DIFFUSIONAL RESISTANCE IN EXTRACTION RATE OF COPPER WITH HYDROXYOXIME EXTRACTANT

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The extraction of copper from sulphate media with a hydroxyoxime chelating extractant was carried out using a stirred transfer cell. Simple physical extraction studies of iodine or acetic acid were also carried out. From a comparison of the results, the extraction mechanism for copper was found to be expressed simply by a series of diffusional processes into the interface for the reactive species and the succeeding interfacial reaction, at least at the initial stages of extraction.

Introduction

In the previous work the reaction scheme and reaction rate of copper extraction from sulphate media with a hydroxyoxime extractant were studied, using a single-drop technique[6]. A simple reaction scheme involving the species adsorbed at the interface was proposed. Assuming the extreme conditions of negligible contribution of the diffusional resistance of the reactive species, the observed rates were found to support the reaction scheme proposed. The resutls obtained in the range of higher extraction rates, however, demonstrated a contribution of diffusional resistance appearing in the observed rates.

In the present work the identical process of copper extraction was carried out using a stirred transfer cell. In addition, the simple physical extraction of iodine or acetic acid between the two phases was carried out to obtain a knowledge of the mass transfer characteristics of the cell. The results were applied to the analysis of the diffusional resistance in the present copper extraction system.

1. Experiment

The stirred transfer cell used for both mass transfer standardization and copper extraction is shown in **Fig. 1**. All parts of the unit in contact with liquid were made of glass, excepting the PTFE gasket used for the stirrer shaft. The two-paddle stirrers were driven in opposite directions in the range 30–170 rpm. The stator plate had an open space containing the aqueous-organic interface, the area of which was either 9.8 cm² or 19.6 cm², according to the stator

plate employed. The volume of aqueous and organic phases was kept constant at 265 cm³ in all runs. A glass electrode and a reference electrode were installed to monitor the aqueous-phase pH value. The temperature was maintained at 25±0.1°C by means of a thermostat bath connected to the outer part of the cell. In all runs the aqueous phase was first added to the cell, and then the organic phase was added gently in order not to disturb the interface. After starting the stirrer, samples were taken at defined time intervals from the appropriate phase via a syringe or through the sampling cock. The amount of sample was 2 cm³ in all runs.

For measurement of the organic-phase film mass transfer coefficient, acetic acid was transferred from n-heptane to aqueous phase. The initial concentration of the acid was 0.1 mol/dm³ and the organic samples were titrated using sodium hydroxide. For
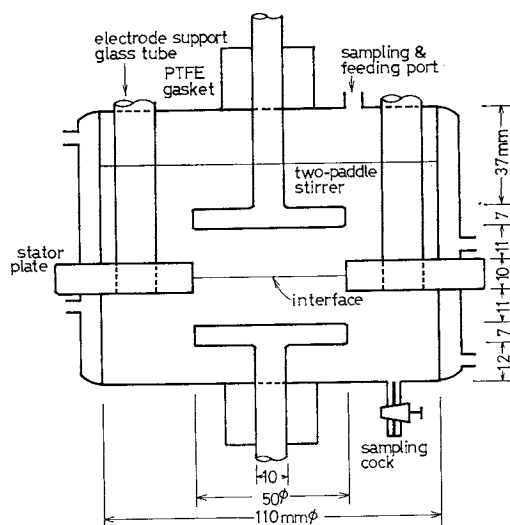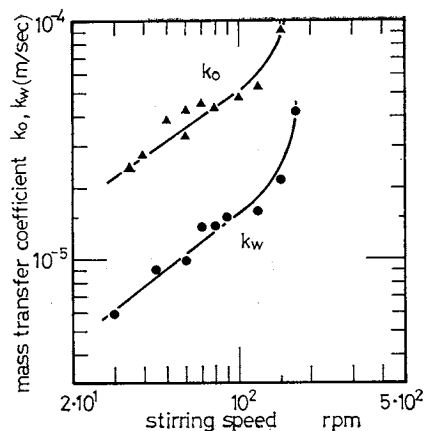

Fig. 1 A sketch of apparatus

Fig. 2 Effect of stirring speeds on mass-transfer coefficient, n-heptane–water system

the aqueous phase, iodine was transferred from aqueous to n-heptane phase. The initial concentration of iodine was 7.1×10^{-4} mol/dm³ and the aqueous samples were titrated using sodium thiosulphate. The acetic acid and iodine were analytically pure reagent-grade materials, and n-heptane and water were purified by simple distillation. Both water and n-heptane were mutually saturated beforehand.

The extraction of copper was carried out by the same procedure as that used in the mass transfer studies. The copper concentration in the aqueous feed was in the range 10^{-2}–2×10^{-1} mol/dm³. The oxime concentration was in the range 1.7×10^{-2}–1.7×10^{-1} mol/dm³ in both diluent systems, n-heptane and toluene. The copper (II) ion and monomeric oxime concentrations were calculated as described in the previous publications[5,6].

The hydrogen ion concentration was in the range 3.2×10^{-3}–10^{-1} mol/dm³ (pH=1.0–2.5). This was restricted to a rather small range compared to that for the previous single-drop study. In the range of pH greater than 3 the variation of pH value was significant during a run, especially at the start. Aqueous and organic solutions were made and analysed as described in the previous publications[5,6].

2. Result

2.1 Mass transfer characteristics of the cell

When a solute is transferred from organic to aqueous phase, the transfer rate is defined by

$$-(V_o/A)(dC_o/dt) = K_o(C_o - C_w/m) = k_o(C_o - C_{o\,int})$$
$$= k_w(C_{w\,int} - C_w) \tag{1}$$

where

$$m = C_{w,e}/C_{o,e} \tag{2}$$

and

$$1/K_o = 1/m \cdot k_w + 1/k_o \tag{3}$$

In the case of a high value of m, the terms C_w/m and $1/m \cdot k_w$ are negligible compared to C_o and $1/k_o$.

Hence, by integrating, a simplified relationship is obtained:

$$k_o = (V_o/A \cdot t) \ln (C_o^0/C_o) \tag{4}$$

In this case the solute was acetic acid and the value of m was 400–800[2]. Similarly, when a solute which is strongly oriented to the organic phase is transferred from aqueous to organic phase, the aqueous-phase film mass transfer coefficient is expressed as

$$k_w = (V_w/A \cdot t) \ln (C_w^0/C_w) \tag{5}$$

In this case the solute was iodine and the value of m was less than 0.025[11].

Linear relationships were found between $-\ln (C_o/C_o^0)$ and t or $-\ln (C_w/C_w^0)$ and t, as predicted by Eq. (4) or (5), for both cases of extraction, allowing the values of k_o and k_w to be calculated from the slope of the resultant lines.

The film coefficients, k_w and k_o, are plotted against stirring speeds in **Fig. 2**. The values of k_w and k_o are seen to increase steadily with increasing stirring speed in the range 30–170 rpm. An appreciable wave formation appeared on the interface at stirrer speeds greater than 150 rpm and the coefficient increased sharply.

McManamey et al.[7] measured the mass transfer characteristics of the cell in which a spacer plate of disc type was fixed at the central part of the liquid-liquid interface. An empirical correlation was obtained from their experiments and from several literature data obtained using similar cells. It is expressed as

$$(Sh_1) = C'(Sc_1)^{0.5}(We')[Re_1 + (\rho_1/\rho_2)(\mu_2/\mu_1)Re_2]^{0.5}$$
$$\times [1 + (\rho_1/\rho_2)(\mu_2/\mu_1)^2(Re_2/Re_1)^2]^{0.5} \tag{6}$$

where the subscripts 1 and 2 denote the phase under consideration and the adjacent phase, respectively. We' is the modified Weber number. The value of constant C' varies from 0.023 to 0.13 depending on the dimensions of a cell and on investigators.

The present value for the n-heptane diluent system are plotted according to the correlation in **Fig. 3**. The values of physical properties used in the calculation are as follows[9]: diffusion coefficient for acetic acid in n-heptane, $D_o = 3.18 \times 10^{-5}$ and iodine in water, $D_w = 1.25 \times 10^{-5}$ cm²/sec, viscosity $\mu_o = 3.88 \times 10^{-3}$ and $\mu_w = 10^{-2}$ g/cm·sec, density $\rho_o = 0.684$ and $\rho_w = 1.0$ g/cm³. The order of magnitude of the values is the same as that predicted from the correlation. The slope in Fig. 3, however, is less than 1 and the organic-phase Sherwood numbers are nearly double compared to the aqueous-phase numbers. These discrepancies may be due to the difference in the shape and dimensions of the apparatus. Consequently, the values of Sherwood numbers of the aqueous and organic phase obtained in the present cell were used to estimate the mass transfer coefficients for the reac-

tive species in the copper extraction system.

2.2 Copper extraction rate

The amount of copper transferred per unit area, $V_o \cdot \overline{C_{CuR_2}}/A$, was plotted against contact time t, and a linear relationship was found in all runs in the rage of organic-phase copper concentration less than 3% of the equilibrium value. The slope of the line, therefore, gives the extraction rate, $N=(V_o/A) \cdot (d\overline{C_{CuR_2}}/dt)$. To confirm this, two runs were carried out, for the n-heptane diluent system varying only the interfacial area, by the use of two stator plates with differing opening area, 9.8 cm² and 19.6 cm², respectively. The concentrations of the species were $[H^+]=3.63$, $[Cu^{2+}]=9.18$ and $[\overline{RH}]=17.0 \text{ mol/m}^3$. The same reaction rates, $(7.1\pm0.1)\times10^{-5} \text{ mol/m}^2\cdot\text{sec}$, were obtained, as expected. An interfacial area of 19.6 cm² was chosen for all subsequent runs. A relatively low stirring speed of 60 rpm was also chosen for all subsequent runs.

In the previous single-drop study[6], the reaction rate for copper extraction was found to obey the following equation.

$$N=k[Cu^{2+}] \cdot [\overline{RH}]/[H^+] \qquad (7)$$

The present rates are plotted according to the above equation in **Fig. 4**, together with the data obtained in the single-drop study. For rates less than 2×10^{-5} mol/m²·sec, the present data are seen to cluster on respective straight lines with a slope of 1 for each diluent system. The rates in a stirred transfer cell are 10 to 15% lower than those in the single-drop study. This difference may not be significant, considering the large difference of conditions in measurement of the rates employed in the two studies, such as the contact time and the ratio of interfacial area to organic bulk volume.

2.3 Contribution by diffusional resistance

In the range of higher extraction rates, the rate data are seen to deviate from the straight line, as shown in Fig. 4. The deviation was considered to be caused by the effect of diffusional resistance on the apparent extraction rates.

An attempt was made to estimate the interfacial concentrations of reactive species and to correlate the rate data with the interfacial concentrations. The situation of the present aqueous and organic phases is much complicated. The aqueous phase contains counter-diffusing electrolytes, especially hydrogen ions with much greater mobility than the other species. Copper sulphate is not completely dissociated in the concentration range of interest and only the copper (II) ion is a reactive species. The oxime is partially aggregated and only the monomeric oxime reacts at the interface.
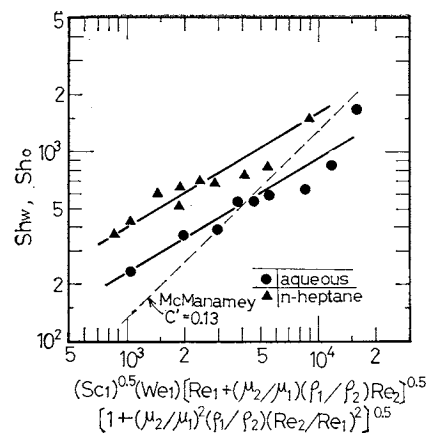
The overall extraction is expressed as

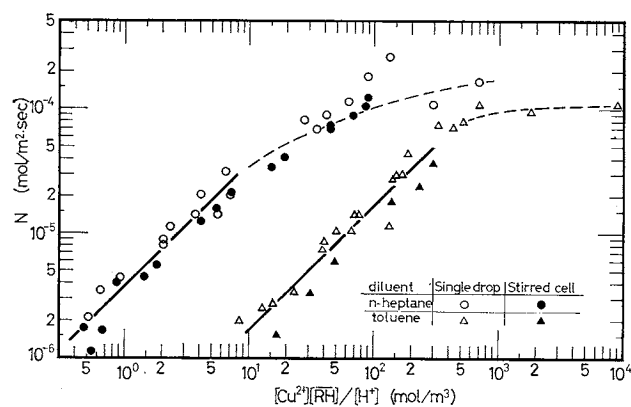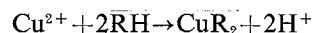Fig. 3 A comparison of present mass-transfer characteristics with McManamey et al.'s correlation[7]

Fig. 4 Correlation of copper extraction rate based on bulk-phase concentrations of species

$$Cu^{2+}+2\overline{RH}\rightarrow\overline{CuR_2}+2H^+$$

Under steady-state conditions, the rate of mass transfer for the species and the extraction rate are equal; thus

$$N=k_{Cu}([Cu_t]_{bulk}-[Cu_t]_{int}) \qquad (8)$$

$$N=(1/2)k_{H^+}([H^+]_{int}-[H^+]_{bulk}) \qquad (9)$$

$$N=(1/2)\overline{k_{oxm}}([\overline{C_{oxm}}]_{bulk}-[\overline{C_{oxm}}]_{int}) \qquad (10)$$

where $[Cu_t]$ is the total concentration of copper (copper sulphate and copper (II) ion), and $[\overline{C_{oxm}}]$ is the total concentration of oxime (monomer and dimer).

As an approximation, the present results for the mass transfer characteristic study were applied to the species involved in the copper extraction system. That is, the mass transfer coefficients were estimated according to the empirical correlation for Sherwood number obtained for the present stirred cell and shown in Fig. 3. The following values for the diffusion coefficients were chosen from published work. i) **Copper sulphate** The value of $D_{Cu,t}=0.85\times10^{-5} \text{ cm}^2/\text{sec}$ was adopted from the work of Hughes et al.[3]. The value of $k_{Cu,t}$ was estimated as 8.2×10^{-6} m/sec. The interfacial concentration of total
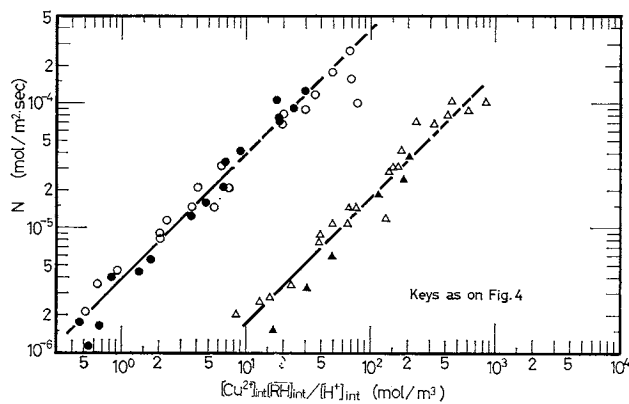
Fig. 5 Correlation of copper extraction rate
based on interfacial concentrations of species

amount of copper (Cu^{2+} and $CuSO_4$) was calculated according to Eq. (8), and then the concentration of copper (II) ion, $[Cu^{2+}]_{int}$, was calculated using the dissociation constants of copper sulphate and sulfuric acid[5,6] together with the interfacial concentration of hydrogen ion, $[H^+]_{int}$.

ii) Hydrogen ion The measured value of D_{H+} was in the range 4.3×10^{-5}–1.3×10^{-4} cm²/sec, depending on the concentration of other ions[10]. An average value of 8.0×10^{-5} cm²/sec was adopted. Hummelstedt[4] adopted the value of 6.0×10^{-5} cm²/sec in the analysis of the diffusional resistance for a system similar to the present system. The value of k_{H+} was estimated as 4.2×10^{-5} m/sec. The interfacial concentration $[H^+]_{int}$ was calculated according to Eq. (9).

iii) Oxime Hughes et al.[3] estimated the diffusion coefficient of the monomeric oxime using the correlation of Wilke and Chang, as 1.02×10^{-5} cm²/sec in n-heptane and 0.79×10^{-5} cm²/sec in toluene at 28°C. The values were assumed to be applicable to the system of a mixture of monomeric and dimeric oximes. The values of $\overline{k_{oxm}}$ were estimated as 1.6×10^{-5} m/sec for n-heptane and 1.5×10^{-5} m/sec for toluene. The total concentration at the interface was calculated according to Eq. (10), allowing the monomeric oxime concentration to be calculated using the dimerization constant $K_m = 120$ for n-heptane and $K_m = 2$ dm³/mol for toluene[5].

The extraction rates are plotted against the resultant interfacial concentrations in **Fig. 5**. Only the values on the abscissa of the data in Fig. 4 are revised. The resultant data are found to cluster on an extension to the line obtained as an expression of the rate under chemical reaction control. For the rate data which are clustered on the straight lines in Fig. 4, the difference between the values based on the bulk and the interfacial concentrations is usually too small to be distinguished, as shown in Figs. 4 and 5. For the toluene diluent system, the deviation was small and

accordingly the difference between the bulk and the interfacial concentration is also small.

3. Discussion

In the previous single-drop study[6] apparent rates greater than 5–7×10^{-5} mol/m²·sec deviated greatly from the straight line, as shown in Fig. 4. This marked deviation was expected from the results shown in Fig. 5 in the previous publication[6], which indicated that the hydrogen ion concentration had little effect on the extraction rate in the range of higher pH values of the bulk phase. The identical process of correlating rates with interfacial concentrations was carried out for the rates obtained in the single-drop study.

Unfortunately, the mass transfer coefficients for the species were not directly measured in the present work. The most probable values to the situation of the drops concerned were therefore assumed. For the aqueous phase, Rowe et al.'s correlation[8] gave $k_{H+} = 2.3 \times 10^{-4}$ and $k_{Cu,t} = 5.2 \times 10^{-5}$ m/sec for the n-heptane drop system, and $k_{H+} = 1.8 \times 10^{-4}$ and $k_{Cu,t} = 3.9 \times 10^{-5}$ m/sec for the toluene drop system*. For the organic drops, Calderbank et al.'s empirical expression for circulating drops[1] gave $\overline{k_{oxm}} = 1.9 \times 10^{-5}$ m/sec for n-heptane drops and $\overline{k_{oxm}} = 1.3 \times 10^{-5}$ m/sec for toluene drops.

The interfacial concentrations of the species were calculated according to the same procedure as that in the preceding section. The extraction rates are plotted against the resultant interfacial concentrations in Fig. 5. These are found to cluster on the straight line extensions. No significant difference is seen between the rates in the stirred cell and the single-drop study.

Consequently, the reaction rate for copper extraction is expressed by Eq. (7), and the rate constant is 3.8×10^{-6} m/hr for the n-heptane diluent system and 1.8×10^{-7} m/hr for the toluene diluent system.

Conclusion

The extraction of copper from sulphate media with a hydroxyoxime extractant was carried out, using a stirred transfer cell. Under conditions of a negligible contribution by diffusional resistance, there appears to be no significant difference between the rates in the present stirred cell and in the previous single-drop study.

The mass transfer characteristics of the cell were determined, using iodine or acetic acid as solutes. Mass transfer coefficients for the reactive species in the copper extraction system were then estimated. The interfacial concentrations of the various reactive

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* For n-heptane drops, drop size $d_p = 0.2$ cm, terminal velocity $u_t = 11$ cm/sec, $L = 130$ cm (average) For toluene drops, $d_p = 0.25$ cm, $u_t = 7.63$ cm/sec.

species during the course of extraction were estimated from the rate data, assuming a diffusional resistance in the apparent rate values. Based on the use of the interfacial concentration terms, all the data were found to be correlated by a single rate equation. The present extraction mechanism is expressed simply by a series of diffusional processes for the reactive species to the interface followed by interfacial reaction, at least at the initial stages of the extraction.

Acknowledgment

Nomenclature

A	= interfacial area	[m²]
C	= concentration	[mol/m³]
D	= diffusion coefficient	[m²/sec]
k	= reaction rate constant	[m/sec]
k_m	= mass transfer coefficient of species m	[m/sec]
m	= distribution coefficient	[—]
N	= flux	[mol/m²·sec]
Re	= Reynolds number	[—]
Sc	= Schmidt number	[—]
Sh	= Sherwood number	[—]
t	= time	[sec]
V	= volume of liquid	[m³]
$[Cu^{2+}]$	= copper (II) ion concentration	[mol/m³]
$[H^+]$	= hydrogen ion concentration	[mol/m³]
$[RH]$	= monomeric oxime concentration	[mol/m³]

⟨Subscripts⟩

bulk	= the species in the aqueous or organic phase
int	= the species adjacent to the aqueous-organic interface, on the aqueous or organic side
o	= organic phase
w	= aqueous phase
oxm	= hydroxyoxime extractant
Cu,t	= total copper

⟨Superscripts⟩

0	= initial concentration
—	= the organic species or organic phase concentration

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