495. *Indium Phosphates: Phase-diagram, Ion-exchange, and* pH *Titration Studies.*

By C. E. A. Brownlow, J. E. Salmon, and J. G. L. Wall.

Phase-diagram studies of the system indium oxide–phosphoric oxide–water have shown the following salts to occur as stable solid phases: (*a*) $In_2O_3,2P_2O_5,11H_2O$; (*b*) $In_2O_3,3P_2O_5,7H_2O$ (both at 25°); and (*c*) $In_2O_3,P_2O_5,4H_2O$ (at 70°). Ion-exchange experiments, together with pH titration studies, have indicated that, in the range of pH 0·05—1·25, the extent of complex formation between indium and the anions of the following acids decreases in the order $HF > H_3PO_4 > HCl > H_2SO_4 > HNO_3 > HClO_4$. The formation of both anionic and cationic phosphato-complexes of indium, under specified conditions, has been detected by ion-exchange techniques.

Apart from the studies of Winkler[1] and Ensslin, Dreyer, and Lessmann[2] on indium phosphates as precipitated from solution, little information is available concerning these compounds. However, pH titration and ion-exchange studies[3,4] have provided indication of complex formation between indium and phosphate ions. In order to establish whether the properties of the indium phosphates were similar to those of iron(III) and aluminium, a more detailed examination has been made.

Experimental

Materials.—*Indium phosphate.* Sodium hydroxide was added to a solution of an indium salt in excess of phosphoric acid until a slight permanent precipitate was formed. The solution was then heated on a steam-bath, and the precipitated indium phosphate washed, with a long period of contact, by decantation with hot 0·5% phosphoric acid, then filtered off and washed with hot water. The product, after drying in air, was shown by analysis to be a hydrated tertiary indium phosphate.

Indium chloride and nitrate solutions. These were prepared by dissolution of indium in the concentrated acid, followed by dilution.

Ion-exchange resins. The cation exchanger Zeo-Karb 225 and anion exchanger Amberlite IRA-400 were used.

Analytical Methods.—Indium was determined by an EDTA method,[5] and phosphate gravimetrically as ammonium phosphomolybdate.

Measurements of pH were carried out by using a commercial pH meter with a glass electrode and a saturated calomel electrode, or (in the case of hydrofluoric acid) narrow-range pH indicator papers.

Cation- and anion-exchanger capacities were determined by standard procedures.[6]

Procedures.—*Phase-diagram studies.* The indium phosphate was added portionwise during 2—3 weeks to phosphoric acid solutions of various strengths until an undissolved residue remained. The suspensions were then kept at the appropriate temperature and stirred at intervals until equilibrium was reached, as indicated by check analyses.

Studies of the removal of indium from cation–exchanger in the indium form. The methods previously given[3,4] were employed.

Cation- and anion-exchange sorption experiments. The procedure previously described was used.[7]

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[1] Winkler, *J. prakt. Chem.*, 1867, **102**, 373.

[2] Ensslin, Dreyer, and Lessmann, *Z. anorg. Chem.*, 1947, **254**, 315.

[3] Holroyd and Salmon, *J.*, 1956, 269.

[4] Genge and Salmon, *J.*, 1959, 1459.

[5] Genge and Salmon, *Lab. Practice*, 1957, **6**, 390.

[6] Salmon and Hale, " Ion Exchange, A Laboratory Manual," Butterworths Scientific Publications, London, 1959, pp. 79 and 86.

[7] Salmon, *Rev. Pure Appl. Chem.*, 1956, **6**, 24.

RESULTS AND DISCUSSION

Phase-diagram Studies at 25°.—A study of the system In_2O_3–P_2O_5–H_2O at 25° for solutions containing up to 62% of phosphoric oxide has indicated the following new compounds as stable solid phases (see Table 1, Fig. 1): (*A*) $In_2O_3,2P_2O_5,11H_2O$ as white irregular microcrystals, 1—2 μ in size, (*B*) $In_2O_3,3P_2O_5,7H_2O$ as rhombohedral plates with bevelled edges. The salt (*A*) could not be formulated exactly, with respect to its degree of hydration, from the convergence of the tie lines, and the formula $InHPO_4,H_2PO_4,4H_2O$ was decided upon in conjunction with the results of experiments in which the compound was washed and then dried at various temperatures.

TABLE 1. *System* In_2O_3–P_2O_5–H_2O *at* 25°. *Stable equilibrium.*

Solutions		Moist solids		Solid phase *
In_2O_3 (%)	P_2O_5 (%)	In_2O_3 (%)	P_2O_5 (%)	
0·10	2·46	41·64	22·65	C
0·38	4·83	20·72	23·18	A
0·62	8·46	23·54	27·24	
0·73	11·46	27·86	30·95	
1·01	15·42	31·63	34·32	
1·17	17·99	28·54	33·98	
1·81	22·44	29·65	34·17	
2·06	26·76	28·21	34·09	
2·80	30·96	27·94	36·28	
3·16	32·69	27·68	37·50	
3·61	36·11	27·62	37·50	
4·46	39·51	27·94	38·10	
5·03	40·25	28·57	38·98	
5·74	40·89	27·54	39·29	A
6·35	42·85	26·11	40·04	
7·42	44·61	27·32	40·50	
9·73	46·51	24·97	42·10	
11·57	48·18	26·03	42·52	
13·19	49·88	—	—	
13·51	50·29	25·53	48·87	
14·20	51·73	24·92	49·98	
11·69	54·36	—	—	
8·97	56·12	20·72	53·67	B
8·29	56·76	28·70	52·07	
6·35	59·61	19·49	55·73	
4·93	61·32	21·20	55·86	

* A = $In_2O_3,2P_2O_5,11H_2O$. B = $In_2O_3,3P_2O_5,7H_2O$. C = $In_2O_3,P_2O_5,4H_2O$.

FIG. 1. *System* In_2O_3–P_2O_5–H_2O *at* 25°.

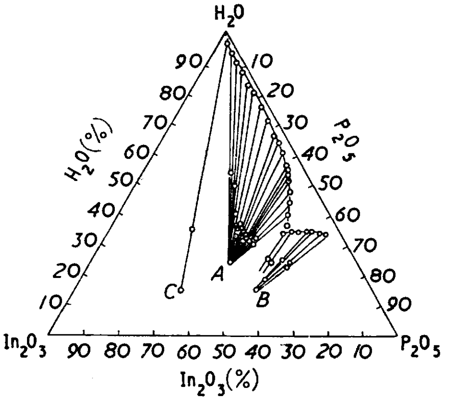
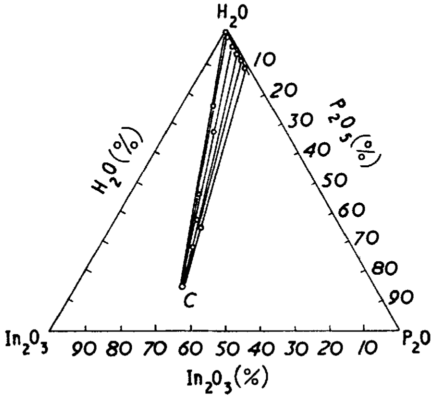


FIG. 2. *Systems* In_2O_3–P_2O_5–H_2O at 70°.



Some evidence was obtained for the existence of a metastable salt in the range 49—53% of phosphoric oxide. In this region, indium oxide has a very high solubility so the solutions were very viscous; hence, the separation of the moist solid from the liquid was more difficult and the resulting tie lines were correspondingly less accurate.

Phase-diagram studies at 70°.—A study of the system at 70° for solutions containing up to 10% of phosphoric oxide has indicated the following as a stable solid phase (see Table 2, Fig. 2): (*C*) $In_2O_3,P_2O_5,4H_2O$ as a white crystalline powder. Again, the degree of hydration was in part deduced from experiments in which the compound was dried at

TABLE 2. *System* In_2O_3–P_2O_5–H_2O *at* 70°. *Stable equilibrium.**

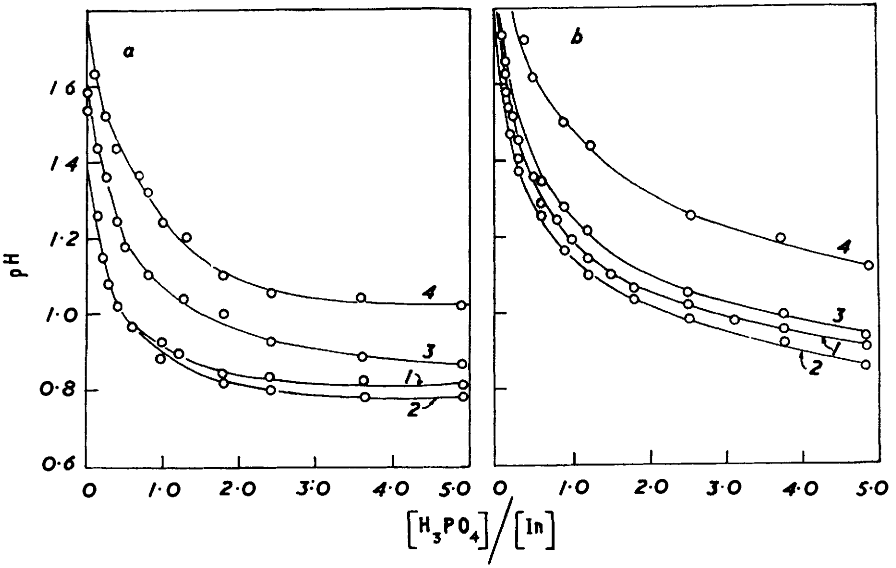
Solutions		Moist solids		Solutions		Moist solids	
In_2O_3 (%)	P_2O_5 (%)	In_2O_3 (%)	P_2O_5 (%)	In_2O_3 (%)	P_2O_5 (%)	In_2O_3 (%)	P_2O_5 (%)
0·10	0·45	16·59	8·75	0·25	6·11	40·48	22·91
0·17	0·99	35·69	19·81	0·42	8·31	46·83	25·97
0·21	2·80	20·93	12·53	0·61	10·91	41·11	25·20

* Solid phase C = $In_2O_3,P_2O_5,4H_2O$ throughout.

various temperatures. The solid (C) ($InPO_4,2H_2O$) has not been described before, although indium tertiary phosphate has been reported [2] as $InPO_4$ after heating at 800°.

pH *Titration Studies.*—The results are given (Fig. 3) of pH titration experiments in which 0·1M-solutions of indium as chloride and nitrate were titrated with 1·5M-phosphoric acid. As in the case of aluminium,[8] the addition of sodium chloride or nitrate (to give a concentration, in the solution to be titrated, of 0·25M of the salt added) had little effect on the course of the pH titration, and the addition of sodium sulphate (0·25M) led to a markedly smaller release of hydrogen ions throughout the titration. In all the indium salt titrations, however, the rapid increase in hydrogen-ion concentration during the titration, compared with the increase obtained in the titration of potassium sulphate [3] which forms complexes to no significant extent, does indicate that complex-forming reactions of the type:

FIG. 3. *Titration of (a) indium nitrate and (b) indium chloride solution with phosphoric acid.*



1, *No added salt.* 2, $NaNO_3$ *added.* 3, NaCl *added.* 4, Na_2SO_4 *added.*

$$In^{3+} + H_3PO_4 \rightleftharpoons InHPO_4^{+} + 2H^{+}$$

take place during the titration. It was found that the extent to which hydrogen ions were liberated during the titration was subject, in some measure, to the previous history of the indium chloride solution, the ageing effects reported in the cation-exchange experiments being evident also in the pH titrations.

Removal of Indium from Cation-exchanger in the Indium Form.—The amounts of indium removed from the cation-exchanger by the various acids indicate the tendency for the reaction:

$$\overline{In}^{3+} + 3H^{+} \rightleftharpoons In^{3+} + 3\overline{H}^{+}$$

(Bars indicate that these ions are in the resin phase.)

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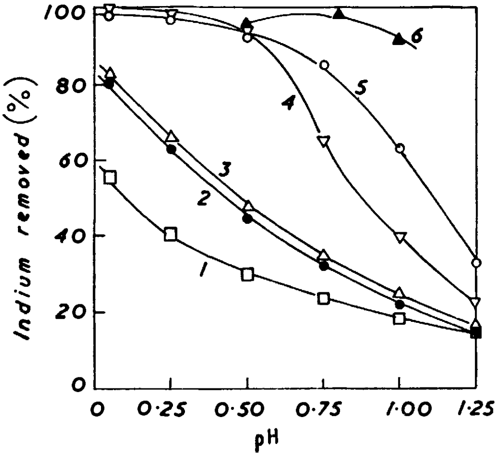
[8] Salmon and Wall, *J.*, 1958, 1128.

to proceed from left to right. Any complex formation in solution will disturb the above equilibrium, with the result that more metal will be removed from the exchange-resin.[8] The amounts of indium removed by hydrofluoric, phosphoric, hydrochloric, sulphuric, nitric, and perchloric acid (Fig. 4) indicate that complex-formation with indium decreases in that order.

Other evidence for the formation of halide complexes of indium has been provided by various workers,[9] indicating that the order of decreasing stability of the complexes is $F > Cl > Br > I$ [9a, b] in accord with the present observation for fluoride and chloride.

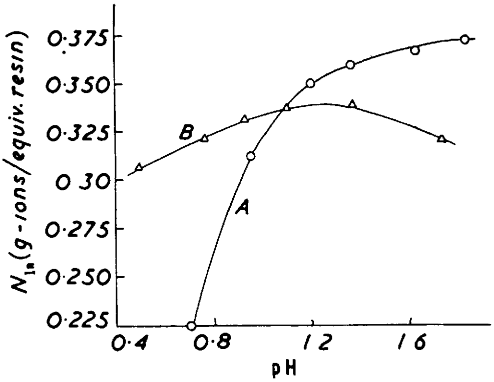
Cation-exchange Experiments with Solutions of Indium Salts.—Experiments were performed to determine the quantity of indium sorbed on the hydrogen form of the cation-exchanger over the pH range 0·5—2·1. Sorption of indium from both indium chloride and indium nitrate solutions has been shown (Fig. 5) to increase with pH, but in different ways for the two anions. The factors most likely to affect this sorption are: (1) hydrolysis of the indium cation, (2) competitive sorption of hydrogen ions, and (3) auto-complex formation. The first of these factors, if it led to the sorption of species of lower ionic charge, such as $In(OH)aq^{2+}$ or $In(OH)_2aq^{+}$, could result in the sorption of more than the 0·33 g.-ion of indium per equiv. of resin that would be expected for the tervalent cation. In fact, the sorption of indium rose only a little above the value of 0·33 g.-ion per equiv.

FIG. 4. *Removal of indium from* Zeo-Karb 225.



1, $HClO_4$. 2, HNO_3. 3, H_2SO_4. 4, HCl. 5, H_3PO_4. 6, HF.

FIG. 5. *Sorption of indium by Zeo-Karb* 225.



A, Indium chloride. *B, Indium nitrate.*

Moeller[10] showed that indium hydroxide was precipitated from sulphate and nitrate solutions when the hydroxide to indium ratio became 0·84 : 1·0 and from chloride solutions when the ratio became only 0·02 : 1·0. It therefore might seem that $In(OH)aq^{2+}$ and $In(OH)_2aq^{+}$ ions are present only to a very small extent in solution and that precipitation of hydroxylated species takes precedence over their formation in solution.

The presence of ions of the type $In[(OH)_2In]_n^{(3+n)+}$, as suggested by Biedermann,[11] with a limiting value for the charge to metal ratio of unity, should result, however, in the sorption of indium on the exchange-resin to the extent of 1·0 g.-ion per equivalent. Such species, however, may have been excluded from the resin because their ionic size is too great to allow the ion to penetrate the resin network.

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[9] (*a*) Carleson and Irving, *J.*, 1954, 4390; (*b*) Schufle and Eiland, *J. Amer. Chem. Soc.*, 1954, **76**, 960; (*c*) Roberts and Laubengayer, *ibid.*, 1957, **79**, 5895; (*d*) Sundén, *Svensk Kem. Tidskr.*, 1954, **66**, 50, 173.

[10] Moeller, *J. Amer. Chem. Soc.*, 1941, **63**, 2625.

[11] Biedermann, *Arkiv Kemi*, 1956, **9**, 277.

At the lower end of the pH range (Fig. 5) the sorption of less than 0·33 g.-ion per equivalent could be due to the second of the factors listed, and in the case of indium nitrate the decrease in sorption of indium at low pH values is probably due mainly to this cause.

Auto-complex-formation which, from the ion-exchange experiments with indium-form resin reported above, should be greater with the chloride than the nitrate system, could cause an increased sorption as $InClaq^{2+}$ or $InCl_2aq^+$, or decreased sorption as reported here, if present in solution as $InCl_3aq^0$ or $InCl_4aq^-$.

Cation-exchange Experiments with Solutions of Indium Salts and Phosphoric Acid.—With both indium chloride and indium nitrate solutions, the addition of phosphoric acid caused an enhanced sorption of indium and also appreciable sorption of phosphate on the cation-exchange resin. This indicated the presence of cationic indium phosphate complexes in the solutions. Tests showed the absence on the resin of chloride and nitrate anions. As with the other tervalent metal phosphate systems no indium was sorbed, from similar solutions, on an anion-exchange resin, thus indicating the absence of anionic indium complexes in the solutions. If the indium chloride solution was first stored for some time there was found to be a consistent and significant fall in the quantity of phosphate sorbed although the enhanced sorption of indium remained essentially constant (Table 3).

TABLE 3. *Sorption of indium and phosphate by Zeo-Karb* 225-H (0·5 *g.*) *from mixtures* (50 *ml.*) *of phosphoric acid* (0·3M) *and indium chloride* * *or indium nitrate* * *solutions* (0·1M).

	Solution		Resin Moles per equiv. resin			
	$\frac{PO_4}{In}$	pH	In	PO_4	*p*	*q*
Indium chloride solution freshly prepared ...	0	1·36	0·358	—	2·79	—
	0·33	1·23	0·405	0·052	—	2·52
	0·73	1·14	0·414	0·067	—	2·31
	1·26	1·10	0·408	0·079	—	1·75
	1·95	1·06	0·400	0·070	—	1·67
Indium chloride solution of age 6 weeks	0	1·36	0·354	—	2·82	—
	0·33	1·23	0·405	0·033	—	4·28
	0·73	1·15	0·409	0·045	—	3·42
	1·26	1·11	0·407	0·043	—	3·47
	1·95	1·07	0·395	0·039	—	2·91
Indium chloride solution freshly prepared ...	0	1·16	0·336	—	2·98	—
	0·36	1·09	0·347	0·026	—	1·19
	0·80	1·04	0·348	0·046	—	0·73
	1·37	1·02	0·354	0·050	—	1·04
	2·12	0·99	0·366	0·050	—	1·75
	3·19	0·98	0·345	0·058	—	0·43
	4·79	1·00	0·344	0·050	—	0·44
Indium chloride solution of age 4 weeks	0	1·16	0·329	—	3·04	—
	0·72	1·12	0·358	0·014	—	6·18
	1·06	1·10	0·358	0·021	—	4·21
	1·72	1·07	0·365	0·026	—	4·24
	2·61	1·05	0·360	0·016	—	5·79
	3·89	1·05	0·357	0·012	—	6·88
Indium nitrate solution of age 7 weeks	0	1·29	0·354	—	2·83	—
	0·33	1·04	0·449	0·072	—	3·78
	0·75	0·96	0·469	0·122	—	2·69
	1·28	0·96	0·467	0·094	—	3·43
	1·99	0·96	0·458	0·090	—	3·30

* pH of the solutions adjusted at time of preparation by addition of the appropriate amounts of hydrochloric or nitric acids.

By following the procedure previously adopted,[8,12] if the phosphate and indium sorbed (designated as $N_{\text{phosphate}}$ and N_{In} moles per equivalent of resin) are attributed to the sorption

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[12] Holroyd and Salmon, *J.*, 1957, 959.

of complex [*e.g.*, $In_vH_w(OH)_y(PO_4)_z{}^{x+}$] and " free " ions [*e.g.*, In $aq.^{3+}$ plus $In(OH)_n{}^{(3-n)+}$, etc.], it can be shown that

$$pN_{In} - qN_{phosphate} = 1$$

where p = the mean charge of the free-metal ions, and $q = (pv - x)/z$, whence $q = (pN_{In} - 1)/N_{phosphate}$. The value of p at any given pH is given by the reciprocal of the moles of indium sorbed per equivalent of resin (Fig. 5). Now the value of p used in the determination of q can be that of the original nitrate or chloride solution, as is the case in Table 3, or adjusted to allow for change in pH with the various amounts of phosphate added. However, in view of the very low values of $N_{phosphate}$ the value of q is much more sensitive to changes in $N_{phosphate}$ than to changes in p. Hence only one set of values for q is recorded.

It can be seen from Table 3 that values for q of the order of 1—2 are generally observed with freshly prepared solutions. These would be consistent with the sorption of species such as $InHPO_4{}^+$ ($q = 2$ for $p = 3$) and $InH_2PO_4{}^{2+}$ ($q = 1$ for $p = 3$). The higher values of q observed with aged indium phosphate solutions indicate that in such solutions, species such as $In_2(OH)_2{}^{4+}$ (formed by dimerisation and similar reactions) are reacting to form species such as $In_2(PO_4)(OH)^{2+}$ ($q = 4$ for $p = 3$) (cf. ref. 10). If either class of solution is set aside for a few weeks precipitation occurs, so that the true state of equilibrium for this system cannot be ascertained. No previous references to this ageing phenomenon in indium chloride solutions could be found in the literature. It may be noted that reactions of the type $2In(OH)^{2+} \longrightarrow In_2(OH)_2{}^{4+}$ would not affect the value of p, which, significantly, did not vary with time. It is not possible, however, to deduce the precise nature of the polymeric species from the present data.

Anion-exchange Experiments with Solutions of Indium Phosphate in Phosphoric Acid.—The sorption of indium and phosphate on samples of anion-exchange resin in the phosphate form from solutions of indium phosphate in phosphoric acid demonstrates the presence in solution of anionic indium phosphate complexes (Table 4). As with other tervalent metal phosphate systems, no phosphate was found to be sorbed from such solutions on a cation-exchanger, indicating that no complex indium phosphate cations were present in the solutions examined.

TABLE 4. *Anion-exchange experiments with solutions of indium phosphate in phosphoric acid.*

Solution (50 ml.)		Resin (1·0 g.) Moles sorbed per equiv. resin		
In_2O_3 (%)	P_2O_5 (%)	In	PO_4	Capacity †
0·5	10·0	0·120	0·719	101
1·5	20·0	0·079	0·693	100
2·5	30·0	0·049	0·675	99

† Percentage capacity of the resin accounted for by assuming sorption of the complex C = $[InH_2(PO_4)_3]^{4-}$ together with $H_2PO_4{}^-$ and $HPO_4{}^{2-}$ (in equal proportions).

Sorption of the following possible anionic indium phosphate complexes was considered: A = $[In(PO_4)_3]^{6-}$, B = $[InH_3(PO_4)_3]^{3-}$, C = $[InH_2(PO_4)_3]^{4-}$, D = $[In(PO_4)_2]^{3-}$, E = $[InH(PO_4)_2]^{2-}$, F = $[InH_2(PO_4)_2]^-$, G = $[InH_8(PO_4)_4]^-$, H = $[InH_4(PO_4)_4]^{5-}$, I = $[InH_3(PO_4)_4]^{6-}$, but the percentage capacity of the resin approached 100 only in the case of complex C. Hence, if one complex alone is sorbed, together with free phosphate, then it is most likely to be $[InH_2(PO_4)_3]^{4-}$.

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