The Infrared Spectra of Tributyl Phosphate Containing Extracted Salts

By Nobufusa SAITO and Akira YAMASAKI

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Tri-*n*-butyl phosphate (TBP) is used as an useful extractant for a number of inorganic salts. In the case of extraction using TBP, some chemical evidence has been presented to indicate that the phosphoryl group of TBP plays an important role in the coordination with the extracted salts[1,2]. It has also been recognized that the extraction of inorganic salts brings about the shift of the phosphoryl stretching vibration band towards a lower frequency[3,4].

This study is concerned with the infrared spectra of TBP phases containing extracted chlorides, nitrates and some inorganic complexes. The infrared spectra of the TBP phases (10% benzene solution) were recorded with a Hitachi EPI-2 double-beam infrared spectrometer equipped with sodium chloride optics.

The maxima of the phosphoryl band which appear at 1285 and 1265 cm^{-1} in pure TBP were found to shift towards lower wave numbers upon extraction. It was observed that there were three groups of compounds producing phosphoryl band shifts of different magnitudes. The maximum of the shifted phosphoryl bands appeared at three different ranges of wave numbers: 1155∼1175 cm^{-1} for group (I), 1195∼1205 cm^{-1} for group (II) and 1260∼1265 cm^{-1} for group (III). Some of the results obtained are summarized in Table I.

It has been reported that the compounds of group (I) form disolvates in TBP phase, whereas those of group (II) form trisolvates[1,2,5-8]. It seems likely to us that the magnitude of the phosphoryl band shift has some relationship with the number of TBP molecules coordinated with the extracted salts.

The compounds which are classified as group (III) in Table I exhibited only slight phosphoryl band shifts. These compounds are presumed to be extracted in the form of such complex acids as H_2TeCl_6[9].

The present results seem to indicate that the phosphoryl band shift depends on the degree of solvation of the extracted salts in the TBP phase as well as on the nature and strength of the bond between the phosphoryl group and the salts. Further investigation concerning this phenomenon is in progress.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo.

TABLE I

Group	Compound	Nature of aqueous phase	Form of solvate reported	Stretching vibration band of phosphoryl group
(I)	UO_2Cl_2	6 M HCl	$UO_2Cl_2\cdot 2TBP$[5]	1165
	$UO_2(NO_3)_2$	8 M HNO_3	$UO_2(NO_3)_2\cdot 2TBP$[1,2,6,7]	1173
	$Zr(NO_3)_4$	8 M HNO_3	$Zr(NO_3)_4\cdot 2TBP$[6]	1163
	$Th(NO_3)_4$	8 M HNO_3	$Th(NO_3)_4\cdot 2TBP$[1,2,7]	1175∼1180
	$(NH_4)_2[Ce(NO_3)_6]$	(solid)	$Ce(NO_3)_4\cdot 2TBP$[1,2]	1155
(II)	$La(NO_3)_3$	8 M HNO_3	$La(NO_3)_3\cdot 3TBP$[1,2,8]	1205
	$Ce(NO_3)_3$	8 M HNO_3	$Ce(NO_3)_3\cdot 3TBP$[1,2,8]	1205
	$FeCl_3$	6 M HCl	—	1195∼1205
	$K_3[TlCl_6]$	6 M HCl	—	1195
(III)	$(NH_4)_2[TeCl_6]$	6 M HCl	$H_2TeCl_6\cdot 2\sim 4\ TBP$[9]	1265
	$(NH_4)_2[SnCl_6]$	6 M HCl	—	1265
	$NH_4[Cr(NCS)_4(NH_3)_2]$	6 M HCl	—	1265
	$HAuCl_4$	6 M HCl	—	1265

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