# Kinetic study of chromium(VI) facilitated transport through a bulk liquid membrane using tri-*n*-butyl phosphate as carrier

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## ARTICLE INFO

## ABSTRACT

The facilitated transport of Cr(VI) through a bulk liquid membrane (BLM) is investigated, using the commercially available solvent tri-*n*-butyl phosphate (TBP) as mobile carrier. The influences of the carrier concentration in the liquid membrane phase, the HCl concentration of the feed phase, and the stripping concentration on the mass transfer process are studied. The transport rate of Cr(VI) increases with increasing the TBP concentration and HCl concentration. The increasing of the stripping concentration improves the stripping process until a plateau is reached. A kinetic model is used to describe the Cr(VI) transport behavior, assuming that it obeys the kinetic laws of two consecutive irreversible first-order reactions. The experimental data fits reasonable well with the derived model. The analysis of the accumulation of Cr(VI) in the liquid membrane phase and the discussion of the rate-controlling step under different experimental conditions are carried out. The magnitude of the value of $k_e$ and $k_s$ is found to be $10^{-4}$–$10^{-5}\,\text{s}^{-1}$, and is well in agreement with other studies.

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## 1. Introduction

The techniques for the removal and recovery of Cr(VI) are of increasing interest because of the growing importance given to environmental protection problems. The Cr(VI) are bioaccumulative due to their high mobility across biological cell membrane [1]. According to the World Health Organization, Cr(VI) is one of the most toxic metals [2]. The vast majority of industrial effluents and waste waters, such as mining effluents, dilute leaching solutions generated during hydrometallurgy, electroplating rinse liquors, etc., carry Cr(VI) in low concentration. Furthermore, due to the worldwide need for Cr(VI) increase and the grades of ore decrease, the incentive to find more effective and efficient Cr(VI) purification methods grows. Attempts to remove and recovery toxic heavy metal ions from the environment have utilized a variety of separation techniques, such as adsorption, precipitation, and solvent extraction.

Compared with solvent extraction, liquid membranes have shown great potential since they combine the process of extrac-

tion and stripping in a single unit operation [3,4]. Especially in case where solute concentration is relatively low and other techniques cannot be applied efficiently. The extraction chemistry of liquid membrane is similar to that found in classical liquid–liquid extraction, but the transport process is governed by kinetic rather than equilibrium parameters, under non-equilibrium mass transfer [5]. Liquid membranes have been successfully used to treat aqueous streams contaminated with heavy metal ions like copper, zinc, cadmium, nickel, mercury, and lead [6–11].

Bulk liquid membrane (BLM) is one of the simplest designs for performing liquid membrane processes, which are often used to investigate the complexation and transport properties of synthetic and natural ionophores with salts [12–14]. BLM has been studied for pre-concentration and separation of different metal ions with a variety of liquid membrane phase [15–17]. The carrier in the liquid membrane phase plays an important role in the liquid membrane process, which must (I) provide a very high extraction distribution coefficient from dilute solutions; (II) react reversibly with the metal so that the metal can be recovered by a stripping reaction; (III) have reasonably fast extraction and stripping kinetic; and (IV) have very low solubility in the aqueous phase for economic and environmental reasons [18]. There has been a number of papers dealing with Cr(VI) transport through different liquid membrane configurations using various kinds of carriers. The choosing of the type of carrier is important in the design of metal separation. Among carriers used

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**Nomenclature**

| | |
|---|---|
| $C$ | solute concentration (mg L$^{-1}$) |
| $C^*$ | dimensionless concentration (−) |
| $k_e$ | apparent rate constant of extraction process (s$^{-1}$) |
| $k_s$ | apparent rate constant of stripping process (s$^{-1}$) |
| $m$ | extraction distribution coefficient (−) |
| $t$ | time (min) |

*Greek symbols*

| | |
|---|---|
| $\xi$ | the volume ratio of the feed phase to the liquid membrane phase (−) |
| $\lambda$ | the volume ratio of the stripping phase to the liquid membrane phase (−) |

*Subscripts*

| | |
|---|---|
| f | feed phase |
| LM | liquid membrane phase |
| s | stripping phase |
| ini | initial condition |

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for Cr(VI) transport, secondary amines, tertiary amines and quaternary ammonium salts have been most extensively studied, such as Amberlite LA-2, Aliquat 336, Alamine 336 and tri-*n*-dodecylamine (TOA) [19–25]. Recently, Alguacil et al. and Lanagan et al. reported the use of the commercially available phosphine oxide, i.e., Cyanex 272, Cyanex 921 and Cyanex 923 [26–29]. Selective transport of Cr(VI) across BLM with *p-tert*-butyl calyx[4]arene 3-morpholino propyl diamide derivative and *p-tert*-butyl calyx[4]arene dioxaoctylamide derivative has been reported by Saf et al. and Yilmaz et al., respectively [30,31].

Tri-*n*-butyl phosphate (TBP) was one of the most widely used organophosphorous extractants in the solvent extraction process. TBP has been showed to be an effective carrier for the separation and purification of a number of metals and organic acids due to its excellent chemical stability, high boiling point and low solubility in water. We have previously reported the extraction performance of Cr(VI) using TBP as extractant [32]. There are only a few reports about the facilitated transport of Cr(VI) using TBP as mobile carrier through emulsion liquid membrane [33] and supported liquid membrane [34]. And there is no available information in the published literatures on the kinetic study of Cr(VI) transport through BLM using TBP as carrier.

One of the objectives of this work is to study the performance of the facilitated transport of Cr(VI) through a BLM contain TBP as mobile carrier in kerosene. The effect of the TBP concentration in the liquid membrane, the HCl concentration of the feed phase and the stripping concentration on the mass transfer process was studied. Besides, a kinetic model was used to analysis the unsteady state transport of Cr(VI) through BLM. The dimensionless concentration of Cr(VI) species in the feed, liquid membrane and stripping phase as a function of time was derived from the model. The discussion of the accumulation of Cr(VI) in the liquid membrane phase and the identification of the rate-controlling step under different experimental conditions were carried out using the kinetic model.

## 2. Experimental

### 2.1. Reagents

The following inorganic salts, acids, and organic solvent are used in the experiments without further purification: potassium dichromate (K$_2$Cr$_2$O$_4$, >99.8%, Beijing), sodium hydroxide (NaOH, >96.0%), hydrochloric acid (HCl, 36%–38%), phosphoric acid (H$_3$PO$_4$, >85%), sulfuric acid (H$_2$SO$_4$, 95%–98%), tri-*n*-butyl phosphate (TBP, >98.5%), kerosene (density, 0.8 kg L$^{-1}$; refractivity, 1.440), 1,5-diphenylcarbazide (DPC, >99%). Deionized water is used for preparing all the aqueous solutions.

### 2.2. Bulk liquid membrane experimental procedure

The experimental setup is similar to literature [5]. The size of the equipment is 20 cm × 10 cm × 16 cm (length × width × height). A glass wall is installed in the middle of the rectangular glass container (height is 12 cm), in which, the aqueous feed phase and the stripping phase are separated by the barrier. The organic liquid membrane phase contacts with the two aqueous liquids and bridges them.

The aqueous feed phase contained 100 mg L$^{-1}$ of Cr(VI), and the pH was adjusted to the desired value by adding hydrochloric acid. The stripping solutions were made from NaOH in a given concentrations. Equal volumes (1000 mL) of aqueous solutions for the feed and stripping phase were placed into the two compartments. The liquid membrane phase (500 mL), prepared by dissolving TBP in kerosene, laid above these aqueous phases. The two aqueous phases were stirred with an appropriate intensity avoiding mixture of the feed and stripping solutions. Besides, the stirs should also make the aqueous phase mix well. The areas of both feed-membrane and membrane-stripping interfaces were 100 cm$^2$.

### 2.3. Analysis

The viscosity of the liquid membrane phase was determined by Ostwald's glass capillary viscometer (diameter = 0.6 mm, purchased from Beijing Glass Factory).

In the course of experiment, the feed and stripping phases were sampled periodically from a fixed position for determination of the Cr(VI) concentrations by UV–vis spectrophotometer (G751, Shanghai, China) at 540 nm wavelength. 1,5-diphenylcarbazide was used as indicator. The initial concentration of H$^+$ in the feed aqueous phase was determined by titration with standardized NaOH solution. The Cr(VI) concentration in the organic phase was calculated from mass balance. All transport experiments were carried out at ambient temperature. Reproducibility was confirmed as ±5% or better.

## 3. The kinetic model

The chromate ions exist in the aqueous solution in different ionic form, such as HCrO$_4^-$, CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$ and HCr$_2$O$_7^-$. According to the literature [33,35], the chromate ions exist as HCrO$_4^-$ in the feed and stripping phase under this experimental condition. And several previous reports have proved that the chromium species extracted by TBP from the HCl medium is Cr(VI)-chloro-oxo complex [32,36].

The facilitated transport of Cr(VI) ions through the bulk liquid membrane (BLM) is illustrated in Fig. 1. As shown in Fig. 1, HCrO$_4^-$,
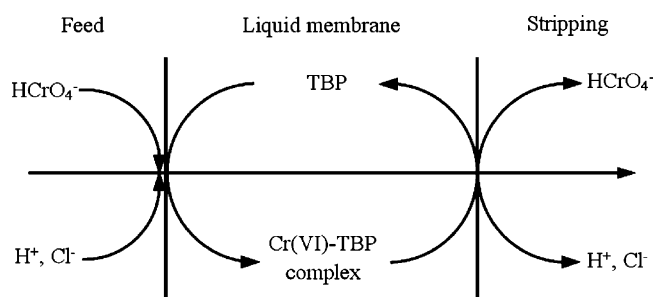


**Fig. 1.** Schematic representation of transport mechanism.

H+ and Cl− react with TBP at the liquid membrane-feed interface, resulting in the formation of the metal complexes. Then, the complexes diffuse through the liquid membrane phase to the liquid membrane-stripping interface, and release Cr(VI) into the stripping phase. The carrier acts as a shuttle. The transport mechanism is a coupled co-transport (symport) mechanism.

Assuming the facilitated transport of metal ions through bulk liquid membranes can be explained by a kinetic law of two consecutive irreversible first-order reactions [37–39]. This behavior can be described according to the following kinetic scheme:

$$Cr_{feed} \xrightarrow[\text{extraction}]{k_e} Cr_{LM} \xrightarrow[\text{stripping}]{k_s} Cr_{strip}$$
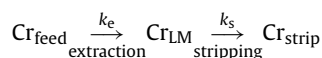
where $Cr_{feed}$ and $Cr_{strip}$ represent the Cr(VI) ions in the feed and stripping phase respectively, while $Cr_{LM}$ is the Cr(VI)-TBP complex in the liquid membrane phase. The Cr(VI) ions present in the different phases are considered as different chemical species obeying the laws of chemical kinetics. $k_e$ and $k_s$ are the "first-order apparent rate constant" of the extraction and the stripping, respectively. Actually, both of the value of $k_e$ and $k_s$ are function of the extraction reaction, stripping reaction and the solute diffusion rate. The value of $k_e$ and $k_s$ are interrelated with each other. The relationship between them is discussed behind.

The transport rate of Cr(VI) can be expressed by the following differential equations:

$$\frac{dC_f^*}{dt} = -k_e C_f^* \tag{1}$$

$$\frac{dC_{LM}^*}{dt} = \xi k_e C_f^* - \lambda k_s C_{LM}^* \tag{2}$$

$$\frac{dC_s^*}{dt} = k_s C_{LM}^* \tag{3}$$

where $\xi$ and $\lambda$ is the volume ratio of the feed phase to the liquid membrane phase and the stripping phase to the liquid membrane phase, respectively ($\xi = \lambda = 2$ in this study). $C_f^*$, $C_{LM}^*$, $C_s^*$ are the dimensionless concentration of Cr(VI) in feed, liquid membrane and stripping phase, respectively. They are defined as:

$$C_f^* = \frac{C_f}{C_{f,ini}} \tag{4}$$

$$C_{LM}^* = \frac{C_{LM}}{C_{f,ini}} \tag{5}$$

$$C_s^* = \frac{C_s}{C_{f,ini}} \tag{6}$$

where $C_{f,ini}$ is the initial concentration of Cr(VI) in the feed phase.

Combining Eq. (1)–Eq. (3), and integration of these differential equations yields

$$C_f^* = \exp(-k_e t) \tag{7}$$

$$C_{LM}^* = \frac{2k_e}{2k_s - k_e} [\exp(-k_e t) - \exp(-2k_s t)] \tag{8}$$

$$C_s^* = 1 - \frac{1}{2k_s - k_e} [2k_s \exp(-k_e t) - k_e \exp(-2k_s t)] \tag{9}$$

**Table 1**
The results of the kinetic model under different HCl concentration[*].

| [HCl] (mol L−1) | m[a] | $k_e$ (×10−5 s−1) | $k_s$ (×10−5 s−1) | $t_{max}$ (min) | $C_{LM,max}^*$ |
|---|---|---|---|---|---|
| 0.03 | 0.3 | 1.8 | 4.8 | 353.7 | 0.26 |
| 0.10 | 1.3 | 14.2 | 5.3 | 135.1 | 0.84 |
| 0.32 | 13.8 | 108.3 | 11.7 | 30.1 | 1.31 |

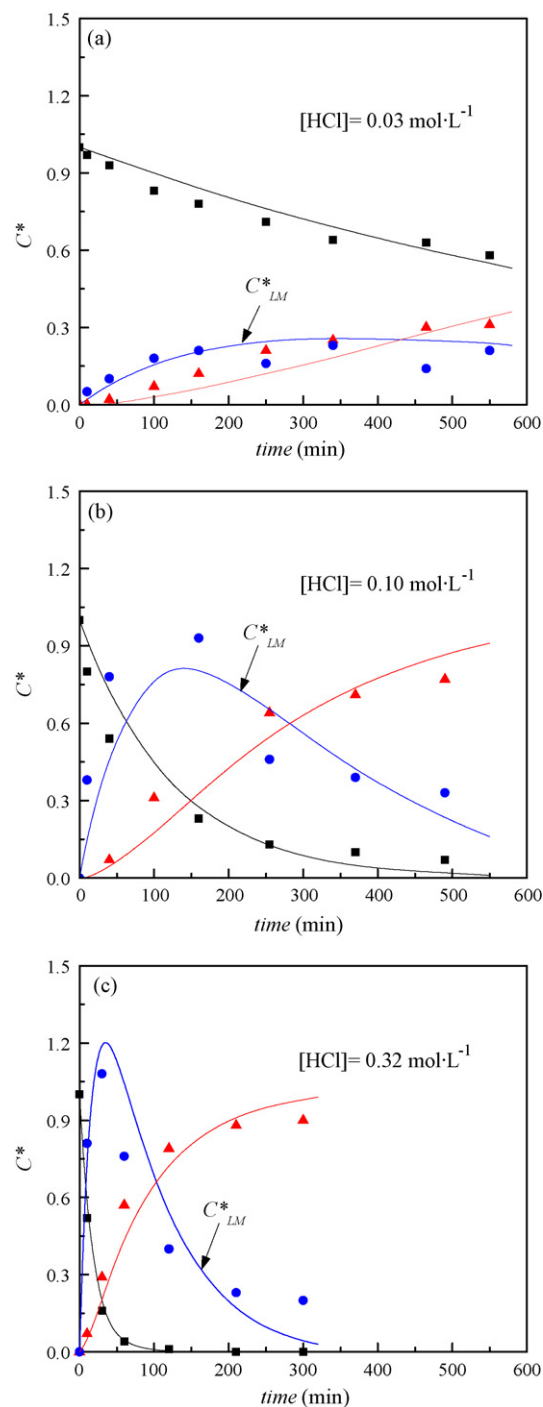[*] $C_{f,ini}$ = 100 mg L−1, [TBP] = 40% (v/v), [NaOH] = 0.5 mol L−1.
[a] Obtained from literature [32].

These equations can be used to describe the kinetic behavior of BLM, which show that the time dependence of $C_f^*$ is mono-exponential, while the time variation of both $C_{LM}^*$ and $C_s^*$ is bi-exponential behavior.

According to Eq. (8), $C_{LM}^*$ has a maximum value and the time is ($dC_{LM}^*/dt = 0$).

$$t_{max} = \frac{\ln(2k_s/k_e)}{2k_s - k_e} \tag{10}$$



**Fig. 2.** The effect of the HCl concentration of the feed phase on the mass transfer process. Feed phase (■): $C_{f,ini}$ = 100 mg L−1. Liquid membrane phase (●): [TBP] = 40% (v/v). Stripping phase (▲): [NaOH] = 0.5 mol L−1. Model (—).
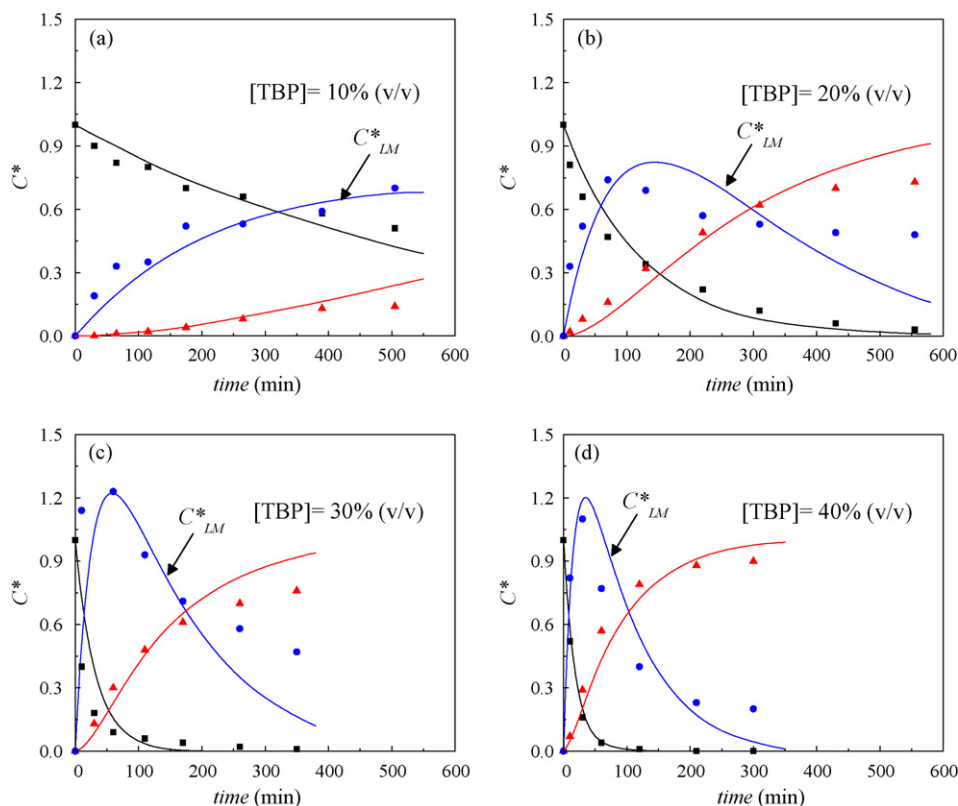
**Fig. 3.** The effect of the carrier concentration on the mass transfer process. Feed phase (■): $C_{f,ini}$ = 100 mg L$^{-1}$, [HCl] = 0.5 mol L$^{-1}$. Liquid membrane phase (●). Stripping phase (▲): [NaOH] = 0.5 mol L$^{-1}$. Model (—).

The maximum value of $C^*_{LM}$ is:

$$C^*_{LM,max} = 2\left(\frac{k_e}{2k_s}\right)^{2k_s/(2k_s-k_e)} \tag{11}$$

## 4. Results and discussion

### 4.1. The influence of the HCl concentration in the feed phase

As it was discussed above, the driving force for the Cr(VI) transport through the liquid membrane was the concentration gradient of both hydrogen and chloride ions across the liquid membrane. In order to assess the effect of the HCl concentration on the Cr(VI) transport through BLM, the studies were conducted with HCl concentration variation in the range of 0.03–0.32 mol L$^{-1}$ keeping the carrier and stripping concentration constant (40% (v/v) and 0.5 mol L$^{-1}$, respectively). The results are shown in Fig. 2.

The Cr(VI) mass transfer behavior through BLM shows significant difference at different HCl concentration. At the highest HCl concentration (0.32 mol L$^{-1}$), 99% of Cr(VI) is removed ($C^*_f$ from 1 to 0.01) and 79% is recovered ($C^*_s$ from 0 to 0.79) within the first 120 min. Meanwhile, the accumulation of Cr(VI) in the liquid membrane phase increases sharply and even more than the initial concentration in the feed phase (the experimental value of $C^*_{LM}$ gets to a maximum of 1.1 at the 30th min). When the HCl concentration is 0.03 mol L$^{-1}$, only 40% of Cr(VI) is removed and 30% is recovered after 550 min. The Cr(VI) concentration in the liquid membrane phase increases over time until it reaches a plateau, and then decreases slightly.

By fitting the experimental data to Eq. (7)–(9), $k_e$ and $k_s$ are obtained, then $C^*_{LM,max}$ and $t_{max}$ can be calculated. All of them are listed in Table 1. With increasing the HCl concentration from (0.03 to

0.32 mol L$^{-1}$), the extraction distribution coefficient increases from (0.3 to 13.8) [32]. More Cr(VI) is extracted into the liquid membrane phase in unit time and the Cr(VI) concentration in the liquid membrane phase increases sharply, which leads to the increase of $k_e$ from (1.8 × 10$^{-5}$ to 108.3 × 10$^{-5}$ s$^{-1}$) and $C^*_{LM,max}$ from (0.26 to 1.31). Higher Cr(VI)-TBP complex concentration in the liquid membrane phase will improve the Cr(VI) transport in the liquid membrane phase as well as the stripping process. Thus, the value of $k_s$ increases from (4.8 × 10$^{-5}$ to 11.7 × 10$^{-5}$ s$^{-1}$). As shown in Fig. 2, the predicated results from Eq. (7)–(9) are in good agreement with the experimental data. The magnitude of the value of $k_e$ and $k_s$ is of the order of 10$^{-4}$–10$^{-5}$ s$^{-1}$. The result is well in agreement with the similar studies reported by Yilmaz et al. [31]. They studied the Cr(VI) transport through BLM containing p-tert-butyl calyx[4]arene dioxooctylamide derivative as carrier, and found that $k_e$ and $k_s$ decreases from 2.59 × 10$^{-3}$ to 0.57 × 10$^{-3}$ min$^{-1}$ and from 2.68 × 10$^{-3}$ to 0.82 × 10$^{-3}$ min$^{-1}$ respectively with increasing pH of the feed phase from 2 to 4 [31].

### 4.2. The influence of the carrier concentration

The experiments were carried out at TBP concentrations ranging from 10% to 40% (v/v) when the HCl concentration and stripping concentration were fixed at 0.32 and 0.5 mol L$^{-1}$, respectively. The experimental results and the predictions are shown in Fig. 3, and good agreement is obtained. The parameters obtained from the kinetic model are listed in Table 2. As expected, both of the transport rate and the accumulation of Cr(VI) in the liquid membrane phase increase with increasing the carrier concentration. The apparent rate constant $k_e$ and $k_s$ increase from (2.8 × 10$^{-5}$ to 10.8 × 10$^{-4}$ s$^{-1}$) and from (1.7 × 10$^{-5}$ to 11.7 × 10$^{-5}$ s$^{-1}$), as well as the maximum of Cr(VI) accumulation in the liquid membrane phase $C^*_{LM,max}$ increase from (0.68 to 1.31) with increasing TBP concentration from 10% to

**Table 2**
The results of the kinetic model under different TBP concentration[*].

| [TBP] (v/v) | $m^a$ | $k_e$ ($\times 10^{-5}$ s$^{-1}$) | $k_s$ ($\times 10^{-5}$ s$^{-1}$) | $t_{max}$ (min) | $C^*_{LM,max}$ |
|---|---|---|---|---|---|
| 10% | 0.5 | 2.8 | 1.7 | 541.7 | 0.68 |
| 20% | 1.8 | 14.2 | 5.0 | 139.3 | 0.87 |
| 30% | 5.1 | 58.3 | 6.7 | 54.7 | 1.29 |
| 40% | 13.8 | 108.3 | 11.7 | 30.1 | 1.31 |

[*] $C_{f,ini} = 100$ mg L$^{-1}$, [HCl] = 0.32 mol L$^{-1}$, [NaOH] = 0.5 mol L$^{-1}$.
[a] Obtained from literature [32].

**Table 3**
The viscosity of the liquid membrane phase at different carrier concentration[*].

| [TBP] (v/v) | Viscosity ($\times 10^{-3}$ Pa s) |
|---|---|
| 10% | 0.803 |
| 20% | 0.886 |
| 30% | 0.894 |
| 40% | 1.801 |

[*] Temperature: 25 °C.

40% (v/v), respectively. The discussion is similar to the effect of the HCl concentration.

The viscosity of the liquid membrane is shown in Table 3. As it can be seen, the viscosity increases from $0.802 \times 10^{-3}$ to $1.081 \times 10^{-3}$ Pa s (by ~25%) when TBP concentration was increased from 10% to 40% (v/v). According to Wilke and Chang equation, the increasing of the viscosity will lead to the decreasing of diffusion coefficient and the diffusion rate. However, the mass transfer rate is still improved. This means that the change of the diffusion coefficient of the complex can be neglected compared with the chemical reaction under this experimental condition.

According to Szpakowska and Nagy [40], the ratio of the initial metal concentration ($C_{f,ini}$) and the carrier concentration ($C_{TBP}$) influenced the kinds of kinetic regime and the shape of kinetic curves. They pointed out that it was possible to change the transport kinetics from non steady state first-order to steady state zeroth-order one by varying the concentration ratio ($C_{f,ini}/C_{TBP}$). In this study, the $C_{f,ini}/C_{TBP}$ ratio is in the range of $1.3 \times 10^{-3}$–$5.4 \times 10^{-3}$, which means that a large excess of carrier is present in the liquid membrane phase to allow Cr(VI) to be extracted. In despite of this, the transport still depends on the carrier concentration, indicating that not only the $C_{f,ini}/C_{TBP}$ ratio but also the extraction distribution coefficient should be properly taken into account in designing the BLM processes.
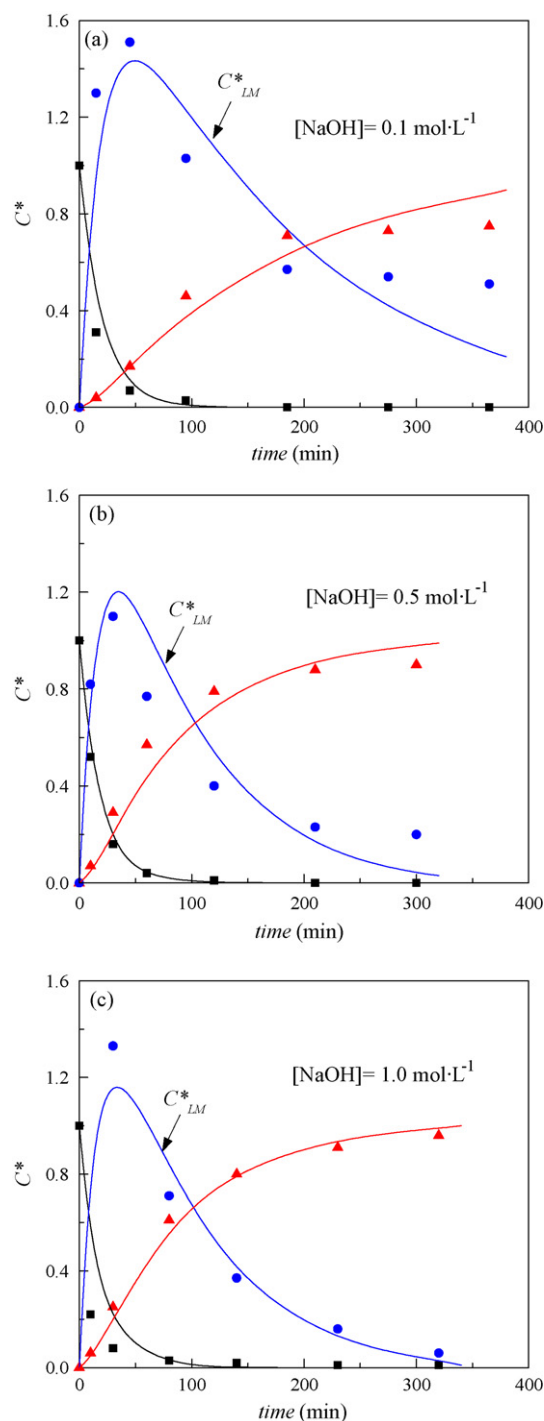
### 4.3. The influence of the stripping concentration

The concentration of the stripping phase determines the rate of the stripping reaction as well as the regeneration of the extractant. The studies were conducted with NaOH concentration variation in the range of 0.1–1.0 mol L$^{-1}$, keeping the HCl concentration of the feed phase and carrier concentration constant (0.32 mol L$^{-1}$ and 40% (v/v), respectively). The results are represented in Fig. 4 and Table 4. The mass transfer rate is increased with increasing stripping concentration from (0.1 to 0.5 mol L$^{-1}$). Further increase in NaOH concentration has no significant improvement on the transport rate. It may be explained that the stripping ability of NaOH

**Table 4**
The results of the kinetic model under different stripping concentration[*].

| [NaOH] (mol L$^{-1}$) | $k_e$ ($\times 10^{-5}$ s$^{-1}$) | $k_s$ ($\times 10^{-5}$ s$^{-1}$) | $t_{max}$ (min) | $C^*_{LM,max}$ |
|---|---|---|---|---|
| 0.1 | 108.3 | 5.17 | 40.0 | 1.56 |
| 0.5 | 108.3 | 11.7 | 30.1 | 1.31 |
| 1.0 | 108.3 | 11.7 | 30.1 | 1.31 |

[*] $C_{f,ini} = 100$ mg L$^{-1}$, [HCl] = 0.5 mol L$^{-1}$, [TBP] = 40% (v/v).



**Fig. 4.** The effect of the stripping concentration on the mass transfer process. Feed phase (■): $C_{f,ini} = 100$ mg L$^{-1}$, [HCl] = 0.5 mol L$^{-1}$. Liquid membrane phase (●): [TBP] = 40% (v/v). Stripping phase (▲). Model (—).

solution is improved with increasing its concentration from 0.1 to 0.5 mol L$^{-1}$, however, no longer increases after 0.5 mol L$^{-1}$. According to the stripping equilibrium data, the recovery efficiency of Cr(VI) would be enhanced by increasing NaOH concentration from 0.1 to 0.5 mol L$^{-1}$, however, further increase (from 0.5 to 1.0 mol L$^{-1}$) had on significant improvement [32]. The apparent rate constant of stripping process, $k_s$, at 0.5 mol L$^{-1}$ NaOH concentration was about twice larger than that at 0.1 mol L$^{-1}$. With a further increase to 1.0 mol L$^{-1}$, $k_s$ remains the same as that with the 0.5 mol L$^{-1}$. The apparent rate constant of extraction process, $k_e$, remains constant ($10.8 \times 10^{-4}$ s$^{-1}$). This suggests that the variation of the stripping
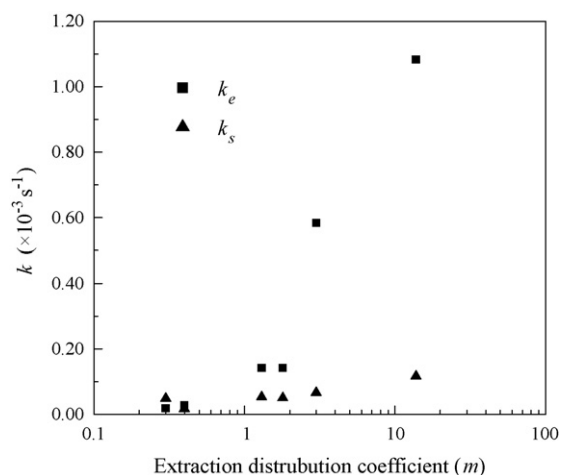
**Fig. 5.** The variation of the apparent rate constant ($k_e$, $k_s$) with extraction distribution coefficient. Stripping phase: [NaOH] = 0.5 mol L$^{-1}$.

concentration almost has no effect on the extraction side under this experimental condition.

### 4.4. The analysis of the accumulation of Cr(VI) in the liquid membrane phase and the rate-controlling step

The accumulation of Cr(VI) in the liquid membrane is dependent on the diffusion rate of complex through the liquid membrane phase, as well as the difference between the extraction and stripping rate. The former is determined by the diffusion distance and the diffusion coefficient of complex in the liquid membrane. In this study, the diffusion distance is invariable due to the fixed experimental setup. The diffusion coefficient of the Cr(VI)-TBP complex can be considered as a constant, which has been proved above.

The difference between the extraction and stripping rate depends on the extraction and stripping distribution coefficient actually, because the extraction and stripping reaction taking place at feed-liquid membrane and liquid membrane-stripping interfaces can be considered as occurring instantaneously compared to the diffusion process [34]. When keeping the same stripping concentration, a higher extraction distribution coefficient means more Cr(VI) are extracted into the liquid membrane phase in unit time. This lead to more Cr(VI) accumulation in the liquid membrane phase occur. In addition, a high concentration of Cr(VI) in the liquid membrane phase can enhance the stripping process. Consequently, the extraction distribution coefficient not only affects the apparent rate constant of extraction process ($k_e$) but also that of the stripping process ($k_s$). The effect of the extraction distribution coefficient on the apparent rate constant $k_e$ and $k_s$ are shown in Fig. 5. The variation of $C_{LM,max}^*$ with extraction distribution coefficient is shown in Tables 1–3. The results are consistent with the analysis.

The value of $k_e$ and $k_s$ can be used to identify the rate-controlling step. At a high extraction distribution coefficient ($m > 10$), the value of $k_e$ is around one order of magnitude higher than $k_s$. The resistance of the extraction process does not dominate the overall mass transfer resistance. That is, the mass transfer process may be governed by combined stripping reaction and the complex diffusion in the liquid membrane phase. When the extraction distribution coefficient in the range of 0.3–10, the value of $k_e$ and $k_s$ are apparently of the same order, indicating that this is a hybrid controlled process.

## 5. Conclusion

The facilitated transport of Cr(VI) through BLM using TBP as mobile carrier is studied. The mass transfer behavior of Cr(VI)

depends on the extraction and stripping distribution coefficient. With the increase of TBP and HCl concentration, the transfer rate increases. The increase of the stripping concentration improves transport rate until a plateau is reached. A kinetic model, based on the kinetic laws of two consecutive irreversible first-order reactions, was used to describe the mass transfer process successfully. By fitting the experimental data, the apparent rate constants ($k_e$, $k_s$) are obtained, and the maximum accumulation of Cr(VI) in the liquid membrane phase ($C_{LM,max}^*$) and the time ($t_{max}$) are calculated. The magnitude of the value of $k_e$ and $k_s$ is of the order of $10^{-4}$–$10^{-5}$ s$^{-1}$. The accumulation of Cr(VI) in the liquid membrane is dependent on the diffusion rate of complex through the liquid membrane phase, as well as the difference between the extraction and stripping rate. The transport of Cr(V) are governed by the combinations of both the stripping reaction and the complex diffusion in the liquid membrane phase at a high extraction distribution coefficient ($m > 10$). When the extraction distribution coefficient in the range of 0.3–10, the transport changes to a hybrid controlled process.

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