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Extraction and Characterization of Indium-[4-(2-Pyridylazo)resorcinol] Complexes

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The extraction of indium complexes with 4-(2-pyridylazo)-resorcinol (PAR = H_2R) was investigated and the nature of the complex species present in the organic and aqueous phases was studied. From the several complex species present in the aqueous acetate solution at pH 6 only one anionic $[InR_2]^-$ species was efficiently extracted by tetraphenyphosphonium chloride as $[Ph_4P]\,[InR_2]$ associate.

INTRODUCTION

Indium(III) forms red coloured complexes with 4-(2-pyridylazo)resorcinol (PAR = H_2R) which are used for the spectrophotometric determination of indium in aqueous solution.[1,2] Several authors have studied the extraction of indium-PAR complexes to improve the selectivity of indium determination or to reduce the possibility of error arising from the fact that different complex species may be formed in aqueous solution depending strongly on the pH and the composition of the solution. By the chloroform solution of capronic acid (HA) indium in extracted at pH 3 as mixed ligand complex $[InRA_2(HA)]$.[3] By addition of diphenylquanidine indium-PAR complex anions $[In(HR)_2R]^-$ and $[In(HR)RCl]^-$ are said to be extracted as associates with the cation of protonated diphenylquanidine.[4] In the presence of an excess of antipyrine (Ant) and the anion of a suitable monobasic acid the indium complex with PAR is extracted into chloroform as an associate of the complex cation $[In(HR)Ant_3]^{2+}$ and the anion of the monobasic acid (CH_3COO^-).[5]

In the present work the extraction of indium-PAR complexes by tetraphenylphosphonium chloride has been studied with particular reference to the optimum conditions for the extraction and spectrophotometric measurement of the complex in the organic phase and the nature of the extracted species.

EXPERIMENTAL

Apparatus

Visible region spectra and absorbance measurements were made on a Perkin-Elmer Coleman 124 spectrophotometer. Absorbance was measured against reagent blank and absorbance differences were plotted in all figures. Infrared spectra of the isolated complex in KBr pellets were recorded on a Perkin-Elmer spectrophotometer Model 257. For the extraction a Griffin Flask Shaker with a time watch was used.

Reagents

The stock solution of indium(III) was prepared by dissolving a weighed amount of indium sulphate in 0.25 M H_2SO_4 solution and diluted to a known volume to give 0.02 M In in 0.05 M sulphuric acid. The solution was filtered and the concentration of indium checked by EDTA titration using PAR as indicator. More dilute solutions were obtained by appropriate dilution of the stock solution with demineralized water immediately before use.

The solutions of PAR, 2.0×10^{-3} and 1.0×10^{-3} M, were prepared by dissolving a weighed amount of the commercial reagent (monosodium salt) in demineralized water. The purity of reagent was checked by determination of nitrogen by the Dumas method. More dilute solutions were prepared by weekly dilution.

Tetraphenylphosphonium chloride was dissolved in chloroform and/or water. The chloroform containing 0.5% ethanol was used without purification or drying.

All the chemicals used were of analytical grade.

Procedure for Comparative Investigation of Complexes in Extract and Relevant Aqueous Solution

From the aqueous solution prepared in a 10 ml volumetric flask containing indium (2×10^{-6} to 4×10^{-5} M), PAR (2×10^{-5} to 4×10^{-4} M), and acetate buffer (0.04 to 0.1 M), 5 ml was pipetted into a conical 50 ml flask and shaken on a mechanical shaker for 15 min with an equal volume of chloroform containing the extraction agent (1×10^{-3} M). The equilibrium was found to be attained in < 5 min shaking. After separation of the layers the absorbance of the organic phase was measured at $\lambda_{max} = 515$ nm and at shoulder at 535 nm against the reagent blank. The other 5 ml of aqueous solution was used for spectrophotometric measurement at $\lambda_{max} = 510$ nm.

Procedure for Extraction and Spectrophotometric Determination of Indium in the Extract

Into a 50 ml conical flask pipette a slightly acidic aqueous solution of indium containing 1 to 25 μg of indium. Add 2 ml of acetate buffer pH 6 (0.2 M) and immediately 2 ml of 2×10^{-3} M PAR. Check the pH. Extract with 10 ml of 1×10^{-3} M tetraphenylphosphonium or tetraphenylarsonium chloride in chloroform, shaking for 15 min on a mechanical shaker. Separate the phases and measure the absorbance of the organic phase at 515 nm in 1 cm cells, against a reagent blank as reference.

The calibration graphs prepared according to this procedure are linear all over the concentration range used, corresponding to 0.2 to 2.5 μg/ml of indium, or 2×10^{-6} to 2×10^{-5} M solutions. The effective molar absorptivity value is 8.2×10^4 l mol^{-1} cm^{-1}.

Preparation of Solid Complexes

To 50 ml of 0.02 M PAR 50 ml of 0.01 M In in 0.05 M H_2SO_4 was added slowly under stirring. During addition the pH of the solution was checked on the pH-meter and kept at pH 6—7 by addition of acetate buffer and NaOH. The reaction mixture was transferred to a separatory funnel and extracted with 100 ml of chloroform containing an equivalent amount of Ph_4PCl (0.38 g). The chloroform phase was separated and its volume reduced, then cooled in the refrigerator and filtered. Petroleum ether was added to the solution. The precipitate obtained as a dark red film on the walls of the flask was dissolved in a minimum amount of ethanol. To the solution a three-fold volume of ether was added and the content was left to stand in the refrigerator. In a few days, red crystals were obtained in a low yield. They were washed with ether and dried in vacuo over calcium chloride.

Elemental Analysis and Infrared Spectrum

Indium in the isolated complex was determined with PAR after decomposition of the substance (0.5 to 2 mg) by the oxygen-flask combustion method. 0.1 M H_2SO_4 (10 ml) was used as absorbing solution.

Phosphorus was determined gravimetrically by the precipitation of ammonium phosphomolybdate and also by ICP-spectrometry after the substance (5 mg) had been destroyed by the Kjeldahl method.

Carbon, hydrogen and nitrogen were determined by the usual microanalytical methods.

TABLE I

Characteristic Bands of Coordinated PAR in IR-spectra of [Ph_4P] [InR_2] and Tentative Assignments

Band, cm^{-1}	Assignment
1595 vs	ν (C $\overset{\text{- - -}}{\text{——}}$ C, C $\overset{\text{- - -}}{\text{——}}$ N, C $\overset{\text{- - -}}{\text{——}}$ O)
1390 vs	ν (N=N)
1280 vs	
1260 vs	
1240 vs	ν (C—O, C—N)
1210 s	δ (C—O, C—N, C—H)
1170 s	
1140 vs	

The analytical data and infrared spectrum were consistent with the formula [$(C_6H_5)_4P$] [InR_2], where R denotes the doubly charged anion of PAR.

Anal. $C_{46}H_{34}N_6O_4PIn$ (M_r = 880,10):
Calc'd.: C 62.74,H 3.89, N 9.54, P 3.52, In 13.04%
Found: C 62.53, H 4.07, N 9.51, P 3.51, In 12.83%.

Infrared spectrum: ν 3480 s (broad), 1595 vs, 1535 w, 1505—1485 (complex), s, 1460 s, 1430 s, 1390 vs, 1280 vs, 1260 vs, 1240 vs, 1210 s, 1170 s, 1140 vs, 1100 s, 1000 m, 930 m, 840 and 830 (unresolved) m, 770 w, 750 w, 720 m, 690 and 670 m cm^{-1}.

RESULTS AND DISCUSSION

Previous investigations have shown that PAR forms different complex species with indium depending on the pH.[1-6] In acidic media, with a pH below 4, complex species with an indium to PAR ratio of 1 : 1 prevail in the solution. Their composition is not always known. At higher pH values another type of complexes is formed with an indium to PAR ratio of 1 : 2. The concentration of 1 : 2 complexes reaches the maximum at pH 6.8. The absorption maxima of 1 : 1 and 1 : 2 complexes are near and appear between 500—510 nm, but the molar absorptivities differ considerably. In the region between pH 4—7 both types of complexes may be present in aqueous solution. As the composition, charge and relative concentration of the different species depend on the pH and the other complex forming concomittants, the absorbance of aqueous solution is greatly affected by a small variation of pH and the concentration of the other ligands present. Constant and reproducible absorbance values may be obtained in the presence of appropriate excess of some second ligand capable of forming mixed complexes with indium and PAR.

In the present work the extraction behaviour of In-PAR complexes with a number of organic solvents alone and in the presence of tetraphenylarsonium and phosphonium chloride was first investigated. The complexes were found to be non-extractible in non-polar extraction solvents and only partly extractible in polar solvents such as isoamyl or isobutyl alcohol and methylisobutylketone. Extraction efficiency is much improved by the addition of tetraphenyl'onium salts in combination with chloroform. Detailed investigations were carried out with tetraphenylphosponium chloride, which is more available than tetraphenylarsonium salt. Most experiments were performed with a solution of indium sulphate, but the behaviour of chloride and nitrate solution was much the same.

Absorption Spectra and the Effect of pH

The chloroform phase obtained by extraction of In-PAR complexes with tetraphenylphosphonium as extraction agent has the absorption maximum (against a reagent blank) at 515 nm with a shoulder at 535 nm. The absorption maximum does not change in wavelength on variation of reactant concentration, pH and buffer composition. The spectrum is given in Figure 1 along with the spectrum of the relevant aqueous solution to illustrate the differences in the shape of bands, the position of absorption maximum and absorptivity.

Figure 2 shows the dependence of the organic phase absorbance upon pH compared to the absorbance dependence of aqueous solution. The maximum absorbance of the extract was achieved at pH 6.0—6.3, at a lower pH than that of the maximum absorbance of the relevant aqueous solution (pH 6.8). As evident, the shape of the »absorbance — pH« curve for the organic phase is more favourable than that of aqueous solution, but the pH region opti-

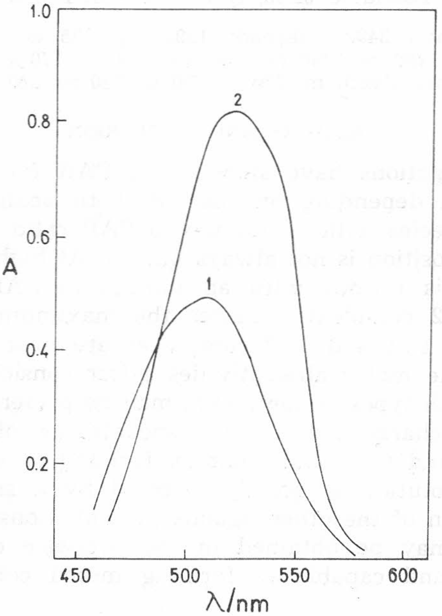

Figure 1. Visible-region spectra of the indium-PAR complexes in aqueous solution at pH 6 and in the extract.

Curve 1 aqueous solution, curve 2 chloroform phase $[In] = 1 \times 10^{-5}$ M, $[PAR] = 1 \times 10^{-4}$ M, acetate buffer pH 6, extracted by 1×10^{-3} M Ph_4PCl in chloroform.

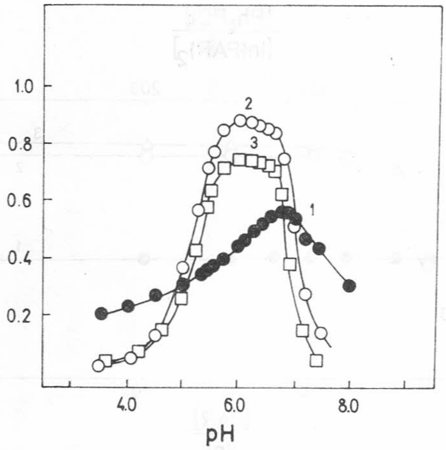

Figure 2. Dependence of absorbance on pH.
Curve 1 aqueous solution at 510 nm, curves 2 and 3 chloroform phase at 515 and 535 nm, respectively. [In] = 1 × 10^{-5} M, [PAR] = 1 × 10^{-4} M, extracted by 1 × 10^{-3} M Ph_4PCl in chloroform.

mum for extraction of the indium-PAR complex is narrower than that of the gallium under similar conditions.[7]

Acetate buffer was used for the maintenance of optimum pH. Phthalate and cytrate buffers were also useful, but phosphate buffer destroyed the indium-PAR complexes. The absorbance of the extract obtained by extraction of complexes from aqueous solution, adjusted to pH 6 with NaOH was noticeably higher but less reproducible. This may be explained by taking into consideration that in the absence of acetate and phthalate as buffer components, the formation of the extracted 1 : 2 indium-PAR complex species in the aqueous phase is favored, but local hydrolysis may occur while adjusting the pH.

The effect of the acetate buffer concentration on the absorbance was also investigated. Constant absorbance values at pH 6 were obtained within 0.04—0.1 M acetate.

The Effect of PAR and Extractant Concentration

The maximum and constant absorbance of the organic phase was achieved with a 10-fold excess of PAR and a 100-fold excess of extractant, as shown in Figure 3 curves 2 and 3. Maximum absorbance of the relevant aqueous solution was obtained already with a three-fold excess of PAR and remained constant up to at least a 30-fold excess (Figure 3 curve 1). This difference in the dependence of absorbance on PAR concentration implies that in aqueous solution under the conditions studied, predominant complex species are the species with a lower indium to PAR ratio rather than those transferred into the organic phase, as was actually found by the complex composition study.

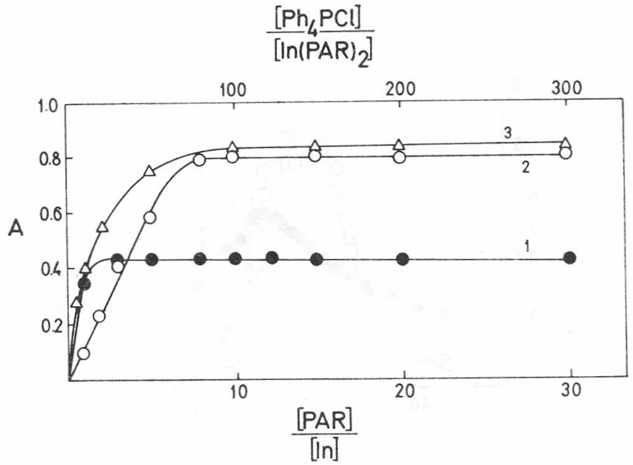

Figure 3. Dependence of absorbance on ligand and extractant concentration. Curve 1 (lower abscissa) aqueous solution, curve 2 (lower abscissa) and curve 3 (upper abscissa) chloroform phases. [In] = 1 × 10^{-5} M.

The Composition of the Complexes

To determine the composition of the complexes present in the extract and in the relevant aqueous solution, Job's and mole ratio methods were used. The results show that in the aqueous acetate and phthalate solution of pH 6 prevailed the complex species with an indium to PAR ratio of 1 : 1 (Figure 4, curves 1 and 3). This is most probably a mixed ligand species, with the acetate or phthalate as a second ligand. At pH 8 Job's method gave an indium to PAR ratio of 1 : 2. In borate medium the 1 : 2 complexes prevailed at pH 6 and pH 8.

For the species present in the organic phase an 1 : 2 : 1 metal to ligand to extractant ratio was obtained (Figure 5). This indicates that the extracted

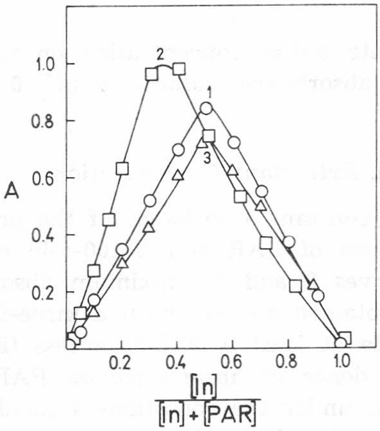

Figure 4. Composition of the indium-PAR complexes in aqueous solution at pH 6. Curve 1 acetate, curve 2 borate and curve 3 phthalate present. [In] + [PAR] = = 1 × 10^{-4} M, at 510 nm.

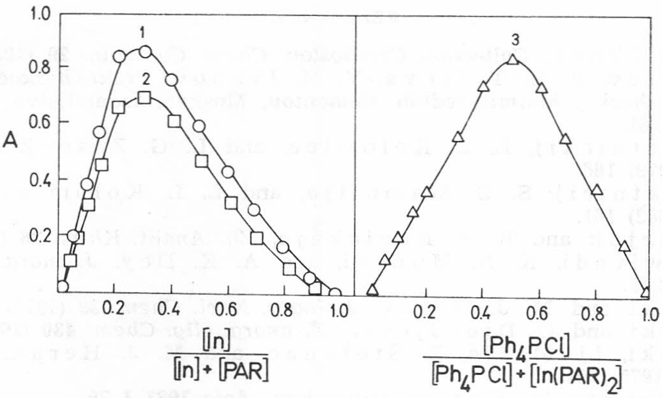

Figure 5. Composition of the extracted complex determined by Job's method. Curves 1 and 2 [In] + [PAR] = 5×10^{-5} M, at 515 nm and 535 nm, respectively. Curve 3 $[In(PAR)_2]$ + $[Ph_4PCl]$ = 1×10^{-4} M, at 515 nm.

species is one with the indium to PAR ratio of 1 : 2 bearing one negative charge. With tetraphenylphosphonium cation as counter ion the anionic indium-PAR complex is therefore extracted as $[Ph_4P]$ $[InR_2]$ associate. We were able to separate the solid compound that corresponded to such composition. In isolation many difficulties arose from the fact that the extracted species is the one present in the reacting solution in low concentration. The excess of PAR which increases the equilibrium concentration of the extracted species in the system must be avoided because of the possibility of PAR-co-extraction and co-precipitation.

The isolated compound is well soluble in chloroform, dimethylsulphoxide and alcohols. The visible spectra of the choloroform solution are identical with the spectra of the extract, indicating that the extracted species and the isolated species are identical.

The infrared spectrum of the isolated complex compound shows absorption bands characteristic of tridentately coordinated PAR (Table I), resembling those of other metal-PAR complexes.[7-11] There are no absorption bands indicative of the presence of oxo, hydroxo and acetate ions as additional ligands. Thus, the elemental analysis data, visible and infrared spectra of isolated complex are consistent with the formula $[Ph_4P]$ $[InR_2]$, which was proposed on the basis of the solution study.

In conclusion, though mixed ligand complexes having composition 1 : 1 with respect to indium and PAR prevailed in the aqueous solution under conditions studied, only an anionic $[InR_2]^-$ species was efficiently extracted by tetraphenylphosphonium chloride in chloroform. By extraction from the system containing an appropriate excess of ligand and extractant, equilibrium is shifted to complete extraction of indium. Quantitative and most reproducible results were obtained with a concentration level of indium between 10^{-6} to 10^{-4} M. At a higher concentration, precipitation occurred which resulted in the loss of indium.

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SAŽETAK

Ekstrakcija i karakterizacija kompleksa indija s 4-(2-piridilazo)rezorcinolom

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Studirana je ekstrakcija kompleksa indija s 4-(2-piridilazo)rezorcinolom (PAR = H_2R) i priroda kompleksnih vrsta prisutnih u organskoj i vodenoj fazi. Utvrđeno je da se od nekoliko kompleksnih vrsta prisutnih u vodenom acetatnom mediju kod pH 6, efikasno ekstrahira samo anionska vrsta $[InR_2]^-$ dajući u prisutnosti tetrafenilfosfonij klorida ionski asocijat $[Ph_4P][InR_2]$.