# Liqiu Yang<sup>1,2</sup> Yuchao Zhao<sup>1</sup> Yuanhai Su<sup>1</sup> Guangwen Chen<sup>1</sup>

<sup>1</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

<sup>2</sup> Graduate University, Chinese Academy of Sciences, Beijing, China.

# **Research Article**

# An Experimental Study of Copper Extraction Characteristics in a T-Junction Microchannel

The extraction performance in a T-junction microchannel was investigated experimentally.  $CuSO_4/H_2SO_4/AD-100/260^{\#}$  solvent oil was chosen as the working system. The velocities of the aqueous and oil phases were varied from 0.0016 to 0.45 m s<sup>-1</sup>, with Re<sub>M</sub> varying between 9 and 200. The experimental results show that the extraction process of copper in the microchannel is controlled by both reaction intrinsic kinetics and mass transfer, depending on the characteristics of the reaction and the fluid hydrodynamics. The maximum extraction efficiency is about 0.96, and the apparent overall volumetric mass transfer coefficient ( $k_{app}a$ ) is in the range of  $0.02-0.2 \text{ s}^{-1}$ . In addition, the effects of the Cu<sup>2+</sup> concentration and the pH in the aqueous phase, the volumetric fraction of AD-100 in the oil phase, and the temperature on the extraction performance were investigated in detail.

**Keywords:** Extraction, Mass transfer, Microchannel, Microreactor, Two-phase system *Received:* August 22, 2012; *revised:* January 03, 2012; *accepted:* January 10, 2013 **DOI:** 10.1002/ceat.201200464

## 1 Introduction

Liquid-liquid extraction, which is also known as solvent extraction, is widely utilized in the process industries such as the petroleum, food, hydrometallurgy and chemical industries, and others. The extraction of copper is a representative process in the hydrometallurgy industry. The introduction of the LIX series extractants by General Mills Company was an exciting innovation for the copper mining industry, creating a great interest in the process of liquid-liquid extraction accompanying chemical reactions [1]. The extraction has been carried out in different contactors, such as the mixer-settler contactors, column contactors, etc. The mixer-settler [2] is free of backmixing between different stages and can be operated under nearly equilibrium conditions between the two phases. However, its recycling solvent and the energy consumption for mechanical stirring are very large. Besides, it requires large space for allocation. Extraction columns, such as sieve plate, pulsed, spray and rotating-disc columns, etc., have also been widely employed [3, 4]. Although these contactors benefit from a simple structure, their utilization is limited due to extreme backmixing, which greatly reduces the extraction efficiency. Moreover, some other contactors are also exploited for extraction

**Correspondence:** Dr. G. Chen (gwchen@dicp.ac.cn), Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. processes. Doungdeethaveeratana and Sohn [5] studied the extraction kinetics in a cylindrical vessel, and a high dispersion performance of the two immiscible liquid-liquid phases could be obtained by gas agitation so that better extraction efficiency was generated. Merchuk et al. [6] experimentally investigated copper extraction with LIX-64N by means of motionless mixing, and an approximate 92% of equilibrium was achieved in the Koch static mixer. Nevertheless, some disadvantages still exist in these contactors, such as rigorous operating conditions, long extraction times, small overall volumetric mass transfer coefficients, etc.

Microchemical engineering technology, as one of the most important process intensification modes, has been in the focus of industry and academia [7-12]. The extremely large surfaceto-volume ratio and the short transport path in microchannels can result in the enhancement of heat and mass transfer performance and hence provide many potential opportunities in chemical process development and intensification. Many researchers tried to apply the microchemical engineering technology to the field of solvent extraction, and some good results have been obtained. Gothsch et al. [13] investigated the effects of the microchannel geometry in the two processes of highpressure dispersion and emulsification. Zhao et al. [14] studied the mass transfer characteristics of the immiscible liquid-liquid two-phase flow in T-junction microchannels. It was found that the overall volumetric mass transfer coefficients of the microchannels were two or three orders of magnitude higher than those of conventional liquid-liquid contactors. Priest et al. [15] carried out the solvent extraction of copper in a confined glass microfluidic chip, and both high efficiency and extraction

rates were obtained even though the solutions involved were not ideal. Dessimoz et al. [16] examined the mass transfer performance of two immiscible fluids in rectangular glass microchannels with Y- and T-junction inlets. Kashid et al. [17] summarized the mass transfer characteristics of gas-liquid and liquid-liquid systems in microstructured reactors. Nevertheless, the previous experimental studies in microfluidic devices emphasized the physical extraction process or the ultra-fast reactions between the two phases in the process, which were totally limited by mass transfer. The extraction processes accompanying chemical reactions in microchannels are not very well understood up to now, particularly for those heterogeneous systems that are commonly controlled by mass transfer and the chemical reaction.

In this work, the main objective was to quantitatively study the extraction process that transfers

 $Cu^{2+}$  from an aqueous to an oil phase in a T-junction microchannel under different operating conditions. Deionized water and AD-100 dissolved in 260<sup>#</sup> solvent oil were selected as the working fluids; AD-100 is a kind of commercial extractant and  $Cu^{2+}$  is the only diffusing species. The effects of the  $Cu^{2+}$  concentration and the pH in the aqueous phase, the volumetric fraction of AD-100 in the oil phase, and the temperature on the extraction process were investigated.

#### 2 Experimental

AD-100 was provided by Luoyang Aoda Chemical Company. The content of the active component, 2-hydroxy-5-nonylbenzaldehyde oxime, was in the range of 70–75 wt %.  $260^{\#}$  solvent oil was obtained from Shanghai Chaoliang Company and used without any further treatment. Copper solution was prepared by dissolving copper sulfate in deionized water and diluted to the desired concentrations; the concentrations of the copper solutions were in the range of  $1.0-10.0 \text{ g L}^{-1}$ . All other chemicals were of analytical grade. The physical properties of the working system are listed in Tab. 1.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The aqueous and oil phases are forced to flow through the horizontal rectangular microchannel (Reactor-1), at the same volumetric flow rate, by two high-precision piston pumps (Beijing Satellite Manufacturing Factory). Two check valves are used in order to maintain continuous flow without pulsation. Two opposing streams enter coaxially from the two inlets arms, begin to contact in the T-junction and flow along

Table 1. The properties of the working system (at 298 K and atmospheric pressure).<sup>a)</sup>

Mass transfer system	Density [kg m <sup>-3</sup> ]	Viscosity [mPa s]
3 g/L CuSO <sub>4</sub> solution	997.6	1.02
30 vol % AD-100 in 260 <sup>#</sup> solvent oil	853.2	3.27

a) Interfacial tension, 19.55 mN m<sup>-1</sup>.



**Figure 1.** Schematic diagram of the experimental setup: (A) liquid tank, (B) piston pump, (C) check valve, (D) separatory funnel, and (E) microchannel.

the main channel, then leave through the outlet. The microchannel has 90 bends of 90° and is fabricated from polymethyl methacrylate (PMMA) substrate by micromachining technology. Tab. 2 shows the dimensions of the T-shaped microchannel. Reactor-2 is a 103-mm-long polytetrafluoroethylene (PTFE) tube with an inner diameter of 2 mm. The experimental procedures were the same as for Reactor-1.

In the experimental runs, the extraction process was carried out at atmospheric pressure and room temperature. However, the extraction process was performed at a given temperature when the effect of the temperature on the extraction performance was studied; the temperature was controlled precisely by a refrigerated/heating circulator (Julabo Technology Co. Ltd). The separatory funnel was directly used to collect samples from the outlet streams when the flow of the two immiscible phases reached stable conditions, and the two immiscible phases could be separated immediately after sampling. The concentrations of Cu<sup>2+</sup> in the aqueous phase at the inlet and outlet of the T-shaped microchannel were measured via titration. The aqueous samples were titrated with disodium ethylenediamine tetraacetate (Na2-EDTA) solution, and a DX264-Cu2+ Copper ISE and a DX1200 reference electrode (1 M KNO<sub>3</sub>) (Mettler-Toledo) were used to indicate the endpoint. Each experimental run was repeated at least two times, and each data point represents the mean value of at least two measurements of the outlet concentration of the aqueous phase; the relative deviation did not exceed  $\pm 5\%$  in all the experiments. The concentrations of Cu<sup>2+</sup> in the oil phase at the outlet were calculated on the basis of mass conservation. Besides, the equilibrium concentrations of copper were measured in flasks. After thorough mixing and long-time standing, the concentrations of the aqueous phase were determined by atomic

Table 2. Dimensions of the T-shaped microchannel.

Inlet-1 and inlet-2 arms		М	lixing chanr	nel	
W[µm]	$H\left[\mu m ight]$	$L_0$ [mm]	W[µm]	$H\left[\mu m ight]$	$L_0$ [mm]
600	600	15	600	600	900

absorption spectroscopy (AA-6650; Shimadzu Corporation). The concentrations of the oil phase were also calculated on the basis of mass conservation.

The solubility of AD-100 in the aqueous phase was negligible; thus, the reaction was assumed to take place only at the interface between the two immiscible liquid-liquid phases [18]. The reaction mechanism involved in this work is given in Eq. (1) [19].

$$Cu^{2+}(aq) + 2HR(org) \rightleftharpoons CuR_2(org) + 2H^+(aq)$$
(1)

where HR represents the extractant AD-100.

## **3** Theoretical Considerations

The residence time  $t^{1}$  was calculated as follows:

$$t = \frac{V}{Q_{\text{total}}} \tag{2}$$

where V is the volume of the microchannel and  $Q_{\text{total}}$  is the volumetric flow rate of the two immiscible phases.

The extraction efficiency *E* and the distribution ratio *D* can be expressed as follows [20, 21]:

$$E = \frac{C_{\rm aq,i} - C_{\rm aq,o}}{C_{\rm aq,i} - C_{\rm aq}^{\rm e}}$$
(3)

$$D = \frac{C_{\text{oil}}^{\text{e}}}{C_{\text{aq}}^{\text{e}}} \tag{4}$$

where  $C_{aq,i}$  and  $C_{aq,o}$  are the concentrations of the solute in the inlet and outlet aqueous phases, respectively.  $C_{aq}^{e}$  and  $C_{oil}^{e}$  are the equilibrium concentrations of the solute in the aqueous phase and in the oil phase after extraction, respectively.

One of our aims was to investigate the apparent overall mass transfer performance in the T-junction microchannel for the extraction process accompanying the chemical reaction. The Reynolds number is also an important parameter, which is always used to describe the hydrodynamics in microchannels. On the basis of our previous experimental results [9, 14], the Reynolds numbers of the two immiscible phases can be calculated by the following equations:

$$\operatorname{Re}_{\mathrm{M}} = \frac{D_{\mathrm{e}} U_{\mathrm{M}} \rho_{\mathrm{M}}}{\mu_{\mathrm{M}}} \tag{5}$$

$$D_{\rm e} = \frac{4S}{2({\rm W}+{\rm H})} \tag{6}$$

$$U_{\rm M} = \frac{Q_{\rm aq} + Q_{\rm oil}}{S} \tag{7}$$

$$\mu_{\rm M} = \left(\frac{\theta_{\rm aq}}{\mu_{\rm aq}} + \frac{1 - \theta_{\rm aq}}{\mu_{\rm oil}}\right)^{-1} \tag{9}$$

$$\theta_{\rm aq} = \frac{Q_{\rm aq}}{Q_{\rm aq} + Q_{\rm oil}} \tag{10}$$

where  $D_{\rm e}$ , *S*,  $Q_{\rm aq}$ ,  $Q_{\rm oib}$ ,  $U_{\rm M}$ ,  $\rho_{\rm M}$ ,  $\mu_{\rm M}$ , and  $\theta_{\rm aq}$  are the hydraulic diameter of the microchannel, the cross-sectional area of the microchannel, the volumetric flow rate of the aqueous phase, the volumetric flow rate of the oil phase, the total superficial flow rate of the two immiscible liquid-liquid phases, the mixture density, the mixture viscosity, and the volume fraction of the aqueous phase in the two phases, respectively.

Due to the unknown effective interfacial area between the immiscible phases in the extraction, the apparent overall volumetric mass transfer coefficients  $(k_{app}a)$  can be calculated from the experimental results. The  $k_{app}a$  is defined by the following:

$$R = k_{\rm aq} A (C_{\rm aq} - C_{\rm aq}^{\rm s}) \tag{11}$$

$$R = V(k_{\rm f}C_{\rm aq}^{\rm s} - k_{\rm r}C_{\rm oil}^{\rm s}) = k_{\rm f}V\left(C_{\rm aq}^{\rm s} - \frac{C_{\rm aq}^{\rm e}}{C_{\rm oil}^{\rm e}}C_{\rm oil}^{\rm s}\right)$$
(12)

$$R = k_{\rm oil} A (C_{\rm oil}^{\rm s} - C_{\rm oil})$$
<sup>(13)</sup>

$$R\left(\frac{1}{k_{\rm aq}A} + \frac{1}{k_{\rm f}V} + \frac{C_{\rm aq}^{\rm e}}{C_{\rm oil}^{\rm e}}\frac{1}{k_{\rm oil}A}\right) = C_{\rm aq} - \frac{C_{\rm aq}^{\rm e}}{C_{\rm oil}^{\rm e}}C_{\rm oil}$$
(14)

$$\frac{1}{k_{\rm app}a} = \frac{1}{k_{\rm aq}a} + \frac{1}{k_{\rm f}} + \frac{C_{\rm aq}^{\rm e}}{C_{\rm oil}^{\rm e}} \frac{1}{k_{\rm oil}a}$$
(15)

$$-\frac{\mathrm{d}(C_{\mathrm{aq}})}{\mathrm{dt}} = \frac{R}{V} = -k_{\mathrm{app}} \mathbf{a} \left( C_{\mathrm{aq}} - \frac{C_{\mathrm{aq}}^{\mathrm{e}}}{C_{\mathrm{oil}}^{\mathrm{e}}} C_{\mathrm{oil}} \right)$$
(16)

Integration over t from 0 to t and over  $C_{aq}$  from  $C_{aq,i}$  to  $C_{aq}$  gives

$$\ln\left(\frac{C_{aq} - C_{aq}^{e}}{C_{aq,i} - C_{aq}^{e}}\right) = -k_{app}a\left(1 + \frac{C_{aq}^{e}}{C_{oil}^{e}}\frac{Q_{aq}}{Q_{oil}}\right)t$$
(17)

where *A*, *a*, *R*,  $k_{aq}$ ,  $k_{oib}$ ,  $k_{f}$ , and  $k_{r}$  are the interfacial area of the two immiscible phases, the interfacial mass transfer area between the two phases per unit volume of the microchannel, the mass transfer rate of copper, mass transfer coefficient in the aqueous phase, mass transfer coefficient in the oil phase, the forward reaction rate constant, and the reverse reaction rate constant, respectively. The superscript s refers to the interface between the two phases.

<sup>1)</sup> List of symbols at the end of the paper.

#### 4 Results and Discussion

#### 4.1 Identification of the Controlling Factor for the Extraction Process in the Microchannel

Two different reactors (Reactor-1 and Reactor-2) with the same volume were used to identify the controlling factor for the extraction process in the microchannel. Fig. 2 a shows the results of  $k_{app}a$  as a function of the residence time in Reactor-1. It can be seen that  $k_{app}a$  in the microchannel decreased with increasing residence time. As is known, the total superficial flow rate of the two immiscible liquid-liquid phases in the microchannel is inversely proportional to the residence time.  $k_{aq}a$  and  $k_{oil}a$  increased with increasing Re<sub>M</sub> (or flow rate) in accordance with our previous research work [9, 14], and this is mainly due to the increase in the interface interaction of the two immiscible fluids. In addition, the interface of the two immiscible fluids can be stretched, folded and distorted. Even



**Figure 2.** Effect of residence time on (a)  $k_{app}a$  in the two reactors and (b) the extraction efficiencies in the two reactors.  $3.0 \text{ g L}^{-1}$  CuSO<sub>4</sub> solution; 30 vol % AD-100 in 260<sup>#</sup> solvent oil; pH = 3.1.

secondary flow occurs when the fluids flow through the channel bends at medium or high total superficial flow rate, and all these phenomena can result in an increase of the interfacial mass transfer area and a decrease of the mass transfer distance. So the mass transfer process can be dramatically intensified. The same trend was also found in Reactor-2, and  $k_{app}a$  was smaller compared to those in Reactor-1. On the one hand, the superficial flow rates in Reactor-1 were larger for the same volume flow in the two reactors, so this can lead to acute mixing of the two immiscible fluids and a larger interfacial mass transfer area. Generally, the interfacial mass transfer area between the two immiscible phases in microchannels is in the range of  $10^3-10^4$  m<sup>2</sup>m<sup>-3</sup>, which is extremely large [7,22]. On the other hand, the decrease of the channel dimensions can also result in a shorter mass transfer distance compared to Reactor-2.

The extraction efficiency characteristics in Reactor-1 and Reactor-2 are shown in Fig. 2 b. The extraction efficiency E in Reactor-1 was higher than that in Reactor-2 at the same residence time. This is attributed to the better mass transfer performance in Reactor-1, as described above.

It is known that the extraction efficiency of the two immiscible phases is not only dependent on  $k_{app}a$  but also on the residence time in the reactor. Generally, a long residence time favors an increase in E. However,  $k_{app}a$  decreases with increasing residence time in the microchannel, and this can inhibit the increase in extraction efficiency to a certain extent. Therefore, E should firstly decrease, then increase and finally decrease with decreasing residence time if the extraction process is controlled by mass transfer, such as in the water/succinic acid/n-butanol system which can be considered an instantaneous reaction [9, 14]. However, Fig. 2 b shows that the extraction efficiency increased monotonically with increasing residence time for the extraction process of copper in this experiment. In fact, the extraction process of copper is the physical process (mass transfer) combined with the chemical reaction. This means that the extraction process in the microchannel is controlled by both reaction-intrinsic kinetics and mass transfer, depending on the characteristics of the reaction and the fluid hydrodynamics.

#### 4.2 Effect of the Concentration of Cu<sup>2+</sup>

Fig. 3 a shows plots of the extraction efficiencies in the microchannel as a function of  $\text{Re}_{M}$  at different concentrations of  $\text{Cu}^{2+}$  in the aqueous phase. The higher the concentration of  $\text{Cu}^{2+}$ , the smaller was the extraction efficiency at the same  $\text{Re}_{M}$ . This can be ascribed to the changes in the distribution ratios of  $\text{Cu}^{2+}$  in the two phases, as shown in Tab. 3. The value of D decreased dramatically when the concentration of  $\text{Cu}^{2+}$  ranged from 1.0 to  $10.0 \text{ g L}^{-1}$ . This means that the  $\text{Cu}^{2+}$  of the aqueous phase is more difficult to be distributed into the oil phase. This is because the concentration of the free extractant in the oil phase becomes lower when the concentration of  $\text{Cu}^{2+}$  in the aqueous phase is higher. Therefore, the actual driving force is relatively low and the reaction rate decreases. As a result, the extraction efficiency becomes lower with increasing concentration of  $\text{Cu}^{2+}$  in the aqueous phase.



Chemical Engineering Technology

a)

**Figure 3.** Effect of the concentration of  $Cu^{2+}$  on (a) the extraction efficiency and (b)  $k_{app}a$ . 30 vol % AD-100 in 260<sup>#</sup> solvent oil; pH = 3.1.

**Table 3.** The distribution ratios of  $Cu^{2+}$ .

	$C = 1.0 \text{ g L}^{-1}$	$C = 3.0 \text{ g L}^{-1}$	$C = 10.0 \text{ g L}^{-1}$
D	1999.0	399.0	24.6

Fig. 3 b shows the plots of the apparent overall volumetric mean mass transfer coefficients as a function of  $\text{Re}_{\text{M}}$  at different concentrations of  $\text{Cu}^{2+}$ . As expected, the larger the concentration of  $\text{Cu}^{2+}$ , the smaller was the apparent overall volumetric mean mass transfer coefficient. This can be explained as follows: The increasing concentration of  $\text{Cu}^{2+}$  leads to worse mass transfer performance, so  $k_{\text{app}}a$  decreases.

#### 4.3 Effect of the Volumetric Fraction of AD-100 in the Oil Phase

Fig. 4 a shows the effect of the volumetric fraction of AD-100 in the oil phase on the extraction efficiency in the micro-

channel. It can be seen that the extraction efficiency increased with increasing volumetric fraction of AD-100 at the same values of Re<sub>M</sub>. The higher the volumetric fraction of AD-100, the larger was the driving force, which favors an increase in the extraction efficiency. Sherwood et al. [23] and Bakker et al. [24] found that the mass transfer performance could be intensified by the interfacial Marangoni instabilities, which are induced by local changes of interfacial tension. As is known, a higher volumetric fraction of AD-100 can result in a larger concentration gradient and a variation in the interfacial tension. Generally, the value of D becomes larger when the concentration of extractant increases. This means that the Cu<sup>2+</sup> of the aqueous phase is much easier to be distributed into the oil phase. In addition, the viscosity of the oil phase will increase with increasing concentration of the extractant, and this can reduce the mass transfer performance and the extraction efficiency. In fact, the viscosity of the oil phase increased from 2.19 to 6.45 mPas, and its negative effect on mass transfer could be



**Figure 4.** Effect of the volumetric fraction of AD-100 in the oil phase on (a) the extraction efficiency and (b)  $k_{app}a$ .  $3.0 \text{ g L}^{-1}$  CuSO<sub>4</sub> solution; pH = 3.1.

compensated for by the other factors described above, which are beneficial for the enlargement of  $k_{app}a$ , as shown in Fig. 4 b.

#### 4.4 Effect of the pH of the Aqueous Phase

Fig. 5 a shows the effects of the pH of the aqueous phase on the extraction efficiency in the microchannel. The extraction efficiencies decreased as the pH of the aqueous phase decreased. From Eq. (1), it can be seen that an increase in H<sup>+</sup> concentration inhibits the reversible reaction equilibrium to tend to the right direction. Besides, an increase in H<sup>+</sup> concentration in the aqueous phase has a negative effect on the distribution of  $Cu^{2+}$  in the two phases, as shown in Eq. (18).

$$\log D = \log k_{ex} + n \log [HR]_{oil} + 2pH$$
(18)

From Eq. (18), it can be seen that the logarithmic value of D increases linearly with the value of pH of the aqueous phase [25]. And from Tab. 4, it is also seen clearly that the distribu-



**Figure 5.** Effect of the pH of the aqueous phase on (a) the extraction efficiency and (b)  $k_{app}a$ . 3.0 g L<sup>-1</sup> CuSO<sub>4</sub> solution; 30 vol % AD-100 in 260<sup>#</sup> solvent oil.

Table 4. The distribution ratios of Cu<sup>2+</sup>.

	pH = 0.1	pH = 0.5	pH = 1.0	pH = 3.1
D	6.1	26.3	106.1	399.0

tion ratio decreases with decreasing pH, i.e. fewer  $Cu^{2+}$  ions are distributed into the oil phase.

Fig. 5 b shows the plots of the apparent overall volumetric mean mass transfer coefficients as a function of  $\text{Re}_{\text{M}}$  at different pH values. As expected, the lower the pH, the smaller was the apparent overall volumetric mean mass transfer coefficient. The explanation is that the decreasing concentration of H<sup>+</sup> is favorable for the extraction of copper, and hence, the mass transfer performance may be enhanced by the increase in pH.

#### 4.5 Effect of Temperature

To study the effect of temperature on the extraction process, the temperature was controlled precisely by a refrigerated/ heating circulator; a section of the PTFE tubing was connected to the outlet in order to collect the liquid samples with the separatory funnel.

As shown in Fig. 6 a, an increase in temperature brought about an increase in the copper extraction efficiency at the same values of  $Re_M$ , and the extraction efficiency reached 0.96 when the temperature was 311 K. The temperature rise led to an improvement in the extraction process, which can be explained as follows: The liquid-liquid mass transfer coefficient is highly dependent on the diffusivity in liquids. An increase in temperature will result in higher diffusivity and thus yield a higher mass transfer coefficient. Moreover, the increasing temperature can cause an increase in the reaction rate. Fig. 6 b shows the effect of the temperature on the apparent overall volumetric mean mass transfer coefficients in the microchannel. As the temperature increased, the diffusivities of the two phases got larger. Therefore,  $k_{app}a$  increased at unchanging values of  $Re_M$ , as did the extraction efficiency.

## 5 Conclusion

The extraction of copper accompanying a chemical reaction was carried out in a T-junction microchannel contactor. The maximum extraction efficiency was 0.96, and  $k_{app}a$  was in the range of  $0.02-0.2 \text{ s}^{-1}$ . Some other operating parameters such as the concentration of  $\text{Cu}^{2+}$ , the volumetric fraction of AD-100, the pH of the aqueous phase, and the temperature had great effects on the mass transfer performance. The extraction efficiency and  $k_{app}a$  decreased with increasing concentrations of  $\text{Cu}^{2+}$  and H<sup>+</sup> in the aqueous phase, and increased with increasing volumetric fraction of AD-100 in the oil phase. When the temperature changed from 288 to 311 K, both the extraction efficiency and  $k_{app}a$  grew obviously. It was found that the reaction has an effect on the extraction process while the mass transfer performance is significantly enhanced in the microchannel.



**Figure 6.** Effect of the temperature on (a) the extraction efficiency and (b)  $k_{app}a$ . 3.0 g L<sup>-1</sup> CuSO<sub>4</sub> solution; 30 vol % AD-100 in 260<sup>#</sup> solvent oil; pH = 3.1.

# Acknowledgment

We gratefully acknowledge the financial support for this project from the Ministry of Science and Technology of China (No. 2012BAA08B02) and the National Natural Science Foundation of China (Nos. 21225627, 21106141).

The authors have declared no conflict of interest.

# Symbols used

Α	$[m^2]$	interfacial area
а	$[m^{-1}]$	interfacial mass transfer area between
		the two phases per unit volume of the
		microchannel (A/V)
$C_{aq}$	$[g L^{-1}]$	concentration of the solute in the
-		aqueous phase

C	[	and a second sec
Coil	[gl]	concentration of the solute in the oil
_	r - 11	phase
C <sub>aq,i</sub>	$[gL^{-1}]$	concentration of the solute in the inlet
		aqueous phase
$C_{\rm aq,o}$	$[g L^{-1}]$	concentration of the solute in the outlet
		aqueous phase
$C_{aa}^{e}$	$[gL^{-1}]$	equilibrium concentration of the solute
uq		in the aqueous phase
$C_{oil}^{e}$	$[gL^{-1}]$	equilibrium concentration of the solute
011		in the oil phase
D	[_]	distribution ratio
D.	[m]	hydraulic diameter of the microchannel
E	[_]	extraction efficiency
H	[m]	microchannel height
k	$[m s^{-1}]$	mass transfer coefficient in the aqueous
vaq		nhase transfer coefficient in the aqueous
k.	$[m e^{-1}]$	mass transfer coefficient in the oil phase
∿oil L	$\begin{bmatrix} 1115 \end{bmatrix}$	forward reaction rate constant
v <sub>f</sub>	[5]	
K <sub>r</sub>	[S]	reverse reaction rate constant
<sub>app</sub> a	[S]	apparent overall volumetric mass
r	r 1	transfer coefficient
L <sub>0</sub>	[m]	microchannel length
Q <sub>total</sub>	$[m^{5}s^{1}]$	volumetric flow rate of the two
	2 1	immiscible phases
$Q_{aq}$	$[m^{2} s^{-1}]$	aqueous phase volume flow rate
$Q_{oil}$	$[m^{3} s^{-1}]$	oil phase volume flow rate
Re <sub>M</sub>	[-]	Reynolds number of the two immiscible
		liquids
R	$[g s^{-1}]$	mass transfer rate of copper
S	$[m^2]$	cross-sectional area of the microchannel
t	[s]	residence time in the microchannel
$U_{\rm M}$	$[m s^{-1}]$	total superficial velocity of the two
		immiscible liquid-liquid phases
V	$[m^3]$	volume of the microchannel
W	[m]	microchannel width
		· · · · ·

#### Greek symbols

ļ

ι	[Pas]	viscosity
)	[kg m <sup>-3</sup> ]	mass density

#### Subscripts/superscripts

- aq aqueous phase
- e equilibrium state
- i inlet
- M mixture of the two immiscible liquid-liquid phases
- o outlet
- oil oil phase
- s interface between the two phases

# References

- [1] R. J. Ma, *Extractive Metallurgy*, 1st ed., Metallurgical Industry Press Publishing, Beijing **2009**.
- [2] T. C. Lo, H. I. M. Baird, C. Hanson, *Handbook of Solvent Extraction*, 1st ed., Wiley Publishing, New York **1983**.

- [3] A. E. Karr, AIChE J. 1959, 5 (4), 446. DOI: 10.1002/ aic.690050410
- [4] R. E. Treybal, Ind. Eng. Chem. Res. 1961, 53 (2), 161. DOI: 10.1021/ie50614a035
- [5] D. Doungdeethaveeratana, H. Y. Sohn, *Hydrometallurgy* 1998, 49 (3), 229. DOI: 10.1016/S0304-386X(98)00028-0
- [6] J. C. Merchuk, R. Shai, D. Wolf, Ind. Eng. Chem. Process Des. Dev. 1980, 19 (1), 91. DOI: 10.1021/i260073a016
- [7] J. Yue, G. W. Chen, Q. Yuan, L. A. Luo, Y. Gonthier, *Chem. Eng. Sci.* 2007, 62 (7), 2096. DOI: 10.1016/j.ces.2006.12.057
- [8] S. T. Tu, X. Yu, W. Luan, H. Löwe, *Chem. Eng. J.* 2010, 163 (3), 165. DOI: 10.1016/j.cej.2010.07.02
- [9] Y. H. Su, G. W. Chen, Y. C. Zhao, Q. Yuan, AIChE J. 2009, 55
   (8), 1948. DOI: 10.1002/aic.11787
- [10] K. P. Nichols, R. R. Pompano, L. Li, A. V. Gelis, R. F. Ismagilov, J. Am. Chem. Soc. 2011, 133 (39), 15721. DOI: 10.1021/ ja206020u
- [11] K. F. Jensen, Chem. Eng. Sci. 2001, 56 (2), 293. DOI: 10.1016/ S0009-2509(00)00230-X
- [12] V. Hessel, H. Löwe, F. Schönfeld, *Chem. Eng. Sci.* 2005, 60 (8/9), 2479. DOI: 10.1016/j.ces.2004.11.033
- [13] T. Gothsch, J. H. Finke, S. Beinert, C. Lesche, J. Schur, S. Büttgenbach, C. Müller-Goymann, A. Kwade, *Chem. Eng. Technol.* 2011, 3 (34), 335. DOI: 10.1002/ceat.201000421

- [14] Y. C. Zhao, G. W. Chen, Q. Yuan, AIChE J. 2007, 53 (12), 3042. DOI: 10.1002/aic.11333
- [15] C. Priest, J. Zhou, S. Klink, R. Sedev, J. Ralston, *Chem. Eng. Technol.* 2012, 7 (35), 1312. DOI: 10.1002/ceat.201100602
- [16] A. L. Dessimoz, L. Cavin, A. Renken, L. Kiwi-Minsker, *Chem. Eng. Sci.* 2008, 63 (16), 4035. DOI: 10.1016/j.ces.2008.05.005
- [17] M. N. Kashid, A. Renken, K. M. Lioubov, *Chem. Eng. Sci.* 2011, 66 (17), 3876. DOI: 10.1016/j.ces.2011.05.015
- [18] D. S. Flett, Acc. Chem. Res. 1977, 10 (3), 99. DOI: 10.1021/ ar50111a005
- [19] F. J. Alguacil, A. Cobo, M. Alonso, *Chem. Eng. J.* 2002, 85 (2/3), 259. DOI: 10.1016/S1385-8947(01)00166-8
- [20] J. Saien, S. A. E. Zonouzian, A. M. Dehkordi, *Chem. Eng. Sci.* 2006, 61 (12), 3942. DOI: 10.1016/j.ces.2006.01.034
- [21] D. M. Fries, T. Voitl, P. R. von Rohr, *Chem. Eng. Technol.* 2008, *31 (8)*, 1182. DOI: 10.1002/ceat.200800169
- [22] K. Jahnisch, V. Hessel, H. Löwe, M. Baerns, Angew. Chem., Int. Ed. 2004, 43 (4), 406. DOI: 10.1002/anie.200300577
- [23] T. K. Sherwood, J. C. Wei, Ind. Eng. Chem. Res. 1957, 49 (6), 1030. DOI: 10.1021/ie50570a038
- [24] C. A. P. Bakker, F. H. Fentener van Vlissingen, W. J. Beek, *Chem. Eng. Sci.* **1967**, *22* (10), 1349. DOI: 10.1016/0009-2509 (67)80025-3
- [25] K. H. Park, H. I. Kim, P. K. Parhi, Sep. Purif. Technol. 2010, 74 (3), 294. DOI: 10.1016/j.seppur.2010.06.018