

Studies of Metal Complexes of Radiobiological Interest

II. The Solubility and Stability Constants of Ca, Sr,
and Ba Croconates

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Using solubility columns the following equilibrium constants (± 0.03) have been determined in K_2A -KCl mixtures at $I = 0.3$ M and 25°C : A^{2-} = croconate ion; $\beta_1 = [MA] [M^{2+}]^{-1} [A^{2-}]^{-1}$; $K_{s1} = [MA]$; $K_{s0} = K_{s1}/\beta_1$ (solubility product).

CaA: $\log \beta_1 = 1.29$,	$\log K_{s1} = -2.76$,	$\log K_{s0} = -4.05$
SrA: $\log \beta_1 = 1.21$,	$\log K_{s1} = -3.87$,	$\log K_{s0} = -5.08$
BaA: $\log \beta_1 = 1.55$,	$\log K_{s1} = -6.73$,	$\log K_{s0} = -8.28$

The Brönsted column method^{1,2} is very convenient and rapid for solubility studies, but for unknown reasons the shaking method is still used in many laboratories. Recently, Dyrssen and Tyrrell³ have described the use of a miniature column with a closed system in a N_2 atmosphere for studying the solubility of mercury oxide (about 2 g). In the present work we show that, by applying the technique of suspending the solid material in a slurry of filter paper, it is possible to decrease the amount of solid in the column even more. In general we have used about 400 mg, although in one series with the barium salt only 200 mg was used.

The strontium and barium salts of rhodizonic acid ($H_2C_6O_6$), which is quite similar to croconic acid ($H_2C_5O_5$), are sparingly soluble. The alkali rhodizonates are used in analysis, and they have also been tested in radiobiology. The effects on the Sr metabolism are ambiguous. Michon and Guilloux⁴ found a marked decrease in ^{90}Sr uptake in the rat skeleton, whereas Kriegel and Melchinger⁵ did not get any effect at all. Corresponding experiments with the more stable croconates have not been described to date.

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EXPERIMENTAL

Potassium croconate ($K_2C_5O_5 = K_2A$) was prepared and analyzed as described previously.⁶ Experimental conditions such as temperature (25°), measurements of pH and spectra were also the same as in that work. The ionic strength (I) was kept constant at 0.3 M with $K_2A + KCl$ (in one series with BaA also $I = 1.0$ M). These solutions were practically neutral. The CaA , SrA , and BaA salts were precipitated from chloride solutions with known specific activities of ^{45}Ca , ^{89}Sr , and ^{140}Ba . The precipitates were suspended in a slurry of filter paper (about 50 % of the bed volume).

Conventional burets were used with a plug of glass wool above and below the filter paper column. The height of the column was about 20 mm and the diameter about 9 mm (4.5 mm in one case). Solutions of increasing as well as decreasing concentrations of K_2A were passed through the columns. The flow rate was about 5 ml/h. The first 5 – 10 ml of the effluent were discarded, and the following 10 – 15 ml were collected, analyzed for M and returned to the column. If the difference in $[M]_{tot}$ was more than 1–2 % a third pass was carried out. The samples of the β -emitting Ca and Sr solutions were dried on steel discs and measured in a GM-counter. The total Ba content was found by counting 5 ml aliquots in a Tracerlab SC-57 well scintillation counter. The standard solutions with known specific activities of ^{45}Ca , ^{89}Sr , and ^{140}Ba contained also 0.3 or 1.0 M KCl to correct for the radiation from ^{40}K and for the absorption by KCl . The concentration of A^{2-} in the effluent was checked spectrophotometrically.

TREATMENT OF THE DATA AND RESULTS

As croconic acid is a strong dibasic acid⁶ ($pK_1 = 0.32$, $pK_2 = 1.51$), we assumed that only the first, neutral complex (MA) was formed. To verify this, the experimental data (shown in Fig.1) were treated by two graphical methods, a linear plot and curve fitting.^{7,8} In the case of only one complex the total metal concentration $[M]_{tot}$ is given by

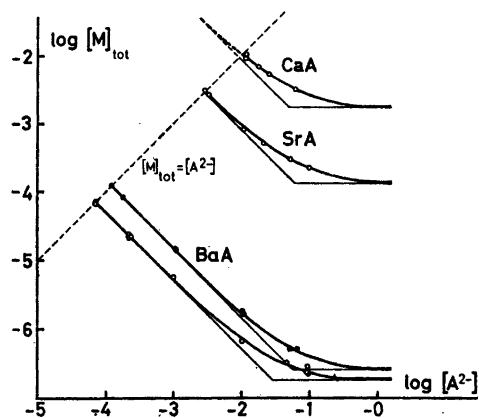


Fig. 1. A plot of $\log [M]_{tot}$ against $[A^{2-}]$ for $M = Ca, Sr, \text{ and } Ba$. The filled circles are data from experiments with an ionic strength of 1 M. For other $KCl - K_2A$ solutions (open circles) the ionic strength was 0.3 M. The limiting solubilities of MA are: $\log K_{s1} = 2.76$ (CaA), -3.87 (SrA), -6.58 (BaA , $I = 1$ M) and -6.73 (BaA). The intercepts of the asymptotes (thin lines) give the $\log \beta_1$ values shown in Table 1. The dashed line represents $[M]_{tot} = [A^{2-}]$, i.e., complete dissociation of MA in 0.3 M KCl (no K_2A added).

$$[M]_{\text{tot}} = [M^{2+}] + [MA] \quad (1)$$

The stability constant of MA is

$$\beta_1 = [MA] [M^{2+}]^{-1} [A^{2-}]^{-1} \quad (2)$$

Elimination of $[M^{2+}]$ in eqn. (1) gives

$$[M]_{\text{tot}} = [MA] (\beta_1^{-1} [A^{2-}]^{-1} + 1) \quad (3)$$

As $[MA]$ is constant in the presence of solid MA we obtain from the definitions (4), (5), and (6)

$$[MA] = K_{s1} \quad (4)$$

$$[M^{2+}] [A^{2-}] = K_{s0} \quad (5)$$

$$\beta_1 K_{s0} = K_{s1} \quad (6)$$

the following expression for $[M]_{\text{tot}}$

$$[M]_{\text{tot}} = K_{s0}/[A^{2-}] + K_{s1} \quad (7)$$

If $[M]_{\text{tot}}$ is plotted against $1/[A^{2-}]$ the data should fall on a straight line. The slope of this line is the solubility product, and the intercept is K_{s1} . As $[A^{2-}]$ varies over several powers of ten, the data will be rather compressed at one end of the linear plot. This is not the case with the curve fitting method since we plot $\log [M]_{\text{tot}}$ against $\log [A^{2-}]$ (Fig. 1).

Eqn. (3) may be written as

$$\log [M]_{\text{tot}} = \log K_{s1} + \log (1 + \beta_1^{-1} [A^{2-}]^{-1}) \quad (8)$$

Data plotted as $\log [M]_{\text{tot}}$ vs. $\log [A^{2-}]$ should then fit the normalized curve $Y = \log (1 + v)$; $X = -\log v$, which has two asymptotes $Y = 0$ and $Y = -X$. These correspond to

$$[A^{2-}] \rightarrow 0: \log [M]_{\text{tot}} = \log K_{s1} - \log \beta_1 - \log [A^{2-}] = \log K_{s0} - \log [A^{2-}] \quad (9)$$

$$[A^{2-}] \rightarrow \infty: \log [M]_{\text{tot}} = \log K_{s1} \quad (10)$$

Table 1. The solubility constants of group IIA salts of croconic acid at 25° and $I = 0.3$ or 1.0 M.

	$-\log K_{s0}$	$\log \beta_1$	$-\log K_{s1}$
CaA ($I = 0.3$ M)			
curve fitting	4.05	1.29	2.76
linear plot	4.03	1.26	2.77
SrA ($I = 0.3$ M)			
curve fitting	5.08	1.21	3.87
linear plot	5.06	1.21	3.85
BaA ($I = 0.3$ M)			
curve fitting	8.28	1.55	6.73
linear plot	8.28	1.54	6.70
($I = 1.0$ M)			
curve fitting	7.82	1.24	6.58
linear plot	7.82	1.26	6.55

At the intersection point of the asymptotes we obtained $\log [M]_{\text{tot}} = \log K_{s1}$ and $\log \beta_1 = -\log [A^{2-}]$. The curves with the best fit are shown in Fig. 1. The results found by the linear plot and curve fitting were in agreement within the experimental errors (± 0.03 ; Table 1).

The solubility decreases in the order $\text{Ca} > \text{Sr} > \text{Ba}$, which is the same as for the corresponding salts of rhodizonic acid.^{9,10} It follows from Fig. 1 and Table 1 that this decrease is principally due to a decrease in K_{s1} . The effect of increasing the ionic strength (without a common ion) is usually an increased solubility, and this is also found in the case of BaA. The increase is due to both a decrease in β_1 and an increase in K_{s1} .

In most cases the complexes of Ba with organic acids are weaker than those of Ca and Sr. With some inorganic ligands, however, the opposite occurs. Since β_1 follows the order $\text{Ba} > \text{Ca} > \text{Sr}$, croconic acid resembles an inorganic acid, which is not entirely unexpected as the acid is very strong.

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REFERENCES

1. Brönsted, J. N. and La Mer, V. K. *J. Am. Chem. Soc.* **46** (1924) 555.
2. Brönsted, J. N. and Pedersen, K.J. *Z. physik. Chem.* **103** (1922) 307.
3. Dyrssen, D. and Tyrrell, V. *Acta Chem. Scand.* **15** (1961) 393.
4. Michon, G. and Guilloux, M. J. *Compt. Rend.* **248** (1959) 2039.
5. Kriegel, H. and Melchinger, H. *Atompraxis* **5** (1959) 425.
6. Carlqvist, B. and Dyrssen, D. *Acta Chem. Scand.* **16** (1962) 94.
7. Dyrssen, D. and Sillén, L.G. *Acta Chem. Scand.* **7** (1953) 663.
8. Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 186.
9. Feigl, F. *Mikrochemie* **2** (1924) 187.
10. Weiss, H. V. and Shipman, W. H. *Anal. Chem.* **29** (1957) 1764.

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