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Selective Extraction of Lithium Chloride from Brines

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NOTE

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Key Words. Lithium chloride extraction; Separation of alkaline earth chlorides; Isoamyl alcohol with admixtures of ethers or 2-ethyl-1,3-hexanediol

INTRODUCTION

Lithium chloride can be recovered from brines by liquid–liquid extraction with alcohols such as *n*-butanol or isoamyl alcohol as well as by precipitation of the lithium aluminate complex (1–3). In most cases, however, certain amounts of magnesium chloride and calcium chloride are coextracted. In order to obtain pure lithium chloride, separation of alkaline earth compounds by special precipitation (4) or extraction procedures (5) is necessary. On the other side, coextraction of alkaline earth chlorides with alcohols can be suppressed by the addition of ammonia (6) or urea (7). For the separation of lithium from magnesium and sodium, extraction with mixtures of butanol and hexanediols is also recommended (8).

The purpose of this study was to find combinations of solvents which are able to extract lithium chloride in good yields without the accompanying chlorides of calcium and magnesium. Lithium chloride is soluble in many solvents. However, because of solubility differences, 2-ethyl-1,3-hexanediol, diisopropyl ether, and diethyl ether were chosen as possible components for mixtures with isoamyl alcohol.

EXPERIMENTAL

The extraction was studied by using solutions of pure metal chlorides as well as a native brine which is a by-product from the winning of natural

TABLE 1
Composition of a Representative Sample of Brine (main components)

Element	Concentration	
	g/L	M
Na	46.945	2.042
Ca	36.072	0.900
K	4.013	0.103
Sr	2.548	0.029
Mg	0.608	0.025
Li	0.426	0.614
Cl	141.360	3.978
Br	0.555	0.007

gas. The composition of a representative sample is given in Table 1. The brine was concentrated at a density of 1.47 g/cm^3 in the extraction process.

To attain equilibrium, equal volumes of the organic and aqueous phases were shaken for 30 minutes at room temperature. If necessary, pH adjustment was made with triethanolamine–hydrochloric acid buffers. The concentrations of lithium, sodium, calcium, and magnesium in the aqueous solution were determined by flame emission spectroscopy (Flapho 4, Carl Zeiss Jena) and atomic absorption spectroscopy (AAS 1100 B, Perkin-Elmer).

RESULTS AND DISCUSSION

The extraction of selected alkali and alkaline earth chlorides from pure solutions with different solvents is reported by Table 2. A pH of 5.4 was chosen to correspond to the pH of the native brine. Table 2 shows that

TABLE 2
Extraction of Metal Chlorides from 10^{-4} M Solutions with Undiluted Extractants at pH 5.4; $V_o:V_w$ = 1:1, t = 30 minutes

Extractant	Extraction rate (%)			
	Li	Mg	Ca	Na
Isoamyl alcohol	25.2	19.2	16.7	5.3
2-Ethyl-1,3-hexanediol	32.8	0.6	0.8	4.1
Diisopropyl ether	11.4	<0.3	<0.2	<0.2
Diethyl ether	9.1	<0.3	<0.2	<0.2

TABLE 3

Extraction of Alkali and Alkaline Earth Ions from Native Brine at Different pH with Isoamyl Alcohol and Binary Solvent Mixtures (1:1) (t = 30 minutes, $V_o:V_w$ = 1:1)

Extractant	pH	Extraction rate (%)			
		Li^+	Na^+	Ca^{2+}	Mg^{2+}
Isoamyl alcohol (*3*)	5.4	90.0	[a]	20.0	50.0
2-Ethyl-1,3-hexanediol/	2.2	42.2	5.5	3.3	2.1
isoamyl alcohol	5.4	38.6	6.1	3.6	2.7
Diisopropyl	2.2	26.7	0.13	2.8	1.7
ether/isoamyl alcohol	5.4	27.6	0.1	2.9	1.6
Diethyl ether/	2.2	24.1	0.12	2.5	1.3
isoamyl alcohol	5.4	23.9	0.09	2.5	1.3

[a] Not determined.

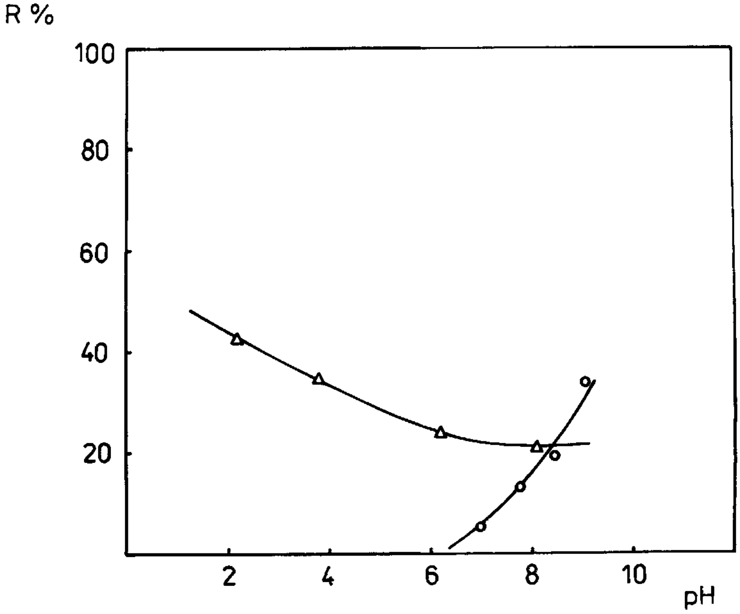

FIG. 1 Extraction of lithium chloride and calcium chloride from 0.01 M solutions with an equimolar mixture of isoamyl alcohol and 2-ethyl-1,3-hexanediol and the dependence on pH ($V_o:V_w$ = 1:1; t = 30 min): (△) Li, (○) Ca.

mixtures of isoamyl alcohol with ethers or 2-ethyl-1,3-hexane-diol should be suitable for extracting lithium chloride whereas suppression of the coextraction of alkaline earth chlorides is to be expected. Results of the extraction of native brine with isoamyl alcohol and mixtures of the extractants mentioned above are summarized in Table 3. It can be seen that the extraction of alkaline earth chlorides barely takes place, but the extraction of lithium chloride also decreases. Furthermore, a dependence on pH is evident in the case of 2-ethyl-1,3-hexanediol. More exact relationships are shown by Fig. 1. While extraction of lithium chloride decreases with pH, extraction of calcium chloride simultaneously increases. Therefore, the best conditions for the specific separation of lithium from native brines involve acidic solutions. However, for any technical application, brine with its original pH of 5.6 must be used because it is unprofitable to consume larger amounts of acid.

CONCLUSIONS

Lithium chloride can be selectively extracted from brines by mixtures of isoamyl alcohol with ethers or 2-ethyl-1,3-hexanediol. The admixtures suppress the coextraction of alkaline earth chlorides but also diminish the extraction of lithium chloride, which must be compensated for by increasing the number of separation stages.

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