

238. *The Condensed Phosphoric Acids and Their Salts. Part VI.*
Dissociation Constants of Strontium Trimetaphosphate and Tetra-
metaphosphate.*

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The conductivities of strontium chloride solutions containing sodium trimetaphosphate or sodium tetrametaphosphate have been used to calculate the dissociation constants of the ion-pairs SrP_3O_9^- and $\text{SrP}_4\text{O}_{12}^{2-}$. The results are supported by the solubilities of strontium iodate in solutions of these sodium salts, and are compared with those of the other alkaline-earth metals in terms of ion radii.

IN Parts IV and V of this series (Jones, Monk, and Davies, *J.*, 1949, 2693; Jones and Monk, *loc. cit.**) the dissociation constants of the ion-pairs formed between some M^{2+} ions and the trimetaphosphate ($\text{P}_3\text{O}_9^{3-}$) and tetrametaphosphate ($\text{P}_4\text{O}_{12}^{4-}$) ions were reported. The method used consisted of mixing dilute solutions of the chlorides MCl_2 with solutions of the sodium metaphosphates, and calculating the extent of ion-association from the difference between the calculated and observed specific conductivities. The solubility of calcium iodate in solutions of the sodium metaphosphates gave confirmatory evidence in the case of calcium.

* Part V, *J.*, 1950, 3475.

It was remarked that the results of magnesium, calcium, and barium were somewhat irregular when compared with the nitrates, iodates, and hydroxides of these cations. With the first two of these anions, the dissociation constants are related to the sizes of the hydrated cations, *i.e.*, $Mg > Ca > Ba$, whereas those of the hydroxides follow the reverse order, namely, according to the radii of the unhydrated cations. This latter aspect has been examined in detail by Davies (*J.*, 1951, 1256), and the value given for strontium hydroxide in the preceding paper fits in with this view. In Parts IV and V (*loc. cit.*) it was suggested that the stronger electrostatic forces resulting from the higher valencies of the metaphosphate ions can at least partly counterbalance the solvation forces of the cations and account for the dissociation constants following an order between the two types discussed above. Accordingly, the intermediate position of strontium between calcium and barium should help to clarify this point.

The dissociation constants of the ion-pairs $SrP_3O_9^-$ and $SrP_4O_{12}^{2-}$ were obtained by the methods used previously (Parts IV and V, *loc. cit.*), namely, from the conductivities of mixed solutions of strontium chloride and the sodium metaphosphates. In addition, supporting evidence has been obtained from the solubility of strontium iodate in solutions of these sodium salts.

EXPERIMENTAL

"AnalaR" strontium chloride was used in the conductivity measurements, which were made with the equipment described previously (Davies, *J.*, 1937, 432; Davies and Monk, *J.*, 1949, 413). Sodium trimetaphosphate was prepared by the method described in Part I (Davies and Monk, *loc. cit.*), and the sodium tetrametaphosphate was taken from the sample described in Part V (*loc. cit.*). The solubility measurements were made as detailed in the preceding paper. A trace of acetic acid was added to the solvent solutions to overcome drifts in the solubilities due to slight hydrolysis.

DISCUSSION

The conductivity data, which are reported in Tables 1 and 2, have been interpreted by the previously described processes (Parts IV and V, *loc. cit.*), the same nomenclature being used. In the tables, c_1 is the concentration of sodium metaphosphate in equiv. per l., c_2 is that of strontium chloride, a and a_1 are those of the $NaP_3O_9^{2-}$ and $NaP_4O_{12}^{3-}$ ion-pairs, b is that of $SrP_3O_9^-$ and $SrP_4O_{12}^{2-}$, d represents $Sr_2P_4O_{12}$, and e represents $NaSrP_4O_{12}^-$. The same dissociation constants were used as before in calculating the concentrations of these ion-pairs, except, of course, those being obtained, namely, $SrP_3O_9^-$ and $SrP_4O_{12}^{2-}$. The derived constants, K , of the latter are given in the last columns of the tables. As before, I represents the ionic strength, and κ the specific conductivity. The limiting mobility of the strontium ion was taken as 59.46 (Shedlovsky and Brown, *J. Amer. Chem. Soc.*, 1934, 56, 1066).

TABLE 1. Conductivities of $Na_3P_3O_9$ solutions containing $SrCl_2$.

$10^4 c_1$	$10^4 c_2$	$10^3 a$	$10^3 b$	$10^4 \kappa$ (calc.)	$10^4 \kappa$ (obs.)	$10^3 I$	$10^4 K$
8.509	3.853	2.2	0.426	1.5569	1.4215	2.02	4.42
8.418	7.343	1.9	0.683	1.9845	1.7695	2.37	4.64
11.428	8.967	3.1	1.109	2.5418	2.2243	3.01	4.33
11.355	12.583	2.8	1.265	2.9809	2.5893	3.39	4.36

TABLE 2. Conductivities of $Na_4P_4O_{12}$ solutions containing $SrCl_2$.

$10^4 c_1$	$10^4 c_2$	$10^3 a_1$	$10^3 a$	$10^3 b$	$10^3 d$	$10^3 e$	$10^4 \kappa$ (calc.)	$10^4 \kappa$ (obs.)	$10^3 I$	$10^4 K$
6.856	1.600	0.86	5.1	0.696	—	2.0	1.1141	0.8619	1.50	7.0
6.825	3.071	0.88	2.7	1.177	1.5	3.4	1.3080	0.8788	1.21	7.0
13.550	11.062	3.16	2.1	3.092	21.4	17.0	3.1617	2.0431	2.45	7.0

The solubility results reported in Tables 3 and 4 have also been obtained by previously established methods (Parts I and V, *loc. cit.*). In these tables, the concentrations are all multiplied by 10^3 . Trial and error methods indicated that a reasonable value for the dissociation constant of $Sr_2P_4O_{12}$ is about 0.0035 and this was used in calculating the amounts of this which are listed in Table 4. When using 0.002, the value adopted in the case of calcium (Part I, *loc. cit.*), marked drifts were found in the evaluation of K for $SrP_4O_{12}^{2-}$.

TABLE 3. *Solubility of Sr(IO₃)₂ in Na₃P₃O₉ solutions.*
(Concentrations × 10³)

Na ₃ P ₃ O ₉	Soly.	[Sr(IO ₃) ⁺]	[NaP ₃ O ₉ ²⁻]	[NaIO ₃]	[SrP ₃ O ₉ ⁻]	10 ³ I	10 ⁴ K
—	5.87	0.37	—	—	—	16.87	—
5.46	7.54	0.35	0.20	0.05	2.80	37.29	4.59
6.75	7.88	0.31	0.30	0.07	3.28	42.87	4.36
8.24	8.20	0.31	0.44	0.09	3.64	50.17	4.45
10.61	8.67	0.30	0.71	0.11	4.21	61.57	4.28

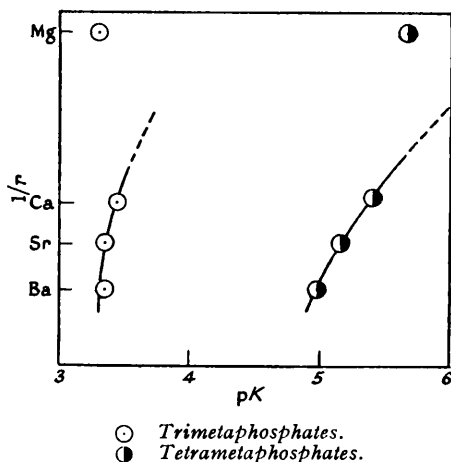
TABLE 4. *Solubility of Sr(IO₃)₂ in Na₄P₄O₁₂ solutions.*
(Concentrations × 10³)

Na ₄ P ₄ O ₁₂	Soly.	[Sr(IO ₃) ⁺]	[NaP ₄ O ₁₂ ³⁻]	[NaIO ₃]	[SrP ₄ O ₁₂ ²⁻]	[Sr ₂ P ₄ O ₁₂]	[NaSrP ₄ O ₁₂ ⁻]	10 ³ I	10 ⁶ K
5.71	9.33	0.26	0.12	0.09	4.30	0.84	0.24	37.14	8.1
8.50	10.87	0.23	0.48	0.16	6.09	0.84	0.45	51.77	10.2
11.87	12.91	0.20	0.87	0.24	8.42	0.78	0.78	68.78	6.6

The average K for SrP_3O_9^- is 4.44×10^{-4} from conductivities and 4.42×10^{-4} from solubilities. The average K for $\text{SrP}_4\text{O}_{12}^{2-}$ is 7.0×10^{-6} from conductivities and 8.3×10^{-6} (approx.) from solubilities; the former of these is probably the more correct since the solubility method involves more assumptions, and these influence the results considerably.

For the purposes of comparison, these results, together with those which have been obtained with the other alkaline-earth metals (Parts IV and V, *loc. cit.*), are given in

Table 5. The strontium results lie between those for calcium and barium, and the order with these three follows the same trend as the crystallographic radii of the cations, r , which are also placed in the table (these are taken from Pauling's "Nature of the Chemical Bond," 2nd edn., Cornell Univ. Press, p. 346). With both the phosphates, the magnesium figures show departure from this rule. The differing results for magnesium may be perhaps interpreted as follows. Since the Mg^{2+} ion has the lowest limiting mobility of the series—the figures (Shedlovsky and Brown, *loc. cit.*) are given in Table 5—the hydrated Mg^{2+} ion is the largest, whereas it has the smallest crystallographic radius, and is consequently the most heavily hydrated. Apparently the cation-anion interaction has less ability to overcome the hydration with this cation than with the other cations, and



this is manifest in the irregular order of the dissociation constants. This irregularity is illustrated by the figure, where $1/r$ (the reciprocal of the crystallographic radius) is plotted against pK . The smooth curves given by calcium, strontium, and barium are similar to those given by the strong hydroxides (Davies, *loc. cit.*, 1951), which suggests that with these the energy of cation-anion interaction energy is sufficient to overcome the energy of cation solvation. In order to fit on to these curves, the pK 's of the magnesium salts would have to be about one unit higher.

To get some idea of the sizes of the ion-pairs, the "Bjerrum distances" of closest approach of the cations and anions are given in Table 5. Subtraction of the crystallographic radii, r , from the Bjerrum distances should give the anion radii if the interaction is between the unhydrated ions. The results for the trimetaphosphates are $3.2 \pm 0.1 \text{ \AA}$, with the exception of Mg (3.9 \AA). From Stokes's law and the limiting mobility of the anion (Part I, *loc. cit.*), which is given in Table 5, the radius of the trimetaphosphate ion is 3.29 \AA , in excellent agreement with the above figure of 3.2 \AA . It would therefore appear that the trimetaphosphate ion is not hydrated, and that the assumption of interaction with the unhydrated cations in the instances of Ca, Sr, and Ba is supported, while the hydration shell of the magnesium ion is only partly penetrated.

On applying the same tests to the tetrametaphosphates, the differences between the Bjerrum distances and the crystallographic radii are 2.6 Å with Ca, Sr, and Ba, whereas the Mg value is 3.1 Å. Stokes's law, on the other hand, indicates that the tetrametaphosphate ion has a radius of 3.91 Å, so that the good agreement found with the trimetaphosphates is not upheld here. It is possible that, since we have two stages of association in these cases,

TABLE 5.

Ions	Trimetaphosphates		Tetrametaphosphates		Δ_i°	Ion radii (Å)	
	10^4K	Bjerrum distances (Å)	10^4K	Bjerrum distances (Å)		Stokes's law	Cryst.
Magnesium	4.89	4.5 ₃	6.7	3.7 ₂	53.06	3.45	0.65
Calcium	3.56	4.2 ₀	3.9	3.5 ₅	59.50	3.08	0.99
Strontium	4.43	4.4 ₂	7.0	3.7 ₄	59.46	3.08	1.13
Barium	4.50	4.4 ₄	10.3	3.8 ₀	63.64	2.88	1.35
Trimetaphosphate	—	—	—	—	83.59	3.29	—
Tetrametaphosphate ...	—	—	—	—	93.69	3.91	—

the probability factor in the Bjerrum expression is not valid in such systems. In spite of this disagreement, the view that the radius of the magnesium ion in the ion-pair lies between that of the bare ion and that when it is fully hydrated is qualitatively supported.

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