



Extraction kinetics of lithium ions by N,N-bis(2-ethylhexyl)acetamide from simulated brine using rising single drop method



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ABSTRACT

Recovery of lithium ions from salt lake brine is becoming more important because of the rapid increase in projected demand for lithium resources. N,N-bis(2-ethylhexyl)acetamide (N523) is a newly developed extractant that presents good lithium extraction ability and selectivity. In this study, the kinetics and mechanism of lithium ion extraction with N523 in kerosene at 298.15 K were investigated using the rising single drop method. Results showed that the extraction process is controlled by diffusion and that the chemical reaction occurs at the interfacial area.

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1. Introduction

Lithium is a crucial resource that is used in batteries, medicines, light aircraft alloys, and thermonuclear fusion reactors (Lemaire et al., 2014; David et al., 2014; Lin et al., 2014; Pratima and Pandey, 2014; Somrani et al., 2013). The demand for lithium resources is estimated to rapidly increase in the near future. Therefore, substantial efforts have been given to the development of lithium recovery technologies from various sources, such as seawater, ore, and salt lake (Sun et al., 2014; James and Palmer, 2000). Among the developed methodologies for lithium recovery, solvent extraction from salt lake brine has attracted considerable interest because more than 80% of lithium resources in China are present in the form of salt lake brine (Sun et al., 2011), which has a high Mg/Li ratio (Zhao et al., 2013).

Extractants with high selectivity toward lithium ions in salt lake brine has been investigated, including several new substances such as 2,6-Dimethyl-4-heptanone (DIBK) (Neilli et al., 1970), N,N-bis(1-methyl heptyl)acetamide (N503) (Xu, 1979), and butyl acetate (BA) (Li et al., 2014), which are considered to be promising lithium-selective extractants. A new extractant, N,N-bis(2-ethylhexyl)acetamide (N523), has been recently proposed. To separate lithium and magnesium effectively from salt lake brine and to increase the extraction rate of lithium,

we built a N523-sulfonated kerosene extraction system (Li et al., 2014; Shi et al., 2013). By using this system, the rate of extracting lithium from salt lake brine can exceed 96% (Shi et al., 2013). Moreover, the impurity content is extremely low in the strip liquor (Shi et al., 2013). However, regardless of the applied extractant, the chemical reaction scheme, mechanism, and mass-transfer models in the extraction process should be studied (Tokerman et al., 2014; Xiong et al., 2010).

The kinetics of metal extraction is complicated because both chemical reaction and diffusion are involved in a heterogeneous system. However, elucidation of the kinetic behavior of an extraction system is important because of their influence on economic parameters, such as equipment model, and extraction reaction temperature and residence time. Hence, several techniques to study the kinetics of metal extraction have been developed over the years, including Lewis cell (Yang et al., 2013; Xiong et al., 2006), rotating diffusion cell (Meng et al., 1996), stirred tank AKUFVE, Kenics mixer (Horner et al., 1980), and the single drop technique (Biswas and Hayat, 2002; Wang et al., 2010). Among the available techniques, the reliable and simple rising single drop method (Zhou et al., 1983; Gai et al., 1986) is considered a promising method.

In the present work, lithium extraction kinetics by N523-sulfonated kerosene extraction system was studied using the rising single drop method. The effects of different parameters, such as interfacial area, column height, temperature, and concentrations of Fe^{3+} , Li^+ , and N523 on the kinetics of extraction were investigated. A mechanism was proposed to explain the obtained results.

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2. Materials and experimental

2.1. Materials and conditions

The new extractant, N523, was prepared by Shanghai Institute of Organic Chemistry of the Chinese Academy of Sciences. The structure of N523 is shown in Fig. 1. Sulfonated kerosene was bought from a local market. (Its density is 0.81 g/cm³, the flash point is below 60 °C and the percent aromatic is below 10%.) All other chemicals were of analytical reagent grade.

A stock solution of the aqueous phase containing 3.50 mol/L MgCl₂, 0.05 mol/L HCl, and 1.40 mol/L LiCl was prepared by mixing appropriate amounts of MgCl₂, HCl, and LiCl. The stock-loaded organic phase was prepared by allowing 500 mL of the organic phase, which contained 1.50 mol/L N523 in sulfonated kerosene, to come into repeated contact with 250 mL of the aqueous phase containing 0.10 mol/L HCl and 0.20 mol/L FeCl₃ in saturated magnesium chloride solution at 298.15 K. The loaded organic phase theoretically contains Mg(FeCl₄)₂·nN523 (Shi et al., 2013). The concentrations of Fe³⁺ and H⁺ in the loaded organic phase were 0.10 and 0.05 mol/L, respectively.

We studied the effects of lithium concentration ranging from 0.90 mol·L⁻¹ to 1.49 mol·L⁻¹ with constant ferric (0.09 mol·L⁻¹) and N523 (1.50 mol·L⁻¹) concentration, those of ferric concentration ranging from 0.05 mol·L⁻¹ to 0.12 mol·L⁻¹ with constant lithium (1.33 mol·L⁻¹) and N523 (1.50 mol·L⁻¹) concentration, and those of N523 concentration ranging from 0.90 mol·L⁻¹ to 1.80 mol·L⁻¹ with constant lithium (1.33 mol·L⁻¹) and ferric (0.09 mol·L⁻¹) concentration. The experiments conditions are listed in Table 1.

2.2. Experimental procedure

The design of the single-drop apparatus for kinetics measurement is shown in Fig. 2.

The organic phase was placed in a 70 cm high vertical glass tube. A series of shorter glass tubes (lengths of 20, 30, 40, and 50 cm, and a uniform diameter of 8 mm) were used to reserve the aqueous phase. Different lengths of glass tubes were used to obtain different extraction rates when the two phases were in contact. A hose with a three-way valve was used to link up the tall column and the short column. One end of the hose was a capillary tube, which was attached to the short column. Hence, the organic phase and aqueous phase can come in contact by opening the valve. Owing to the difference in two-phase pressure, the liquid drops of organic phase can escape from the capillary nozzle and enter the aqueous phase. The lithium loaded organic drops can form a continuous organic phase when the drops reach the top of the short column and can be collected from the overflow pipe.

Formation of organic phase drops was strictly regulated to ensure the same intervals between organic phase drops. The volume of a drop was averaged from the volumes of 100 drops collected in the measuring tube. Changes in lithium concentration in the aqueous phase were neglected while drops run in the short column. The extraction rate was calculated using Eq. (1). The running time of a drop for a particular short column was calculated by averaging the running time of 20 drops. Experiments were conducted at (298.15 ± 1) K.

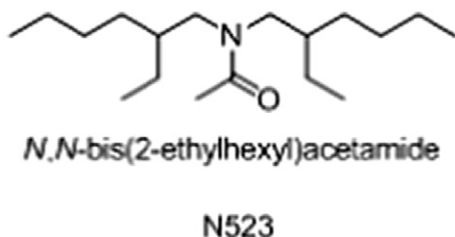


Fig. 1. The structure of new extractant N523.

Table 1
The experimental condition of reagent concentration.

[Li ⁺]/(mol L ⁻¹)	[Fe ³⁺]/(mol L ⁻¹)	[N523]/(mol L ⁻¹)
0.90	0.09	1.50
1.13	0.09	1.50
1.33	0.09	1.50
1.49	0.09	1.50
1.33	0.053	1.50
1.33	0.077	1.50
1.33	0.09	1.50
1.33	0.12	1.50
1.33	0.09	0.90
1.33	0.09	1.20
1.33	0.09	1.50
1.33	0.09	1.80

$$a = 26.45 \text{ cm}^{-1}, T = 298.15 \text{ K.}$$

2.3. Lithium analysis

Lithium analysis in the organic phase was performed in two steps. A weighed sample was completely back-extracted with 6 mol/L hydrochloric acid. The lithium concentration of the aqueous phase (containing 2 mg/L to 10 mg/L lithium) was then analyzed at a wavelength of 670.8 nm with Analyst 800 atomic absorption spectrophotometer (Perkin Elmer Company, US).

2.4. Mathematical relationships

In this paper, the mass of Li⁺ transfer per second (extraction rate, *R*) during extraction at the experimental temperature was calculated using the following equation (Gai et al., 1986):

$$R = \frac{dm}{Adt} = \frac{Vd[c(Li^+)]_{(o)}}{Adt} \text{ (mol/cm}^2 \cdot \text{s)} \quad (1)$$

where *V* is the average volume of a drop, which can be obtained through the collective volume of the organic phase and drops counted in the experiment, *A* is the superficial area of a drop, *c(Li⁺)* is the concentration of lithium in the organic phase drop, and *t* is the running time of the organic phase drop.

Given that ferric ion is the synergist in this experiment, it existed in the form of [FeCl₄]⁻ in salt lake brine. Lithium can be extracted by N523 only with the existence of [FeCl₄]⁻. Hence, at a constant time, the extraction rate can also be expressed as

$$R = k[Li^+]_{(aq)}^a [FeCl_4^-]_{(o)}^b [N523]_{(o)}^c \quad (2)$$

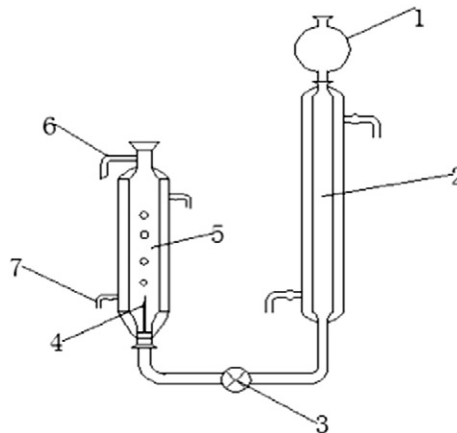


Fig. 2. Experimental set-up of the rising drop technique. 1—Head tank; 2—feed column; 3—three way control valve; 4—glass capillary nozzle; 5—extraction column; 6—overflow pipe; 7—thermostated jacket.

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