CHEMISTRY LETTERS, pp. 43-46, 1988.

Ion-pair Extraction of Gallium(III) from Hydrochloric Acid with Various Methoxy-substituted Triarylphosphines

Yuko YAMASHOJI,* Takayuki MATSUSHITA, Masanori WADA,† and Toshiyuki SHONO
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka 2-1, Suita, Osaka 565
†Department of Industrial Chemistry, Faculty of Engineering,
Tottori University, Koyamacho-minami, 4-101, Tottori 680

A series of methoxy substituted triarylphosphines $R_nPh_{3-n}P$, where R can be 2-MeOPh, 4-MeOPh, 2,6-MeOPh, and 2,4,6-MeOPh and n=1, 2, and 3, has been prepared and employed as extractants for gallium(III) from hydrochloric acid solutions. Their extractabilities for gallium(III) were found to become more effective with their increased basicities.

Previously one of the authors has reported that tris(2,4,6-trimethoxyphenyl)-phosphine $(2,4,6\text{-MeOPh})_3P$ possesses a high basicity comparable to piperidine (pKa=11.2), which was determined by ^1H NMR spectroscopy.1) This is ascribed to the electron-donating ability of the methoxy group. On the other hand, triphenylphosphine Ph_3P is well known to be one of the most effective extractants for metal ions such as silver and platinum from acidic media,2-3) even though it's pKa value is low (pKa=2.73).4) It can be expected that higher the basicity of this type of extractants becomes, much more effective its extractability should become.

In this paper, we describe the extraction behavior of gallium(III) ion with a series of methoxy substituted triarylphosphines from hydrochloric acid solutions. We have found that their extractabilities of gallium(III) can be correlated with their basicities, which were determined by nonaqueous titrimetry. All the methoxy substituted triarylphosphines listed in Table 1 were prepared according to the methods described in the literatures.5-6) These compounds were identified by elemental analyses, mass spectra and melting points. The basicities of the compounds were measured by nonaqueous titrimetry in nitromethane according to the method reported by Streuli7) using a Horiba pH meter F-8 DP equipped with a glass-calomel electrode. The pKa (H_2O) values were calculated from the half-neutralization potential values obtained in the nonaqueous titrimetry. The titration was performed with a standard hydrochloric acid (0.004 M, 1 M = 1 mol dm^{-3}). Diphenylguanidine was used as the reference standard for all the nonaqueous titration. As shown in Table 1, the basicities of the triarylphosphines become high with increasing the number of the methoxy groups. In addition, the substitution of para-position on the phenyl ring results in a slightly higher basicity than that of ortho-position.

Extraction and analytical procedures were carried out as follows. Equal volumes (5 cm^3) of a chloroform solution of an extractant and a hydrochloric acid solution of gallium(III) ion were placed into a centrifuge glass tube(10 cm^3), followed by shaking for 15 min at 25 ± 0.1 °C and centrifuging for phase separation. The concentration of gallium(III) ion remaining in the aqueous phase was determined by atomic absorption spectrometry. The concentration of gallium(III) ion in the organic phase was calculated from mass balance using that in the aqueous phase.

The extraction behavior of gallium(III) ion with the triarylphosphines from various concentrations of hydrochloric acid solutions are shown in Figs. 1A-D, where the concentration of the extractants in the organic phase is equal to the initial concentration of the gallium(III) ion in the aqueous phase(5.0×10^{-4} M). Figures 1A and B show the extraction isotherms obtained by using $(2\text{-MeOPh})_n\text{Ph}_{3-n}\text{P}$ and $(4\text{-MeOPh})_n\text{Ph}_{3-n}\text{P}$ (n=1,2,3), respectively. Figure 1A also includes that obtained by using Ph_3P for comparison. It can be seen in both cases that maximum extractions of gallium(III) ion were achieved at lower concentrations of hydrochloric acid in the order of $n=1 < 2 < 3$. This order is fairly consistent with the increasing order of their basicities (see Table 1). The percentage extraction of gallium(III) ion with Ph_3P was reached only about 80% at more than 7.3 M hydrochloric acid. The pKa value of Ph_3P is 2.73, being the lowest basicity examined in the present work.

Figures 1C and D show the extraction isotherms obtained by using $(2,6\text{-MeOPh})_n\text{Ph}_{3-n}\text{P}$ and $(2,4,6\text{-MeOPh})_n\text{Ph}_{3-n}\text{P}$ (n=1, 2, and 3), respectively. A similar relationship was observed between their extractabilities and basicities. Moreover,

Table 1. pKa values for triarylphosphines

Compound	pKa (H_2O)	Compound	pKa(H_2O)
Ph_3P	2.73[7)]	(2,6-MeOPh)Ph_2P	5.39
(2-MeOPh)Ph_2P	3.33	(2,6-MeOPh)$_2$PhP	7.28
(2-MeOPh)$_2$PhP	4.01	(2,6-MeOPh)$_3$P	9.33
(2-MeOPh)$_3$P	4.47	(2,4,6-MeOPh)Ph_2P	5.77
(4-MeOPh)Ph_2P	3.67	(2,4,6-MeOPh)$_2$PhP	8.22
(4-MeOPh)$_2$PhP	4.06	(2,4,6-MeOPh)$_3$P	11.02 (11.2)[1)]
(4-MeOPh)$_3$P	4.75 (4.57)[4)],(4.46)[7)]		

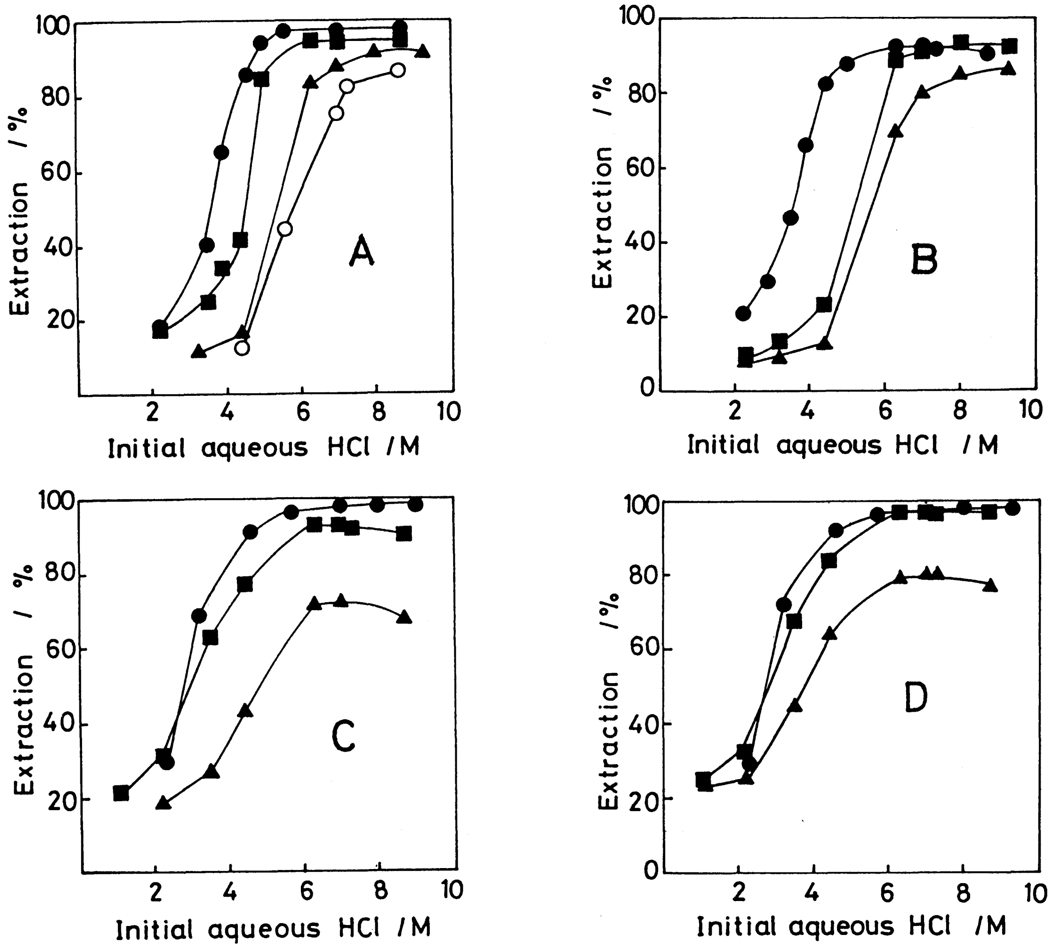

Fig. 1. Effects of HCl concentration on extraction of Ga(III) (5×10^{-4} M) with triarylphosphines (5×10^{-4} M).

A : (2-MeOPh)$_n$Ph$_{3-n}$P n=1 ; (▲), n=2 ; (■), n = 3 ; (●), Ph_3P ; (○)

B : (4-MeOPh)$_n$Ph$_{3-n}$P n=1 ; (▲), n=2 ; (■), n=3 ; (●)

C : (2,6-MeOPh)$_n$Ph$_{3-n}$P n=1 ; (▲), n=2 ; (■), n=3 ; (●)

D : (2,4,6-MeOPh)$_n$Ph$_{3-n}$P n=1 ; (▲), n= 2 ; (■), n=3 ; (●)

the extractions nearly equal to 100% were obtained in the cases of $(2,6\text{-MeOPh})_3P$ and $(2,4,6\text{-MeOPh})_3P$ which are highly basic. These results indicate that $(2,6\text{-MeOPh})_3P$ and $(2,4,6\text{-MeOPh})_3P$ are the most effective extractant among the triarylphosphines investigated here.

In the present extraction system, it is assumed that gallium (III) ions are transferred into the organic phase through the formation of the ion-pair complex $[R_3P^+H][GaCl_4^-]$. This was confirmed by the molar ratio method and IR spectroscopy. The extraction percentage of gallium(III) ion increased linearly until the molar ratio of $(2,4,6\text{-MeOPh})_3P$ in the organic phase to gallium(III) ion in the aqueous phase was reached unity and then became constant at this ratio and above it. This clearly indicates that the extracted species of gallium(III) ion consists of the 1 : 1 molar ratio of the extractant to the gallium(III) ion. The IR spectra of the extracted species of gallium(III) ion with Ph_3P and $(2,6\text{-MeOPh})_3P$, which were isolated by evaporating their chloroform extracts, show a strong absorption band at 375 and 372 cm^{-1}, respectively. These bands can be assigned to Ga-Cl stretching vibrations in the $GaCl_4^-$ anion.8)

The extraction behavior of other metal ions by these highly basic phosphines is the subject under investigation.

References

1) M. Wada and S. Higashizaki, J. Chem. Soc., Chem. Commun., 1984, 482.

2) Z. Skorko-Trybulowa, Z. Boguszewska, and B. Rozanska, Mikrochimica Acta[Wien] 1979I, 151.

3) M. Mojski, Talanta, 27, 7 (1980).

4) T. Allman and R. G. Goel, Can. J. Chem., 60, 716 (1982).

5) W. E. McEwen, W-I Shau, Y-I Yeh, D. N. Schulz, R. U. Pagilagan, J. B. Levy, C. Symmes Jr., G. O. Nelson, and I. Granoth, J. Am. Chem. Soc., 97, 1787 (1975).

6) M. Wada, S. Higashizaki, and A. Tsuboi, J. Chem. Res. (M), 1985, 0467-0490.

7) C. A. Streuli, Anal. Chem., 32, 985 (1960).

8) P. L. Goggin and T. G. Buick, J. Chem. Soc., Chem. Commun., 1967, 290.

(Received September 30, 1987)