J. Chem. Research (S), 1999, 299
J. Chem. Research (M), 1999, 1401–1414

Study of Solvent Extraction of Mercury(II) with Dibenzo-18-Crown-6 from Hydrochloric Acid Solution into Benzene

Rita Giovannetti,*[a] Vito Bartocci[b] and Laura Petetta[a]

[a] *Centro Interdip. Grandi Apparecchiature, Università di Camerino, 62032 Camerino, Italy*
[b] *Dipartimento di Scienze Chimiche, Università di Camerino, 62032 Camerino, Italy*

The effect of Li^+, K^+, NH_4^+, Ca^{2+} or Sr^{2+} in the extraction of mercury(II) as chloro-complexes from solutions in hydrochloric acid with dibenzo-18-crown-6 (DB18C6) into benzene and the stoichiometries of the reactions have been studied. The crystalline extracted species were characterized by morphological and microanalysis measurements by scanning electron microscopy and energy dispersive X-ray spectrometry respectively.

Crown ethers are a class of selective ligands that form fairly stable stoichiometric complexes with metal ions or cationic compounds with high selectivity; for this reason they have largely applied to analytical chemistry especially in solvent extraction.[3,4] Here, we report a study of the extraction mechanism of mercury(II) as chloro-complexes with DB18C6 (L) into benzene in the presence of Li^+, K^+, NH_4^+, Ca^{2+}, Sr^{2+} and the characterization of the solid extracted complex by morphological and microanalysis measurements.

The study has showed that mercury(II) was prevalently extracted as $HgCl_4{}^{2-}$ by forming ion-pair compounds $[(L_2M_2)^{2+}(HgCl_4)^{2-}]$ ($M = Li^+, K^+$ or NH_4^+), or $[(LM)^{2+}(HgCl_4)^{2-}]$ ($M = Ca^{2+}$ or Sr^{2+}) and $[(LH)^+(HHgCl_4)^-]$. The extractability of Hg^{II} in the presence of these cations decreased in accordance with their ionic diameter (Fig. 1). The log $K_{M,ex}$ values ($K_{M,ex}$ = extraction conditional constants) were: 3.03 ± 0.09 for $[(L_2K_2)^{2+}(HgCl_4)^{2-}]$, 2.76 ± 0.02 for $[(L_2Li_2)^{2+}(HgCl_4)^{2-}]$, 2.71 ± 0.03 for $[(LNH_4)_2{}^{2+}(HgCl_4)^{2-}]$, 0.86 ± 0.01 for $[(LH)^+(HHgCl_4)^-]$, 1.76 ± 0.03 for $[(LCa)^{2+}(HgCl_4)^{2-}]$ and 2.05 ± 0.03 for $[(LSr)^{2+}(HgCl_4)^{2-}]$. The global conditional extraction constants ($K_{M,H,ex}$) increased with HCl concentration for the growth of the $[(LH)^+(HHgCl_4)^-]$ species. Morphological and microanalysis measurements of the DB18C6 and (DB18C6)KCl crystals show characteristic needle-shaped structures, while, for $(DB18C6)_2K_2HgCl_4$ a highly modified sheet structure is seen.

Techniques used: inductively coupled plasma, UV–VIS spectroscopy, scanning electron microscopy, energy dispersive-X-ray spectrometry.

Table 1: Extraction conditional constants for the complexes $[(LM)^{2+}(HgCl_4)^{2-}]$ (M = monovalent cation), $[(L_2M_2)^{2+}HgCl_4^{2-})]$ (M = bivalent cation) and $[(LH_2)^{2+}(HgCl_4)^{2-})]$ at 25 °C (M = 0.9 mol l^{-1} and HCl = 1.5 mol l^{-1})

Table 2: Analytical data of extracted complex mixtures of $L_2K_2HgCl_4$, LH_2HgCl_4 and LKCl with DB18C6 (1.3×10^{-2} mol l^{-1}), KCl (0.9 mol l^{-1}) and HCl (1.5 mol l^{-1})

References: 13

Fig. 2: Extraction of Hg^{II} as a function of HCl concentrations by a benzene solution of DB18C6 (1.30×10^{-2} mol l^{-1}).

Fig. 3: Concentration of $[(LH)^+(HHgCl_4)^-]$ species as a function of HCl concentration for a benzene solution of DB18C6 (1.30×10^{-2} mol l^{-1}).

* To receive any correspondence (*e-mail:* Giovannetti<bartocci@camserv.unicam.it>).

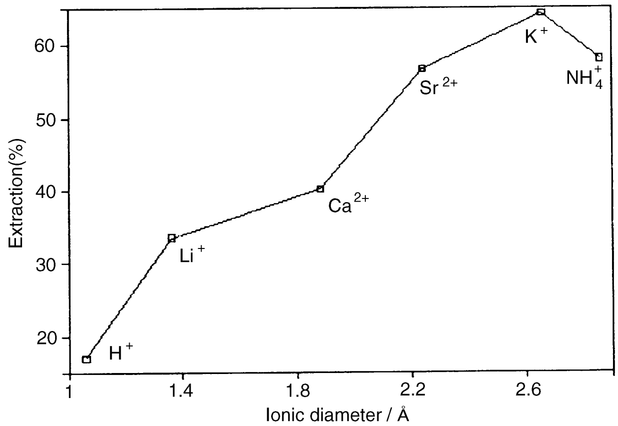

Fig. 1 Extraction of Hg^{II} as function of ionic diameter of cations. Conditions: $Hg^{II} = 8.00 \times 10^{-5}$ mol l^{-1} in HCl (1.50 mol l^{-1}); KCl, $SrCl_2$, $CaCl_2$, NH_4Cl or LiCl (0.90 mol l^{-1}); DB18C6 (1.30×10^{-2} mol l^{-1})

Fig. 4: log $K_{M,H,ex}$ as a function of HCl concentration and ionic strength.

Fig. 5: log $K_{M,H,ex}$ as a function of HCl concentration and ionic strength.

Fig. 6: Scanning electron micrographs of DB18C6 and solid extracted complex.

Fig. 7: EDS spectrum obtained during microanalysis of $(DB18C6)_2K_2HgCl_4$ and $(DB18C6)H_2HgCl_4$ crystals.

Fig. 8: Scanning electron micrographs of a mixture of $(DB18C6)_2K_2HgCl_4$ and (DB18C6)KCl crystals and backscattered electron image of the same region.

Fig. 9: EDS spectra obtained during microanalysis of a mixture of $(DB18C6)_2K_2HgCl_4$, $(DB18C6)H_2HgCl_4$ and (DB18C6)KCl crystals in the light and grey zone of Fig. 5.

Fig. 10: Scanning electron micrographs showing fuller details of $(DB18C6)_2K_2HgCl_4$ and $(DB18C6)H_2HgCl_4$ corresponding to the light zone in the backscattered electron image.

Received, 11th August 1998; Accepted, 2nd February 1999
Paper E/8/06361C

References cited in this synopsis

3 H. K. Frensdorff, *J. Am. Chem. Soc.*, 1971, **93**, 4684.
4 *Macrocyclic Compounds in Analytical Chemistry; Chemical Analysis*, ed. Yu. A. Zolotov, Wiley, New York, 1977, vol. 143, ch. 3.