

AQUO AND HALO COMPLEXES OF Zn^{2+} ION IN ISOMOLAR SERIES PERCHLORATE-HALIDE*

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The formation of halo complexes of Zn^{2+} ion in isomolar series $Ca(ClO_4)_2$ - $CaCl_2$, $NaClO_4$ - $NaBr$ and $NaClO_4$ - NaI was studied by means of the method of molar volumes. Using isomolar series in which the concentration of halide ions was increased independently of the activity of water it was demonstrated that dehydration of octahedral complexes to tetrahedral ones is not caused by the decrease of water activity but by the penetration of halide ions into the inner coordination sphere of the complex. Concentration stability constants were calculated and the conditions were found where this method can be employed for evaluating the experimental data on molar volumes.

Using the method of molar volumes, as described in earlier communications¹⁻⁴ it was found⁵ that in aqueous solutions of halides alone, the hexaquo zinc(II) cation is transformed, with increasing concentration of the complexing background solutions (in the range of 1-5 mol/l of halide ions) to halo zincate anions with coordination number 4. The intermediates, containing more water molecules, $[ZnX_3 \cdot (H_2O)_3]^-$ and $[ZnX_4(H_2O)_2]^{2-}$, where X = Cl, Br or I could not be detected in the solution of halide alone.

Since in these solutions the water activity decreases with increasing concentration of halide ions, the observed dehydration can have two possible causes: either it is due to the decrease of water activity, or it is caused by the entering of halide ligands into the coordination sphere of the complex of Zn^{2+} ion, where it leads, for sterical and quantum chemical reasons, to the rearrangement of coordination polyhedron from octahedral to tetrahedral coordination. This could not be decided by experiments carried out in solutions of halide alone, since with increasing halide concentration its activity increases, whereas that of water decreases.

In order to elucidate this problem which is of principal importance in the studies of general coordination relationships, we have performed analogous measurements of apparent molar volumes of zinc(II) salts under the conditions when the activity

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of water remained approximately constant and only the activity of halide ions changed. This was realized in isomolar series perchlorate-halide in which the halide concentration was adjusted to constant total molarity by adding perchlorate as "inert" electrolyte whose anion does not form aniono complexes with Zn^{2+} ion in appreciable amounts.

THEORETICAL

The values of molar volume of a particle in anhydrous form, V_i^0 , and at infinite dilution, V_i^∞ serve as basic data for determining molar volume V' at different concentrations. According to the Masson rule⁶ stating that molar volume of ions is a linear function of the square root of molar concentration, the value of molar volume can be calculated for a given concentration of the isomolar series using relation (1)

$$V' = V_i^\infty + (V_i^0 - V_i^\infty) \cdot \sqrt{(c/c^0)}, \quad (1)$$

where c is molar concentration of the respective isomolar series, c^0 is molar concentration corresponding to the hypothetical "anhydrous" state of the solution, and V' is molar volume corresponding to concentration c .

If concentration of anhydrous solution is approximately the same for both electrolytes of the isomolar series, then the theoretical value of molar volumes depends only on total concentration of the respective electrolytes and is independent of the X^-/ClO_4^- ratio. Consequently, the theoretical values of molar volumes V' are then graphically represented by horizontal straight lines with constant final volume of the given reaction.

The use of isomolar series allows, in addition to the investigation of the causes of dehydration of halo complexes of Zn^{2+} ions, also to evaluate quantitatively the experimental data on molar volumes and to determine the corresponding stability constants.

Molar volume V' (ml/mol) of the sample of the studied salt whose cation exists in the complex-forming solution of the electrolyte in n complex forms, is given by the expression for calculating the mean value \bar{V}'

$$\bar{V}' = \frac{\sum_0^n c_i V_i'}{\sum_0^n c_i}, \quad (2)$$

where c_i are concentrations of individual complex forms and V_i' are their molar volumes.

If the cation of the sample M forms in the given solution besides free aquo ions ($i = 0$) only one-nucleus aniono complexes MX_i with total stability constants β_i^+ ,

defined as

$$\beta'_i = [MX_i^{2-i}]/[M^{2+}][X^-]^i, \quad (3)$$

then it holds for the concentration c_i of the i -th complex

$$c_i = c_0 \beta'_i c_X^i, \quad (4)$$

where the total concentration $[X^-]$ of free ions X^- in the solution is put approximately equal, at low concentrations of the sample with respect to excess background electrolyte, to the analytical concentration of ions X^- in the background solution, c_X .

On substituting Eq. (4) into Eq. (2), we obtain, after reducing by c_0 , the expression for the total molar volume of the system V'

$$V' = \sum_0^i \beta'_i V'_i c_X^i / \sum_0^i \beta'_i c_X^i. \quad (5)$$

In isomolar series the activity coefficients of ions can be taken, in rough approximation, as constants, since at low total concentrations (up to $2M$) their changes in the interval from solution of pure halide to solution of pure perchlorate are negligible at the given accuracy of the densimetric measurements of molar volumes of small sample weights. At high total concentrations the formation of complexes is finished in most cases by 1 to $2M-X^-$, when even perchlorate prevails in this series so that even in this case the ions are present in a constant ionic medium. For this reason the total stability constants β'_i in Eq. (5) can be considered, within each series, as adjusted constant parameters.

The values of these constants for a given isomolar series can be determined by comparing the experimentally found $V'-c_X$ -dependence with the calculated courses of the Bjerrum function (5) for variously chosen concentration stability constants β'_i .

This quantitative evaluation of experimental curves $V'-c_X$ - describes fairly well the existence of the i -th kinds of acido complexes in aqueous solutions of electrolytes and at the same time identifies the change of total coordination number of the true complex according to the system of theoretical curves to which the experimentally found values can be well fitted when assigning constants $\beta'_1 - \beta'_4$.

The change of coordination number of aniono complex from 6 to 4, accompanied by the release of two water molecules from the inner coordination sphere, results in the change of molar volume V'_i by 10 to 12 ml/mol, which exceeds by 1 order of magnitude the inaccuracy of the measurement of V' , inherent to the float method.

The course of experimental curves makes it possible to decide, whether the change in coordination number of the complex takes place immediately when the first ligand enters or whether it occurs only during some higher intermediate step. A good guide in solving this question is the initial course of the curves in series with

low electrolyte concentration where the activity coefficients approach unity. Here the lower steps can be distinguished. The stability constant $\beta'_1 = K'_1$ increases with the first power of activity coefficients of ions, whereas β'_i increases with their i -th power. Series with high electrolyte concentration are therefore not suitable for determining the change in coordination number, since the activity coefficients are higher than 1 and consequently β'_4 is considerably greater as compared to β'_1 and the formation of the highest complex becomes a dominant process already at low concentrations of the ligand-forming component.

This modified method of the determination of stability constants from molar volumes in isomolar series allows to evaluate the first valid decimal in the order of tenths to tens, in the case of higher values at least to estimate their order of magnitude, thus representing an approximate method even when using the mentioned approximations in the evaluation of data. The method was employed for calculating the stability constants of halide complexes of Zn^{2+} ion in isomolar series perchlorate-halide.

EXPERIMENTAL

The chemicals used were of the reagent grade purity. Zinc(II) perchlorate was prepared by dissolving zinc(II) carbonate in perchloric acid and was twice recrystallized. Measurement of molar volumes was performed in isomolar series $CaCl_2$ - $Ca(ClO_4)_2$, $NaBr$ - $NaClO_4$ and NaI - $NaClO_4$, all adjusted to the acidity of $0.1M-HClO_4$. The experimentally found values of molar volumes V' and the values of V_i^0 and V_i for a given electrolyte and a given form of the complex were determined using the method described earlier¹⁻⁵. Concentration of salts of basic solutions in isomolar series was determined from their densities and the concentration of zinc(II) perchlorate was determined chelatometrically.

RESULTS AND DISCUSSION

Comparison of the measured apparent volumes of salts of divalent zinc with the values calculated for different halo-aquo complexes of Zn^{2+} ion shows that Zn^{2+} ion is present in perchlorate solution containing no halide ions, up to highest ClO_4^- concentrations as an aquo ion with the coordination number 6 (Figs 1-3).

In isomolar transfer from perchlorate to halide medium during which water activity does not change and in the case of chloride it even increases⁷, the entering of halide ions into the coordination sphere of Zn^{2+} is accompanied by dehydration under the formation of a complex with coordination number 4. At high concentration of halides (2-3M) the curve of molar volumes approaches in all cases asymptotically the values corresponding to anhydrous halo complexes $[ZnX_4]^{2-}$ and that even in the case of iodide systems, if we use the coordination volume of the ligand I^- $V_i^k = 32.1$ ml/mol, i.e. $V_i^k = 1.21V_i$, as it was found for the coordination volumes of ligands Cl^- and Br^- in $HgBr_4^{2-}$ and $HgCl_4^{2-}$ complexes¹⁻³.

The problem is now whether the change in the coordination number of the complex occurs immediately when the first ligand enters or whether it takes place only during one of the higher steps. The cue to this question may be the initial course of the curves in the region of low concentrations. Here the values of apparent volumes increase proportionally to the concentration of halide ions. This indicates that monohalo complex is formed predominantly in the initial stages at low concentrations. If the aquo ion were converted directly to higher complexes, the tangent of the curve V' had to be zero in the initial point and the curve would take a course of a parabol of the second or higher order.

TABLE I

Theoretical Values of Apparent Molar Volumes, V'_i (ml/mol), of Aquo and Chloro Complexes of Zn^{2+} Ion (Evaluated for $Zn(ClO_4)_2$ in solutions of $CaCl_2$)

Complex	V'_i^0	V'_i^∞	V'_1	V'_2	V'_4	V'_6
$[Zn(H_2O)_6]^{2+}$	82.5	60.0	65.9	68.4	71.8	74.4
$[Zn(H_2O)_5Cl]^+$	86.2	72.5	76.1	77.6	79.7	81.3
$[Zn(H_2O)_4Cl_2]$	92.0	83.0	85.4	86.3	87.7	88.0
$[Zn(H_2O)_2Cl_4]^{2-}$	96.7	78.5	83.3	85.2	88.0	92.0
$[Zn(H_2O)_4]^{2+}$	94.0	69.5	75.5	78.3	82.1	85.0
$[Zn(H_2O)_3Cl]^+$	98.2	84.0	87.7	89.3	91.4	93.1
$[Zn(H_2O)_2Cl_2]$	101.7	94.7	96.5	97.3	98.4	99.2
$[Zn(H_2O)Cl_3]^-$	105.2	99.5	101.0	101.6	102.5	103.2
$[ZnCl_4]^{2-}$	109.1	88.5	93.9	96.1	99.3	101.7

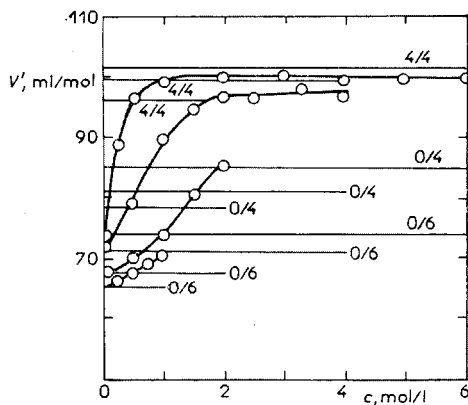


FIG. 1

Apparent Molar Volume of $Zn(ClO_4)_2$ in Isomolar Series $CaCl_2-Ca(ClO_4)_2$

0/6 Theoretical curves of the $[Zn(H_2O)_6]^{2+}$ complex, 1/6 $[Zn(H_2O)_5Cl]^+$, 0/4 $[Zn(H_2O)_4]^{2+}$, 4/4 $[ZnCl_4]^{2-}$ ($c = 1, 2, 4$ and 6 mol/l).

In further course an indication can be observed that the curve approaches asymptotically the theoretical value for monohalo complex with coordination number 6. This asymptotic course is most pronounced in isomolar iodide series 1M and 2M (Fig. 3), it is indicated in a detectable amount also in bromides in series 2M (Fig. 2), whereas in chloride series it is totally overlapped by the formation of higher complexes (Fig. 1, Table I), which are the most stable ones of all three halo complexes. Even here, however, the initial linear increase of the curves in 1M and 2M-Cl⁻-ClO₄⁻ proves the presence of monochloro complex and there is no reason to assume why, in the case of the Cl⁻ ligand which is the smallest of all halides, this complex could also not have the coordination number 6 as the other two complexes.

After the region of formation of [ZnX(H₂O)₅]⁺ complexes the curves V'-c in all cases leave very quickly the region of complexes with coordination number 6, passing relatively steeply into the region of complexes with coordination number 4 where finally they attain the value corresponding to the [ZnX₄]²⁻ complex. From this we can estimate that complexes higher than ZnX⁺, as far as they are present in the solution in a detectable amount, have the coordination number 4.

On the basis of these findings an attempt was made to analyze quantitatively the obtained V'-c_X- dependences. Total concentration stability constants β_i as evaluated from the curves of molar volumes for individual isomolar series chloride-perchlorate are the following: for series 1M-Cl⁻-ClO₄⁻ β₁ = 0.5; for 2M β₁ = 0.5; β₄ = 0.1; for 4M β₁ = 3.0, β₂ = 2.5, β₄ = 1.0; for 6M β₁ = 5.0, β₂ = 10.0, β₄ = 100. The existence of higher chloro complexes was verified also by other methods⁸⁻¹².

TABLE II

Theoretical Values of Apparent Molar Volumes, V'_i (ml/mol), of Aquo and Bromo Complexes of Zn²⁺ Ion (Evaluated for Zn(ClO₄)₂ in solutions of NaBr)

Complex	V' ₁ ⁰	V' ₁ [∞]	V' ₁	V' ₂	V' ₃	V' ₅
[Zn(H ₂ O) ₆] ²⁺	82.5	60.0	66.6	69.3	71.2	74.7
[Zn(H ₂ O) ₅ Br] ⁺	86.7	71.9	76.1	77.9	79.1	81.4
[Zn(H ₂ O) ₄ Br ₂]	90.4	81.0	83.7	84.8	85.6	87.0
[Zn(H ₂ O) ₃ Br ₃] ⁻	93.8	85.2	87.7	88.7	89.4	90.7
[Zn(H ₂ O) ₂ Br ₄] ²⁻	96.8	78.0	83.4	85.6	87.2	90.1
[Zn(H ₂ O) ₄] ²⁺	94.0	69.5	76.5	79.4	81.6	85.2
[Zn(H ₂ O) ₃ Br] ⁺	98.7	83.5	87.8	89.5	90.9	93.0
[Zn(H ₂ O) ₂ Br ₂]	102.4	93.0	95.7	96.8	97.7	99.9
[Zn(H ₂ O)Br ₃] ⁻	107.1	98.0	100.6	101.7	102.5	103.8
[ZnBr ₄] ²⁻	110.3	88.5	94.6	97.3	99.3	102.5

The transformation of aquo zinc(II) complex to tetrabromozincate complex proceeds also in bromide solutions even in the highest isomolar series $NaClO_4$ - $NaBr$ via $[ZnBr(H_2O)_5]^+$ (Fig. 2, Table II). The found stability constants indicate a lower tendency to form higher bromo complexes than have been found in chloride solution. The same results were found also in solutions of pure bromides⁵. Here the stability constants for the highest complex β_4 are by two orders of magnitude lower than β_4 for the $[ZnCl_4]^{2-}$ complex. For the series $2M-Br^- - ClO_4^-$ $\beta_1 = 1.0$; for $3M$ $\beta_1 = 1.0$, $\beta_4 = 0.06$ and for $5M$ $\beta_1 = 3.0$, $\beta_2 = 2.0$, $\beta_4 = 0.1$.

The tendency towards iodide complexes formation is still lower than that found with bromide systems. If we compare the rate of conversion of the aquo complex $[Zn(H_2O)_6]^{2+}$ to iodo complexes (Fig. 3, Table III), it follows from the calculated

FIG. 2

Apparent Molar Volume of $Zn(ClO_4)_2$ in Isomolar Series $NaBr-NaClO_4$

0/6 Theoretical curves of the $[Zn(H_2O)_6]^{2+}$ complex, 1/6 $[Zn(H_2O)_5Br]^+$, 2/6 $[Zn(H_2O)_4Br_2]$, 2/4 $[Zn(H_2O)_2Br_2]$, 3/4 $[Zn(H_2O)Br_3]^-$, 4/4 $[ZnBr_4]^{2-}$ ($c = 1, 2, 3$ and 5 mol/l).

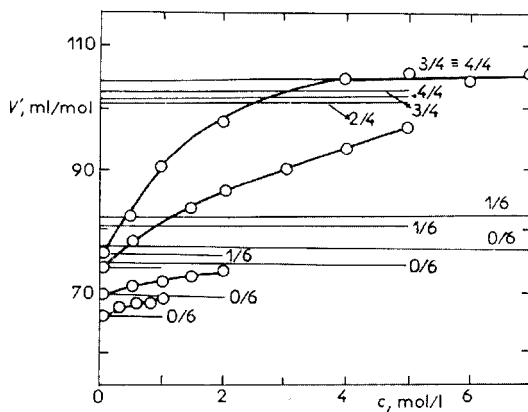
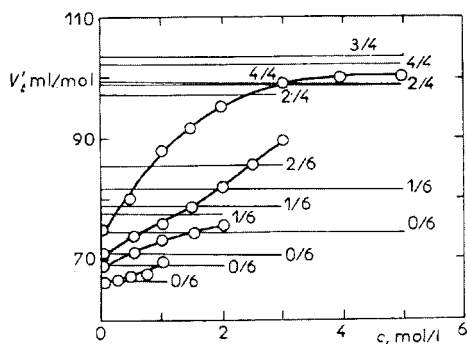


FIG. 3

Apparent Molar Volume of $Zn(ClO_4)_2$ in Isomolar Series $NaI-NaClO_4$

0/6 Theoretical curves of the $[Zn(H_2O)_6]^{2+}$ complex, 1/6 $[Zn(H_2O)_5I]^+$, 2/4 $[Zn(H_2O)_2I_2]$, 3/4 $[Zn(H_2O)I_3]^-$, 4/4 $[ZnI_4]^{2-}$ ($c = 1, 2, 5$ and 7 mol/l).

TABLE III

Theoretical Values of Apparent Molar Volumes, V'_i (ml/mol), of Aquo and Iodo Complexes of Zn^{2+} ion (Evaluated for $Zn(ClO_4)_2$ in solutions of NaJ)

Complex	V_i^0	V_i^∞	V'_1	V'_2	V'_5	V'_7
$[Zn(H_2O)_6]^{2+}$	82.5	60.0	66.4	69.1	74.4	77.0
$[Zn(H_2O)_5I]^+$	87.3	71.0	75.7	77.6	81.4	83.3
$[Zn(H_2O)_4I_2]$	91.6	79.0	82.6	84.1	87.1	88.5
$[Zn(H_2O)_3I_3]^-$	94.9	80.5	84.6	86.3	89.7	91.4
$[Zn(H_2O)_2I_4]^{2-}$	98.2	75.0	81.6	84.4	89.5	92.6
$[Zn(H_2O)_4]^{2+}$	94.0	69.5	76.5	79.4	85.2	88.0
$[Zn(H_2O)_3I]^+$	99.3	81.5	86.6	88.7	92.9	94.9
$[Zn(H_2O)_2I_2]$	104.6	92.0	95.6	97.1	100.1	101.5
$[Zn(H_2O)I_3]^-$	107.9	94.5	98.3	99.9	103.1	104.6
$[ZnI_4]^{2-}$	111.2	88.0	94.6	97.4	102.8	105.6

values of stability constants that the degree of conversion found in 4M- $CaCl_2$ - $-Ca(ClO_4)_2$ occurs in the series NaI- $NaClO_4$ in the same extent only at 7M concentration. The values of β_i , corresponding to V'_i - c_1 curves are the following: for series 1M $\beta_1 = 0.7$; for 2M $\beta_1 = 0.7$; for 5M $\beta_1 = 2.5$, $\beta_2 = 0.12$, $\beta_4 = 0.07$; for 7M $\beta_1 = 1.7$, $\beta_4 = 1.0$. The found values of stability constants of halo complexes of the Zn^{2+} ion are in accordance with the values determined by means of other methods¹³⁻¹⁵.

Zn^{2+} ion can be ranged among the group of light transition metals, characterized by the same relation describing the formation of halo complexes. In this group the Zn^{2+} ion behaves as anion forming the most stable halo complexes. The stability increases in the sequence $Ni^{2+} < Mn^{2+} < Cu^{2+} < Zn^{2+}$ and the tendency to form halogeno complexes decreases in the series $Cl^- > Br^- > I^-$, ranging Zn^{2+} among "hard" complex-formers.

The second problem of which we have tried to find a solution, was whether the change of coordination number, occurring as the result of the formation of higher halo complexes of the Zn^{2+} ion, is due to the decrease of water activity or to the inherent properties of halo ions. Here the answer is unambiguous: The change of the coordination number from 6 to 4 takes place at constant water activity as the result of entering of the second halide ion. All higher forms show the total coordination number 4 and this change is not caused by the decrease of water activity.

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