611. *Ion-exchange Studies of Solutions of Borates.*

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The sorption of borate ions on an anion-exchange resin in the chloride form from 0·6, 0·4, 0·2, and 0·02M-boron solutions * was studied, by means of equilibrium experiments, at pH ~5·6—11·5. It reached a maximum at pH values which depended on the boron concentration.

Polyborate ions were sorbed from $\nless$0·2M-boron solutions at all but the highest pH values, the degree of condensation increasing with decreasing pH and increasing boron concentration. From the quantity of boron and chloride sorbed by the resin, it is calculated that there is sorption of a mixture of $B_5O_8^-$, $B_4O_7^{2-}$ (or $HB_5O_9^{2-}$), and monoborate ions, the relative amounts varying with the total boron concentration and the pH. The results appear to exclude the existence of a unique equilibrium in solution between $HB_5O_9^{2-}$ and $H_2BO_3^-$ existing over the whole pH range.

THE chemical constitution of aqueous solutions of boric acid has been much studied. In one of the first systematic investigations Kolthoff [1,2] concluded from conductivity measurements of borate solutions that both tetra- and penta-borate ions were present.

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* Throughout this paper, concentrations of borate solutions are given as molar with reference to single boron atoms; amounts given as " moles of boron " have similar significance.

[1] Kolthoff, *Rec. Trav. chim.*, 1926, **45**, 501.

[2] Kolthoff and Bosch, *ibid.*, 1927, **46**, 180.

Menzel,[3] from cryoscopic and conductivity data, concluded that monoborate ions BO_2^-, tetraborate ions $B_4O_7^{2-}$, and pentaborate ions $B_5O_8^-$ aq. were all present in aqueous borate solutions, the pentaborate ions being extensively dissociated. Thygesen,[4] by means of conductivity measurements on boric acid solutions, attempted to calculate the various dissociation constants K_1, K_2, K_3, and K_4 for the hypothetical di-, tri-, tetra- and penta-boric acid: his calculated values of K_3 had the greatest constancy, indicating that univalent triborate ions predominated in solution. However, for reasons which are a little obscure Thygesen considered that the presence of a mixture of univalent tetraborate ions $HB_4O_7^-$ and bivalent $B_4O_7^{2-}$ ions would better explain his results. More recently the constitution of aqueous solutions of boric acid and borates has received much attention from the French schools of Souchay and of Carpeni.

In their first publication Carpeni and Souchay,[5] following the previous theoretical treatment by Bye,[6] concluded, from a study of the neutralisation curves of solutions of boric acid between 0·03 and 0·262M, that $B_5O_8^-$, $HB_4O_7^-$, and BO_2^- ions were formed successively during the neutralisation. They emphasised that condensation of boric acid would be affected by two separate factors, the total boron concentration and the pH of the solution, the importance of which had not been fully appreciated by previous workers.

Subsequently Carpeni has reconsidered these conclusions: in particular he has differently interpreted the point of intersection of the neutralisation curves of boric acid at various concentrations. This point, which he calls the isohydric point,[7] is considered to show the existence in solution of an equilibrium between two, and only two, borate ions, one species being simple ($H_2BO_3^-$) and the other condensed ($HB_5O_9^{2-}$).[8] The existence of the simple species is favoured by high pH values and by high dilution. Recently, in a more detailed study of borate solutions, he has found [9] that the position of the isohydric point is unchanged on varying the boron concentration from 0·01M to saturation, or on varying the temperature from 5° to 95°, also that at room temperature KB_5O_8 is the borate salt in equilibrium with the isohydric solution, whilst at 85° and 95° it is $K_2HB_5O_9$. He has again emphasised his view that only $HB_5O_9^{2-}$ and $H_2BO_3^-$ ions occur in borate solutions.

These revised conclusions of Carpeni have been strongly criticised by Souchay and others on theoretical grounds.[10] The views of Souchay's school on the nature of solutions of borates have been recently summarised and extended by Lourijsen-Teyssedre,[11] who used pH measurements, partition coefficient data on the distribution of boric acid between water and pentyl alcohol, and cryoscopic methods based on the depression of the transition point between sodium sulphate decahydrate and the anhydrous salt.

Lourijsen-Teyssedre concluded that in boric acid solutions un-ionised HBO_2 molecules were largely present. On addition of alkali their concentration decreased, being offset by an increased concentration of $B_5O_8^-$, $B_4O_7^{2-}$, and BO_2^- ions in solution. Initially it was the $B_5O_8^-$ ions which were the most quickly formed, their concentration reaching a maximum at an alkali : boron ratio of *ca.* 0·2 : 1 (for a 0·25M-boron solution), when about one-third of the total boron was present as $B_5O_8^-$ ions. Further addition of alkali caused a rapid decomposition of these ions, which had entirely disappeared from solution at an alkali : boron ratio of *ca.* 0·4 : 1. The concentration of $B_4O_7^{2-}$ ions reached a maximum at an alkali : boron ratio of *ca.* 0·5 : 1, about 50% of the boron then being present as this ion. At higher alkali : boron ratios the concentration of $B_4O_7^{2-}$ ions decreased smoothly until it reached zero at an alkali : boron ratio of 1 : 1. The concentration of BO_2^- ions increased only slowly on the first additions of alkali, but at high alkali : boron ratios it became the most important borate ion in solution. Lourijsen-Teyssedre also pointed out that the condensation of boric acid was concentration-dependent,

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[3] Menzel, *Z. anorg. Chem.*, 1927, **164**, 22.

[4] Thygesen, *ibid.*, 1938, **237**, 101.

[5] Carpeni and Souchay, *J. Chim. phys.*, 1945, **42**, 149.

[6] Bye, *Ann. Chim. (France)*, 1945, **20**, 463; *Compt. rend.*, 1945, **221**, 99.

[7] Carpeni, *Compt. rend.*, 1948, **226**, 807; *Bull. Soc. chim. France*, 1948, 505.

[8] *Idem, Compt. rend.*, 1949, **228**, 89; *Bull. Soc. chim. France*, 1948, 629; 1950, 1280; 1952, 1010.

[9] *Idem, ibid.*, 1955, 1327.

[10] Souchay, *ibid.*, 1951, 932; Souchay and Teyssedre, *ibid.*, 1951, 938; *Compt. rend.*, 1953, **236**, 1965; Bye, *Bull. Soc. chim. France*, 1953, 390; Souchay, *ibid.*, 1953, 395.

[11] Lourijsen-Teyssedre, *ibid.*, 1955, 1111.

an increase in the boron concentration causing corresponding increases in the proportion of condensed borate ions present. Below a boron concentration of *ca.* 0·1M no $B_5O_8^-$ ions could be detected in solution, whilst the quantity of $B_4O_7^{2-}$ ions was greatly reduced.

This concentration-dependence of the condensation of boric acid is further illustrated by Stetten's work.[12] He showed, by means of pH measurements, that in the concentration range 0·1—0·6M a polyboric acid existed in solution with an average composition of 3·2 atoms of boron per molecule. This acid did not occur in <0·1M-solutions.

In view of the success of ion-exchange methods in studying the condensation of germanic acid,[13, 14] and of the close agreement of the resulting conclusions with those of Lourijsen-Teyssedre [15] for germanate solutions (based on different experimental methods), it was considered that an ion-exchange study might throw new light on the condensation reactions of boric acid. Boric acid has been found to be sorbed by the strong-base anion-exchange resin Amberlite IRA-400 in the chloride form (cf. Costa and Camus [16]); by measuring the amount of boron and chloride sorbed per equivalent of resin it has been possible to identify the various borate ions formed, and to obtain information concerning their behaviour on varying the pH or the boron concentration.

EXPERIMENTAL

Solutions.—Stock solutions (*ca.* 0·9, 0·6, 0·3, and 0·03M) were prepared by dissolving Analytical Grade orthoboric acid in boiled-out distilled water. Samples (50 ml.) were adjusted to the required pH by sodium hydroxide solution and were then made up to a total of 75 ml. by water, giving solutions *ca.* 0·6, 0·4, 0·2, and 0·02M in boron. Chloride was added as resin chloride (*ca.* 3·0 milliequiv. of chloride per g. of resin), additional chloride being introduced as sodium chloride.

Anion-exchanger.—Analytical Grade Amberlite IRA-400 in the chloride form was used. It was prepared from the hydroxide form by treatment with 2N-hydrochloric acid, and was washed free from excess of acid and air-dried before use. 1·0 or 0·5 g. resin samples were used.

Equilibrium Experiments.—Nine days were allowed for equilibration between solution and resin phase, each solution being mechanically shaken for at least 2 hr. each day. Experiments for longer times showed this to be adequate. The solution was then filtered through a dry column (1 cm. in internal diameter, 10 cm. long) containing a glass-wool plug. The filtrate was retained and used for analysis of the boron sorbed (by difference) and for pH measurements. The resin was then transferred to the column and rapidly washed with water (*ca.* 50 ml.) under suction, to prevent interaction between the resin and the partially diluted solution; a further 300 ml. of water were then passed slowly through the column to complete the washing. All the washings were rejected. The chloride sorbed on the resin was eluted with 300 ml. of 2N-nitric acid during 8 hr. and determined in the eluate. The resin was then completely converted into the chloride form by treatment with 300 ml. of 2N-hydrochloric acid and washed free from excess of acid. Final elution with 300 ml. of 2N-nitric acid for 8 hr., and determination of the chloride so removed, gave the capacity of the resin sample used. The capacity was found to vary from sample to sample and the results have been expressed in moles sorbed per equiv. of resin.

Analytical Methods.—Boron was determined by first neutralising the solution to methyl-red by dilute hydrochloric acid, adding excess of glycerol, and titrating the solution to phenolphthalein with standard sodium hydroxide. Chloride was determined gravimetrically as silver chloride. Measurements of pH were made with a commercial pH meter incorporating a glass electrode and a saturated calomel electrode. For strongly alkaline solutions a Cambridge Instrument Co.'s " Alki " glass electrode was used.

RESULTS

The sorption of boron and of chloride from solutions containing 45, 30, and 15 mmoles of boron and, in each case, 1·5 milliequivs of chloride (the resin chloride from 0·5 g. of resin) in

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[12] Stetten, *Analyt. Chem.*, 1951, **23**, 1177.
[13] Everest and Salmon, *J.*, 1954, 2438.
[14] Idem, *J.*, 1955 1444.
[15] Lourijsen-Teyssedre, *Bull. Soc. chim. France*, 1955, 1118.
[16] Costa and Camus, *Ann. Chim. (Italy)*, 1955, **45**, 598.

75 ml. of solution is illustrated (Figs. 1 and 2). For these ranges of concentration (0·6, 0·4, and 0·2M-boron) the sorption of boron reached a maximum at pH *ca.* 7·5, 8·0, and 8·5, and of chloride a minimum at pH *ca.* 8·5, 8·7, and 9·1 respectively. There was, therefore, a divergence between the pH values for these maxima and minima, this " chloride shift " increasing with increasing boron concentration.

When 1·0 g. of resin and solutions containing 15 mmoles of boron and 4·0 milliequivs. of chloride in 75 ml. of solution were used (Fig. 2), the overall boron sorption was reduced and the pH values for maximum boron and minimum chloride sorption were slightly higher than when only 1·5 milliequivs. of chloride were present.

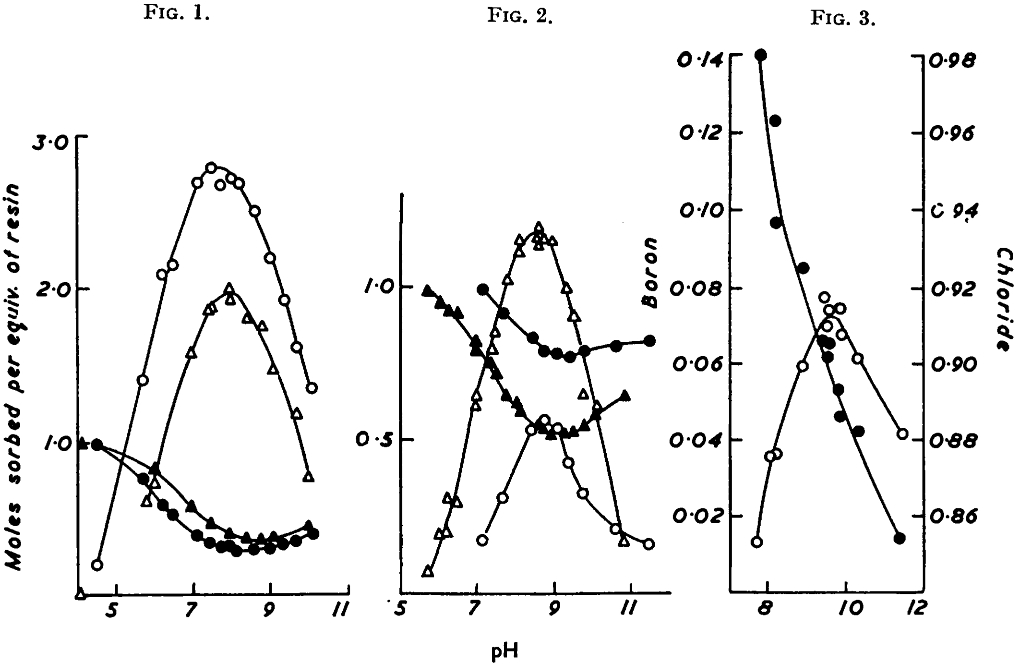
FIG. 1. FIG. 2. FIG. 3.

Sorption of boron and chloride by IRA-400 (Cl) (0·5 g.).

	Concn. (M) of boron soln.	Mmoles added		Sorbed on resin	
		B	Cl	B	Cl
Fig. 1	0·6	45	1·5	○	●
	0·4	30	1·5	△	▲
Fig. 2	0·2	15	1·5	△	▲
		15	4·0 *	○	●
Fig. 3	0·02	1·5	3·0 *	○	●

* 1·0 g. of resin used.

With only 1·5 mmoles of boron and 3·0 milliequivs. of chloride in solution the boron sorption was low, reaching a maximum at pH 9·4 whilst the chloride sorption decreased over the whole pH range studied (Fig. 3). The maximum amount of boron sorbed from solution by 0·5 g. of resin was 9%, 11%, and 12% for the 0·6, 0·4, and 0·2M-boron solutions: for 0·02M-boron solutions with 1·0 g. of resin this figure was 13%. The pH values at which boron sorption could first be detected were *ca.* 4·9, 5·2, 5·7, and 7·6 for these four boron concentrations.

The values of *R* (the number of boron atoms present in one equiv. of borate ions sorbed) were calculated as previously described,[13] and are given in the Table.

The number of boron atoms present in one equivalent of borate ions sorbed (*R*).

pH	*R*	pH	*R*	pH	*R*	pH	*R*	pH	*R*
(*A*) IRA-400 (Cl) (0·5 g.), 45 *mmoles of boron and* 1·5 *milliequivs. of chloride.*									
5·68	5·74	7·08	4·46	7·95	4·01	8·98	3·19	9·64	2·50
6·21	4·99	7·42	4·23	8·07	3·88	9·32	2·91	10·04	2·28
6·47	4·63	7·69	3·89	8·58	3·58				
(*B*) IRA-400 (Cl) (1·0 g.), 45 *mmoles of boron and* 3·0 *milliequivs. of chloride.*									
5·62	4·84	5·75	4·96	5·90	4·98	5·98	4·52	6·00	4·43
5·63	5·25	5·79	4·88						
(*C*) IRA-400 (Cl) (0·5 g.), 30 *mmoles of boron and* 1·5 *milliequivs. of chloride.*									
6·02	3·95	7·48	3·46	7·98	3·30	8·78	2·74	9·62	1·88
6·98	3·69	7·97	3·21	8·41	2·84	9·06	2·33	9·98	1·37
7·40	3·51								
(*D*) IRA-400 (Cl) (1·0 g.), 15 *mmoles of boron and* 4·0 *milliequivs. of chloride.*									
7·64	3·71	8·71	2·72	9·38	1·80	10·60	1·10	11·48	0·89
8·41	3·10	9·05	2·27	9·76	1·49				
(*E*) IRA-400 (Cl) (0·5 g.), 15 *mmoles of boron and* 1·5 *milliequivs. of chloride.*									
5·68	3·43	7·46	2·99	8·50	2·51	8·62	2·49	9·45	1·86
6·06	3·08	7·76	2·87	8·52	2·59	8·69	2·46	9·73	1·40
6·15	3·30	8·02	2·93	8·53	2·54	8·90	2·31	10·03	1·45
6·96	2·86	8·05	2·91	8·57	2·47	9·23	2·03	10·80	0·47
7·39	3·08	8·11	2·83						
(*F*) IRA-400 (Cl) (1·0 g.), 15 *mmoles of boron and* 3·0 *milliequivs. of chloride.*									
6·14	2·98	6·52	2·98	6·63	2·99	6·76	3·09	6·96	2·86
(*G*) IRA-400 (Cl) (1·0 g.), 1·5 *mmoles of boron and* 3·0 *milliequivs. of chloride.*									
7·73	0·69	8·85	0·80	9·43	0·72	9·78	0·69	10·26	0·52
8·01	0·97	9·39	0·82	9·49	0·78	9·84	0·60	11·40	0·29
8·17	0·59								

In all experiments 75 ml. of solutions were present and all pH values are those of the equilibrated solutions.

DISCUSSION

0·02M-*Boron Solutions.*—The *R* values obtained (section *G* of Table) indicate the sorption of monoborate ions by the resin at pH >7. Monoborate must also be the predominant borate species in solution at this concentration as monoborate ions would be less readily sorbed by the resin than would any ions derived from the relatively strong polyboric acids. That the experimental *R* values are less than unity at higher pH values may be due to the sorption of small amounts of HBO_3^{2-} (*R* 0·5) or BO_3^{3-} (*R* 0·33) ions. This is indicated by the maximum in boron sorption at pH 9·6 whereas the chloride sorption decreases through the whole range studied (Fig. 3). However, overmuch significance cannot be attributed to the variations observed, as the *R* values cannot be calculated with great accuracy owing to the small amount of boron sorbed from 0·02M-boron solutions. Also the possibility of hydrolysis of the borate form of the resin at higher pH values, to give fractional *R* values, cannot be completely discounted.

It is of interest that no boron sorption could be detected from 0·002M-boron solutions (containing 0·15 mmole of boron and 0·75 milliequiv. of chloride in 75 ml. solution, with 0·25 g. of resin).

0·6, 0·4, *and* 0·2M-*Boron Solutions.*—The *R* values (sections *A*, *B*, *C*, *E*, and *F* of Table) indicate that condensed borate ions are being sorbed by the resin at pH <*ca.* 10, the degree of condensation being greater at lower pH or higher boron concentration. At pH >*ca.* 10 the *R* values tend towards unity, indicating the progressive sorption of a univalent monoborate ion by the resin. This would agree with the views of Carpeni,[8,9] Souchay,[10] and Lourijsen-Teyssedre,[11] who consider that monoborate ions are the chief species existing in solution in this pH region at all boron concentrations. That monoborate ions are present in sodium borate solutions (which will possess pH >10) over a wide concentration range has been shown by other workers using cryoscopy [17, 18] and Raman spectra.[19]

According to Lourijsen-Teyssedre [11] successive formation of $B_5O_8^-$, $B_4O_7^{2-}$, and BO_2^- ions occurs on addition of alkali to boric acid solutions, although the formation of these ions overlaps to some extent. A good interpretation of our results at pH <*ca.* 10 can be given if Lourijsen-Teyssedre's conclusions are accepted, and if it is assumed that the affinities of the pentaborate ion $B_5O_8^-$ (R 5) and the tetraborate ion $B_4O_7^{2-}$ (R 2) for the resin do not differ widely. That this assumption is reasonable can be deduced from the work of Kolthoff,[1, 2] Thygesen,[4] and Stetten [12] who showed that the polyboric acids were of comparable strengths, although considerably stronger than monoboric acid.

At the highest boron concentration used (0·6M) the maximum R value, obtained at pH *ca.* 6, approximated closely to five, indicating almost exclusive sorption of pentaborate ions by the resin at this pH. With the 0·4 and 0·2M-boron solutions the maximum R values were also obtained at pH *ca.* 6, although the proportion of pentaborate ions sorbed by the resin appeared to decrease with decreasing boron concentration.

Lourijsen-Teyssedre [11] considers that as the pH of the boron solutions is raised above six a rapid increase in the concentration of pentaborate ions and a rather slower increase in the concentration of tetraborate ions takes place. These two ions will be taken up by the resin, giving rise to the rapid increase observed in the overall boron sorption (Fig. 1). This increase will be accompanied by a fall in the values of R due to the sorption of a higher proportion of tetraborate ions than at pH 6. The pentaborate ions in solution reach maximum concentration at a pH dependent on the boron concentration, and are then rapidly replaced by tetraborate ions. Pentaborate ions on the resin will then be replaced by tetraborate ions with a resulting decrease in the overall amount of boron sorbed by the resin and a continued fall in the values of R. As a univalent ion is now being replaced on the resin by a bivalent one, with approximately the same resin affinity, the sorption of chloride will continue to fall at pH values above that at which the sorption of boron by the resin has reached a maximum (Fig. 2), thus explaining the occurrence of the "chloride shift."

At higher pH values (*ca.* 9) the sorption of tetraborate ions will reach a maximum and they will then be progressively replaced on the resin by univalent monoborate ions (R 1), thus continuing the fall in the values of R and in the overall boron sorption. The chloride sorbed by the resin will now increase, however, owing to replacement of a bivalent ion on the resin by a univalent one, and to the lower affinity of monoborate ions for the resin. This behaviour is similar to the replacement of pentagermanate ions [13, 14, 20] on the resin by monogermanate ions at pH >9·2.

The increase in the "chloride shift" observed with increasing boron concentration (Figs. 1 and 2) is due to the relative increase in the concentration of pentaborate ions in solution and to the greater overlap in the pH range in which both penta- and tetra-borate ions can co-exist. Both these factors will cause the replacement of pentaborate ions on the resin by tetraborate ions to take place over a wider pH range.

In the experiments with 0·2M-boron solutions, added chloride (Fig. 2) slightly increased the R values (section D of Table). This indicates that tetraborate ions are more easily displaced from the resin than are pentaborate ions, and implies that the affinity of the pentaborate ion for the resin is greater than that of the tetraborate ions, despite the smaller charge on the former. However, the effect of added chloride is here much less than it is in the germanate system where a marked change was afforded in the ratio of penta- and mono-germanate ions sorbed by the resin.[14] This provides additional evidence that the affinities of the different polyborate ions for the resin do not differ widely.

Although our results can be completely interpreted on the basis of Lourijsen-Teyssedre's conclusions,[11] nevertheless other interpretations of our work could be advanced. Our

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[17] Menzel and Shultz, *Z. anorg. Chem.*, 1943, **251**, 167.
[18] Doucet and Rollin, *Compt. rend.*, 1948, **226**, 1967.
[19] Edwards, Morrison, Ross, and Shultz, *J. Amer. Chem. Soc.*, 1955, **77**, 226.
[20] Everest, *J.*, 1955, 4415.
[21] Lefebvre, *Compt. rend.*, 1955, **241**, 1037, 1295.

results could be equally well explained by assuming the ion $HB_5O_9^{2-}$ (*R* 2·5), postulated by Carpeni,[8,9] to be sorbed over the middle pH range instead of the tetraborate ion, or even that it is a mixture of these ions which is so sorbed. It is also possible that the ion $HB_4O_7^-$ (*R* 4) [21] occurs as an intermediate between the $B_5O_8^-$ and $B_4O_7^{2-}$ ions. However, our results appear to exclude the existence of a unique equilibrium in borate solutions between $HB_5O_9^{2-}$ and $H_2BO_2^-$ ions over the whole pH range as postulated by Carpeni, although such a unique equilibrium could exist at pH $>$*ca.* 9·5. Not only are the *R* values which we find at pH $<$9·5 too large for the sorption of $HB_5O_9^{2-}$ ions, but our results definitely point to the sorption of more than one polyborate ion in the pH range 6—9·5.

It is significant that previous studies on germanates [13,14] show that, unlike the case of borate solutions, only one condensed germanate ion is taken up by the resin, and as the germanate species sorbed all possessed the same charge no " chloride shift " was observed.

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