

Study on the Hydrolysis of Metal Ions

Part 56. Solvent Extraction Study of the Hydrolysis of Zinc(II)
in 3 M NaClO₄ at Low Concentration

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The mononuclear hydrolysis of Zn(II) in 3 M NaClO₄ has been studied by a distribution method. The mononuclear species, Zn(OH)₂, was extracted into a benzene phase containing 5 % (by volume) of the long-chain liquid amine Amberlite LA-1. The net distribution ratio of Zn(II) could be explained by the relation $D = \frac{[\text{Zn(II)}]_{\text{org, total}}}{[\text{Zn(II)}]_{\text{aq, total}}} = \frac{[\text{Zn(OH)}_2\text{L}_2]_{\text{org}}}{([\text{Zn}^{2+}] + [\text{Zn(OH)}_2] + [\text{Zn(OH)}_3^-] + [\text{Zn(OH)}_4^{2-}])}$ where L denotes the amine.

The hydrolysis constants and the distribution constant of the Zn(OH)₂ species between the organic and the aqueous phases were calculated by a generalized least squares method, using the LETAGROP VRID computer program.

The "best-fit" constants thus obtained were

$$\begin{aligned} \log \beta_2^* &= \log \frac{[\text{Zn(OH)}_2][\text{H}^+]^2}{[\text{Zn}^{2+}]} = -20.10 \pm 0.14 \\ \log \beta_3^* &= \log \frac{[\text{Zn(OH)}_3^-][\text{H}^+]^3}{[\text{Zn}^{2+}]} = -28.83 \pm 0.09 \\ \log \beta_4^* &= \log \frac{[\text{Zn(OH)}_4^{2-}][\text{H}^+]^4}{[\text{Zn}^{2+}]} = -38.72 \pm 0.09 \\ \log K_D &= \log \frac{[\text{Zn(OH)}_2\text{L}_2]_{\text{org}}}{[\text{Zn(OH)}_2]} = 2.88 \pm 0.12 \end{aligned}$$

(Amberlite LA-1, 5 % in benzene)

(The range of error gives three times the standard deviation, 3σ)

No ZnOH⁺ has been observed within the experimental accuracy. The concentration of Zn(OH)₂ was also very low in the whole -log [H⁺] region studied (Fig. 6).

It has been known for a long time that a zinc(II) hydroxide precipitate is dissolved on addition of excess of sodium or potassium hydroxide solution. Crystalline zincates of definite composition have often been prepared.¹

Stability constants for hydrolyzed zinc species have been given by many authors. Some authors, from solubility or emf measurements concluded that Zn(OH)₃⁻ and Zn(OH)₄²⁻ exist in the higher pH region, and reported the stability constants β₃ and β₄.²⁻³ The solubility product of zinc hydroxide

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has also been reported by many authors.²⁻³ However, it was pointed out by Feitknecht and Häberli⁴ that the solubility product is very different for different crystal phases and $\log K_{s0}$ (25°C) ranges from -16.92 for ϵ -Zn(OH)₂ to ≈ -15.7 for amorphous zinc hydroxide.

Previous studies have given scattered values of the stability constant of ZnOH⁺ (*cf.* Ref. 2), even though most of the values for $\log \beta_1$ fall in the range 4 to 5.

Recently, emf measurements of zinc hydrolysis were carried out by Biedermann and Row⁵ in this laboratory. They reported only one positively-charged hydrolyzed species, Zn₂OH³⁺, in the concentration range for Zn(II) between 0.25 and 1.45 M in 3 M LiClO₄ and gave the stability constant, $\log \beta_{1,2}^* = -8.7 \pm 0.1$.

I have found no paper describing the stability constant of the species Zn(OH)₂.

Thus it seems that even though the existence of the negatively charged species, Zn(OH)₃⁻ and Zn(OH)₄²⁻ have been well confirmed, the existence of ZnOH⁺ and Zn(OH)₂ has not been established beyond doubt.

The low solubility product of zinc hydroxide, and the previous studies on ZnOH⁺, suggest that the concentration of these species in solution is low over the entire pH range. Hence, in the study of ZnOH⁺ and Zn(OH)₂ one must make very accurate measurements at low zinc concentrations; if one uses the solubility method, one must be sure always to have the same crystal phase of zinc hydroxide.

The distribution method gives another approach to the study of hydrolyzed zinc species. One can work at very low zinc concentrations by the use of a radioactive isotope, and thus avoid the formation of precipitates. Since the distribution constant for the neutral species is high, one can detect it in the organic phase, separately from any charged species, even if its concentration is much lower than those of other species. As will be discussed in the next section, it is also possible to study a system where a third phase is present, for example, some form of solid zinc hydroxide, provided that the system is in an equilibrium state and that one can separate the organic and the aqueous phases without contamination by the third phase.

Studies of distribution equilibria of neutral hydrolyzed species with an organic phase have been applied to the hydrolysis of vanadium(V) and cadmium(II) in this laboratory.^{6,7} In these cases, the results were explained by a stepwise mononuclear hydrolysis in the aqueous phase followed by the extraction of HVO₃ or Cd(OH)₂ into the organic phase.

This paper describes solvent extraction studies of zinc(II) hydrolysis from Zn²⁺ to Zn(OH)₄²⁻. The neutral species, Zn(OH)₂, in 3 M NaClO₄ was extracted with a high molecular weight organic secondary amine, Amberlite LA-1, in the neutral form. The distribution of Zn(II) between the organic phase and aqueous phases of various hydrogen ion concentrations was determined by the use of ⁶⁵Zn radioactive tracer.

Some experiments were carried out with 0.1 M NaClO₄ to see the influence of the perchlorate concentration on the distribution ratio. Experiments were also carried out at different metal ion concentrations in the aqueous phase. The influence of carbonate, which might come from the air with the present

experimental procedure, was checked, and the recovery of the radioactive zinc from both phases was determined.

From these data, the stability constants of the mononuclear hydrolyzed species and the distribution constant of the neutral hydrolyzed species were calculated. The constants were finally improved by a generalized least squares method.

APPLICATION OF THE LAW OF MASS ACTION

In this section, we make the following assumptions.

1) No polynuclear species is formed in the aqueous phase or in the organic phase.

2) Only Zn(OH)_2 is dissolved in the organic phase. The extraction of other neutral species such as $\text{Zn(ClO}_4)_2$, ZnOHClO_4 , NaZn(OH)_3 etc. is negligible.

3) No complex formation other than with OH^- occurs in the aqueous phase.

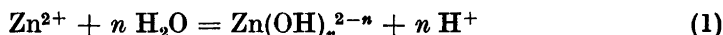
4) The composition of the organic phase is constant.

5) The volumes of the organic and the aqueous phases are the same.

6) The highest hydrolyzed species is Zn(OH)_4^{2-} .

The suffix "org" denotes concentrations in the organic phase, and "aq" or no suffix denotes those in the aqueous phase.

The hydrolysis reactions of Zn^{2+} , and the overall hydrolysis constants, are

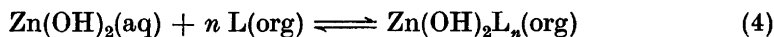


$$\beta_n^* = [\text{Zn(OH)}_n^{2-n}] [\text{H}^+]^n / [\text{Zn}^{2+}] \quad (2)$$

At equilibrium with solid Zn(II) hydroxide, we have a series of equilibrium constants

$$K_{s_n}^* = [\text{Zn(OH)}_n^{2-n}] [\text{H}^+]^{n-2} = K_s^* \beta_n^* \quad (3)$$

The distribution equilibrium of Zn(OH)_2 is assumed to be



where L is an organic neutral ligand. At constant $[\text{L}]_{\text{org}}$, the apparent equilibrium constant is

$$K_D = [\text{Zn(II)}]_{\text{org, total}} / [\text{Zn(OH)}_2] \quad (5)$$

The net distribution ratio of Zn(II) between the organic and the aqueous phase is determined from radioactivity measurements as

$$D = \frac{\text{radioactivity of Zn per ml organic phase}}{\text{radioactivity of Zn per ml aqueous phase}} \quad (6)$$

$$= [\text{Zn(II)}]_{\text{org, total}} / [\text{Zn(II)}]_{\text{aq, total}} \quad (7)$$

From our assumptions

$$[\text{Zn(II)}]_{\text{org, total}} = K_D [\text{Zn(OH)}_2] = K_D \beta_2^* [\text{Zn}^{2+}] [\text{H}^+]^{-2} \quad (8)$$

$$\begin{aligned} [\text{Zn(II)}]_{\text{aq, total}} &= [\text{Zn}^{2+}] + [\text{ZnOH}^+] + [\text{Zn(OH)}_2] + [\text{Zn(OH)}_3^-] + [\text{Zn(OH)}_4^{2-}] \\ &= [\text{Zn}^{2+}] (1 + \beta_1^* [\text{H}^+]^{-1} + \beta_2^* [\text{H}^+]^{-2} + \beta_3^* [\text{H}^+]^{-3} + \beta_4^* [\text{H}^+]^{-4}) \quad (9) \end{aligned}$$

From eqns. (7), (8), and (9)

$$D = K_D \beta_2^* [H^+]^{-2} / (1 + \beta_1^* [H^+]^{-1} + \beta_2^* [H^+]^{-2} + \beta_3^* [H^+]^{-3} + \beta_4^* [H^+]^{-4}) \quad (10)$$

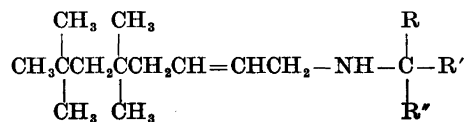
Even if a third phase such as a solid is present or if there is adsorption on the vessel wall, eqn. (10) is valid as long as the third phase is at equilibrium with the organic and aqueous phases, because when the equilibrium constant between the third phase and Zn^{2+} (or any one of the species) is introduced, it cancels out and does not appear in eqn. (10).

EXPERIMENTAL

Tracer. Zinc tracer, ^{65}Zn , was used in this study. It was made by the nuclear reaction, $^{64}Zn(n, \gamma)^{65}Zn$, and was obtained from the Radiochemical Center, Amersham, England, as a zinc chloride solution.

This tracer solution was diluted with a mixture of perchloric acid and sodium perchlorate solution to make the stock solution, which contained 1×10^{-3} M Zn^{2+} , 0.1 M $HClO_4$ and 2.9 M $NaClO_4$.

Reagents. Amberlite LA-1, a commercially available liquid anion exchanger, was used as the extracting ligand. This is a mixture of highly branched unsaturated secondary aliphatic amines. A structural formula for the mixture has been indicated as follows,



where $R + R' + R'' = 11$ to 14 carbon atoms. It is a liquid at room temperature. The mean molecular weight of the commercial product is 372 and its molarity at 25°C is about 2.25.

It was purified as follows: Commercially-available LA-1 in bottles was diluted with very pure benzene which had been purified by recrystallization. This LA-1-benzene solution was then washed successively with 0.1 M $HClO_4$, with 1 M $NaOH$, and then several times with a 2.9 M $NaClO_4 + 0.1$ M $Ba(OH)_2$ solution.

Sodium perchlorate was prepared by dissolving sodium carbonate in perchloric acid. The solution was first brought to pH 3 with $HClO_4$, boiled to expel CO_2 , and then brought to pH 9 with $NaOH$. The solution was left to stand for a few days, and the precipitate of hydroxide impurity was filtered off. The solution was then neutralized with $HClO_4$ and evaporated, and the solid purified by two recrystallizations. "Carbonate-free" $NaOH$ solutions were made from 50 % $NaOH$ solution. The concentrations of the stock $NaOH$ solutions were 1 M and 0.1 M, and the Na^+ concentration was made 3 M with $NaClO_4$. Other reagents were used without further purification.

Procedures. Glass tubes with stopper were used for the distribution experiments. The volume of each tube was about 50 ml and the shape as well as the inside area was nearly the same in all tubes. A barium perchlorate solution was added to a sodium perchlorate solution, the mixture was allowed to stand for few days and the barium carbonate precipitate was filtered off under a nitrogen atmosphere. The final solution contained 0.01 M $Ba(ClO_4)_2 + 3$ M $NaClO_4$. Various amounts of a perchloric acid solution (0.1 M $HClO_4 + 2.9$ M $NaClO_4$) or a sodium hydroxide solution (0.1 M $NaOH + 2.9$ M $NaClO_4$), and 0.1 ml of $Zn(II)$ tracer stock solution, were added to the tubes. The volume of the aqueous phase was finally made up to 10.0 ml by the addition of 3 M $NaClO_4$. Thus the initial $Zn(II)$ concentration in the aqueous phase was 1×10^{-5} M. To this, 5.0 ml of a 10 % (by volume) LA-1-benzene solution was added followed by 5.0 ml of pure benzene or benzene containing 0.02 M phenol.

Some experiments were carried out in solutions prepared by different procedures: (a) 0.5 ml or 0.01 ml $Zn(II)$ tracer solution was used to see whether D changes if the initial

metal concentration is different (the initial Zn(II) concentration was then 5×10^{-5} or 1×10^{-5} M). (b) 1 M NaOH solution was added to the Zn(II) stock tracer solution (in 0.1 M HClO₄) to convert the initial form of Zn(II) from Zn²⁺ to Zn(OH)₂²⁻. This tracer solution was added to the aqueous phase. (c) No Zn(II) tracer was added to the aqueous phase but an organic solution of Zn(II) tracer was added which had been prepared by the extraction of Zn(OH)₂ with 5 % LA-1 solution.

To study the dependence of the distribution on [LA-1]_{org}, Zn(II) was equilibrated with 10 %, 5 %, 3 %, 2 %, 1 %, and 0.5 % LA-1 in benzene. For these experiments, $-\log [H^+]$ was kept in the range 8 to 9 because here the slope of the plot $\log D$ versus $-\log [H^+]$ is nearly 2.0 and one can compare the distribution ratio for different $-\log [H^+]$ by using the normalized values $D [H^+]^2$.

To see how the distribution varies with the ionic medium, the Zn(II) distribution was measured between 0.1 M NaClO₄ and benzene containing 5 % LA-1. The hydrogen ion concentration was buffered by 0.01 M phenol, and 5 mM Ba²⁺ was added to mask the carbonate ion.

After the samples had been prepared, the tubes with the two phases were set in a framework which was rotated mechanically for 2–3 hours so that the distribution equilibrium was attained. Then they were centrifuged. A 4-ml portion of each phase was pipetted out and transferred to a small polyethylene tube. Each phase was pipetted carefully to avoid contamination by the other phase.

A portion of the aqueous phase was also transferred into a small plastic vessel with a glass cover, and the hydrogen ion concentration was measured quickly. As the reference solution, 0.01 M HClO₄ + 2.99 M NaClO₄ ($-\log [H^+] = 2.00$), or 0.01 M NaOH + 2.99 M NaClO₄ ($-\log [OH^-] = 2.00$) was used.

A reference half-cell containing a silver-silver chloride electrode in a 2.9 M NaClO₄ + 0.1 M AgClO₄ solution was connected with the test solution and a glass electrode ("Radiometer red") through a 3 M NaClO₄ salt bridge. The emf was measured with Radiometer type PHM 3ik.

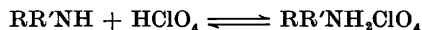
For the experiments in the 0.1 M NaClO₄ solution, a standard reference solution of 0.01 M HClO₄ + 0.09 M NaClO₄ was used in the same apparatus. The use of this solution ($I = 0.1$ M) introduces a constant error, a parallel shift in the $-\log [H^+]$ scale, caused by the liquid junction potential.⁹ However, this error does not influence our discussion about the zinc species in the organic phase.

The γ radioactivity of the solutions in the polyethylene tubes was measured with a well-type scintillation counter, Tracerlab SC-57.

The following factors have been studied to find the most suitable experimental conditions.

Reaction time. Two hours of agitation by the mechanical rotator was enough to obtain distribution equilibrium, both for the extraction from the aqueous phase to the organic phase and the back-extraction from the organic to the aqueous phase.

Buffering reagent. Attempts were made to find a buffering reagent which does not change the distribution. The addition of 0.01 M boric acid, diethylbarbituric acid, etc. decreased the distribution ratio to some extent. Finally it was found that the addition of 0.01 M phenol or cresol to the organic phase buffered the aqueous solution to a $-\log [H^+]$ around 10, and caused practically no decrease in the extraction if the concentration was less than 0.015 M. However, they were not effective when $-\log [H^+]$ was below 9. In this region, LA-1 reacts with perchloric acid and changes into the acid form of the amine. This reaction,



buffered the system to some extent when the two phases were in contact with each other by agitation but as there was only a small amount of the amine in the aqueous phase, this buffering reaction was weak when the two phases were separated, and so it was necessary to measure $-\log [H^+]$ as soon as possible.

The decrease in the extraction caused by the addition of boric acid, etc., became negligible in the $-\log [H^+]$ region above 10.5 where Zn(OH)₂²⁻ is dominant. The distribution ratio was not changed in this $-\log [H^+]$ region even by the addition of some other ligand, for example, carbonate ion.

Influence of carbonate ion. With this experimental procedure, some CO₂ from the air could be absorbed by the aqueous solution. It was found that an addition of a millimolar

amount of sodium carbonate decreased the distribution ratio markedly when $-\log [\text{H}^+]$ was below 10.5. However, by an addition of Ba^{2+} ion, the carbonate in the aqueous solution seemed to be masked very well. For example, after the addition of 0.01 M Ba^{2+} ion to the aqueous solution, an addition of 0.001 M Na_2CO_3 did not change D .

RESULTS

The net distribution ratio of Zn(II). The net distribution ratio of Zn(II) was calculated from the radioactivity measurements as

$$D = (\gamma \text{ activity in 4 ml organic phase}) / (\gamma \text{ activity in 4 ml aqueous phase})$$

Table 1 gives the distribution ratio of Zn(II) between the benzene phase containing 5 % Amberlite LA-1 and 3 M NaClO_4 aqueous phase of various hydrogen ion concentrations. Fig. 1 gives the plot $\log D$ versus $-\log[\text{H}^+]$ for the data in Table 1. Fig. 2 shows the plots of $\log D$ versus $-\log[\text{H}^+]$ when

Table 1. The distribution of Zn(II) between 3 M NaClO_4 and benzene containing 5 % (by volume) Amberlite LA-1.

$-\log [\text{H}^+]$ ($\log D$); 8.424 (−0.503); 8.570 (−0.231); 8.571 (−0.130); 8.585 (−0.085); 8.607 (−0.131); 8.636 (0.068)(a); 8.637 (−0.018); 8.705 (0.212)(a); 8.715 (0.158); 8.764 (0.255); 8.774 (0.356)(a); 8.779 (0.272); 8.810 (0.375); 8.818 (0.223); 8.820 (0.452); 8.828 (0.443); 8.867 (0.494); 8.874 (0.572); 8.896 (0.614); 8.906 (0.677); 8.962 (0.637); 8.970 (0.740); 9.008 (0.758); 9.013 (0.732); 9.040 (0.754)(b); 9.045 (0.895); 9.075 (0.872)(b); 9.090 (1.004); 9.134 (1.107); 9.156 (1.097); 9.177 (1.100); 9.217 (1.146); 9.217 (1.230); 9.227 (1.233); 9.227 (1.238)(c); 9.285 (1.318); 9.305 (1.408); 9.317 (1.410); 9.320 (1.324); 9.339 (1.350); 9.354 (1.420); 9.369 (1.441); 9.444 (1.458); 9.444 (1.525); 9.456 (1.537); 9.471 (1.547); 9.508 (1.600); 9.510 (1.550) (c); 9.518 (1.509); 9.528 (1.539); 9.574 (1.568); 9.594 (1.637); 9.596 (1.634); 9.623 (1.558); 9.630 (1.591); 9.637 (1.611); 9.677 (1.560)(c); 9.684 (1.596); 9.699 (1.548); 9.713 (1.526); 9.745 (1.624); 9.763 (1.487); 9.779 (1.556); 9.797 (1.462); 9.799 (1.494); 9.804 (1.425)(d); 9.823 (1.382) (c); 9.836 (1.441); 9.843 (1.467); 9.860 (1.352); 9.882 (1.328)(d); 9.905 (1.312); 9.909 (1.384); 9.936 (1.243)(d); 9.973 (1.286); 9.988 (1.318)(c); 9.995 (1.149); 10.010 (1.179); 10.022 (1.228); 10.036 (1.104); 10.095 (1.017); 10.105 (1.114); 10.113 (0.999); 10.139 (0.894); 10.149 (0.950); 10.152 (1.013); 10.166 (0.907); 10.179 (0.953); 10.198 (0.870); 10.205 (0.903)(c); 10.233 (0.843); 10.252 (0.793); 10.252 (0.759); 10.262 (0.820); 10.269 (0.824); 10.342 (0.677); 10.365 (0.666); 10.365 (0.649); 10.365 (0.603); 10.396 (0.525); 10.423 (0.516); 10.456 (0.511); 10.462 (0.462); 10.462 (0.461); 10.534 (0.356); 10.565 (0.286); 10.620 (0.218); 10.622 (0.127); 10.795 (−0.061); 10.889 (−0.375); 10.908 (−0.338); 10.935 (−0.330); 11.013 (−0.629); 11.094 (−0.740); 11.121 (−0.688); 11.287 (−1.095); 11.298 (−1.075); 11.369 (−1.243); 11.440 (−1.357);

(a) 0.003 M Na_2CO_3 was added to see the effect of 0.01 M Ba^{2+} in the aqueous phase as the masking reagent for CO_3^{2-} .

(b) Tracer in 1 M NaOH was added to the aqueous phase.

(c) Back-extraction from the organic phase to the aqueous phase.

(d) Initial concentration of Zn(II) in the aqueous phase was 5×10^{-5} M.

the initial concentration of Zn(II) in the aqueous phase was 1×10^{-6} M and 5×10^{-5} M, or when Zn(II) tracer in 1 M NaOH was added to the aqueous phase, or Zn(II) tracer in benzene containing 5 % LA-1 was added to the organic phase. The solid curves in Fig. 1 and 2 give the calculated distribution ratio from the hydrolysis constants and the distribution constant of $\text{Zn}(\text{OH})_2$, which were obtained from the data in Table 1 as will be described later. Fig. 3

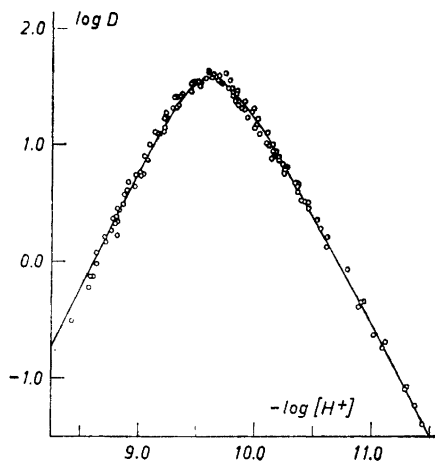


Fig. 1. The distribution of Zn(II) between 3 M NaClO_4 and benzene containing 5% Amberlite LA-1. The solid curve shows the calculated distribution ratio from the constants in Table 3.

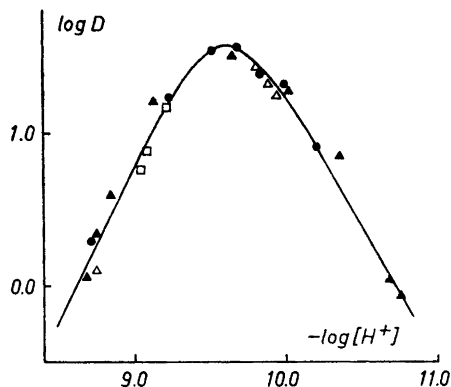


Fig. 2. The distribution of Zn(II) between 3 M NaClO_4 and benzene containing 5% Amberlite LA-1 in samples prepared in different ways: open triangles, initial $[\text{Zn(II)}]_{\text{aq. total}} = 5 \times 10^{-5}$ M; closed triangles, initial $[\text{Zn(II)}]_{\text{aq. total}} = 1 \times 10^{-6}$ M; squares Zn(II) tracer in 1 M NaOH was added, initial $[\text{Zn(II)}]_{\text{aq. total}} = 1 \times 10^{-5}$ M; closed circles, Zn(II) tracer in benzene containing 5% LA-1 was added, initial $[\text{Zn(II)}]_{\text{org. total}} \text{ around } 5 \times 10^{-5}$ M. The solid curve gives the calculated distribution ratio from Fig. 1.

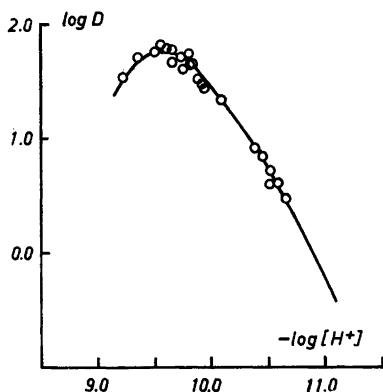


Fig. 3. The distribution of Zn(II) between 0.1 M NaClO_4 and benzene containing 5% Amberlite LA-1.

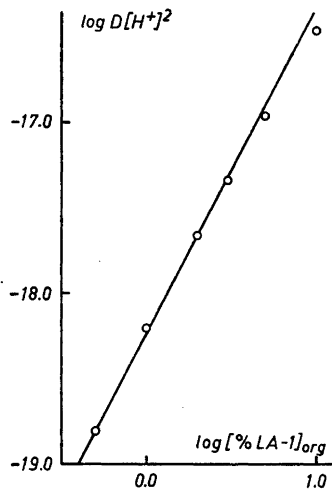


Fig. 4. The distribution of Zn(II) between 3 M NaClO_4 and benzene containing various amounts of Amberlite LA-1, together with a line of slope 2.

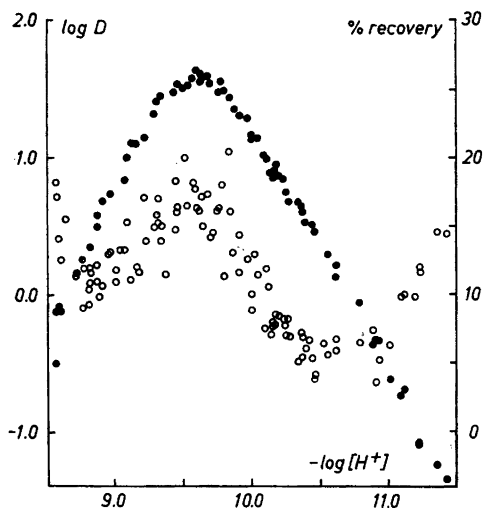


Fig 5. The recovery of zinc from the aqueous and the organic phase. Open circles; % recovery of zinc calculated from γ radioactivity; closed circles, the distribution ratio of Zn(II) (only representative points are given).

gives the plot of $\log D$ versus $-\log [H^+]$ when the aqueous phase was 0.1 M NaClO_4 and the organic phase was benzene containing 5% LA-1. Fig. 4 gives the influence of the LA-1 amine concentration on the distribution ratio, on the «acidic» side where Zn^{2+} predominates. To compare D in solutions of different $-\log [H^+]$, $\log D [H^+]^2$ was plotted versus $\log [\% \text{LA-1}]_{\text{org}}$.

Fig. 5 gives the recovery of Zn radioactive tracer from both phases when 1×10^{-5} M Zn^{2+} was added to the aqueous phase. Table 2 gives $[\text{Zn(II)}]_{\text{org, total}}$, $[\text{Zn(II)}]_{\text{aq, total}}$ and the recovery at some representative points under various experimental conditions. The Zn(II) concentration was calculated from the proportion of γ radioactivity added and recovered from the two phases and the percentage recovery of zinc was calculated as

$$\% \text{ recovery} = ([\text{Zn}]_{\text{org}} + [\text{Zn}]_{\text{aq}}) \times 100 / [\text{Zn}]_{\text{initial}}$$

Here $[\text{Zn}]$ denotes the total amount of zinc calculated from γ radioactivity.

Determination of the equilibrium constants

The first estimation of the equilibrium constants was made graphically. In Fig. 1, the points approach two straight lines of slope 2 and -2 in the two regions where Zn^{2+} or Zn(OH)_4^{2-} is predominant in the solution. From the intersections of these two lines with $D = 0$, the values of $K_D \beta_2^*$ and β_4^* were estimated and using these estimates, a first guess for β_1^* , β_2^* , β_3^* , β_4^* and K_D was made. These estimated constants were then refined by a generalized least squares method using the LETAGROP VRID which is an improved version of the LETAGROP computer program.⁹

Using eqn. (10) and estimates of the parameters one may for each $[H^+]$ value obtain the calculated distribution ratio D_{calc} and LETAGROP VRID searched for the constants which minimized the error-square sum, U ,

$$U = \sum (\log D_{\text{calc}} - \log D_{\text{exp}})^2$$

Table 2. The Zn(II) concentration in the organic and the aqueous phase in the equilibrium state and the recovery of zinc from both phases.

	Zn(II) Initially added	$-\log[\text{H}^+]$	$[\text{Zn(II)}]_{\text{total, org}}$	$[\text{Zn(II)}]_{\text{total, aq}}$	Recovery
	M		M	M	%
A	5×10^{-5}	8.751	3.6×10^{-6}	2.9×10^{-6}	13.0
	»	9.804	6.0×10^{-6}	2.3×10^{-7}	12.4
	»	9.882	6.5×10^{-6}	3.1×10^{-7}	13.6
	»	9.936	4.4×10^{-6}	2.5×10^{-7}	9.4
	1×10^{-5}	8.818	7.5×10^{-7}	3.4×10^{-7}	10.8
	»	9.320	1.4×10^{-6}	6.8×10^{-8}	15.2
	»	9.528	1.6×10^{-6}	4.6×10^{-8}	16.5
	»	9.699	1.4×10^{-6}	3.9×10^{-8}	14.2
	»	9.843	1.5×10^{-6}	5.3×10^{-8}	16.0
	»	10.022	1.2×10^{-6}	7.2×10^{-8}	12.9
	»	10.365	4.7×10^{-7}	1.1×10^{-7}	6.1
	»	10.795	3.1×10^{-7}	3.5×10^{-7}	7.4
	1×10^{-6}	8.839	4.5×10^{-8}	1.2×10^{-8}	5.7
	»	9.645	6.6×10^{-8}	2.1×10^{-9}	8.7
	»	10.019	3.3×10^{-8}	1.8×10^{-9}	5.1
	»	10.348	1.9×10^{-8}	2.8×10^{-9}	2.0
B	1×10^{-5}	9.040	1.1×10^{-6}	1.9×10^{-7}	12.6
	»	9.075	1.2×10^{-6}	1.6×10^{-7}	13.3
	»	9.205	1.4×10^{-6}	9.4×10^{-8}	14.6
C	1×10^{-5}	8.636	1.7×10^{-7}	1.5×10^{-7}	3.2
	»	8.705	1.6×10^{-7}	9.8×10^{-7}	2.5
	»	8.774	2.2×10^{-7}	9.7×10^{-8}	3.1
D	5.7×10^{-5}	9.227	1.1×10^{-6}	6.4×10^{-8}	2.3
	5.7×10^{-5}	9.510	1.2×10^{-6}	3.4×10^{-8}	2.1
	4.8×10^{-5}	9.677	1.5×10^{-6}	4.1×10^{-8}	3.1
	3.6×10^{-5}	9.988	7.2×10^{-7}	3.5×10^{-9}	2.1

A. Tracer in Zn^{2+} form was added to the aqueous phase.

B. Tracer in $\text{Zn}(\text{OH})_4^{2-}$ form was added to the aqueous phase.

C. 0.003 M Na_2CO_3 was added to the aqueous phase and BaCO_3 may be formed.

D. Tracer in $\text{Zn}(\text{OH})_2\text{L}_2$ form was added to the organic phase.

Calculations with five parameters, β_1^* , β_2^* , β_3^* , β_4^* and K_D gave a larger error when β_1^* was larger than zero. This seems to agree with the observation in Fig. 1 that in the plot of $\log D$ versus $-\log [\text{H}^+]$ the slope is first 2 in the lower $-\log [\text{H}^+]$ region, then changes very sharply to zero close to $-\log [\text{H}^+] \approx 9.6$ and then again changes gradually from -1 to -2 in the higher $-\log [\text{H}^+]$ region. The sharp change of slope from 2 to 0 may indicate that ZnOH^+ is negligible within the experimental accuracy of the present work.

Table 3. The hydrolysis constants and the extraction constants of Zn(II) at 25°C.

Aqueous phase: 3 M NaClO₄. Organic phase: benzene containing 5 % Amberlite LA-1.

$$\begin{aligned} \log \beta_2^* &= \log[\text{Zn}(\text{OH})_2][\text{H}^+]^2/[\text{Zn}^{2+}] = -20.10 \pm 0.14 \\ \log \beta_3^* &= \log[\text{Zn}(\text{OH})_3^-][\text{H}^+]^3/[\text{Zn}^{2+}] = -28.83 \pm 0.09 \\ \log \beta_4^* &= \log[\text{Zn}(\text{OH})_4^{2-}][\text{H}^+]^4/[\text{Zn}^{2+}] = -38.72 \pm 0.09 \\ \log K_D &= \log[\text{Zn}(\text{OH})_2]_{\text{org}}/[\text{Zn}(\text{OH})_2]_{\text{aq}} = 2.88 \pm 0.12 \end{aligned}$$

$\log \beta_1^* = \log[\text{ZnOH}^+][\text{H}^+]/[\text{Zn}^{2+}]$ is 0 within the experimental accuracy. The range of error gives three times the standard deviation.

Table 3 gives the "best-fit" values of the four remaining constants. It was concluded that any positive value of β_1^* would give a larger error-square-sum than that obtained with $\beta_1^* = 0$. Thus these calculations seem to indicate that ZnOH⁺ is negligible in the whole $-\log [\text{H}^+]$ region, within the accuracy of the present work.

The distribution of the mononuclear Zn(II) hydrolyzed species as a function of $-\log [\text{H}^+]$ was calculated from these hydrolysis constants and is given in Fig. 6.

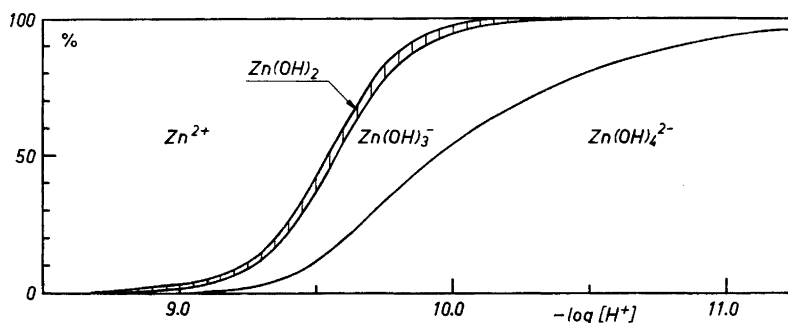


Fig. 6. Distribution of mononuclear Zn(II) hydrolyzed complexes as a function of $-\log [\text{H}^+]$.

DISCUSSION

Chemical form of Zn(II) in the aqueous and the organic phases. As we see in Fig. 2, the distribution ratios of Zn(II) from the experiments when (a) 1×10^{-6} M or 5×10^{-5} M Zn(II) tracer was added, (b) Zn(II) tracer in the Zn(OH)₄²⁻ form was added, or (c) Zn(II) tracer was added with the organic phase, fall practically on the calculated curve for the distribution ratio from Fig. 1.

As we see from Fig. 5 and Table 2, the zinc tracer initially added was not recovered completely. The concentration of zinc in a certain phase may vary, even when the distribution ratio is nearly the same. However, from Table 2, we can see that the final concentration in each phase is roughly 4 to 9 times larger when the initial concentration is 5 times larger and smaller than 1/10

when the initial concentration was one tenth as large. The fact that in spite of such differences in the Zn(II) concentration in the aqueous phase, the distribution ratio of Zn(II) can be regarded as the same, seems to indicate that zinc hydrolysis in these systems is independent of the Zn(II) concentration in the aqueous phase which indicates that the hydrolyzed zinc species are mononuclear.

On the other hand, as we can see in Figs. 1 and 3, the peak of the plot of $\log D$ versus $-\log [H^+]$ is shifted from $\log D \approx 1.6$, $-\log [H^+] \approx 9.6$ in 3 M NaClO₄ to $\log D \approx 1.7$ to 1.8, $-\log [H^+] \approx 9.0$ to 9.1 in 0.1 M NaClO₄. The change of the sodium perchlorate concentration changes not only the concentration of Na⁺ and ClO₄⁻ in the solution but also the activity of the chemical species in the system. This may change the dissociation constant of water (pK_w is 13.8 in 0.1 M NaClO₄ and 14.2 in 3 M NaClO₄), the hydrolysis constants of zinc and the distribution constant of the extractable species. The change of pK_w and the hydrolysis constants of zinc may shift the peak in the horizontal direction (and the latter may also shift it in the vertical direction to some extent). The change of the distribution constant by the change in the ionic strength may shift the peak slightly in the vertical direction. Even though further information is necessary to discuss these factors more completely, the result that a change in the concentration of Na⁺ or ClO₄⁻ from 3 M to 0.1 M does not change the values of D very much seems to indicate that the zinc hydrolyzed species in the organic phase do not contain Na⁺ or ClO₄⁻.

In Fig. 4, we see that the slope of the plot, $\log D[H^+]^2$ versus $\log [\% \text{ LA-1}]_{\text{org}}$, is approximately 2 between 0.5 % and 10 % LA-1 when $-\log [H^+]$ of the aqueous phase is 8 to 9. If we assume that the activity of the amine is approximately proportional to $[\% \text{ LA-1}]_{\text{org}}$, we may conclude that two molecules of amine are attached to one Zn.

From these observations, we may conclude the following about the chemical forms of Zn(II) in the aqueous and the organic phases: (1) Only mononuclear hydrolyzed species are found in the aqueous phase. The calculation of the hydrolysis constants shows that Zn(OH)₂, Zn(OH)₃⁻, and Zn(OH)₄²⁻ are formed from Zn²⁺, and that ZnOH⁺ is negligible. (2) The zinc species in the benzene phase is in the form Zn(OH)₂L₂ where L denotes Amberlite LA-1 amine.

The recovery of zinc tracer. As we see from Table 2 and Fig. 5, the recovery of zinc tracer from both phases is rather low and not reproducible and the concentration of Zn(II) in the two phases does not show any clear trend. However, we may summarize these results approximately, as follows: (i) When the samples are prepared in the same way, the concentration of Zn(II) in both phases is roughly proportional to the amount of Zn(II) initially added at the same $-\log [H^+]$ (*cf.* Part A, Table 2). (ii) The final concentration and the recovery is the same whether the tracer is initially in the form of Zn²⁺ or Zn(OH)₄²⁻ (*cf.* Table 2, Part A and B). (iii) The recovery and the final Zn(II) concentration are smaller when BaCO₃ particles are formed or when the tracer is added with the organic phase (*cf.* Table 2, Part C and D). (iv) Even though the final concentration and the recovery are not very reproducible, still the distribution ratio is reproducible.

The zinc which was not recovered from either the organic or the aqueous phase may have collected on the surface of the glass tube or in the inner surface between the two phases, and its loss cannot be explained only by the formation of solid zinc hydroxide. When we calculate the solubility product from $[\text{Zn(II)}]_{\text{aq, total}}$ in Table 2 assuming that the aqueous phase is in equilibrium with solid Zn(OH)_2 , the $\log K_{s0}^*$ is, for instance, 12.0, 11.2, and 9.8, when the initial $[\text{Zn(II)}]_{\text{aq, total}}$ are 5×10^{-5} , 1×10^{-5} , and 1×10^{-6} , respectively, and $-\log [\text{H}^+]$ is about 8.8. (Here $[\text{Zn(II)}]_{\text{aq, total}}$ is nearly the same as $[\text{Zn}^{2+}]$; cf. Fig. 6.) The calculated K_{s0}^* seem to vary too much even when we take into account the fact that there are different crystal phases of Zn(OH)_2 .⁴ The small recovery of zinc when BaCO_3 particles are formed seems to indicate some kind of adsorption of zinc on the surface of the particles.

The chemical errors. The main chemical errors may be caused by the error of $-\log [\text{H}^+]$ measurements and by the contamination of one phase by another.

As the hydrogen ion concentration is buffered by the amine, only for the extraction of perchloric acid into the organic phase below $-\log [\text{H}^+] \approx 9$, there could be an error in $-\log [\text{H}^+]$ in this region but this should be less when $-\log [\text{H}^+]$ is above 9.

According to our experience in this laboratory, the error caused by the contamination of the organic and the aqueous phases by each other seems to be very small when the samples are taken carefully by pipets after centrifugation. However, even after centrifugation contamination of the phases may occur by solid particles such as zinc hydroxide or basic perchlorate salts, or dust particles which can adsorb zinc if they are very small or their density is almost the same as that of the solutions. This might be possible especially in the present study where most of the zinc is present in the third phase.

Zn(II) hydrolyzed species. It is remarkable that ZnOH^+ has not been found in this study within the experimental accuracy even though MOH^+ species of Cu(II) and Cd(II) have been well confirmed.^{2,10} The relative concentration of Zn(OH)_2 is very small over the entire $-\log [\text{H}^+]$ region as seen in Fig. 6. However, it was possible to detect this species, and to study Zn(II) hydrolysis from the change in its relative concentration in the aqueous phase. In this work this could be measured as the change in the distribution ratio because the distribution constant for this species, K_D , is so large that one can determine $[\text{Zn(II)}]_{\text{org}}$ and D . This may be one of the advantages of the distribution method for the study of a system which contains one neutral species together with various charged species.

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