Comparison of Stability Constants of Alkaline Earth Chlorides between Conductometric and Potentiometric Studies

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The stability constants of alkaline-earth metal chlorides, MCl^+ (M^{2+}=Ca, Sr, Ba), were determined by conductometric and potentiometric measurements in methanol. The conductometric study was made at 5, 15, 25, 35, and 45 °C; the potentiometric study was at 25 °C. The formation of MCl_2 was neglected in the conductometric study, while in the potentiometric study it was taken into account, though it was too slight to determine a reliable value of the stability constant of MCl_2. The stability constants of MCl^+, K_1, determined by conductometric measurements were compared with the previous conductometric results of the same metal(II) perchlorates, K_{1A}. The magnitudes of K_1 and K_{1A} increase in the orders $Ca \simeq Sr < Ba$ and $Ca < Sr < Ba$, respectively. K_1 is larger than K_{1A} for calcium and strontium, though the K_1 and K_{1A} values for barium are similar to each other; that is, the degree of such an increase in K_{1A} is larger than that in K_1. Both enthalpy and entropy changes determined by conductometric measurements were positive for all the chlorides and perchlorates. However, the enthalpy changes of the chlorides were 1.2—1.4 times as large as those of the perchlorates. On the other hand, the K_1 from potentiometry was smaller for every chloride and also increased more steeply (in the order $Ca < Sr < Ba$) than that from conductometry. Therefore, the difference of K_1 between conductometry and potentiometry decreases in going from Ca to Ba.

We previously studied the stability constants of Ca(II), Sr(II), and Ba(II) chlorides in methanol with a potentiometric method.[1] Then, the K_1 of Sr(II) was about 4-times larger than those of Ca(II) and Ba(II). Regarding this abnormal results, we gave no explanation in the previous work, though we had a little doubt about the influence of impurities in the metal salts used on the stability constants. On the other hand, we were a little anxious about the accuracy of our potentiometric determination in the case of small stability constants, such as the alkaline-earth chlorides. Thus, with the main purpose of checking the abnormal result of Sr(II) chloride, we have made conductometric measurements. At the same time, the potentiometric experiment was repeated. However, the experimental method has been partly improved in order to determine the small stability constant more accurately. We also made a careful purification of the metal(II) salts, especially strontium perchlorate.

It is frequently thought that an ion pair, which is generally less stable than a highly covalent metal complex, does not exist as only one type of contact structure (contact ion pair) but also has various types of solvent-separated structures in which the cation and/or anion remain solvated (solvent-separated ion pair).[2] Therefore, in varying degrees of solvent-separation, if species detected as an ion pair vary according to experimental methods, it is natural that a different experiment yields a different stability constant of the ion pair. Being interested in the relation between ion pairing and solvation, we have carefully examined the results obtained by two quite different methods of conductometry and potentiometry in this study; the former showed an increase in the solution resistance but the latter showed a decrease in the concentration of the free anions caused by ion pairing.

Experimental

Materials. Conductometry: Calcium(II) and Strontium(II) chlorides hexahydrates were prepared by neutralizing the corresponding carbonates with hydrochloric acid and purifying by triple recrystallizations from distilled deionized-water. The calcium chloride was dried on a vacuum line over diphosphorus pentaoxide during heating under an infrared lamp for 1 day; the strontium chloride was vacuum dried in an oven over silica gel at 120 °C for 10 hours. After drying, these chlorides became nearly anhydrous salts. Barium(II) chloride anhydrous of a commercially available material (Rare Metallic, 99.99%-grade) was vacuum dried in an oven over silica gel at 120 °C for 10 h.

Potentiometry: By dissolving in perchloric acid, calcium(II) perchlorate trihydrate was prepared from calcium nitrate purified by double recrystallizations from distilled deionized-water and strontium(II) perchlorate dihydrate from strontium carbonate. The calcium perchlorate was recrystallized from distilled deionized-water and dried on a vacuum line over diphosphorus pentaoxide for 3 d and monohydrate was obtained. The strontium perchlorate was recrystallized from distilled deionized-water, and furthermore from purified methanol, and then vacuum dried in an oven over silica gel at 120 °C for 1 day and anhydrous perchlorate was obtained. Barium(II) perchlorate anhydrous (Wako, special grade) which was vacuum dried in an oven over silica gel at 120 °C for 1 day was used without any purification.

The purification of methanol has been described previously.[1,3] Stock solution of these metal(II) salts (except barium chloride) were standardized by titration with EDTA; the barium chloride stock solution was standardized by a gravimetric method.

Measurements. The detailed procedure of conductometric measurements has been described previously.[3] However, in this experiment temperatures were controlled within an accuracy of ±0.01 °C by a Neslab RTE-5 refrigerated circulating bath which was monitored by a Guildline digital platinum resistance thermometer (model 9535).

Outline of potentiometric measurements could be found in previous manuscripts.[4–6] All potentiometric measurements were made at 25.0±0.1 °C, and ionic strength, I, was kept nearly constant at 0.05 M (M=mol dm^{-3}). In order to attain an accurate determination of a small K_1, measurements of the standard electromotive force, emf, were improved as follows. In the previous method, standardization was achieved by measuring the emf of a standard solution free from metal(II) ions (which were prepared aside) after every potentiometric titration was performed in the usual way. In this manner, a titrated sample solution must be replaced with a standard solution in a measuring cell when the standardization is carried out. It is possible that this displacement becomes a cause of experimental errors. In order to remove such a cause of errors, we rechecked the standard emf by measuring the emf of a solution which was prepared by the addition of an appropriate amount of metal(II) ions to the usual metal(II)-free standard solution already measured.

If K_2 is negligible relative to K_1, K_1 can be determined merely by the above standardization procedure. Using this procedure, the K_1 of Ca(II) and Ba(II) have been determined at several metal-ion concentrations, because it is assured by the previous study[1] and the present results of Sr(II) that K_2 of Ca(II), Sr(II), and Ba(II) chlorides are negligibly small.

Data Treatment

In a sample solution,

$$M^{2+} + Cl^- \rightleftarrows MCl^+ \quad (K_1) \tag{1}$$

$$MCl^+ + Cl^- \rightleftarrows MCl_2 \quad (K_2) \tag{2}$$

$$M^{2+} + ClO_4^- \rightleftarrows MClO_4^+ \quad (K_{1A}) \tag{3}$$

are major equilibria: However, the last case (Eq. 3) does not take place in the solution of conductometric measurements since no salts other than MCl_2 are contained in that solution.

Conductometry. Conductometric data were treated by a modified Fuoss and Edelson method[3] in which the equilibrium (Eq. 2) was not completely taken into account. The modified Fuoss and Edelson equation is

$$\Lambda F = \Lambda_o - XK_1/\Lambda_o, \tag{4}$$

where

$$X = cy_{2+}\Lambda F(\Lambda F - \Lambda_o/2)$$

and

$$F = [\{1 - \delta_c{}^{1/2}/(1 + BaI^{1/2})\}^{-1} + (\Lambda_o - \lambda_o)/2\Lambda]/$$
$$\{1 + (\Lambda_o - \lambda_o)/2\Lambda_o\}.$$

Here, Λ and Λ_o are the molar and the limiting molar conductances of $1/2MCl_2$, respectively. λ_o and c are the limiting molar conductance of Cl^- and the total concentration of Cl^-, respectively. Onsager's slope divided by Λ_o is δ. The ion activity coefficient of M^{2+}, y_{2+}, was calculated by the Debye-Hückel second approximation:

$$\log y = -Az_i{}^2I^{1/2}/(1 + BaI^{1/2}), \tag{5}$$

where a is an ion-size parameter which has been 5 Å (for Sr^{2+} and Ba^{2+}) or 6 Å (for Ca^{2+}). The ionic strength, I, is 1.5 times as large as the total concentration of Cl^-, c.

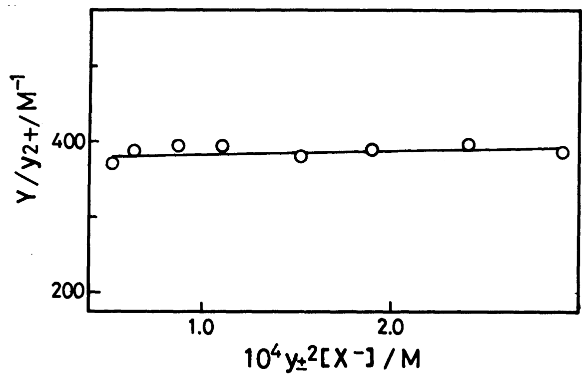

Fig. 1. The plot according to Eq. 6 for strontium chloride. C°_M=8.072×10^{-3} M, C°_I=0.035 M.

Potentiometry. Our latest treatment of potentiometric data was previously described in detail.[4] According to the treatment,

$$Y/y_{2+} = K_1 + 2K_1K_2(y_\pm{}^2[X^-]), \tag{6}$$

where

$$Y = (C^\circ_X - [X^-])/([M^{2+}][X^-]),$$

is a key equation. Here, C°_X is the total concentration of NaCl and $y_\pm$ is the ion activity coefficient of a monovalent ion which has been calculated by Eq. 5 at a=4 Å. In the present study, X^- is Cl^-. In order to plot Y/y_{2+} against $y_\pm^2$ [Cl^-], it is necessary to calculate the [M^{2+}], [Cl^-], and y's. The detailed procedure of the calculation could he found in a previous manuscript.[4]

If K_2 is negligible relative to K_1, we can determine the K_1 value from the data of a change in [Cl^-] caused by the addition of M^{2+}, C°_X-[Cl^-], and [M^{2+}] after the M^{2+}-addition, which are obtained by the preceding standardization of emf.

Results and Discussion

Conductometry. From plots according to Eq. 3, Λ_o and K_1 were determined (Tables 1 and 2). In the tables, K_{1A} of perchlorate salts is included; however, these values were determined by the recalculation of previous data[7] in the modified Fuoss and Edelson method. The difference between the modified and original Fuoss and Edelson methods was discussed in a previous manuscript.[3] Lee and Wheaton studied Ca, Sr, and Ba chlorides in methanol by using their original conductance equation; according to their results at 25 °C, K_1 were 410±2.6, 425±4.3, and 430±7.7 M^{-1} for Ca, Sr, and Ba, respectively (Λ_o were 110.0, 112.2, and 112.9 S cm^{2}mol^{-1}, respectively).[8] Pethybridge recalculated these values using the data and calculation of Lee-Wheaton; K_1 were 450, 393, and 480 M^{-1} for Ca, Sr, and Ba, respectively.[9] In spite of our quite different data treatment, our K_1 are in relatively good agreement

Table 1. Limiting Molar Conductances ($\mathrm{S\,cm^2\,mol^{-1}}$) of $1/2\mathrm{MCl_2}$ and $1/2\mathrm{M(ClO_4)_2}$ in Methanol at 278.15—318.15 K

M(II)	278.15K	288.15K	298.15K	308.15K	318.15K
			$\mathrm{MCl_2}$		
Ca	81.6±0.1	95.1±0.1	109.9±0.1	126.3±0.2	144.2±0.2
Sr	84.7±0.2	98.9±0.2	114.5±0.2	131.7±0.3	150.0±0.4
Ba	85.2±0.2	99.5±0.2	115.3±0.2	132.6±0.3	151.7±0.3
			$\mathrm{M(ClO_4)_2}$[a]		
Ca	99.0±0.3	114.9±0.3	132.1±0.3	150.7±0.4	171.5±0.4
Sr	95.8±0.2	111.3±0.3	128.0±0.3	146.4±0.4	166.9±0.6
Ba	101.6±0.3	118.1±0.3	135.7±0.4	154.7±0.5	176.1±0.6

a) Recalculated from the previous data (Ref. 6) by the modified Fuoss and Edelson method.

Table 2. Stability Constants of $\mathrm{MCl^+}$ and $\mathrm{MClO_4^+}$, K_1 and K_{1A} ($\mathrm{M^{-1}}$), in Methanol at 278.15—318.15 K

M(II)	278.15K	288.15K	298.15K	308.15K	318.15K
			$\mathrm{MCl^+}$		
Ca	253± 7	309± 8	408± 7	549± 8	758±10
Sr	249±10	313±11	403±12	534±13	715±19
Ba	275± 8	353± 9	464±11	623±12	863±16
			$\mathrm{MClO_4^+}$[a]		
Ca	173±10	209±11	254±12	309±12	386±14
Sr	227±10	277±11	345±12	430±15	551±21
Ba	293±13	363±15	451±17	562±20	717±24

a) Recalculated from the previous data (Ref. 6) by the modified Fuoss and Edelson method.

Table 3. Thermodynamic Functions of the Formation of $\mathrm{MCl^+}$ and $\mathrm{MClO_4^+}$ at 298.15 K

M(II)	$\Delta H_1^{\ominus}$	$\Delta S_1^{\ominus}$	$-\Delta G_1^{\ominus}$
	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{JK^{-1}\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$
		$\mathrm{MCl^+}$	
Ca	20.6±0.5	119±2	14.90±0.04
Sr	19.7±0.8	116±3	14.87±0.07
Ba	21.2±0.6	122±2	15.21±0.06
		$\mathrm{MClO_4^+}$	
Ca	14.8±1.1	96±4	13.72±0.11
Sr	16.4±0.9	104±3	14.49±0.09
Ba	16.5±0.9	106±3	15.15±0.10

with theirs. The λ_o of $\mathrm{Cl^-}$ is 52.35 $\mathrm{S\,cm^2 mol^{-1}}$ at 25 °C.[10] The other λ_o, which have been evaluated proportionally to the λ_o of $\mathrm{ClO_4^-}$ in methanol.[3,7] are 39.5, 45.7, 59.8, and 67.9 $\mathrm{S\,cm^2\,mol^{-1}}$ at 5, 15, 35, and 45 °C, respectively.

According to the familiar Gibbs-Helmholtz equation, thermodynamic functions have been determined at 25 °C (Table 3). The results of perchlorates are also listed there for reference. The shapes of $\ln K_1$ vs. T^{-1} plots for the chloride systems were strikingly identical to those for the perchlorate systems, which were slightly concave downward (Fig. 2 in Ref. 7).

On the basis of previous discussions,[3,7] we wil give some explanations for the next two problems: 1) Why K_1 is larger than K_{1A} at Ca and Sr whereas those are similar to each other at Ba and 2) why both $\Delta H_1^{\ominus}$ and $\Delta S_1^{\ominus}$ of chlorides are larger than those of perchlorates. Relating to the problems, there are the following properties of $\mathrm{M^{2+}}$, $\mathrm{Cl^-}$, and $\mathrm{ClO_4^-}$ in methanol: a) The solvation of $\mathrm{M^{2+}}$ becomes strong in the order of Ba<Sr<Ca.[7] b) The solvation of $\mathrm{Cl^-}$ seems to be stronger than that of $\mathrm{ClO_4^-}$, because of $\lambda_o(\mathrm{Cl^-})<\lambda_o(\mathrm{ClO_4^-})$: the hydration free energies, $\Delta G_h^{\ominus}$, of $\mathrm{Cl^-}$ and $\mathrm{ClO_4^-}$ are −317 and −190 $\mathrm{kJ\,mol^{-1}}$, respectively.[11] c) The degree of covalency in $\mathrm{MCl_2}$ bonding is in the order of Ca>Sr>Ba and the binding energy of $\mathrm{MCl_2}$ is also in the same order in gas phase.[12] d) $\mathrm{Cl^-}$ has a greater preference for covalent bonding than $\mathrm{ClO_4^-}$, because almost all metal perchlorates seem to be very unstable in solutions even if these metals are typical soft acids.[13]

As an important remark, here we propose from the previous discussion concerning the solvent-separated ion pair[7] that ion pairs separated with over one methanol molecule of solvent contribute little to their stabilities; that is, in this system we just consider the coexistence of ion pairs from a directly contacted one to a solvent-separated one with one methanol molecule though the two extremes may be major species on a time-average. Consequently, it means that anion ($\mathrm{Cl^-}$ or $\mathrm{ClO_4^-}$) solvation is forced to reduce considerably by ion pairing since anion solvation is very weak relative to divalent cation solvation. This must be a direct cause of problem 2), because of property b).

Using property a), we previously explained why the stability of the perchlorate, K_{1A}, is of the order Ca<Sr<Ba.[7] That explanation can be simply summarized as: In the case that a cation is solvated more weakly than a certain limit, the cation forms a more stable ion

pair as the cation solvation becomes weaker. Examining problem 1) under the consideration of property d), we infer that the above rule regarding the stability of an ion pair depending on its cation solvation is more pronounced for an ion pair having a higher ionic bonding. Strictly speaking, since the bonding nature of Ba (Ba is the most ionic metal of them; Property c)) is so ionic, that Property d) has little effect on the stability constsnts. Hence, K_1 and K_{1A} are similar to each other for Ba. However, because, as shown in the binding energies of chlorides in gas phase, K_1 probably gains some larger contribution from covalency in $CaCl^+$ and $SrCl^+$ bonding than from that in $BaCl^+$ bonding (Property c)), the difference of K_1 and K_{1A} increases for Ca and Sr. Thus, problem 1) can be well explained by Properties a), c), and d).

Potentiometry. Since the slopes of plots according to Eq. 6 were very gentle (Fig. 1), K_2 of Sr was so small relative to K_1 that it was impossible to make an accurate determination of K_2. The K_1 values are summarized in Table 4; here the conductometric results at 25 °C are also listed. Only the reference a-value of Ca is 6 Å;[6,14] however, the stability constants calculated at a=5 Å are also indicated in the table in order to check the contribution of a to the results. According to the results, the values at a=5 Å are lower by 3% for conductometry and higher by 3.5% for potentiometry than those at a=6 Å. These differences will probably have little importance in our present discussion and, thus, even in comparison with their standard deviations.

Before the potentiometric and conductometric results are compared, we must explain the discrepancies between the previous[1] and present potentiometry results. In our potentiometry, stability constants are determined by measuring the concentration of free anions ([Cl^-] in this study) which remain after combining with M^{2+}. Therefore, some metal compounds as impurities which form very stable chloride compounds have a considerably large influence on potentiometric data, even if the amount is so small that there is no problem in conductometric experiments. In fact, a measurement using a metal perchlorate of insufficient purification yielded a large stability constant; furthermore, the obtained stability constants varied with the total metal concentration, C°_M. Thus, the previous abnormally large K_1 of $SrCl^+$ was probably caused by some metal impurities. It is sure that the present K_1 of $CaCl^+$ and BaCl have also gained a higher reliability than the previous ones due to the experimental improvement.

Table 4. Comparison of Stability Constants between Potentiometry and Conductometry at 298.15 K

	a/Å	K_1/M^{-1} Poten.	K_1/M^{-1} Conduc.	K_{1A}/M^{-1} Conduc.
Ca	6	288± 8	408± 7	254±12
	5[a)]	298± 8	398± 8	245±12
Sr	5	343±27	403±12	345±12
Ba	5	399±27	464±11	451±17

a) Calculated to know the effect of a.

As shown in Table 4, K_1 from potentiometry is smaller than that from conductometry for all the metals. This is a cause for neglecting K_2 in conductometry, though it may have only a negligibly small effect. That is to say, if the formation of MCl_2 is not taken into account in the data treatment, K_1 is evaluated to a higher value by a decrease in conductance caused by the MCl_2 formation than would be expected.

Regarding K_1(potentiometry)<K_1(conductometry), there is another general explanation which was slightly mentioned in the introduction: Simply expressed, a different measurement yields a different result. With this simple explanation our discussion may come to the end; however, it would be interesting to discuss the result that the difference in K_1 between conductometry and potentiometry increases in going from Ba to Ca. At least, here, we will be able to infer that the Ag–AgCl electrode responds to the Cl^- which weakly binds to M^{2+}, where the weak ion pair works to reduce the net conductance a little. That is, there is a weak ion pair which is potentiometrically detected as being dissociated, but conductometrically as being associated. Therefore, K_1(potentiometry)<K_1(conductometry). According to the previous discussion,[7] on the other hand, $CaCl^+$ is probably separated by solvent molecules more strongly than $BaCl^+$ because of the strong solvation and small K_1 of Ca^{2+} compared to Ba^{2+}. That is, Cl^- enters into the solvation shell of Ba^{2+} more deeply than into that of Ca^{2+}. Therefore, it is inferred that the fraction of weak ion pairs which may be detected as dissociated by other experimental methods is larger for Ca than for Ba. Consequently, if the solvent-separated species take a larger part of properties relating to ion pairing (that is, if the ion solvation is stronger and the stability of an ion pair is smaller) such an investigated system will have a higher possibility of yielding different results from other measurements.

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