Note**Simultaneous Recovery of Lithium Bromide with Ion Exchange Method**

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Abstract

The simultaneous recovery of LiBr from aqueous solution such as seawater and industrial effluent using ion exchange method has been investigated, employing quaternary ammonium salt type adsorbent. The quaternary ammonium salt type adsorbent prepared possesses sufficient adsorption ability for Br⁻ and the adsorption was found to progress with Langmuir mechanism. The selectivity for Br⁻ against Cl⁻ depends on the counter anion of the adsorbent and the adsorbent with counter anion OH⁻ shows the sufficient selectivity for Br⁻. The Br⁻ loaded was also eluted by LiOH from the adsorbent to produce LiBr.

Key words: recovery, ion exchange, lithium bromide, quaternary ammonium salt type adsorbents

1 Introduction

The demands for lithium bromide have been increasing in recent years as a refrigerant for absorption-type chiller and air conditioner. In previous works [1], we have successfully recovered lithium from seawater by using a benchmark plant, employing λ -MnO₂ adsorbent. In the present work, we attempt to simultaneously recover LiBr by eluting Br⁻ from the loaded adsorbent with LiOH. We investigated the batchwise adsorption of Br⁻ with quaternary ammonium salt type adsorbent to elucidate the adsorption mechanism and the effect of counter anion of the adsorbent on the selectivity of Br⁻ against Cl⁻ in aqueous solution. In addition, we carried out the column separation of Br⁻ by elution from the loaded adsorbent with LiOH solution as an elutant.

2 Experimental

The quaternary ammonium salt type adsorbent, based on styrene and divinylbenzene co-polymer (OT-K 1020, Muromachi Chemicals), was employed for the adsorbent. The adsorbent was treated twice with 1.0 mol/dm³ HCl, LiOH or HNO₃, to obtain Cl type, OH type and NO₃ type adsorbents, respectively. The aqueous solution was prepared by dissolving LiBr and/or LiCl solution to adjust the concentrations of Br⁻ and Cl⁻ ($C_{\text{Br}} = 0 \sim 12.5$ mmol/dm³, $C_{\text{Br}} = C_{\text{Cl}} = 7.5$ mmol/dm³). The pH of aqueous solution was adjusted by adding of NaOH or HCl solution (pH = 4.0 ~ 12.0). The batchwise adsorption was carried out by shaking the mixture of 20 mg of the adsorbent (Cl type, NO₃ type, OH type) and 10 cm³ of the aqueous solution at 298 K for 2 h. Concentration of each anion in the aqueous solution was measured by ion chromatography (Metrohm 761Compact IC).

The chromatographic operation was carried out using a column packed the adsorbent (wet volume = 0.89 cm³). The aqueous feed solution ($C_{\text{Br}} = C_{\text{Cl}} = 100$ ppm, pH = 8.0) was fed upward with 0.39 cm³/min to the

column using a reciprocal pump (UNIOWS uf-7005PSB2). After the break thorough of Br^- , deionized water was fed to wash out the aqueous feed solution. LiOH solution of 5 mmol/dm^3 was then fed for scrubbing the loaded column. The Br^- was then eluted from the loaded adsorbent with 1.0 mol/dm^3 LiOH solution. The effluent was collected with a fraction collector (Advantec CHF122SA), to measure the concentrations of Br^- and Cl^- by ion chromatography.

3 Results and Discussion

3.1 Adsorption equilibria of bromide ion

The adsorption mechanism of Br^- with Cl type adsorbent was revealed to be Langmuir mechanism, and the maximal adsorption amount and equilibrium constant at $\text{pH}_{\text{eq}} = 4.9$ were determined as 2.82 mmol/g and $1.90 \text{ dm}^3/\text{mmol}$, respectively. The adsorption behaviors at $\text{pH}_{\text{eq}} = 4.9$ with OH and NO_3 types of the adsorbents are quite identical to that with Cl type adsorbent. Figure 1 shows the effect of pH on the adsorption amount of Br^- , q_{Br} , from binary Br^-/Cl^- aqueous solution, with the various type adsorbent having different counter anions. The q_{Br} gradually decreases with increasing pH in aqueous solution in cases of Cl and NO_3 types of the adsorbents. In the case of OH type adsorbent, the excellent adsorption of Br^- was observed in acidic and neutral region ($\text{pH} < 7$), while the adsorption decreased in alkali region ($\text{pH} > 8$). This result indicates that the OH type adsorbent has the potential for the selective recovery and elution of Br^- .

3.2 Eluted recovery of lithium bromide

Figure 2 shows the elution profiles of Br^- and Cl^- from the loaded OH type adsorbent. Br^- was concentrated up to 1600 ppm, while Cl^- was suppressed to 1200 ppm. Since eluted amounts of Br^- and Cl^- are 1.01 mmol/g and 0.62 mmol/g , respectively, the separation ratio of Br^-/Cl^- , $S_{\text{Br/Cl}}$, was reached to 1.6. In case of corresponding experiments without scrubbing step using diluted LiOH solution, the $S_{\text{Br/Cl}}$ was remained close to unity. This enhancement of $S_{\text{Br/Cl}}$ is due to the scrubbing off of Cl^- away from the adsorbent, suggesting the affinity of Cl^- to the present adsorbent is possibly lower than OH^- .

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References

- 1) A. Kitajou, T. Suzuki, S. Nishihama, K. Yoshizuka, *Ars Separatoria Acta*, **2**, 97-106 (2003); A. Kitajou, Y. Suzuka, S. Nishihama, T. Suzuki, K. Yoshizuka, *J. Ion Exchange*, **16(1)**, 49-54 (2005)

Fig. 1 Effect of pH on the adsorption amount of Br^- using the adsorbent with different counter anion.

Fig. 2 Elution profiles of Br^- and Cl^- from the loaded adsorbent.