

Separation of Europium from Crown Ether Complex Solutions

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Europium is separated from dichloromethane phase in the solvent extraction with benzo-15-crown-5 in the presence of picrate anion by the use of a diaphragm electrolyser.

Crown ethers are important extractants,¹ which are now becoming widely used for the solvent extraction of rare earths.²⁻³ Since europium is a valuable rare earth, the selective extraction of europium is highly important.⁴ However, it is difficult to separate metal ions from metal ion-crown ether complexes.⁵ The back-extraction of rare earth ions from the organic to the aqueous phase by using $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$ as a back-extractant^{3,6} cannot effectively separate the rare earth from crown ether and picrate. As can be seen from Fig. 1(a), the spectrum of the back-extractive phase using $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$ acting on the organic phase containing $0.615 \text{ mmol dm}^{-3}$ complex of europium picrates with benzo-15-crown-5 (B15C5) is a composite of B15C5 and picric acid, which have the respective absorptions of 221 and 275 nm and 207 and 356 nm. However, the electrochemical method using a diaphragm electrolyser can effectively dissociate crown ether complexes.⁷

The diaphragm electrolyser has been widely used in the electrolytic separation^{7,8} and the electrodialysis.⁹ Here, an

H-type electrolyser is employed. The diaphragm is a cation-exchange membrane (Type F101, Jangyen Chemical Engineering No. 1 Factory, Jangsu) effective surface 1.0 cm^2 . The major characteristic of the cation-exchange membrane is strong binding strength. The cathode and anode are platinum plates ($0.35 \times 1.20 \text{ cm}$). The pole distance is 5 cm. The catholyte and anolyte (both volumes 5 cm^3) are an aqueous solution of $0.1 \text{ mol dm}^{-3} \text{ NaCl}$ and an organic solution obtained by the solvent extraction, respectively. All the electrochemical experiments were carried out at room temp.

The solvent extraction and back-extraction experiments were performed according to procedures described in previous papers.^{3,6} Europium is extracted at pH 6 with 50 mmol dm^{-3} B15C5 in dichloromethane from an aqueous solution of lithium picrate (50 mmol dm^{-3}) and europium nitrates of known concentration, shown in Table 1 as C_0 . The initial volumes of the organic phase and the aqueous phase were 10 and 50 cm^3 , respectively. The mixture in a stoppered flask was shaken in a water bath kept at $30.0 \pm 0.5 \text{ }^\circ\text{C}$ for 30 min. Equal volumes of a dichloromethane solution obtained by the solvent extraction and of $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$ solution in a stoppered glass tube were shaken for 15 min at room temp. The concentration of the picrate was determined spectrophotometrically at 356 nm. The concentration of B15C5 in each organic phase was calculated from a calibration curve. The curve was obtained spectrophotometrically at 275 nm at constant concentration of the picrate, which was similar to that in that organic phase. In the back-extraction, concentration of B15C5 in the aqueous phase was its initial concentration minus final concentration in the organic phase. The concentration of europium was measured by the quantitative analysis reported recently.¹⁰ EDTA was used as a titrant and xylenol orange as an indicator. A microscale burette was employed. Data analyses of the determination done three times afforded the values of the quantity of europium. The extractability (E_x) of europium from picrate media by using B15C5 in dichloromethane, the recovery (E_B) of europium using $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$, and the concentration (C_p , C_c) of the picrate and B15C5 in the aqueous phase after the back-extraction are listed in Table 1. These results show that the back-extraction of europium is quantitative with $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$, but there are losses of the crown ether and picrate during the back-extraction. This is in agreement with the one previously reported.^{3,6} The experiments in Table 1 show that the loss, as the ratio of the quantity in the aqueous phase to the initial quantity in the organic phase in the back-extraction, of the picrate is 7.5–8.0% and that the loss of B15C5 is ca. 0.5%. In

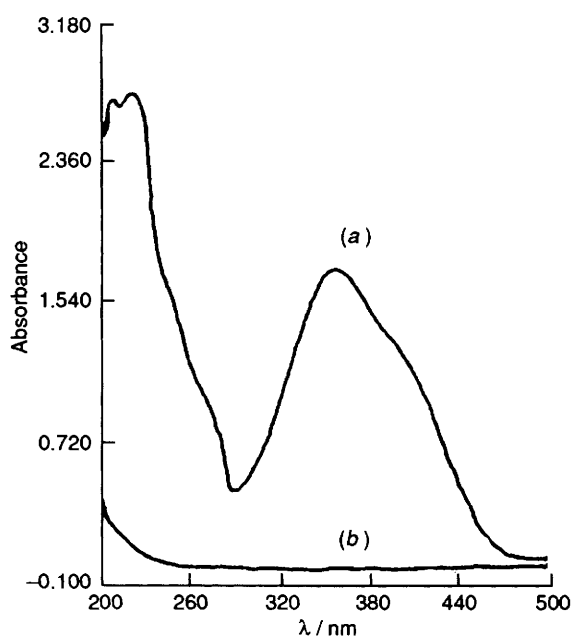


Fig. 1 Absorption spectra for (a) the back-extractive solution using $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$ and (b) the catholyte using the electrolyser

Table 1 Extraction of europium using B15C5 from picrate media, back-extraction of europium using $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$ and electrolytic separation of europium using the electrolyser from the complex solutions

C_0 / mmol dm^{-3}	E_x (%)	E_B (%)	C_p / mmol dm^{-3}	C_c / mmol dm^{-3}	D_E (%)	W_E ($10^6 \text{ J mol}^{-1} \text{ Eu}^{3+}$)	η (%)
0.125	56.8	100.0	0.085	0.202	69.4	19.3	45
0.253	48.2	100.0	0.138	0.210	58.5	14.5	60
0.505	43.6	100.0	0.263	0.208	45.8	11.0	79
1.01	35.6	99.9	0.440	0.215	30.4	12.0	72

addition, the extraction of europium is not quantitative with 50 mmol dm^{-3} B15C5 in dichloromethane.

We define an electro-separation coefficient (D_E), which is the ratio of the concentration of europium in the catholyte to the initial concentration of europium in the anolyte. The electrolytic separation of europium was performed at a cell voltage of 30 V. After electrolysis for 60 min. The values of D_E , energy consumption (W_E), and current efficiency (η) are also shown in Table 1 and a colourless solution [Fig. 1(b)] was obtained. The absorption spectra of picrate and B15C5 are clearly absent and this indicates that the crown ether and picrate are only in the anolyte and that there are no losses of the expensive extractant during the electrolytic separation. The organic solution can be used in the circulating way between the solvent extraction and the electrolytic separation.

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