568. *The Condensed Phosphoric Acids and their Salts. Part IV. Dissociation Constants of Some Trimetaphosphates.*

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By addition of various bivalent metal chloride solutions to solutions of sodium trimetaphosphate, the dissociation constants of the corresponding MP_3O_9' ions have been determined by analysis of the resulting conductivities. The conductivities of nickel chloride solutions at 25° from 0·0002 to 0·004N. are reported.

It has been shown (Davies, *J.*, 1938, 448) that the deviations, from additivity, of the conductivities of solutions of mixed salts may be almost entirely accounted for if the dissociation constants of the possible ion-pairs are taken into consideration. These deviations become more marked with ions of higher charge, and in the present instance they have been used to calculate the extent of association between $M^{\cdot\cdot}$ and P_3O_9''' ions. The trimetaphosphate ion has previously been well characterised by conductivity studies (Davies and Monk, this vol., p. 413).

The method used to obtain the results reported below consisted of adding various chlorides, MCl_2, to solutions of sodium trimetaphosphate, and measuring the resultant specific conductivities. To evaluate the extent of formation of MP_3O_9' ions, the following treatment was used. For a solution containing c_1 equivalents per l. of sodium trimetaphosphate and c_2 of MCl_2, if a g.-ions of NaP_3O_9'' and b g.-ions of MP_3O_9' are present per l., then

$$10^3\kappa(\text{obs.}) = \Lambda_{Na^\cdot}(c_1 - a) + 3\Lambda_{P_3O_9'''}(c_1/3 - a - b) + 2\Lambda_{NaP_3O_9''}(a) + 2\Lambda_{M^{\cdot\cdot}}(c_2/2 - b) + \Lambda_{Cl'}(c_2) + \Lambda_{MP_3O_9'}(b)$$

where κ is the specific conductivity. It is assumed that no $MCl^\cdot$ ions are present, as judged by the available evidence (Righellato and Davies, *J.*, 1930, 592). 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 this difference may be regarded as negligible. Thus if the conductivity of the MP_3O_9' ion is taken as one-third of that of the trimetaphosphate ion, the above equation reduces to

$$10^3\kappa(\text{obs.}) = c_1\Lambda_{Na_3P_3O_9} + c_2\Lambda_{MCl_2} - 2\tfrac{2}{3}b\Lambda_{P_3O_9'''} - 2b\Lambda_{M^{\cdot\cdot}}$$

where the first two equivalent conductivities can be found from known data. The equivalent conductivities of the two ions can be found from the corresponding Onsager equations

$$\Lambda_{P_3O_9'''} = 83{\cdot}59 - 141{\cdot}0I^{\frac{1}{2}}$$

and

$$\Lambda_{M^{\cdot\cdot}} = \Lambda^0_{M^{\cdot\cdot}} - BI^{\frac{1}{2}}$$

where 83·59 is the conductivity at zero concentration of the trimetaphosphate ion (Davies and Monk, *loc. cit.*) and 141·0 is calculated with respect to the sodium ion. B is the theoretical Onsager value for the $M^{\cdot\cdot}$ ion calculated with respect to the chloride ion. The ionic strength $I = \frac{1}{2}(4c_1 + 3c_2 - 6a - 12b)$, a being obtained from the dissociation constant of sodium trimetaphosphate (Davies and Monk, *loc. cit.*); b is at first ignored until a first value for the dissociation constant of MP_3O_9' has been obtained. Better values of a and b are then calculated by successive approximation. If no MP_3O_9' formation occurred, we would have

$$10^3\kappa(\text{calc.}) = c_1\Lambda_{Na_3P_3O_9} + c_2\Lambda_{MCl_2}$$

Hence by subtraction,

$$10^3\{\kappa(\text{calc.}) - \kappa(\text{obs.})\} = b(2\tfrac{2}{3}\Lambda_{P_3O_9'''} + 2\Lambda_{M^{\cdot\cdot}})$$

With the final values of a and b, the dissociation constant K for the equilibrium $MP_3O_9' \rightleftharpoons M^{\cdot\cdot} + P_3O_9'''$ can be calculated from

$$K = \frac{[M^{\cdot\cdot}][P_3O_9''']f_1f_2}{[MP_3O_9']\,f_3} = \frac{(c_2/2 - b)(c_1/3 - a - b)f_1f_2}{bf_3}$$

where the ion-activity coefficients f_1, f_2, and f_3 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 data are given in Table I. The calculated specific conductivities were obtained by plotting the equivalent conductivities against $I^{\frac{1}{2}}$ and interpolating, and the concentrations of the MCl_2 stock solutions were determined gravimetrically. The conductivities of calcium, barium, and magnesium chloride were taken from the literature (Shedlovsky and Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 1066). That of manganous chloride was kindly supplied by Dr. J. C. James (The University, Glasgow); for this salt $\Lambda_0 = 129{\cdot}4$ and Onsager's treatment shows it to be completely dissociated at high dilutions. No conductivities were available for dilute solutions of nickel chloride at 25°, so these have been measured and are given in Table II and the figure; in the latter the line is drawn with the theoretical Onsager slope, and dissociation at these low concentrations is clearly complete. Extrapolation gives $\Lambda_0 = 130{\cdot}0_5$, so by taking 76·34 for the chloride ion (Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Co., 1943), $53{\cdot}7_1$ is the limiting mobility of the nickel ion.

The average dissociation constants, all $\times 10^4$, are: calcium, $3{\cdot}5_6$; barium, $4{\cdot}5_0$; magnesium, $4{\cdot}8_9$; manganese, $2{\cdot}7_2$; and nickel, $6{\cdot}0_3$. There are no comparable figures except in the case of calcium for which solubility studies give 3·3 (Davies and Monk, *loc. cit.*).

TABLE I.

Data for the dissociation constants of MP_3O_9' *at* 25°.

Run.	10^4c_1.	10^4c_2.	10^6a.	10^4b.	$10^2\kappa$ (calc.).	$10^2\kappa$ (obs.).	10^3I.	10^4K.
				M·· = calcium.				
1	10·045	7·198	2·48	0·891	2·1666	1·8860	2·502	3·68
	9·985	14·086	1·77	1·373	3·0157	2·5890	3·286	3·58
	9·800	28·629	1·12	1·887	4·7738	4·2020	5·121	3·38
2	7·994	6·448	2·61	0·697	1·8228	1·6021	2·155	3·67
	7·937	12·030	2·14	1·038	2·5181	2·1931	2·786	3·63
	7·803	25·491	1·75	1·461	4·1609	3·7154	4·451	3·40
				M·· = barium.				
1	10·639	3·510	3·08	0·454	1·7784	1·6285	2·381	4·43
	10·548	7·021	2·59	0·812	2·2227	1·9629	2·696	4·32
	10·387	16·152	1·98	1·320	3·3712	2·9503	3·728	4·61
2	9·297	3·197	2·58	0·358	1·5774	1·4591	2·118	4·60
	9·242	6·379	2·13	0·665	1·9866	1·7716	2·413	4·56
	9·124	13·190	1·70	1·079	2·8504	2·5060	3·175	4·50
				M·· = magnesium.				
1	7·364	5·841	1·40	0·515	1·6314	1·4748	2·088	4·73
	7·267	13·130	1·16	0·843	2·4918	2·2394	2·931	4·96
	7·166	26·054	0·78	1·122	3·9855	3·6590	4·799	5·02
2	6·764	7·039	1·403	0·555	1·7061	1·5374	2·076	4·75
	6·718	13·202	1·062	0·804	2·4357	2·1947	2·857	4·84
	6·639	24·321	2·70	1·029	3·7281	3·4267	5·375	5·03
				M·· = manganese.				
1	9·451	7·510	1·97	1·073	2·0886	1·7640	2·355	2·60
	9·385	12·710	1·53	1·447	2·7005	2·2673	2·902	2·65
	9·234	24·527	0·97	1·839	4·0625	3·5246	4·435	2·71
2	7·091	8·849	1·04	0·910	1·9624	1·6861	2·166	2·80
	7·044	13·831	0·81	1·170	2·5548	3·5117	2·779	2·74
	6·935	25·118	0·59	1·398	3·8615	4·3337	4·334	2·83
				M·· = nickel.				
1	6·267	3·025	1·33	2·227	1·1518	1·0882	1·670	6·09
	6·227	6·277	1·01	3·903	1·5462	1·4262	2·122	6·20
	6·146	13·051	0·71	6·167	2·3435	2·1597	3·094	6·29
2	6·265	3·148	1·33	2·203	1·1732	1·1051	1·689	6·40
	6·229	6·183	1·04	3·888	1·5347	1·4161	2·112	5·96
	6·150	12·699	0·77	6·112	2·3033	2·1198	3·043	6·23

TABLE II.

Conductivity of nickel chloride at 25°.

Run.	$10^6\kappa_{H_2O}$.	10^4c.	Λ.	Run.	$10^6\kappa_{H_2O}$.	10^4c.	Λ
1	0·232	2·1550	127·58	2	0·233	2·7232	127·00
		4·4397	126·41			6·7205	125·44
		7·9681	125·20			12·691	123·74
		10·852	124·35			21·831	121·86
		13·710	123·72			42·223	119·62
		17·259	122·96				

(c, in equivalents per l.)

TABLE III.

Dissociation constants of some ion-pairs.

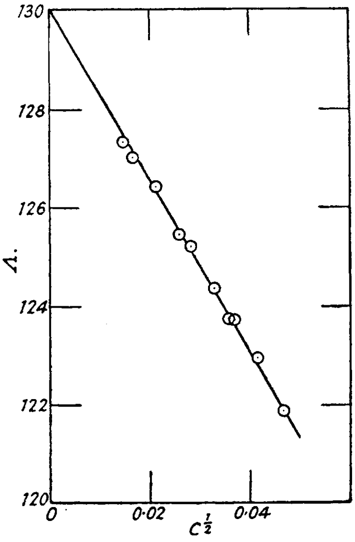
	Mg.	Ca.	Ba.
Hydroxide	0·0026 [1]	0·034 [2]	0·23 [3]
Oxalate	0·00037 [4]	0·001 [5]	0·0047 [5]
Malonate	0·0014 [6]	0·0032 [6]	0·020 [6]
Nitrate	1 [7]	0·52 [7]	0·12 [7]
Iodate	0·19 [8]	0·13 [9]	0·09 [10]

[1] Stock and Davies, *Trans. Faraday Soc.*, 1948, **44**, 856; [2] Davies, *J.*, 1938, 277; Hoyle and Davies, unpublished; [3] Davies, *J.*, 1939, 349; [4] Davies, *Trans. Faraday Soc.*, 1927, **23**, 351; [5] Money and Davies, *ibid.*, 1932, **28**, 609; [6] Stock and Davies, this vol., p. 1371; [7] Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592; [8] Davies, *J.*, 1930, 2410; [9] Davies, *J.*, 1938, 271; [10] Macdougall and Davies, *J.*, 1935, 1416.

The dissociation constants obtained by the conductivity method correspond on Bjerrum's electrostatic theory of ion association to the following values for the closest approach of the $M^{\bullet\bullet}$ and trimetaphosphate ions: Ca, 4·2; Ba, 4·4; Mg, 4·5; Mn, 4·0; and Ni, 4·8 A.

An interesting feature of the results is that the calcium salt has a lower dissociation constant than either the magnesium or the barium salt. In Table III the data are compared with some previous results, and it is possible to trace in a qualitative way the relative importance of the two factors on which the measured dissociation constants mainly depend, *i.e.*, the hydration energy of the cation, and the energy of interaction of the associating ions.

In the hydroxides no water molecules can intervene between cation and hydroxy-group, and the order is that of the radii of the unhydrated cations. The interaction energy also predominates in the weak oxalates—where chelation probably occurs at any rate with the smaller cations—and to a markedly lesser extent in the malonates. With the nitrates, iodates, and some other inorganic salts, on the other hand, only moderate electrostatic forces seem to be involved in the interaction energy, and the order of strength is reversed, the most strongly hydrated cation giving the highest K. In the 2–3-valent salts considered here the stronger electrostatic attraction appears to balance more equally the solvation energy, thus leading to the irregular order of dissociation constants. The same phenomenon has been found with 1–1-valent salts in solvents of lower dielectric constant (Davies, "Conductivity of Solutions," 2nd Edn., p. 231, Chapman and Hall, 1933).



EXPERIMENTAL.

Sodium trimetaphosphate was prepared by the method described previously (Davies and Monk, *loc. cit.*). "AnalaR" Chlorides were used without further purification, and duplicate gravimetric silver chloride analyses on the stock solutions were ±0·03% or better in all cases. The equipment for the conductivity measurements has been described previously (Davies, *J.*, 1937, 432; Davies and Monk, *loc. cit.*).

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[*Received, June* 13*th*, 1949.]