# Effect of Lix984N content on phase disengagement dynamics in copper-SX [①]

LIU Xiao-rong( 刘晓荣) [1], QIU Guan-zhou( 邱冠周) [2], HU Yue-hua( 胡岳华) [2],

YANG Jun-he( 杨俊和) [1], JIN Ming-lin( 金鸣林) [1]

( 1. Department of Materials, Shanghai Institute of Technology, Shanghai 200233, China;

2. School of Resource Processing and Bioengineering,

Central South University, Changsha 410083, China)

**Abstract:** Lix984N is intimately related to the dynamic characteristics of phase disengagement in copper solvent extraction because of its interfacial activity. With increasing Lix984N content, the phase disengagement time is prolonged and the mechanism dominating phase disengagement process transfers from sedimentation to coalescence. The rate of droplet coalescence is faster than that of droplet sedimentation in the dense dispersion band when the volume fraction of Lix984N is less than 3.0%. The former almost equaled to the latter at Lix984N content of 3.0% and finally becomes lower than the latter when the volume fraction of Lix984N is more than 3.0%. The relationship between the adhesion force of two equal droplets and physical properties of fluids is deduced, which explains that the change of physical properties of organic phase with Lix984N content can make droplet coalescence more difficult and phase disengagement slower.

**Key words:** copper solvent extraction; phase disengagement; hydroxyoxime; Lix984N; dynamics; interfacial activity; coalescence

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## 1 INTRODUCTION

Hydroxyoxime extractants show an amphiphilic character as a result of the presence of a long alkyl chain and characteristic hydrophilic fragments, such as oxime and phenolhydroxy that are usually chemically active and can react with metal ions. They exhibit surface activity and can be adsorbed at the interface between the organic and aqueous solutions resulting in the decrease of interfacial tension. Many researchers agreed that the reaction between copper and hydroxyoxime extractants occurred at the interface or in an aqueous film near the interface[1−4]. Due to this reason, the interfacial properties of hydroxyoxime extractants, including interfacial tension, interfacial population and molecule orientation at the interface are important parameters and may be considered as initial data for further discussion of the extraction rate and mechanism. A high interfacial activity of hydroxyoxime extractants, indicating a large interfacial excess is desirable. However this activity should not be too large because of the problems then caused by poor phase disengagement and formation of stable emulsions.

Up to now a lot of researches have been done on the effects of interfacial activity of hydroxyoxime extractants on extraction properties and mechanism[1−4]. However the effects on the aspects of phase disengagement are rarely reported in literature. Lix984N is one of hydroxyoxime extractants commonly used in solvent extraction now. Therefore, studying the effects of Lix984N on separated droplet coalescence during phase disengagement is helpful to understand its interfacial properties and its all-sided effects on copper-SX process.

## 2 EXPERIMENTAL

The copper extractant and diluent used in this study were Lix984N and kerosene, respectively. The aqueous phase containing 0. 25 g/ L $Cu^{2+}$, 1. 30 g/ L $Fe^{3+}$ at pH = 2. 5 and acid-strip solution containing 160 g/ L $H_2SO_4$, 30 g/ L $Cu^{2+}$ was prepared from $CuSO_4·5H_2O$, $Fe_2(SO_4)_3·xH_2O$ and $H_2SO_4$ ( all AR grade) according to the composition of corresponding solution of Dexing Copper Mine in Jiangxi Province, China. The scale of Lix984N content from 0. 5%− 5. 0% ( volume fraction) was considered correspond to 0. 25 g/ L $Cu^{2+}$ in the aqueous phase.

The experimental apparatus is illustrated in Fig.

**Correspondence:** LIU Xiao-rong, Associate professor, PhD; Tel: + 86-21-64942811; E-mail: xr− Liu117@ sohu. com
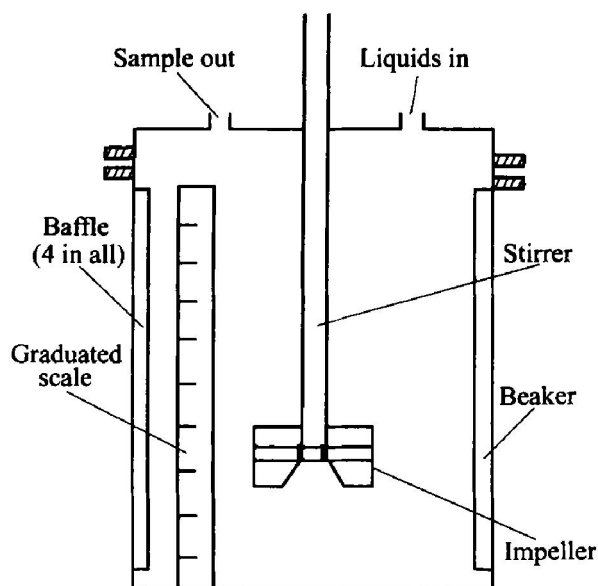
**Fig. 1** Phase disengagement apparatus

1, which was self-made according to Zeneca's standard methods of test. The vessel consisted of a cylindrical, flat-bottomed beaker with internal diameter of 10 cm and depth of 14 cm. The impeller diameter was 5 cm, with six blades regularly spaced beneath a circular disc, and two spoiler blades fixed to the upper surface.

Prior to any extraction experiment, the vessel should be washed down with kerosene, water, methanol and acetone in turn. Then transfer 400 mL organic phase to the vessel, start the stirrer ( pre-set at about 600 r/min) and add 400 mL aqueous phase. Maintain stirring for 5 min then stop the stirrer and simultaneously start a stop-clock. Record the time taken to pass convenient scale markings for the lower interface to break away from the bottom of the vessel and arrive at the final clear interface. Meanwhile record the time taken to pass convenient scale markings for the upper interface moving from the top of fluids to the final clear interface in the same way. When the last droplet disappeared at the interface it was defined as the final clear interface. Define the lower interface, that was the interface between the clear aqueous phase and the dispersion band as coalescence front, also the interface of the clear organic phase-dispersion band ( the top interface) as sedimentation front. Plot a graph of both depths of coalescence front and sedimentation front against time and a settling curve could be formed.

In all tests keep organic phase continuous by stirring it at first and O/A= 1: 1. The experimental temperature was at ( 25 ±1) ℃.

The density, viscosity of organic phase and interfacial tension were measured with Mettler Toledo Ag204 densimeter, NDJ-85 viscosimeter and JYW-

200A auto-interfacial tensiometer respectively. The Cu concentration of organic phase was calculated according to that of aqueous phase measured by AAS.

## 3　RESULTS AND DISCUSSION

### 3. 1　Effects of Lix984N on physicochemical properties of organic phase

Fig. 2 shows the change of Cu concentration in loaded organic phase with the increase of Lix984N content from 0. 5% to 5. 0%. It can be seen that the Cu concentration is low in loaded organic phase, and when Lix984N content is larger than 1. 5% it reaches a constant loading. The interfacial tension between the aqueous phase and the organic phase decreases and the density and viscosity of organic phase increase correspondingly with the increase of Lix984N concent, as shown in Fig. 3 and Fig. 4. It is believed that lower interfacial tension, larger viscosity of organic phase and less density difference between two liquids are detrimental to phase disengagement in copper solvent extraction[5-7].
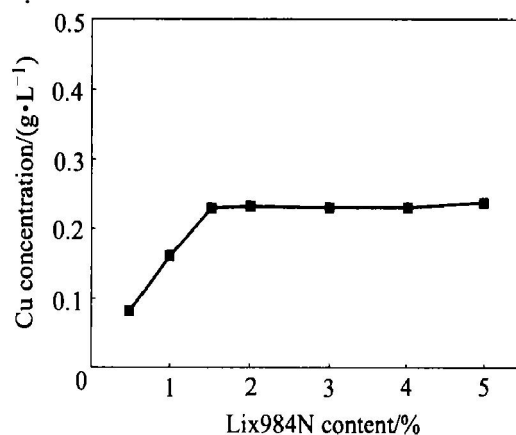


**Fig. 2**　Change of Cu concentration in loaded
organic phase with Lix984N content
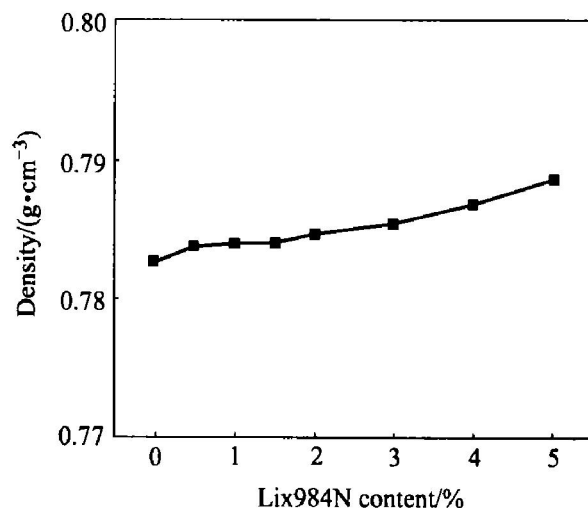( 0. 25 g/ L Cu in aqueous feed, O/ A= 1: 1, 298 K)



**Fig. 3**　Effect of Lix984N content on
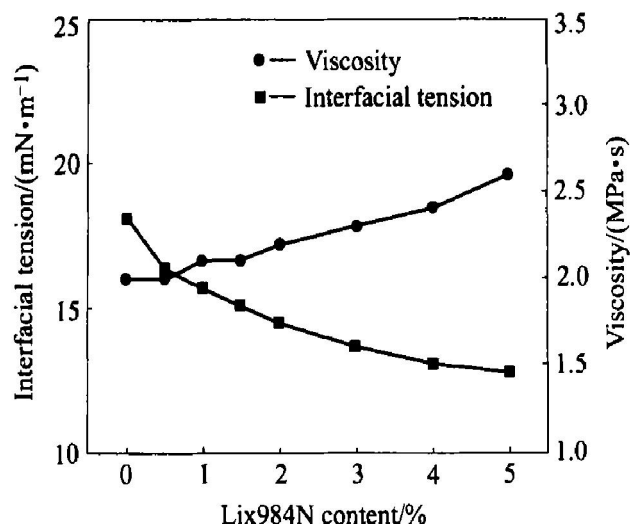organic phase density
( 0. 25 g/ L Cu in aqueous feed, 298 K)

**Fig. 4**  Effect of Lix984N content on
organic phase viscosity and interfacial tension
( 0. 25 g/ L Cu in aqueous feed,  O/ A= 1: 1,  298 K)



**Fig. 5**  Illustration of dense dispersion band
with heavily dispersed liquid

### 3. 2  Effects of Lix984N on droplet coalescence in phase disengagement process

The behavior of droplet coalescence during phase disengagement process is observed. A dense dispersion band of equal thickness appears immediately after stopping intensive mixing in batch extraction experiments carried out in the apparatus shown in Fig. 1. A multizone structure in the course of phase disengagement is observed and illustrated in Fig. 5 following the method of Ref. [ 9] . The droplets enter into the dispersion band through flocculation zone. No coalescence takes place there, but separated droplets arrang themselves in the most compact way by a sedimentation motion and trap the continuous phase in the interstices. Passing into the packing zone, the droplets grow by drop-drop coalescence and adapt their shape to their immediate environment. In the coalescing zone droplets are densely pressed together and deform into the shape of dodecahedron. These deformed drops flow into the clear

buck phase by drop-interface coalescence[8, 9].

Fig. 6 is a schematic illustration of the settling curve at a Lix984N content of 1. 5%. It is clear that the coalescence front arrives at the final clear interface earlier than the sedimentation front. This means that the sedimentation of droplets predominate the phase disengagement rate at  φ( Lix984N) = 1. 5%. Contrarily, a lower rate of drop-interface coalescence than that of sedimentation refers to a coalescence controlled mechanism. The time for the most slowly moving front to arrive at the final clear interface is defined as phase disengagement time t, as shown in Fig. 6. The settling curve can be used to describe the dynamic characteristics of phase disengagement.

Settling curves with different dynamic characteristics of phase disengagement in the extraction experiments at different Lix984N contents are brought to
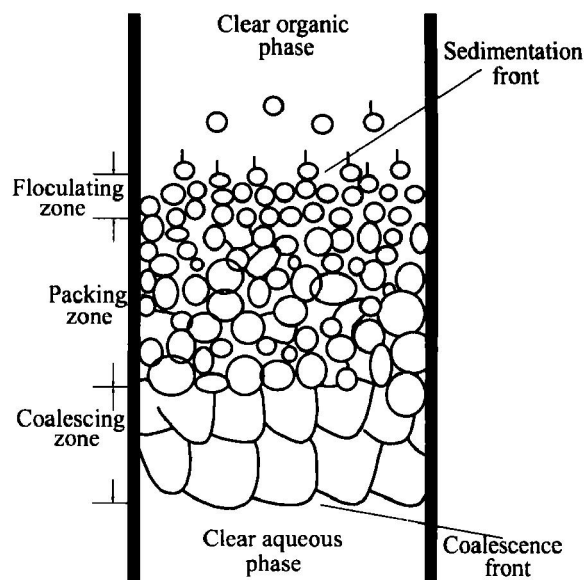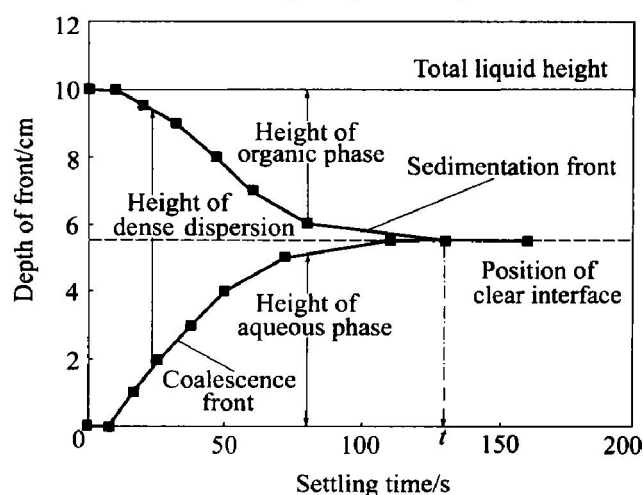


**Fig. 6**  Extractoin settling curve
( 0. 25 g/ L Cu in aqueous feed,
φ( Lix984N) = 1. 5%,  O/ A= 1: 1,  298 K)

gether in Fig. 7. It is easy to find firstly that the phase disengagement time extends with the increase of Lix984N content, so that more Lix984N in the organic phase results in a longer phase disengagement time. Table 1 lists the time taken for the coalescence front and sedimentation front to arrive at the final clear interface ( denoted

**Table 1**  Time indicating phase disengagement
characteristics at different Lix984N contents

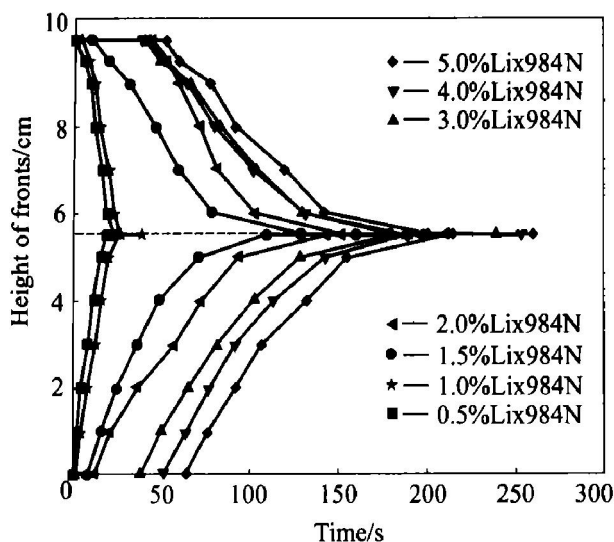| φ( Lix984N) / % | $t_c$/ s | $t_s$/ s | $t$/ s |
|---|---|---|---|
| 0. 5 | 20 | 23 | 23 |
| 1. 0 | 26 | 28 | 28 |
| 1. 5 | 110 | 130 | 130 |
| 2. 0 | 144 | 152 | 152 |
| 3. 0 | 181 | 180 | 181 |
| 4. 0 | 198 | 189 | 198 |
| 5. 0 | 214 | 200 | 214 |

**Fig. 7** Extractoin settling curve at
different Lix984N contents
( 0. 25 g/ LCu in aqueous feed, O/ A= 1: 1, 298 K)

as $t_c$ and $t_s$) and phase disengagement time ( denoted as $t$) at different Lix984N contents.

When the volume fraction of Lix984N is less than 3. 0%, the rate of droplet coalescence is faster than that of sedimentation. When the volume fraction of Lix984N is 3. 0%, the rate of coalescence is almost equal to that of sedimentation. And when the volume fraction of Lix984N is more than 3. 0%, the rate of coalescence becomes lower than that of sedimentation. The mechanism dominating phase disengagement process transfers from sedimentation to coalescence and the droplet coalescence becomes more and more difficult with the increase of Lix984N content.

The phase disengagement process is mainly depended on the sedimentation behaviors and coalescence behaviors of droplets which is influenced by such factors as diameter of droplets, density difference of two immiscible liquids, viscosity of continuous phase, interfacial tension and strength of interfacial film. Lix984N, being surface-active, has a crucial influence on the interfacial tension. In the low Lix984N content range ( less then 3. 0%), the factors dominating phase disengagement are density difference of two immiscible liquids and viscosity of continuous phase. With the increase of Lix984N content more Lix984N molecules are adsorbed at the droplet interface and the interfacial films of droplets are strengthened. As a result, interfacial properties of droplets play more important roles and the phase disengagement rate is controlled by droplet coalescence. At the Lix984N content of 3. 0% the interfacial properties and physical properties of the fluids play almost the same roles and the sedimentation mechanism and coalescence mechanism control phase disengagement process simultaneously.

**3. 3　Droplet hydrodynamic behavior under extrac-**

**tion condition**

According to turbulence theory for locally isotropic flow[10, 11], if velocity fluctuations in the external fluid cause the normal pressure difference across the droplet to exceed the interfacial tension pressure, the droplet will break up. The critical diameter for the break-up of droplets is

$$d_{max}= c_1 \rho_c^{\frac{3}{5}} \gamma^{\frac{3}{5}} n^{-\frac{6}{5}} D^{-\frac{4}{5}} \qquad (1)$$

The critical diameter for droplet coalescence which takes place only if the energy of adhesion is greater than the kinetic energy of the droplets when they are colliding is

$$d_{min}= c_2 \rho_c^{-\frac{3}{8}}[ A ( h_0)]^{\frac{3}{8}} n^{-\frac{3}{4}} D^{-\frac{1}{2}} \qquad (2)$$

There is a critical impeller speed[12], at which $d_{max}$ is almost equal to $d_{min}$:

$$n_c= c_4\left[\frac{\Delta \rho}{\rho_c}\right]^{0.26} D^{-0.67} v^{0.11} \qquad (3)$$

Combining $n_c$, $d_{max}$ with $d_{min}$, the force of adhesion between two equal spheres separated by a distance $h_0$ can be deduced as:

$$A ( h_0)= [ c \cdot \gamma \rho_c^{0.108} \Delta \rho^{-0.117} v^{-0.05}]^{\frac{8}{3}} \qquad (4)$$

where　$c$ is dimensionless constants, $\gamma$ is the interfacial tension between two immiscible liquids, $v$ is the kinetic viscosity, $\rho_c$ and $\Delta \rho$ is the density of continuous-phase and the density difference between two immiscible liquids respectively.

The equation indicates that $A ( h_0)$ is uniquely determined by the physical properties of the fluids of which $\gamma$ plays an important role in this determination. Dropping of $\gamma$ results in the decline of $A ( h_0)$ obviously. Meanwhile, the changes of $\rho_c$ and viscosity of organic phase as shown in Fig. 3 and 4 hasten the declining of $A ( h_0)$ in a way. Consequently, with the increase of Lix984N content the droplet coalescence becomes more and more difficult and the rate of phase disengagement becomes lower and lower.

**4　CONCLUSIONS**

1) A setting curve, which is drawn according to the relationship of height of coalescence front and sedimentation front in the dense dispersion band and time, can be used to describe the dynamic characteristics of phase disengagement in copper extraction experiments.

2) With the increase of Lix984N content, the phase disengagement time is prolonged. The mechanism dominating phase disengagement process transfers from sedimentation to coalescence and the droplet coalescence becomes more and more difficult.

3) The adhesion force of two equal droplets separated by a distance $h_0$ can be deduced from turbulence theory for locally isotropic flow and described as $A ( h_0)= [ c \cdot \gamma^{0.6} \rho_c^{0.108} \Delta \rho^{-0.117} v^{-0.05}]^{\frac{8}{3}}$. This e-

quation explains that the change of physical properties of organic phase with Lix984N content can make the coalescence of droplets more difficult and the phase disengagement slower.

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