BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 620—623 (1968)

Solvent Extraction of Cadmium(II) from Aqueous Chloride and Bromide Solutions by Tri-*n*-octylamine

Hiroto WATANABE and Kunihiko AKATSUKA

Department of Industrial Chemistry, The Muroran Institute of Technology, Muroran

(Received October 11, 1967)

The distribution of cadmium(II) between dilute hydrochloric or hydrobromic acid solution and tri-*n*-octylamine dissolved in a number of diluents has been measured for several cadmium(II) loadings and amine concentrations. Diluents investigated are *n*-hexane, cyclohexane, benzene, xylene, toluene, carbon tetrachloride, chloroform, chlorobenzene and *o*-dichlorobenzene. The results show that all the species extracted into various diluents are present in the form of bis(tri-*n*-octylammonium)tetrahalocadmium(II). The specific ability of each diluent in extracting cadmium(II) from acidic halide solutions is approximately correlated with the dielectric constant of the pure diluent, suggesting that the dissociation of ion paired alkylammonium salt in the organic phase is responsible for the extraction.

It has been shown in our previous papers[1,2] that the formation of binegatively charged thiocyanate complexes is responsible for the extraction of iron(III) and cobalt(II) from acidic thiocyanate media with tri-*n*-octylamine in various organic diluents. The influence of diluents on the extraction of these metal ions was approximately correlated with the dielectric constant of the diluents. A similar study was carried out in the present investigation for the extraction of cadmium(II) from hydrochloric or hydrobromic acid solutions with tri-*n*-octylamine.

It is well known that cadmium(II) easily forms halo-complexes which are extractable into an organic phase with amines dissolved in various diluents,[3-6] and is generally accepted that the cadmium(II) species thus extracted is the tetrahalo-complexes of cadmium(II).[7,8] The present investigation was undertaken to obtain further information about the diluent influence on the extraction behavior of cadmium(II).

Experimentals

Apparatus. An Iwaki-V-S Shaking Unit was employed to carry out the equilibration. A Hitachi Model-139 Spectrophotometer was used to determine the concentration of cadmium(II) spectrophotometrically

Reagents. All reagents used were of analytical grade, and were further purified, if necessary. Tri-*n*-octylamine obtained from Kao Soap Co., Ltd. was converted to the chloride or bromide form by equilibrating the amine solution (0.1 N) in an appropriate dilutent twice with an equal volume of 0.5 N hydrochloric or hydrobromic acid. Then, the organic phase was separated and diluted to cover the concentration range studied. The concentration of the alkylammonium salt dissolved in various diluents was determined by potentiometric titration with a standard sodium hydroxide solution in ethanol medium.

The stock solution of cadmium(II) bromide was obtained by precipitation of the cadmium(II) hydroxide and subsequent dissolution in hydrobromic acid.

Diluents used and their dielectric constants in Debye Units were as follows[9]: *n*-hexane (1.9), cyclohexane (2.0), xylene, benzene (2.3), toluene (2.4), carbon tetrachloride (2.2), chloroform (5.0), chlorobenzene (5.8) and *o*-dichlorobenzene (9.9). The xylene used in this study was a mixture of three isomers and hence the dielectric constant was not given above.

Procedure. For all operations, 20 m*l* each of amine-halide solution and cadmium(II) halide solution were mixed together in a 100 m*l* glass separatory funnel and the mixture was equilibrated at room temperature. Fifteen minute shaking period at a rate of 120 strokes per minute was more than adequate. Then, the aqueous phase was filtered through paper to remove entrained organic phase. Aliquot portions were taken

---

1) H. Watanabe and M. Murozumi, This Bulletin, **40**, 1006 (1967).
2) H. Watanabe and K. Akatsuka, *Anal. Chim. Acta*, **38**, 542 (1967).
3) G. Nakagawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **81**, 1533 (1960).
4) T. Suzuki and T. Sotobayashi, *Bunseki Kagaku (Japan Analyst)*, **12**, 910 (1963).
5) S. Hirano, A. Mizuike and Y. Iida, *ibid.*, **11**, 1127 (1962).
6) T. Suzuki and T. Sotobayashi, *ibid.*, **13**, 1103 (1964); *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 587 (1966).
7) A. A. Morozov and N. A. Kisel, *Chem. Abstr.*, **63**, 12392c (1963).
8) T. Sato, K. Abe and H. Baba, Preprints for the 20th Annual Meeting of the Chemical Society of Japan, Tokyo (1967), II, 105.
9) International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. VI (1929). (McGraw Hill Book Company, Inc.).

and the cadmium(II) content in the aqueous phase was determined either spectrophotometrically with 4-(2-pyridylazo)resorcinol or complexometrically with Eriochrome Black T as an indicator. Spectrophotometric determination of cadmium(II) with 4-(2-pyridylazo)resorcinol has not yet been reported, but the following procedure used in our preliminary experiments is adequate both in the sensitivity and in the reproducibility for the purpose of the present investigation. One m*l* of aqueous 4-(2-pyridylazo)-resorcinol solution (2.5×10^{-3} M) is added to the aliquot of the aqueous phase. Adjusting the pH to 9.8 with a sodium hydroxide solution and a borate buffer solution prepared by the standard method, the orange color was developed and the solution was diluted to 25 m*l* with pure water. The absorbance was measured at 495 mμ in a 10 mm quartz cell using a reagent blank as a reference. Beer's law was followed up to 2 mg/*l* of cadmium(II) in the 20 m*l* of aqueous phase.

The amount of cadmium (II) in the organic phase was calculated by material balance.

Results

The effects of amine concetration on the distribution of cadmium(II) between both phases were examined at fixed concentrations of cadmium(II) and hydrochloric or hydrobromic acid. The distribution ratio, *q*, is defined as the total concentration of cadmium(II) in the organic phase divided by that in the aqueous phase,

$$q=\sum[\mathrm{Cd}]_o/\sum[\mathrm{Cd}]_w$$

where subscripts o, w stand for the organic and aqueous phase respectively. Figures 1 and 2 summarize the results on the various diluents. It is apparent that there is a close relationship between the extractability of the amine and the dielectric constant of the diluents. On the influence of diluents the order of increasing extractability agrees fairly well with those obtained by previous studies[1,2] for the extraction of iron(III) and cobalt(II) from acidic thiocyanate media.

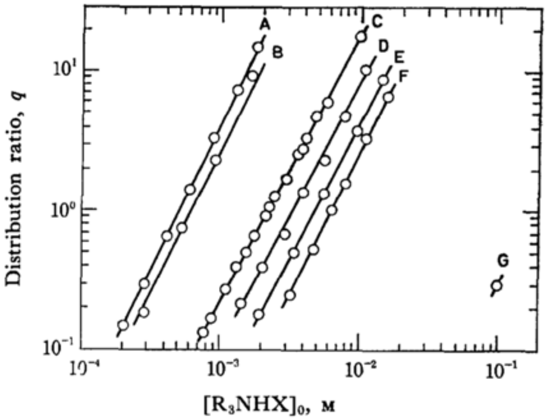

Fig. 1. Distribution of cadmium(II) as a function of amine concentrations from 0.50 N hydrochloric acid; 4.54×10^{-5} M total cadmium.
(A) *n*-hexane, (B) cyclohexane, (C) benzene, toluene, xylene, (D) chlorobenzene, (E) *o*-dichlorobenzene, (F) carbon tetrachloride, (G) chloroform

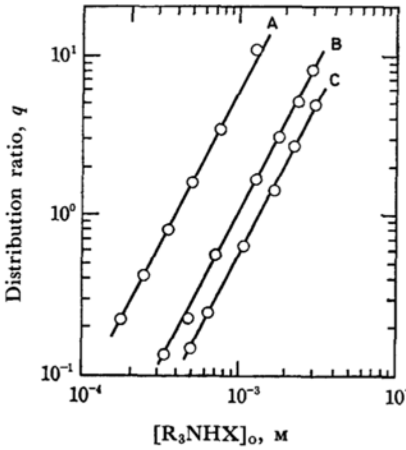

Fig. 2. Distribution of cadmium(II) as a function of amine concentrations from 0.10 N hydrobromic acid; 4.54×10^{-5} M total cadmium.
(A) benzene, (B) chlorobenzene, (C) *o*-dichlorobenzene

To determine the stoichiometry of the organic cadmium(II) species by measuring the maximum loading number which is the maximum equivalents of amine per mole of cadmium(II) in organic phase, loading curves were determined in a fixed concentration of amine (5×10^{-3} M) dissolved in cyclohexane and toluene. The results are shown in Figs. 3 and 4, which indicate a maximum $\sum[\mathrm{Cd}]_o/\sum[\mathrm{Amine}]_o$ for conditions of maximum loading being close to 0.5.

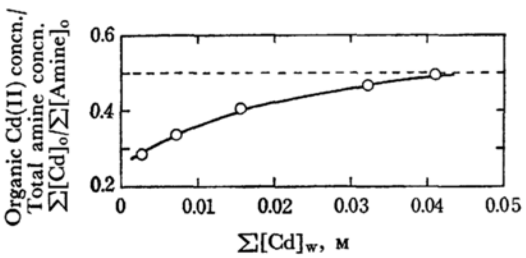

Fig. 3. Loading curve; 4.86×10^{-3} M tri-*n*-octylamine in cyclohexane, 0.5 N hydrochloric acid in aqueous phase.

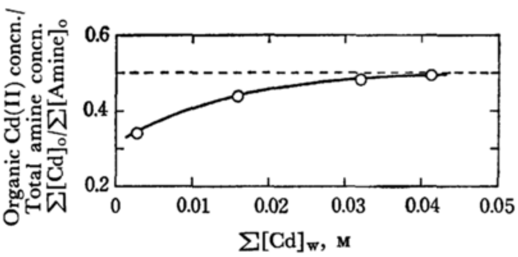

Fig. 4. Loading curve; 5.06×10^{-3} M tri-*n*-octylamine in toluene, 0.5 N hydrochloric acid in aqueous phase.

Discussions

In the present investigation, where the acids used are not over 0.5 N, the extraction of the excess acid by tri-*n*-octylamine can be assumed to be negligibly small.[10,11] Thus, the reaction between the amine in various diluents and hydrochloric or hydrobromic acids can be written as:

$$R_3N + H^+ + X^- \rightleftharpoons R_3NHX \qquad (1)^{12)}$$

where R_3N refers to the tri-*n*-octylamine and R_3NHX indicates its ammonium salt form. As it has been indicated by several authors,[11,13] the equilibrium constant of reaction (1) is in the order of magnitude 10^6. Therefore, under the conditions of the present study, one equivalent of amine combines with one equivalent of hydrochloric or hydrobromic acid and the species, R_3NHX, is formed in the organic phase almost quantitatively.

The simplest generalized equation for the extraction of cadmium(II) can be written as follows:

$$mR_3NHX + CdX_2 \rightleftharpoons (R_3NH)_mCdCl_{2+m} \qquad (2)$$

Assuming that the amine salts exist as monomeric species and that the activity coefficients of each species in both phases are essentially unchanged throughout the experiments, the corresponding mass action law expression in terms of concentration is derived as

$$K_m = [(R_3NH)_mCdX_{2+m}]_o / [R_3NHX]^m_o[Cd^{2+}][X^-]^2\beta_2 \qquad (3)$$

where β_2 denotes the cumulative formation constant of the aqueous species, CdX_2. Then the distribution ratio, q, may be expressed in terms of K_m;

$$q = A\sum_{m=1}^{M} K_m[R_3NHX]^m_o \qquad (4)$$

where A denotes $\beta_2[X^-]^2/(1+\sum_{n=1}^{4}\beta_n[X^-]^n)$. If halide concentration $[X^-]$ in aqueous phase is kept constant, the product of $[R_3NHX]_o$ by the derivative of q with respect to $[R_3NHX]_o$ is given by;

$$dq[R_3NHX]_o/d[R_3NHX]_o = A\sum_{m=1}^{M} mK_m[R_3NHX]^m_o \qquad (5)$$

Using Eq. (3), we can now introduce the average number of amine molecules combined with cadmium(II) halo-complexes in the organic phase.

$$\bar{m} = \sum_{m=1}^{M} mK_m[R_3NHX]^m_o / \sum_{m=1}^{M} K_m[R_3NHX]^m_o \qquad (6)$$

From Eqs. (4) and (5), the average number of combined amines, $\bar{m}$, can be written as follows:

$$\bar{m} = d\log q/d\log [R_3NHX]_o \qquad (7)$$

Equation (7) shows that, if halide concentration $[X^-]$ is kept constant, the slope of the $\log q$ *vs.* $\log[R_3NHX]_o$ gives the average number of amine molecules combined with halide complex of cadmium(II) in the organic phase. As shown in Figs. 1 and 2, log-log plots of q *vs.* $[R_3NHX]_o$ for different diluents at a fixed concentration of the aqueous hydrochloric or hydrobromic acid yield straight lines of slope ~2 within the experimental error. This means that only a single species is extracted and the binegatively charged CdX_4^{2-} complexes are formed in the organic phase.

In Eqs. (4) and (7), $[X^-]$ and $[R_3NHX]_o$ denote the equilibrium concentrations. As the total concentration of cadmium(II) is in the order of magnitute of 10^{-5} M, the analytical concentrations of the amine ($>10^{-4}$ M) and the hydrohalic acids ($>10^{-1}$ M) are large enough and they can be assumed to be kept unchanged throughout the extraction.

The results in Figs. 1 and 2 are confirmed by the loading curves shown in Figs. 3 and 4. The maximum loading numbers indicate two equivalents of amine per mole of cadmium(II) in cyclohexane and toluene and presumably in other diluents. From these results it is concluded that the charge of the cadmium complex extracted is -2 and hence the species present is CdX_4^{2-}.

The influences of diluents on the extraction of cadmium(II) from the same aqueous phase by tri-*n*-octylamine are also shown in Figs. 1 and 2. These figures indicate that the extractability is correlated approximately with the dielectric constant of diluent; the smaller the value of dielectric constant, the larger the extractability. In the present results, the diluent effect is not so apparent compared with the previous ones on the extraction of iron(III) and cobalt(II) from acidic thiocyanate solutions, that is, in Fig. 1 benzene, toluene and xylene behave identically and carbon tetrachloride shows smaller extractability than that of aromatic diluents irrespective of the comparable magnitude of the dilelectric constant. However, in a series of the diluents of similar structures it can be said that the extractability is lowered with increasing dielectric constant except for nitrobenzene in the aromatic diluents which was examined in the previous study.[2] From the examination of the Eq. (1), Diamond *et al.*[13] reported that the alkylammonium salts dissociate in nitrobenzene. Assuming that the alkylammonium salt behaves as a Bjerrum type ion pair, the increase of the dissociation of $R_3NH^+X^-$ would occur with increasing the dielectric constant of the diluent. In other diluents the ion paired alkylammonium salt presumably dissociates to a smaller extent depending

---

[10] A. S. Wilson and J. A. Wogman, *J. Phys. Chem.*, **66**, 1552 (1962).

[11] U. Bertocci and G. Rolandi, *J. Inorg. Nucl. Chem.*, **23**, 323 (1961).

[12] X^- denotes chloride or bromide ions.

[13] J. J. Bucher and R. M. Diamond, *J. Phys. Chem.*, **69**, 1565 (1965).

on the dielectric constant of the diluent. From such considerations in the medium of smaller dielectric constants such as *n*-hexane or benzene, ion paired alkylammonium salts will not appreciably dissociate and hence the activity coefficient of amine salts should be unity under these experimental conditions. This may be an important factor illustrating the high extractability for these diluents. On the contrary, as a result of the dissociation of the ion pairs in the medium of the larger dielectric constant, the activity of amine salt is considered to be smaller than in the previous case, irrespective of the increased solvation by the dipole of the diluent molecules.

Such consideration may lead to the conclusion that the higher the dielectric constants is the lower is the extractability. However, as it has been shown in our previous paper,[2] nitrobenzene has the high extractability which is comparable to that of cyclohexane. In this case the interaction between the dipole of the dilutent molecules and the ion paired alkylammonium salt must be strong enough compared with other diluents used in the present study. Therefore, if strong dissociation may occur, the activity coefficient of amine salt would be approximately unity because of the strong affinity of nitrobenzene to the ion pairs. In a series of our researches the alkylammonium cation is tri-*n*-octylammonium ion, so the small difference in behavior between the thiocyanate, chloride and bromide systems must be due to the anion size. From such considerations it is evident that the dissociation of the ion paired alkylammonium salt and the solvating properties of the diluent molecules to the ion pairs are the important factors goverining the extraction of metal ions.

The authors wish to express their thanks to Professor Masayo Murozumi of The Muroran Institute of Technology for his encouragement and valuable discussions and to Professor Masaichi Nagayama, Dr. Katsumi Goto and Mr. Takao Yotsuyanagi of The Hokkaido University for their helpful discussions and for citicizing the manuscript. We are also indebted to Mr. Sakae Matsumura for assistance with part of the experimental work.