Bull. Chem. Soc. Jpn., 62, 1817—1821 (1989)

Solvent Extraction of Indium with 3-Hydroxy-2-methyl-1-phenyl-4-pyridone

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(Received September 17, 1988)

Extraction behavior of indium has been investigated with 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HMPP) at 25 ± 0.1 °C and an ionic strength of 0.2. The values of the proton-dissociation constants, pK_{a1} and pK_{a2}, of HMPP were determined spectrophotometrically to be 3.02 and 9.56. The value of the partition coefficient, $\log K_D$, of HMPP between 1,2-dichloroethane and water was determined to be 1.35. Indium(III) was extracted into 1,2-dichloroethane by forming a 1 : 3 (metal : ligand) complex with HMPP. The extraction constant, K_{ex}, the overall formation constant, β_3, and the distribution constant, K_{DC}, of the indium(III)–HMPP complex were determined, their values being as follows: $\log K_{ex}=2.16$, $\log \beta_3=32.63$, and $\log K_{DC}=2.26$.

Since Herak and his co-workers[1] used 2-ethoxycarbonyl-5-hydroxyl-1-phenyl-4-pyridone and its analogues to the extraction and separation of tantalum(V) and niobium(V), 4-pyridones including 1-aryl-2-ethoxycarbonyl-5-hydroxy-4-pyridones and 1-aryl-3-hydroxy-2-methyl-4-pyridones[2,3] were synthesized and proposed as chelating and extracting reagents for various metal ions. As is apparent from their structures, these pyridones are *O,O*-donating chelating reagents, so they seem to be promising chelating and/or extracting reagents for metal ions classified into the hard acids including indium(III), gallium(III), and aluminium(III), investigations on the extraction of gallium(III) with some of these pyridones having already been done.[4,5]

On the other hand, indium is an element widely dispersed in nature, about 0.1 ppm of indium being contained in the earth's crust. Minerals containing indium as a major constituent are not known. Indium is usually recovered as a by-product in the zinc industry. Taking into consideration that indium is used not only as a constituent of corrosion-resisting alloys for bearings and a semi-conductor but also in many fields such as non-ferrous metallurgy, electric contacts and reflectors and so on, the separation and/or concentration of indium by solvent extraction with the above 4-pyridones are much attractive as well as of practical and theoretical importance.

Thus to start with, we investigated the extraction of indium(III) with 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HMPP), the results of which are described in this paper.

Experimental

Reagents. All reagents used were of analytical-reagent grade unless stated otherwise. All aqueous solutions were prepared with distilled, deionized water.

HMPP solutions. Prepared by dissolving HMPP in 1,2-dichloroethane or 1,4-dioxane. The HMPP was synthesized by heating a mixture of 3-hydroxy-2-methyl-4-pyrone, aniline and water in a sealed, thick-walled glass tube for 46 h at 150 °C.[3]

Standard indium(III) solution, 5.0×10^{-2} M (1M=1 mol dm^{-3}). Prepared by dissolving the required mass of metallic indium (99.99 % pure), with heating, in a sufficient volume of nitric acid (1+1) to give an acidity of 0.1 M in the final solution. Working solutions were prepared by diluting this solution with water.

Buffer solutions. Buffers consisting of 1 M chloroacetic acid–1 M sodium chloroacetate, 1 M acetic acid–1 M sodium acetate, (0.2 M boric acid+0.05 M sodium chloride)–0.05 M sodium borate, 0.2 M tris(hydroxymethyl)aminomethane–0.2 M hydrochloric acid or 0.2 M sodium hydrogencarbonate–0.2 M sodium carbonate system was used according to the pH values required.

Apparatus. The following instruments were used: a Hitachi 139 spectrophotometer and a Hitachi 340 automatic recording spectrophotometer with 10-mm quartz cells, a Toa HM-5B pH meter, an Iwaki KM shaker and a Haake FK-2 thermoelectric circulating bath. All extractions were performed by shaking samples in 50-cm^3 separating funnels jacketed so that the system could be kept at a constant temperature (25±0.1 °C) by means of water circulated from the thermostatic bath.

Procedures. Proton Dissociation Constants: The proton dissociation constants of HMPP were determined spectrophotometrically[6] in aqueous dioxane of various concentrations (8—32% v/v) at 25±0.1 °C and at an ionic strength of 0.2. The ionic strength was adjusted with sodium chloride. Values of pH measured in aqueous dioxane solutions were not corrected because logarithmic values of U_H were very small (−0.03 at a dioxane concentration of 32% v/v), where U_H is a conversion factor in the equation proposed by Uitert et al.[7]

Partition of HMPP: A 10-cm^3 aliquot of an aqueous solution containing 2.7—5.3 cm^3 of 0.1 M sodium hydroxide solution and sodium nitrate to maintain the ionic strength to 0.2 was placed in a 50-cm^3 separating funnel along with 10 cm^3 of a 1.1×10^{-4} M HMPP solution in 1,2-dichloroethane. The funnel was shaken for 30 min and allowed to stand for 15 min for the phase separation. The organic phase was transferred into a flask containing about 1 g of anhydrous sodium sulfate in order to dehydrate it. The absorbance of the organic phase was measured at 292 nm against 1,2-dichloroethane, the concentration of HMPP being calculated by using the molar absorptivity of HMPP in 1,2-dichloroethane, obtained beforehand. The equilibrium concentration of HMPP in the aqueous phase was calculated by subtracting the organic equilibrium concen-

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tration from the initial concentration.

Distribution of Indium: The distribution of indium between 1,2-dichloroethane and aqueous phases was determined as a function of the hydrogen ion concentration.

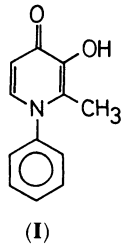
A 10-cm^3 aliquot of an aqueous solution containing 14.9 μg of indium (III), dilute perchloric acid to adjust the pH to the required value and potassium nitrate to maintain the ionic strength to 0.2 was placed in a 50-cm^3 separating funnel along with 10 cm^3 of 4.1×10^{-4} M HMPP solution in 1,2-dichloroethane. The funnel was shaken for 30 min and then allowed to stand for 15 min for the phase separation. The equilibrium concentration of indium in the organic phase was determined by measuring the absorbance of the extract at 319 nm against a reagent blank prepared under the identical conditions. The equilibrium concentration of indium in the aqueous phase was calculated by subtracting the organic equilibrium concentration from the initial concentration.

Formation Constant: To an aliquot containing 1.50 mg of indium(III) in a 25-cm^3 calibrated flask were added 10 cm^3 of a dilute nitric acid solution of 2.5×10^{-4} M HMPP, dilute perchloric acid to adjust the pH to the required value and sodium chloride to maintain the ionic strength to 0.2. Then the solution was diluted to the mark with water. After allowing to stand for 30 min at 25±0.1 °C, the absorbance of the solution was measured at 315 nm against water as a reference.

Results and Discussion

Proton Dissociation Constants, Species Distribution Diagram and Absorption Spectra of HMPP. HMPP is insoluble in water and practically insoluble in nonpolar organic solvents such as benzene and hexane, but very soluble in ethanol, dioxane, chloroform and 1,2-dichloroethane. It is also soluble in weakly acidic and alkaline solutions, but it decomposes in solutions of pH below 1 and above 12.5.

As is evident from the structure of HMPP shown in **I**, at least 3 species, H_2L^+, HL, and L^-, are involved in



(I)

its acid-base equilibria, the probable equilibria being as follows:

$$H_2L^+ \overset{K_{a1}}{\rightleftharpoons} HL \overset{K_{a2}}{\rightleftharpoons} L^- \qquad (1)$$

where L denotes the undissociable part of HMPP and, K_{a1} and K_{a2} are the proton dissociation constants. The value of K_{a2} is already determined by Herak et al.,[7] but that of K_{a1} is not determined yet. So both proton dissociation constants were determined by extrapolating the linear plot of apparent pK_a values obtained by the procedure stated already versus dioxane concentrations (8—32% v/v) to the intercept. The result was shown in Fig. 1. Values of apparent pK_{a1} decrease, whereas those of apparent pK_{a2} increase, with increasing the dioxane concentration. The values of pK_{a1} and pK_{a2} thus obtained were 3.02 and

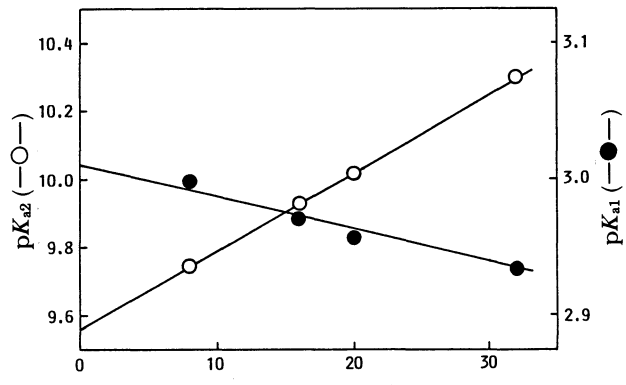


Fig. 1. Plots of pK_a values vs. 1,4-dioxane concentration.

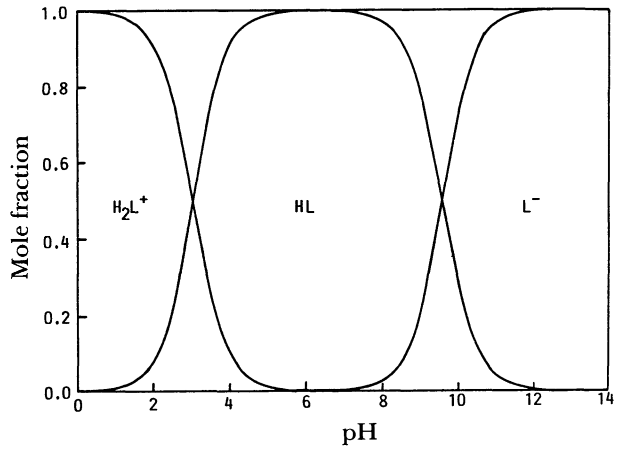


Fig. 2. Species distribution diagram.

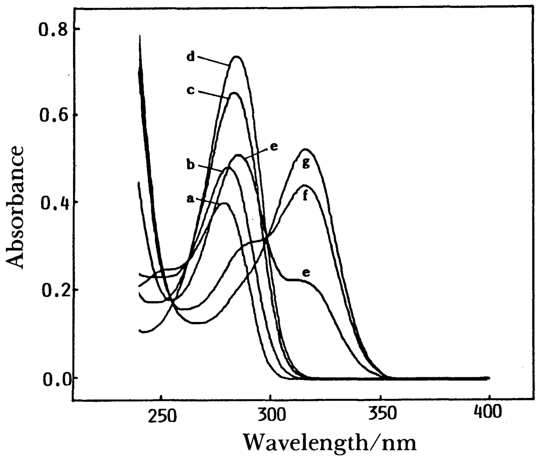


Fig. 3. Absorption spectra of HMPP in 8% v/v 1,4-dioxane. HMPP, 4.1×10^{-5} M; reference, 8% v/v 1,4-dioxane; pH—a, 1.1; b, 2.7; c, 3.7; d, 6.0; e, 9.6; f, 10.5; g, 12.0.

9.56, respectively. The latter value is near to the pK_{a2} value (9.88) reported by Herak et al.[8] K_{a1} and K_{a2} are considered to correspond to the deprotonations of the protonated pyridone-nitrogen and the hydroxyl group, respectively.

Figure 2 shows the species distribution diagram of HMPP prepared on the basis of the above results.

Figure 3 indicates absorption spectra of HMPP in 8% v/v dioxane solutions of various pHs. Spectra a, d, and g correspond to species of H_2L^+, HL, and L^-, respectively. The absorption maximum, λ_{max}, and the molar absorptivity, ε, of each species and the isosbestic points are summarized in Table 1.

Partition Coefficient of HMPP. The distribution ratio, D_L, of HMPP between an aqueous and a 1,2-dichloroethane phase can be expressed as Eq. 2 and is rewritten as Eq. 3 by using the proton dissociation constants and the partition coefficient K_D:

$$D_L = \frac{[HL]_{org}}{[H_2L^+]+[HL]+[L^-]} \tag{2}$$

$$D_L = \frac{K_D}{\dfrac{[H^+]}{K_{a1}} + 1 + \dfrac{K_{a2}}{[H^+]}} \tag{3}$$

where the subscript org denotes the concentration in the organic phase. When $[H^+] \ll K_{a1}$, K_{a2}, Eq. 3 can be approximated by Eq. 4 and rewritten as Eq. 5

$$D_L = \frac{K_D}{K_{a2}}[H^+] \tag{4}$$

$$\log D_L = \log K_D + pK_{a2} - pH \tag{5}$$

Equation 5 implies that the plot of $\log D_L$ against the pH gives a straight line with a slope of −1, the value of K_D being calculated from the intercept of this line. Such a relation was experimentally obtained as shown in Fig. 4, from which the value of 1.35 was obtained as $\log K_D$. This value is close to that (1.69) obtained in the chloroform-water system.[8]

Table 1. Spectral Characteristics of HMPP in 8% v/v 1,4-Dioxane

	H_2L^+	HL	L^-
Absorption maximum/nm	279	285	316
Molar absorptivity/M^{-1} cm^{-1}	9900	18000	13000
Isosbestic point/nm		264	256, 299

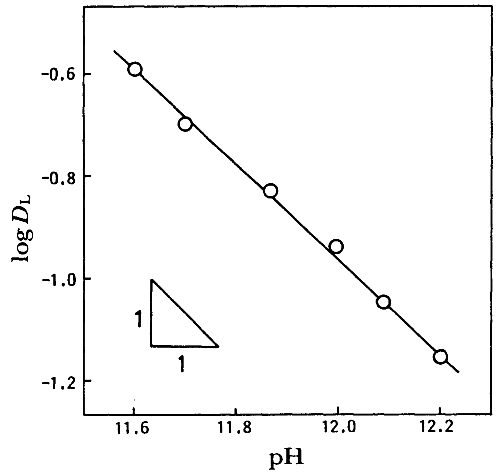


Fig. 4. Plot of $\log D_L$ vs. pH for the partition of HMPP between 1,2-dichloroethane and water at an ionic strength of 0.2 and at 25±0.1 °C. HMPP, 1.1×10^{-4} M; $V_{aq}/V_{org}=1$ ($V_{org}=10$ cm^3); shaking time, 30 min.

Absorption Spectra. Absorption spectra of HMPP and its indium(III) complex extracted into 1,2-dichloroethane are shown in Fig. 5 along with those of aluminium(III) and gallium(III) complexes measured for comparison. The absorption maxima of indium(III), gallium(III), and aluminium(III) complexes lie at nearly the same wavelengths, i.e., 319, 319, and 318 nm, respectively. The absorption maxima and the shape of the spectra did not vary in the pH range 2—12 and the molar ratio range of metal to ligand of 1 : 10—10 : 1, which suggests that only one species of each complex is extracted.

Shaking Time and Stability of the Extract. In general, as the shaking time needed to attain the extraction equilibrium increases with decreasing the pH, the influence of the shaking time on the extraction of the indium(III)-HMPP complex was examined at indium(III) and HMPP concentration of 1.3×10^{-5} and 4.1×10^{-4} M, respectively, and at pHs 2.7

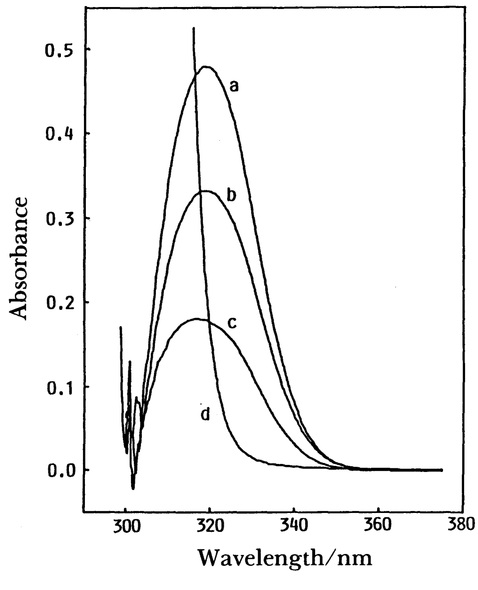


Fig. 5. Absorption spectra of HMPP and its metal complexes in 1,2-dichloroethane. HMPP, 4.1×10^{-4} M; In(III), 1.3×10^{-5} M; Ga(III), 1.1×10^{-5} M; Al(III), 9.9×10^{-6} M; a, In(III) complex; b, Ga(III) complex; c, Al(III) complex; d, HMPP alone (Reagent blank); reference—a,b,c, reagent blank; d, 1,2-dichloroethane.

and 1.9, by varying the shaking time from 15 to 60 min. The results revealed that shaking for 15 min is sufficient at either pH. The complex, once extracted, was very stable, the absorbance of the extract remaining unchanged for more than 2 h.

Influence of pH on Extraction. The degree of extraction of indium(III) with HMPP dissolved in 1,2-dichloroethane, as a function of the pH, is shown in Fig. 6 together with results on the extraction of gallium(III) and aluminium(III) carried out for comparison. Indium(III), gallium(III), and aluminium(III) were quantitatively extracted at pH above 2.6, 2.8, and 4.3, respectively, within 30 min, except for the extraction of indium(III) in the pH range 5—7 and that of gallium(III) in the pH range 4—6, where more than 14 hour's shaking was needed to attain equilibrium presumably because of hydrolysis of these ions. Values of half-extraction pHs, $pH_{1/2}$, for indium(III) and aluminium(III) were 2.16 and 3.15, respectively, but that for gallium(III) could not be obtained because no reliable extraction curve for gallium(III) was obtained below pH 1.7.

Extraction Constant of Indium. The overall reaction in the extraction of indium(III) with HMPP may be expressed as

$$In^{3+} + n\,HL_{org} \rightleftarrows InL_{n,org} + n\,H^+ \qquad (6)$$

The extraction constant, K_{ex}, is defined as Eq. 7 and is rewritten as Eq. 8 by using the distribution ratio of indium, D_{In}, if it is assumed that (a) indium(III) forms no appreciable amounts of hydrolysis or anion coordination complexes, (b) the complex concentration in the aqueous phase is negligible, (c) the concentrations of intermediate complex species are negligible and (d) the volume of the organic phase is equal to that of the aqueous phase.

$$K_{ex} = \frac{[InL_n]_{org}[H^+]^n}{[In^{3+}][HL]^n_{org}} \qquad (7)$$

$$\log D_{In} = \log K_{ex} + n \log [HL]_{org} + n\,pH \qquad (8)$$

Equation 8 implies that the plot of $\log D_{In}$ against the pH at a constant HMPP concentration gives a straight line with a slope of n for indium(III), the value of K_{ex} being calculated from the intercept of this line. In fact, a linear relationship with a slope of about 3 was obtained experimentally as shown in Fig. 7, from which it can be concluded that only a 1 : 3 complex, InL_3, is extracted into 1,2-dichloroethane in this extraction system. The logarithmic value of K_{ex} was calculated to be 2.16 from the intercept of the line in Fig. 7.

Formation Constant of the Complex. Since HMPP and its indium(III) complex have enough solubilities in slightly and/or weakly acidic solution to investigate the complexation reaction in aqueous solution and in addition, the formation constant of the complex was expected to be large, the formation constant was determined in aqueous solution according to the same method as was used by Musha et al.[9]

On the basis of the results stated above, the overall complexation reaction may be written as

$$In^{3+} + 3\,HL \rightleftarrows InL_3 + 3\,H^+ \qquad (9)$$

The equiliblium constant, K_{eq}, is defined as Eq. 10

$$K_{eq} = \frac{[InL_3][H^+]^3}{[In^{3+}][HL]^3} \qquad (10)$$

In the pH region 2.5—3.5, where the experiment was carried out, HMPP exists as species of HL and

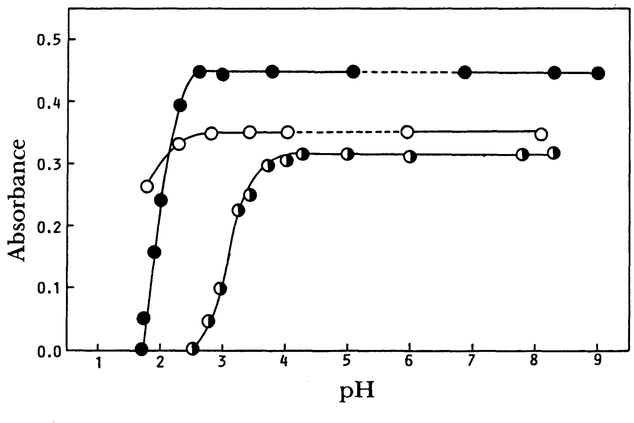


Fig. 6. Extraction curves for In(III)-, Ga(III)-, and Al(III)-HMPP complexes. HMPP, 4.1×10^{-4} M; V_{aq}/V_{org}=1 (V_{org}=10 cm^3); shaking time, 30 min; reference, reagent blank.

		Concentration/M	Wavelength/nm
—●—	In(III)	1.3×10^{-5}	319
—○—	Ga(III)	1.1×10^{-5}	319
—◑—	Al(III)	9.9×10^{-6}	318

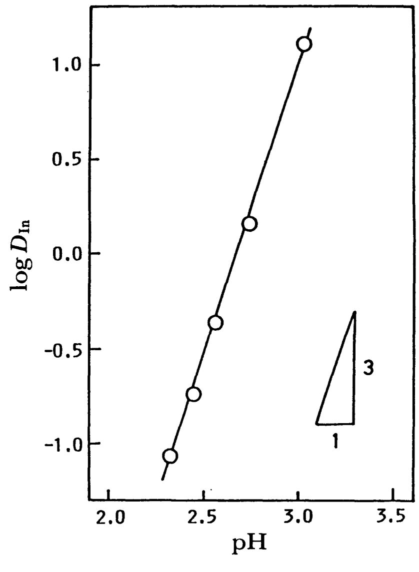


Fig. 7. Plot of $\log D_{In}$ vs. pH for the extraction of indium(III) with HMPP into 1,2-dichloroethane at an ionic strength of 0.2 and at 25±0.1 °C. In(III), 1.3×10^{-5} M; HMPP, 4.1×10^{-4} M; shaking time, 30 min; V_{aq}/V_{org}=1 (V_{org}=10 cm^3).

H_2L^+. So if the initial concentration of indium(III), C_{In}, is much higher than that of HMPP, C_{HL}, Eq. 10 can be expressed as

$$K_{eq}=x[H^+]^3\left(1+\frac{[H^+]}{K_{a1}}\right)^3/C_{In}(C_{HL}-3x)^3 \qquad (11)$$

where x is the equilibrium concentration of the complex formed. At a specified wavelength where the ligand, HMPP, shows no absorption, Eqs. 12 and 13 exist.

$$A=\varepsilon x \qquad (12)$$

$$A_\infty=\frac{1}{3}\varepsilon C_{HL} \qquad (13)$$

where ε is the molar absorptivity of the complex, A is the absorbance at a given pH of the solution containing indium(III) and HMPP and A_∞ is the limiting absorbance when all of the HMPP is complexed quantitatively with indium(III) at a higher pH. From Eqs. 11, 12, and 13, Eq. 14 can finally be obtained:

$$\log\frac{A}{27(A_\infty-A)^3}=\log C_{In}-2\log\varepsilon-pK_{eq}+3\log\frac{K_{a1}}{[H^+]^2+K_{a1}[H^+]} \qquad (14)$$

Equation 14 implies that at a constant value of C_{In} a plot of $\log A/27(A_\infty-A)^3$ vs. $\log K_{a1}/\{[H^+]^2+K_{a1}[H^+]\}$ should yield a straight line with a slope of 3. Such a relation was experimentally obtained as shown in Fig. 8. The pK_{eq} value was evaluated to be −3.95 by entering the value of $\log K_{a1}/\{[H^+]^2+K_{a1}[H^+]\}$ obtained when $\log A/27(A_\infty-A)^3$ is equal to zero in Eq. 14.

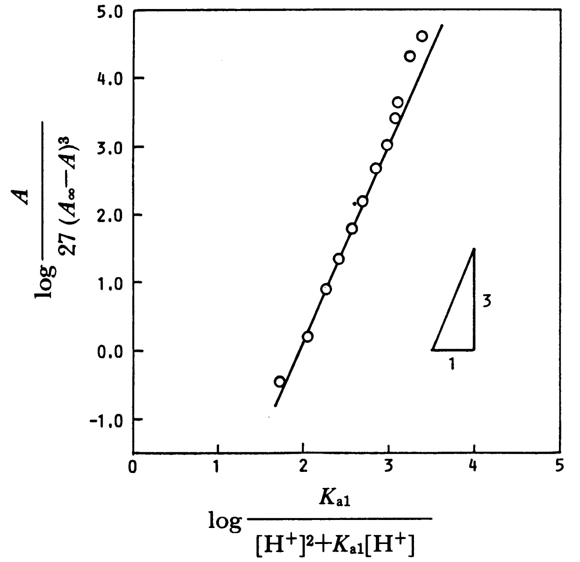


Fig. 8. Plot of $\log A/27(A_\infty-A)^3$ vs. $\log k_{a1}/\{[H^+]^2+K_{a1}[H^+]\}$ for the determination of the equilibrium constant, K_{eq}, at an ionic strength of 0.2 and 25±0.1 °C. In(III), 5.2×10^{-4} M; HMPP, 1.0×10^{-4} M; wavelength, 315 nm.

The overall formation constant, β_3, of this complex defined by

$$In^{3+}+3L^- \rightleftarrows InL_3$$
$$\beta_3=[InL_3]/[In^{3+}][L^-]^3 \qquad (15)$$

can be calculated from the values of K_{eq} and K_{a2} as follows:

$$\begin{aligned}\log\beta_3 &= 3\,pK_{a2}-pK_{eq}\\ &= 3\times9.56-(-3.95)=32.63 \qquad (16)\end{aligned}$$

Distribution Constant of the Complex. The distribution constant of the indium(III) complex, K_{DC}, is defined by

$$InL_3 \rightleftarrows InL_{3,org}$$
$$K_{DC}=[InL_3]_{org}/[InL_3] \qquad (17)$$

and K_{ex} is finally represented by

$$K_{ex}=K_{DC}K_{a2}^3\beta_3/K_D^3 \qquad (18)$$

From Eq. 18 the value of K_{DC} is calculated as follows:

$$\begin{aligned}\log K_{DC} &= \log K_{ex}+3\log K_D-3\log K_{a2}-\log\beta_3\\ &= 2.16+3(1.35)-3(-9.56)-32.63\\ &= 2.26\end{aligned}$$

Conclusion

From the results described above, it is concluded that the value of the overall formation constant of the indium(III)-HMPP complex is very large, but those of the partition coefficient of HMPP and the distribution constant of the complex are not so large as expected. So it is desirable to increase these two values, for example, by introducing a hydrophobic group into the HMPP molecule and enhance the practical usefulness of HMPP as an extractant, which is now in progress.

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