474. *Ion-exchange Studies of Solutions of Arsenites.*

By D. A. Everest and W. J. Popiel.

The sorption of arsenic and of chloride by Amberlite I.R.A-400 (Cl) from arsenious acid solutions has been studied over the pH range 5—13. The results have been interpreted in terms of the sorption of $As_3O_5^-$, $As_2O_4^{2-}$, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}, the actual ion sorbed depending on the pH and the arsenic concentration of the solution studied. Supporting evidence has been obtained from measurement of the ultraviolet absorption spectra of these solutions, and evidence has been obtained that a correlation exists between the ions sorbed by the resin and those present in solution.

The tendency of arsenious acid to undergo condensation in neutral or weakly alkaline solutions was first observed by Auerbach,[1] who investigated 0·03—0·23M-arsenious acid by means of partition experiments between pentyl alcohol and water and by competition experiments between arsenious acid and boric acid for limited quantities of bases. In addition to the presence of simple monoarsenite ions he inferred the presence in more concentrated solutions of diarsenite ions, and possibly some more highly condensed species also. The concentration of condensed arsenious acid species was considered to be low in dilute solution. Garret, Holmes, and Laube[2] determined the solubility of arsenious oxide in sodium hydroxide solution and concluded that the condensed species $HAs_2O_4^-$ and $H_2As_3O_6^-$ were present in the more concentrated arsenious acid solutions.

In other work with more dilute solutions of arsenious acid, formation of condensed arsenite ions could not be detected. Thus Roth and Schwartz,[3] from freezing-point measurements on 0·008—0·06M-arsenious acid, concluded that arsenious acid was entirely in the monomeric form. Similarly Carpeni and Souchay,[4] from pH titrations of arsenious acid solutions up to 0·2M, could obtain no evidence for condensation.

More recently Souchay and Teyssedre[5] repeated and modified the earlier work. They conclude that in 0·2—0·8M-arsenious acid the only condensed species present is $As_3O_5^-$, and that the $HAs_2O_4^-$ ion does not exist or is present in only undetectable quantities. The relative concentration of condensed species does not appear to be very high—in 0·2M-arsenious acid solution only 10% of the arsenic is present as $As_3O_5^-$ ions.[6]

In strongly alkaline solution arsenious acid appears to be always present in the monomeric form, even at relatively high concentrations. Brintzinger and Ratanarat,[7] from dialysis experiments, concluded that arsenious acid was present in strongly alkaline solution as $As(OH)_6^{3-}$. Goldfinger and von Schweinitz[8] observed an absorption line in the ultraviolet absorption spectrum of arsenious acid (up to 0·1M) which they attributed to $H_2AsO_3^-$ ions. On increase in the alkali concentration to 10—12M a second absorption line was obtained which was attributed to the presence of $HAsO_3^{2-}$, and it was considered that these solutions might contain also small amounts of AsO_3^{3-} ions.

The success of ion-exchange methods in the investigation of the condensation of germanic and boric acid[9, 10] suggested that similar methods could be used to study condensation of arsenious acid, and its dependence on pH and total arsenic concentration. Preliminary experiments showed that arsenic is sorbed from arsenious acid solutions by the strongly basic ion-exchanger Amberlite I.R.A.-400 in the chloride form.

---

[1] Auerbach, *Z. anorg. Chem.*, 1903, **37**, 353.

[2] Garret, Holmes, and Laube, *J. Amer. Chem. Soc.*, 1940, **62**, 2024.

[3] Roth and Schwartz, *Ber.*, 1926, **59**, 338.

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

[5] Souchay, *Bull. Soc. chim. France*, 1951, 932; Souchay and Teyssedre, *Compt. rend.*, 1953, **236**, 1965.

[6] Lourijsen-Teyssedre, *Bull. Soc. chim. France*, 1956, 1118.

[7] Brintzinger and Ratanarat, *Z. anorg. Chem.*, 1935, **222**, 317.

[8] Goldfinger and von Schweinitz, *Z. phys. Chem.*, 1932, **19**, 219.

[9] Everest and Salmon, *J.*, 1954, 2438; 1955, 1444.

[10] Everest and Popiel, *J.*, 1956, 3183.

EXPERIMENTAL

Solutions.—Stock solutions, containing *ca.* 0·27 and 0·15 g.-atom of arsenic, were prepared by dissolving " AnalaR " arsenious oxide in the minimum amount of boiling water and diluting it to the required volume.[11] The maximum solubility of arsenious oxide at 25° is stated to be 0·1035 molal,[8] but it was found that more concentrated solutions could be prepared and that they were stable at room temperature for *ca.* 2 days. Portions of these stock solutions (50 ml.) were adjusted to the required pH by addition of sodium hydroxide, and then made up to 75 ml. by addition of water before addition of resin (1·0 g.), thus giving solutions containing 0·18 or 0·10 g.-atom of arsenic per l.

Anion-exchanger.—Amberlite I.R.A.-400 (Cl) (1·0 g.) was used, being prepared from the hydroxide form by treating it with 2N-hydrochloric acid, washing it free from acid and air-drying it before use.

Equilibrium Experiments.—These were carried out as previously described.[10] All wash-water was de-ionised by passage through Permutit " Biodeminrolit " mixed-bed resin.

Analytical Methods.—Arsenic was determined in the filtrate, after separation of the resin phase, by acidification with hydrochloric acid (methyl-red), addition of sodium hydrogen carbonate (*ca.* 1 g.), and titration of arsenic with iodine (starch). Chloride was determined gravimetrically as silver chloride. The quantity " chloride desorbed " from the resin was found from the difference between the total capacity and the chloride loading at equilibrium for any given resin sample.

Measurements of pH were made with a pH meter of commercial type, a glass electrode, and a saturated calomel electrode. For strongly alkaline solutions a Cambridge Instrument Co. " Alki " glass electrode was used.

Ultraviolet Absorption Spectra.—Measurements on arsenious acid solutions were carried out with a Unicam single-beam spectrophotometer. Reference solutions were identical with the test solutions except that arsenic was absent.

RESULTS

The quantity of arsenic sorbed by the resin, the chloride desorbed, and the ratio of g.-atoms of arsenic sorbed to g.-atoms of chloride desorbed (referred to in the discussion as the *R* value) are represented in Figs. 1 and 2. The *R* value, which is in effect the average number of arsenic atoms sorbed per " active site " of the resin, is used to determine the number of arsenic atoms present in the actual arsenite ions sorbed.[9, 10] The quantity of arsenic removed from solution did not exceed 12% for either of the arsenic concentrations studied.

The ultraviolet spectrograms obtained show sharp absorption edges, which move to longer wavelengths as the pH of the solution is increased. This bears a close similarity to a colour change in the visible region, as is shown in the chromate–dichromate system, and suggests that a pH-dependent ionic change takes place in solution. The results for solutions containing 0·18 g.-atom of arsenic per l. are given in Fig. 3. Similar observations were recorded for solutions containing 0·1 g.-atom of arsenic per l. although the displacement of the absorption curves was somewhat less marked.

DISCUSSION

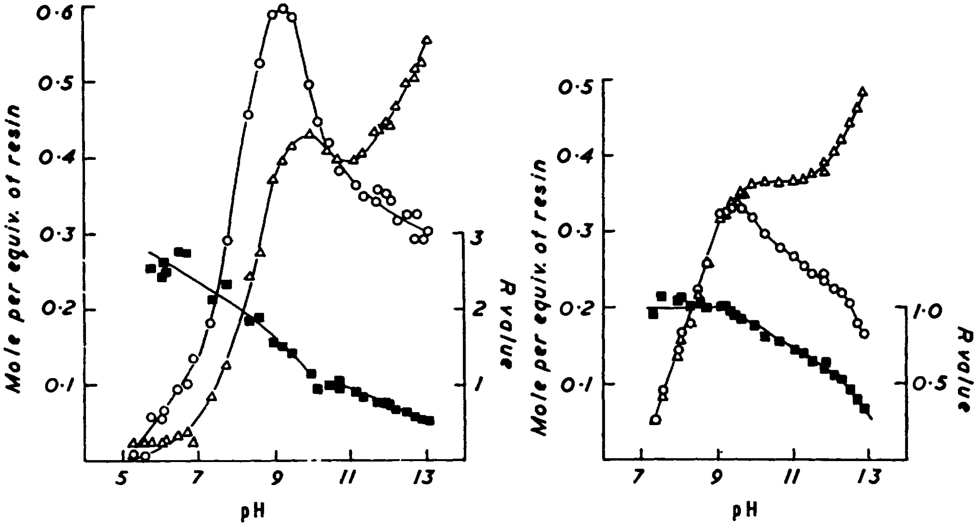
Solutions containing 0·18 *g.-atom of Arsenic per l.*—Maximum sorption of arsenic is found at *ca.* pH 9·2 whereas a maximum in the desorption of chloride occurs at pH 10. As in the ion-exchange investigation of boric acid,[10] this " chloride shift " indicates that as the pH of the arsenious acid solution increases, a transition occurs from the sorption of a univalent condensed ion by the resin to the sorption of a multivalent ion of lower *R* value. This transition would cause the overall sorption of arsenic to come to a maximum and then to decrease, as is found, since a condensed ionic species is being gradually replaced on the resin by a less condensed one. However, the desorption of chloride ions will continue since a univalent ion is being replaced on the resin by a multivalent one. In this way the desorption of chloride ions comes to a peak at a higher pH value than that at which the maximum in the arsenic sorption occurs.

---

[11] Margulis and Ganc, *Ann. Agron.*, 1947, **17**, 568.

The sorption of a mixture of $As_3O_5^-$ (*R* 3) [2, 6] and $As_2O_4^{2-}$ (*R* 1) in the pH region 5—9 would explain our results, the equilibrium in solution between these ions changing in favour of $As_2O_4^{2-}$ as the pH increases, thus explaining the decrease in the value of *R* from *ca.* 2·8—2·5 down to 1 (Fig. 1). The multivalent species reaches a maximum concentration

FIG. 1. FIG. 2.



FIGS. 1 *and* 2. *Sorption of arsenic and chloride by resin* I.R.A.-400 (Cl) (1·0 *g*.).
Concn. (*g.-atom per l.*) *of* As *in soln.*: *Fig.* 1, 0·18; *Fig.* 2, 0·1. ○ *Sorption of* As, *and* △ *desorption of* Cl *by resin* (1 *g*.). ■ *R value.*

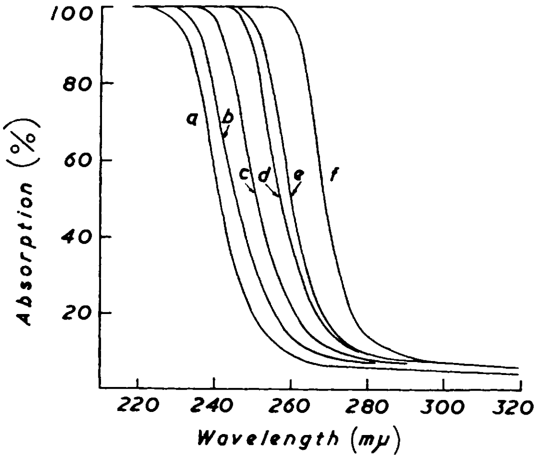


FIG. 3. *Absorption spectrograms* (1 *cm. cells*) *of* 0·18 *g.-atom of arsenic at* pH : *a*, 5·0; *b*, 7·42; *c*, 8·02; *d*, 8·88; *e*, 11·46; *f*, 12·10.

near the peak of the chloride desorption (pH 10), and it is significant that the values of *R* in this region of pH closely approach unity. But whereas the value of *R* remains steadily at unity in the pH region 10—11, the desorption of chloride ion decreases, which implies a further change from $As_2O_4^{2-}$ to $H_2AsO_3^-$ (both of *R* 1).

Above pH 11 the chloride-desorption curve rises steadily, whereas the arsenic sorption curve falls and flattens out, whilst the *R* values tend towards 0·5. This implies that at higher pH values the species $HAsO_3^{2-}$ is being sorbed, and is in agreement with the observations of Goldfinger and von Schweinitz.[8]

Solutions containing 0·1 *g.-atom of Arsenic per l.*—A maximum R value of unity is maintained in the pH region 7—9·5 (Fig. 2), which indicates sorption of $As_2O_4^{2-}$ or $H_2AsO_3^-$ ions. Although the presence of monoarsenite ions only in this concentration range would be in agreement with the results of other workers,[3, 4, 5] our spectrophotometric studies indicate a large displacement of the absorption edges in the pH region 7—9, suggesting a marked ionic change in solution. This implies a transition from $As_2O_4^{2-}$ to $H_2AsO_3^-$ in this range. The chloride-desorption curve shows a point of inflection in the pH range 10—11 (Fig. 2), corresponding to a steady decrease in the value of R. This indicates the progressive formation of $HAsO_3^{2-}$ ions in solution (R 0·5), the tendency for sorption of this ion becoming greater at pH 11·5 as is shown by the sudden increase in slope of the chloride-desorption curve. At pH 12·5 the R value of 0·5 shows that the $HAsO_3^{2-}$ ion is then the principal species sorbed by the resin. Above this pH value there is a rapid decrease in the sorption of arsenic, coupled with an increase in the desorption of chloride. This suggests the sorption of OH^- ions by the resin, the concentration of which in solution is now becoming appreciable. It is not precluded however that a species such as AsO_3^{3-} (R 0·33) may be taken up by the resin in this pH region. The existence of this ion in solution above pH 12 has been suggested by the work of Goldfinger and von Schweinitz [8] and of Brintzinger and Ratanarat.[7] That the sorption of the hydroxyl ion is not as great as might be expected at such a high alkalinity is shown by the fact that, although at pH $\nless 12$ the pH values of the equilibrium solutions were found to be consistently lower than those of the initial solutions, nevertheless this discrepancy was never greater than *ca.* 0·2 pH unit over the whole pH range studied.

Our formulation of the various arsenite ions occurring in arsenious acid solutions is consistent with the results obtained by Nelson [12] for the As_2O_3–Na_2O–H_2O system. He found the following arsenites to be formed: $Na_2O,3As_2O_3$ ($Na_2As_6O_{10}$); Na_2O,As_2O_3 ($Na_2As_2O_4$); $2Na_2O,As_2O_3,7H_2O$ ($Na_4As_2O_5,7H_2O$); $2Na_2O,As_2O_3$ ($Na_4As_2O_5$). The first two compounds can be considered to contain $As_3O_5^-$ and $As_2O_4^{2-}$ ions respectively. The last two can be considered as derived from the $H_2As_2O_5^{2-}$ ion by the replacement of the two hydrogen atoms, the $H_2As_2O_5^{2-}$ ion being simply the hydrated form of $As_2O_4^{2-}$.

The sorption of a species such as $HAs_3O_6^{2-}$ (R 1·5), instead of the $As_2O_4^{2-}$ ion, might on our evidence be considered possible. From the previous discussion of the chloride shift the sorption of either $HAs_3O_6^{2-}$ or $As_2O_4^{2-}$ ions by the resin would be expected to reach a maximum at the pH value corresponding to the peak in the chloride-desorption curve. However, at both the concentrations studied, the value of R at this point has been on or just below unity. The sorption of $As_2O_4^{2-}$ ions by the resin rather than $HAs_3O_6^{2-}$ is thus considered more likely.

It is significant that, in the ultraviolet absorption studies, the maximum displacement of the absorption edges occurs in the pH regions at which our ion-exchange results indicate a maximum change in the ionic species sorbed by the resin (*i.e.*, at *ca.* pH 7—9·5 and above pH 11 for the higher arsenic concentration, and pH 7—9 and above 12 for the lower arsenic concentrations). These results indicate a definite correlation between the ions present in solution and those sorbed by the resin.

It is worth mention that similar spectrograms to ours have been observed with solutions of telluric acid,[13] indicating similar behaviour.

BATTERSEA POLYTECHNIC, LONDON, S.W.11.

[*Received, November 14th*, 1956.]

---

[12] Nelson, *J. Amer. Chem. Soc.*, 1941, **63**, 1870.

[13] Scott and Leonard, *Analyt. Chem.*, 1954, **26**, 445; Stüber, Braida, and Jander, *Z. phys. Chem.*, 1934, **171**, *A*, 320.