239. *The Condensed Phosphoric Acids and Their Salts. Part VII.* Ion Association between Some Tervalent Cations and the Tri- and Tetra-metaphosphates.*

By C. B. MONK.

The extent of ion-pair formation between lanthanum, some complex cobaltic cations, and the trimetaphosphate and tetrametaphosphate ions has been calculated from the conductivities of mixed solutions of the cation chlorides containing solutions of the sodium metaphosphates. The resulting dissociation constants are qualitatively related to the cation sizes.

IN continuation of previous studies of the extent of ion-pair formation between cations and $P_3O_9^{3-}$ and $P_4O_{12}^{4-}$ ions (see Part VI *), attention has now been directed to the kind of interaction that occurs when tervalent cations are used. The same procedure has been adopted as in the previous cases, namely use of the differences between the calculated and observed specific conductivities of mixtures of the sodium metaphosphates and the cation chlorides.

Considering, first, the trimetaphosphates, where MP_3O_9 ion-pairs are formed (M representing a tervalent cation), for a solution containing c_1 equiv. per l. of sodium trimetaphosphate and c_2 of MCl_3, if a g.-ions of $NaP_3O_9^{2-}$, b g.-ions of MCl^{2+}, and d g.-ions of MP_3O_9 are present per l., then

$$10^3\,\kappa\text{ (obs.)} = \Lambda_{Na^+}(c_1 - a) + 3\Lambda_{P_3O_9^{3-}}(c_1/3 - a - d) \\ + 2a\Lambda_{NaP_3O_9^{2-}} + 3\Lambda_{M^{3+}}(c_2/3 - b - d) + \Lambda_{Cl^-} - (c_2 - d) + 2b\Lambda_{MCl^{2+}}$$

where κ is the specific conductivity. The value of a is slightly different from what it would be in sodium trimetaphosphate solutions of the same ionic strength as the mixtures, but for the purposes of calculation this difference may be neglected, and similarly for b (both a and b are relatively small). Accordingly, the above expression becomes

$$10^3\,\kappa\text{ (obs.)} = c_1\Lambda_{Na_3P_3O_9} + c_2\Lambda_{MCl_3} - 3d(\Lambda_{P_3O_9^{3-}} + \Lambda_{M^{3+}})$$

where the first two equivalent conductivities (Λ) can be found from known data, and those of the two ions from the appropriate Onsager equation $\Lambda_i = \Lambda_i^\circ - BI^{\frac{1}{2}}$, I being the ionic

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* Part VI, preceding paper.

strength and B the theoretical Onsager value. The values of Λ_i°, the equivalent ionic conductivity at zero ionic strength, and of B are listed in Table 2. The ionic strength is given by

$$I = 0{\cdot}5\{4c_1 + 4c_2 - 6a - 5d - 18d\}$$

a being obtained from the known dissociation constant of $NaP_3O_9^{2-}$ (Davies and Monk, *J.*, 1949, 413) and b from the corresponding data for MCl^{2+} in the cases of the complex cobaltic chlorides (Jenkins and Monk, *J.*, 1951, 68). The other tervalent chloride used, lanthanum chloride, appears to ionise fully in the concentration range used here (James and Monk, *Trans. Faraday Soc.*, 1950, **46**, 141). The true values of a, b, and d were found by successive approximations.

If no MP_3O_9 were formed, we would have

$$10^3\,\kappa\text{ (calc.)} = c_1\Lambda_{Na_3P_3O_9} + c_2\Lambda_{MCl_3}$$

Hence, by subtraction,

$$10^3\{\kappa\text{ (calc.)} - \kappa\text{ (obs.)}\} = 3b(\Lambda_{P_3O_9^{3-}} + \Lambda_{M^{3+}})$$

which gives b. The final values of a, b, and d thus obtained were used in calculating the dissociation constants of the equilibria

$$MP_3O_9 \rightleftharpoons M^{3+} + P_3O_9^{3-},$$

i.e.,

$$K = (c_2/3 - b - d)(c_1/3 - a - d)f_1f_2/b$$

where the ion activity coefficients f_1 and f_2 are found from the Debye–Hückel limiting equation $-\log f_i = 0{\cdot}509z_i^2I^{\frac{1}{2}}$, z_i being the ion valency. The calculated specific conductivities were obtained from known data (Davies and Monk; Jenkins and Monk; James and Monk, *locc. cit.*) for sodium trimetaphosphate, cobaltammine chlorides, and lanthanum chloride respectively. The average dissociation constants from Table 1 (which contains the experimental results and the calculated data) are given in Table 4.

TABLE 1. *Data for the dissociation constants of* MP_3O_9.

10^4c_1	10^4c_2	10^6a	10^5b	10^6d	$10^4\,\kappa$ (calc.)	$10^4\,\kappa$ (obs.)	10^3I	10^5K
			M = Lanthanum					
17·640	17·465	1·0	53·23	—	4·5645	2·3152	2·22	0·19
9·614	6·303	2·0	20·29	—	2·0851	1·2103	1·35	0·19
17·938	11·483	5·0	37·27	—	3·7965	2·2006	2·51	0·21
17·798	14·292	2·5	45·78	—	4·1492	2·2157	2·29	0·20
			M = Hexamminocobalt(III)					
11·709	6·926	2·9	15·93	1·1	2·5768	1·7668	2·28	3·69
11·498	14·786	1·5	25·41	7·4	3·8403	2·5101	2·95	3·70
10·028	4·113	2·6	9·84	0·4	1·9263	1·4231	1·94	3·58
9·999	6·332	2·1	14·09	1·0	2·2844	1·5646	2·00	3·64
			M = Trisethylenediaminocobalt(III)					
4·062	2·909	0·4	5·01	1·0	0·9334	0·7076	0·94	4·07
4·023	5·159	0·3	7·37	1·2	1·2435	0·9134	1·16	3·90
3·247	1·228	0·3	2·27	0·7	0·5934	0·4904	0·67	3·80
3·229	2·495	0·3	3·97	0·8	0·7718	0·5918	0·78	3·99
			M = Trispropylenediaminocobalt(III)					
9·768	7·360	2·5	6·60	3·6	2·1464	1·8788	2·81	24·4
9·690	15·201	2·0	10·22	15·0	3·0893	2·6837	4·06	21·7
11·705	5·524	3·5	5·58	1·9	2·0269	1·8007	2·73	22·4
10·583	16·918	2·3	11·48	18·0	2·9411	2·3949	4·46	21·7

TABLE 2. *Constants used in the calculations.*

	La^{3+}	$Co(NH_3)_6^{3+}$	$Co(en)_3^{3+}$	$Co(pn)_3^{3+}$	$P_3O_9^{3-}$	$P_4O_{12}^{4-}$
Λ_i°	69·61	99·20	74·71	65·06	83·59	93·69
B	127·6	147·5	130·9	124·7	141·0	190·8
	$LaCl_3$	$Co(NH_3)_6Cl_3$	$Co(en)_3Cl_3$	$Co(pn)_3Cl_3$	$Na_3P_3O_9$	$Na_4P_4O_{12}$
Λ°	145·95	175·55	151·05	141·40	133·70	143·80
E	198·6	260·0	254·0	232·0	212·0	313·0

(E represents the experimental slope in the equation $\Lambda = \Lambda^{\circ} - EI^{\frac{1}{2}}$; for B, see p. 1317.)

The method of calculating the concentrations of $MP_4O_{12}^-$ ion-pairs in mixtures of MCl_3 and $Na_4P_4O_{12}$ is similar to that described above, except that the type of assumption used previously (Part V, *loc. cit.*) is used, namely, that the equivalent conductivity of the $MP_4O_{12}^-$ ion is one-quarter of that of the $P_4O_{12}^{4-}$ ion. The ionic-strength expression is

$$I = 0{\cdot}5\{5c_1 + 4c_2 - 8a - 9e - 24b\}$$

where c_1 now represents the equivalent concentration of sodium tetrametaphosphate c_2 is that of MCl_3, a and b are the $NaP_4O_{12}^{3-}$ and $MP_4O_{12}^-$ concentrations respectively. The latter is obtained from

$$10^3\{\kappa\ (\text{calc.}) - \kappa\ (\text{obs.})\} = b(3{\cdot}75\Lambda_{P_4O_{12}^{4-}} + 3\Lambda_{M^{3+}})$$

The dissociation constants K were calculated from

$$K = (c_2/3 - b - d)(c_1/4 - a - b)f_1f_2/bf_3$$

where the activity coefficients f_i were calculated from the expression given previously. The data are given in Table 3.

TABLE 3. *Data for the dissociation constants of* $MP_4O_{12}^-$.

10^4c_1	10^4c_2	10^5a	10^5b	10^6d	$10^4\ \kappa$ (calc.)	$10^4\ \kappa$ (obs.)	10^3I	10^6K
			M = Lanthanum					
11·454	9·155	0·7	27·83	—	2·7815	1·3351	1·35	0·25
9·944	7·075	1·4	22·94	—	2·3073	1·1076	1·14	0·19
			M = Hexamminocobalt(III)					
10·735	11·741	1·0	25·51	3·0	3·3214	1·7962	1·95	1·85
13·387	8·680	6·0	26·55	0·4	3·1699	1·5802	1·87	1·65
13·238	10·334	3·4	29·28	1·0	3·4246	1·6700	1·85	1·80
13·174	11·036	2·8	29·84	1·6	3·5268	1·7410	1·90	1·88
			M = Trisethylediaminocobalt(III)					
10·537	6·682	4·4	20·35	0·4	2·3305	1·2470	1·51	1·72
10·476	9·380	1·5	24·34	2·2	2·6999	1·4056	1·56	1·54
11·490	6·043	8·0	18·90	0·2	2·3484	1·3493	1·78	1·78
11·422	8·822	2·5	25·12	1·0	2·7431	1·4087	1·59	1·73
			M = Trispropylenediaminocobalt(III)					
8·556	5·346	6·5	9·87	1·2	1·8111	1·3196	1·99	24·5
8·508	7·359	5·5	11·93	2·5	2·0576	1·4699	2·15	24·7
9·980	5·745	9·0	11·00	0·5	2·0344	1·4900	2·29	25·0
9·832	11·098	5·5	15·58	6·0	2·6847	1·9229	2·79	25·6

DISCUSSION

A summary of the dissociation constants is given in Table 4, together with those of the corresponding sulphates (Jenkins and Monk, *loc. cit.*). In each series it will be noticed that

TABLE 4.

	La^{3+}	$Co(NH_3)^{3+}$	$Co(en)_3^{3+}$	$Co(pn)_3^{3+}$
Average dissociation constants				
Sulphates ($\times 10^4$)	2·0	2·77	3·55	17·5
Trimetaphosphates ($\times 10^5$)	0·20	3·65	3·94	22·6
Tetrametaphosphates ($\times 10^6$)	0·22	1·80	1·69	25·6
Bjerrum distances (Å)				
Sulphates	3·8	4·0	4·2	7·3
Trimetaphosphates	3·9	5·3	5·3	7·7
Tetrametaphosphates	4·7	5·5	5·5	7·6
Radii of ion-pairs from Stokes's law (Å)				
Sulphates	6·2	5·1	6·0	6·5
Trimetaphosphates	7·2	6·1	7·0	7·5
Tetrametaphosphates	7·9	6·7	7·6	8·1

the values for lanthanum are the smallest, those for $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ show little difference, and those for $Co(pn)_3^{3+}$ are much the largest. The Bjerrum distances of closest approach of the ions, and the radii of the ion-pairs as calculated by Stokes's law from the limiting mobilities of the ions, are also included in Table 4.

The difference between the radii of the ion-pairs as calculated by the two methods is most marked with the lanthanum series, and supports the suggestion made previously (Part IV, *loc. cit.*; also Part VI), namely, that with these high valency forces the energy of interaction is sufficiently large to overcome, at least, in part, the energy of ion-hydration. The lanthanum ion is undoubtedly heavily hydrated, since the crystallographic radius is 1·15 Å (Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 2nd edn., p. 346) whereas application of Stokes's law gives the ion radius as 3·95 Å. Using the 1·15 Å value together with the Stokes's law values for the three anions, we get 3·4, 4·4, and 5·1 Å for the radii of the lanthanum ion-pairs, in much better agreement with the Bjerrum distances. This would only be admissible if the anions were hydrated to a relatively small extent, and this conclusion is upheld by the trimetaphosphate results (Part VI, *loc. cit.*). Some reserve must be placed on this conclusion, however, since the comparison with the tetrametaphosphates of bivalent metals does not fit into this scheme (probably because of the complication that two equilibria are involved).

The relatively close agreement between the Bjerrum and the Stokes's law distances found with the complex cobaltic ions indicates that both cations and anions are comparatively unhydrated. This applies particularly to the last of these cations, $Co(pn)_3^{3+}$, where, by analogy with the alkali and alkaline-earth metals, we would expect the largest ion of the series to be the least solvated.

EXPERIMENTAL

The conductivity equipment used was that referred to in Part VI, where the sources of the sodium metaphosphates were also given. The lanthanum chloride was made by boiling an excess of " Spec-pure " lanthanum oxide with a 50% solution of A.R. hydrochloric acid until the pH was about 5·5, filtering it, and diluting it with conductivity water. The complex cobaltic salts were taken from samples used for previous conductivity work (Jenkins and Monk, *loc. cit.*). In order to obtain the concentrations of the stock solutions of the salts, conductivity measurements were made with each one, and the concentrations found by interpolation from the known data.

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