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Studies of the Liquid-Liquid Partition Systems. VII. The Solvent Extraction of Mercury(II) Chloride, Bromide, Iodide and Thiocyanate with Some Organic Solvents

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The liquid-liquid distribution of mercury(II) has been determined when the organic phase was benzene, hexane containing tributylphosphate(TBP), methylisobutylketone(MIBK), or nitrobenzene, and when the aqueous phase was 0.5M sodium perchlorate containing chloride, bromide, iodide, or thiocyanate ions. The stability constants for the mercury(II) complexes in the aqueous phase and the distribution constants for the extractable complexes were determined by a graphic analysis of the distribution data, which were measured as a function of the ligand concentration. It was concluded that the stability constants determined from the present results agree almost entirely with the previous values and that the only extracted species into benzene and hexane containing TBP is the non-charged complex (HgX_2, where X^- is the ligand) in all cases, whereas those extracted into MIBK or nitrobenzene include not only the non-charged but also the charged species (HgX_3^- and sometimes HgX_4^{2-}) except in the case of the chloride system. The distribution ratio in the hexane-TBP system was further determined by changing the TBP concentration in the hexane phase, and the equilibrium constants for the adduct formation between the HgX_2 species and TBP molecules were determined. Finally, some discussion was made of the relation between the distribution behavior of the mercury(II) complexes and the natures of the ligands and the solvents.

It has been known for a long time that mercury(II) halides are somewhat soluble in organic solvents, while they are rather insoluble in water. This has been explained in terms of the formation of stable coordinate complexes which dissociate only slightly into mercuric ion and halide ions in aqueous solutions.

The stability constants of these complexes have been determined repeatedly by many authors by using various different experimental methods.[1] Of these, Sillén and his co-workers[2] determined these constants very comprehensively in a 0.5M sodium perchlorate constant ionic medium; their findings are listed in Table 1. Later, Marcus[3] published a series on the solvent extraction of mercuric halides or mixed halides with benzene. He concluded that the distribution ratio of mercury(II) between benzene and aqueous halide solutions can be explained in terms of the complex formation in the aqueous phase and the extraction of the non-charged dihalide mercury(II) complex into the benzene phase.

TABLE 1. STABILITY CONSTANTS FOR Hg(II) COMPLEXES AT 25°C

Previous work

	Cl^-	Br^-	I^-	SCN^-	
$\log K_1$	6.74*	9.05*	12.87*	—**	—***
$\log K_2$	6.48	8.28	10.95	—	—
$\log K_3$	0.85	2.41	3.78	2.71	2.88
$\log K_4$	1.00	1.26	2.23	1.98	1.99

Present work

	Cl^-	Br^-	I^-	SCN^-
$\log K_3$	0.85	2.27	3.78	2.73
$\log K_4$	1.00	1.60	2.23	2.02

* in 0.5M Na (X, ClO_4), from Ref. 2
** in 0.2M Na (X, NO_3), from Ref. 7
*** in 1M Na (X, ClO_4), from Ref. 8

In the present investigation, the authors have studied the solvent extraction of mercury(II) in aqueous chloride, bromide, iodide, and thiocyanate solutions with four organic solvents, benzene, hexane containing tributylphosphate (TBP), methylisobutylketone (MIBK), and nitrobenzene. These solvents were chosen in order to examine how the nature of the organic solvent influences the distribution behavior of mercury(II) complexes. We determined that benzene has no lone-pair electrons, but can form π-complexes with an acceptor, that TBP coordinatedly solvates metal ions rather strongly in non-

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[1] L. G. Sillén and A. E. Martell, "Stability Constants," The Chemical Society Spec. Pub. **17** (1964).

[2] L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949).

[3] Y. Marcus, *ibid.*, **11**, 329, 599, 610, 811 (1957).

polar solvents such as hexane, that MIBK also can solvate the metal ion, and the solvent itself is somewhat polar, and that nitrobenzene has one of the highest dielectric constants among the water immiscible organic solvents. The aqueous phase was kept as a 0.5M sodium perchlorate constant ionic medium in order to compare the present results with the previous results obtained in the same medium.

The changes in the distribution ratio, determined as a function of the ligand concentration, has been analyzed graphically, and the equilibrium constants in these systems were determined. There is some discussion of the distribution behavior of the complexes in these systems in connection with the chemical properties of the solvent and the ligand. The role of sodium ions in the organic phase for the extraction of the anionic complexes is also discussed.

Experimental

Reagents. About 0.2 g of mercuric dichloride was irradiated with thermal neutrons in the Triga III reactor at the Nuclear Research Laboratory of St. Paul's University, Kanagawa. It was dissolved in 5 m*l* of concentrated hydrochloric acid and then to the solution there was added an excess of zinc powder; the mixture was left standing overnight in order to reduce the mercury(II) to metallic mercury, and then the supernatant solution was decanted off. To the residue there was added a small amount of sulfuric acid in order to dissolve the excess of the zinc powder, and then the metallic mercury which remained was washed with water several times and finally dissolved in nitric acid. The solution was then evaporated in order to expel the excess acid, dissolved in 0.05M nitric acid, and stored for about one month in order to make the Hg-197 isotope decay out. The solution thus prepared was used as the stock tracer solution. The sodium-24 was obtained from the Japan Atomic Research Institute as a sodium chloride solution. It was diluted with a large amount of water and used as the stock solution. All of the reagents used were reagent-grade. The sodium perchlorate was recrystallized twice from water. The MIBK or TBP was washed with 0.1M perchloric acid, water, and 0.1M sodium hydroxide, and then several times with water. The other reagents were used without further purification. The concentration of the sodium thiocyanate solutions was determined by means of argentmetry, but the other concentrations were determined by means of gravimetry.

Procedures. All of the procedures were carried out in a thermostatted room at 25°C. Stoppered glass tubes (volume, 20 m*l*) were used to equilibrate the two phases. Five-milliliter portions of an aqueous solution containing mercury(II) labelled by the Hg-203 isotope, various amounts of ligand anions, and a 5-m*l* portion of one of the organic solvents were placed in the tubes. The initial concentration of the hydrogen ions in the aqueous phase was 1×10^{-3}M, and that of the mercury(II) ions was 1×10^{-5}M. The two phases were agitated mechanically for 30 min and then centrifuged off. A two-milliliter portion was pipetted from each phase and transferred into small test tubes. The γ-radioactivity in the sample solutions was measured with a well-type (NaI) scintillation counter, and the distribituion ratio of mercury(II) was calculated as follows:

$$D = [\mathrm{Hg(II)}]_{org,total}/[\mathrm{Hg(II)}]_{total} = \frac{\gamma\text{-count-rate per m}l\text{ of the org. phase}}{\gamma\text{-count-rate per m}l\text{ of aq. phase}}$$

Statistical

The complex formation of mercury(II) with these monovalent anions, X^-, can be described as follows:

$$\mathrm{Hg}^{2+} + n\mathrm{X}^- \rightleftarrows \mathrm{HgX}_n{}^{2-n} \qquad (1)$$

$$\beta_n = [\mathrm{HgX}_n{}^{2-n}]/[\mathrm{Hg}^{2+}][\mathrm{X}^-]^n \qquad (2)$$

or the stepwise formation constants can be described as follows:

$$\mathrm{HgX}_{n-1}{}^{3-n} + \mathrm{X}^- \rightleftarrows \mathrm{Hg}_n{}^{2-n} \qquad (3)$$

$$K_n = [\mathrm{HgX}_n{}^{2-n}]/[\mathrm{HgX}_{n-1}{}^{3-n}][\mathrm{X}^-] \qquad (4)$$

The solvent extraction of the neutral mercury(II) complexes may be described as follows;

$$\mathrm{HgX}_2 \rightleftarrows \mathrm{HgX}_2(org) \qquad (5)$$

$$K_{\mathrm{D}2} = [\mathrm{HgX}_2]_{org}/[\mathrm{HgX}_2] \qquad (6)$$

It would be also possible to extract the ion-pairs of the mercury(II) complex anion with sodium ions as:

$$\mathrm{HgX}_3{}^- + \mathrm{Na}^+ \rightleftarrows \mathrm{NaHgX}_3(org) \qquad (7)$$

$$\mathrm{HgX}_4{}^{2-} + 2\mathrm{Na}^+ \rightleftarrows \mathrm{Na}_2\mathrm{HgX}_4(org) \qquad (8)$$

These ion-pairs could dissociate in the organic phase as:

$$\mathrm{NaHgX}_3(org) \rightleftarrows \mathrm{Na}^+(org) + \mathrm{HgX}_3{}^-(org) \qquad (9)$$

$$\mathrm{Na}_2\mathrm{HgX}_4(org) \rightleftarrows \mathrm{Na}^+(org) + \mathrm{NaHgX}_4{}^-(org) \qquad (10)$$

$$\rightleftarrows 2\mathrm{Na}^+(org) + \mathrm{HgX}_4{}^{2-}(org) \qquad (11)$$

The third complex in the organic phase may be treated as follows. The equilibrium constant for the ion-pair extraction in Eq. (7) is:

$$K_{ex3} = \frac{[\mathrm{NaHgX}_3]_{org}}{[\mathrm{HgX}_3{}^-][\mathrm{Na}^+]} \qquad (12)$$

The dissociation constant for Eq. (9) is:

$$K_{diss3} = \frac{[\mathrm{HgX}_3{}^-]_{org}[\mathrm{Na}^+]_{org}}{[\mathrm{NaHgX}_3]_{org}} \qquad (13)$$

The total concentration of the third complex in the organic phase can, then, be described from Eqs. (12) and (13) as follows;

$$[\mathrm{NaHgX}_3]_{org} + [\mathrm{HgX}_3{}^-]_{org} = [\mathrm{HgX}_3{}^-](K_{ex3}[\mathrm{Na}^+] + K_{ex3}K_{diss3}[\mathrm{Na}^+]/[\mathrm{Na}^+]_{org}) \qquad (14)$$

From this, the distribution of the $\mathrm{HgX}_3{}^-$ species in the organic phase could be said to be dependent on the sodium concentration in the aqueous and the organic phases. However, it was concluded that both the aqueous and the organic sodium concentrations can be regarded as practically constant under the conditions employed in the present study, thus, the terms in parentheses in Eq. (14) can be regarded as constant. The terms in parentheses will be denoted in this study by a constant, "K_{D3}", as:

$$K_{D3} = ([\mathrm{NaHgX_3}]_{org} + [\mathrm{HgX_3^-}]_{org})/[\mathrm{HgX_3^-}] \qquad (15)$$

The same type of arguement, but a more complicated one, could be made for the fourth complex species in the organic phase, and for the same reason a "K_{D4}" constant can be defined as:

$$K_{D4} = ([\mathrm{Na_2HgX_4}]_{org} + [\mathrm{NaHgX_4^-}]_{org} + [\mathrm{HgX_4^{2-}}]_{org})/[\mathrm{HgX_4^{2-}}] \qquad (16)$$

In the ligand-concentration range where the $\mathrm{Hg^{2+}}$ and $\mathrm{HgX^+}$ species are negligible, the distribution ratio may be generally described as:

$$D = \frac{[\mathrm{HgX_2}]_{org} + [\mathrm{HgX_3^-}]_{org,total} + [\mathrm{HgX_4^{2-}}]_{org,total}}{[\mathrm{HgX_2}] + [\mathrm{HgX_3^-}] + [\mathrm{HgX_4^{2-}}]} \qquad (17)$$

where $[\mathrm{HgX_3^-}]_{org,total}$ and $[\mathrm{HgX_4^{2-}}]_{org,total}$ stand for the total organic concentrations of the third complex species ($\mathrm{HgX_3^-}$ and $\mathrm{NaHgX_3}$) and of the fourth complex species ($\mathrm{HgX_4^{2-}}$, $\mathrm{NaHgX_4^-}$ and $\mathrm{Na_2HgX_4}$) respectively.

When the organic sodium-ion concentration is assumed to be constant, it can be described from Eqs. (4), (6), (15), and (16) as;

$$D = \frac{K_{D2} + K_{D3}K_3[\mathrm{X^-}] + K_{D4}K_3K_4[\mathrm{X^-}]^2}{1 + K_3[\mathrm{X^-}] + K_3K_4[\mathrm{X^-}]^2} \qquad (18)$$

When to the non-charged mercury(II) complex in an organic solvent there is added a non-charged organophilic ligand, L, the equilibrium constants can be described as:

$$\mathrm{HgX_2}(org) + \mathrm{L}(org) \rightleftarrows \mathrm{HgX_2L}(org) \qquad (19)$$

$$\mathrm{HgX_2}(org) + 2\mathrm{L}(org) \rightleftarrows \mathrm{HgX_2L_2}(org) \qquad (20)$$

$$\beta_1^\circ = [\mathrm{HgX_2L}]_{org}/[\mathrm{HgX_2}]_{org}[\mathrm{L}]_{org} \qquad (21)$$

$$\beta_2^\circ = [\mathrm{HgX_2L_2}]_{org}/[\mathrm{HgX_2}]_{org}[\mathrm{L}]_{org}^2 \qquad (22)$$

When the organic phase contains these adduct complexes as well as the $\mathrm{HgX_2}$ species, but no charged complexes, the following holds;

$$\begin{aligned}[\mathrm{Hg(II)}]_{org,total} &= [\mathrm{HgX_2}]_{org} + [\mathrm{HgX_2L}]_{org} + [\mathrm{HgX_2L_2}]_{org} \\ &= [\mathrm{HgX_2}]_{org}(1 + \beta_1^\circ[\mathrm{L}]_{org} + \beta_2^\circ[\mathrm{L}]_{org}^2)\end{aligned} \qquad (23)$$

When the ligand-anion concentration in the aqueous phase, $[\mathrm{X^-}]$, is kept at "a", the following equation may be introduced from Eqs. (18) and (23);

$$D = \frac{K_{D2}(1 + \beta_1^\circ[\mathrm{L}]_{org} + \beta_2^\circ[\mathrm{L}]_{org}^2)}{1 + K_3a + K_3K_4a^2} \qquad (24)$$

When the distribution ratio at the same anionic-ligand concentration, but in the absence of the adduct-forming ligand, is denoted by D_0, the following equation is obtained;

$$\log D = \log D_0 + \log(1 + \beta_1^\circ[\mathrm{L}]_{org} + \beta_2^\circ[\mathrm{L}]_{org}^2) \qquad (25)$$

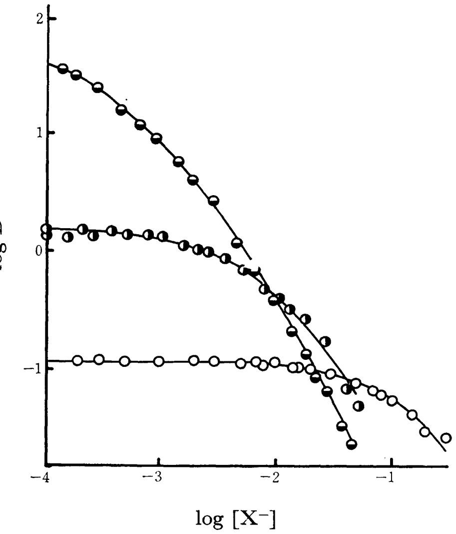

Fig. 1. Distribution of Hg(II) between benzene and 0.5M Na(X, ClO$_4$).
○: Cl⁻, ◑: Br⁻, ◒: I⁻
Distribution ratio in the thiocyanate system is very low.

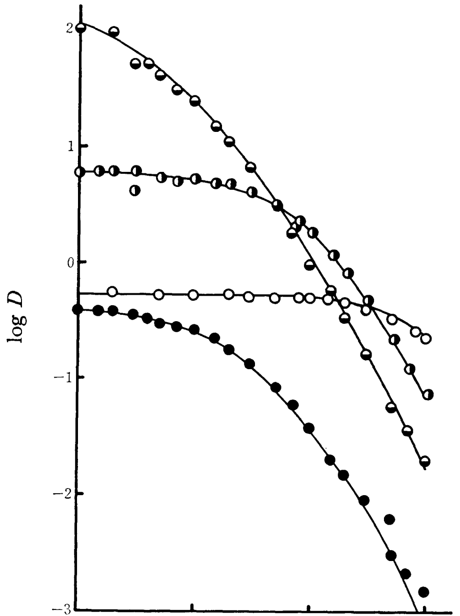

Fig. 2. Distribution of Hg(II) between hexane containing 0.1M TBP and 0.5M Na(X, ClO$_4$).
○: Cl⁻, ◑: Br⁻, ◒: I⁻, ●: SCN⁻

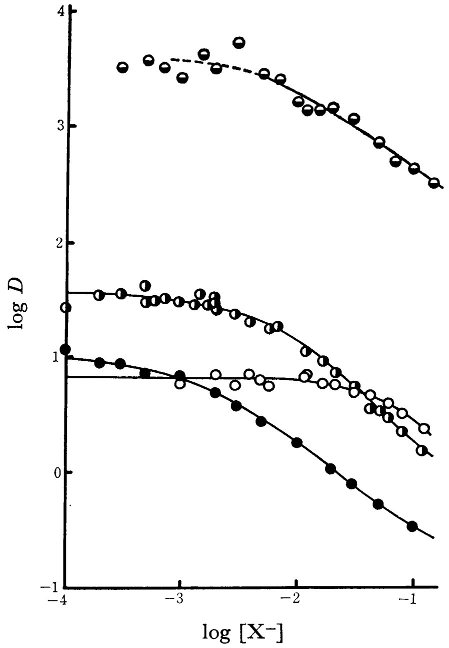

Fig. 3. Distribution of Hg(II) between MIBK and 0.5M Na(X, ClO$_4$).
○: Cl$^-$, ◑: Br$^-$, ⊖: I$^-$, ●: SCN$^-$

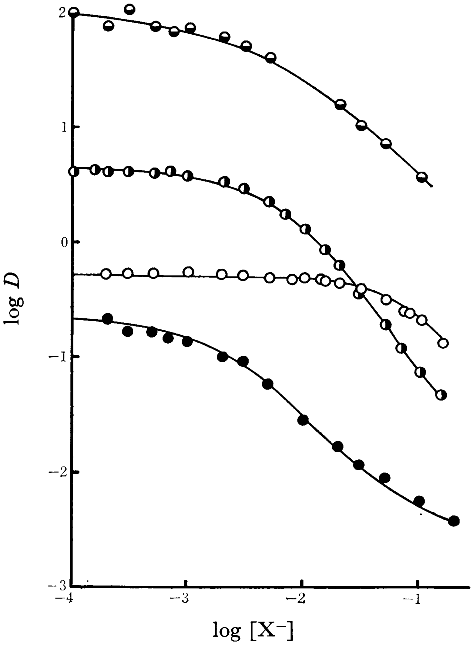

Fig. 4. Distribution of Hg(II) between nitrobenzene and 0.5M Na(X, ClO$_4$).
○: Cl$^-$, ◑: Br$^-$, ⊖: I$^-$, ●: SCN$^-$

Results

Figures 1 to 4 give the changes in the distribution ratio as a function of the ligand concentration in the aqueous 0.5M perchlorate constant ionic medium when the organic phase was benzene, hexane containing 0.1M TBP, MIBK, and nitrobenzene, respectively.

It can be assumed that the concentration of the Hg^{2+} or HgX$^+$ species is very small in the ligand-concentration range studied[2]; when it is assumed that the extraction of the ion-pair species, NaHgX$_3$ and Na$_2$HgX$_4$, into benzene or into hexane containing a small amount of the extractant, TBP, is almost negligible, the follwing equation can be employed for the analysis of the data in Figs. 1 and 2;

$$D = \frac{K_{\mathrm{D2}}}{1 + K_3[\mathrm{X}^-] + K_3K_4[\mathrm{X}]^{-2}} \tag{18'}$$

By using the following family of standard curves:

$$Y = -\log(1+pv+v^2),\ X = \log v \tag{26}$$

the equilibrium constants for the data in Figs. 1 and 2 were determiend by a curve-fitting method.[4–6] The stability constants and the distribution constants thus determined are listed in Tables 1 and 2. It was concluded that the stability constants for the HgX$_3^-$ and HgX$_4^{2-}$ complexes agree well with the values previously pointed by Sillén[2] within the limits of experimental error except for those for the bromide complexes. The equilibrium constants in the benzene system also agreed very well with the values reported by Marcus.[3] The stability constants for the thiocyanate complexes were also determined from Fig. 2; they are given in Table 1. They also agree with the constants in 0.2M nitrate media reported by Tanaka, Ebata, and Murayama[7] and with those in 1M perchlorate media reported by Nyman and Alberts.[8]

By introducing the constants, K_3 and K_4, determined from Figs. 1 and 2 into Eq. (18), the data in Figs. 3 and 4 were also analyzed graphically in order to obtain the distribution constants. After several attempts, it was found that the extraction constants for the charged complexes, K_{D3} and K_{D4}, should be taken into account as well as that for the non-charged complex, K_{D2}. However, the extraction curve of iodide in the MIBK system could be explained only in terms of the extraction of the charged complexes, HgI$_3^-$ and HgI$_4^{2-}$, for a reason to be given below.

In order to ascertain the effect of the coexisting salt, some experiments were carried out in the absence of sodium perchlorate in the aqueous phase; that is, the aqueous phase contained only sodium halide, and the ionic concentration was not con-

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[4] D. Dyrssen and L. G. Sillén, *Acta Chem. Scand.* **7**, 663 (1953).

[5] L. G. Sillén, *ibid.*, **10**, 186 (1956).

[6] T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).

[7] N. Tanaka, K. Ebata and T. Murayama, *ibid.*, **35**, 124 (1962).

[8] C. J. Nyman and G. S. Alberts, *Anal. Chem.*, **32**, 207 (1960).

Table 2. Extraction constants for Hg(II) complexes

		Benzene	Hexane	0.1M TBP-Hexane	MIBK	Nitrobenzene
Cl^-	$\log K_{D2}$	−0.95(−0.96*)	−2.1	−0.72	0.83	−0.28
	$\log K_{D3}$	—	—	—	—	—
Br^-	$\log K_{D2}$	0.16(0.155*)	−1.70	0.79	1.57	0.63
	$\log K_{D3}$	—	—	—	0.81	−0.84
I^-	$\log K_{D2}$	1.84(1.760*)	0.39	2.28	—**	2.10
	$\log K_{D3}$	—	—	—	3.68	1.81
	$\log K_{D4}$	—	—	—	2.28	—
SCN^-	$\log K_{D2}$	<−2(−2.2*)	−2.4	−0.38	1.00	−0.66
	$\log K_{D3}$	—	—	—	0.31	−1.60
	$\log K_{D4}$	—	—	—	−0.82	−2.57

$$K_{D2}=\frac{[HgX_2]_{org}}{[HgX_2]}\qquad K_{D3}=\frac{[NaHgX_3]_{org}+[HgX_3^-]_{org}}{[HgX_3^-]}$$

$$K_{D4}=\frac{[Na_2HgX_4]_{org}+[NaHgX_4^-]_{org}+[HgX_4^{2-}]_{org}}{[HgX_4^{2-}]}$$

* Taken from Ref. 3

** This value could not be determined but it was supposed that the extraction constant for the HgI_2 species with MIBK should be very large.

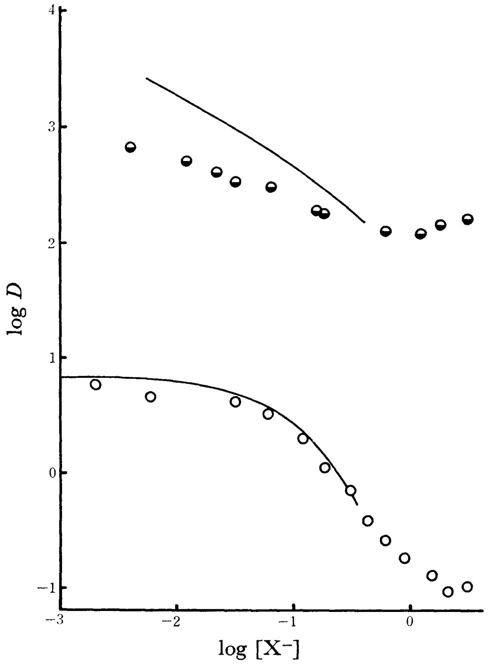

Fig. 5. Changes in the distribution of Hg(II) into MIBK when the aqueous phase containes sodium chloride(○) or sodium iodide(◒) but no sodium perchlorate (concentration of the ionic medium is not kept constant).

stant. Figure 5 gives some of the results of these experiments. In Fig. 5, the half-closed circles and the open circles show the extraction of mercury(II) with MIBK from aqueous sodium iodide and chloride solution respectively. The solid lines show the MIBK extraction curves from the 0.5M constant ionic media taken from Fig. 3. It can be seen that the extraction is not very different in the chloride system, but it is somewhat different in the iodide system.

The coextraction of sodium as ion-pairs with the anionic mercury(II) complex was also studied by using a sodium-24 radioactive tracer. An aqueous 0.1M sodium iodide solution containing no mercury(II) was equilibrated with MIBK, and from the measurement of the γ-radioactivity of sodium-24 in the two phases, the organic sodium concentration was determined. Then, from 0.002M to 0.01M of mercury(II) nitrate, (which was not labelled) was added to this aqueous 0.1M sodium iodide solution, the aqueous phase was equilibrated with MIBK, and the organic sodium concentration was determined. In the absence of mercury, the sodium content in the organic phase was about 1×10^{-4}M; this is probably due to the extraction of sodium iodide. Upon the extraction of mercury, the organic sodium concentration increases; when the total organic mercury concentration was 0.002M, 0.003M, 0.005M, and 0.01M, the organic sodium concentration was 1.8×10^{-3}M, 3.4×10^{-3}M, 7.8×10^{-3}M, and 1.3×10^{-2}M. These results indicate that one molecule of the mercury iodide complex coextracts one or two sodium ions. As has been pointed out, the extracted mercury-iodide complexes in this iodide concentration are the HgI_3^- and HgI_4^{2-} species, and they should coextract one and two sodium ions respectively. The results of the above sodium coextraction, determined by means of radiometry, seem to be explained by this assumption regarding the complex species in the organic phase.

Figure 6 shows the dependence of the distribution ratio on the TBP concentration in hexane when the

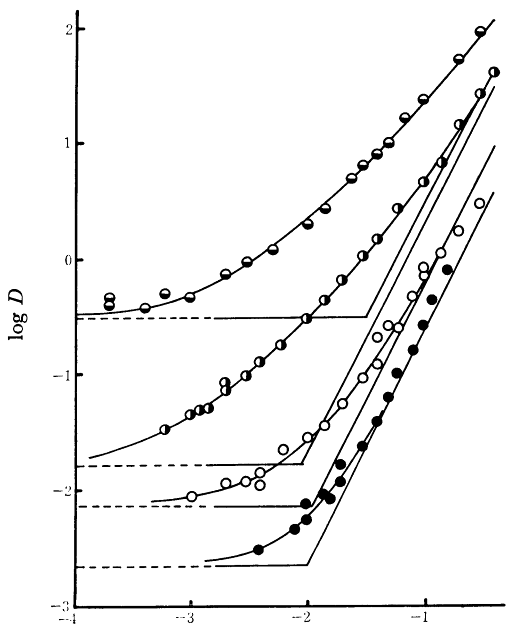

Fig. 6. The increase in the distribution of Hg(II) into hexane by the addition of TBP into the organic phase.

○: Cl⁻, ◑: Br⁻, ⊖: I⁻, ●: SCN⁻.

The aqueous phase is 0.5M $NaClO_4$ containing 1×10^{-3}M of the ligand. The broken lines represent the distribution ratio of the HgX_2 in the absence of TBP in hexane.

aqueous phase contains ligands at 1×10^{-3}M. It was found that some mercury(II) is extracted from these aqueous phases even into hexane containing no TBP. The distribution ratio into pure hexane is given in Table 3 as D_0. The distribution ratio increases as the TBP concentration increases. The plot was also analyzed by the curve-fitting method by using Eq. (24). The adduct-formation constants in Eqs. (21) and (22) thus determined are given in Table 3.

Table 3. Equilibrium constants for the extraction TBP and adduct formation of HgX_2 in hexane when the aqueous phase is 0.5M $NaClO_4$ containing 1×10^{-3}M of the ligand

	log D_0	log K_{D2}	log β_1°	log β_2°
$HgCl_2$	−2.1	−2.1	2.24	3.88
$HgBr_2$	−1.80	−1.70	3.32	4.08
HgI_2	−0.52	0.39	2.80	3.00
$Hg(SCN)_2$	−2.7	−2.4	1.70	4.00

$$D_0=\frac{[HgX_2]_{org}}{[HgX_2]+[HgX_3^-]+[HgX_4^{2-}]}$$

(org. phase; pure hexane)

$$K_{D2}=\frac{[HgX_2]_{org}}{[HgX_2]}\quad \text{(org. phase; pure hexane)}$$

$$\beta_1^\circ=\frac{[HgX_2TBP]_{org}}{[HgX_2]_{org}[TBP]_{org}}\qquad \beta_2^\circ=\frac{[HgX_22TBP]_{org}}{[HgX_2]_{org}[TBP]_{org}^2}$$

The distribution constant of the HgX_2 complex between pure hexane and the aqueous phases given by Eq. (6) was calculated by using the D_0 values and the stability constants in Table 1, for at this ligand concentration (1×10^{-3}M), the aqueous phases contain not only the HgX_2 but also the HgX_3^- and HgX_4^{2-} species except in the case of the chloride system. The K_{D2} values are also given in Table 3.

Discussion

The results given in Figs. 1 to 6 and in Tables 1, 2 and 3 may be summarized as follows; i) In the benzene and 0.1M TBP-hexane systems, the only metal species in the organic phase is the HgX_2 species.

ii) In the MIBK and nitrobenzene systems, only the HgX_2 species is extracted from the chloride media, but anionic complexes, HgX_3^- and HgX_4^{2-} species, are also extracted as ion-pairs with sodium ions from other media.

iii) The extraction of the HgX_2 species into pure hexane grows larger in this order; $Hg(SCN)_2 < HgCl_2 < HgBr_2 < HgI_2$. This extraction is increased by the addition of TBP. The increase can be explained in terms of the formation of TBP adduct complexes, HgX_2TBP and $HgX_2(TBP)_2$, in hexane. No systematic explanation has yet been made of the stability order of these adduct complexes of the different mercury(II) complexes.

iv) The stability constants for the HgX_3^- and HgX_4^{2-} species in the chloride and iodide systems agreed well with the data given by Sillén,[2] but those in the bromide system are slightly different. The same type of disagreement in the stability constants of the bromide complexes was also observed in the distribution work by Marcus[3] (log K_3 and log K_4 for the bromide complexes are 2.27 and 1.75), but the present results are closer to his values. Equilibrium constants in the benzene system agreed very well with the values reported by Marcus,[3] who also did his work in 0.5M sodium perchlorate constant ionic media.

The stability constants of the thiocyanate complexes obtained in the present study also agreed almost entirely with the previous data.[7,8]

As has been pointed out, the data in Figs. 3 and 4 were analyzed by using Eq. (18); that is, no effect of the organic sodium concentration on the distribution of the charged species was assumed. This is reasonable for the following reasons. According to the other studies, the sodium concentration in the organic phase equilibrated with 0.5M sodium perchlorate is about 5×10^{-5}M for nitrobenzene[9] and almost 1.5×10^{-3}M for MIBK (a small part of

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[9] T. Sekine and D. Dyrssen, *Anal. Chim. Acta*, **45**, 433 (1969).

these sodium ions could associate with perchlorate ions and form ion-pairs in MIBK).[10] The sodium concentration in the organic phases in the present systems can be described as follows:

$$[\mathrm{Na}^+]_{org} = [\mathrm{ClO_4}^-]_{org} + [\mathrm{X}^-]_{org} + [\mathrm{HgX_3}^-]_{org} + [\mathrm{NaHgX_4}^-]_{org} + 2[\mathrm{HgX_4}^{2-}]_{org} \quad (27)$$

In the ligand-concentration range studied, the aqueous sodium perchlorate concentration was kept pratically at 0.5M and the sums of the first and the second terms on the right side of Eq. (27) were 5×10^{-5}M and 1.5×10^{-3}M in nitrobenzene and MIBK respectively. On the other hand, as the total mercury concentration in the initial aqueous phase was 1×10^{-5}M, the maximum of the sum of the third, fourth and the fifth terms of Eq. (27) should be 2×10^{-5}M (when the $\mathrm{HgX_4}^{2-}$ species is dominant in the organic phase). However, as may be seen from Figs. 3 and 4 and Tables 1 and 2, this does not happen under the present experimental conditions. On the contrary, it is most probable that this sum is smaller than 1×10^{-5}M. From these points, it can be assumed that the sodium ions coextracted with the anionic mercury(II) complexes do not change the total organic sodium concentration seriously; in other words, the total sodium in the organic phase given by Eq. (27) is practically constant: 5×10^{-5}M in nitrobenzene and 1.5×10^{-3}M in MIBK.

Until now, not very much seems to have been discovered about the activity coefficient of ionic species in the organic phase in solvent extraction systems. The present results indicate that the activity coefficients of the ionic species in the organic phase can be controlled if the concentration of the metal complexes is very low. When the organic concentration of sodium perchlorate is much larger than that of the extracted metal ions in the organic phase, and when the aqueous phase is kept at a constant ionic medium by using sodium perchlorate, the concentration of the bulk sodium perchlorate in the organic phase is kept constant; in other words, this organic phase is a kind of constant ionic medium.

The distribution ratio of the complexes in these systems is probably influenced by many factors. When the interactions in the organic phase are not large as in hexane, the distribution ratio should be affected mainly by the interactions with the aqueous phase. Thus, the K_{D2} into pure hexane shown in Table 3 reflects the differences in the interactions with the aqueous phase. The order of the values of this K_{D2}, $\mathrm{HgCl_2}<\mathrm{HgBr_2}<\mathrm{HgI_2}$, is the same as the order of the sizes of these complexes, which is in turn parallel with the difficulty of the dissolution into water with a hydrogen-bonded structure. The small distribution ratio of the thiocyanate complex could be due to another effect of the polyatomic nature of this ion.

The extraction of the dihalides into benzene becomes larger than that into hexane, but the difference is rather small with the dithiocyanate. This increase in the extraction can be explained in terms of the π-complex formation of the mercury dihalides, and the data seem to show a smaller tendency toward π-complex formation in the dithiocyanate.

The TBP adduct formation also increases the extraction, as may be seen from Fig. 6 and Table 3. Many neutral metal complexes have been known to be extracted into various solvents as TBP adducts, and the solvation number of TBP has been given to many of them on the basis of the TBP dependence of the extraction. As the neutral complex is usually extracted into an "inert diluent" only very poorly, not very much has been known about the adduct-formation constants, β°, except for the adduct metal chelate complexes which are known as "synergic complexes." Thus, although it is known to be a general tendency, for complexes of a certain metal with a series of similar ligands to be extracted better with a neutral extractant such as TBP when the size of the ligand is large, there has been little discussion as to whether this is due to the larger extraction into the diluent or whether it is due to the larger stability of the adduct complexes. The results shown in Table 3, however, indicate that the greater extraction into hexane, in other words, the larger "aquofobic" tendency, is more important in causing the larger extraction (the larger K_{D2} in Table 3) of the bis-mercury(II) complexes into hexane containing TBP.

It is remarkable that the extraction of the ion-pairs of the third complex anion and the sodium ion is larger in this order; chloride (no extraction) <thiocyanate<bromide<iodide, an order which is parallel to the order of K_{D2}. The extraction of the ion-pairs should be effected by the dissociation and the solvation in the organic phase, and when the extracted complexes dissociate more in the organic phase, the distribution ratio should be higher. As has been pointed out, no information about the dissociation of the ion-pairs in the organic phase has been obtained from the present distribution constant, not only for the neutral complex (K_{D2}), but also for the anionic complexes (K_{D3} and K_{D4}), probably indicates a larger contribution of the solvation than of the dielectric constant, because nitrobenzene has a higher dielectric constant ($\varepsilon=34.82$ at 25°C)[11] than MIBK ($\varepsilon=13.11$ at 20°C)[11]: However, the latter is obviously more favorable for the solvation than the former; this higher ability of solvation should make MIBK a better extractant of the charged complexes than nitrobenzene.

The distribution ratio of the iodide complexes in MIBK is too high to allow an accurate determina-

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[10] Y. Hasegawa, T. Ishii and T. Sekine, to be published.

[11] A. A. Maryott and E. A. Smith, Table of Dielectric Constant of Pure Liquids NBS Circular 514 Aug. 10 1951.

tion, especially in the lower-iodide-concentration region, where an extraction of the HgI_2 species could be expected ($[I^-]<10^{-2}$M). Thus, the data used for the analysis were taken from the region where the iodide concentration was above 5×10^{-3}M when the concentration of the HgI_2 species was calculated to be lower than 1.8% of the mercury(II) content, neglecting the extraction of this species; the K_{D2} value for the iodide complex could not be determined. The K_{D2} for this species in the MIBK system, however, is probably very large because the K_{D2} can be assumed to be larger than the very large K_{D3}, $10^{3.68}$.

Due to the change in the ionic concentrations in the experiments in Fig. 5, no statistical analysis of the data has been carried out. However, the following qualitative discussion is possible. In the chloride system, the addition of the sodium perchlorate may change the activity coefficients of the species, but we observed a not very large effect in the experimental data. In the iodide system, however, the extraction of the ion-pairs is probably influenced by the change in the sodium concentration, as can be seen from Eq. (14) or from the discussion which has been given above. Therefore, the extraction of mercury(II) can be increased by an increase in the aqueous sodium concentration (*cf.* Eqs. (21) to (24)). Figure 6 shows the rather prominent independence of the iodide extraction on the sodium iodide concentration. This may be explained as follows; the increase in the sodium iodide concentration will increase the concentration of iodide ions, which in turn changes the metal species from the HgI_3^- species to the less extractable HgI_4^{2-} species. In consequence, this should decrease the extraction. At the same time, however, the increase in the salt concentration of the sodium ions may increase the extraction, as we can see from Eq. (14). By the combination of these two inverse effects, the increase or the sodium iodide concentration has a rather small effect on the net distribution ratio.

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