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Competitive Extraction of Pb^{2+} by Dicyclohexano-18-crown-6 from Heavy Metal Aqueous Solutions

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Dicyclohexano-18-crown-6 was found to selectively remove Pb^{2+} from aqueous solutions containing it alone, and with other cations. Distribution ratios for liquid−liquid extraction of heavy metal cations such as Pb^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} by some crown ethers (dicyclohexano-18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5) were reported. SCN^-, NO_3^-, and Cl^- were used as anions while nitrobenzene, chloroform, toluene, and an equimolar mixture of nitrobenzene and chloroform were the solvents.

Introduction

In solvent extraction of metallic ions, it is possible to use a variety of ligands as extracting agents, that can form chelate complexes or ion pairs with metallic ions. In particular, macrocyclic ligands, such as certain crown ethers, complex selectively with cations and have played an important role in removing toxic metals from waste water (Izatt *et al.*, 1987, 1991; Bacon and Kirch, 1987; Lindoy, 1991; Parham and Shamsipur, 1994).

This work, which is part of a study on the use of crown ethers as possible extracting agents (Dernini *et al.*, 1991, 1992), deals with the ability of certain crown ethers (benzo-15-crown-5, dibenzo-18-crown-6, and dicyclohexano-18-crown-6) to remove lead from aqueous solutions containing lead alone, and lead with other cations. In addition, the role of the solvent in the metal extraction was considered. Measurements were also made using a mixed solvent.

Experimental Section

Materials. The following inorganic salts, macrocyclic polyethers, and organic solvents (Aldrich Chemie) were used in the experiments without further purification: $PbCl_2$ (98%), $NiCl_2$ (99%), $CoCl_2$ (97%), $CuCl_2{\cdot}2H_2O$ (>99%), $ZnCl_2$ (98%), $Pb(SCN)_2$ (99.5%), $Pb(NO)_3$ (99%), dicyclohexano-18-crown-6, benzo-15-crown-5, benzo-15-crown-5 (all 98%), nitrobenzene, chloroform, toluene (all >99%). The purity of the materials was always expressed in mass %.

Measurements of Extraction Equilibria. Distilled water and the organic solvents were pre-equilibrated with each other in order to minimize volume changes during extractions. Equal volumes of aqueous solutions of the inorganic salts (1×10^{-4} to 1×10^{-2}) mol dm^{-3} and organic solvent containing the crown (1×10^{-4} to 1×10^{-2}) mol dm^{-3} were shaken in a thermostatic bath at (25 ± 0.5) °C for 15 min. The phases were allowed to settle overnight in the bath.

Then samples of the aqueous solution were withdrawn, appropriately diluted, and analyzed for cation concentration on an atomic absorption spectrophotometer (IL VIDEO 12). Each experiment was repeated three times for each system, and the results agreed within 3%. The results are expressed as the distribution ratio $D = (c_M)_o/(c_M)_a$ of the molar concentration of the metal between the two phases, where the subscripts a and o refer to the aqueous and organic phases respectively.

Blank experiments were performed with the solvent containing no crown ether, and in no case was there detectable extraction of the cation from the aqueous phase.

Results

Complexation and Stoichiometry. When equilibrium is achieved between an aqueous phase containing a metal ion M^{m+} and a counteranion A^- and an organic phase containing a neutral crown ether L, a crown ether complex ML_nA_m is considered to be formed (Frensdorff, 1971; Tanigawa *et al.*, 1988) and the overall equilibrium

$$\mathrm{M_a}^{m+} + m\mathrm{A_a}^{-} + n\mathrm{L_o} \rightleftarrows (\mathrm{ML}_n\mathrm{A}_m)_\mathrm{o} \tag{1}$$

can be expressed by means of the overall equilibrium constant K:

$$K = \frac{[\mathrm{ML}_n\mathrm{A}_m]_\mathrm{o}}{[\mathrm{M}^{m+}]_\mathrm{a}[\mathrm{A}^-]_\mathrm{a}{}^{m}[\mathrm{L}]_\mathrm{o}{}^{n}} \tag{2}$$

Under the assumption that the crown ether complex scarcely dissociates in the organic phase the extraction reaction (1) might be expressed through the following reaction scheme:

$$\mathrm{L_a} \rightleftarrows \mathrm{L_o} \tag{3}$$

$$K_\mathrm{DL} = \frac{[\mathrm{L}]_\mathrm{o}}{[\mathrm{L}]_\mathrm{a}} \tag{4}$$

$$n\mathrm{L_a} + \mathrm{M_a}^{m+} \rightleftarrows (\mathrm{M}^{m+}\mathrm{L}_n)_\mathrm{a} \tag{5}$$

$$K_\mathrm{ML} = \frac{[\mathrm{M}^{m+}\mathrm{L}_n]_\mathrm{a}}{[\mathrm{M}^{m+}]_\mathrm{a}[\mathrm{L}]_\mathrm{a}{}^{n}} \tag{6}$$

$$(\mathrm{M}^{m+}\mathrm{L}_n)_\mathrm{a} + m\mathrm{A_a}^{-} \rightleftarrows (\mathrm{ML}_n\mathrm{A}_m)_\mathrm{o} \tag{7}$$

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$$K^1 = \frac{[\mathrm{ML}_n\mathrm{A}_m]_\mathrm{o}}{[\mathrm{M}^{m+}\mathrm{L}_n]_\mathrm{a}[\mathrm{A}^-]_\mathrm{a}^{\,m}} \qquad (8)$$

where $\mathrm{M}^{m+}\mathrm{L}_n$ = crown−cation complex.

Since the K_DL values in the dicyclohexano-18-crown-6 systems examined are large, the material balance of each component becomes

$$[\mathrm{M}^{m+}]_\mathrm{a} = c_\mathrm{s}^\circ - [\mathrm{ML}_n\mathrm{A}_m]_\mathrm{o} \qquad (9)$$

$$[\mathrm{L}]_\mathrm{o} = c_\mathrm{L}^\circ - n[\mathrm{ML}_n\mathrm{A}_m]_\mathrm{o} \qquad (10)$$

$$[\mathrm{A}^-]_\mathrm{a} = m[\mathrm{M}^{m+}]_\mathrm{a} \qquad (11)$$

where c_s° is the initial salt concentration and c_L° the initial crown concentration.

Equation 2 can be written as

$$\log \frac{[\mathrm{ML}_n\mathrm{A}_m]_\mathrm{o}}{[\mathrm{M}^{m+}]_\mathrm{a}[\mathrm{A}^-]_\mathrm{a}^{\,m}} = n \log\,[\mathrm{L}]_\mathrm{o} + \log K \qquad (12)$$

Using the measured values of $[\mathrm{M}^{m+}]_\mathrm{a}$, the weighed values of c_s° and c_L°, and the calculated values of $[\mathrm{ML}_n\mathrm{A}^m]_\mathrm{o}$, and $[\mathrm{L}]_\mathrm{o}$, the relationship between $\log\,[\mathrm{ML}_n\mathrm{A}^m]_\mathrm{o}/[\mathrm{M}^{m+}]_\mathrm{a}[\mathrm{M}^{m+}]_\mathrm{a}^{\,m}$ and $\log\,[\mathrm{L}]_\mathrm{o}$ was plotted, according to eq 12, and it was possible to calculate n and $\log K$ values using the least squares method. Activities equal to concentrations were always assumed in calculations, because the activity coefficients of organic species were not calculable failing literature information on the subject.

Combination of Crown Ether and Cation. In this work the dicyclohexano-18-crown-6, dibenzo-18-crown-6, and benzo-15-crown-5 crowns ethers (Figure 1) were considered for the removal of Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, and Pb^{2+} from waste water. Since 1967 (Pedersen, 1967) it has been reported that the size match between the cavity radius of the crown ether and the cation radius is an important parameter in metal extraction from aqueous solutions. In Table 1 the diameters of the crown ethers and the cations examined are reported. Figure 2 shows the extraction results: only Pb^{2+} is selectively and quantitatively extracted by means of dicyclohexano-18-crown-6. The much lower distribution ratio D obtained for the Pb^{2+} extraction by dibenzo-18-crown-6, compared with that of the extraction by dicyclohexano-18-crown-6, can be attributed to the electron withdrawing effect of benzo groups (Izatt *et al.*, 1986).

The very low distribution ratios obtained for Cu^{2+}, Co^{2+}, and Zn^{2+} with benzo-15-crown-5 are not explained by the fit between the carrier cavity and the size of metal ion: other factors, like the substitution groups and the number of oxygen atoms in the crown ether molecule, and also possible changes in the conformation of the macrocycle during complexing, have an important influence on extraction (Izatt *et al.*, 1983, 1988; Morosanova *et al.*, 1984; Tanigawa *et al.*, 1988).

Effect of Anion Type. Salts are extracted by neutral macrocyclic carriers via a cation−macrocycle−anion pair in the organic solvent. The distribution ratio D varies greatly with anion type for a given cation−carrier combination. According to Marcus and Asher (1978) extraction is efficient only if the anion is large and higly polarizable. In this work chloride, nitrate, and thiocyanate anions have been used, and only the large and lipophilic thiocynate anion gave good extraction (Muray *et al.*, 1990; Updhyay *et al.*, 1994). The experimental results for Pb^{2+} extraction by dicyclohexano-18-crown-6 in nitrobenzene with the different anions are shown in Figure 3 and are reported in Table 2.

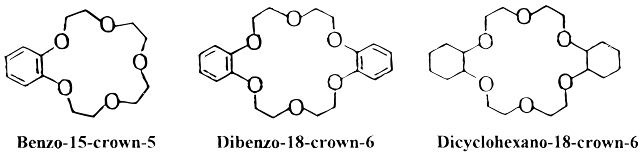

Figure 1. Chemical structure of dicyclohexano-18-crown-6, dibenzo-18-crown-6, and benzo-15-crown-5.

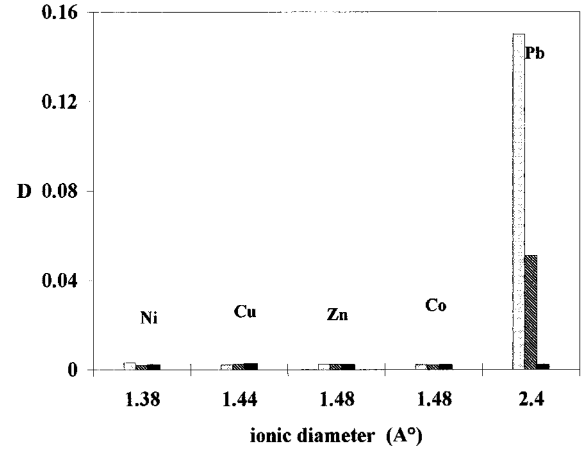

Figure 2. Extraction of M^{2+} from aqueous solutions containing $\mathrm{M(Cl)_2}$, in nitrobenzene containing different crown ethers: (dots) dicyclohexano-18-crown-6; (stripes) dibenzo-18-crown-6; (solid) benzo-15-crown-5; $c_\mathrm{L}^\circ = 1 \times 10^{-2}$ mol dm^{-3}, $c_\mathrm{s}^\circ = 1 \times 10^{-3}$ mol dm^{-3}.

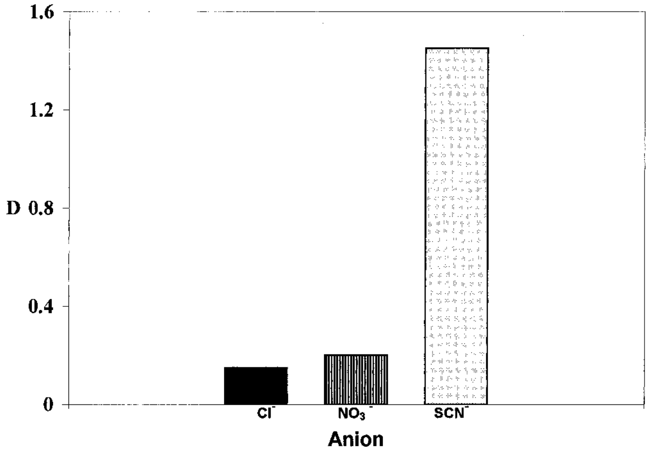

Figure 3. Extraction of Pb^{2+} from aqueous solutions with different anions, in nitrobenzene containing dicyclohexano-18-crown-6; $c_\mathrm{s}^\circ = 8 \times 10^{-4}$ mol dm^{-3}, $c_\mathrm{L}^\circ = 1 \times 10^{-2}$ mol dm^{-3}.

Table 1. Cation and Crown Ether Cavity Diameters, *d*

cation	d/Å[a]	crown	d/Å[b]
Ni^{2+}	1.3	benzo-15-crown-5	1.72−1.84
Cu^{2+}	1.44	dibenzo-18-crown-6	2.68−2.86
Zn^{2+}	1.48	dicyclohexano-18-crown-6	2.68−2.86
Co^{2+}	1.48		
Pb^{2+}	2.4		

[a] Henderson (1982). [b] Izatt *et al.* (1983).

Effect of Solvent. The Pb^{2+} extraction experiments were performed using toluene, chloroform, nitrobenzene, and a mixed solvent consisting of an equimolar mixture of the last two. For low crown concentrations (1×10^{-4} to 1×10^{-2}) mol dm^{-3} the ability of the solvents to remove Pb^{2+}

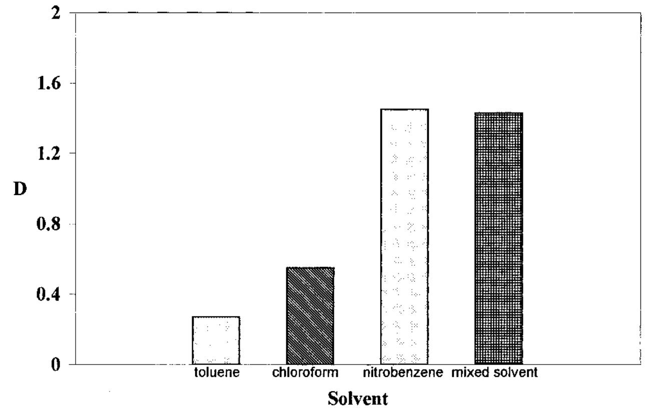

Figure 4. Extraction of Pb^{2+} from aqueous solutions containing $Pb(SCN)_2$, in different solvents containing dicyclohexano-18-crown-6; $c_L^\circ = 1 \times 10^{-2}$ mol dm^{-3}, $c_S^\circ = 8 \times 10^{-4}$ mol dm^{-3}.

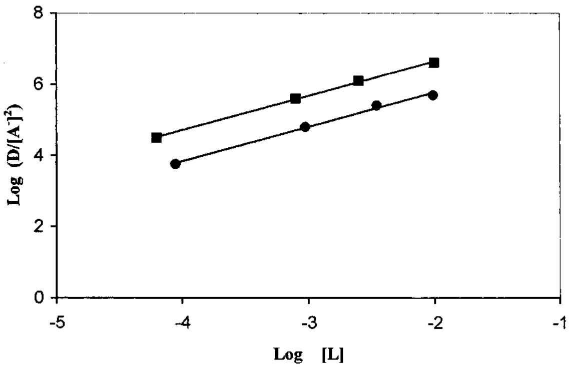

Figure 5. Plot of log $(D/[A^-]_a{}^m)$ *vs* log $[L]_o$ for the $Pb(SCN)_2$–dicyclohexano-18-crown-6 system at 25 °C; $c_S^\circ = 8 \times 10^{-4}$ mol dm^{-3}.

Table 2. Extraction Data for PbA_2 in a 10^{-2} mol dm^{-3} Dicyclohexano-18-crown-6 Organic Solvent

		D		
A^-	$c_{Pb^{2+}}$/(mol dm^{-3})	$CHCl_3$	$C_6H_5NO_2$	$CHCl_3 + C_6H_5NO_2$
Cl^-	1×10^{-3}	0.05	0.15	0.13
NO_3^-	1×10^{-3}	0.056	0.2	0.21
SCN^-	8×10^{-4}	0.553	1.45	1.43

decreased in the order nitrobenzene ≅ mixed solvent > chloroform > toluene, as shown in Figure 4, and in Table 2, where the obtained distribution ratios for nitrobenzene, chloroform, and mixed solvent systems are reported. In this sequence the polarity of the solvent seems to be important (Izatt, 1986; Marcus and Asher, 1978; Shukla *et al.*, 1992).

Effect of Crown Concentration. A number of Pb^{2+} extraction experiments were carried out using different concentrations of crown. In the range (1×10^{-4} to 1×10^{-2}) mol dm^{-3} the plots of log $(D/[A^-]_a{}^m)$ as a function of log $[L]_o$ were reported in Figure 5. Straight lines were obtained, and always slope values of near unity confirmed the 1:1 complex stoichiometry.

The following values of overall extraction equilibrium constants, calculated as intercepts, were obtained for the Pb^{2+} cation:

$$\mathrm{Pb(SCN)_2 + dicyclohexano\text{-}18\text{-}crown\text{-}6 + chloroform + H_2O} \qquad \log K = 7.71$$

$$\mathrm{Pb(SCN)_2 + dicyclohexano\text{-}18\text{-}crown\text{-}6 + nitrobenzene + H_2O} \qquad \log K = 8.58$$

Competitive Extraction. Extraction experiments were conducted on equimolar binary cation mixtures containing Pb^{2+} with one other cation (Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}). Pb^{2+} was always extracted selectively over the others, and the measured *D* values were similar to that obtained in single extractions.

Extraction experiments on a mixture containing Pb^{2+} with all the other cations (Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}) were also performed. In this case not only was the Pb^{2+} extracted selectively but also the *D* values observed were much higher than those in single extraction. For the system nitrobenzene + water, using a dicyclohexano-18-crown-6 concentration of 1×10^{-2} mol dm^{-3}, and a metallic chloride concentration of 1×10^{-3} mol dm^{-3} for all the cations, *D* of Pb^{2+} increased from 0.15, for single extraction, to 5.1, for multiple competitive extractions.

This result shows that very often in a competitive system, the selective extraction of a cation over the others cannot be determinated from a single cation system. Also Izatt, when investigating the selective separation of Ag^+ from $Ag^+{-}M^{n+}$ mixtures (Izatt *et al.*, 1983, 1988a) or that of Pb^{2+} from $Pb^{2+}{-}M^{n+}$ mixtures, using macrocycles, obtained results not expected from single cation experiments (Izatt *et al.*, 1982).

The results obtained confirmed the possibility of using dicyclohexano-18-crown-6 to remove Pb^{2+} from waste water even if the Pb^{2+} is at very low concentrations. In fact, a number of extraction experiments were also performed at different salt concentrations; the examined range was (1×10^{-4} to 1×10^{-2}) mol dm^{-3}. In the case of the system nitrobenzene + dicyclohexano-18-crown-6 + water + $PbCl_2$ using a crown concentration of 1×10^{-2} mol dm^{-3}, the metal distribution ratio value increased from 0.12 to 0.19 when the Pb^{2+} concentration varied from (1×10^{-2} to 1×10^{-4}) mol dm^{-3}, respectively.

In conclusion, it might be interesting and worthwhile to employ dicyclohexano-18-crown-6 in a membrane-based Pb^{2+} extraction process.

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