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**Critical Evaluation of Equilibrium Constants in Solution
Part A: Stability Constants of Metal Complexes**

**CRITICAL SURVEY OF STABILITY
CONSTANTS OF COMPLEXES OF
INDIUM**

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CRITICAL SURVEY OF STABILITY CONSTANTS OF COMPLEXES OF INDIUM

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I. INTRODUCTION

In the introduction to this series of IUPAC review articles, Beck (75B) has identified some of the problems involved in the measurement and critical evaluation of stability constants. Many of the difficulties which Beck discusses clearly apply in the case of complexes of indium, and in particular, the failure of 'constants' which nominally describe a given system to agree within reasonable limits is readily apparent on examination of the standard compilations of such data (64S, 71Sa). A critical review of this information, and that which has been published since the appearance of these standard references, is therefore appropriate.

It may well be that the easy availability of a useful radioactive tracer [$^{114\text{m}}\text{In}$, $t_{1/2}$ 50d, from (n, γ) on indium metal] provoked many of the studies of stability constants of indium complexes by ion exchange and solvent extraction methods. Equally, the use of the metal as a working electrode has led to a number of electrochemical investigations of complex formation. Whatever the reasons, a large number of stability constants of indium complexes has been reported, especially in the period 1950-1975, but unfortunately these results did not lead to any clear understanding of the solution chemistry of the element, even in such apparently uncomplicated systems as In/Cl (see (77J)). It therefore seems reasonable to discuss the reported stability constants in terms of the structural information which is available on those species which exist, or have been postulated to exist, in aqueous solution, and to examine the measure of agreement between these differing approaches to the chemistry of the element. A general comment which can be made at the outset is that despite the implicit chemical information contained in a given stability constant, few authors have discussed their results in the context of the overall chemistry of the element, and it is equally true that stability constant measurements have contributed little to our knowledge of the coordination chemistry of indium in solution.

The material in this review is organised into a series of discussions by ligand, or groups of ligands, and individual or collective results are evaluated in terms of the criteria laid down by the I.U.P.A.C. Commission on Equilibrium Data. Wherever possible, a brief structural introduction serves to establish a point of departure. Thus a survey of studies of cationic $\text{In}^{3+}(\text{aq})$ leads to a discussion of the crucial matter of hydrolysis: inorganic ligands (halide, pseudohalide, oxyanion) are then considered: and

carboxylic acids, monobasic chelating agents, and various polydentate organic ligands, complete the review. The information is essentially restricted to complexes of indium(III), since only sparse information is available on the aqueous solution chemistry of indium(I) and (II), despite the increased interest in these oxidation states in recent years (75C).

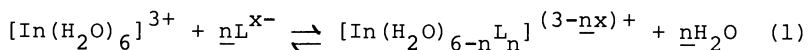
The general chemistry of indium is dealt with in various standard texts, and a number of reviews have appeared in recent years (73W, 75C, 75P, 75T). The electrochemistry of the element has been discussed by Losev and Molodov (76L).

II. NEUTRAL CATIONIC SPECIES

II. 1. The In^{3+} (aq) cation

There is now an overwhelming accumulation of evidence that the indium species in non-complexing aqueous solutions (e.g. aqueous perchloric acid) is $[\text{In}(\text{H}_2\text{O})_6]^{3+}$. Firstly, there is extensive preparative evidence on the existence of InL_6^{3+} cations, where L is some monodentate oxygen donor ligand (64C, 75C). Secondly, n.m.r. studies (both ^1H and ^{115}In) of indium(III) perchlorate in aqueous solution (66C, 68Fa) have identified the predominant species as $[\text{In}(\text{H}_2\text{O})_6]^{3+}$, and this conclusion has been confirmed independently by dilatometric measurements of ionic volumes (74Ca), and more recently by X-ray diffraction methods (77M). Rapid exchange between bound water and the bulk phase has also been demonstrated (68Gb). Finally, with acetone/water (71F), and with trimethyl phosphate (TMP), TMP/water, TMP/acetone, and TMP/water/acetone (72C), one finds $[\text{In}(\text{H}_2\text{O})_6]^{3+}$, $[\text{In}(\text{TMP})_6]^{3+}$, or mixed hexa-coordinate cationic species. A similar conclusion has been reported for solutions in N,N'-dimethylformamide and DMF/ H_2O , and confirmed preparatively (65Ga).

The formation of complexes of indium(III) under conditions in which hydrolysis has been completely suppressed (see below) must therefore be via equilibria of the general form



implying that the substituted products also involve six-coordinate indium. While accepting that this statement is indeed valid for the great majority of systems, it must also be emphasised that four- and five-coordination is well established in the chemistry of indium (III), especially with ligands which are 'soft' and/or stereochemically demanding (75C), so that there may well be ligands for which specific values of \underline{n} in eq. (1) will involve changes in coordination number, in particular by the elimination of water molecules. We return to this matter below in the context of indium (III)-halide complexes.

II. 2. Cationic complexes with ligands

The cation $[\text{In}(\text{NH}_3)_6]^{3+}$ which has been identified in liquid ammonia solution (76G), is clearly analogous to $[\text{In}(\text{H}_2\text{O})_6]^{3+}$, and a large number of related cationic complexes is known (75C). Few stability constant measurements have been reported. McBryde (78M) has critically reviewed the results for the

2,2'-bipyridine (bipy) and 1,10-phenanthroline complexes of a large number of elements. For indium, the values given are:

1,10-phenanthroline

	log K_1	log K_2	log K_3	Ref.
1M NaNO ₃ , 25°C	5.51	4.59	4.40	(71Ka)
1M K ₂ SO ₄	5.70	4.34	3.96	(72K)

2,2'-bipyridine

1M NaNO ₃	3.45	4.61	-	(71Ka)
1M K ₂ SO ₄	4.75	3.25	-	(72K)

For the bipy experiments, agreement between the two series of measurements is lacking, and in one case $K_2 > K_1$. McBryde also quotes results for In(III)/bipy in 50% aqueous ethanol (25°C, 1.0M electrolyte), for which $\log K_1 = 4.18$. All of these results are rated as doubtful. A similar rating is given by the present author to values for 2,3-dihydroxypyridine, 2-amino- and 2-thiol-3-hydroxy-pyridine, for which β_1 and β_2 have been determined polarographically (77S). A related polarographic study (78T) of thiourea complexation yielded a tentative value of $\log K_1 = 1.97 \pm 0.07$ ($I = 0.5(\text{NaClO}_4)$, $T = 25^\circ\text{C}$), said to be in agreement with unpublished measurements (75Kc) based on distribution experiments. These few results emphasise the need for reliable values for simple cationic indium (III) complexes, and for some thermochemical information.

III. HYDROLYSIS OF In^{3+} (aq) AND RELATED TOPICS

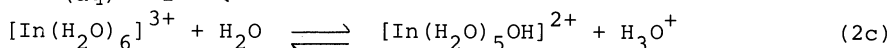
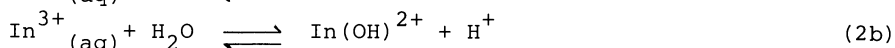
III. 1. Introduction

The pH range in which the solution chemistry of indium (III) can be studied is defined in practice by the onset of hydrolysis, since it is common experience that increasing alkalinity results in the formation of hydroxy complexes. Precipitation eventually occurs, unless the formation of soluble complexes with other ligands predominates, and here one immediately encounters an important experimental fact established by early work (41Mb), namely that precipitation takes place well before the $[\text{OH}^-]:[\text{In}^{3+}]$ ratio reaches 3.0. It has also been reported that the kinetics of the redissolution of metastable precipitates and polynuclear complexes are complex (67P). In general then it is crucial in quantitative studies of indium (III) solution chemistry to ensure that all polymeric species have been completely destroyed before proceeding to other work.

The present section attempts to establish reliable thermodynamic results for the range of possible $\text{In}^{3+}/\text{OH}^-$ species, recognising that a proper accounting of the formation of such complexes is a sine qua non in the measurement of other stability constants, as has been demonstrated in the case of In^{3+} /halide complexes (67L). The whole field of cation hydrolysis of indium (and other elements) has been extensively reviewed by Baes and Mesmer (76B), who have recalculated certain of the literature results.

III. 2. Hydrolysis constants for In^{3+} (aq)

The hydrolysis of the In^{3+} (aq) ion can be represented by one of the related equations:



where all species are aquated. Electrode kinetics have demonstrated that dissociation, not substitution, is involved in the hydrolysis (67L), so that we shall discuss the processes in terms of equations

such as (2b) with
$$^*\beta_{1,n} = \frac{[\text{In}(\text{OH})_n^{(3-n)+}] [\text{H}^+]^n}{[\text{In}^{3+}]}$$
. In view of the

relationship
$$^*\beta_{1,n} = ^*\beta_{1,n} \cdot K_w^n$$
, the assumed value of K_w is noted in Table 1.

The earliest measurements of $^*K_{1,1}$ refer to uncertain standard states (36H, 41Ma, 42M), and take no account of competing equilibria (but see (52H)). The careful emf work of Biedermann (56B, 56Ba) gave a value subsequently confirmed in the same laboratory by solvent extraction studies (72Fa), despite detailed differences in the relevant aqueous phases. The series of measurements by Kul'ba and co-workers (74Kb, 75Ka, 75Kb) refer to 3M LiClO_4 solution, and therefore do not provide confirmation of the type necessary in recommending a value for $^*K_{1,1}$. The tentative values are:

$$-\log ^*K_{1,1} (3M \text{ NaClO}_4) = 4.42 \pm 0.05$$

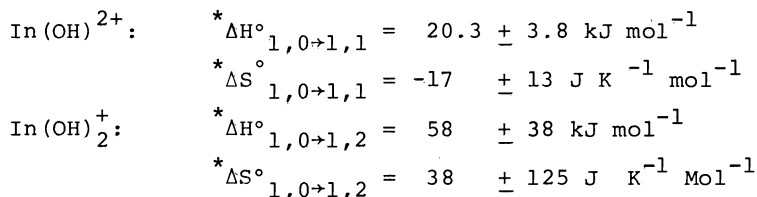
$$-\log ^*K_{1,1} (3M \text{ LiClO}_4) = 4.25 \pm 0.04$$

Later work employing electrochemical cells similar to those used by Kul'ba et al. gave results for $\log K_{1,1}^*$ over the range 0 - 1.0M LiClO_4 in good agreement with the earlier results, and the values (81Y; Table 1) are also tentatively accepted. The hydroxide stability constants $\log K_{1,1}$ corresponding to the above values are 9.80 and 9.97 ($\log K_w = -14.22$).

Of the other results recorded in Table 1, the value derived from Biedermann's results by an unspecified least squares treatment (76B) is in good agreement with the tentative values above, but the results of the extraction studies of Aziz and Lyle (69A) differ by an amount which exceeds the sum of the reported errors. The results in 65H appear to contain a serious error. It is unfortunate that the studies of the effect of variation of ionic strength (69B) agree so poorly with other similar results (e.g. 81Y), not only because of the intrinsic interest of such work, but also because only these papers and ref. 65H quote values for the constants beyond $^*K_{1,1}$. It may be that the formation of $\text{In}(\text{OH})_n$ species was not the only set of acid dependent equilibria in the experimental solutions used in this work (69B); for example, deprotonation of the competing alizarin-3-sulphonic acid beyond the assumed HL^- anion may also have been significant (cf. section IX).

The range of values reported for $K_{1,2}^*$ is such as to raise doubts about the correct identification of the processes being studied. The two sets of solvent extraction experiments agree closely in this respect, but differ from other work, and the agreement for $K_{1,1}^*$ between NaClO_4 and LiClO_4 solutions breaks down completely for $K_{1,2}^*$. The two sets of studies with LiClO_4 solution are again in good agreement, but further work is required; at present, $-\log K_{1,2}^* = 2.9 \pm 0.1$ can be used for 3M LiClO_4 , but must be regarded as doubtful (but see ref. 76B). A value of $\log \beta_{1,3}^* = -12.4$ has been derived by Baes and Mesmer (76B) from the low solubility of $\text{In}(\text{OH})_3$ in nearly neutral solution ($4.8 \times 10^{-5} \text{ mol l}^{-1}$ at pH 7.22). The results in Table 1 suggest that $K_{1,1}^* \approx K_{1,2}^* \approx K_{1,3}^*$, which therefore implies that $\log \beta_{1,3}^* \approx -12$, in reasonable agreement with the derived result, but such arguments do not lead to any reliable numerical value for $K_{1,3}^*$ at the present time.

Finally we note that Schlyter (61S) has measured ΔH° and ΔS° for the formation of $\text{In}^{3+}/\text{OH}^-$ complexes in 3M NaClO_4 at 25°C, relying upon Biedermann's values for $K_{1,1}^*$ etc. in interpreting his results. The enthalpy values are of poor accuracy because of the low concentrations of the species involved:



The nature of the experimental method renders these results of inherently doubtful value.

III. 3. Hydrolysis in mixed aqueous — non-aqueous media

Russian workers have reported some interesting measurements of $K_{1,1}^*$ and $K_{1,2}^*$ in the systems water/dimethylsulphoxide (74Kb, 81Y), water/dimethylformamide (74Kb), water/acetone (75Kb) water/acetonitrile (75Ka) and water/1,4-dioxane (81Y). With acetone and acetonitrile, hydrolysis increases with increasing mole fraction of organic solvent, whereas with dimethylsulphoxide the reverse is observed. These results have been qualitatively explained in terms of changing dielectric constant, increasing proton affinity of the bulk phase, and the formation of $[\text{In}(\text{H}_2\text{O})_{6-n}\text{L}_n]^{3+}$ species. A detailed analysis of the results would be valuable, especially since these effects may be important in aqueous systems in terms of ionic strength changes and the like.

III. 4. The solubility product of $\text{In}(\text{OH})_3$

The hydrolysis of $\text{In}^{3+}(\text{aq})$ leads eventually to the precipitation of $\text{In}(\text{OH})_3$ (but see III. 6. below), and the existence of this compound, rather than a hydrated oxide, has been confirmed (37M). Measurements of the solubility product of $\text{In}(\text{OH})_3$ have been reviewed by Feitknecht and Schindler (63F), who emphasise the difficulty of establishing reliable values for such constants.

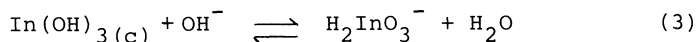
TABLE 1. Hydrolysis constants for the In^{3+} (aq) ion.

Method	Medium (concn. M)	T (°C)	$K_{1,1}^*$	$K_{1,2}^*$	$K_{1,3}^*$	Comments	Ref.
pH titration	Various concns. of $\text{In}_2(\text{SO}_4)_3$	23	3.7			No allowance for $\text{In}/\text{SO}_4^{2-}$ complexing	36H
pH titration	Various concns. of InCl_3 , InBr_3 or InI_3	25	3.85			Recalcn. allows for In^{3+} complexing with Cl^- , Br^- , I^- . recalc. $\log^* K$ is unweighted average (52H).	41Ma, 42M by 52H
pH titration, In by emf	3.0 NaClO_4	25	4.42±0.05	3.9±0.2		pH range 1.91 - 3.86 Lower values for $K_{1,1}^*$ (4.25) recalc. by (76B). Results later confirmed (72Fa).	56B, 56Ba
pH titration, In by extraction	3.0 NaClO_4 in equil. with TTA in benzene	25	4.4±0.1	4.4±0.3		pH range 2.7 - 4.5 ($\log K_w = -14.22$)	56R
emf	3 NaCl	25	6.95±0.1			pH range 4.20 - 5.40	61B
In by extraction	I = 1? in equil. with BHPA in C_6H_6 or toluene	20	2.11	2.45	2.68	pH range 2 - 3.5	65H
H^+ by emf, In by extraction	3.0 NaClO_4 in equil. with DEHP in toluene	25	4.63±0.05	4.38±0.05		pH range 3.25 - 4.75 ($\log K_w = -14.22$)	69A
In by spectroscopy	NaClO_4 :I = 0 0.1 0.3 0.5 1.0	25	3.54 3.48 3.40 3.33 3.11	4.28 4.19 4.01 3.92 3.54	5.16 5.08 4.96 4.85 4.48	pH range 4.6 - 5.6 ($\log K_w = -14.0$) no error limits quoted. Values at I = 0 by extrapolation by authors	69B
pH titration	3.0 LiClO_4	25	4.22±0.04	2.92±0.05		pH range 0.5 - 4.0 K_w not quoted	74Kb
pH titration, In by emf	3.0 LiClO_4	25	4.22±0.04 4.26±0.04	2.92±0.05 2.84±0.05		-results from $[\text{H}^+]$ expts. -results from In expts. K_w not quoted.	75Ka
pH titration	3.0 LiClO_4	25	4.26±0.02			pH range 0.6 - 2.2 K_w not quoted.	75b
emf	LiClO_4 :I = 0 0.1 0.3 1.0	25 25 25 25	3.66±0.06 4.00±0.04 4.04±0.04 4.15±0.04	2.40±0.08 2.79±0.05 2.77±0.05 2.83±0.05		K_w not quoted Values at I = 0 by extrapolation by authors	81Y

The early workers reported values for $\log K_{sp}$ at 25°C of -33.2 (380) and -33.1 (41Mb) based on pH measurements alone. Moeller (41Mb) also demonstrated that K_{sp} is temperature dependent, but the relevant numerical values cannot be regarded as reliable, at least in part because no account was taken of complex formation with the balancing anion (chloride, sulphate). The importance of establishing that equilibrium has actually been reached was demonstrated by Aksel'rud and Spivakovskii (59A), who showed that the value of K_{sp} obtained after 76 days aging is significantly different from that after only 1 day. Their value for K_{sp} is $\log K_{sp} = -36.92 \pm 0.1$ (tentative), but independent confirmation of this result would be welcome. The value reported by Kovalenko (61Ka), $\log K_{sp} = -32.85$, obviously suffers from the fact that only 1 h was allowed for equilibration, and should be rejected.

III. 5. Anionic hydroxo complexes of indium(III)

A small number of papers bear upon the existence in aqueous solution on mono-nuclear complexes of the type $[\text{In}(\text{OH})_n]^{(n-3)-}$ ($n > 3$), which should be structurally related to $\text{InF}_n^{(n-3)-}$ and similar anions. The lack of even qualitative agreement is the first point to strike the reviewer. Both Lacroix (49L) and Deichman (58D) claim that $\text{In}(\text{OH})_3$ does not undergo further reaction with aqueous caustic soda to yield either soluble or insoluble indates, whereas Thompson and Dacer (63T) reported a measurable solubility in the range 0.76 - 6.03 M NaOH, and derived constants for an equilibrium which they write as



but which could equally well involve $[\text{In}(\text{OH})_4]^-$, $[\text{In}(\text{OH})_4(\text{H}_2\text{O})_2]^-$ etc., as the solution species. From their experimental result, $\log \{[\text{H}_2\text{InO}_3^-]/a_{\text{OH}^-}\} = -3.0 \pm 0.5$ at 25°C, it has been estimated that $\log^* \beta_{1,4} = -22.07 \pm 0.1$ ($\log K_w = -14.0$). Aksel'rud (60A) has concluded from mass-action arguments, that $[\text{In}(\text{OH})_4]^-$ is indeed formed in such solutions, and has used earlier experimental results (56A, 58A) to derive $\log \beta_{1,4} = 35.23$, or $\log^* \beta_{1,4} = -20.8$ ($\log K_w = -14.0$).

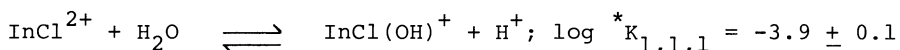
Unfortunately even this measure of agreement is called into question by the work of Ivanov-Emin et al. (60Ia), who find that the solubility of $\text{In}(\text{OH})_3$ in aqueous NaOH (1-17 M) goes through a sharp maximum at 11.33 M, a concentration higher than that reached in any of the experiments just discussed. It is further claimed that the solid in equilibrium with these solutions is $\text{In}(\text{OH})_3$ below this maximum, but hydrated $\text{Na}_3[\text{In}(\text{OH})_6]$ above it. None of the papers quoted apparently takes account of the aging of precipitates (cf. (59A) or of possible peptisation (cf. (41Mb)).

In the circumstances, no value can be recommended for $\log^* \beta_{1,4}$. This whole topic of anionic hydroxo complexes of indium (III) could benefit from combined thermodynamic, preparative and structural studies.

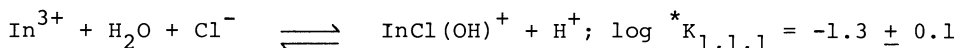
III. 6. Mixed hydroxo-halogeno compounds

The formation of mixed In/OH/L complexes is always a potential problem in both quantitative and preparative work. A number of mixed hydroxo/anion complexes have been identified in the solid state (41Mb, 49L, 60A, 67P, 68Db). In particular, basic chlorides are said to be formed during the addition of NaOH to aqueous InCl₃ solution, including In(OH)_{2.8}Cl_{0.2} (57D, 59A), In(OH)_{1.5}Cl_{1.5} and In(OH)_{1.75}Cl_{1.75} (59A); log K_{sp} for In(OH)_{1.5}Cl_{1.5} = -22.38 at I → O (doubtful, since no error limits given).

Some quantitative results are available on the information of In/OH/Cl solution species. Biedermann, Li and Yu (61B) concluded that in chloride media, the formula 'InOH²⁺' actually represents mixed In/ClOH species, although the difference in their *K_{1,1} for 3M NaCl and that for 3M NaClO₄ hardly seems explicable in such terms, or in changes in the medium. On the evidence from higher species, [In(OH)Cl]⁺ is the more convincing (see (76B)). Ferri (72Fa) gave results (25 C) for



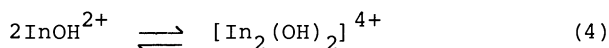
or



(tentative), using K_{1,1} for InCl⁺ = 2.8 (see below). The agreement between *K_{1,1,1} and *K_{1,2} implies that the dissociation of XIn(OH)₂²⁺ → XInOH⁺ is independent of the nature of X, within the limits of the data. This is not surprising, given that K (i.e., ΔG) for any system involves an important common term for the formation of H₃O⁺, but nevertheless further results on this matter would be welcome.

III. 7. Polymeric indium(III)-hydroxo complexes

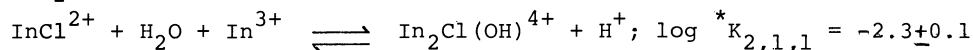
The detailed nature of the processes which intervene between the formation of [In(H₂O)₅OH]²⁺ and the precipitation of In(OH)₃ is largely unestablished. Eyring and Owen (70Ea) have studied the fast forward reaction in



identifying the rate-determining step as the loss of a water molecule from the coordination shell of one InOH²⁺ ion. Biedermann (56B, 56Ba) explained his thermodynamic results in terms of further core-linked species

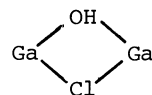
[In₂(OH)₂]⁴⁺, [In₃(OH)₄]⁵⁺, [In_{n+1}(OH)_{2n}]⁽ⁿ⁺¹⁾⁺, with *log β_{n+1,2n} = -0.52 - 4.69_n + 0.04_n (doubtful) (but see 76B). A later result (61B), log *β_{2,2} = -10.1 ± 0.1, is in reasonable agreement with the more generalized formula.

Questions as to the number of polymeric species which exist in significant concentrations and their relative importance find no satisfactory answer at present, and a similar comment applies to the matter of mixed polynuclear complexes. A tentative constant (72Fa) applies to the formation of [In₂(OH)Cl]⁴⁺;



The existence of such species is strongly supported by the crystal structure

identification of a gallium hydrolysis product containing the



unit (72D). Any discussion of formation constants for higher species is clearly not justified given our present knowledge.

III. 8. Sulphide species

The solubility product of In_2S_3 ($I = 1M \text{ NaClO}_4$, $T = 20^\circ\text{C}$) is

$$\log K_{\text{sp}} = -77.4 \pm 2.4$$

and the formation constants for the complexes $\text{In}(\text{SH})^{2+}$ and $[\text{In}(\text{SH})_2]^+$ are

$$\log K_{1,1} = 10.5 \pm 1.3$$

$$\log K_{1,2} = 6.6 \pm 0.1$$

(all doubtful) (70Tb). An earlier report ($\log K_{\text{sp}} = -73.24$, $I \rightarrow 0$, $T = 25^\circ\text{C}$) (62T) has been criticized (70Tb). Further work in this area is required.

IV. HALIDE AND PSEUDOHALIDE COMPLEXES

IV. 1. Structural information

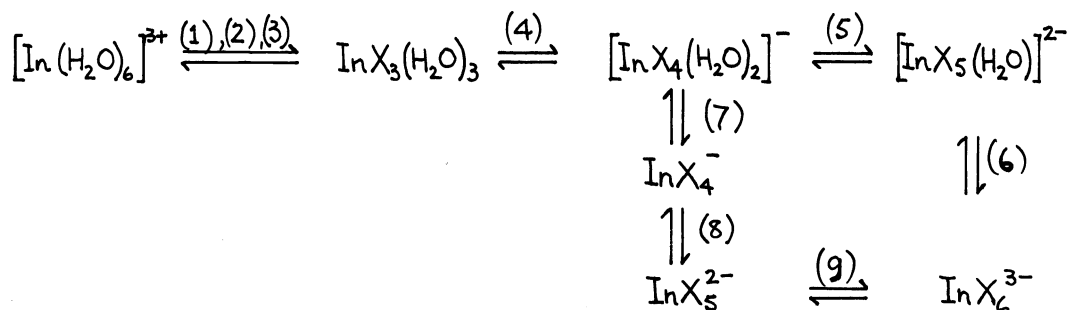
The matter of the species which can exist in aqueous solutions containing indium(III) and halide anion has provoked such debate that a review of the species known to be stable in the solid state seems an appropriate starting point for our discussion. In adopting this approach, one must emphasize that the existence of a specific complex in the crystalline state is in itself no proof of the stability of that same species in aqueous solution, given the very different nature of the energy factors involved in the two phases. On the other hand, an understanding of those species which can exist is at least a reasonable basis from which to examine the evidence as to those which are claimed to do so.

There appear to be no X-ray structural determinations on monosubstituted cations $[\text{In}(\text{H}_2\text{O})_5\text{X}]^{2+}$, nor of $[\text{In}(\text{H}_2\text{O})_4\text{X}_2]^+$, but complexes related to the latter, namely $[\text{InCl}_2(\text{bipy})_2]^+$ (and other bidentate ligands) (48S, 69W, 78C) and $[\text{InI}_2(\text{dmsO})_4]^+$ (70E) have been identified. A large number of InX_3L_3 complexes have been reported (75C), and in particular the crystal structure of $\text{InCl}_3(\text{H}_2\text{O})_3$ has been elucidated (75W), as has that of $\text{InF}_3(\text{H}_2\text{O})_3$ (66Ha); both are six-coordinate monomers. Thus far no difficulties arise, but for anionic complexes the information is less complete, and in particular the question of the coordination number at indium remains difficult. Fluoride complexes are known to include InF_6^{3-} (70S), in which indium is six-coordinate, and the hydrated salts $\text{MInF}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MInF}_5 \cdot \text{H}_2\text{O}$ may well contain aquo-fluoro anionic complexes. For chloride, six-coordination has been unambiguously characterized in the anions $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ (75Z), $[\text{InCl}_5(\text{H}_2\text{O})]^{2-}$ (48K), and InCl_6^{3-} (72 Sd, 760, 77C), thus confirming earlier preparative and spectroscopic studies (64T, 71G). At the same time, anhydrous InCl_4^- (tetrahedral) and InCl_5^{2-} (square-based pyramidal) (69Ba) are also known, both in the solid state (69Ba, 69T) and in non-aqueous solution (60Wa, 68Wa). With bromide as ligand, only InBr_4^- and InBr_6^{3-} have been identified both

spectroscopically (55W, 71G) and crystallographically (81K, 82K) but neither InBr_5^{2-} nor substituted species are known at present. The only anionic iodo-complex unambiguously identified in either solid state or non-aqueous solution is InI_4^- (58W, 70E, 75C). Mixed halogeno complexes $\text{InX}_n\text{Y}_{4-n}^-$ are also known (80D, 80M, 82K).

No information appears to be available on cationic or neutral aquo-pseudo-halide complexes, although InX_3L_3 adducts are known for $-\text{NCS}$ and $-\text{NCO}$ with organic donors. The anions $[\text{In}(\text{NCS})_5]^{2-}$ and $[\text{In}(\text{NCS})_6]^{3-}$ have been prepared, and X-ray crystallography has confirmed that the latter involves six-coordinate indium(III) and N-bonded ligands (75C). The species $[\text{In}(\text{NCS})_6]^{3-}$, $[\text{In}(\text{NCO})_4]^-$ and $[\text{In}(\text{CN})_4]^-$ have also been reported, but structural information on these is lacking. In general, chemical evidence suggest that pseudohalide systems are qualitatively very similar to the chloride analogues.

The solution equilibria which must be postulated if all species are to be included are



SCHEME 1

There can be little doubt as to the reality of equilibria (1)-(3) (77J), but the relative concentration of the two tetrahalogeno InX_4^- and $[\text{InX}_4(\text{H}_2\text{O})_2]^-$ species in solution appears to depend on the halide involved. The Raman studies of Hanson and Plane (69H) confirmed the conclusion reached by Woodward et al. (55W, 60Wa) that neither InCl_4^- nor InBr_4^- exist in aqueous solution, even at high halide concentrations, even though the species extracted from such solutions into basic organic solvents (55W, 60Wa, 73Hb), and sorbed on anion exchange resins (70Db) is InX_4^- . In contrast, InI_4^- has been identified spectroscopically in aqueous hydriodic acid (58W). In all cases, the addition of hydrophilic solvents (e.g., methanol) to these aqueous solutions increases the concentration of InX_4^- , in the order $\text{I} > \text{Br} > \text{Cl}$ (69H, 70Da). The recent detailed Raman studies of Irish et al. (77J) confirm that aquo-complexes up to $[\text{InCl}_4(\text{H}_2\text{O})_4]^-$ exist in aqueous solution (chloride only).

In summary, it is clear that complexes up to $\underline{n} = 4$ must be considered for all four halides, and possibly for pseudohalides. A detailed understanding of the inter-relationships between the possible anions is at present lacking, and further quantitative and spectroscopic studies are required. Such results will surely reveal more about these interesting systems than recent conductance results (e.g., 73C) which are capable of a variety of qualitative explanations. Equally importantly, a discussion of stability constant measurements based on anion exchange or solvent extraction should recognize

that these processes may involve species (e.g., InX_4^-) which are present in aqueous solution only in extremely low concentrations, and that partition may involve a major change in the aqueous phase equilibria, including changes in the coordination number of indium. It is not always clear that such considerations have been given proper weight in the discussion of experimental results.

IV. 2. Fluoro complexes

The literature values for the stability constants for indium(III)-fluoride complexes are given in Table 2, and the corresponding thermochemical results in Table 3. For 1M NaClO_4 at 25°C three sets of results (68A, 69R, 71W) are in satisfactory agreement, extending to K_4 , and the values for 20°C 2M NaClO_4 (54Sa) support these results. The (unweighted) means of the three sets of data for these complexes are

$\log K_1$	3.70	\pm 0.03	<u>recommended</u>
$\log K_2$	2.66	\pm 0.15	<u>tentative</u>
$\log K_3$	2.30	\pm 0.20	<u>tentative</u>
$\log K_4$	1.2	\pm 0.2	<u>tentative</u>

It is worth noting that the uncertainty in $\log K_1$ is close to the variation in the values of $pK_1(\text{HF})$ adopted in different calculations.

The early cation exchange results (54Sd) are almost certainly in error because of the high pH (3.8) of the solutions, for although the authors state that no precipitation occurred, hydrolysis must be a significant competing process under such conditions (cf. Section II). A study of the temperature dependence (55H) unfortunately lacks any independent confirmation, but the results at 25°C are in reasonable agreement with those given, allowing for the different media involved, and for the fact that not only the values of $pK_1(\text{HF})$, but also K_1 , K_2 , K_3 and K_h for iron(III)-fluoride complexes, are involved in the calculation.

The agreement amongst the thermochemical results (Table 3) is not so satisfactory. Of the three ΔH° values, that of Walker, Twine and Choppin (71W) exceeds the other two by an amount which is higher than the stated experimental error. From the work of Rhyll (69R) and Vasilev (74V) with 1M NaClO_4 , one finds

ΔH°_1	9.1 ± 0.2	kJ mol^{-1}	ΔS°_1	101 ± 1	$\text{J K}^{-1} \text{mol}^{-1}$	(recommended)
ΔH°_2	8.0 ± 0.4	" "	ΔS°_2	81 ± 4	"	(tentative)
ΔH°_3	10 ± 3	" "	ΔS°_3	75 ± 10	"	(doubtful)
ΔH°_4	10 ± 2	" "	ΔS°_4	56 ± 7	"	(doubtful)

One may note in passing that although the percentage error in ΔS° cannot be less than that in ΔG° and/or ΔH° , the published errors do not always obey this restriction.

The changes in ΔH° with n are only slight, implying that the replacement of In-OH_2 by In-F involves essentially constant changes in bonding and solvation factors at each stage. Vasilev and Kozlovskii (74Va) have extended their

Table 2. Stability constants for indium(III)/fluoride species.

Method	Medium (concn. M)	T (°C)	1	2	3	4	Comments	Ref.
cation exchange, resin (In)	1 NaClO ₄	25	3.00	2.8	2.8	-	log K ₁ (HF) 2.85 (assumed) pH 3.8 No errors quoted; K ₂ & K ₃ "only orders of magnitude"	54Sd
emf: In electrode	2 NaClO ₄	20	3.70±0.03	2.56±0.09	2.36±0.15	1.09±0.40	log K ₁ (HF) 2.91; K ₂ 0.70 pH 1.7 Values confirmed by ligand displacement method. Na ₃ InF ₆ ppts. at [F ⁻] > 0.1M	54Sa
emf (In)	0.5 NaClO ₄	15	3.70	2.55	-	-	log K ₁ (HF) 2.85	55H
		25	3.75	2.61	-	-	" " 2.91	
		35	3.83	2.78	-	-	" " 3.00	
cation exchange resin + extraction (In)	1.0 NaClO ₄ in equil. with DEHP in toluene	25	3.67±0.03	2.58±0.06	2.36±0.10	-	No errors quoted. pH 1.3	68A
emf (F ⁻)	1.0 NaClO ₄	25	3.69±0.03	2.83±0.04	2.11±0.10	1.27±0.10	log K ₁ (HF) 2.95, log K ₂ (HF) 0.58 pH 1.65 - 2.0	69R
H ⁺ by emf.	1.0 NaClO ₄	25	3.72±0.03	-	-	-	log K ₁ (HF) 2.94, pH 0.7 - 1.30 K ₂ not calc'd because errors too large	71W

TABLE 3. Thermochemical parameters for InF_n(3-n)⁺ complexes (all at 298K)

Medium	-ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° J K ⁻¹ mol ⁻¹	Comments (See also Table 2)	Ref.
$\frac{n=1}{0.5 \text{ NaClO}_4}$	21.1	10.3	105	Recalc'n (55H) assumes ΔH ₁ ⁰ (HF) = 12.4, ΔS ₁ ⁰ (HF) = 96; No errors quoted.	55H, 56P
1.0 NaClO ₄	21.0±0.1	9.20±0.17	101.2±0.8	Assumes ΔH ₁ ⁰ (HF) = 11.7, ΔH ₂ ⁰ (HF) = 3.4	69R
1.0 NaClO ₄	21.3±0.2	12.5±0.6	114±7		71W
1.0 NaClO ₄	-	8.9±0.2	100.7±0.8	Stability consts. of (69R) assumed throughout Hydrolysis (1-2%) allowed for; K _{1,1} = 10 ⁻⁴	74V
$\frac{n=2}{\text{"}}$	16.2±0.2	7.7±0.4	80±2		69R
"	-	8.3±0.6	82±2		74V
$\frac{n=3}{\text{"}}$	12.0±0.4	13.8±1.3	87±2		68R
"	-	6.9±1.0	63±4		74V
$\frac{n=4}{\text{"}}$	7.3±0.5 (69R)	10±2	56±7		74V

calorimetric measurements to the temperature range 15-35°C at ionic strengths 0 - 2M NaClO₄, and report that the monotonic increase in ΔC_p (from 105 J K⁻¹ mol⁻¹, for $\underline{n} = 1$, to 293 J K⁻¹ mol⁻¹ for $\underline{n} = 4$) is in agreement with a series of consecutive replacements of H₂O by F⁻ in the indium coordination sphere. It follows that all the complexes are of the type [In(H₂O)_{6- \underline{n}} F _{\underline{n}}]^{(3- \underline{n})⁺, in agreement with the proposal that the stability constants do indeed refer to equilibria (1)-(4) in Scheme 1.}

IV. 3. Chloro complexes

In contrast to the fluoride systems, the indium-chloride stability constants show a surprising range of values. For example, the reported log K₁ results vary from 4.3 to 0.05, and even when the more obviously inconsistent results are eliminated, no single value predominates. The situation is also complicated by an almost perverse refusal to use a standard medium, even in studies from the same laboratory. That this is no trivial matter is shown by the work of Mikhailova et al. (69M), who found K₁ varying by almost a power of ten when different alkali metal nitrates were used as background electrolyte (see Table 4), and in addition claimed that no complexes higher than $\underline{n} = 1$ exist in lithium nitrate media. No allowance for the possible formation of indium-nitrate species appears to have been made in this work.

Of the experimental methods used, the polarographic technique seems to be the least satisfactory in this particular system. Doubts have been expressed as to the polarographic reversibility of the reduction processes (62M), with the implication that all constants derived from such experiments are unreliable. Other authors (60I, 67L) claim that the three-electron reduction is reversible, but opine that Cozzi and Vivarelli (53C, 54C) used an incorrect value for E°_{1/2}, and that recalculation with the correct value would lower the derived log K₁ by 1.3 units. Given these problems, and the failure of other workers to report stepwise stability constants (51S, 58Z), it seems appropriate to remove all the polarographic data from further consideration. The most recent polarographic results (75K) must also be subject to considerable doubt, for although K₁ is close to that from other methods, the fact that K₂ shows no such agreement, and that K₃ > K₂, does not inspire confidence. One can, for other reasons, eliminate from consideration the values reported by Schufle and Eiland (54Sd) (suspect because of probable hydrolysis (see IV. 2. above)), and those involving anion exchange (63M), which are based on the surely invalid assumption that β₃ = 0.

What then remain are values which unfortunately show no constancy as to experimental conditions. In perchloric acid media, one finds

acid strength (M)	log K ₁	log K ₂	log K ₃	Ref
0.5	2.47	0.64	0.83	64V
0.69	2.36	1.27	0.32	54C
1.0	2.52	-	-	61W
2.0	2.51	-	-	61W

and confidence in the last two sets is reduced by the failure to identify any higher complexes. Accordingly, over the range 0.5 - 0.69M perchloric acid,

one has

log K_1	2.41 \pm 0.05	<u>recommended</u>
log K_2	0.95 \pm 0.4	<u>doubtful</u>
log K_3	0.5 \pm 0.3	<u>doubtful</u>

with the use of the rather broadly defined standard state being justified by the agreement within the limits stated and by the present lack of detailed knowledge as to the effect of changes of ionic strength on the stability constants.

For sodium perchlorate solutions with pH < 3.0, the reported values are:

NaClO ₄ concn. (M)	log K_1	log K_2	log K_3	Ref.
1	2.18	-	-	54Sb
	2.20	1.35	-	54Sc
2	2.43	1.0	0.2	54S, 72F
3	2.58	1.26	0.4	72F
4	2.61	1.57	-	70H

and again it seems justifiable to state average values valid for the concentration range 1 - 4M sodium perchlorate.

log K_1	2.40 \pm 0.2	<u>tentative</u>
log K_2	1.30 \pm 0.3	<u>doubtful</u>
log K_3	0.30 \pm 0.3	<u>doubtful</u>

The cation exchange results for various concentrations of alkali metal nitrates (69M) are regarded as doubtful for lithium nitrate, and tentative for the other two salts.

In concluding this part of the discussion, one can only lament the lack of reliable recommended values for these stability constants, given the amount of effort and the range of experimental methods which have been applied to the problem.

The only thermochemical work is that of Rhyll (69R), who finds the following values, based on values of $K_1 - K_3$ refined from Sunden (54S):

$\underline{n} = 1$	ΔG°	-12.0 \pm 0.2	kJ mol ⁻¹ } <u>tentative</u>
	ΔH°	5.1 \pm 0.2	
	ΔS°	57.3 \pm 1.2	
$\underline{n} = 2$	ΔG°	-8.6 \pm 0.2	} <u>tentative</u>
	ΔH°	3.3 \pm 0.3	
	ΔS°	39.7 \pm 1.7	
$\underline{n} = 3$	ΔG°	1.4 \pm 0.5	} <u>doubtful</u>
	ΔH°	33 \pm 8	
	ΔS°	108 \pm 17	

(2M NaClO₄, at 25°C, pH 2.0). These results do not lend themselves to any thermochemical analysis of the type performed for the fluoride system.

TABLE 4. Stability constants for indium(III)/chloride species.

Method	Medium (concn. M)	T (°C)	1	2	$\log K_{n-3}$	4	Comments	Ref.
polarography	0.01 - 11.6 HCl corr. I = 0	25	-	$(\beta_2) \sim 1.7$	-	$(\beta_4) \sim 1$	cf 62M	51S
	varying; aq. soln of InCl ₃	25	2.35	-	-	-	pH 2.7 - 3.8 recalcn. of results of Moeller (41Ma)	52H
polarography	2 NaClO ₄	25	4.3±0.1	1.8±0.2	-	-	pH 1.0 cf (67L)	53C, 54Ca
cation exchange resin	0.69 HClO ₄	20	2.36±0.02	1.27±0.08	0.32±0.12	-	cf (59Ba)	54C
cation exchange resin	1 NaClO ₄	25	1.42	0.81	1.00	-	pH 3.8 No errors reported.	54Sd
emf, In electrode	2 NaClO ₄	20	2.15±0.03	1.44±0.03	-	-	Higher consts. not calculable from results pH 1.7 Values confirmed by ligand displacement method.	54S
cation exchange	1 NaClO ₄	20	2.18±0.03	-	-	-	pH 2.5 Higher consts. not calculable. No consts. from anion exchange resin expts.	54Sb, 54Sc
extraction into naphthalene-l- carboxylic acid in di-iso-propyl ether	1 NaClO ₄ in equil. with org. phase	20	2.20±0.03	1.35±0.05	-	-	pH 2.7 - 3.0	54Sc
polarography	corr to I= 0	25	-	$(\beta_2) 6.28$	-	$(\beta_4) 7.44$	Only InCl ₂ ⁺ and InCl ₄ assumed.	58Z

TABLE 4. (continued)

Method	Medium (concn. M)	T (°C)	1	2	log K_n	3	4	Comments	Ref.
extraction into DNNS in heptane and TNOA in benzene	1 HClO ₄ in equil. with org. phase 2 HClO ₄ in equil. with org. phase	25	2.52	-	-	-	-	No errors quoted	61W
Cl, by AgCl electrode	corr. to I = 0	25	1.72	0.92	-	-	-	No errors quoted. ? acid added.	62A
polarography potentiometric	4 NaNO ₃ 4 NaNO ₃	25 25	2.26 -	0.24 -	- 1.05	- -	- -	No errors quoted. ? acid added Mixed Br/Cl species identified.	62F
anion exchange resin, solvent extraction into TIOA in xylene	corr. to 0	25	0.05	0.45	0	-1.6	-	β_3 assumed = 0 in mechanism. [HCl] 0.08 - 9.0 No errors quoted.	63M
cation exchange resin	0.5 HClO ₄	?	2.47	0.64	0.83	-	-	Also values in mixed H ₂ O/EtOH	64V
cation exchange resin	1.5 LiNO ₃ 1.5 NaNO ₃ 1.5 KNO ₃	25 25 25	1.75 2.49 2.66	- 1.54 1.74	- -0.50 0.51	- -	-	pH 1.75 No errors quoted. No complexes higher than $\bar{n} = 1$ in LiNO ₃	69M
extraction (In) by TTA in CHCl ₃	4 NaClO ₄ in equil. with org. phase	25	2.61	1.59	-	-	-	pH 2.0 - 4.0 No errors quoted.	70H
potentiometric (In, Cl)	3 NaClO ₄ 2 NaClO ₄	25 20	2.58+0.02 2.43+0.05	1.26+0.04 1.0+0.1	0.4+0.1 0.2+0.2	- -	-	pH 1 Recalc. by (72F) assuming $\bar{n} = 3$ complex present	72F 54S, 72F
polarography			2.70	0.50	1.00	-0.90	-		75K

IV. 4. Bromo complexes

Using the criteria established in IV. 3., we can reject values based on polarography (54Ca, 54Cb, 62F, 75K), and the cation exchange studies at high pH (54Sd), and are then left with a set of results (Table 5) for 0.69M perchloric acid (54C):

$\log K_1$	2.01 ± 0.02	<u>tentative</u>
$\log K_2$	1.09 ± 0.09	<u>tentative</u>
$\log K_3$	0.18 ± 0.12	<u>doubtful</u>

and values which apply to various concentrations of sodium perchlorate

Concn. (M)	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	Ref.
1	1.93	0.67	-	-	54Sc
	1.90	-			
2	1.98	0.58	-	-	54S
4	2.08	1.28	0.60	0.85	57B
	2.36	0.80	-	-	
	-	1.42	-0.08	-1.06	70H

It is then possible to derive constants which can be taken as valid over this whole concentration range

$\log K_1$	2.10 ± 0.02	<u>tentative</u>
$\log K_2$	0.95 ± 0.3	<u>tentative</u>
$\log K_3$	0.3 ± 0.3	<u>doubtful</u>
$\log K_4$	0 ± 1	<u>rejected</u>

The thermochemical results reported by Rhy1 (69R) yield

$\underline{n} = 1$	ΔG°	-11.3 ± 0.1	kJ mol^{-1}	} <u>tentative</u>
	ΔH°	1.95 ± 0.05	kJ mol^{-1}	
	ΔS°	44.3 ± 0.8	$\text{J K}^{-1} \text{mol}^{-1}$	
$\underline{n} = 2$	ΔG°	-3.4 ± 0.2	kJ mol^{-1}	} <u>doubtful</u>
	ΔH°	5.65 ± 0.2	kJ mol^{-1}	
	ΔS°	30.5 ± 1.2	$\text{J K}^{-1} \text{mol}^{-1}$	

IV. 5. Iodo complexes

From the results in Table 6, and following the previous argument, one finds for 0.69M perchloric acid

$\log K_1$	1.64 ± 0.05	<u>tentative</u>
$\log K_2$	0.91 ± 0.22	<u>doubtful</u>
$\log K_3$	-0.08 ± 0.25	<u>doubtful</u>

The results for sodium perchlorate media are few in number, and rendered unreliable by the fact that Sunden (54Sa) reports $K_2 > K_1$; while such a result is not impossible, there is no other evidence to support such a finding for indium-halide systems. The values for 2 - 4M NaClO_4 solutions are therefore

$\log K_1$	1.5 ± 0.5	<u>doubtful</u>
$\log K_2$	0.6 ± 0.5	<u>doubtful</u>
$\log K_3$	0 ± 0.5	<u>doubtful</u>

Given these findings, the thermochemical results (69R) must also be treated

with reservation:

$\underline{n} = 1$	ΔG°	-5.9	± 0.8	kJ mol^{-1}	} <u>doubtful</u>
	ΔH°	-3.05	± 0.08	kJ mol^{-1}	
	ΔS°	10	± 3	$\text{J K}^{-1} \text{mol}^{-1}$	
$\underline{n} = 2$	ΔG°	-7.1	± 1.3	kJ mol^{-1}	} <u>doubtful</u>
	ΔH°	3.4	± 0.1	kJ mol^{-1}	
	ΔS°	35	± 4	$\text{J K}^{-1} \text{mol}^{-1}$	

Despite the reported experimental accuracy, these values must bear the doubts expressed about the stability constants (54Sa), on which ΔG° , and hence ΔH° and ΔS° , are based.

IV. 6. Pseudohalide complexes

A number of the constants reported for thiocyanate complexes (see Table 7) can be rejected immediately. Three series of spectrophotometric measurements either make assumptions, or reach conclusions, about the absence of complexes beyond $\text{In}(\text{NCS})_2^{2+}$ or $\text{In}(\text{NCS})_2^+$ which are at variance with work on the known chemistry of indium-thiocyanate systems, and of the analogous halides (64K, 68D, 62S). The polarographic results again suffer from uncertainties as to the reversibility of the reduction processes (63R, 65Na, 73R) said to be 'quasi-reversible' (65Na), and are rejected, despite the fact that one analysis produces values for K_5 and K_6 (but note $K_5 > K_4$). One is then left with two emf (54Sa, 63G) and one solvent extraction (70H) results, from which for 1.6 - 4M sodium perchlorate, 20 - 25°C

$\log K_1$	2.53 ± 0.05	<u>tentative</u>
$\log K_2$	1.35 ± 0.3	<u>doubtful</u>
$\log K_3$	0.92 ± 0.3	<u>doubtful</u>

The reservations about K_1 apply because the three results involved are based on different standard states and temperatures. The effects of pressure (3000 atm) on the formation of indium-thiocyanate complexes have been reported (77P, 78P).

The thermochemical results yield

$\underline{n} = 1$	ΔG°	-14.6	± 0.2	kJ mol^{-1}	} <u>tentative</u>
	ΔH°	-6.9	± 0.2	kJ mol^{-1}	
	ΔS°	25.5	± 0.8	$\text{J K}^{-1} \text{mol}^{-1}$	
$\underline{n} = 2$	ΔG°	-5.60	± 0.25	kJ mol^{-1}	} <u>doubtful</u>
	ΔH°	-15.9	± 0.9	kJ mol^{-1}	
	ΔS°	35	± 3	$\text{J K}^{-1} \text{mol}^{-1}$	
$\underline{n} = 3$	ΔG°	-6.0	± 0.4	kJ mol^{-1}	} <u>doubtful</u>
	ΔH°	10	± 1	kJ mol^{-1}	
	ΔS°	53	± 4	$\text{J K}^{-1} \text{mol}^{-1}$	

The doubts expressed as to the $\underline{n} = 2$ and 3 results arise from the values of ΔG° (i.e., K), since $K_3 > K_2$, following Sunden (54Sa).

No stability constant results have been reported for other pseudohalides. Indeed it may be that certain of these systems are not experimentally accessible since it has been reported (73R) that at the acidity required to prevent

TABLE 5. Stability constants for indium(III)/bromide species.

Method	Medium (concn. M)	T (°C)	1	2	log K_n	3	4	Comments	Ref.
polarography	varying; aq. soln. of InBr_3	25	2.20	-	-	-	-	Recalcn. of results of Moeller (42M) pH 2.6 - 3.4	52H
cation exchange resin	2 NaClO_4	25	3.8±0.1	1.0±0.2	-	-	-	pH 1.0 See (67L)	54Ca, 54Cb
cation exchange resin	0.69 HClO_4	20	2.01±0.02	1.09±0.09	0.18±0.12	-	-	54C	54C
cation exchange resin	1 NaClO_4	25	1.20	0.58	0.70	-	-	pH 3.8 No errors reported	54Sd
emf. In electrode	2 NaClO_4	20	1.98±0.03	0.58±0.04	-	-	-	Higher constns. not calculable. pH 1.7	54S
extraction (see Table 4)	1 NaClO_4 in equil. with org. phase	20	1.93±0.03	0.67±0.05	-	-	-	pH 2.7 - 3.0	54Sc
cation exchange resin	1 NaClO_4	20	1.90±0.03	-	-	-	-	pH 2.5. Higher constns. not calculable	54Sc
spectrophotometric	4 NaClO_4	21.7	2.08	1.28	0.60	0.85	-	pH 1.0. Na_2SO_3 added. No errors reported. No higher complexes.	57B
(i) polarography (ii) emf, In/Hg electrode	4 NaNO_3		1.36(i)	1.52(ii)	1.72(ii)	-	-	Acid added? No errors reported Mixed Cl/Br complexes also identified	62F
anion exchange resin	0.1 - 9.3 LiBr	'room temp'	-	1.3	0.59±0.08	-0.52±0.07	-	log K_5 - 1.6; log K_6 ~ -2.2 K_1 not determinable Resin species assumed to be R_3InBr_6 . pH 1.7	62Aa
extraction (In) into TTA in CHCl_3	4 NaClO_4 in equil. with org. phase	25	2.36	0.80	-	-	-	No errors reported. pH 2.0	70H
extraction (In) into TBP in hexane	"	25	~1.9	1.42	-0.08	-1.06	-	Assume $\text{InBr}_3(\text{solv})$. in organic phase	
polarography			2.10	0.30	0.10	-0.90	-		75K

TABLE 6. Stability constants for indium(III)/iodide species.

Method	Medium (concn. M)	T (°C)	1	2	3	Comments	Ref.
	varying: aq. solns. of InI ₃	25	1.98	-	-	pH 3.4 - 2.6 No errors reported.	52H
polarography	2 NaClO ₄	25	3.1	0.7	-	No errors reported. See (67L). pH?	54Ca, 53C
cation exchange resin	0.69 HClO ₄	20	1.64±0.05	0.91±0.23	-0.08±0.25		54C
cation exchange resin	1 NaClO ₄	25	0.30	-	-	pH 3.8	54Sd
emf, In electrode	2 NaClO ₄	20	1.00±0.20	1.26±0.30	-	pH 1.7	54Sa
extraction (In) into TTA in CHCl ₃	4 NaClO ₄ in equil with org. phase	25	1.97	0.31	-0.39	pH 2.0 No errors reported.	70H
extraction into TBP in hexane	"	~2.0	0.18	0.02	0.02	Assume InI ₃ (solv) extracted log K ₄ = -1.06	
polarography	"	1.35	0.05	-0.10	-0.10	log K ₄ - 0.80	75K

TABLE 7. Stability constants for indium(III)/thiocyanate species.

Method	Medium (concn. M)	T (°C)	1	2	log K _n	3	4	Comments	Ref.
emf: In electrode	2 NaClO ₄	20	2.58±0.02	1.02±0.03	1.03±0.05	-	-	pH 1.7	54Sa
spectrophotometric	1 NaClO ₄	25	-	(β ₂) ₄	-	-	-	Job's plot shows only In(NCS) ₂ ⁺ present. pH 1.60	62S
emf: In/Hg electrode	1.6 NaClO ₄	20	2.58	1.42	0.74	0.06			63G
polarography	2 NaClO ₄	30	2.08	1.13	1.04	-0.01		log K ₅ 0.58 log K ₆ 0.03 Errors? pH = 1	63R
spectrophotometric (comp. formation of FeNCS ₂ ⁺)	0.6 HClO ₄	20	2.34±0.02	-	-	-	-	Assuming no complexes beyond InNCS ₂ ⁺ . Assume log K ₁ for FeNCS ₂ ⁺ = 2.15	64K
polarography	2 NaClO ₄	25	1.7	0.6	-0.22	1.14		Assume no complexes beyond $\bar{n} = 4$ pH 3.0. No errors quoted.	64Na
spectrophotometric	0, corr.	30-32	3.15±0.01	-	-	-	-	pH 2.3 {Analysis said to show absence of higher complexes.	68D
emf: Ag/AgSCN	"	35	3.26±0.04	-	-	-	-	pH 2.0 {	70H
extraction (In) into TTA in CHCl ₃	4 NaClO ₄ in equil. with org. phase	25	2.44	1.67	0.99	-	-	pH 3.0	
extraction (In) into TBP in hexane	"	"	~2.4	1.71	0.99	-0.63		log K ₅ = 0.88 Assume In(NCS) ₃ in org. phase.	
polarography	2 NaNO ₃	27	0.78	1.71	1.42	-	-	? added acid No complexes beyond $\bar{n} = 3$	73R

preprecipitation of indium hydroxide, decomposition of SeCN^- occurs, with preprecipitation of red selenium; the abstract of this paper has a misprint which leads the reader to expect results for In/SeCN complexes.

IV. 7. General discussion

In view of the efforts which have been expended on the experiments reviewed in this section, the yield of 'recommended' stability constants is very disappointing. There are no firm results for complexes higher than $\underline{n} = 1$ in any system, and the results for $\underline{n} > 3$ are all extremely tenuous. Equally regrettably, the data cast no light on the problem of the species in solution beyond $\underline{n} = 3$, discussed in sub-section IV. 1. All in all, the indium(III)-halide systems clearly lack definitive stability constants, and one final irony is that the results for K_1 for InCl^{2+} , InBr^{2+} and InI^{2+} derived in 1952 (52H) from the early results of Moeller (41Ma, 42M) are remarkably close to the values recommended.

Given the problems of establishing recommended values for K_3 etc., any comparison of the stability constants for the different halides must be restricted to K_1 , K_2 , ΔH°_1 , and ΔS°_1 . The results for 1 - 4M sodium perchlorate give

	$\log K_1$	$\log K_2$	ΔH°_1	ΔS°_1
F	3.70	2.66	9.1	101
Cl	2.40	1.30	5.1	57
Br	2.10	0.95	1.95	44
I	1.5	0.6	-3	10
<u>NCS</u>	2.53	1.35	-7	25

It is immediately obvious that the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$ holds for both K_1 and K_2 , this being the classical order for a hard cation such as In^{3+} . The same order also holds for ΔH° , and ΔS° , and a detailed analysis of these results might lead to some insight into the bonding terms. The order for $\beta_{\underline{n}}$ ($\underline{n} = 1 - 4$) in methanol is $\text{Cl} > \text{Br} > \text{NCS} > \text{I}$ (80S). Finally we should note that K_1 and K_2 for thiocyanate would imply strong similarity to chloride, but that this cannot be extended to the thermochemical results.

V. OXYANION COMPLEXES

Compared with the number of publications dealing with halide complexes, the study of the ligation of indium(III) by oxyanion ligands have been almost neglected. Equally, there is no firm base of preparative chemistry from which to discuss those results which are available. The present review is ordered in terms of Group V-VI-VII ligands, there being no results on indium-carbonate, silicate, etc.

V. 1. Oxyanions of Group V

Indium(III)-nitrite complexes have been identified in anhydrous methanol solutions of $\text{In}(\text{NO}_2)_3$ and NaNO_2 ; conductimetric and potentiometric studies gave $\log K_{\underline{n}}$ (at 25°C) = 5.20, 3.50, 3.38, 2.32, 2.00 and 0.64, for $\underline{n} = 1 - 6$ (all tentative). Crystalline $\text{In}(\text{NO}_2)_3 \cdot 1\text{MeOH}$ was obtained from solution (74G).

Both cationic and anionic indium nitrate complexes have been prepared; the latter are salts of the $[\text{In}(\text{NO}_3)_4]^-$ anion (65S, 66T, 73I), while the cationic species are of the type $[\text{InL}^{\text{II}}(\text{NO}_3)_2]^+$ (L^{II} = bipy or phen) (66T). The formation of indium-nitrate complexes in solution has been demonstrated by Raman spectroscopy (63H, 64H). Two quantitative studies of complex formation gave

0.69M HClO_4 , 20°C, cation exchange resin (68F)

$$\left. \begin{array}{l} \log K_1 = 0.18 \pm 0.08 \\ \log K_2 = -0.48 \pm 0.10 \end{array} \right\} \text{(tentative)}$$

4M $\text{Na}(\text{ClO}_4)$, 25°C, pH = 2.0, extraction into TTA in CHCl_3 (70H)

$$\log K_1 = -0.43 \quad \text{(doubtful)}$$

Indium orthophosphate precipitates quantitatively from solution (pH 3.25) as $\text{InPO}_4 \cdot 2\text{H}_2\text{O}$, for which the solubility product (68Da)

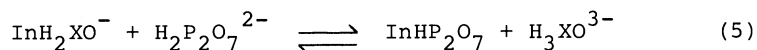
$$\log K_{\text{sp}} = -21.63 \quad \text{(doubtful)}$$

(25°C, $I = 1 \text{ NaClO}_4$). Aging of the precipitate is said to be important, but no information is given on the relevance, if any, of this factor in the measurement of K_{sp} (cf. Section III. 4.). Mixed hydroxo-phosphate complexes were also detected. No stability constants have been reported for higher complexes of PO_4^{3-} , although salts containing $[\text{In}(\text{PO}_4)_2]^{3-}$ and $[\text{In}_2(\text{PO}_4)_4]^{6-}$ anions have been characterized (65D). A 1:1 complex with the H_2PO_4^- anion is reported, with $\log K_1 = 1.43$ (ion exchange, $I = 0.9$, 20°C, $[\text{H}^+] 0.1 - 0.51\text{M}$) (doubtful) (74F).

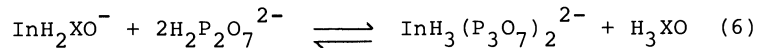
Two insoluble indium pyrophosphates have been prepared and their solubility products measured at 20°C, pH 0.6 -1.5 (64G).

$$\left. \begin{array}{l} \text{In}_4(\text{P}_2\text{O}_7)_3 \quad \log K_{\text{sp}} \quad -64.47 \pm 0.15 \\ \text{InHP}_2\text{O}_7 \quad \log K_{\text{sp}} \quad -12.44 \pm 0.16 \end{array} \right\} \text{tentative}$$

Other pyrophosphates have also been prepared and examined (67D). A study of competitive complex formation (In/Xylenol Orange/pyrophosphate) has led to values for the equilibrium.

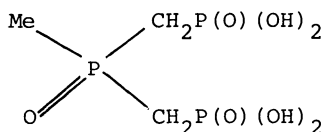


for which $\log \beta(\text{InHP}_2\text{O}_7) = 10.23 \pm 0.18$ at $I = 0.1 \text{ NaClO}_4$, 20°C, pH 3.65-5.53, and $= 12.31 \pm 0.18$ at $I \rightarrow 0$. For the process



$\log \beta(\text{InH}_3(\text{P}_2\text{O}_7)_2) = 15.77 \pm 0.15$ at $I \rightarrow 0$ (69S). It is assumed that $\text{H}_2\text{P}_2\text{O}_7^{2-}$ is the predominant (> 90%) pyrophosphate species present under the conditions used. These results should be regarded as doubtful, since the complex presumed to be formed in (5) is reportedly insoluble (see above). The stability constants of the pyrophosphate complexes $[\text{In}(\text{HP}_2\text{O}_7)_2]^{4-}$ ($\log \beta_1 = 21.99 \pm 0.02$) and $[\text{In}(\text{P}_2\text{O}_7)_2]^{5-}$ ($\log \beta_2 = 23.80 \pm 0.02$) (tentative) have been determined by a partition method ($I = 0.1(\text{NaClO}_4)$, pH 6.9 - 8.3) (78Mb). The xylenol orange competitive method (67A) has been used in studying the triphosphate complex $[\text{In}(\text{H}_2\text{P}_3\text{O}_{10})_2]^{3-}$, for which $\log K = 12.18 \pm 0.22$ at $I = 0.1 (\text{NaClO}_4)$, $T = 20^\circ\text{C}$, pH 3.65-5.53 (doubtful). No complexes of indium(III) with arsenate, antimonate, etc. have been reported, but it is

relevant to include here the organophosphorus complexing agent I



which forms soluble 1:1 and 1:2 complexes with indium: $\log K_1 = 15.4$, $\log K_2 = 3.3$ (potentiometric titration, 0.1 KCl) (68K) (doubtful).

V. 2. Oxyanions of Group VI

Detailed studies of indium-sulphato complexes constitute the most important entry in this section. Infrared (64L) and Raman (63H, 64H) work has shown that such complexes exist in aqueous solution, whilst other physical measurements have been interpreted in terms of $[\text{In}(\text{SO}_4)_2]^{2-}$ and $[\text{In}(\text{SO}_4)_3]^{3-}$ anions (61D); phase rule studies have identified the crystalline solids $\text{NaIn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{In}(\text{OH})(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ (66D). Table 8 shows that the measured stability constants lead to the unweighted mean for 1M NaClO_4 , 20-25°C.

$\log K_1$	1.78 ± 0.02	<u>recommended</u>
$\log K_2$	0.75 ± 0.05	<u>recommended</u>
$\log K_3$	0.4 ± 0.1	<u>tentative</u>

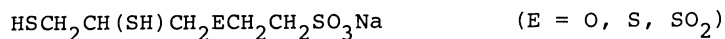
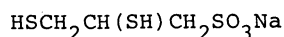
The single value for K_1 in 2.0M NaClO_4 (54Sc) is essentially indistinguishable from the value recommended above, given the reported experimental errors.

Thermochemical results (69I) corrected to zero ionic strength give

$\underline{n} = 1$	$\log K_1$	3.04 ± 0.09	
	$\Delta G^\circ =$	-17.3 ± 0.5	kJ mol^{-1}
	$\Delta H^\circ =$	29.0 ± 0.4	kJ mol^{-1}
	$\Delta S^\circ =$	155.5 ± 1.3	$\text{J K}^{-1} \text{mol}^{-1}$
$\underline{n} = 2$	$\log K_2$	1.96 ± 0.08	
	$\Delta G^\circ =$	-11.2 ± 0.5	kJ mol^{-1}
	$\Delta H^\circ =$	-7.32 ± 0.25	kJ mol^{-1}
	$\Delta S^\circ =$	13.0 ± 1.3	$\text{J K}^{-1} \text{mol}^{-1}$

The reported stability constants are in poor agreement with those recommended above, and while any errors in K may be reduced in their effect on ΔH and ΔS , as the authors claim, the differences are such that all of these results must be rated doubtful.

A series of sulphonic acid derivatives have also been studied (71E) and may be included here



All are said to form 2:3 complexes with indium, with $\log K_{2,3}$ in each case ≈ 55 (doubtful).

TABLE 8. Stability constants for indium(III)/sulphate species.

Method	Medium (concn. M)	T (°C)	log K _n			Comments	Ref.
			1	2	3		
cation exchange resin	1 NaClO ₄	20	1.74±0.09	-	-	pH 2.5	54Sb
extraction into α-oxynaphthoic acid in di-isopropyl ether	1 NaClO ₄ in equil. with org. phase	20	1.85±0.07	0.77±0.06	0.4±0.1	pH 2.7 - 3.0	54Sc
cation exchange	2 NaClO ₄	20	1.74±0.09	-	-		54Sc
solubility	I = 2		1.78	-	-		66D
extraction into DEHP in toluene	1 NaClO ₄ in equil. with org. phase	25	1.79±0.01	0.72±0.02	-	pH 3.2	68A
thermochem. titration	I → 0 (corr)	25	3.04±0.09	1.96±0.08	-	"enough acid to suppress hydrolysis".	69I

V. 3. Oxyanions of Group VII

The following values have been reported by Hasegawa (70H), using extraction into TTA in chloroform, 25°C, 4M NaClO₄, pH 2.0 (ClO₃⁻, BrO₃⁻) or 3.0 (IO₃⁻).

	log K ₁	log K ₂	
ClO ₃ ⁻	-0.37	-	<u>doubtful</u>
BrO ₃ ⁻	-0.12	-	<u>doubtful</u>
IO ₃	1.02	1.62	<u>rejected</u>

The order of K₁ is the order of the anion basicities, but for iodate the conclusion that K₂ > K₁ must reduce confidence in these results.

Finally we should note that perchlorate shows no evidence of complexing with indium(III) in solution (Raman spectroscopy) (63H, 64H)), which is a welcome conclusion in view of the number of authors who have used aqueous perchlorate media in the study of complexing by other ligands.

VI. INDIUM(I) COMPLEXES

The halides of indium(I) are insoluble in aqueous solution, and indium(I) species generated in situ (e.g. electrochemically) undergo oxidation and/or disproportionation. Despite these difficulties, a small number of stability constants have been determined by studying the disappearance of In^I in various media, using polarographic methods to follow such reactions (82R). The results (25°C, pH 2.80, I = 0.7 (various Group I nitrates)) are as follows:

F ⁻	log β ₂ = 2.46	} <u>doubtful</u>
Cl ⁻	log K ₁ = 2.37	
Br ⁻	log K ₁ = 1.56, log K ₂ = 0.55	

These experiments give some hope of further studies of the solution chemistry of indium(I).

VII. CARBOXYLATO COMPLEXES

VII. 1. Introduction

A thorough analysis of the stability constants of complexes of indium(III) with carboxylate anions is rendered difficult both by the general absence of duplicate results, and by the lack of a firm base of preparative and/or structural information. Thus although a number of neutral indium-tricarboxylato compounds are known in the solid state (75C), there are no reports on the preparation of either cationic or anionic complexes apart from oxalate (see below) and one negative result in respect of acetate species (73Ha), and in consequence, the reality of the anionic complexes implied by K_4 , K_5 and K_6 , (c.f. Table 9) is not as yet supported by other work.

Table 9 presents the published results in the order of increasing ligand molecular weight, grouping the parent acids in the sequence monobasic > substituted monobasic, (including aromatic compounds) > dibasic > tribasic. The very considerable problem of the unambiguous identification of the structure of the ligand actually bound to the metal, i.e., of the number of ionized protons and the sites of ionization, becomes increasingly important.

VII. 2. Monobasic acids

Sunden's results for the series $\text{HCOOH} - \text{CH}_3\text{COOH} - \text{C}_2\text{H}_5\text{COOH}$ are regarded as tentative, since the reported experimental errors are all less than ± 0.2 and the results are confirmed by other workers within the limits of available evidence. Thus for acetic acid, the polarographic values (53C, 54Ca, 57C) give $\log \beta_3 = 9.8 \pm 0.8$, but since the work of these authors give high results for halide complexes (see Section IV. 3.), a corrected value of $\log \beta_3 \approx 8.5$ would be more reasonable; Sunden finds $\log \beta_3 = 7.9$, which gives some confidence in his other values for constants up to K_3 . The most recent results (73T) appear to be too low, and are rejected, as are those for chloroacetic acid, both because of a lack of correlation with pKa and because of the order $K_2 > K_3 > K_1$. For di- and trichloroacetic acids, the K_1 values are doubtful, in part because $K_2 > K_1$ in each case, but the K_1 values appear to have a reasonable dependence upon pKa (see Fig. 1, and below).

For glycolic acid, Sunden's value for K_1 is supported by three separate measurements, from which one finds

$$\log K_1 = 2.99 \pm 0.05 \quad (\text{recommended})$$

for the range 0.3 - 2.0 perchlorate (H or Na). The values for K_2 and K_3 in such media are also in good agreement

$$\left. \begin{array}{l} \log K_2 = 2.49 \pm 0.1 \\ \log K_3 = 1.70 \pm 0.1 \end{array} \right\} \quad \text{tentative}$$

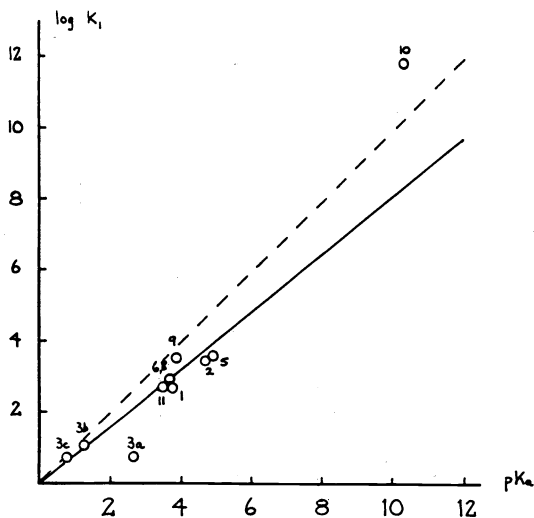
and the K_4 and K_5 values in Table 9 (entry 6a) must also be treated as better than doubtful. The polarographic value for β_3 again appears to be too high and is rejected.

For lactic acid, the two series of measurements are in good agreement, but since the temperature and pH range of one study (72Sd) are not stated by the

authors, the earlier set of results are tentatively accepted. A similar agreement exists in the case of the isomer 3-hydroxypropionic acid, where the solvent extraction work (68T) supports the extensive potentiometric titration studies (72Sa), so that the latter values for K_1 and K_2 are tentatively accepted, as are the measurements by the same workers on other 3-substituted propionic acids.

There is little to be said concerning the results for the remaining monobasic acid systems. All (i.e. entries (2-23) are doubtful or rejected either because the experimental accuracies are not known, or because the conditions are not specified, or both. The two sets of measurements on amino acids (76K, 77K) unfortunately show little agreement in those cases for which duplicate values are available (Entries 24 and 27), and neither paper quotes experimental errors.

Fig. 1 shows a graph of $\log K_1$ versus pK_a for those cases where K_1 values are tentative or recommended; the pK_a values are either from measurements associated with the determination of K_1 , or from refs 64S and 72Sa. The points generally lie within ~ 0.25 log units of a straight line drawn through the



origin, except for 3-hydroxy and 3-mercaptopropionic acid (latter point not shown on the graph). It is obviously tempting to discuss such deviations in terms of differing degrees of ligand chelation (see, e.g. (72Sa)), but such speculation seems profitless in the absence of structural information on the mode of ligation in such systems. The value for K_1 for chloroacetic acid does not lie on the line drawn, which must call this determination into question.

VII. 3. Dibasic acids

Preparative studies have shown that $[\text{Inox}_3]^{3-}$ and $[\text{Inox}_2(\text{H}_2\text{O})_2]^-$ anions are stable in the crystalline state (75C), but the stability constants for oxalate complexes of indium lack any certainty. The values of $\log K_1 = 5.30$, $\log K_2 = 5.22$ (66H) are of unstated accuracy, but are in keeping with $\log \beta_3 = 14.7$ (63S), which is tentatively accepted. The earlier value for β_2 (49L) is rejected; the remaining results are doubtful. Re-investigation of this system is obviously needed.

TABLE 9. Stability constants for indium(III) carboxylate species.

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
1	Formic acid CH ₂ O ₂ HL	53S	emf (ligand, In)	2 NaClO ₄	20	?	K ₁ 2.74±0.03 K ₂ 1.98±0.02 K ₃ 0.98±0.05 K ₄ 1.0 ±0.1	Hydrolysis not significant Polynuclear complexes negligible	Tentative K ₁ -K ₄
2a	"	80Sa	polarography	0.5 ClO ₄ ⁻	?	?	K ₁ 2.60		Rejected
	Acetic acid C ₂ H ₄ O ₂ HL	53S	emf (ligand, In)	2 NaClO ₄	20	?	K ₁ 3.50±0.02 K ₂ 2.45±0.05 K ₃ 1.95±0.05 K ₄ 1.18±0.08 K ₅ 0.15±0.15 K ₆ 1.11±0.2	See (1)	See text
2b	"	53C, 54Ca	polarography	2 NaClO ₄	25	4.64	β ₃ 9.0 ±0.2	Soln. buffered by HL + NaL	"
2c	"	57C	polarography	0.5 ClO ₄ ⁻	25	3-4	β ₃ 10.6	InL ₃ prepared	"
2d	"	73T	extraction into BEHP	0.2-2 NaClO ₄	25	?	K ₁ 2.91 K ₂ 2.11	Values for I = 0 by extrapolation	"
2e	"	80Sa	polarography	0.5 ClO ₄ ⁻	?	?	K ₁ 3.26		Rejected
3	Chloroacetic acids Cl _n CH _{3-n} COOH								
3a	ClCH ₂ COOH	73L	as (2d)	as (2d)	25	?	K ₁ 0.71 K ₂ 1.61 K ₃ 1.07		Rejected
3b	Cl ₂ CHCOOH	74La	as (2d)	1.0	25		K ₁ 1.03 K ₂ 1.27		Doubtful Rejected
3c	Cl ₃ CCOOH	74La	"	"	"		K ₁ 0.80 K ₂ 0.81		Doubtful Rejected

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
4	Glyoxylic acid HCO ₂ COOH C ₂ H ₂ O ₃	76C	polarography	1	30	?	K ₁ 7.30		} Rejected
							K ₂ 0.40		
							K ₃ 1.00		
							K ₄ 0.70		
							K ₅ 2.50		
5a	Propionic acid	53S	as (1)	2 NaClO ₄	20	?	K ₁ 3.57±0.02	See (1)	} All tentative
							K ₂ 2.79±0.04		
							K ₃ 1.79±0.10		
							K ₄ 0.93±0.15		
							K ₅ 1.03±0.2		
5b	"	80Sa	polarography	0.5 ClO ₄ ⁻	?	?	K ₁ 3.61		} Rejected
6a	Glycolic acid C ₂ H ₄ O ₃ HOCH ₂ COOH	53S	emf, ligand	2 NaClO ₄	20	?	K ₁ 2.93±0.03	See (1)	} See text
							K ₂ 2.59±0.04		
							K ₃ 1.69±0.09		
							K ₄ 0.67±0.06		
							K ₅ 0.73±0.15		
6b	"	57C	polarography	0.5 ClO ₄ ⁻	25	3.0-5.0	β ₃ 9.5	InI ₃ prepared	} "
6c	"	60W	extraction into DNNS in heptane	0.3 HClO ₄	25	-	K ₁ 3.15	pK(HI) 3.64 No higher complexes proposed	} "
6d	"	60W	pH titration,	corr. to μ=0.14	25	1.5-12.0	K ₁ 2.95		} "
6e	"	76S	TTA extraction	1 NaClO ₄	30	?			} "

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
6f	"	68T	extraction into BEHP in toluene	0.5 ClO ₄ ⁻	25	2.04	K ₁ 2.94 K ₂ 2.40 K ₃ 1.61	pK(HL) 3.61	See text
6g	"	70Ka	conductimetric, various non-aq. solvents		25	-	K ₁ given for solvent systems studied.	evidence of complex formation	Doubtful
7	Thioglycolic acid HSCH ₂ COOH	76S	TTA extraction	1 NaClO ₄	30	?	?		
8a	Lactic acid, 2-hydroxy- propionic acid C ₃ H ₆ O ₃	68T	see (6f)	0.5 NaClO ₄	25	2.00	K ₁ 2.96 K ₂ 2.60 K ₃ 1.64	pK(HL) 3.68	See text
8b	"	72Sd	extraction into TTA in CHCl ₃	1 NaClO ₄	?	?	K ₁ 3.17 K ₂ 3.10 K ₃ 1.98	"pH low enough to suppress hydrolysis"	" "
9a	3-hydroxy- propionic acid C ₃ H ₆ O ₃	68T	See (6f)	0.5 NaClO ₄	25	2.10	K ₁ 3.52 K ₂ 2.66 K ₃ 2.06	pK(HL) 3.92 alternative value K ₂ 2.81	" "
9b	"	72Sa	pH titration	0.1-0.4 NaClO ₄	25, 35, 45		μ=0.1, 25C K ₁ 3.75±0.03 K ₂ 3.04±0.05	pK(HL) measured over range of T and μ. Values given for 3 temps and 4 ionic strengths; data extrapolated to μ = 0	
9c	"	72Sa		0.1 NaClO ₄			ΔH ₁₊₂ +36+6 ΔS 250±13	Values also at μ = 0. ΔH derived from temp. dependence of β ₂	Tentative

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K_n	Comments	Rating
10	3-mercaptopropionic acid $C_3H_6O_2S$	72Sa	as above	0.1 NaClO ₄	25, 35, 45		$\mu=0.1, 25^\circ C$ K_1 11.87±0.03 K_2 7.66±0.05 K_3 6.25±0.05 ΔH_{1+2} -70±8 ΔS_{1+2} 260±20	as above	All tentative
11	3-aminopropionic acid $C_3H_7O_2N$	72Sa	as above	"	25, 35, 45		$\mu=0.1, 25^\circ C$ K_1 2.72±0.03 K_2 2.54±0.05 ΔH_{1+2} +31±6 ΔS_{1+2} 200±13	as above pK(HL) 3.58	All tentative
12	Levulinic acid $C_5H_8O_3$ $CH_3COCH_2CH_2COOH$	71P	polarography	?			K_1 3.0 K_2 1.6 K_3 1.0 K_4 0.5		Doubtful
13	DL-pencillamine, 2-amino-3-methyl- 3-mercaptopbutyric acid $C_5H_{11}NO_2S$ HL	76Ka	potentiometric	0.1 KNO ₃	21		K_1 15.33 K_2 14.46 K(InLH) 18.86 K(InL(LH)) 33.39 K(In(L)OH) 11.25		Doubtful
14	Methionine $C_5H_{11}O_2NS$ $CH_3SCH_2CH_2CH(NH_2)COOH$	77R	polarography	I = 1	30		K_1 8.23 K_2 5.69		Doubtful
15	Gluconic acid $C_6H_{12}O_7$	70P	?	?	?	?	?	complex formation reported	-
16	Quinic acid 1,3,4,5 tetra- hydroxycyclohexane- 1-carboxylic acid $C_7H_{12}O_6$	70T	solvent extraction BEHP	?	?	?	K_1 2.56 K_2 2.83	pK(HL) 3.3 $K_2 > K_1$	Rejected

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
17	Salicylic acid C ₇ H ₆ O ₃	73S	?	0.2 NaClO ₄ 75% EtOH	30	?	K ₁ 2.59		Doubtful
18	Anthranilic acid C ₇ H ₇ O ₂ N	73S	?	"	"	?	K ₁ 11.1 K ₂ 8.90 K ₃ 5.96		Doubtful
19	5-nitrosalicylic acid C ₇ H ₅ O ₅ N HL	70K, 71K	potentiometric	?			K ₁ 7.5 K ₂ 6.3 K ₃ 5.9	IR study of complexes	Doubtful
20	Phenylacetic acid C ₈ H ₈ O ₂ HL	57C	polarography	0.5 ClO ₄ ⁻ 20% EtOH	25	3.0- 3.75	β ₃ 10.2	InL ₃ prepared	Doubtful
21	Mandelic acid 2-phenyl-2-hydroxy- acetic acid C ₈ H ₈ O ₃ HL	70T	solvent extraction See (16)	?	?	?	K ₁ 2.58 K ₂ 2.82	K ₂ > K ₁ !	Doubtful
21b	"	57C	polarography	0.5 ClO ₄ ⁻	25	3.0-	β ₃ 9.3	InL ₃ prepared	Rejected
21c	"	76S	TTA extraction	?	?	?	?	?	?
22	Acetylsalicylic acid C ₉ H ₈ O ₄ HL	68Ga	polarography	1 NaClO ₄	30	?	K ₁ 4.48 K ₂ 0.22 K ₃ 1.78 K ₄ 0.33 K ₅ 1.32	Reduction "quasi -reversible" Order of K _n !	Rejected
23	1-hydroxy-1- (dibutylphosphinyl)- propionic acid C ₁₁ H ₂₃ O ₄ P HL	70Ta	spectropho- metric	0.1 NaClO ₄	25	5	K ₁ ~ 8.8	pK[HL] 2.94 Metal hydroxides ppts. at pH at which complex formation should be studied.	Rejected
24a	DL-α- Alanine	76K	pH titration	0.01 HL, 3.3mM InCl ₃	24	?	K ₁ 8.40 K ₂ 8.25	No errors quoted	Doubtful

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
24b	DL-α- Alanine	77K	polarography	0.2 NaClO ₄	30	5	K ₁ 10.25 (10.67) K ₂ 5.96 (5.55)	Two different methods of calculation. No errors quoted.	Doubtful
24c	"	81M	polarography	0.5 (KNO ₃)	30	?	K ₁ 9.18 K ₂ 7.31	No errors quoted.	Doubtful
25	β- Alanine	76K	pH titration	as (24a)	24	?	K ₁ 8.30 K ₂ 8.22	as (24a)	Doubtful
26	L- Asparagine	76K	"	"	"	"	K ₁ 7.17 K ₂ 7.21	"	Doubtful
27a	Glycine	76K	"	"	"	"	K ₁ 8.22 K ₂ 8.02	"	Doubtful
27b	"	77K	polarography	0.2 NaClO ₄	30	5	K ₁ 9.85 (10.10) K ₂ 6.08 (5.82)	as (24b)	Doubtful
28	DL- Leucine	76K	pH titration	as (24a)	24	?	K ₁ 7.76 K ₂ 7.65	as (24a)	Doubtful
29	L- Leucine	76K	"	"	"	"	K ₁ 8.26 K ₂ 7.48	"	Doubtful
30	DL- Methionine	76K	"	"	"	"	K ₁ 7.75 K ₂ 7.42	"	Doubtful
31	DL- Phenylalanine	76K	pH titration	as (24a)	24	?	K ₁ 7.36 K ₂ 7.22	as (24a)	Doubtful
32	L- Proline	76K	"	"	"	"	K ₁ 9.04 K ₂ 8.64	"	Doubtful
33	DL- Serine	76K	"	"	"	"	K ₁ 7.53 K ₂ 7.05	"	Doubtful
34	DL- Taurine	76K	"	"	"	"	K ₁ 7.44 K ₂ 7.13	"	Doubtful

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
35	DL- Valine	76K	pH titration	as (24a)	24	?	K ₁ 8.28 K ₂ 7.52	as (24a)	Doubtful
36a	Oxalic acid H ₂ L C ₂ H ₂ O ₄	49L	pH titration		18 (?)	3- 8	β ₂ 8.6	pptn. of InL ₂ ⁻ complexes noted pK ₁ [H ₂ L] 3.18	See text Rejected
36b	"	60W	extraction into DNNS in heptane	0.3 HClO ₄	25	-	In ³⁺ + HL ⁻ ⇌ InHL ₂ ⁺ K 3.08	pK ₁ [H ₂ L] 1.28	Doubtful
36c	"	63S	extraction into 8-quinolol in CHCl ₃	0.1 KClO ₄	20	3-5	β ₃ 14.7+0.1		Tentative
36d	"	66H	extraction into TTA in CHCl ₃	1 NaClO ₄	25	3- 3.4	K ₁ 5.30 K ₂ 5.22	No need to postulate InL ₃ ³⁻	Doubtful
37	Maleic acid, H ₂ L (cis) HOOC.C ₂ H ₂ .COOH C ₄ H ₄ O ₄	67Na	polarography 0.2 NaClO ₄		25	3- 4.5	K ₁ 5.0 K ₂ 2.1 K ₃ 3.8	K ₃ > K ₂ !	Rejected
38	Succinic acid, H ₂ L C ₄ H ₆ O ₄	53C, 54Ca	polarography	0.5 ClO ₄ ⁻	25	3.3	K ₁ 6.8+0.3 [In(OH)L ₂] ₂ ⁻ 18.5+0.3	In(OH)L prepared	Rejected
39a	Malic acid, H ₂ L C ₄ H ₆ O ₅	53C, 54Ca	polarography	0.5 ClO ₄ ⁻	25	2.7- 3.4	K ₁ 6.8+0.2 [In(OH)L ₂] ₂ ⁻ 18.9+0.1	dL H ₂ L used	Rejected
39b	"	72Sb	pH titration, temp. dependence	0.1-0.4 NaClO ₄	25, 35, 45		I 0.1, 25°C K ₁ 4.60 K ₂ 3.61	Values for K ₁ , K ₂ and pK ₁ , pK ₂ at 3 temps and 4 ⁻ ionic strengths; also corr. to I=0 pK ₁ [H ₂ L] 4.59, pK ₂ 3.05 No ionization of OH group	Doubtful
			Corr. to I=0		35		ΔG ₁₊₂ ⁰ -50.4 ΔH ₁₊₂ ⁰ +43.5 ΔS ₁₊₂ ⁰ +304	Errors?	

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
40	Aspartic acid, H ₂ L H ₂ N-CH-COOH H ₂ C-COOH C ₄ H ₇ O ₄ N	72Sb	as above	0.1-0.4 NaClO ₄ Corr. to I = 0	25, 35, 45 35		I 0.1, 25°C K ₁ 3.26 K ₂ 2.84 ΔG ₁₊₂ ^o -37.7 ΔH ₁₊₂ ^o +41.8 ΔS ₁₊₂ ^o +304	as above pK ₁ [H ₂ L] 3.70, pK ₂ 1.84 Errors?	Doubtful
41	Thiomalic acid, H ₂ L HS-CH-COOH H ₂ C-COOH C ₄ H ₆ O ₄ S	72Sb	as above	0.1-0.4 NaClO ₄ Corr. to I = 0	25, 35, 45 35		I 0.1, 25°C K ₁ 14.47 K ₂ 11.29 ΔG ₁₊₂ ^o -158 ΔH ₁₊₂ ^o -51 ΔS ₁₊₂ ^o +346		Doubtful
42a	Tartaric acid, H ₂ L 2, 3-dihydroxybutane -dioic acid, C ₄ H ₆ O ₆	53C, 54Ca	polarography	0.5 ClO ₄ ⁻	25	1.75 -3.5	In (dHL) ₂ 6.8±0.1 In (mesoHL) ₂ 7.5±0.1	Crystalline In(OH) (L) ₂ H ₂ O identified. pK ₁ [H ₂ L] 3.77, pK ₂ 2.60	Rejected
42b	"	63C	extraction into 8-quinolol in CHCl ₃	0.1 KClO ₄	20	4.5- 12	K ₁ 4.48±0.04 In (OH) (dL) ₂ 18.5±0.1 In (OH) (mesoL) ₂ 18.9±0.1		Doubtful
42c	", but treated as H ₄ L	71B	pH titration	1 NaNO ₃	?	3-9	K ₁ [In(HL)] ₃ 12.37 K ₂ [In(HL) ₂] ₆ 10.80 K ₃ [In(HL) ₃] ₃ 7.15		Rejected
43	Iminodiacetic acid, H ₂ L HN(CH ₂ COOH) ₂ C ₄ H ₇ NO ₄	66M	potentiometric titration	0.3 KCl	25	3- 11	K ₁ 9.54 K ₂ 8.87	Reversibility of Rejected electrode pro- cess? K ₂ may refer to ₂ InL ₂ or [InL ₂ OH]	Rejected
44	HIMDA, H ₂ L C ₆ H ₁₁ O ₅ N ₂	63Ra	ion exchange	0.5	?	?	K ₁ 11.0±0.1		Doubtful

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
45	Phthalic acid, H ₂ L C ₈ H ₆ O ₄	78S	polarography	?	30	1.25- 4.5	K ₁ 5.00 K ₂ 2.81 K ₃ 1.22		Doubtful
46a	Citric acid, H ₃ L 2-hydroxypropane, 1, 2, 3-carboxylic acid C ₆ H ₈ O ₇	63Rb	potentiometric titration, anion exchange resin cation exchange resin	0.1 KNO ₃ 0.5 NaClO ₄	?	1- 11 0.6 -1	In ³⁺ + H ₃ L ⇌ InLH ⁺ + 2H ⁺ K 1.05+0.04 K ₁ 6.18	Na[InL(H ₂ O) ₂] and H[InL(H ₂ O) ₂] prepared. charge on com- plexes identified by ion exchange	Rejected Rejected
46b	"	77L	extraction into BEHP	1 NaClO ₄	25	7.1 1.5- 2.5	K (ML) 10.58+ 0.03 K (MHL) 6.17+ 0.09		Rejected
46c	" , H ₄ L:	78Ta	polarography	3.2 NaClO ₄	25	0.01 -0.5	In ³⁺ + H ₄ L ⇌ In(H ₂ L) ⁺ + 2H ⁺	Evidence for H ₂ L ₂ ⁻ as predom- inant ion	Rejected (see text)
47a	Nitrilotriacetic acid, H ₃ L N(CH ₂ COOH) ₃	63S	extraction (see entry 33)	0.1 KClO ₄	20	?	β ₂ 24.4		See text
47b	"	63Rb	cation exchange resin	0.5 NH ₄ ClO ₄	?	0.3 -1	K ₁ 14.88±0.09	pK ₁₊₂₊₃ 13.53	"
47c	"	65Za	spectrophotometric (FeL complex)	?	20- 22	2.5- 3.4	K ₁ 15.88		"
47d	"	67B	redox emf (FeII/FeIII)	0.1 NaClO ₄	20	2	K ₁ 16.9		"
48	HEDTA, H ₃ L C ₁₀ H ₁₈ O ₇ N ₂	63Ra	ion exchange	0.5	?	?	K ₁ 17.16±0.03		Doubtful
49	EDTA, H ₄ L C ₁₀ H ₁₆ O ₈ N ₂	78A	See Comments	0.1 KNO ₃ 0.1 NaClO ₄	20 20	-	K ₁ 24.95 K ₁ 24.37 pK[InHL] 1.5 pK[InL] 8.63	Critical review of refs 54Se, 56S, 63Ra, 63S, 65B, 65Z, 67B by 78A	All tentative

TABLE 9. (continued)

Entry	Parent Acid	Ref.	Method (concn. M)	Medium	T (°C)	pH	log K _n	Comments	Rating
50	(trimethylene- dinitro)-tetra acetic acid, H ₄ L C ₁₁ H ₁₈ O ₈ N ₂	67B	redox (Fe ^{II} / Fe ^{III})	0.1 NaClO ₄	20	?	K ₁ 21.15 pK [InL] 1.64		Doubtful
51a	EDTA, H ₄ L C ₁₂ H ₂₀ O ₈ N ₂	65Z	spectroscopic	?	18- 20	?	K ₁ 22.67		Doubtful
51b	"	65B	redox (Fe ^{II} / Fe ^{III})	0.1 NaClO ₄	20	?	K ₁ 25.5		Doubtful
52a	[(2,2'-thiodi- ethylene)dinitrilo] tetra-acetic acid, H ₄ L C ₁₂ H ₂₀ O ₈ N ₂ S	66Z	spectroscopic	I ≈ 0	18- 20	?	K ₁ 24.1		Doubtful
52b	"	67B	redox (Fe ^{II} / Fe ^{III})	0.1 NaClO ₄	20	?	K ₁ 20.26 pK (InHL) 1.88 InL + OH ⁻ ⇌ InOHL ²⁻ K 4.2		Doubtful
53a	CDTA, H ₄ L C ₁₄ H ₂₂ O ₈ N ₂	63Ra	ion exchange	0.5	?	?	K ₁ 25.05±0.09		Doubtful
53b	"	67B	redox (Fe ^{II} / Fe ^{III})	0.1 NaClO ₄	20	?	K ₁ 28.74		Doubtful
54	HDTA, H ₄ L C ₁₄ H ₂₄ O ₈ N ₂	65Z	spectroscopic	?	18- 20	?	In ³⁺ + HL ³⁻ ⇌ InHL K 9.03		Doubtful
55a	DTPA, H ₅ L C ₁₄ H ₂₃ O ₁₀ N ₃	63Ra	ion exchange	0.5	?	?	K ₁ 27.65±0.04		} (Mean) Doubtful
55b	"	65Z	spectroscopic	?	18- 20	?	K ₁ 28.42	mean 28.4±0.8	
55c	"	67B	redox (Fe ^{II} / Fe ^{III})	?	20	?	K ₁ 29.0		
55d	DTPA, H ₅ L C ₁₄ H ₂₃ O ₁₀ N ₃	74Lb	extraction	1.0 NaClO ₄	?	?	K [InL] 27.25±0.02 K [InHL] 18.45±0.02 K [InH ₂ L] 11.68±0.02 K [In(H ₃ L) ₂] 14.17±0.02		} Rejected

The polarographic results on maleic, succinic acid and malic acids are all rejected, in line with the previous discussion. The measurements on malic, aspartic and thiomalic acids (72Sb) are all tentatively accepted, despite the absence of stated errors, given the confirmation by others of the work by the same authors on substituted propionic acids (72Sa) (see VI. 2. above).

The results for tartaric acid raise a point noted earlier and to which we shall return later, namely the problem of identifying the ligand(s) involved in the equilibria being studied. The three sets of values are all predicated on different species, and even on differing numbers of ionizable protons (i.e., H_2L or H_4L) (cf. entries 42a, 42c). Here surely is a case, as elsewhere, in which the use of thermodynamics and the law of mass action has little point unless coupled with (say) spectroscopic identification of the species present in solution. For the present, the results on tartaric acid are all regarded as doubtful or rejected. Similarly, for iminodiacetic acid, doubts have been registered by the authors (66M) as to the reversibility of the electrode process, leading to uncertainty as to the equilibria actually being studied, and here again the results are therefore rejected.

VII. 4. Tribasic and higher acids

The problems noted in the last paragraph are the more important with tribasic acids, as illustrated by citric acid, where the results are all rejected because of the failure to identify the equilibria unambiguously. There is even disagreement as to whether citric acid is to be regarded as tri- or tetrabasic (63Rb, 78Ta). Other authors (78Sa) have commented on the complications of the polarographic reduction processes in In^{3+} /citrate media.

The parent acids in this section include many of the derivatives or analogues of ethylenediaminetetraacetic acid, which itself has been the subject of a critical review by Anderegg (78A), and results for this ligand are therefore not discussed in the present work. Complexes of this and similar ligands with ^{111}In have been used for in vivo investigations (79G). For nitrilotriacetic acid (entry 47), three reports yield a mean of $\log K_1 = 15.9$ (doubtful) for differing media. In other cases (eg. EDTA, CDTA), the agreement between different authors is poor, and one can only suggest that the results of 67B can be treated as being reliable because the values derived in this paper for the $In/EDTA$ system find some independent confirmation. For DTPA, the mean of 28.4 for $\log K_1$ again confirms the work in 64B.

In general, one can only repeat the opinion that physical methods must be coupled to thermodynamic studies if the equilibria involved in such complicated systems are to be properly understood.

VII. 5. Mixed ligand systems

Despite the problems of arriving at a satisfactory series of results for such ligands as NTA, EDTA, etc., a number of investigations have been made of systems in which more than one ligand is involved. Results have been published on $In/EDTA/halide$ (78F), $In/EDTA/NCS$ (78E) and $In/NTA/NCS$ (79E)

systems. Other authors have reported stability constants for In/NTA with various polybasic acids (78A), and for In/NCS with complexones (79Ea). The comments made above as to thermodynamic significance must also apply to these mixed ligand systems.

VIII. MONOBASIC BIDENTATE CHELATING AGENTS

Because of the importance of bidentate chelating agents such as acetylacetonone (Hacac, 2,4-pentanedione) in the development of coordination chemistry, it seems appropriate to give separate consideration to the stability constants for complexes of these ligands. The appropriate neutral InL_3 complexes are structurally well established, and the solution chemistry (e.g., ligand exchange) has been the subject of spectroscopic and other investigations (75C).

The three sets of results for indium/acac (Table 10) are not in particularly good agreement, and the unweighted means of the values (0-0.5 $NaClO_4$, 25-30°C) give

log K_1	8.20 \pm 0.2	<u>tentative</u>
log K_2	6.9 \pm 0.5	<u>doubtful</u>
log K_3	6.2	<u>doubtful</u>

The β_3 value for In/benzoylacetone is doubtful; the results of extraction into different organic solvents are accepted as giving different stability constant results (cf. Beck (75B)). For thenoyltrifluoroacetone (TTA) the apparent agreement between two sets of experiments would be more encouraging if one set of conditions were clearly defined (72Sc). The values of Schweitzer and Anderson (68S) are tentatively accepted, being confirmed both by other $K_1 - K_3$ results, and by a previously reported value for β_2 (56R). The results for a series of substituted diketonates, including TTA (72B), apply to mixed aqueous-organic solutions, and so cannot be compared with the results just noted.

For 8-hydroxyquinoline (Hoxine) the agreement between the similar but independent measurements is such that one can recommend the results (0.1 $NaClO_4$, 25°C)

log K_1	12.00 \pm 0.05
log K_2	11.95 \pm 0.05
log K_3	11.45 \pm 0.05

The situation with the solubility product of $In(oxine)_3$ is less satisfactory, and in view of the disagreement between the two results, both should be rejected. A recent study by Thompson (78Tb) refers to 50% (w/w) aqueous dioxane; constants for In/oxine are tentatively accepted, as are the conclusions for the apparently more complicated system involving 2-methyl-8-hydroxyquinoline in the same medium.

There are a number of papers, not available to the present reviewer, dealing with various derivatives of 8-hydroxyquinoline. In particular, the effect of halogen substitution at the C5-position of 8-mercaptoquinoline has been studied, with the order of stability (β_3) being 5-HL > 5-FL > 5-ClL > 5-BrL > 5-lL (68C, 69C); similarly 8-mercapto > 8-hydroxyquinoline (66B). Mixed

TABLE 10. Stability constants for indium(III) complexes with monobasic bidentate chelating agents.

Entry	Ligand	Ref.	Method	Medium (concn. M)	T (°C)	pH	log K_n	Comments	Rating
1a	2,4-pentanedione HL $C_5H_8O_2$	55I	potentiometric	corr. to I = 0	30		K_1 8.0±0.2 K_2 7.1±0.2	pptn. prevents detrn. of K_3 No interference from hydrolysis	See text
1b	"	58R	extraction into $CHCl_3$, C_6H_6 , CCl_4	I = 0.1	var- ied	var- ied	K_1 8.06 K_2 6.20	Quoted in (60S)	"
1c	"	66Ca	polarography	0.5 $NaClO_4$	25	0.7- 3.5	K_1 8.8 K_2 7.3 K_3 6.2		"
2	Benzoylacetone, HL $C_6H_5COCH_2COCH_3$	59R	extraction into $CHCl_3$, C_6H_6 or CCl_4		?	?	CCl_4 : β_3 20.7 C_6H_6 , or $CHCl_3$: β_3 20.85	Quoted in (60S)	Doubtful
3a	Thenoyltrifluoro- acetone, HL $C_4H_3SCOCH_2COCF_3$	56R	extraction into benzene	3 $NaClO_4$	25	2.7- 4.3	β_2 12.4	pptn. occurs at pH >5	See text
3b	"	68S	extraction into $CHCl_3$	0.1 $NaClO_4$	25	1-7	K_1 6.0±0.2 K_2 6.0±0.2 K_3 5.6±0.2 $In^{3+} + L^- + OH^-$ $\rightleftharpoons InL(OH)^+$ K_1 16.8 $In^{3+} + L^- + 2OH^-$ $\rightleftharpoons InL(OH)_2$ K_2 26.0 $In^{3+} + 2L^- + OH^-$ $\rightleftharpoons InL_2OH$ K_3 22.0		Tentative $K_1 - K_3$
3c	"	72sc	extraction into CCl_4	1 $NaClO_4$?	?	K_1 6.51 K_2 5.46 K_3 5.20	"pH low enough to suppress hydrolysis"	See text

TABLE 10. continued

Entry	Ligand	Ref.	Method	Medium (concn. M)	T (°C)	pH	log K _n	Comments	Rating
4	Substituted 1,1,1 trifluoro- methyl-β-di- ketonates CF ₃ COCH ₂ COR (HL)	72B	pH titration	0.1 Et ₄ NClO ₄ 46% dioxan	25		R 2-furyl 2-thienyl phenyl 2-naphthyl i-Bu t-Bu	K ₁ 5.93 K ₂ 5.45 0.05 throughout 5.97 5.76 5.85 5.95 pKa values also 6.93 6.65 reported in 6.78 6.40 same solvent. 6.85 6.56 K ₂ for phenyl probably too high	K ₁ Tentative K ₂ Doubtful
5a	8-hydroxy- quinoline, HL C ₉ H ₇ ON	68S	extraction into CHCl ₃	0.1 NaClO ₄	25	1- 6	K ₁ 12.0±0.2 K ₂ 11.9±0.2 K ₃ 11.4±0.2		See text
5b	"	65Zb	extraction into CHCl ₃ , C ₆ H ₆ , iAmOH	0.1 ClO ₄ ⁻	25	?	K ₁ 12.00 K ₂ 11.99 K ₃ 11.48	'Hydrolysis only affects values at high pH'	"
5c	"	78Tb	potentio- metric	50% (W/W) aq. dioxane I = 0.1	25	?	K ₁ 13.30±0.01 K ₂ 12.16±0.01 K ₃ 10.97±0.02		"
5d	"	49L	pH titration	?	18?	2.65	K _{sp} -36.7		Rejected
5e	"	57P	?	?	?	?	K _{sp} -31.34		Rejected
6	2-methyl-8- hydroxyquinoline HL	78Tb	potentio- metric	50% (W/W) aq. dioxane I = 0.1	25	?	β _{1,2,2} 32.00±0.08 β _{1,0,2} 25.97±0.05 β _{1,-1,2} 20.74±0.01	values for InpHg ^{I_n} complexes	Tentative
7	8-mercapto- quinoline C ₉ H ₇ NS HL	66B	extraction into CHCl ₃	?	20?	?	β ₃ 41.3	InL ₃ ppt. at pH > 3.5 (68Sa)	Doubtful
8	5-bromo-8- mercaptoquinoline	67C	extraction into CHCl ₃	I = 0.1	20	9- 8.3	β ₃ 43.6		Doubtful

complexes of oxine and acetate (68Sa) and of oxine and 8-mercaptoquinoline (66A) have also been reported. The whole field of oxine complexes has been reviewed by Stary, Zolotov and Petrukhin (79Sc).

IX. MISCELLANEOUS ORGANIC LIGANDS

In this section are collected together the stability constants for a number of ligands which do not conveniently fit into any of the previous sections. (Table 11) In many cases the parent compounds, and/or the complexes are coloured, and these systems therefore readily lend themselves to spectrophotometric investigation. Many of the compounds studied are in fact indicators, and have been used as such in complexometric titrations, so that knowledge of the extent of their interaction with a metal ion is therefore of considerable use to the analytical chemist, and the results in Table 11 represent valuable source material in this context. A quantitative understanding of the complexation of ^{111}In by biochemically active molecules may also become important as the use of this radioactive tracer increases, and an interesting study (79K) reports values for complexes with transferrin ($\log K_1 = 30.5$, $\log K_2 = 25.5$; doubtful). As reliable stability constants however, most of the values in Table 11 are at best doubtful, since in only very few cases is the ligand which actually complexes unambiguously identified, so that the reported constant may apply to an ill-defined equilibrium, and in many cases to undefined temperature. The few cases in which two sets of results are reported for the same ligand do not give concordant values. As noted earlier, the precise structural identification of the structure of the anion(s) derived from the parent acids under different pH conditions is itself a major problem which cannot be solved by mass action studies alone. One paper (71D) claims to offer a theoretical approach to this problem. Until such questions are capable of solution, it is inevitable that stability constants derived as in most of the work reported in Table 11 must be of little value. The only system for which tentative values are available is in the case of N-phenylbenzohydroxamic acid, where the work of Schweitzer and Anderson (68S) is preferred over that of the Russian workers (65H) because the latter gives no experimental errors.

A small number of studies have reported stability constants for such systems as $\text{In}(\text{OH})\text{L}_2\text{Y}_2$ (80G) and InL_2Br_4 (79Ca), where L = bromopyrogallol red and Y = 2,2'-bipyridine or 1,10-phenanthroline (cf. Table 11, entry 14). The comments made earlier about such measurements (Section VII. 5.) must also apply here.

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TABLE 11. Stability constants for complexes of indium(III) with miscellaneous organic ligands.

Entry	Ligand	Ref.	Method	Medium (concn. M)	T (°C)	pH	log K _n	Comments	Rating
1	pyrocatechol C ₆ H ₆ O ₂	74Ka	spectrophotometric	0.1 NaClO ₄	?	1.5- 10.5	K ₁ 18.71 β ₃ 34.63	Refs to prep. studies of InL, InL ₂ , InL ₃ Correction made for In ³⁺ hydrolysis	Doubtful
2	pyrogallol C ₆ H ₆ O ₃	74Ka	"	"	?	1.5 -7	K ₁ 18.64 β ₃ 34.44	"	Doubtful
3a	Tiron C ₆ H ₆ O ₈ S ₂	74Ka	"	"	?	1.5- 10.5	K ₁ 18.12 β ₃ 33.66	"	Rejected
3b	"	65N	spectrophotometric	varying I	29	3.5	I=0 (extrap). 4.46 I=0.05 3.91±0.03 I=0.1 3.79±0.05 I=0.2 3.72±0.04 ΔH 6.0±0.5 ΔS 93 ±1	ppn. of In(as hydroxide?) at pH > 4 K by Job's plot	Rejected
4	purpuric acid, H ₅ L C ₈ H ₅ O ₆ N ₅ (murexide = H ₄ L.NH ₃)	65G	spectrophotometric	0.1 KNO ₃	12	3.0	In ³⁺ + H ₄ L ⁻ ⇌ InH ₄ L ₂ ⁺ K 4.61±0.2	kinetics investi- gated by temp. Jump	Tentative
5	TAR H ₂ L C ₉ H ₇ O ₂ N ₃ S	67N	potentiometric titration, & spectrophotometric	0.1 NaClO ₄ , 50% MeOH	25	?	In ³⁺ + HL ⇌ InH ₂ L *K 10.8±0.2		Doubtful
6	4-COOH-TAR C ₁₀ H ₇ O ₄ N ₃ S H ₃ L	71D	spectrophotometric	? Ethanol soln of ligand	?	1- 10	K ₁ 4.36±0.4 K ₂ 7.40 ⁻	Both const. conditional ML in pH range 1 - 3 ML ₂ at pH 5.5 Calcs. on structure of H ₃ L at diff. pH	Rejected
7a	pyridylazo- resorcinol (PAR) H ₂ L C ₁₁ H ₉ O ₂ N ₃	66Da	Spectrophotometric	?	25	4.0	β ₂ (?) 9.3	K not identified. Complex said to be anionic (ML ₂ ?)	

TABLE 11. (continued)

Entry	Ligand	Ref.	Method	Medium (concn. M)	T (°C)	pH	log K_{L}	Comments	Rating
7b	Pyridylazo- resorcinol (PAR) H_2L $\text{C}_{11}\text{H}_9\text{O}_2\text{N}_3$	78Sb	Spectrophotometric	50% (v/v) aq. dioxan I = 0.2 (NaClO ₄) ?		>5.0	K_1 12.54 K_2 11.46	No errors quoted	Rejected
8	2,2'-dihydroxyazo- benzene H_2L $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2$	62K	Spectrophotometric	0.1 KCl 35% EtOH	25	5.5- 6.5	$\text{In}^{3+} + \text{H}_2\text{L}$ $\rightleftharpoons \text{InL}^{2+} +$ 2H^+ K = 5.2 $\text{InL}^{2+} + \text{H}_2\text{L}$ $\rightleftharpoons \text{InL}_2^+ +$ 2H^+ K = 8.0	no chelation below pH 4	Doubtful
9	4-methyl-2- (2'-pyridylazo) phenol HL $\text{C}_{12}\text{H}_{11}\text{ON}_3$	68W	spectrophotometric	2.0 (HOAc + OAc ⁻) 0.4% dioxan	25	2- 5	K_1 11.8 $\text{InL}_2^{2+} + \text{A}^-$ $\rightleftharpoons \text{InAL}$ K 3.03 $\text{InL}_2^+ + \text{A}^-$ $\rightleftharpoons 2\text{InAL}_2$ K 1.92 $\text{InL}_3 + \text{A}^- \rightleftharpoons$ InAL_3 K 1.25 (HA = CH ₃ COOH)		Doubtful
10a	N-phenylbenzo- hydroxamic acid $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}$ HL	68S	extraction into CHCl ₃	0.1 NaClO ₄	25	1- 7	K_1 9.2+0.2 K_2 9.2+0.2 K_3 7.9+0.2	InL_3 shown to org. phase species	Tentative
10b	"	65H	extraction into CHCl ₃ or benzene	I = 1	20	2- 3.5	K_1 9.40 K_2 8.94 K_3 8.58		See text
11	Leucoalizarin-S $\text{C}_{14}\text{H}_9\text{O}_7\text{S}$ H_4L	71N	spectrophotometric	1 NaClO ₄	?	1- 6	$\text{In}(\text{H}_4\text{L})^{2+}$ (pH 1.6) $\text{In}(\text{H}_3\text{L})^+$ K 8.4 (pH 6.0)	deoxygenated solns, under argon	Rejected
12	Kaempferol H_4L $\text{C}_{15}\text{H}_{10}\text{O}_6$	74M	spectrophotometric	? 34-40% EtOH	?	5.9- 6.3	K_1 10.51	$[\text{In}(\text{OH})(\text{H}_3\text{L})_2]$	Rejected
13	Thoron $\text{C}_{16}\text{H}_{13}\text{O}_{10}\text{N}_2\text{S}_2\text{As}$	68G	spectrophotometric	?	25	3.0	K 9.9+0.4	site of complex- ing speculative Complex anionic, stable in pH range 3.5 - 6.5	Rejected
14	Bromopyrogallol red $\text{C}_{19}\text{H}_{10}\text{O}_8\text{Br}_2\text{S}$	69Pa	spectrophotometric	?	25	3.0	K_1 10.97		Rejected
15	Chrome Azurol S $\text{C}_{23}\text{H}_{16}\text{O}_9\text{Cl}_2\text{S}$	64M	spectrophotometric	?	25	4.0	4.4+0.1	equil. not identified. Complex stable at pH 3.5 - 5.5	Rejected

TABLE 11 continued

Entry	Ligand	Ref.	Method	Medium (concn. M)	T (°C)	pH	log K _n	Comments	Rating
16a	Xylenol orange C ₃₁ H ₃₂ O ₁₃ N ₂ S	66Db	spectrophotometric	?	25	4.0	5.0±0.1	Complex anionic Electrolytes cause pptn. of coloured complex Complex stable at pH 3.0 - 6.5	Rejected
16b	"	77Ka	spectrometric, pH titration	~0.1 NaClO ₄	20		K(In(H ₂ L) ⁻) 14.31 K(In(H ₂ L) ₂ ⁵⁻) 24.63		Rejected
17	5-(5-bromo-2- pyridylazo)-2- (methylamino)-p- cresol	66Gb	spectrophotometric	?	?	3- 5	6.62		Rejected
18	5-(3,5-dibromo-2- pyridylazo)-2- (ethylamino)-p- cresol	66Gb	spectrophotometric		?	2- 5	6.22		Rejected
19a	1-(2'-pyridylazo) -2-naphthol (PAN)	73T	polarography	I 0.06 50% EtOH	?	?	K 13.05±0.06		Rejected
19b	1-(2'-pyridylazo) -2-naphthol (PAN)	78Sb	spectrophotometric	50% (v/v) aq. dioxan I = 0.2 (NaClO ₄)	?	5.0	K ₁ 12.19 K ₂ 10.57	No errors quoted	Rejected
20	3,4-dihydroxy- benzene-azo 1'-naphthalene- sulphonic acid HL	76D	"			5	K [InL ₂] 8.21		Rejected
21	Calgamite	78Sb	spectrophotometric	50% (v/v) aq. dioxan I = 0.2 (NaClO ₄)	?	5.0	K ₁ 17.09 K ₂ 14.87	No errors quoted	Rejected
22	Socochrome Dark Blue	78Sb	spectrophotometric	50% (v/v) aq. dioxan I = 0.2 (NaClO ₄)	?	5.0	K ₁ 16.48 K ₂ 14.66	No errors quoted	Rejected
23	4-sulphonaphthol- (1-azo-1')-2,4- dioxylbenzene	77P	spectrophotometric	I = 0.1	20	?	K ₁ 13.60 K ₂ 32.39	Formation of InOH ₂ ²⁺ In(OH) ₂ ⁺ corrected	Rejected

Abbreviations Used Throughout Tables.

TTA	1-(2'-Thienyl)-4,4,4-trifluorobutane-1,3-dione (thenoyltrifluoroacetone)
BEHP	Bis-(2-ethylhexyl)phosphoric acid
BPHA	N-Benzoylphenylhydroxylamine
TNOA	Tri-n-octylamine
TIOA	Triisooctylamine
DNNS	Dinonylnaphthalenesulphonic acid
TBP	Tri-n-butyl phosphate

Proper Names of Polycarboxylic Acids in Table 9.

32.	HLMDA	N-2-Hydroxyethyliminodiacetic acid
35.	HEDTA	N'-(2-hydroxyethyl)ethylenediamine-N,N,N' triacetic acid
36.	EDTA	Ethylenediamine-N,N,N',N'-tetraacetic acid
38.	EEDTA	[(2,2'-Oxydiethylene)dinitrilo]tetraacetic acid
40.	CDTA	(trans-1,2-Cyclohexylenedinitrilo)tetraacetic acid
41.	HDTA	(Hexamethylenedinitrilo)tetraacetic acid
42.	DTPA	[(N-Carboxymethyl-2,2'-iminodiethylene)dinitrilo- tetraacetic acid

Proper Names of Ligands in Table 11.

Entry		
3	Tiron	4,5-Dihydroxybenzene-1,3-disulphonic acid
4	Purpuric acid	N-(4'-Hydroxy-2',6'-dioxo-1',3'-diazin-5'-yl)-5-imino (perhydro-1,3-diazine-2,4,6-trione)
5	TAR	4-(2'-Thiazolylo)-1,3-hydroxybenzene
6	4-COOH-TAR	4-(2-4'-Carboxythiazolylo)-resorcinol
7	PAR	1,3-Dihydroxy-4-(2'-pyridylazo)benzene- (pyridylazoresorcinol)
11	Leuco- alizarin-S	1,2,9,10-Tetrahydroxyanthracene-3-sulphonate anion
12	Kaempferol	3,5,7',4'-Tetrahydroxyflavone
13	Thoron	1-(2'-Arsonophenylazo)-2-hydroxy-naphthalene- 3,6-disulphonic acid
15	Chrome Azurool S	2",6" - Dichloro - 4'-hydroxy - 3,3'-dimethyl - 3" - sulphofuchsone - 5,5'- dicarboxylic acid
16	Xylenol Orange	5,5'-Bis -N,N-bis(carboxymethyl)aminomethyl- 4'-hydroxy - 3,3'-dimethylfuchsone - 2" - sulphonic acid
21	Calganite	3-Hydroxy-4-[(6-hydroxy-m-tolyl)azo]-1-naphthalene sulphonic acid
22	Socochrome Dark Blue	3-Hydroxy-4-[(2-hydroxynaphthyl)azo]-1-naphthalene sulphonic acid

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