

Chapter 2

Interaction Between Minerals and Reagents

As well known, mechanisms of reagents in the flotation process are very complicated. Much progress on interaction between collectors and mineral surface has been made using modern testing methods. However, there are still many problems to be solved. There have been many books and papers related to the mechanism of flotation reagents. Considering that the interaction mechanism of flotation reagents is not the key content of this book and also it is difficult to clearly illustrate the subject in one chapter, this chapter just briefly introduces a few significant theories and the related research results to this book. And collector is mainly concerned with this chapter. Other reagents will be introduced in the following chapters.

2.1 Various Theories on Interaction Between Collectors and Minerals

2.1.1 *Main Interactions Between Collector and Mineral*

Main interactions between collector and mineral include [1, 2]:

(1) **Physical adsorption**

The adsorption heat or energy (0.01–0.1 eV/mol) of physical adsorption is very low. The distance between adsorption molecules and mineral surface is large. Meantime, the adsorption forces include van der Waals force and electrostatic force. There are not shared electrons or electron transfer between reagent and mineral. It is not selective adsorption and is easy to desorption. Usually, the adsorption capability decreases with increasing temperature.

(2) **Chemical adsorption**

The adsorption heat or energy (1 eV/mol) is high. The distance between adsorption molecules and mineral surface is small. Meantime, the adsorption force is essentially the chemical force. The adsorption between reagent and mineral involves bonding force of electrons. It is selective adsorption and is hard to desorption. Adsorption capability increases with increasing temperature.

(3) **Surface chemical reaction**

The further development of chemical adsorption often leads to chemical reaction on the mineral surface. The difference between surface chemical reaction and chemical adsorption lies in the production of new independent phase of product on the mineral surface of the former.

2.1.2 Adsorption Models of Collector on Mineral

The main adsorption models of collector on mineral are as follows:

(1) **Physical adsorption of nonpolar molecule**

It refers to the adsorption of various nonpolar hydrocarbon oils onto mineral. The adsorption force is dipolar force or London force. According to research results, the adsorption of nonpolar oil occurs at the three-phase wetting interface when the bubble adheres to mineral surface.

(2) **Adsorption theory of electric double layer**

If the mineral surface is charged, then there must be a corresponding excess of oppositely charged ions (counterions) to maintain electrical neutrality. The combined system of surface charge and the excess charge is known as the electrical double layer and its inside is called interlayer and the outside is expand layer. A fundamental concept in electric double layer is that there is a plane of shear (stern layer), which separates the fixed and mobile charge. The electric potential at the plane of shear is universally known as the zeta potential and given the symbol ζ . The adsorption of collector and other ions is able to change the zeta potential with the help of electrostatic force. When the concentration value of collector is low, the adsorption of collector occurs in form of ions. When the concentration value of collector is high, the adsorption of collector occurs in form of semi-micelle and ion-molecule reaction [3–5]. If collector ions are able to enter into the inner of stern layer (IHP), superfluous compensating ions in the solution can make the charge reverse. Specific adsorption forms at the interface of mineral and reagent under such circumstances. And specific adsorption is a very important method for destabilization of charged mineral particles.

A conceptual picture of the collector adsorption onto mineral surface is shown in Fig. 2.1.

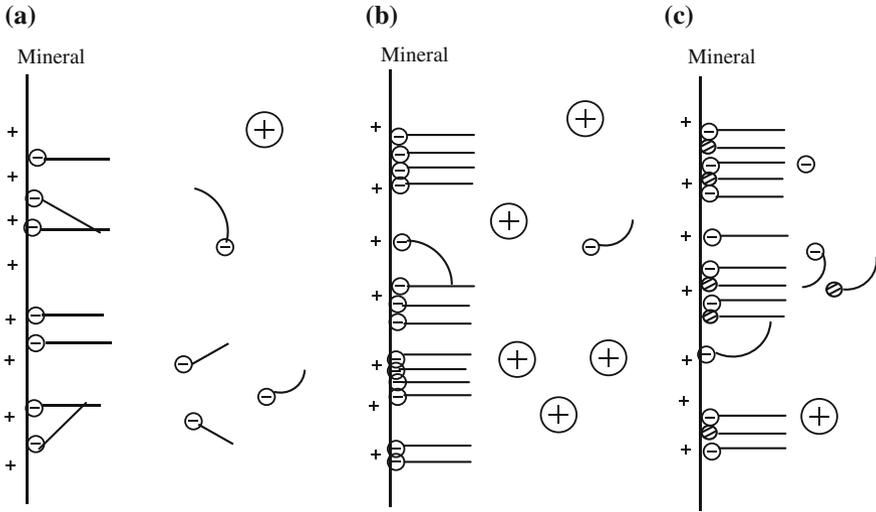
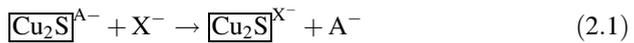


Fig. 2.1 A conceptual picture of sodium laurate adsorption onto hematite. **a** dilute solution, single-ion adsorption; **b** concentrate solution, semi-micelle adsorption; **c** ion–molecule coadsorption

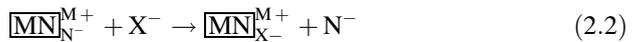
(3) Exchange adsorption of isonym ions

The experimental results of Gaudin (MIT) revealed that the concentration of sulfur-bearing ion increase with decrease of anion concentration of residual xanthate in the solution system of xanthate and sulfide mineral. Based on the results as above, the model of exchange adsorption is given by the following [6]:



where X^- refers to the xanthate anion, A^- refers to the anionic from mineral.

Wark and Cox also proposed another model, which is similar to Eq. 2.1. The model becomes following [7]:



where X^- refers to the xanthate anion; M^+ refers to the cation, and N^- refers to the anion from mineral.

According to their results, collector’s effective style is its ions and occur competitive adsorption with OH^- in water on mineral surface. For studying the critical condition of flotation occurring, Wark et al. (Melbourne University) reported that the collector concentration and the solution pH of sulfide *mineral* showed a relationship. Taking the adsorption of potassium ethyl xanthate onto galena, for example, the relationship between reagent concentration and solution pH is presented by the following:

| | | | | | |
|-----------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Concentration of KEX (mg/L) | 625 | 500 | 100 | 25 | 5 |
| pH | 12.5 | 11.9 | 11.4 | 10.4 | 9.1 |
| $C \cdot [H^+]$ | 1.3×10^{-15} | 4.2×10^{-15} | 2.7×10^{-15} | 6.7×10^{-15} | 2.7×10^{-14} |

where $C \cdot [H^+]$ is the product value of two factors (reagent concentration C and solution H^+).

From above results, Barsky found that the product value of reagent concentration and solution pH is a constant value under the flotation critical condition. The results are explained by people in favor of ionic theory as follows. The dissociation constant of xanthic acid is $K_a = 10^{-5}$ – 10^{-3} ; the ion concentration is approximately equal to the reagent concentration in alkali solution, that is, $[X^-] = C$, and $[X^-] \cdot [H^+] = \text{constant}$. Under alkaline conditions, $[H^+] \cdot [OH^-] = 10^{-14}$, the following equation can be drawn based on these relations:

$$\frac{[X^-]}{[OH^-]} = K \quad (2.3)$$

The Eq. (2.3) is called Barsky relation—the famous concept in flotation research history. To the adsorption of potassium ethyl xanthate on galena, $K_a = 10^{-1}$ – 1 is the quantitative relation of competitive adsorption between OH^- and collector anion. It can be concluded that xanthic acid ion is an effective fraction of reagent.

In fact, $[OH^-]$ is not in direct ratio to $[X^-]$. The actual relation between $[OH^-]$ and $[X^-]$ is as follows:

$$[X^-] = K[OH^-]^y$$

This problem will be discussed further in Chap. 7.

(4) Molecular adsorption

Cook et al. (University of Utah) gave another explanation about the adsorption of potassium ethyl xanthate with galena [8]. Although the adsorption of negative xanthate ion is decreased owing to the resistance of negatively charged sulfide mineral, there is no resistance of the adsorption of xanthate molecule by hydrolysis on the mineral surface. For xanthate, the dissociation equation is as follows:

$$K_a = \frac{[H^+](C - [HX])}{[HX]}$$

K_a is far greater than $[H^+]$ in alkaline solution. Therefore, it can be drawn by the following:

$$[\text{HX}] = \frac{[\text{H}^+] \cdot C}{K_a}$$

where K_a is the dissociation constant of xanthic acid; C is the reagent concentration.

Thus, it can be seen that $[\text{HX}]$ is also a constant on the basis of $C \cdot [\text{H}^+]$ reported by Wark et al. This is an excellent proof that that xanthate molecule is the effective fraction of reagent. Thus, Barsky relation expression can be given by the following:

$$(1 - \theta) + [\text{HX}] = \theta$$

Therefore,

$$\frac{1}{[\text{HX}]} \left(\frac{\theta}{1 - \theta} \right) = K \quad (2.4)$$

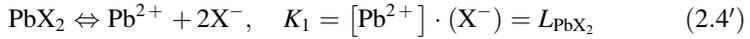
where θ is the proportion of collector coverage on mineral surface.

Although the theories of ion adsorption and molecular adsorption are on the basis of the same experimental results, there also is contradiction between them for some time. For enhancing the interactions of xanthate and mineral, ore pulp pH should be increased in order to $[\text{X}^-]$ increasing according to ion adsorption theory. The pH of ore pulp should be decreased in order to increase $[\text{HX}]$ according to molecular adsorption theory. However, the competitive adsorption of OH^- increases with increase of solution pH. And it is not conducive to the adsorption of X^- . The decomposing rate of xanthate increases with decrease of solution pH. And it is also not good for the selectivity of collector toward different minerals. However, it is worth mentioning that, the calculated experimental data about the ion adsorption and the molecular adsorption agree with each other in a particular alkaline solution. We shall not go into details here. The details will be discussed further in Chap. 7.

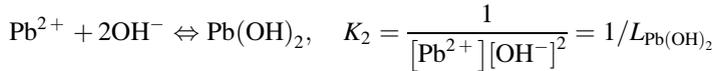
(5) Chemical adsorption

The interaction between collector and mineral involves electron transfer, that is, chemical adsorption. Taggart (Columbia University) proposed the solubility product theory, which is used to explain the behavior of chemical adsorption and flotation. But there is distinction between flotation process and chemical reaction in solution. The distinctions are as follows: (1) Mineral flotation takes place at solid-liquid interface; (2) The concentration ratio of collector to metal ion is over that of chemical reaction in solution. Someone, however, insist that the data of solubility product does not conform to actual condition. For instance, the solubility product of lead xanthate is bigger than that of lead sulfide. But chemical adsorption of xanthate still occurs on the surface of galena. Someone, thus, proposes that the solubility product value of surface reaction may be smaller than that of solution reaction.

In addition, the mineral is not pure one in the flotation processing. For example, after surface oxidation, the surface of galena is not component of PbS. But the calculation of the solubility product of reaction is still adopted at present. The reason is that it is helpful to explain the role of flotation reagent in many cases. Taking the adsorption of galena and xanthate, for example, the process of dissociation of lead xanthate formed on the surface of galena can be given as follows:



And then the adsorption reaction of Pb^{2+} with OH^- becomes following:



From above two-step reactions, it can be given as follows:



The equilibrium constant of reaction is as follows [9] (L refers to solubility product):

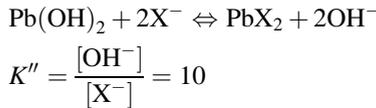
$$K' = K_1 \cdot K_2 = \frac{[\text{X}^-]^2}{[\text{OH}^-]^2} = \frac{L_{\text{PbX}_2}}{L_{\text{Pb}(\text{OH})_2}}$$

or

$$K = \frac{[\text{X}^-]}{[\text{OH}^-]} = \sqrt{K'}$$

where $L_{\text{Pb}(\text{OH})_2} = 4.2 \times 10^{-15}$; For isopropyl xanthate, $L_{\text{PbX}_2} = 1.58 \times 10^{-18}$, $K_{\text{isopropyl}} = 1.9 \times 10^{-2}$; For ethyl xanthate, $L_{\text{PbX}_2} = 1.7 \times 10^{-17}$, $K_{\text{ethyl}} = 1.2 \times 10^{-1}$.

For the adsorption of galena and xanthate, meantime, the reaction process and K'' were expressed in another way by Kakovski. The new expression for reaction and K'' become the following:



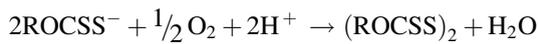
It suggests that the value of $[X^-]/[OH^-]$ is 10^{-1} . By comparing this value with that calculated value of Barsky ($C \cdot [H^+] = 10^{-15}$, and $[H^+]/[OH^-] = 10^{-14}$), while, it can be found that the value of $[X^-]/[OH^-]$ acquired by both of them is same with each other. To sum up, although those theories analyze the results from different aspects, they can reflect the actual conditions of flotation process and reagent to some extent.

In most cases, the interaction between coordination collector and mineral involves chemical adsorption [8]. Taking the flotation of chrysocollite with salts of hydroxamic acid, for example, the interaction is attributed to chemical adsorption. In fact, coordination chemistry theory is the application and development of solubility product theory. Based on this theory, dissociation constant of complex K_a is closely related to its stability. The stability of coordination increases with decrease of K_a . Therefore, K_a may serve as a criterion for chemical adsorption and chemical reactivity of flotation reagent.

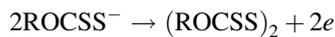
(6) Adsorption of reaction product

The interaction between mineral and reagent is not as simple as it seems. There is a series of complicated reactions in the flotation process. Mineral reacts with not only air (or oxygen) but also with impurities in pulp. And it leads to changes of the surface properties. There are side reactions occurring such as oxidation-reduction reaction, catalytic reaction, and some other special reactions. Among these side reactions, reaction product adsorption influences the flotation performance remarkably.

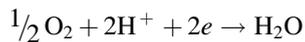
Lots of reaction products of xanthate with sulfide mineral are studied [10–13]. Research shows that the adsorption products of xanthate with sulfide surface include usually dixanthogen (X_2) and its existent, and quantity is relationship with mineral flotation. The interpretations of this relation are varied. One of those interpretations is based on the scanning potential study by R. Woods. The electrode reaction of xanthate occurs on the surface of sulfide mineral and the xanthate is further oxidized to dixanthogen. The expression for electrode reaction of xanthate is given by the following:



The anodic oxidation reaction is as follows:



The cathodic reduction reaction is as follows:



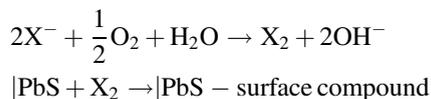
Sulfide *mineral* acted as a catalyst of these reactions. The anodic oxidation reaction and the cathodic reduction reaction can be expressed as follows:



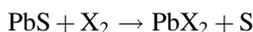
R. Woods reports that, under the condition of the concentration of potassium ethyl xanthate 6.25×10^{-4} and solution $\text{pH} \approx 7$, the reversible potential of dixanthogen in which xanthate is oxidized to dixanthogen is 0.13 V. The rest potentials of various minerals such as pyrite, chalcopyrite, covellite, bornite, and galena are 0.22, 0.14, 0.05, 0.06, and 0.06 V, respectively.

It is reported that dixanthogen product can improve the flotation performance of mineral. For example, under the condition of low pH, electrode oxidation of xanthate starts first, and the oxidation of mineral itself is followed. Under the condition of high pH, electrode oxidation of xanthate does not occur. The flotation tests show that the flotability of mineral is good at low pH but bad at high pH.

Another interpretation is that the adsorption of dixanthogen to mineral can improve the flotation performance of mineral on condition that xanthate ion is preferentially oxidized to dixanthogen. The reaction process can be given by the following:



Someone proposes that the reaction of dixanthogen with mineral can also be given by the following:

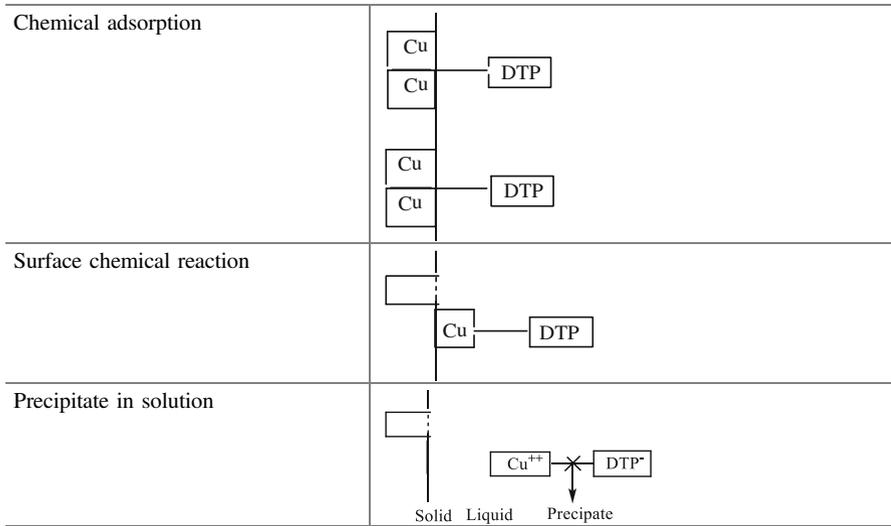


It is experimentally reported that the reaction product of xanthate with sulfide exists of dixanthogen and it is the main adsorption product especially on the surface of chalcopyrite, covellite, pyrite, and so on.

(7) Surface chemical reaction

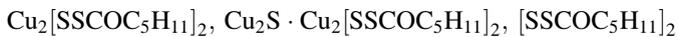
The chemical adsorption of reagent on mineral surface should result in surface chemical reaction. Through testing the reaction product of xanthate with sulfide, it can be found that the crystals of metal salts xanthate are found on the surface of mineral. Taking the reaction product of fatty acid with oxidized ore, for example, it can be found that metal salt of fatty acid can be dissolved in some solvents.

There are some differences among chemical adsorption, surface chemical reaction, and solution chemical reaction. Taking the adsorption of dithiophosphate on copper mineral, for example, the differences can be given by the following [14]:



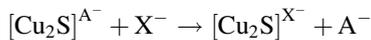
The effect of the occurrence of surface chemical reaction on flotation behavior has been unknown now. Someone insist that surface chemical reaction is bad for flotation because the surface chemical reaction does not lead to nonpolar group of reagent in hydrophobic-oriented arrangement. However, someone insist that the product of surface chemical reaction is necessary for flotation. For instance, the presence of dixanthogen is good for flotation.

From above results, it can be seen that those theories and hypothesis are proposed from different conditions (minerals, reagents, and reaction environments), research methods, and reaction stages. In fact, there may be some relation among those reactions in flotation. The practical results also indicate that collector exists in the form of free molecule, ion, and the reaction product on the surface of mineral. According to Dewey, after a longtime reaction of chalcocite with high concentrate potassium amyl xanthate, the reaction products dissolved in methanal, acetone, and ether extract are given by the following:

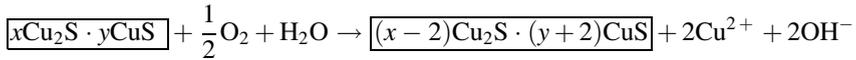


Therefore, the reactions may be given by the following:

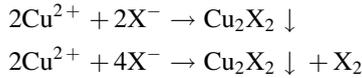
Exchange adsorption:



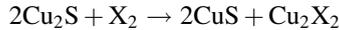
Surface oxidation of chalcocite:



Reaction of copper ion with xanthate ion:



Reaction of chalcocite with dioxanthogen:



2.2 Adsorption Equation of Flotation Reagent on Mineral Surface

The adsorption process of reagent on mineral surface can be described by various adsorption equations in surface chemistry. At first, some typical adsorption isotherm models and adsorption kinetics equations are introduced in this section. Subsequently, the adsorption equations of flotation reagent on mineral surface are derived.

2.2.1 Adsorption Isotherm Model

(1) Langmuir model

It has been found that the monolayer adsorption of gas molecules on solid surface can be expressed by Langmuir equation. The following gives a rough deduce for Langmuir adsorption of flotation reagent on mineral surface:



where M is mineral surface; A is reagent; MA is adsorption product; C_A is the reagent concentrate; C_M is the proportion of residual active site in which mineral surface is not covered by reagent; C_{MA} is the proportion of active site in which mineral surface is covered by reagent.

When the adsorption reaches to reaction equilibrium, the equilibrium constant (K) is given by the following:

$$K = \frac{C_{MA}}{C_M \cdot C_A}$$

It is obvious that the value of C_{MA} is same as that of adsorption amount (Γ). Because of $C_M + C_{MA} = 1$, a modified equation is as follows:

$$\Gamma = \frac{KC_A}{1 + KC_A} \quad (2.5)$$

The equation above can be further modified, and Langmuir equation is as follows:

$$\frac{C}{\Gamma} = \frac{b}{a}C + \frac{1}{a} \quad (2.5')$$

Langmuir equation shows that it is a linear relation between C/Γ and C .

(2) Freundlich model

Freundlich equation, as an empirical model, is base on the multilayer adsorption of reagent. The following gives a rough deduce for Freundlich adsorption of flotation reagent on mineral surface:

$$|M + nA \Leftrightarrow |MA_n$$

$$\Gamma = \frac{KC_A^n}{1 + KC_A^n}$$

When the values of K and C_A^n both are small, the equation above can be further modified, and Freundlich equation is as follows:

$$\Gamma = KC_A^n \quad (2.6)$$

$$\log \Gamma = a + n \log C \quad (2.6')$$

Freundlich equation indicates that it is a linear relation between $\log \Gamma$ and $\log C$.

Under the condition of mineral reacting with two or more reagents, the rough deduce process is given by the following:

$$|M + nA \Leftrightarrow |MA_n, \quad |M + mB \Leftrightarrow |MB_m$$

$$C_{MA} = K_A \cdot C_A^n \cdot C_M, \quad C_{MB} = K_B \cdot C_B^m \cdot C_M$$

That is:

$$\frac{\Gamma_A}{\Gamma_B} = K \frac{C_A^n}{C_B^m} \quad (2.7)$$

As shown in Eq. 2.7, there exists competitive adsorption between reagent A and reagent B on mineral. If one of the adsorption amounts of reagents keeps unchanged and $n = m$, Eq. 2.7 can be given as follows:

$$\log \Gamma = a + b \log \frac{C_A}{C_B} \quad (2.7')$$

(3) Temkin model

Temkin equation applies to the situation that the reagent adsorption changes with surface coverage. With increase of adsorption density, the interaction of adsorbing particulate gradually diminishes. The relationship between adsorption energy and adsorption amount is as follows:

$$-\Delta E = -\alpha(1 - \beta\Gamma)$$

where α and β refer to constants, respectively.

When the adsorption reaches to reaction equilibrium, the adsorption and the desorption processes are given by the following:

$$\begin{aligned} K_A C_M \cdot C_A &= K_B C_{MA} \cdot e^{-\frac{\alpha(1-\beta C_{MA})}{RT}} \\ C_A &= K \frac{C_{MA} \cdot e^{-\frac{\alpha(1-\beta C_{MA})}{RT}}}{C_M} \end{aligned}$$

When the value of C_{MA} is close to C_A , that is, coverage is 0.5. The expression of C_A is given by the following:

$$C_A = e^{-\frac{\alpha}{RT}} \cdot e^{-\frac{\alpha\beta C_{MA}}{RT}} \cdot K$$

The equation above can be further modified, and Temkin equation is as follows:

$$\Gamma = a + b \log C \quad (2.8)$$

where a is equivalent to $\frac{1}{\beta} - \frac{RT}{\alpha\beta} \ln K$; and b is equivalent to $\frac{RT}{\alpha\beta}$.

It can be found that it is a linear relation between Γ and $\log C$. Under the condition of mineral reacting with two reagents, Temkin equation can be given by the following:

$$\Gamma = a + b \log \frac{C_A}{C_B} \quad (2.8')$$

2.2.2 Adsorption Isotherm of Flotation Reagent on Mineral Surface

As mentioned before, the interactions of flotation reagent with mineral include physical adsorption by van der Waals force, electric double layer adsorption, chemical adsorption, and surface chemical reaction. There have been lots of reports on the experimental data and mathematical relations of interactions. Adopting various adsorption isotherm models, the analysis on main interactions between reagent and mineral are given by the following:

(1) Monolayer physical adsorption

The process of various reagents adsorption on the mineral surface can be adequately described with monolayer Langmuir equation, under the condition of low concentration of reagent. Under the condition of high concentration of reagent, however, Langmuir equation is not adaptable for describing the adsorption process. The reason lies in that multilayer adsorption and chemical adsorption are hard to occur under the condition of low concentration of reagent. Usually, the adsorption of flocculant with mineral is in conformity with Langmuir equation.

(2) Electric double layer adsorption

Electric double layer adsorption includes the adsorption of counterions in diffusion layer, the adsorption of surface-active ion and electrolyte in stern layer, and specific ion adsorption.

1. Adsorption of counterions in diffusion layer

Counterions is called inactive (indifferent) electrolyte. The monolayer coverage decides the maximum adsorption density of counterions. The most famous equation in electric double layer theory, Gouy-Chapman Equation, is given as follows:

$$\Gamma = kC^{1/2}e^{k'\zeta-1} \quad (2.9)$$

where k and k' refers to a constant, respectively; C is the concentration of counterions; ζ is the zeta potential of mineral surface.

Equation 2.9 is same with Freundlich equation (Eq. 2.6) in form. It indicates the adsorption of counterions in diffusion layer is a multilayer adsorption process. It is in accordance with the desorption theory of electric double layer. The thickness of the diffusion layer is larger than the diameter of monolayer ions.

2. Adsorption of surface-active ion and electrolyte in stern layer

The adsorption of surface-active ion and electrolyte in stern layer can be described with Stern-Grahame Equation, which is important for explaining the adsorption process.

Firstly, we assume that the chemical potentials of reagent and mineral surface are, respectively, μ_i and μ_i^s . The values of μ_i and μ_i^s can be obtained by the following:

$$\begin{aligned}\mu_i &= \mu_i^o + RT \ln a_i \\ \mu_i^s &= (\mu_i^o)^s + RT \ln a_i^s\end{aligned}$$

where μ_i^o and a_i are, respectively, the standard chemical potential and the activity of reagent of the solution; $(\mu_i^o)^s$ and a_i^s are, respectively, the standard chemical potential and the activity of mineral surface; R is the gas constant ($\text{J} (\text{mol T})^{-1}$); T is the absolute temperature.

When the adsorption reaches to reaction equilibrium (that is, $\mu_i = \mu_i^s$), the equation above is given by the following:

$$\frac{a_i^s}{a_i} = \exp \frac{\mu_i^s - (\mu_i^o)^s}{RT}$$

If the value of a_i is same as that of solution concentration (C), the adsorption standard free energy ΔG_{ads}^o (J/mol) can be obtained by the following:

$$\begin{aligned}\Delta G_{\text{ads}}^o &= (\mu_i^o)^s - \mu_i^o \\ \Gamma_{\delta} &= 2rCe^{-\Delta G_{\text{ads}}^o/RT} \\ \Delta G_{\text{ads}}^o &= \Delta G_{\text{elec}}^o + \Delta G_{\text{Chem}}^o + \Delta G_{\text{CH}_2}^o + \Delta G_{\text{CH}_2}^*\end{aligned} \quad (2.10)$$

where Γ_{δ} is the adsorption density in stern layer ($\text{mol}/\text{cm}^{-2}$); r is the effective diameter of the adsorbed ion (cm); $a_i^s = \Gamma_{\delta}/2r$; ΔG_{elec}^o (J/mol) is the free energy of electrostatic adsorption; ΔG_{Chem}^o (J/mol) is the free energy of chemical adsorption; $\Delta G_{\text{CH}_2}^o$ (J/mol) is the free energy of hydrocarbon chain association in nonpolar group; $\Delta G_{\text{CH}_2}^*$ (J/mol) is the free energy of association between nonpolar group and mineral.

When the adsorption is actuated by the electrostatic force, the standard adsorption free energy ΔG_{ads}^o (J/mol) can be obtained by the following:

$$\Delta G_{\text{ads}}^o = \Delta G_{\text{elec}}^o = vF\psi_{\delta}$$

where v is the valence of the adsorbed ion; F is the faraday constant; ψ_{δ} is the surface potential of a certain distance (δ) from mineral surface.

For the n -alkyl, the free energy $\Delta G_{\text{CH}_2}^o$ (J/mol) can be obtained by the following:

$$\Delta G_{\text{CH}_2}^o = n\Phi$$

where n is the number of $-\text{CH}_2-$; Φ is the free energy of each $-\text{CH}_2-$ (2.50–4.184 kJ/mol).

ΔG_{chem}^o means the chemical bond energy of reagent and mineral. In general, the value of ΔG_{chem}^o is about several tens kJ/mol. It was reported that the adsorption heat of hexyl mercaptan on the ZnO or ZnSiO₄ surface is 42 kJ/mol; the adsorption heat of ethyl xanthate on the PbS surface is 83 kJ/mol; the adsorption heat of Cu²⁺ on the ZnS surface is 63 kJ/mol.

Specific adsorption includes the chemical adsorption and molecular chain association adsorption except the electrostatic adsorption. The free energy of specific adsorption ΔG_{spec}^o (J/mol), hence, can be given by the following:

$$\Delta G_{\text{spec}}^o = \Delta G_{\text{chem}}^o + \Delta G_{\text{CH}_2}^o$$

From those equations above, it can be found that Eq. (2.10) is similar to Eq. (2.6). Both equations belong to the type of Freundlich model. If the adsorption is confined to the reaction between mineral and indifferent electrolyte, ΔG_{spec}^o only includes ΔG_{elec}^o . If the adsorption is extended to the reaction between mineral and active reagent, ΔG_{spec}^o includes ΔG_{elec}^o and ΔG_{chem}^o . But ΔG_{chem}^o and $\Delta G_{\text{CH}_2}^o$ are seldom displayed under the condition of low reagent concentration. Taking the adsorption of sodium dodecylsulphonate on alumina, for example, the adsorption isotherm can be divided into three regions. In the first region (reagent concentration $< 10^{-5}$ mol), the collector just act as counterion, and $\Delta G_{\text{ads}}^o = \Delta G_{\text{elec}}^o$. In the second region ($10^{-5} < \text{reagent concentration} < 3 \times 10^{-4}$ mol), the absorption amount increases remarkably as increasing collector concentration; the hydrocarbon chain association reaction occurs, that is, $\Delta G_{\text{ads}}^o = \Delta G_{\text{elec}}^o + \Delta G_{\text{CH}_2}^o$; the free energy of each $-\text{CH}_2-$ (Φ) is 2.51 kJ/mol. When the reagent concentration (C) is 5×10^{-5} mol and the monolayer coverage is 1/10, the semi-micelle adsorption takes place. In the third region (reagent concentration $> 3 \times 10^{-4}$ mol), the abundant absorption of the collector anion makes the zeta potential of mineral reverse (from positive potential to negative potential); the free energy of each $-\text{CH}_2-$ (Φ) is 2.929 kJ/mol; the electrostatic force becomes a repulsion force of antiadsorption at this case.

According to the testing of de Bruyn, the adsorption equation of lauryl amine hydrochloride on quartz can be presented by the following:

$\Gamma = 8.1 \times 10^{-9} C^{1/2}$, when $10^{-7} < \text{reagent concentration } (C) < 2 \times 10^{-4}$ mol
or $\Gamma = 2.2 \times 10^{-6} C^{1.16}$, when reagent concentration (C) $> 2 \times 10^{-4}$ mol

The lauryl amine ion absorbs on the quartz in the form of semi-micelle. Although the exponents of two equations vary, the adsorptions of reagents both in diffusion layer and stern layer are in line with the Freundlich model.

3. Adsorption of potential-determining ion in stern layer

The special role of the crystal lattice ions is recognized by referring to them as the potential-determining ions in electric double layer theory. Based on actual

results, the half-logarithm equation of the adsorption of potential-determining ion in stern layer is given by the following:

$$\Gamma = a \pm b \ln C$$

It shows the adsorption of potential-determining ion in stern layer is in accordance with the Temkin model (Eq. 2.8). That is, the adsorption of potential-determining ions in stern layer affects the electrical properties of mineral surface.

(3) Chemical adsorption

Xanthate collectors adsorb on the surface of sulfide ore mainly via multilayer chemical adsorption. The adsorption equation of these reagents, thus, is in line with the Freundlich model in most circumstances. For instance, the exponent (n) of Freundlich equation of xanthate adsorbing on sphalerite in the solution of potassium ethyl xanthate is 0.203 (from M Tokorozawa Liming). According to the report by Mukai, the Freundlich equation of xanthate adsorbing on sulfide ore is given by the following:

$$\Gamma = a[X^-]^{1/n}$$

For

$$\text{MoS}_2: a = 4.96 \times 10^{-5}, 1/n = 0.28;$$

$$\text{HgS}: a = 2.12 \times 10^{-5}, 1/n = 0.32;$$

$$\text{PbS}: a = 5.24 \times 10^{-5}, 1/n = 0.33;$$

$$\text{FeS}_2: a = 2.58 \times 10^{-6}, 1/n = 0.38;$$

$$\text{Sb}_2\text{S}_3: a = 3.98 \times 10^{-5}, 1/n = 0.45;$$

According to de Bruyn's results, the Freundlich equation of hexyl mercaptan adsorbing on gold ore is given by the following:

$$\Gamma = 1.68 \times 10^{-6} C^{0.52}$$

According to study results from Plaksin, the Freundlich equation of tridecylamine adsorbing on oxidized ore is given by the following:

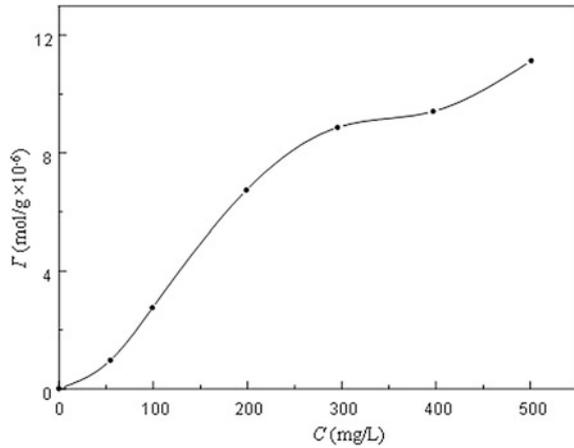
$$\Gamma = kC^{1/n}$$

where $1/n$, hubnerite: 0.51; wolframite: 0.58; quartz: 0.47; fluorite: 0.60; spar: 1.07.

The adsorption of tridecylamine on the inactive quartz, fluorite, and calcite may belong to multilayer physical adsorption. The adsorption of tridecylamine on the wolframite may belong to chemical adsorption.

In the course of studying the flotation of wolframite with 8-hydroxyquinoline as collector, the adsorption isotherm was obtained and shown in Fig. 2.2 [15]. By comparing with five types of adsorption isotherms in surface chemistry, the

Fig. 2.2 Adsorption isotherm of 8-hydroxyquinoline on wolframite



adsorption isotherm of 8-hydroxyquinoline on the wolframite is similar to type II. It indicates that there is no obvious point of saturated adsorption. But the point B is equivalent to point of saturated monolayer adsorption. By data processing using those adsorption isotherm equations, the adsorption of 8-hydroxyquinoline on the wolframite is in accordance with Freundlich and BET equations rather than Langmuir equation. And Fig. 2.3 shows that the adsorption isotherm accords with Freundlich equation much more. The results indicate that the adsorption of collector on the mineral is mainly multilayer adsorption of uneven distribution. Based on the analysis of adsorbate components, the adsorption includes physical and chemical adsorption. Under the condition of $\text{pH} \approx 8.5$, they are almost competitive equally. But the chemical adsorption plays a decisive role in improving the mineral flotation.

(4) Competitive adsorption of two reagents

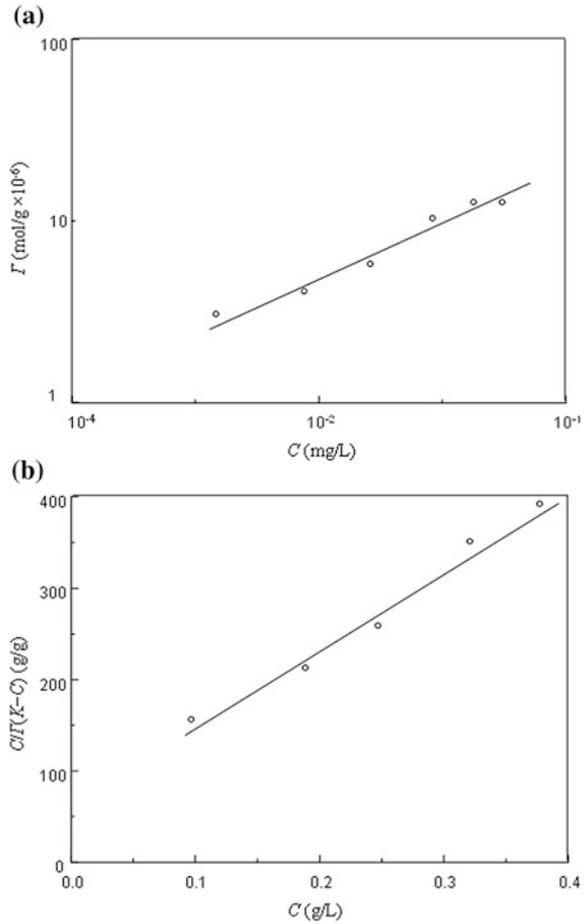
Based on *experimental* results, when competitive adsorption occurs between collector and depressant, the adsorption of reagent on the mineral is in accordance with Freundlich equation. Considering the effect of the concentrations of collector and depressant on the adsorption amount of collector, the adsorption of collector on mineral is given by the following:

$$\log \Gamma = a + b \log \frac{[A]}{[D]}$$

where Γ is the adsorption amount of collector; $[A]$ is concentration of collector; $[D]$ is the concentration of depressant. If the concentration of collector is fixed, the following equation can be obtained:

$$\log \Gamma = a \pm b \log [D]$$

Fig. 2.3 Adsorption isotherms of 8-hydroxyquinoline on wolframite. **a** Freundlich isotherm, **b** BET isotherm



And if $[D]$ is $[H^+]$ or $[OH^-]$, therefore

$$\log \Gamma = a \pm b pH$$

According to the experimental determination by Mitrofanov, the half-logarithm equation of competitive adsorption is expressed as follows:

$$\Gamma = a + b \log \frac{[A]}{[D]}$$

According to the discussions above, the competitive adsorption occurs between collector and depressant is in accordance with Temkin model.

(5) Surface chemical reaction

If the surface chemical reaction belongs to double decomposition reaction, the equilibrium constant can be calculated by the following equation:

$$K = \frac{L_1^a}{L_2^b} = \frac{C_1^c}{C_2^d}$$

where K is the equilibrium constant; C_1 and C_2 are the reagent concentrations; L_1 and L_2 are the solubility products; a , b , c , and d are the reaction constants. This equation is in accordance with the equation of solubility product theory (2.4').

2.2.3 Adsorption Kinetics Equation of Flotation Reagent on Mineral Surface

The adsorption amount of reagent varies with time. And the adsorption kinetics equation, usually, can be expressed by the following form:

$$\Gamma = at^{1/n}$$

where t is the adsorption time; a and n are constants. For example, $1/n$ is 0.1–1.02 when sodium sulfide reacts with oxidized ores by Mitrofanov.

According to the experimental determination by Gaudin, the adsorption kinetics equation of Cu^{2+} adsorbing on sphalerite can be expressed by the following:

$$\Gamma = 0.82 + 0.165 t^{1/2}$$

The adsorption rate, usually, is very fast. For instance, the time of the adsorption equilibrium is from 10^{-11} to several seconds. The report shows that reagent molecule keeps to-and-fro motion at the interface when the adsorption equilibrium is reached, the motion of which could last for about 10^{-9} s [16].

2.3 Structure of Adsorption Film and Flotation Behavior of Mineral

2.3.1 Structure of Adsorbed Layer

There have been many determination and opinions on the structure and composition of the adsorbed layer on mineral surface. As far as we know, the adsorption is multilayer in general. Based on the study on the adsorption of fatty acid on hematite and cassiterite, the single adsorbed layer can reach to 70 layers. The adsorbed reagent is in the form of molecule, ion, semi-micelle, and surface chemical reaction products.

The combination and arrangement of the adsorbed reagent on the mineral is not clear now. It is an accepted fact that the nearest layer of the adsorbed reagent is the product of chemical adsorption and then is the physical adsorption to minerals. For electrostatic adsorption in electric double layer, the adsorption of potential-determining ion occurs in inner layer; the adsorption of counterions occurs in the outer diffusion layer.

The ratio of chemical and physical adsorption is different under different conditions. The chemical adsorption increases with increasing activity of mineral. Experimental result in our laboratory shows that the proportion of chemical to physical adsorption is 4:1 for the adsorption of xanthate on galena surface, 1:1 for the adsorption of 8-hydroxyquinoline on wolframite, and 1:(3–4) for the adsorption of fatty acid on hematite.

For the arrangement of the adsorbed collector on the mineral, nonpolar groups direct outward in order to improve the hydrophobicity of mineral. However, flotation is depressed under the condition of too high reagent concentration. The explanation is that outward of polar groups of reagent molecule in adsorption outermost layer leads to increase of hydrophilicity.

The reasons for heterogeneous distribution of the adsorbed collector include mainly two aspects as follows: First, there is crystal defect, impurity, surface chemical reaction, and electrochemistry on the mineral surface; second, the differences in crystalline properties and residual chemical bonds on broken faces lead to the adsorption variation of reagent on the high-energy or low-energy zones of mineral. According to reports by isotopic analysis, the adsorbed collector is in the form of fascicles; the adsorption density at edge and corner of mineral is bigger than that in other zones. In addition, there is a relation between distribution of the adsorbed collector and lattice structure of mineral.

2.3.2 Relationship of Collector Adsorption and Mineral Flotation

Within a certain range of reagent concentration, the flotation recovery is improved with increasing reagent concentration and increasing adsorption amount. If the reagent concentration reaches a fixed value, however, the recovery rate varies not significantly with increasing reagent concentration and adsorption amount. When the reagent concentration reaches a higher value, adsorption amount increases and the flotation recovery decreases on the contrary. Corton and Bogdanov had found these similar results. The following Fig. 2.4 is the common relation between reagent concentration and adsorption amount of ethyl xanthate on the galena. And Fig. 2.5 is the relation between adsorption density of ethyl xanthate and flotation recovery of galena (from Gaudin and Bogdanov).

As shown in Fig. 2.5, the flotation recovery rate of galena reaches a maximum when the monolayer coverage of ethyl xanthate is 40 %. The study of Gaudin

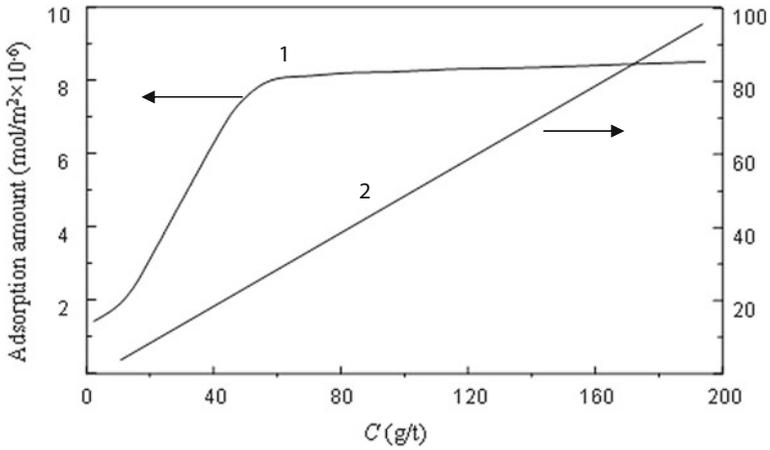


Fig. 2.4 Relation between reagent concentration and adsorption amount of ethyl xanthate on the galena (from Gaudin)

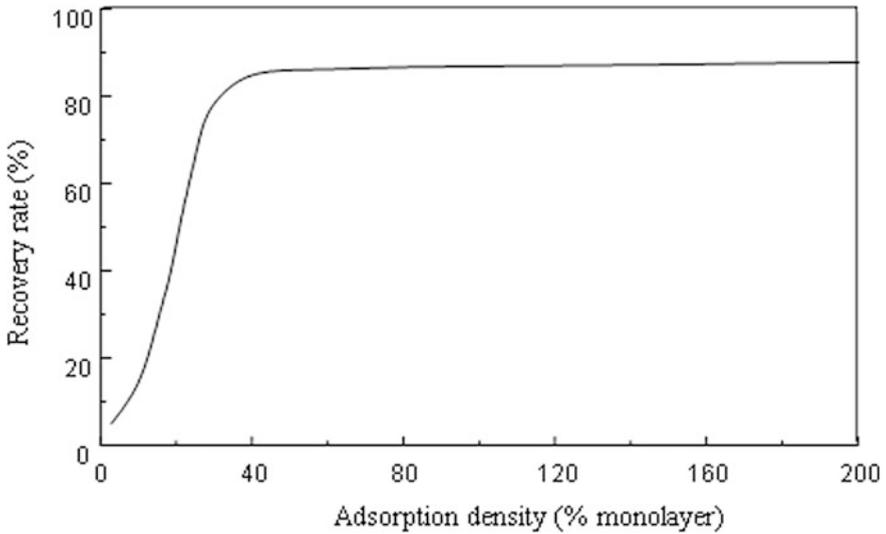


Fig. 2.5 Relation between adsorption density of ethyl xanthate and flotation recovery of galena (from Bogdanov)

showed that, however, the flotation recovery rate of mineral reaches a maximum when the monolayer coverage of reagent is 70 %.

The following Fig. 2.6 is the relation between reagent concentration and adsorption amount and flotation recovery rate of 8-hydroxyquinoline on wolframite surface (By Wang).

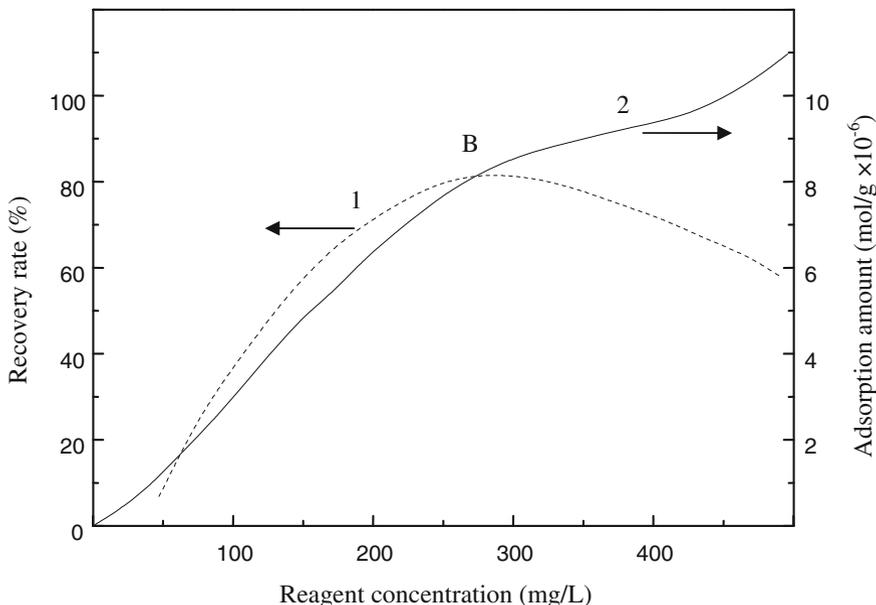


Fig. 2.6 Relation between reagent concentration and adsorption amount and flotation recovery of 8-hydroxyquinoline on wolframite surface

It can be shown in Fig. 2.6 that, within a certain range of reagent concentration, the flotation recovery rate and the adsorption amount increase consistently with reagent concentration. The adsorption amount increases all along when the reagent concentration reaches a higher value (point B). However, the flotation recovery rate decreases with reagent concentration. The point B is equivalent to the whole monolayer coverage.

The following Fig. 2.7 is the relation between solution pH and adsorption amount and flotation recovery rate of 8-hydroxyquinolinato on wolframite surface. It can be shown in Fig. 2.7 that, within a certain range of solution pH, the flotation recovery rate and the adsorption amount increase similarly with solution pH. When the pH reaches a higher value, however, the adsorption amount and the flotation recovery rate decreases with solution pH, respectively. The variation trends have also been found in other documents. The following Fig. 2.8 is the relation between solution pH and adsorption amount and flotation recovery rate of butyl and benzyl xanthate on galena surface.

Chemical adsorption, as the most important adsorption, affects the flotation behavior of mineral markedly. FT-IR results of Wadsworth showed that [3, 4] around wavelength of 5.8 μm assigned physical adsorption of oleic acid molecule; around wavelength of 6.4 μm is chemical adsorption of calcium oleate. The adsorption between oleic acid and fluorite is presented in following Figs. 2.9 and 2.10.

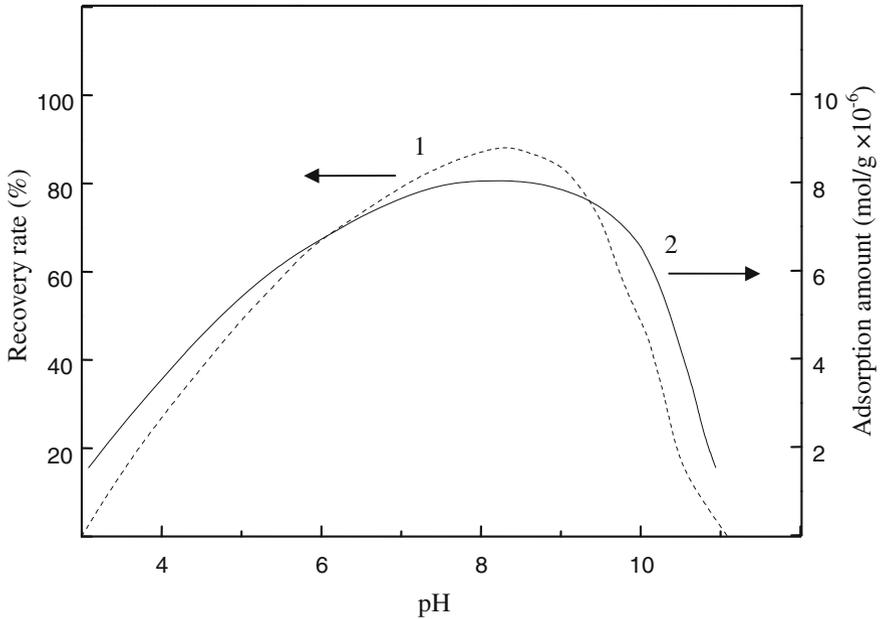


Fig. 2.7 Relation between solution pH and adsorption amount and flotation recovery of 8-hydroxyquiloninato on wolframite surface

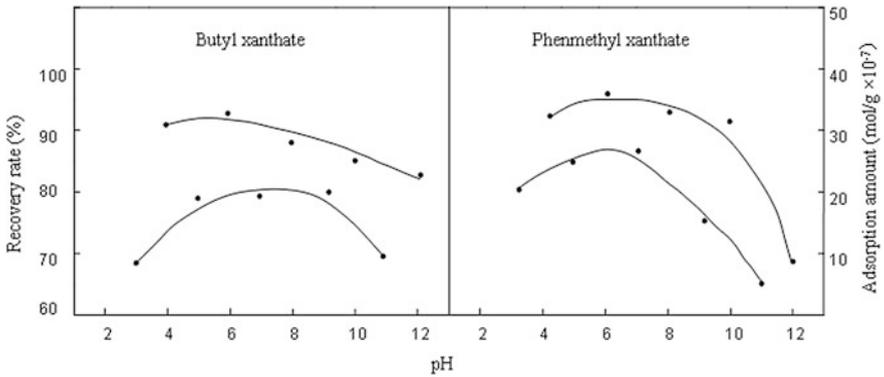


Fig. 2.8 Relation between solution pH and adsorption amount and flotation recovery of butyl and benzyl xanthate on galena surface

The flotation behaviors of fluorite show that the flotation recovery rate is small at low pH; while the flotation recovery rate becomes better under the condition of high pH. Chemical adsorption of reagent increases with increasing pH. Meantime, the effect of chemical adsorption on flotation behavior of mineral is bigger than that of physical adsorption. It is reasonable that the flotation recovery rate increases with increasing pH.

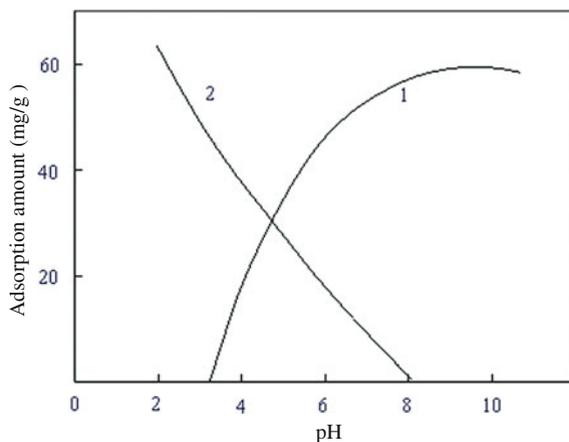


Fig. 2.9 Adsorption of oleic acid on fluorite. 1 Chemical adsorption; 2 Physical adsorption

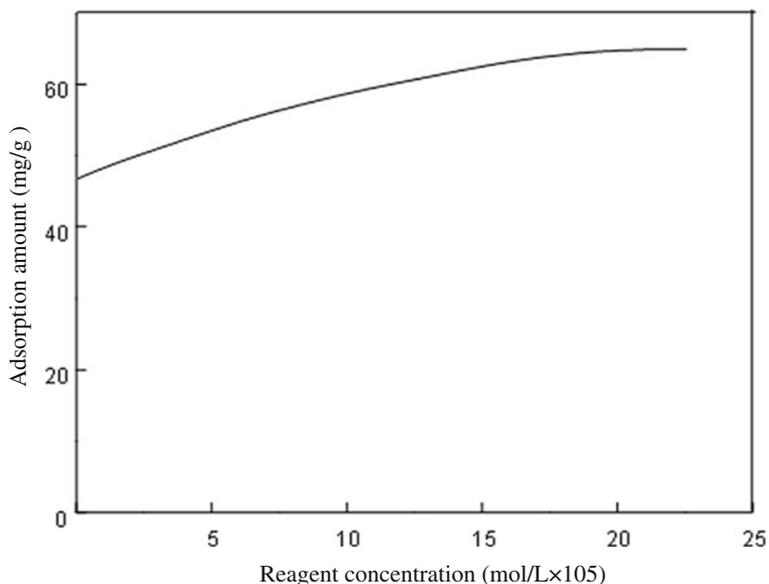


Fig. 2.10 Chemical adsorption of oleic acid on fluorite (by Wadsworth)

We have studied the relationship of chemical adsorption and flotation behavior by means of the flotation of wolframite with 8-hydroxyloquinolinate as collector. The Fig. 2.11 is the critical curve for wolframite flotation with 8-hydroxyloquinolinate. The results show that the critical curve for flotation is in line with the critical curve for chemical adsorption of collector. That is, the flotation behavior of mineral is strongly linked to the chemical adsorption.

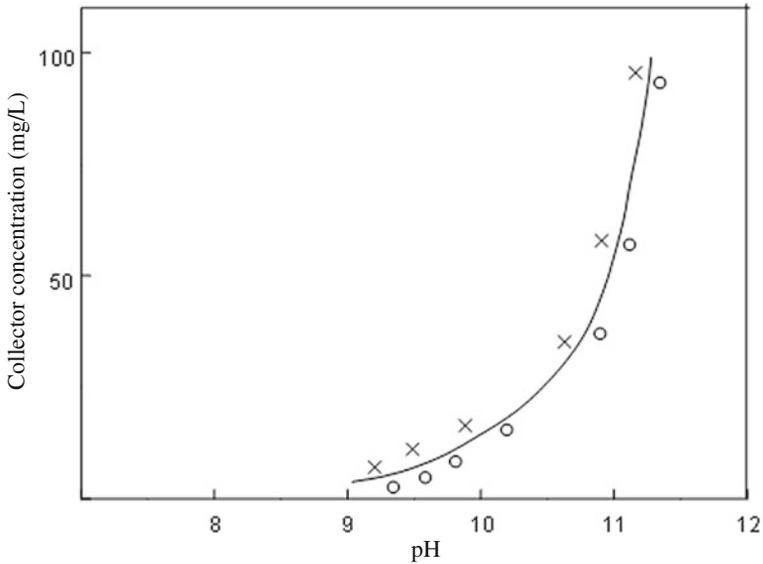


Fig. 2.11 The critical curve for wolframite flotation with 8-hydroxylquiloninato [17]. ×-occurrence of chemical adsorption and contact of bubble and mineral; ○-not occurrence of chemical adsorption and contact of bubble and mineral

2.4 Mineral Structure, Bonding Characteristics, and the Reaction of Reagents

2.4.1 Geochemical Classification of Mineral Elements and Their Interaction With reagent

According to electronic structure, chemical affinity, and characteristic geochemical, the classifications of mineral elements are as follows:

(1) Lithophile elements

Lithophile elements refer to the main elements in the rocks. Electronic structure of their cation is similar to that of inert gaseous element. The number of outer shell electron is 2 or 8. If lithophile elements are ionized, they lose s or p electrons. For instance:

| | |
|---|----------|
| Electronic structure of $1s^2$: Li^+ , Be^{2+} | He model |
| Electronic structure of $1s^2 2s^2 2p^6$: Na^+ , Mg^{2+} | Ne model |
| Electronic structure of $3s^2 3p^6$: K^+ , Ca^{2+} | Ar model |

Other elements such as Al, Ba, rare elements and anions such as O, Cl, F, P, Si, and B belong to lithophile elements, too. These elements, as the principal part of pegmatite, mainly formed in the late stage of magmatism. These elements are prone

to combine with O and Cl and further form ionic bonding compounds of large electronegative difference (Δx). Those compounds are characterized by stable chemical properties, widespread, and long-term preservation. Usually, physical adsorption (including electric double layer adsorption) of flotation collector occurs on the mineral which are comprised of these elements. Chemical adsorption only occurs on the minerals which are comprised of those elements with large atomic number or high valence number (such as Ca and Ba and so on).

(2) Chalcophile elements

Chalcophile elements include the elements of heavy nonferrous metals and precious metals. Their cation possesses electronic structure of d^{10} or $d^{10}s^2$, such as Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Au^+ , Hg^{2+} , As^{3+} , Sn^{2+} , Sb^{3+} , Pb^{2+} , Bi^{3+} , and so on. Nonmetallic anion includes S and Se. These elements, as the principal part of polymetallic ore, mainly formed in the hydrothermal stage. These elements are prone to combine with S and further form covalent bond compounds of small electronegative difference. Because of unstable chemical properties, those compounds are more easily weathered away into secondary mineral deposit. In general, chemical adsorption of flotation collector occurs on the minerals which are comprised of these elements.

(3) Siderophile elements

Siderophile elements include the elements of transition metals. Their cation possesses electronic structure of d^x ($x, 0-8$), such as Ti, V, Cr, Mn, Zr, Ta, Nb, Fe, Co, Ni, Mo, and rare precious metals. Nonmetal includes C and P. These elements mainly formed in the early stage of magma. These elements are prone to combine with C, P, and N and further form compounds of medial electronegative difference. In general, both chemical and physical adsorptions of flotation collector occur on the minerals which are comprised of these elements.

2.4.2 *Structure and Valence Bond of Mineral and Their Reactions with Reagents*

Considering the flotation process and variety of reagents, minerals are divided into two classes by flotation scientists: sulfide minerals and nonsulfide minerals. Sometimes, nonsulfide minerals are also called oxidized minerals, although nonsulfide minerals contain some salineoxy acid of nonoxides or various saline minerals that do not contain oxygen.

The flotability of sulfide minerals are good, in general. For example, adopting low dosage of selective thio-organic collector, the multimetal polymetallic sulfide

ore can be separated effectively. Although nonsulfide minerals are divided into many types, nonsulfide minerals (except for a few nonpolar minerals such as sulfur, coal, talc, and mica) own bad flotability. For example, using a large reagent dosage of carboxylic acids or amines as collector, sulfide ore cannot be separated well. From the view of geochemical classification of mineral elements, sulfide minerals are mainly comprised of chalcophile elements (or some siderophile elements such as Fe, Co, and Ni); nonsulfide minerals are mainly comprised of lithophile and siderophile elements. As for those minerals in secondary oxide deposits such as cerussite, smithsonite, and malachite, they are product oxidized from sulfide minerals. First, presulfurization of secondary oxide minerals is applied in the flotation process. Subsequently, secondary oxide minerals are separated by adopting selective thio-organic collector. That is, flotation reagents for these secondary oxide minerals are still same as those for sulfide minerals.

Valence bond properties of minerals have been mentioned. On the whole, the oxide minerals are ionic bonding; the sulfide minerals are covalent bond.

Crystal structure properties of minerals are strongly linked to their natural flotability and the reaction of flotation reagent. It is listed in Table 2.1.

Crystal structure can affect the crushing behavior of minerals, hydrophilicity or hydrophobicity of surface, and accumulation mode of mineral elements. For example, molybdenite is one of the sulfide minerals with covalent bond of Mo–S. But nonpolar bond of S–S is exposed to the cleavage plane of molybdenite due to its stratiform crystal lattice. The natural flotability of molybdenite is so good that it can be floated by using hydrocarbon oil as collector. Because of the occurrence of nonpolar bond on the cleavage plane, some oxide minerals including talc and mica own good natural flotability. They can be separated even though frother is only used in flotation.

Meantime, the impurities and defect of minerals also make influence on the crystal structure and flotability of minerals. For example, the presence of various impurities such as Fe, Mn, and Cd in sphalerite leads to the changes of ionic fraction and lattice parameter. As is well known, the flotability of marmatite with large ionic fraction is worse than that of pure sphalerite. And the content of Fe also affects the ionic fraction and lattice parameter. The following are the flotation results of sphalerites with single bubble flotation tube. It shows that there is a relation between lattice parameter and flotability of minerals.

| | | | |
|------------------------------|--------|--------|--------|
| Lattice parameter of ZnS (Å) | 5.4234 | 5.4187 | 5.4139 |
| Results of flotation (%) | 8.0 | 0.0 | 30.0 |

Table 2.1 Crystal structure of minerals and their flotation behavior

| Crystal structure | Valence bond | Typical mineral | Interaction with reagent and flotability |
|-----------------------|--------------------------------|---|---|
| Needle-like, schistic | Covalent bond | Se element: needle-like, atomic separation in needle: $d = 2.32 \text{ \AA}$, Atomic separation between needles: $d = 3.46 \text{ \AA}$; Graphite: schistic, atomic separation in sheet: $d = 1.42 \text{ \AA}$, atomic separation between sheets: $d = 3.40 \text{ \AA}$; Molybdenite: atomic separation in sheet: S-S, $d = 2.98 \text{ \AA}$, S-Mo, $d = 2.35 \text{ \AA}$; Atomic separation between sheets: S-S, $d = 3.66 \text{ \AA}$ | Cleavage along the van der Waals force direction; Nonpolar cleavage plane; Having natural flotability and can be floated by hydrocarbon oil; Physical adsorption between reagent and mineral |
| Diamond type | Covalent bond | Diamond, C-C tetrahedron, $d = 1.54 \text{ \AA}$ | No cleavage; Having natural flotability and can be floated by hydrocarbon oil; Physical adsorption between reagent and mineral |
| Metallic crystal | Metallic bond | Natural gold, silver, copper; Cu: $d = 2.55 \text{ \AA}$ | Floated by thio-organic collector; Chemical adsorption |
| Semi-metallic crystal | Covalent bond Metallic bond | Nonferrous metals sulfide ores such as: galena: metallic bond Pb-Pb, $d = 4.18 \text{ \AA}$; S-S, $d = 5.93 \text{ \AA}$; Pb-S, $d = 2.96 \text{ \AA}$; Sphalerite: 50 % ionicity, Zn-Zn, $d = 3.83 \text{ \AA}$; Pyrite: S appearing covalent double ion, $d = 2.14 \text{ \AA}$; Fe-S, $d = 2.26 \text{ \AA}$; Fe-Fe, $d = 3.83 \text{ \AA}$ | Having cleavage; Weak polarity; Having natural flotability and can be floated by Thio-organic collector; Chemical adsorption |
| Silicates | Covalent bond Ionic bond | The fundamental structure appearing in forms of silicon-oxygen tetrahedron; Si-O ionicity 40 %; (1) orthosilicates, tetrahedron, example: olivine (2) polysilicate, ditetrahedron, example: akermanite (3) metasilicate, free ring, example: beryl (4) metasilicates, single stranded, example: diopside (5) metasilicates, duplex, example, tremolite | Floated by fatty acid or amine, or activation flotation; Physical adsorption (1) imperfect cleavage, polarity, no natural flotability; (2) imperfect cleavage, polarity, no natural flotability; (3) appearing cleavage, polarity, no natural flotability; |

(continued)

Table 2.1 (continued)

| Crystal structure | Valence bond | Typical mineral | Interaction with reagent and flotability |
|---------------------|--------------|---|---|
| | | (6) layer silicates, example, talcum (7) framework, silicates, example: quartz | (4) appearing cleavage, polarity, no natural flotability; (5) appearing cleavage, polarity, no natural flotability; (6) appearing cleavage, no polarity, natural flotability; (7) no cleavage, polarity, no natural flotability; |
| Metallic oxide | Ionic bond | Corundum, rutile, hematite | Appearing cleavage, polarity, And can be floated by fatty acid; Physical and chemical adsorption |
| Complex ion crystal | Ionic bond | Oxysalts such as CO_3^{2-} , PO_3^{2-} , and SO_3^{2-} ; The inner of complex ion appearing covalent bond, anion-cation is electrovalent bond; Example: CaSO_4 S-O, $d = 1.56 \text{ \AA}$; Ca-Ca, $d = 3.11 \text{ \AA}$; Ca-S, $d = 3.48 \text{ \AA}$; Ca-O, $d = 2.42 \text{ \AA}$ | Appearing cleavage, polarity; And can be floated by fatty acid; Physical and chemical adsorption |
| Simple ion crystal | Ionic bond | Halide salts | Appearing cleavage, polarity; And can be floated by fatty acid; Physical adsorption |

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