the following were taken: $A = 0,3 \cdot 10^{-13}$ erg (this value is known only to order of magnitude); $D = 80$; ζ in units

CGSE; d is the reciprocal of the Debye-Hückel parameter x : $d = 1/x = 4.31 \cdot 10^{-8}/\sqrt{C}$ cm, where C is the concentration in mol/l of a monovalent electrolyte—determined conditionally in terms of NaCl from the specific electrical conductivity measured in the experiment; $C = 1000\chi/\lambda$ g-equiv/l; at $\lambda = 100$ (from the mobilities of Na and Cl ions at 18°) $C = 10\chi$ g-equiv/l.

Flotation experiments on antimonite of size $0.15 + 0.043$ mm were carried out in a flotation machine designed by G. A. Khan, with a capacity of 70 ml, at an S:L ratio of 1 : 7 and initial solution pH values of 3, 4, 5, 6, and 9. As frother, n -hexyl alcohol was used, calculated as 5 mg/l in the flotation of antimonite from the Zopkhito deposit and 125 mg/l in the flotation of antimonite from the Marguzor and Kadam-Dzhai deposits. The mixing time in all experiments was 2 min.; the flotation time was 2 min. Recovery was calculated from the weight of the froth product and the initial material.

The results given in Table 1 show that the concentration of hydrogen ions substantially affects the magnitude of the electrokinetic potential and the floatability of antimonite from the deposits studied.

To determine the influence of the frother on the ζ -potential, measurements were carried out in the presence of n -hexyl alcohol (in amounts corresponding to its dosage during flotation). The measurement results showed that the frother had practically no effect on the magnitude of the ζ -potential of antimonite. At the same time it is evident that, at values of the criterion $m \equiv aD\zeta^2/A$ less than 3.0, in accordance with theory, recovery exceeds 90%. At criterion values greater than 3-4, recovery falls to very low values.

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