[Contribution from the School of Chemistry of the University of Minnesota]

# A Quantitative Expression for the Extractability of Metals in the Form of Dithizonates from Aqueous Solutions. The Equilibrium Constant of Zinc Dithizonate. Preliminary Paper

By I. M. Kolthoff and E. B. Sandell

An excellent review of the dithizone method for the determination of traces of heavy metals has been given by Wichmann.[1] From this paper and the abundant literature on the subject, it is evident that a great number of procedures for the determination and separation of several metals by the dithizone method has been worked out. These procedures are more or less empirical in nature. It may be expected that the usefulness of the dithizone method would be greatly extended if a quantitative expression could be given for the extractability of metal dithizonates from aqueous media by organic solvents. Wichmann[1] expresses the same view, but is of the opinion that "such a complex system of simultaneous equilibria cannot be expressed in simple equations or curves."

In the present paper it is shown that a quantitative expression for the extractability of the dithizonates can be derived simply on the basis of the mass action and distribution laws. We have confined our derivations to systems in which the metal in the aqueous phase is present as the aquo ion or in which the metal ion is more or less completely hydrolyzed. Experimentally, the distribution equation has been tested in a preliminary way for zinc. A more accurate experimental procedure and more extensive investigations, also with other metals, under widely varying experimental conditions are desirable and are planned. The present study, however, shows that the theoretical expression for the extractability of zinc dithizonate is in satisfactory agreement with the experimentally determined data.

In the following expressions HDz denotes dithizone and $MDz_2$ the keto dithizonate of a divalent metal. We first consider a range of *p*H in which the metal ion is present as aquo ion (denoted by $M^{++}$). It is assumed that the dithizone and the metal dithizonate are present in the non-associated forms HDz and $MDz_2$ in the aqueous and organic phases. From the agreement between the final expression and the experimental values it appears that this assumption is correct and that it is not necessary to derive more complicated expressions which involve association. For the sake of simplicity the following equations are written in terms of concentrations, although theoretically activities should be used.

Concentrations in the aqueous layer are denoted by the subscript w, and in the organic solvent (usually chloroform or carbon tetrachloride) by the subscript o. The distribution constant $D_{HDz}$ of dithizone between water and the organic solvent is given by

$$D_{HDz} = [HDz]_w/[HDz]_o \qquad (1)$$

and

$$D_{MDz_2} = [MDz_2]_w/[MDz_2]_o \qquad (2)$$

The formation of the metal dithizonate (keto form) in the aqueous phase is given by the equation

$$M^{++} + 2HDz \rightleftharpoons MDz_2 + 2H^+ \qquad (3)$$

Application of the mass action law yields

$$\frac{[MDz_2]_w[H^+]_w^2}{[M^{++}]_w[HDz]_w^2} = K' \qquad (4)$$

The concentrations of HDz and $MDz_2$ in water are extremely small and unknown. Upon shaking with the organic solvent both are extracted by the latter solvent. From equations (1), (2) and (4) we find

$$\frac{[MDz_2]_o[H^+]_w^2}{[M^{++}]_w[HDz]_o^2} = K'\frac{D_{HDz}^2}{D_{MDz_2}} = K \qquad (5)$$

The ratio $[MDz_2]_o$ to $[M^{++}]_w$ which is the experimentally determined distribution of the metal between the organic phase and water is given by

$$\frac{[MDz_2]_o}{[M^{++}]_w} = K\frac{[HDz]_o^2}{[H^+]_w^2} \qquad (6)$$

or more exactly by

$$\frac{[MDz_2]_o}{[M^{++}]_w} = K\frac{[HDz]_o^2 f_{M^{++}}}{[H^+]_w^2 f^2_{H^+}} \qquad (6a)$$

in which $f_{M^{++}}$ and $f_{H^+}$ represent the activity coefficients of the metal and hydrogen ions in the aqueous phase. Equation (6) shows that the extractability of a divalent metal at a given *p*H increases with the square of the concentration of the excess of dithizone in the organic phase, and that with constant excess of dithizone it decreases with the square of the hydrogen ion concentration (activity) in the aqueous phase.

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(1) H. J. Wichmann, *Ind. Eng. Chem., Anal. Ed.*, **11**, 66 (1939).

TABLE I

ZINC–DITHIZONE EQUILIBRIUM

| No. | $pH$ | Vol. aq. phase, ml. | Vol. $CHCl_3$ phase, ml. | Zn added, γ | Dz added, γ | Zn in | | $\frac{[Zn]_{CHCl_3}}{[Zn]_{H_2O}}$ | $K$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $CHCl_3$, γ | $H_2O$, γ | | |
| 1 | 3.97 | 10.0 | 10.0 | 10.0 | 100 | 2.3 | (7.7) | 0.30 | 3.4 |
| 2 | 3.97 | 10.0 | 10.0 | 10.5 | 245 | (6.2) | 4.3 | 1.44 | 2.8 |
| 3 | 3.97 | 10.0 | 10.0 | 10.0 | 250 | (6.2) | 3.8 | 1.63 | 3.0 |
| 4 | 3.97 | 10.0 | 10.0 | 10.5 | 490 | (9.2) | 1.3 | 7.1 | 3.1 |
| 5 | 3.97 | 10.0 | 10.0 | 10.0 | 750 | (9.64) | 0.36 | (27) | (4.5) |
| 6 | 3.05 | 10.0 | 10.0 | 11.0 | 588 | 2.5 | (8.5) | 0.29 | 4.7 |
| 7 | 3.05 | 10.0 | 10.0 | 11.0 | 980 | 4.2 | (6.8) | .62 | 3.6 |
| 8 | 3.05 | 5.0 | 10.0 | 5.7 | 1000 | (3.7) | 2.0 | .93 | 5.1 |
| 9[a] | 3.71 | 7.5 | 5.0 | 5.5 | 150 | 2.1 | 3.4 | .93 | 3.25 |
| 10[a] | 3.71 | 7.5 | 5.0 | 5.3 | 150 | 1.8 | 3.5 | .77 | 2.6 |
| 11[b] | 3.71 | 7.5 | 5.0 | 4.9 | 150 | 1.5 | 3.4 | .66 | 2.3 |

[a] Aqueous solution 1 *M* in sodium nitrate. [b] Aqueous solution 1 *M* in sodium chloride.

If the $pH$ of the aqueous solution is such that the metal ion is more or less completely hydrolyzed, the hydrolysis constants are also introduced in equation (6).

$$[M^{++}] + H_2O \rightleftarrows [MOH^+] + H^+ \qquad (7)$$

$$[M^{++}] + 2H_2O \rightleftarrows [M(OH)_2] + 2H^+ \qquad (8)$$

$$\frac{[MOH^+][H^+]}{[M^{++}]} = K_{1_{\text{hydr.}}} \qquad (9)$$

$$\frac{[M(OH)_2][H^+]^2}{[M^{++}]} = K_{2_{\text{hydr.}}} \qquad (10)$$

If the total metal concentration in the solution is denoted by [M] we have

$$[M] = [M^{++}] + [MOH^+] + [M(OH)_2] \qquad (11)$$

From (9), (10) and (11) it is found that

$$[M^{++}] = [M] \left\{ \frac{[H^+]^2}{[H^+]^2 + K_{1_{\text{hydr.}}}[H^+] + K_{2_{\text{hydr.}}}} \right\} \qquad (12)$$

Introducing this value in equation (6) yields

$$\frac{[MDz_2]_o}{[M]_w} = K \frac{[HDz]_o^2}{\{[H^+]_w^2 + K_{1_{\text{hydr.}}}[H^+]_w + K_{2_{\text{hydr.}}}\}} \qquad (13)$$

When $K_{1_{\text{hydr.}}}[H^+]_w + K_{2_{\text{hydr.}}}$ is small as compared to $[H^+]^2$, equation (13) becomes identical with equation (6). On the other hand when all of the metal may be considered present in the form of $M(OH)_2$ we find

$$\frac{[MDz_2]_o}{[M]_w} = K \frac{[HDz]_o^2}{K_{2_{\text{hydr.}}}} \qquad (14)$$

and the extractability becomes independent of the $pH$ of the aqueous layer. If the metal hydroxide has amphoteric properties and reacts with hydroxyl ions to form metalate anions another expression has to be derived.

## Experimental

**Materials.**—Water was redistilled in an all-Pyrex apparatus. Standard zinc solution, 0.0010% zinc as the chloride in 0.01 *N* hydrochloric acid. Dithizone, 0.010% in chloroform. The solution was standardized against silver nitrate by extractive titration.[2]

Biphthalate buffers, of $pH$ 3 and 4, according to Clark and Lubs. These were shaken with 0.01% dithizone to remove most of the zinc and other reacting heavy metals present. The buffer of $pH$ 3 could not conveniently be entirely freed from zinc in this manner, and the trace of metal remaining was determined and taken into consideration in the calculations.

The $pH$ of the solutions before shaking with the dithizone solution in chloroform was determined with the aid of the quinhydrone electrode, a proper correction being made for the salt error.

Sodium acetate was a saturated solution. Reacting metals were removed by shaking with dithizone.

**Procedure.**—The mixtures of dithizone, chloroform, buffer and zinc solution were shaken mechanically for two hours at room temperature (25 ± 2°) in glass-stoppered Pyrex tubes. Zinc was then usually determined in the phase which contained the smaller fraction of the total amount of metal present. When the chloroform phase was to be analyzed, a suitable aliquot was shaken with an equal or greater volume of 0.05 *M* hydrochloric acid for five minutes to transfer the zinc to the acid layer. The latter was separated and treated with sufficient sodium acetate solution to make the $pH$ approximately 6. Zinc was then determined with dithizone by the mixed-color method.[3] The comparison solutions used had the same composition as the sample solution. The error of the visual comparison should not exceed 5%.

When the aqueous phase of the mixture was analyzed, an aliquot portion was brought to a $pH$ of approximately 6 with sodium acetate and compared against standards of identical composition by the mixed-color method.

The results are given in Table I. It is seen that at constant $pH$ (3.97) the extractability of the zinc varies greatly with the excess of dithizone used. In the experiments described, the ratio $[ZnDz_2]_{\text{chloroform}}/[Zn^{++}]_w$ varied from 0.30 to 27, or about a hundred-fold. Still the value of $K$ of

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[2] H. Fischer, G. Leopoldi and H. von Uslar, *Z. anal. Chem.*, **101**, 5 (1935).

[3] *Cf.* E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **9**, 469 (1937).

equation (6) was found to be sensibly constant and equal to 3.2 ± 0.3. At a $p$H of 3.05 equation (6) was also found to be satisfied although a slightly greater value of $K$ of 4.5 ± 0.5 was found. This difference may be partly due to experimental errors in the measurement of the distribution and of the $p$H of the aqueous solution (a small error in the measurement of $a\text{H}^+$ has a large effect on $K$ since the value of $K$ depends on $a\text{H}^{+2}$) and to the fact that the activity coefficient of the zinc ions has not been taken into account (equation 6a). Experiments 9 and 10 in Table I show that in 1 $M$ sodium nitrate the value of $K$ was only slightly less than in the absence of this salt. The observed variation of $K$ in the experiment in 1 $N$ sodium chloride is either accidental or the result of the tendency of chloride to form a complex ion with zinc.

## Summary

A simple quantitative expression for the extractability of a metal in the form of its dithizonate from water by an organic solvent has been derived. Experiments carried out with zinc showed that the theoretical expression is valid under widely varying experimental conditions.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE UNIVERSITY OF IOWA]

# Physical Studies of Non-aqueous Solvates. IV. The Solubility of Zinc Bromide in Diethyl Ether[1]

BY H. H. ROWLEY AND ROBERT B. ANDERSON

Recent investigations in this Laboratory[1a] of the diethyl etherates of zinc bromide through vapor pressure measurements, indicated the existence of a dietherate at low temperatures. At about +5° this dietherate decomposes to form a monoetherate which exists up to about +20°. Above +20° the non-solvated zinc bromide appeared to be the stable form of the solid in contact with ether solution and vapor. These results differed markedly from those of Raynaud,[2] who claimed a monoetherate of zinc bromide existing at +100°.

The present study was undertaken to clear up the incongruities in the results of Raynaud and those found in this Laboratory and to ascertain more precisely the transition points by solubility determinations over the temperature range −20 to +35°.

## Experimental

**Apparatus and Materials.**—The anhydrous zinc bromide and the diethyl ether were prepared as previously described.[1a]

The solubility cells were large test-tubes which were closed with rubber stoppers carrying two glass tubes for removing the saturated liquid. Agitation in the solution was provided by a solenoid stirring device suitable for use in constricted spaces.[3] The various temperatures −20 to +35° were maintained to less than ±0.3° by using a thermostat (water-bath), various freezing mixtures and acetone cooled by the addition of dry-ice.

**Procedure.**—In the handling of materials and apparatus, great care was taken at all times to exclude atmospheric moisture. The solutions of zinc bromide were prepared in a dry atmosphere chamber by adding ether to the anhydrous zinc bromide. The solutions were stirred for varying periods of time, depending upon the temperature of the determination, and then allowed to settle. Below +15°, the stable system required shorter periods for settling out due to the lower viscosity of these less concentrated solutions and the crystalline character of the solid compared to the "amorphous" solid above +20°. The conversion of the "amorphous" solid to the crystalline (solvated) phase was effected readily only by cooling the mixture to about −78°. It was then warmed to about one degree above the required temperature, stirred, and then permitted to approach equilibrium for a period of about eighteen hours, at the required temperature.

After settling, the clear supernatant liquid was forced by dry air into tared glass-stoppered Erlenmeyer flasks. The flasks were weighed immediately, and the samples dissolved in water and analyzed for bromine content by a modification of the Volhard method as revised by Caldwell.[4] A few samples also were analyzed for zinc and the results calculated as zinc bromide checked the bromine analyses very closely.

The wet solids in contact with the saturated solutions at the various temperatures were analyzed. The instability of the etherates in air at room temperature prevented complete removal of the adhering solution but they were drained as thoroughly as possible before analysis by pressing on filter paper pads at the equilibrium temperature.

**Results.**—Solubility data for the system zinc bromide–diethyl ether are gathered in Table I.

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(1) Original manuscript received July 22, 1940.

(1a) Rowley and Olson, THIS JOURNAL, **61**, 1949 (1939).

(2) Raynaud, *Bull. soc. chim.*, **39**, 195 (1926).

(3) Rowley and Anderson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 397 (1939).

(4) Caldwell, *ibid.*, **7**, 38 (1935).