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THE EXTRACTION OF MERCURY(II) IODIDE*

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Abstract—The extraction of mercury(II) iodide into benzene at various acid and iodide concentrations was used as a means of determining the formation constants of the HgI_3^- and $HgI_4^=$ species. Radioactive tracer techniques were used to measure the extent of extraction at low mercury concentrations. With reasonable assumptions about activity coefficients the thermodynamic values of the constants for the formation of HgI_3^- and $HgI_4^=$ from HgI_2 and I^- were found to be $5{\cdot}0 \times 10^3$ and $5{\cdot}1 \times 10^5$, respectively.

THE equilibria which exist between mercury(II) iodide and iodide ion have been studied by using the extraction of the mercury species into benzene from dilute aqueous solutions as a phenomenon by which the extent of complex ion formation in the aqueous phase could be measured. A radioactive tracer, Hg^{203}, was used to determine the amount of extraction.

The application of an extraction technique to this equilibrium is not new,⁽¹⁾ but the use of a tracer permits the determination of lower concentrations of mercury and thus affords a worthwhile improvement in that the iodide ion concentration of the solution can easily be established. The amount of iodide undergoing combination can be neglected, since it is small compared to the total amount present.

EXPERIMENTAL

Solutions of nitric acid, potassium nitrate, and potassium iodide were prepared with reagent-grade chemicals and doubly-distilled water. A solution of mercury(II) nitrate containing radioactive Hg^{203} was obtained from the Oak Ridge National Laboratory. A standard solution of mercury(II) nitrate was prepared from this by precipitating the mercury as metal with hypophosphorous acid, weighing it, and dissolving it in concentrated nitric acid.

Distribution experiments were performed by shaking the aqueous solutions of mercury iodide with an equal volume of thiophene-free benzene for a period of about 12 hours at 25°C. The ratios of the concentrations of mercury in each phase were determined radiochemically. Aliquots from the equilibrated solutions were added to mercury(II) nitrate carrier, and the sulphide was precipitated and mounted for counting. Enough acetone was added to the benzene-mercury nitrate carrier mixture to make it one phase. After evaporation of the acetone and benzene, the sulphide was precipitated and mounted as mentioned above.

The distribution of mercury(II) between benzene and aqueous solutions was measured at an ionic strength of 0·03, nitric acid concentration of 0·01 M, and various potassium iodide concentrations in the range 0·001–0·02 M. Similar measurements were made with the nitric acid concentration being varied in the range 0·001–0·02 M, while the ionic strength was kept at 0·03 and the iodide ion concentration at 0·01 M. The total mercury present was in the range of 10^{-5} to 10^{-6} M and was always less than 1/300 of the total iodide concentration.

The distribution of mercury(II) iodide in the absence of excess iodide in the aqueous phase was measured by equilibrating a nearly saturated solution of HgI_2 in benzene (about 5×10^{-3} M) with a 0·01 M nitric acid–0·02 M potassium nitrate solution.

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⁽¹⁾ M. S. SHERRILL *Z. physik. Chem.* **43**, 705 (1903).

RESULTS

The extraction ratio, E, was found to be invariant with hydrogen ion concentration in the range tested as shown in Table 1. This indicates that species such as $HHgI_3$ and H_2HgI_4 are not extracted into the benzene phase. It is reasonable to assume that mercury(II) iodide dissolved in benzene exists as HgI_2 molecules, since any ionization in this non-polar solvent is extremely unlikely.

TABLE 1.—THE DISTRIBUTION OF MERCURY(II) BETWEEN BENZENE AND 0·01 M KI SOLUTIONS OF VARYING HNO_3 CONCENTRATION

conc. HNO_3 (moles/litre)	E
0·001	0·39
0·006	0·37
0·010	0·39
0·020	0·38

The measurements of the distribution as a function of iodide concentration can be interpreted on the basis of the following equilibria in the aqueous phase.

$$HgI_2\,(aq) + I^- \underset{}{\overset{K_1}{\rightleftharpoons}} HgI_3^- \tag{1}$$

$$HgI_2\,(aq) + 2I^- \underset{}{\overset{K_2}{\rightleftharpoons}} HgI_4^{=} \tag{2}$$

An extraction ratio E and an extraction constant E^0 are defined as:

$$E = [HgI_2]_0/[Hg]_{tot,aq} \quad \text{and} \quad E^0 = [HgI_2]_0/[HgI_2]_{aq}.$$

Brackets denote concentrations in moles per litre. If equations (1) and (2) represent the prevailing reactions in the aqueous phase, then:

$$[Hg]_{tot,aq} = [HgI_2]_{aq} + [HgI_3^-] + [HgI_4^{=}]. \tag{3}$$

This equation can be expressed in terms of the known iodide concentration, the concentration of mercury(II) iodide in benzene, the constants E^0, K_1, and K_2, and the activity coefficients of the ions I^-, HgI_3^-, and $HgI_4^{=}$, symbolized as γ_-, γ_1, and γ_2, respectively. The activity coefficient of uncharged mercuric iodide in the benzene phase at these concentrations is certainly close to unity, and it has been assumed to be that. In the aqueous-phase, calculations by LONG[2,3] indicate that at an ionic strength of 0·03, the deviation from unity for the activity coefficient of an uncharged species would be less than 0·5 per cent. This was considered to be negligible.

Thus:

$$[Hg]_{tot,aq} = \frac{[HgI_2]_0}{E^0}\left[1 + K_1[I^-]\frac{\gamma_-}{\gamma_1} + K_2[I^-]^2\frac{\gamma_-^2}{\gamma_2}\right]$$

or

$$\frac{1}{E} = \frac{1}{E^0}\left[1 + K_1[I^-]\frac{\gamma_-}{\gamma_1} + K_2[I^-]^2\frac{\gamma_-^2}{\gamma_2}\right] \tag{4}$$

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(2) W. F. McDEVIT and F. A. LONG *J. Amer. chem. Soc.* **74**, 1090 (1952).

(3) F. A. LONG and R. L. BERGEN JR. *J. phys. Chem.* **58**, 166 (1954).

While it is possible to evaluate the constants in equation (4) with measurements in the presence of iodide, the errors involved make such evaluation quite inaccurate. Better estimates of K_1 and K_2 can be obtained by the use of the independent determination of E^0, in which a value of 47·2 was obtained for this constant.

The designation of this value as E^0 implies the assumption that aqueous mercury(II) iodide is not ionized in the concentration range of the experiment. Published measurements of the conductivity of mercury(II) iodide solutions(4) and the potentials of various couples involving mercury(II) iodide(5) indicate that it is largely in molecular form in aqueous solutions near the saturation point. The present measurement of E^0 was made with near-saturation conditions in both phases.

With the use of a measured value of E^0, equation (4) can be rearranged for better graphical interpretation into the form:

$$\frac{E_0 - E}{E[\mathrm{I}^-]} = \frac{K_1\gamma_-}{\gamma_1} + \frac{K_2\gamma_-^2\,[\mathrm{I}^-]}{\gamma_2} \qquad (5)$$

Experimental data expressed in this form as a function of iodide concentration are shown in Fig. 1. The satisfactory linearity of the plot justifies the use of equation (5) to interpret the data.

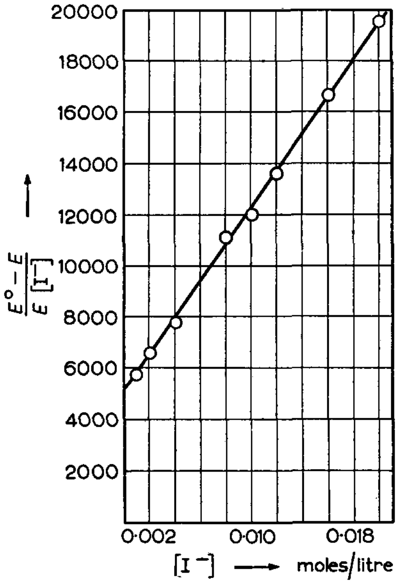

FIG. 1.—Mercuric iodide distribution study using benzene as extractant for HgI_2 0·0100 M HNO_3. μ = 0·03 (HNO_3, KNO_3, KI).

Values of (5·05 ± 0·12) × 10^3 and (7·24 ± 0·11) × 10^5 were determined for the intercept and slope of Fig. 1 by applying the method of least-squares for equally weighted measurements. Only the ordinate values were assumed liable to error. The above figures can be considered as nonthermodynamic values of K_1 and K_2 at an ionic strength of 0·03. They can be compared to the values of (6·1 ± 2·4) × 10^3 and

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(4) F. KOHLRAUSCH and F. ROSE *Z. physik. Chem.* **12**, 241 (1893).

(5) I. QVARFORT and L. G. SILLÉN *Acta chem. scand.* **3**, 505 (1949).

$(10{\cdot}3 \pm 1{\cdot}1) \times 10^5$ which were determined by the use of electrometric measurements(5) in solutions of the same acidity and ionic strength.

For a calculation of the thermodynamic values of K_1 and K_2 some assumptions regarding the activity coefficients are necessary. The "effective diameter" of the I^- ion was estimated by KIELLAND(6) to be 3×10^{-8} cm. He also estimated values of 4×10^{-8} and $4{\cdot}5 \times 10^{-8}$ cm for the effective diameters of ions similar in type and size to HgI_3^- and $HgI_4^=$. By the use of these values and the Debye-Hückel expression:

$$-\log \gamma_i = \frac{AZ_i^2\mu^{1/2}}{1 + Ba_i\mu^{1/2}},$$

activity coefficients of 0·84, 0·85, and 0·52 were calculated for the I^-, HgI_3^-, and $HgI_4^=$ ions in these solutions, in which $\mu = 0{\cdot}03$. The ratios γ_-/γ_1 and γ^2_-/γ_2 were estimated to be 0·99 and 1·35, using the above values of the activity coefficients, and thermodynamic values of K_1 and K_2 equal to $(5{\cdot}1 \pm 0{\cdot}2) \times 10^3$ and $(5{\cdot}4 \pm 0{\cdot}2) \times 10^5$ were calculated.

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(6) J. KIELLAND *J. Amer. chem. Soc.* **59**, 1675 (1937).