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Studies of the Alkaline Earth Complexes in Various Solutions. V. Calcium(II) and Strontium(II) Complexes with Carbonate Ions in 1M Sodium Chloride Media

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The complex formation of calcium(II) and strontium(II) with carbonate ions in 1 M sodium chloride media at 25°C has been determined by a liquid-liquid distribution method. The metal ions in the aqueous phase were extracted with a mixture of benzoylacetone and tributylphosphate in hexane as adduct chelate complexes. The distribution ratio was determined by radiometry as a function of the carbonate-ion concentration in the aqueous phase. The decrease in the metal distribution caused by the addition of carbonate ions to the aqueous phase has been explained in terms of the complex formation, and the stability constants have been determined from these data by a "curve-fitting" method. It has been concluded from the results that the stabilities of these complexes are about the same magnitude of those of the sulfate complexes of these metal ions and that the concentration of the carbonate complexes in usual natural waters is probably negligibly small.

The formation of calcium(II) and strontium(II) complexes with carbonate ions may influence the chemical behavior of these metal ions in various aqueous solutions in equilibrium with atmospheric carbon dioxide, such as in the sea or in living bodies. Since the chemical behavior of these ions, especially of calcium(II), has attracted the attention of many chemists for many years, the solubility or solubility products of these metal carbonates have been reported repeatedly by many authors, but only few of these investigators have determined the stability constants of carbonate complexes in aqueous solutions.[1] The present authors have studied the solvent extraction of calcium(II) and strontium(II) in 1 M sodium chloride media containing various amounts of carbonate ions, and have determined the distribution ratio as a function of the carbonate concentration.

For the solvent extraction of calcium(II) and strontium(II), 8-hydroxy-quinoline has very often been used.[2-4] However, the solvent extraction method with this reagent seems to be unsuitable for the determination of complexes in aqueous solutions because the distribution behavior of the 8-hydroxyquinolinates of these metal ions is complicated due to the formation of an aqueous chelate with this extractant.[4] The use of thenoyltrifluoroacetone (TTA) in methylisobutylketone(MIBK) has been also suggested for the extraction of these metal ions.[5-6] The extraction equilibria of calcium(II)

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[1] L. G. Sillén and A. E. Martell, "Stability Constants," The Chemical Society, Spec. pub. 17, London (1964).

[2] G. H. Morrison, H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley & Sons., New York (1957).

[3] J. Stary, "The Solvent Extraction of Metal Chelates", Pergamon Press, Oxford (1964).

[4] D. Dyrssen, *Svensk Kem. Tidskr.*, **67**, 311 (1955).

[5] T. Kiba and S. Mizukami, This Bulletin, **31**, 1007 (1958).

[6] T. Kiba and M. Kametani, *ibid.*, **31**, 1013 (1958).

or strontium(II) with TTA in carbon tetrachloride containing MIBK, tributylphosphate(TBP), or trioctylphosphine oxide (TOPO) have been studied in detail,[7] and these adduct-chelate extraction systems have been used for the study of the oxalate and sulfate complexes of alkaline earth metal ions in previous papers of this series.[8–11]

In the present study, the hydrogen-ion concentration of the aqueous phase had to be kept much lower than in the previous studies because carbonic acid is a weaker acid (the pK_{a_1} and pK_{a_2} in 1 M Na(ClO$_4$) are 6.04 and 9.57 respectively[12]) than sulfuric or oxalic acid; thus, it was necessary to keep the $-\log[H^+]$ above 8.5 in order to prevent the dinegative carbonate ions from associating with protons.

However, if the $-\log[H^+]$ is kept high, a chelating acid of a higher dissociation constant, such as TTA (pK_a is 6.23[7]), in the organic phase will be distributed into the aqueous phase due to the acid dissociation;[7] it was, therefore, concluded that the use of TTA as the extractant was unsuitable for the present purpose. For this reason, benzoylacetone (BZA) (pK_a is 8.96[3]) was employed in conjunction with TBP, which was found to form adduct complexes with the BZA chelates in hexane and which enhances the extraction considerably. The ionic media used in the previous studies were 1 M Na(ClO$_4$). These media, however, were found to be unsuitable for the present work because of the extraction of the mixed chelate or the metal perchlorate at higher TBP concentrations, as has been pointed out previously,[13] and so the 1 M Na(Cl) media were employed throughout this study instead of the perchlorate media. The distribution ratio was determined from the radioactivity in the two phases. A decrease in the distribution ratio of the metal ions was caused by the addition of carbonate ions to the aqueous phase; this decrease was explained in terms of the complex formation. The stability constants were determined graphically from these data by using a curve-fitting method. These complexes were then discussed.

Experimental

Tracers. The calcium-45 was obtained from the Nuclear Science and Engineering Co., U. S. A., as a hydrochloric acid solution. The strontium-85 was obtained from the New England Nuclear Corp. as a hydrochloric acid solution. They were both diluted with a 1 M sodium chloride solution. The calcium stock solution thus prepared contained 1.5×10^{-5} M calcium, while the strontium stock solution contained 7.5×10^{-6} M strontium.

Reagents. All the reagents were of an analytical grade. The TBP and MIBK were obtained from the Tokyo Kasei Co. In order to remove impurities, they were washed successively with 0.1 M perchloric acid, water, and a 0.1 M sodium hydroxide solution, and then several more times with water. The other reagents were used without further purification.

Procedures. All the procedures were carried out in a thermostatted room at 25±0.5°C. Hexane containing BZA and 0.6 M TBP was used as the organic solvent. The concentrations of BZA were 0.1 M and 0.2 M for the calcium and the strontium extractions respectively. The two phases were equilibrated in stoppered glass tubes (volume 20 m*l*). Various amounts of a 0.5 M sodium carbonate solution and/or a 1 M sodium acid carbonate solution were placed in the tubes. When it was necessary, a small amount of sodium borate (0.0025 M at initial) was added to the aqueous phase as a buffer. The tracer (calcium-45 or strontium-85) was then added to this solution, and finally the aqueous phase was made up to 5 m*l* with a 1 M sodium chloride solution. A 5-m*l* portion of the organic phase was then placed in the tubes, and the two phases were agitated mechanically for 30 min and then centrifuged. After the two phases had then been separated, a small portion of the aqueous phases was transferred into a glass vessel and the hydrogen ion concentration was determined potentiometrically by using 1 M sodium chloride containing 1.00×10^{-2} M hydrochloric acid as the standard of $-\log[H^+]$ 2.00.

The radioactivity in the two phases was determined as follows. Calcium: A 2-m*l* portion of the aqueous phase was transferred into another stoppered glass tube and agitated with 2 m*l* of MIBK containing 0.2 M TTA in order to extract the calcium into the MIBK phase. A 1-milliliter portion of this MIBK solution was pipetted out, placed on a stainless steel dish, and then decomposed gradually on a hot plate under controlled heating. The β-radioactivity of the sample in the dish was measured with an end-window-type G. M. counter. The calcium in the organic phase containing TBP was first back-extracted into 4m*l* of 0.1 M nitric acid, and then a 2-m*l* portion of this aqueous phase was transferred into another tube and 2-m*l* of 0.1 M sodium hydroxide were added. The calcium in this aqueous solution was treated just as has been described above.

Strontium. A two-milliliter portion was pipetted from each phase; these portions were then transferred into small test tubes. The γ-radioactivity of the samples was then measured with a well-type (NaI) scintillation counter.

Statistical Treatment

The complex formation of a dipositive metal

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[7] T. Sekine and D. Dyrssen, *Anal. Chim Acta*, **37**, 217 (1967).

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[9] T. Sekine and M. Sakairi, *ibid.*, **40**, 261 (1967).

[10] Y. Hasegawa, M. Maki and T. Sekine, *ibid.*, **40**, 1845 (1967).

[11] T. Sekine, Y. Kawashima, T. Unnai and M. Sakairi, *ibid.*, **41**, 3013 (1968).

[12] M. Frydman, G. Nilsson, T. Rengemo and L. G. Sillén, *Acta Chem. Scand.*, **12**, 878 (1958).

[13] T. Sekine and Y. Hasegawa, Proceedings of 5th International Conference of Solvent Extraction Chemistry, Jerusalm, September 1968. The full paper will be published from John Wiley & Sons.

ion, M^{2+}, with dinegative ligand ions, L^{2-}, in the aqueous phase may be described as:

$$M^{2+} + nL^{2-} \rightleftharpoons ML_n^{2-2n} \tag{1}$$

$$\beta_n = [ML_n^{2-2n}]/[M^{2+}][L^{2-}]^n \tag{2}$$

The extraction of this metal ion into an organic phase containing a chelating acid, HA, and an adduct-forming ligand, E, may be described as follows:

$$M^{2+} + 2HA(org) + eE(org) \rightleftharpoons MA_2E_e(org) + 2H^+ \tag{3}$$

$$K = [MA_2E_e]_{org}[H^+]^2/[M^{2+}][HA]^2_{org}[E]^e_{org} \tag{4}$$

In the present study, the concentration of the adduct-forming ligand (TBP) is kept constant (0.6M) throughout the experiments, and so the terms of this adduct-forming ligand will not be presented in the equations. Thus, the organic metal species will be denoted by MA_2, and the extraction constant, K_{ex} will be defined and described as;

$$K_{ex} = [MA_2]_{org}[H^+]^2/[M^{2+}][HA]^2_{org} \tag{5}$$

When no ligand exists in the aqueous phase, the distribution ratio is:

$$D_0 = [MA_2]_{org}/[M^{2+}] \tag{6}$$

Then, the K_{ex} in Eq. (4) can be described as:

$$K_{ex} = D_0[H^+]^2[HA]^{-2}_{org} \tag{7}$$

Here, this K_{ex} should give a constant value at a certain temperature.

When the complex-forming ligand is present in the aqueous phase and when the concentration is $[L^{2-}]$, the distribution ratio may be described from Eqs. (2) and (5) as:

$$\begin{aligned} D &= [MA_2]_{org}/([M^{2+}] + [ML] + [ML_2{}^{2-}] + \cdots) \\ &= D_0/(1+\sum\beta_n[L^{2-}]^n) \end{aligned} \tag{8}$$

From Eqs. (7) and (8), the following can be described:

$$D[H^+]^2[HA]^{-2}_{org}/K_{ex} = (1+\sum\beta_n[L^{2-}]^n)^{-1} \tag{9}$$

The dissociation constants of carbonic acid are described as follows:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3{}^-$$

$$K_{a_1} = \frac{[H^+][HCO_3{}^-]}{[H_2CO_3]}$$

$$HCO_3{}^- \rightleftharpoons H^+ + CO_3{}^{2-}$$

$$K_{a_2} = \frac{[H^+][CO_3{}^{2-}]}{[HCO_3{}^-]}$$

The values in 1M $NaClO_4$ at 25°C are 9.12×10^{-7} and 2.70×10^{-10} respectively for K_{a_1} and K_{a_2}.[12]

The total concentration of carbonate ions is, then;

$$\begin{aligned} [\text{carbonate}]_{total} &= [H_2CO_3] + [HCO_3{}^-] + [CO_3{}^{2-}] \\ &= [CO_3{}^{2-}]\left(1 + \frac{[H^+]}{K_{a_2}} + \frac{[H^+]^2}{K_{a_1}\cdot K_{a_2}}\right) \end{aligned} \tag{10}$$

The concentration of the dinegative carbonate ions at a certain hydrogen-ion and a certain total carbonate concentration can be calculated from Eq. (10), while the stability constants, β_n, can be determined from the distribution data by a curve-fitting method[7-10] using Eq. (9).

Results

Dependence of *D* on the Hydrogen-ion Concentration. In order to determine the extraction constant, K_{ex}, in Eq. (5), the distribution ratio of the metal ions between 1M NaCl containing no carbonate ions and hexane containing 0.6M TBP and 0.1M BZA (extraction of Ca(II)) or 0.2M BZA (extraction of Sr(II)) was determined as a function of $-\log[H^+]$. The results are shown in Fig. 1. We can see from Fig. 1 that the plots of both the calcium(II) and strontium(II) extractions have a slope of +2. Thus, the extraction equilibria can be represented by Eq. (4); that is, neither the aqueous chelate formation nor the decrease in the $[HA]_{org}$ occurs in the hydrogen-ion concentration

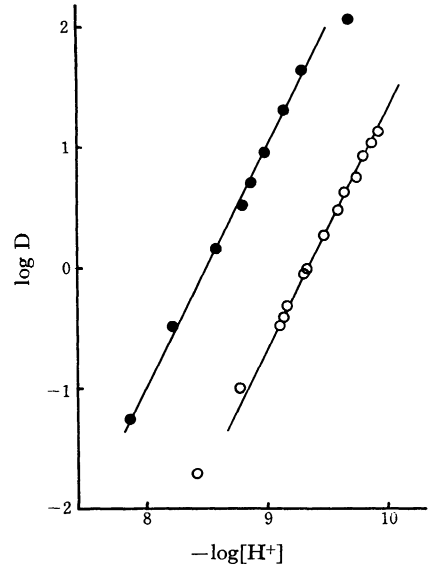

Fig. 1. Distribution ratio of calcium(II) (closed circles) and strontium(II) (open circles) as a function of the hydrogen ion concentrations.
Aqueous phase: 1M Na(Cl).
Organic phase: Ca(II), 0.1M BZA+0.6M TBP in hexane.
Sr(II), 0.2M BZA+0.6M TBP in hexane.
The straight lines give $\log D = -2\log[H^+] - 17.04$ ··· (Ca(II)) and $\log D = -2\log[H^+] - 18.75$ ··· (Sr(II))

Table 1. The stability constants of alkaline earth complexes

	CO_3^{2-}*			SO_4^{2-}**			$C_2O_4^{2-}$**	
	log β_1	log β_2	log β_3	log β_1	log β_2	log β_3	log β_1	log β_2
Be(II)	—	—	—	—	1.78	2.08	3.55	5.40
Ca(II)	1.22	1.38	—	1.10	1.36	—	1.64	2.68
Sr(II)	1.28	1.60	1.70	0.72	1.29	—	1.25	1.90
Ba(II)	—	—	—	0.66	1.42	—	0.58	2.20

* In 1 M Na(Cl) data are taken from the present work.

** In 1 M Na(ClO_4) data are taken from Ref. 8 (Ba(II)), Ref.9 (Be(II)) and Ref. 10 (Ca(II) and Sr(II)).

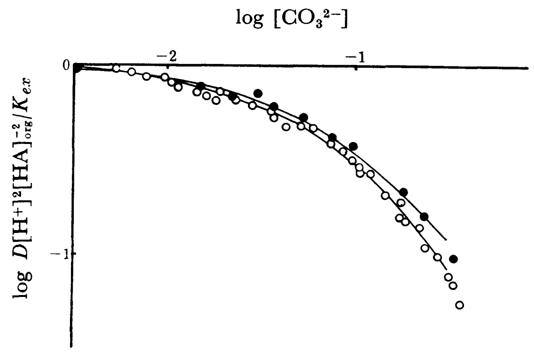

Fig. 2. Decrease in the calcium(II) (closed circles) and strontium(II) (open circles) extraction as a function of the carbonate ion concentration. The solid lines represent the followings;

Ca(II): $\log D[H^+]^2[HA]_{org}^{-2}/K_{ex} = -\log(1+10^{1.22}[CO_3^{2-}]+10^{1.38}[CO_3^{2-}]^2)$

Sr(II): $\log D[H^+]^2[HA]_{org}^{-2}/K_{ex} = -\log(1+10^{1.28}[CO_3^{2-}]+10^{1.60}[CO_3^{2-}]^2+10^{1.70}[CO_3^{2-}]^3)$

range studied in Fig. 1. The decrease in the extraction of metal ions by the addition of carbonate ions into the aqueous phase is given in Fig. 2. The results in Fig. 2 were analyzed by the curve-fitting method. The extraction curve of calcium(II) (closed circles) was found to fit with a standard curve by assuming the first and the second complexes. From the parameters of this best-fit standard curve, the stability constants were obtained as shown in Table 1. The extraction curve of strontium(II) (open circles), on the other hand, could be fitted to none of the standard curves drawn by assuming the formation of the first and the second complexes. Therefore, the curve-fitting was further carried out by assuming the formation of the third complex, and finally the best-fit standard curve was found. The three stability constants determined from the parameters of the standard curve for the strontium extraction are given in Table 1. Table 1 also gives the stability constants previously obtained in this series to facilitate comparison with the present results.

Discussion

From the present results, it may be concluded that the complexes containing the acid carbonate ion, HCO_3^-, are negligible within the limits of experimental accuracy. The data in Fig. 2 were plotted against the carbonate concentration disregarding the acid carbonate ions, but this seems to have caused no systematic deviation.

The stability constants of calcium(II) and strontium(II) carbonate complexes in Table 1 are rather similar to each other, except for the third complex of strontium(II), which has not been observed in calcium(II). Such similarity in the magnitude of the constants——in other words, the small difference in the stability constants among the complexes of metal ions of different ionic sizes——can also be seen in the sulfate complexes of alkaline earth ions given in Table 1. Although no direct evidence showing the nature of the interactions between the metal and the ligand ion could be obtained from only these distribution data, we might assume the following. Among these, the oxalate complexes should be the inner-sphere chelate complexes. On the other hand, the sulfate complexes should be mainly outer-sphere complexes (ion-pairs), as has been suggested by the kinetic data.[14] The similarity in the stabilities of sulfate and carbonate complexes can be explained if we assume that the carbonate complexes are also outer-sphere complexes.

The stability constants of carbonate complexes in Table 1 seem to show that the contribution of carbonate complexes to the total concentrations of these metal ions in usual natural water is negligibly small. For example, in a 1 M aqueous sodium chloride solution at pH 8, the total carbonate concentration necessary to convert a 1% portion of the total calcium(II) into carbonate complexes can be calculated from these data as about 2×10^{-2} M; this is about ten times larger than the carbonate con-

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centration in sea water (0.6M NaCl, pH 8.1 and $[HCO_3^-]=2.3\times10^{-3}$M.[15,16]).

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