

Application of extended DLVO theory in emulsion stability research^①

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Abstract: The extended DLVO theory was used to analyze the stability of emulsion stabilized by solid particles. It was emphasized that emulsion droplets covered by solid particles behaved as congener solid granules with the same diameter as droplets. The interaction potential energy curves between emulsion droplets stabilized by mica particles in the copper solvent extraction system were calculated. The results show that the effect of hydration repulsive forces are more powerful than that of electrostatic forces on stabilizing droplets for O/W emulsions. The energy barrier between droplets increases dramatically by about 7×10^3 kT when the hydration repulsion is considered.

Key words: emulsion; solid interfacial film; hydration force; coalescence; extended DLVO theory; solvent extraction

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1 INTRODUCTION

The stability study is crucial for emulsion forming or breaking. Emulsion is a system in which one immiscible liquid is highly dispersed in another in the form of very small droplets. The increase of the droplet interface areas during the emulsion process results in very high interface energy, so that emulsion is an unstable thermodynamic system. However, relying on emulsifier, the system can be kinetically stable. Usually, emulsifiers are surfactants. While, some very small solid particles can also stabilize emulsions^[1-7]. There are a lot of these kind of solid stabilized emulsions in chemical, hydrometallurgical, petrochemical, food, and medicinal industries.

The surfactants stabilize emulsions through reducing interfacial tension, forming interfacial films or liquid crystal adsorption layer to prevent the coalescence of emulsion droplets^[8, 9]. Small solid particles stabilize emulsions by adsorbing at interface to form physical barriers around droplets^[1-7]. In all emulsions, whether stabilized by surfactants or small solid particles, there are double electric layers and potential drops at both sides of the droplet interface. The electrostatic repulsive force on the droplet surface keeps the droplets apart so that reducing the chance of coalescence. This electrical repulsive effect is particularly important for O/W emulsions, or for the systems using small solid particles as emulsifiers. The DLVO theory is commonly used to study the stability of

emulsion^[1, 10]. Generally speaking, for small solid particles stabilized emulsions, their stability is believed to depend on the strength of interfacial film and electrostatic repulsive force.

The mechanisms of stabilization of small solid particles on emulsions were studied by analyzing the forces between emulsion droplets in copper solvent extraction system.

2 EXPERIMENTAL

All materials were provided by Dexing Copper Mine Company in JiangXi Province. Lix984N was used as extraction agent, and kerosene 260[#] was used as diluent. Real bioleaching solution containing $0.25 \text{ g} \cdot \text{L}^{-1} \text{Cu}^{2+}$ and $1.30 \text{ g} \cdot \text{L}^{-1} \text{Fe}^{3+}$ from Dexing Copper Mine and an artificial solution were used as the aqueous feed. The later was a solution made from analytical pure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ and deionized water in the same proportion as in the real bioleaching solution. The pH of the solution was adjusted to 2.46 by using $5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ and $10 \text{ mol} \cdot \text{L}^{-1} \text{NaOH}$. The volume fraction of extraction agent was 1.5% based on the $0.25 \text{ g} \cdot \text{L}^{-1}$ of copper concentration in the aqueous feed.

Extraction experiments were done in a 250 mL baffled Erlenmeyer flask at $(25 \pm 1)^\circ\text{C}$. Two immiscible liquids were stirred by an electrical stirrer at speed of 200 r/min for 5 min. The phase ratio O/A was 1:5 and the aqueous phase was kept continuous.

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The pH of solutions was measured by using a PHSJ-4A pH meter. The diameter distribution of emulsion droplets was determined by microscopic counting using Nikon ECLIPSE E400POL electrical optical microscopy, counting more than 5 000 droplets. The chemical composition of solids was analyzed by using atomic absorption spectrometry. The analysis of crystallographic components of the solids in emulsion was performed using a Simmons D-500 X-ray diffractometer. The micromorphic study of emulsion was performed using a KYKY-2800 Scanning Electronic Microscopy. The ζ potential of dispersed droplets in aqueous phases was measured by using Zetaplus Zeta potentiometer.

3 RESULTS AND DISCUSSION

3.1 Study of ζ potentials of emulsion droplets and small solid particles

The measured ζ potential of the solid particles in the real Dexing bioleaching solution was -50.5 mV. The self-made artificial solution was mixed with organic phases with different volume fraction of Lix984N(φ) to form O/W emulsions. This artificial solution was solid free so that there was no solid particles interface surrounding the droplets. The measured ζ potentials of those naked droplets are shown in Fig. 1. It is very clear that they are positive, and decrease with the increase of the volume fraction of Lix984N.

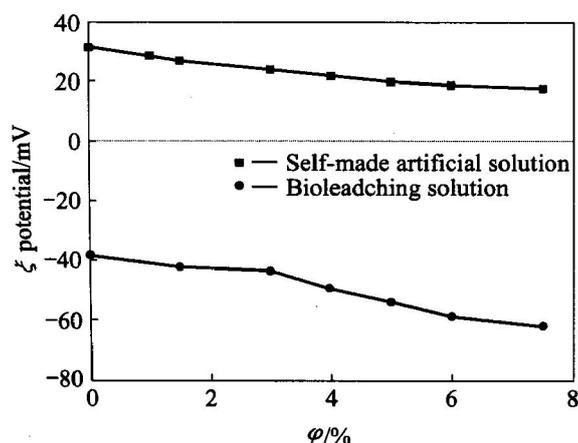


Fig. 1 ζ potentials of droplets with or without solid interfacial film

There are a lot of very small solid particles dispersed in the real Dexing bioleaching solution. During the extraction processes, this bioleaching solution forms emulsions with different volume fraction of Lix984N. The newly formed positive charged emulsion droplets quickly attract negative charged small solid particles to develop a solid particle film. These solid particle film surrounded emulsion droplets is

negative charged eventually. The ζ potentials then turn to be negative as shown in Fig. 1, which also decrease with the increase of Lix984N volume fraction.

The ζ potential study indicates that it is very easy to form a lot of solid particle surrounded droplets during extraction process due to the opposite charged small solid particle surface and droplet surface. Fig. 2 shows SEM micrograph of those solid surrounded droplets. The solid films formed at emulsion droplet interfaces are clearly shown in this image. It is also very evident that solid films are unevenly distributed at interface, and some individual solid particles as well as some solid particle flocculates randomly disperse between droplets.

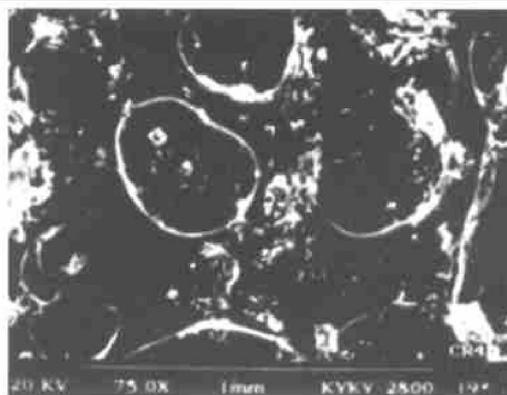


Fig. 2 SEM micrograph of solid films formed at emulsion droplet interface

3.2 Composition profiles of solid films at emulsion droplets

Acetone was used to isolate small solid particles from the emulsion. Those particles were then analyzed by using atomic absorption spectrometry for their chemical composition. The major elements in the solid particles are silicon, aluminum, iron, magnesium, sulfur, and calcium as shown in Table 1, in which silicon and aluminum are most richly abundant.

Table 1 Chemical compositions of solid particles separated from interfacial emulsion (mass fraction, %)

MgO	TFe	CaO	Al ₂ O ₃	SiO ₂	S
2.58	2.58	1.14	10.14	24.27	4.86

Fig. 3 shows the X-ray diffraction spectra of solid particles. The crystallographic component complexity of the particle is clearly shown. There are more than twenty components, and most of them are mica-type silicates. The major components are Na₃Fe₂Si₄O₁₀(OH)₂·4H₂O, KMgAlSi₄O₁₀(OH)₂ and other silicates. SiO₂, Fe(OH)₃, CaSO₄·2H₂O and Na₂Ca(SO₄)₂·4H₂O are also

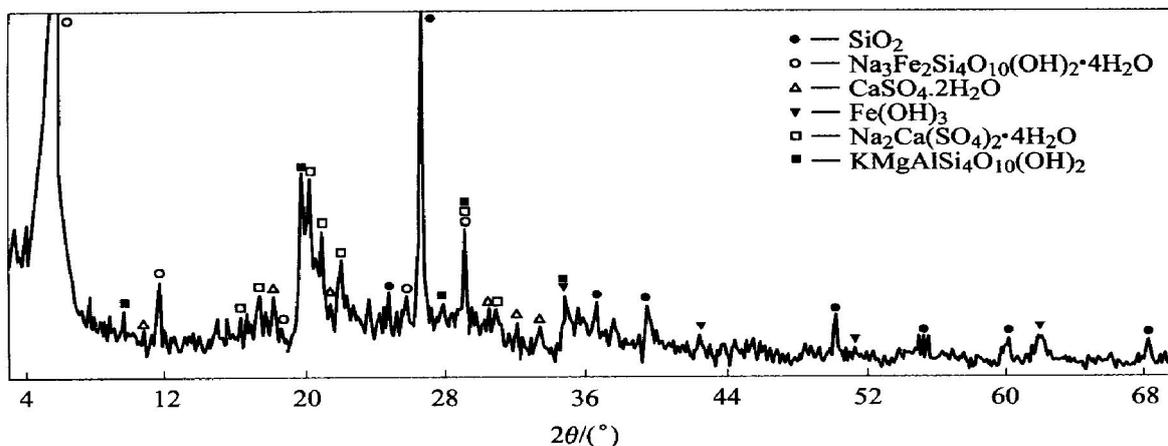


Fig. 3 XRD pattern of solid particles separated from interfacial emulsion

identified in the particles.

3.3 Application of EDLVO theory on emulsion stability study

DLVO is a theory to explain colloidal stability, which also involves in emulsion stability study. The theory points out that emulsion stability depends on the interaction between the double electric layer's electrostatic repulsive forces and Van der Waals attractive forces when droplets approach each other. The total energy (V_T) between droplets is:

$$V_T = V_W + V_E$$

where V_W is the Van der Waals' attractive potential between droplets; V_E is electrostatic repulsive potential.

Some recent studies indicate that classical DLVO theory can't give a satisfactory explanation for the mechanism of colloidal stability^[11, 12]. Therefore, an extended DLVO theory (ie EDLVO) has been developed. The EDLVO theory involves the hydration repulsive force between hydrophilic particles, hydrophobic force between hydrophobic particles and steric repulsive force between polymer compounds in consideration, too. The total energy between particles is^[11, 12]:

$$V_T = V_W + V_E + V_{HR} + V_{HA} + V_{SR} + V_{MA}$$

where V_{HR} is the hydration repulsive potential between hydrophilic particles; V_{HA} is the hydrophobic potential between hydrophobic particles; V_{SR} is the steric stabilization energy and V_{MA} is the magnetic attraction energy.

Applying the EDLVO theory to a real system, the interaction between particles should be considered based on the system characteristics.

In the case of interfacial emulsion in copper solvent extraction, if only Van der Waals force and electrostatic force between droplets are accounted, the total interaction potential between droplets is calculated as follows:

$$V_T = V_W + V_E \tag{1}$$

$$V_W = - \frac{AR_d}{12H} \tag{2}$$

$$V_E = 2\pi\epsilon_a R_d \zeta^2 \ln[1 + \exp(-\kappa H)] \tag{3}$$

where $\kappa = \left[\frac{4e^2 N_A I}{\epsilon_a kT} \right]^{\frac{1}{2}}$; κ^{-1} is Debye length, thickness of double electric layer, m or nm; A is Hamaker constant; e is electric charge, $1.062 \times 10^{-19} \text{C}$; H is distance between two droplets, nm; k is Boltzmann constant, $1.381 \times 10^{-23} \text{J} \cdot \text{K}^{-1}$; N_A is Avogadro constant, $6.022 \times 10^{23} \text{mol}^{-1}$; R_d is droplet radius, m; T is system temperature, K; ϵ_a is absolute dielectric constant in the dispersion medium; $\epsilon_a = \epsilon_0 \epsilon_r$, ϵ_0 is absolute dielectric constant in vacuum, ϵ_r is dielectric constant in dispersion medium, for water, $\epsilon_r = 78.5$.

Since the droplets are surrounded by solid particles, interactions between them is considered the same as that between the equal sized solid particles. Based on the result of X-ray diffraction analysis of the small solid particles, mica is selected to represent them for calculating the potential curve of real emulsion droplets. According to the fact that the solution is electric neutral and through the mass balance, the calculated SO_4^{2-} concentration in the real bioleaching solution is $0.2 \text{mol} \cdot \text{L}^{-1}$, and ionic strength I is $0.98 \text{mol} \cdot \text{L}^{-1}$. The average radius of the droplets determined through microscopic counting method is $5 \times 10^{-6} \text{m}$. When extraction is performed at $\text{pH} = 2.43$ with $\varphi(\text{Lix984N}) = 1.5\%$, ζ potential is -43.45mV . The Hamaker constant of mica is selected as $A_{11} = 10 \times 10^{-20} \text{J}^{[11]}$, and Hamaker constant of water $A_{33} = 3.7 \times 10^{-20} \text{J}^{[11]}$. $1kT = 4.12 \times 10^{-21} \text{J}$, $T = 298 \text{K}$.

Effective Hamaker constant A_{mica} is:

$$A_{\text{mica}} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2 = 1.54 \times 10^{-20} \text{J}$$

$$\kappa = \left[\frac{4e^2 N_A I}{\epsilon_a kT} \right]^{\frac{1}{2}} = 0.097 \text{nm}^{-1}$$

$$V_{W, \text{mica}} = - \frac{6.42 \times 10^{-18}}{H} \text{J}$$

$$= - \frac{1.58 \times 10^3}{H} \text{ kT} \quad (4)$$

$$V_E = 4.035 \times 10^{-17} \ln[1 + \exp(-0.097H)] \text{ J}$$

$$= 9.79 \times 10^3 \ln[1 + \exp(-0.097H)] \text{ kT} \quad (5)$$

Potential vs distance curve as shown in Fig. 4 is drawn from Eqns. (1), (4) and (5). It is apparent that there is an energy barrier of $5.09 \times 10^3 \text{ kT}$ to keep droplets apart because of the stabilization effect of the electrostatic repulsive potential.

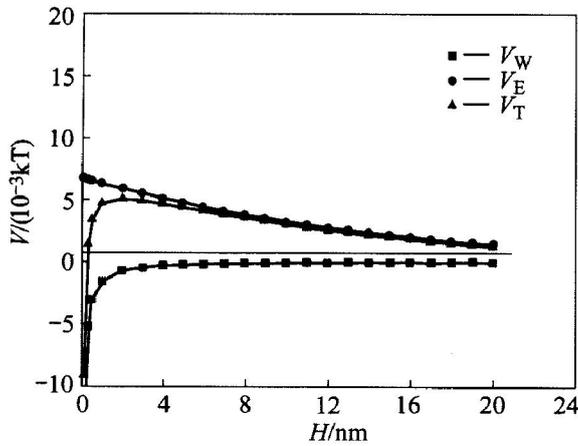


Fig. 4 DLVO potential energy curve between emulsion droplets stabilized by mica particles

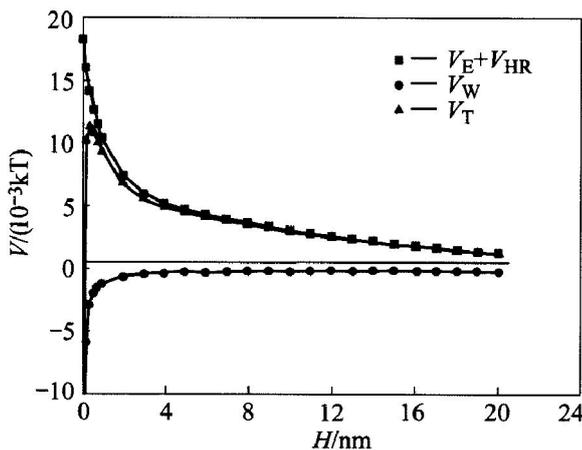


Fig. 5 EDLVO potential energy curve between emulsion droplets stabilized by mica particles

Hydration force is formed when positive charged ions are absorbed on the surface of hydrophilic particles, or when water molecules near by the polar zone of particle surface are polarized^[11-15]. The hydration force behaves repulsively when two droplets are getting closer.

During the process of copper solvent extraction, particles absorbed on the surface of emulsion droplets, such as mica, SiO₂, and etc, are highly hydratable hydrophilic particles. Once surrounded by these particles, emulsion droplets tend to be highly hydratable as well. Fig. 6 shows a liquid droplet surrounded by

small solid particles in an aged emulsion. The witness of hydrated water layer outside of a droplet indicates that the solid particle film has a strong hydration effect. Therefore, hydration repulsive forces between droplets should be considered for the emulsion stability study, and the extended DLVO theory should be applied. Then, the total interaction potential between droplets is calculated as follows:

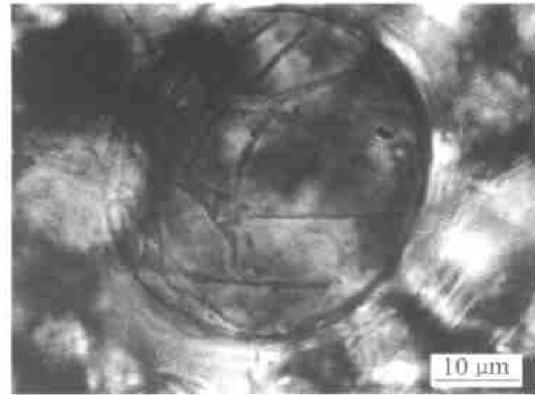


Fig. 6 Microscope photo of droplet stabilized by solid particles with hydrated water layer

$$V_T + V_W + V_E + V_{HR} \quad (6)$$

The hydration repulsive potential V_{HR} can be calculated empirically by^[11-15]

$$V_{HR} = \pi R_d h_0 V_{HR}^0 \exp\left\{\frac{-H}{h_0}\right\} \quad (7)$$

where V_{HR}^0 is an interaction potential constant relating to surface wettability; h_0 is attenuation length.

For mica, the parameters are the same as Ref. [13]:

$$V_{HR}^0 = 3 \times 10^{-3} \text{ J} \cdot \text{m}^{-2}, \quad h_0 = 1.0 \text{ nm}, \text{ then}$$

$$V_{HR} = 4.71 \times 10^{-17} \exp(-H) \text{ J}$$

$$= 1.14 \times 10^4 \exp(-H) \text{ kT} \quad (8)$$

The EDLVO potential vs distance curve drawn from Eqns. (4), (5), (6) and (8) is shown in Fig. 5. Comparing Fig. 5 with Fig. 4, it is evident that the contact energy barrier between emulsion droplets increases dramatically by about $7 \times 10^3 \text{ kT}$ when hydration repulsive force is considered. It is also very clear that hydration repulsive effect is much bigger than electrostatic repulsive effect, so that it contributes more to the stability of the emulsion. Therefore, for O/W emulsions, when the droplet stability is provided by small solid particles surrounding it, its stability relies not only on the strength of interface film and electrostatic repulsive force, but also on the hydration repulsive force of the interface film.

4 CONCLUSIONS

1) Small solid particles can stabilize emulsions. In copper solvent extraction system, the solid film surrounding the liquid droplet is consisted of mica sili-

cates, SiO_2 , $\text{Fe}(\text{OH})_3$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{Ca}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, etc.

2) Because the small solid particles suspended in the bioleaching solution are negatively charged, while naked emulsion droplets in the emulsion are positive charged, those small solid particles are very easily absorbed on the surface of emulsion droplets to form solid films. The ζ potential of the emulsion is therefore negative, decided by those solid films.

3) For the droplets surrounded by solid particles, interaction between them is considered the same as that between the equal sized solid particles.

4) For O/W emulsion such as that formed in the copper solvent extraction system, considering the strong hydration repulsion of hydrophilic particles on the interface of emulsion droplets, the extended DLVO theory can provide better explanation about its stability than classical DLVO theory. In some cases, hydration force is stronger than electrostatic force, so that has a larger influence on the emulsion stability. Therefore, hydration repulsive force of solid films should be a very important factor for small solid particle stabilized emulsions.

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