Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

EXTRACTION OF MERCURY(II) WITH DICYCLOHEXANO-18-CROWN-6, AND ITS APPLICATION TO INDUSTRIAL WASTES

T. Francis[a]; R. Meera[a]; M. L. P. Reddy[a]
[a] Inorganic and Analytical Chemistry Unit, Regional Research Laboratory (CSIR), Trivandrum, India

To cite this Article Francis, T. , Meera, R. and Reddy, M. L. P.(2001) 'EXTRACTION OF MERCURY(II) WITH DICYCLOHEXANO-18-CROWN-6, AND ITS APPLICATION TO INDUSTRIAL WASTES', Separation Science and Technology, 36: 10, 2341 — 2353

To link to this Article: DOI: 10.1081/SS-100105922

URL: http://dx.doi.org/10.1081/SS-100105922

SEPARATION SCIENCE AND TECHNOLOGY, 36(10), 2341–2353 (2001)

EXTRACTION OF MERCURY(II) WITH DICYCLOHEXANO-18-CROWN-6, AND ITS APPLICATION TO INDUSTRIAL WASTES

T. Francis, R. Meera, and M. L. P. Reddy*

Inorganic and Analytical Chemistry Unit,
Regional Research Laboratory (CSIR),
Trivandrum-695019, India

ABSTRACT

As part of the study of hazardous metal ion separation from industrial wastes, the extraction behavior of Hg(II) from dilute hydrochloric acid solutions with dicyclohexano-18-crown-6 (DC18C6) in 1,2-dichloroethane was investigated. For comparison, extraction studies also were carried out with 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), and dibenzo-18-crown-6 (DB18C6). The extraction data were analyzed by both graphical and theoretical methods that account for aqueous phase complexation with inorganic ligands and all plausible complexes extracted into the organic phase. The results demonstrate that Hg(II) is extracted into dichloroethane as $HgCl_2 \cdot 2$Crown Ether. The $HgCl_2 \cdot$DC18C6 solid complex was prepared and characterized by elemental analysis, and IR (infrared) and ^{1}H-NMR (nuclear magnetic resonance) spectral studies. The possible means of extracting and separating Hg(II) from other metal ions, such as Mg(II), Ca(II), Ba(II), and Fe(III), that are present in the industrial wastes

---

*Corresponding author. E-mail: reddy@csrrltrd.ren.nic.in

www.dekker.com

of the chlor-alkali industry is discussed. The potential of the DC18C6 for decontaminating mercury from the brine sludge of a chlor-alkali plant has been assessed.

Key Words: Mercury (II); Solvent extraction; Crown ethers; Industrial wastes

INTRODUCTION

Mercury is considered by the Environmental Protection Agency (EPA) a highly dangerous element because of its accumulative and persistent character in the environment and biota. Today, both inorganic and organic mercury compounds are produced in industrial processes for agricultural products, paper, pharmaceuticals, and the chlor-alkali industry. Methylmercury is a neurotoxin; it causes blockages of enzyme binding sites and interferes in protein synthesis. Moreover, inorganic mercury can be transformed into methylmercury by the action of microorganisms under aerobic conditions. Thus the control and removal of mercury from industrial waste streams has received considerable attention in recent years (1). Conventional mercury-treatment technologies include carbon adsorption, cementation and roasting (2). More recently, solvent extraction processes have also been used for mercury recovery from industrial waste (3).

The discovery that crown ethers selectively complex alkali and alkaline-earth metals led to many studies of their use in solvent extraction processes (4,5). In early research efforts, workers noted that a match between the cavity size of the crown ether and the ionic diameter of the metal ion corresponded to high extraction selectivity (6,7). Thus, appropriately sized crown ethers could be chosen to obtain selective extraction of particular cations. The nature of substituent groups on the macrocyclic ring is another factor that influences the selectivity of crown ethers. Recently, Giovannetti, Bartocci, and Petetta (8) investigated the extraction of Hg(II) from hydrochloric acid solutions (1–7 mol/L) with DB18C6 into benzene in the presence of lithium, potassium, ammonium, and calcium chlorides and reported that Hg(II) was extracted prevalently as $HgCl_4^{2-}$ by forming ion-pair compounds of $[(DB18C6)_2(M^+)_2(HgCl_4^{2-})]$, where $M^+ = Li^+, K^+$, or NH_4^+, or $[(DB18C6)(M^{2+})(HgCl_4^{2-})]$, where $M^{2+} = Ca^{2+}$, and $[(DB18C6)(H^+)(HgCl_4^{2-})]$. Talanova et al. reported remarkable extraction selectivity for Hg(II) for the series of proton-ionizing calix[4]arene di(*N*-X-sulfonyl carboxamides) (9) and with a calixarene-based fluorogenic reagent (10). Selective complexation of Hg^{2+} by *bis*-calix[4]arene nitriles has also been reported by Shahabuddin Memon et al. (11).

In the research presented in this paper, the extraction behavior of Hg(II) from dilute hydrochloric acid solutions through the use of dicyclohexano-18-

crown-6 (DC18C6) was investigated to elucidate the nature of the complexes extracted into the organic phase and also to investigate the selectivity of this ligand toward Hg^{2+}. For comparison, extraction studies were carried out with 18-crown-6 ether (18C6), benzo-18-crown-6 ether (B18C6), and dibenzo-18-crown-6 ether (DB18C6). The potential of the DC18C6 for the recovery of mercury from the brine sludge of a chlor-alkali plant was also investigated.

EXPERIMENTAL

The tracer solution of ^{203}Hg was obtained from the Board of Radiation and Isotope Technology, India. The crown ethers, DC18C6 (mixture of *cis*-syn-*cis* and *cis*-anti-*cis*), 18C6, B18C6, and DB18C6 were obtained from Aldrich Chemical Company, Inc., Milwaukee, WI. All the other chemicals used were of analytical reagent grade.

Distribution Studies and Analytical Procedures

Equal volumes of the aqueous phase containing 0.01 mmol/L Hg(II) labeled with radioisotope and the organic phase were equilibrated in a glass, stoppered vial using a mechanical shaker at 303 ± 1 K. Preliminary experiments showed that the extraction equilibrium is attained within 60 min. The 2 phases were then separated and assayed radiometrically with a well-type NaI (Tl) gamma ray scintillation counter supplied by Nucleonix Systems Pvt. Ltd, India. The distribution ratio, D, is defined as the ratio of tracer activity in the organic phase to that in the aqueous phase.

Hg(II) in the chlorinated brine sludge of a chlor-alkali plant was analyzed spectrophotometrically with Rhodamine-6G (12). A Hitachi 220 double-beam, microprocessor-controlled spectrophotometer was used for measuring the absorbances. Metal ions, such as Mg(II), Ca(II), Ba(II), and Fe(III), were determined through standard volumetric methods (13). The amount of Hg(II) in the crown ether complex was determined by the following method: The complex was decomposed by heating in a minimum amount of 1:1 HNO_3:$HClO_4$ solution and the excess acid was evaporated. This was diluted with distilled water, and Hg(II) levels were determined by an ethylenediaminetetraacetic acid (EDTA) titration method (13).

Preparation of Solid Complex

The $HgCl_2 \cdot DC18C6$ complex was prepared as follows: Solutions containing 1 mmol $HgCl_2$ in 20 mL 1-butanol and 1 mmol DC18C6 in 20 mL 1-butanol were heated almost to boiling and then mixed. A Nicolet FTIR 560 Magna spectrometer using KBr (neat) was used to obtain the IR spectra of the metal complex. C, H, and N analysis was performed with a Perkin Elmer Series 2 Elemental Analyzer 2400. The Bruker 300MHz NMR spectrometer was used to obtain the ^{1}H-NMR spectra of the complex.

RESULTS AND DISCUSSION

Extraction of Hg(II) with Crown Ether

The complex formation of Hg(II) with chloride ions can be described as follows:

$$Hg^{2+} + nCl^- \overset{\beta}{\longleftrightarrow} HgCl_n^{2-n} \tag{1}$$

or the stepwise formation constants (K_n) can be described as follows :

$$\begin{aligned} &HgCl_{n-1}^{3-n} + Cl^- \overset{K_n}{\longleftrightarrow} HgCl_n^{2-n} \\ &K_n = \frac{[HgCl_n^{2-n}]}{[HgCl_{n-1}^{3-n}][Cl^-]} \end{aligned} \tag{2}$$

The extraction of neutral Hg(II) complexes into the organic phase with crown ether can be described as follows:

$$HgCl_{2\mathrm{aq}} + nCE_{\mathrm{org}} \overset{K_{\mathrm{ex,n}}}{\longleftrightarrow} HgCl_2 \cdot nCE_{\mathrm{org}} \tag{3}$$

where $n = 0$, 1, or 2.

The concentration of Hg^{2+} and $HgCl^+$ species can be assumed to be very small in the ligand concentration range studied (14,15). Then the distribution ratio, D, may be described as

$$D = \frac{[HgCl_2]_{\mathrm{org}} + [HgCl_2 \cdot CE]_{\mathrm{org}} + [HgCl_2 \cdot 2CE]_{\mathrm{org}}}{[HgCl_2]_{\mathrm{aq}} + [HgCl_3^-]_{\mathrm{aq}} + [HgCl_4^{2-}]_{\mathrm{aq}}} \tag{4}$$

From Eqs. (2), (3), and (4), a fundamental equation for D can be described as

$$D = \frac{K_{\mathrm{ex},0} + K_{\mathrm{ex},1}[CE]_{\mathrm{org}} + K_{\mathrm{ex},2}[2CE]_{\mathrm{org}}^2}{1 + K_3[Cl^-]_{\mathrm{aq}} + K_3K_4[Cl^-]_{\mathrm{aq}}^2} \tag{5}$$

where $[CE]_{\mathrm{org}} = [CE]_{\mathrm{initial}} / [\,1 + (1/K_D)]$

The values of partition coefficients (K_D) of various crown ethers were obtained from the literature: $\log K_{D,18C6} = -0.04$; $\log K_{D,DC18C6} = 2.29$; $\log K_{D,B18C6} = 4.00$) (16–18). The values of stepwise stability constants ($\log K_3 = 0.85$;

$\log K_4 = 1.0$) were taken from the literature (19). The equilibrium constants of the extracted complexes were determined by nonlinear regression analysis as follows:

1. Values were assumed for $K_{ex,0}$, $K_{ex,1}$, and $K_{ex,2}$.
2. The equilibrium concentrations of the crown ether described in Eq. (5) were determined with the knowledge of initial concentrations of crown ether and K_D.
3. The distribution ratio values D under the given conditions were calculated (D_{cal}) and compared with the experimental values (D_{exp}).
4. The values of the assumed equilibrium constant, which lead to minimum, root, mean-square fractional error, y, where

$$y = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{D_{cal,i} - D_{exp,i}}{D_{exp,i}}\right\}^2}$$

for all the experimental values were assumed to be the equilibrium constant for the system under consideration.

For confirming the above extraction equilibrium, 0.01 mmol/L Hg(II) was investigated with varying concentrations of hydrochloric acid (0.05–0.1 mol/L) and 0.002 mol/L DC18C6 in 1,2-dichloroethane. The results are shown in Fig. 1. The results show that the extraction of Hg(II) decreases continuously with increasing hydrochloric acid concentrations in the aqueous phase. This may be due to the formation of $HgCl_3^-$ and $HgCl_4^{2-}$ in the aqueous phase with increased hydrochloric acid concentration.

The effect of DC18C6 concentration (0.002–0.01 mol/L) on the extraction of 0.01 mmol/L Hg(II) from 0.1 mol/L hydrochloric acid solutions was investi-

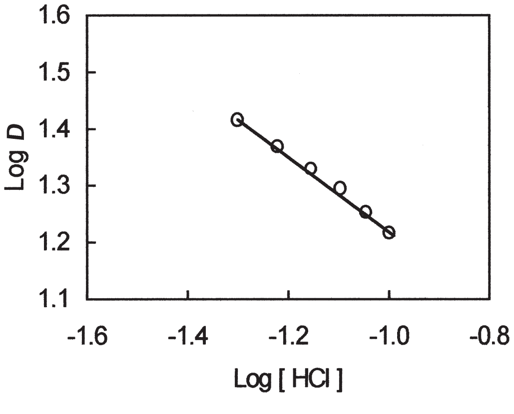

Figure 1. Effect of hydrochloric acid concentration on the extraction of Hg(II). DC18C6 = 0.002M; Hg(II) = 0.01mM.

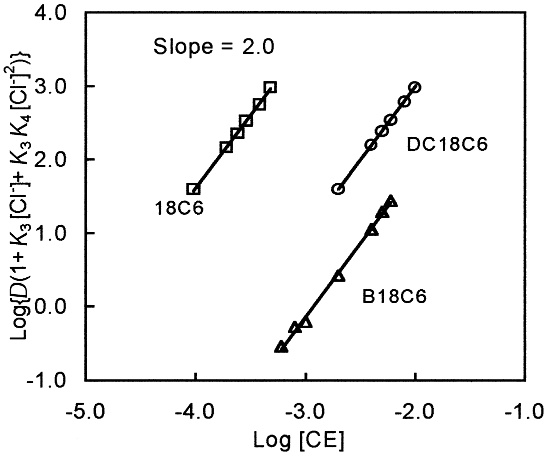

Figure 2. Effect of crown ether concentration on the extraction Hg(II). HCl = 0.1M; Hg(II) = 0.01mM.

gated, and the results are shown in Fig. 2. For comparison, extraction of Hg(II) was also carried out with 18C6, B18C6, and DB18C6 used as extractants. The distribution ratio, *D*, of Hg(II) increased linearly with increased crown ether concentrations and the slope of the log-log plot shows that two molecules of either DC18C6, 18C6, or B18C6 were associated with extractable complexes. However, the extraction of Hg(II) was negligible when DB18C6 from dilute hydrochloric acid solutions was used. Giovannetti, Bartocci, and Petetta (8) have reported ion-pair complexes of $[(DB18C6)_2(M^+)_2(HgCl_4^{2-})]$, where $M^+ = Li^+$, K^+, or NH_4^+, or $[(DB18C6)(M^{2+})(HgCl_4^{2-})]$, where $M^{2+} = Ca^{2+}$ or Sr^{2+}, for the extraction of Hg(II) from concentrated hydrochloric acid solutions (1–7 mol/L).

The effect of metal ion concentration (0.01–0.1 mmol/L) on the extraction process of Hg(II) was investigated through the use of 0.002 mol/L DC18C6 in 1,2-dichloroethane from 0.1 mol/L hydrochloric acid solutions. The log-log plot (Fig. 3) of the equilibrium organic-phase Hg(II) concentration against the aqueous-phase Hg(II) concentration is linear with slope = 1, indicating that only mononuclear species are extracted into the organic phase.

These distribution data (Figs. 1 and 2) were further analyzed for confirming the stoichiometry of the extracted complexes by nonlinear regression analysis with Eq. (5) where n = 0, 1, or 2. The best fit between the experimental and calculated *D* values was obtained only when the formation of the complex $HgCl_2 \cdot 2DC18C6$ (i.e., n = 2) was assumed. The values of equilibrium constants determined by nonlinear regression analysis of various crown ethers are given in Table 1. The extraction efficiency of Hg(II) with various crown ethers follows the order: 18C6 >

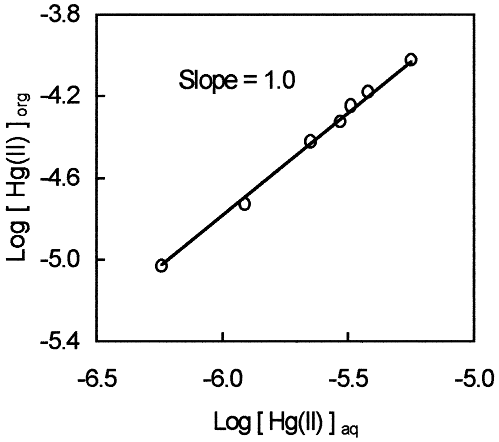

Figure 3. Effect of ion concentration on the extraction of Hg(II). DC18C6 = 0.02M; HCl = 0.1M.

DC18C6 > B18C6, which is also the basicity sequence of these crown ethers. The sharp decreases in the extraction efficiency of Hg(II) from 18C6 to DC18C6 and B18C6 mostly reflects increasing steric effect and decreasing basicity. The higher extractability of Hg(II) with 18C6 or DC18C6 can be explained on the basis of the "size-fitting effect "of these crown ethers. The 18C6 and DC18C6, with cavity sizes of 0.26 to 0.32 nm (20), complexes more strongly with metal ions having ionic diameter close to the cavity size, such as the Hg(II) of 0.22 nm (4). The theory of cavity-ion fit leads to the assumption that Hg(II) of 0.22 nm is too small to be stabilized by the size effect of DB18C6 (0.4 nm) (4). For practical application in solvent extraction, crown ethers must exhibit both high solubility in organic diluents and low distribution to the aqueous phase (highly lipophilic). Hence, for subsequent study for the recovery of Hg(II) from the brine sludge of the chlor-alkali plant, DC18C6 was chosen as an extractant due to its high solubility in organic diluents and its lipophilic nature in the 2-phase system.

Table 1. Equilibrium Constants of Various Crown Ethers for the Extraction of Hg(II)

Extractant	Log $K_{ex,2}$
18C6	9.62 ± 0.02
DC18C6	6.99 ± 0.03
B18C6	5.86 ± 0.04

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Table 2. Effect of Nature of Diluent on the Extraction of Hg(II) with 0.01 mol/L DC18C6

Diluent	D
Benzene	1.51
Toluene	5.34
Xylene	7.10
Chloroform	1.98
1,2-Dichloroethane	3.98

The extraction of 0.01 mmol/L Hg(II) from 0.1 mol/L hydrochloric acid solution with 0.01 mol/L DC18C6 in various diluents was investigated and the results are shown in Table 2. The extraction of Hg(II) varies with the nature of the diluent. The weak hydrogen bonding between the ether oxygen of crown ethers and dichloroethane results in higher extraction efficiency of Hg(II). When chloroform is used as the diluent, low extraction of Hg(II) was observed. This may be due to strong acid-base interaction, through hydrogen bonds, between the basic extractant CE and the acidic diluent. Among aromatic hydrocarbons, the extraction progresses in the order xylene $>$ toluene $>$ benzene.

Hg(II) stripping from a loaded organic system consisting of 0.02 mol/L DC18C6 in 1,2-dichloroethane and 0.01 mmol/L Hg(II) was investigated using various stripping agents, and Hg(II) is stripped almost entirely ($>$99.9%) through a single stage in which 5% NH_4Cl (in 1:10 NH_3) was used as the stripping agent. The results are given in Table 3.

Elemental Analysis, and IR and ^{1}H NMR Spectral Data

Elemental analysis of the extracted complex gave C 38.27%, H 5.61%, and Hg 30.77%, which compared with calculated values for $HgCl_2 \cdot$DC18C6 of C 37.3%, H 5.63%, and Hg 31.15%. This study clearly shows that $HgCl_2$ and

Table 3. Stripping Efficiency for Hg(II) with Different Reagents

Reagent	% Recovery of Hg(II)
5%Thiourea (pH = 11)	41.3
5% NH_4Cl (1:10 NH_3)	99.9
4 mol/L NaCl + 0.1 mol/L NaOH	0.0
0.01 mol/L $Na_2S_2O_3$ (pH = 11)	0.0

DC18C6 form a 1:1 complex. Paige and Richardson with crystallographic studies reported a similar 1:1 complex with $HgCl_2$ and 18C6 (21).

Infrared spectra of compounds, DC18C6 and the complex were recorded in the 4000–500 cm^{-1} region. The very intense, very broad, and probably multicomponent CH_2 stretching vibration band of the free ligand has a peak at 2865 cm^{-1}; on complexation the intensity is much reduced and the band becomes asymmetrical with a peak at 2926 cm^{-1}. However, the medium intensity peak, due to bending of CH_2 modes of the free ligand, at 1349 cm^{-1} is slightly downshifted to 1341 cm^{-1} for the complex. Likewise, the bands at 1120 and 847 cm^{-1} are shifted down to 1103 and 838 cm^{-1} respectively upon complexation. The metal-oxygen bands are most likely found to be in the far infrared region.

The ^1H NMR spectral data for DC18C6 and $HgCl_2 \cdot$DC18C6 was obtained in $CDCl_3$. The observed chemical shifts (ppm), and multiplicity and the number of protons are given in Table 4. The crown ether protons of the free ligand were observed as a multiplet at 3.67 ppm, and the CH_2 protons of cyclohexane were observed as a multiplet at 1.50 ppm (4). In the complex, the crown ether protons were observed as a multiplet at 3.71 ppm and the CH_2 protons of cyclohexane as a multiplet at 1.64 ppm. The observed NMR data confirms the formation of the complex $HgCl_2 \cdot$DC18C6.

Selectivity Studies Using DC18C6

The extraction of Mg(II) (0.02 mol/L), Ca(II) (0.02 mol/L), Ba(II) (0.02 mol/L) and Fe(III) (0.2 mol/L) from solutions containing 0.05 mol/L hydrochloric acid and through the use of 0.02 mol/L DC18C6 in 1,2-dichloroethane was investigated, and results showed that none of these metal ions were extracted into the organic phase. This finding is in good agreement with earlier reports for the extraction of Ca(II) and Ba(II) with DC18C6 (22). However, Hg(II) was found to be mostly (>99.9%) extracted under the above conditions. Thus, Hg(II) can be selectively separated from the above metal ions through the use of DC18C6.

Table 4. ^1H NMR Spectral Data

Compound	Crown Ether Protons (ppm)	CH_2 Protons of Cyclohexane (ppm)
DC18C6	3.67 (m, 20 H)	1.5 (m, 16 H)
$HgCl_2 \cdot$DC18C6	3.71 (m, 20 H)	1.64 (m, 16 H)

m represents multiplet.

Recovery of Mercury from Brine Sludge

The developed solvent extraction procedure for the extraction of mercury using DC18C6 was applied for the removal and recovery of mercury from the brine sludge of a chlor-alkali plant. One gram of the brine-sludge sample in 10 mL of 0.05 mol/L hydrochloric acid was chlorinated for 5–10 min for converting mercury into highly soluble mercuric chloride complexes. The chlorinated sludge was then subjected to solid-liquid separation and the filtrate was analyzed with a Rho-

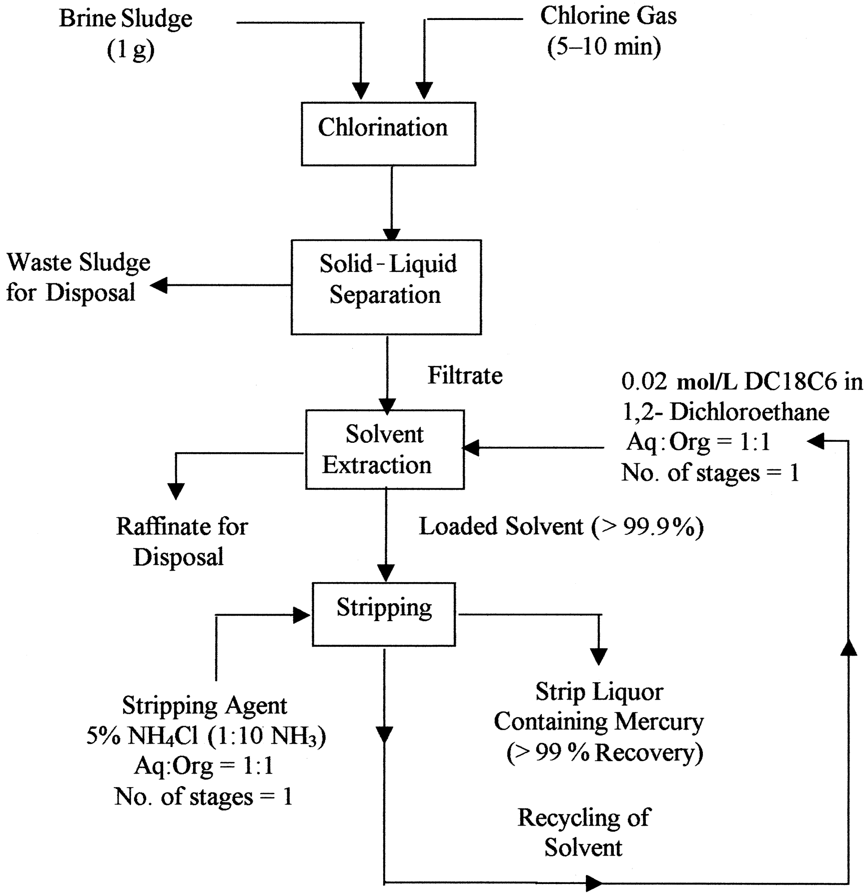

Figure 4. A Schematic diagram for the extraction of mercury from brine sludge of a chloralkali industry.

damine-6G spectrophotometer to determine the mercury content in the brine-sludge sample. The mercury content in the brine-sludge sample was found to be 160 μg/g of the sludge.

The extraction process of mercury from the brine sludge of a chlor-alkali plant is comprised of the following steps:

1. chlorination of the brine sludge;
2. solid-liquid separation;
3. bringing the resultant filtrate liquor (pH = 1–2) from solid-liquid separation containing the mercury (Hg^{2+} = 16 μg/mL) into contact with a substantially immiscible extractant phase, which is comprised of DC18C6 in 1,2-dichloroethane (0.02 mmol/L; Aq:Org = 1:1, whereupon the mercury to be separated selectively reversibly transfers into the extractant phase (single-stage extraction >99.9%);
4. backwashing the extractant phase with an aqueous system consisting of 5% NH_4Cl (in 1:10 NH_3) to recover all the mercury contained in the extractant phase (Aq:Org = 1:1; number of stages = 1).

A schematic procedure for the extraction process is given in Fig. 4. The investigations reveal that >99% mercury can be recovered selectively through a single-stage extraction and stripping process from the brine sludge of a chlor-alkali plant through the use of 0.02 mol/L DC18C6 in 1,2-dichloroethane.

CONCLUSIONS

This study clearly demonstrates the usefulness of DC18C6 as a selective reagent for the extraction of Hg(II) over Mg(II), Ca(II), Ba(II), and Fe(III) from dilute hydrochloric acid solutions (pH = 1–2). The extraction equilibrium of Hg(II) can be explained by a simple chemically based model presented in this paper. Furthermore, the results also indicate that DC18C6 can be used as a potential extractant for the selective extraction and separation of mercury from the brine sludge of a chlor-alkali plant.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Environment and Forests, Government. of India. The authors wish to thank Dr. G.D. Surender, Head, Mineral Processing Division, and Dr. G. Vijay Nair, Director, Regional Research Laboratory (CSIR), Trivandrum, for their constant encouragement.

REFERENCES

1. Sanchez Uria, J.E.; Sanz-Medel, A. Inorganic and Methylmercury Speciation in Environmental Samples. Talanta **1998,** *47*, 509–524.
2. de Carvalho, J.M.R.; Anacleto, A. Cementation of Mercury(II) from Chlor-Alkali Effluents by the Use of Zn and Fe. In *Hydrometall.'94*, Proceedings of the International Symposium on Hydrometallurgy, Chapman & Hall: London, 1994; 579–590.
3. Baba, Y.; Inoue, K.; Yoshizuka, K.; Yasukawa, R.; Tazaki, M. Removal of Mercury from Wastewaters by Extraction with Alkylthiol Compounds. Jpn. Kokai Tokkyo Koho JP 04164817 A2 .1992.
4. Pederson, C.J. Cyclic Polyethers and Their Complexes with Metal Salts. J. Am. Chem. Soc. **1967,** *89* (26), 7017–7036.
5. Izatt, R.M.; Pawlak, K.; Bradshaw, J.S.; Bruening, R.L. Thermodynamic and Kinetic Data for Macrocycle Interaction with Cations and Anions. Chem. Rev. **1991,** *91*, 1721–2085.
6. Christensen, J.J.; Hill, J.O.; Izatt, R.M. Ion Binding by Synthetic Macrocycle Compounds. Science **1971,** *174*, 459.
7. Lamb, J.D.; Izatt, R.M.; Christensen, J.J.; Eatough, D.J. Thermodynamics and Kinetics of Cation-Macrocyclic Interaction. In *Coordination Chemistry of Macrocyclic Compounds;* Melson, G.A., Ed.; Plenum: New York, 1979; 146.
8. Giovannetti, R.; Bartocci, V.; Petetta, L. Study of Solvent Extraction of Mercury (II) with Dibenzo-18-Crown-6 from Hydrochloric Acid Solution into Benzene. J. Chem. Res. (M) **1999,** *299,* 1401–1414.
9. Talanova, G.G.; Hwang, H.S.; Talanov, V.S.; Bartsch, R.A. Calix[4]arenes with Hard Donor Groups as Efficient Soft Cation Extractants: Remarkable Extraction Selectivity of Calix[4]arene *N*-(X)sulfonyl Carboxamides for Hg(II). Chem. Commun. **1998,** *13*, 1329–1330.
10. Talanova, G.G.; Elkarim, N.S.A.; Talanov, V.S.; Bartsch, R.A. A Calixarene-Based Fluorogenic Reagent for Selective Mercury (II) Recognition. Anal. Chem. **1999,** *71* (15), 3106–3109.
11. Memon, S.; Yilmaz, M.; Uysal, G. Selective Complexation of Hg^{2+} by Biscalix[4]arene Nitriles. Sep. Sci. and Tech. **2000,** *35* (8), 1247–1256.
12. Ramakrishna, T.V.; Aravamudan, G.; Vijayakumar, M. Spectrophotometric Determination of Hg(II) with Rhodamine 6G and Iodide. Anal. Chim. Acta **1976,** *84*, 369–372.
13. Vogel, A.I. *A Textbook of Quantitative Chemical Analysis*, 5th ed.; ELBS, Longman: Harlow, England, 1996; 329.
14. Sekine, T.; Ishii, T. Studies of the Liquid-Liquid Partition Systems VII. The Solvent Extraction of Mercury (II) Chloride, Bromide, Iodide, and Thiocyanate with Some Organic Solvents. Bull. Chem. Soc. Jpn. **1970,** *43* (8), 2422–2429.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

15. Reddy, M.S.; Reddy, M.L.P.; Damodaran, A.D. Extraction Equilibrium of Mercury(II) with bis(2-Ethylhexyl) Sulphoxide. J. Radioanal. Nucl. Chem. **1995,** *199* (2), 331–336.
16. Kolthoff, I.M.; Chantooni, M.K.J.; Wang, W. Partitioning of Crown Ether Complexed Univalent Metal Dichloropicrates Between Water and 1,2-Dichloro Ethane at 298K: Thermodynamic Representation. J. Chem. Eng. Data **1993,** *38* (1), 556–559.
17. Izatt, R.M.; Bruening, R.L.; Clark, G.A.; Lamb, J.D.; Christensen, J.J. Effect of Co-anion on DC18C6 [Dicyclohexane-18-Crown-6]-Mediated Tl+ [Thallium$^{(+)}$] Transport Through an Emulsion Liquid Membrane. J. Memb. Sci. **1986,** *28* (1), 77–86.
18. Kina, K.; Shiraishi, K.; Ishibashi, N. Fluorometric Determination of Potassium by Ion-Pair Extraction with Macrocyclic Compounds and Anilinonaphthalene Sulfonate. Bunseki Kagaku **1978,** *27* (5), 291–295.
19. Smith, R.M.; Martell, A.E. *Critical Stability Constants: Inorganic Complexes*; Plenum Press: New York, 1976; Vol. 4, 108.
20. Pedersen, C.J. Ionic Complexes of Macrocyclic Polyethers. J. Am. Chem. Soc. **1970,** *92* (2), 386–390.
21. Paige, C.R.; Richardson, M.F. Complexes with Macrocyclic Ligands. II. The Crystal Structures of $HgCl_2 \cdot$18-Crown-6 and $CdCl_2 \cdot$18-Crown-6 and the FAB Mass Spectrum of $HgCl_2 \cdot$18-Crown-6. Can. J. Chem. **1984,** *62* (2), 332–335.
22. Bond, A.H.; Chiarizia, R.; Huber, V.J.; Dietz, M.L. Synergistic Solvent Extraction of Alkaline Earth Cations by Mixtures of Di-*n*-Octyl Phosphoric Acid and Stereoisomers of Dicyclohexano-18-Crown-6. Anal. Chem. **1999,** *71* (4), 2757–2765.

Received August 2000
Revised February 2001

Downloaded At: 10:46 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100105922