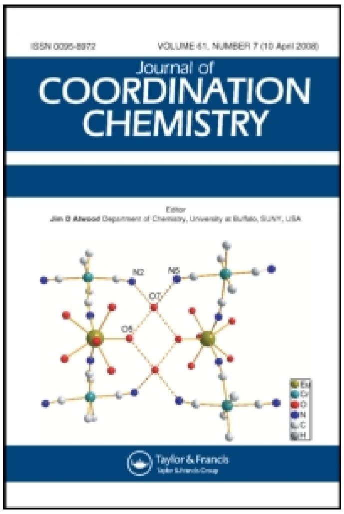

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POLY(METHYLPHENYLSILOXANE) COMPLEX OF SILVER(I) TRIFLUOROACETATE AND ITS LIGAND EXCHANGE REACTIONS WITH BENZENE AND CYCLOHEXENE

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POLY(METHYLPHENYLSILOXANE) COMPLEX OF SILVER(I) TRIFLUOROACETATE AND ITS LIGAND EXCHANGE REACTIONS WITH BENZENE AND CYCLOHEXENE

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A nonpolar organic polymer, poly(methylphenylsiloxane), dissolves silver(I) trifluoroacetate through coordination of the phenyl group. The resultant complex readily exchanges the ligand with benzene or cyclohexene. Two different methods have been developed to evaluate the ligand exchange constants at very high concentrations of the constitutents: a) by vapor pressure of the ligands and b) by the vapor composition in the presence of an inert compound, cyclohexane, employed as an internal standard. Similar values were obtained in these methods: The discrepancies are discussed.

KEYWORDS: poly(methylphenylsiloxane), silver(I), ligand exchange

INTRODUCTION

It is well documented that silver(I) interacts weakly with a variety of aromatic[1-3] and olefinic compounds[4] attaining equilibrium: $Ag^+ + L \rightleftharpoons [AgL]^+$.

We found that poly(methylphenylsiloxane) (PhSi), commonly known as OV-17, dissolves silver(I) salts of anions such as trifluoroacetate and trifluoromethanesulfonate. Since pure siloxane is available commercially and is very stable thermally, the resulting solution might be useful as a selective absorbent for olefins and aromatic hydrocarbons. The solution might be used to purify, to separate from a

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mixture, or to store olefins and aromatic hydrocarbons. The nonvolatile nature of the siloxane is a big advantage as a volatile solvent must be removed to recover the absorbed ligands.[5,6]

Poly(ethyleneglycol) has been widely employed to dissolve silver salts in gas chromatography to separate olefins.[7] However, its thermal instability is always problematic and a silver solution can be employed only at low temperatures in the liquid phase. We previously showed that a silver(I) solution of PhSi successfully separates olefinic and aromatic hydrocarbons in gas chromatography.[8]

In this paper, we report coordination of phenylsiloxane to silver trifluoroacetate (Agtac) and its ligand exchange reactions with benzene and cyclohexene. The equilibrium constants have been determined by analysis of vapor pressures of benzene and cyclohexene and also by the vapor phase compositions of chemical species in a high concentration region of the constituents.

EXPERIMENTAL

Materials

Benzene, cyclohexene, and cyclohexane were of reagent grade (J.T. Baker, Xalostoc, Mexico) and distilled in *vacuo*. Chloroform (J.T. Baker) was passed through a silica column to remove methanol and then fractionally distilled in *vacuo*. 1,4-Bis(trichloromethyl)benzene (Aldrich Chemical, Milwaukee, WI) and poly(methylphenylsiloxane) (Supelco, Supelco Park, PA) were used without further tratment. Silver(I) trifluoroacetate was synthesized as described previously.[9]

Vacuum Vapor Pressure Osmometry (vvpo)

The vvpo method was used as described previously.[9,10] 1,4-Bis(trichloromethyl) benzene was employed to calibrate the apparatus at 30.1 °C.

Ligand Vapor Pressure Measurements

Figure 2 illustrates the apparatus used to measure the vapor pressure of benzene and cyclohexene dissolved in PhSi at various concentrations.

PhSi, 7.00 g, was placed in the reaction vessel *F* and degassed at 100°C for 1 h under magnetic stirring. Approximately 1.8 mL of C_6H_6 or C_6H_{10} was transferred to a thin burette *C* by vacuum distillation from a reservoir in another part of the vacuum system. The level of liquid was measured by aid of a cathetometer. An aliquot of the ligand was transferred to the vesel *F* by vacuum distillation and the liquid level was recorded. The whole apparatus was then immersed into a constant temperature bath at 40.0°C to measure the equilibrium pressure by use of the mercury manometer *G*.

Ligand addition and subsequent vapor pressure determinations were repeated. After an experimental run, the ligand was recovered to the burette by cooling it with liquid nitrogen while heating the reaction vessel *F*. then, 1.14 g (5.14 mmole) of Agtac was added to vessel *F* and degassed. The ligand was successively transferred to the silver solution by vacuum distillation and the vapor pressure was determined.

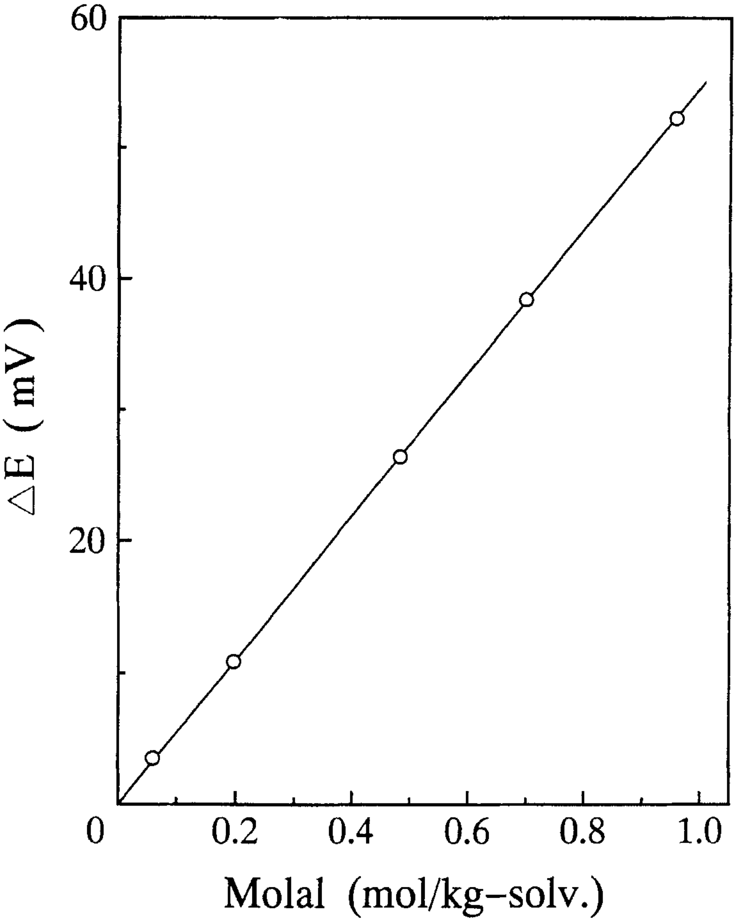

Figure 1 The linear relationship between the observed potential (ΔE, mV) *vs.* concentrations (molal) of *p*-bis(trichloromethyl)benzene in chloroform.

Determination of Vapor Composition

Fig. 3 illustrates the system used to determine the vapor phase composition. PhSi, 5.178 g, was placed in reaction vessel *G* and degassed at 100°C. An aliquot (0.3–0.4 mL) of C_6H_6 or C_6H_{10} containing 5% C_6H_{12} was introduced to the ampule *D* and degassed. After the solution in the ampule was completely transferred to the vessel by vacuum distillation, the reaction vessel was immersed into a constant temperature bath at 40.0°C. The vapor in the reaction vessel was introduced to the system by opening stopcock *F* slowly. One of the capillaries, *H*, was cooled by liquid nitrogen to condense the vapor (8–12 μL).

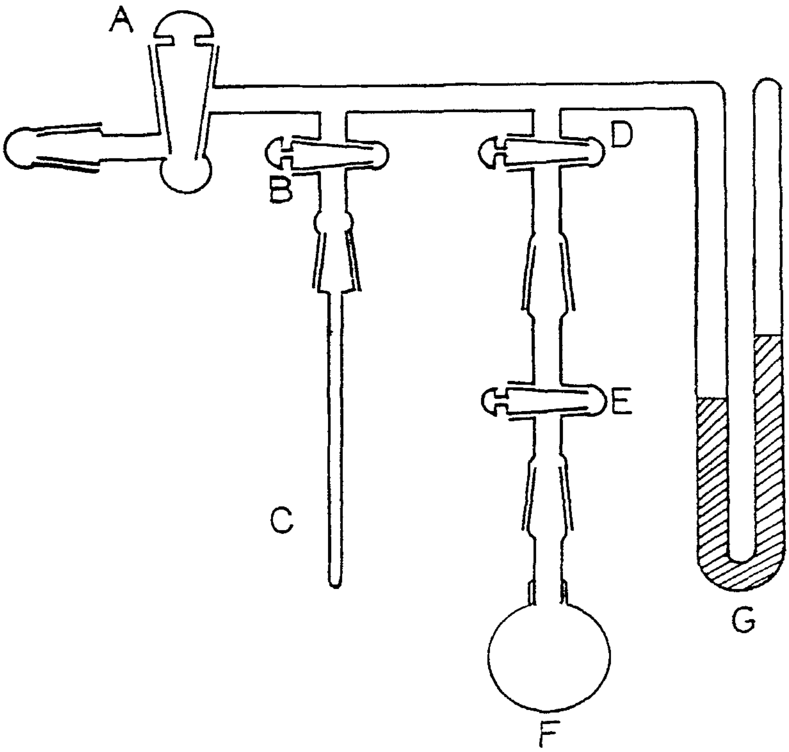

Figure 2 The apparatus used to measure the vapor pressures of benzene or cyclohexene in SiPh in the absence or presence of Agtac. A, B, and E stopcocks, C thin burette, F reaction vessel, and G mercury manometer.

The condensed phase was assayed by gas chromatography to determine the ratio, C_6H_6/C_6H_{12} or C_6H_{10}/C_6H_{12} based on the calibration curves. Three or four determinations were averaged for each condensation.

The gas chromatograms were obtained with Perkin-Elmer 990 using a packed column of DOP 5% on acid washed and silylated diatomaceous earth (Neosorb NCS, Nishio Kogyo, Japan).

The resultant siloxane solution was heated to 100°C under stirring and the ampule was cooled by liquid nitrogen to remove volatile compounds. Then, 0.839 g (3.80 mmole) of Agtac was added to the siloxane and the procedures were followed again.

RESULTS

Vvpo

Figure 1 shows the calibration curve for the vvpo apparatus using chloroform solutions of bis(trichloromethyl)benzene ($C_8H_2Cl_6$) at 30.1°C. The line is expressed

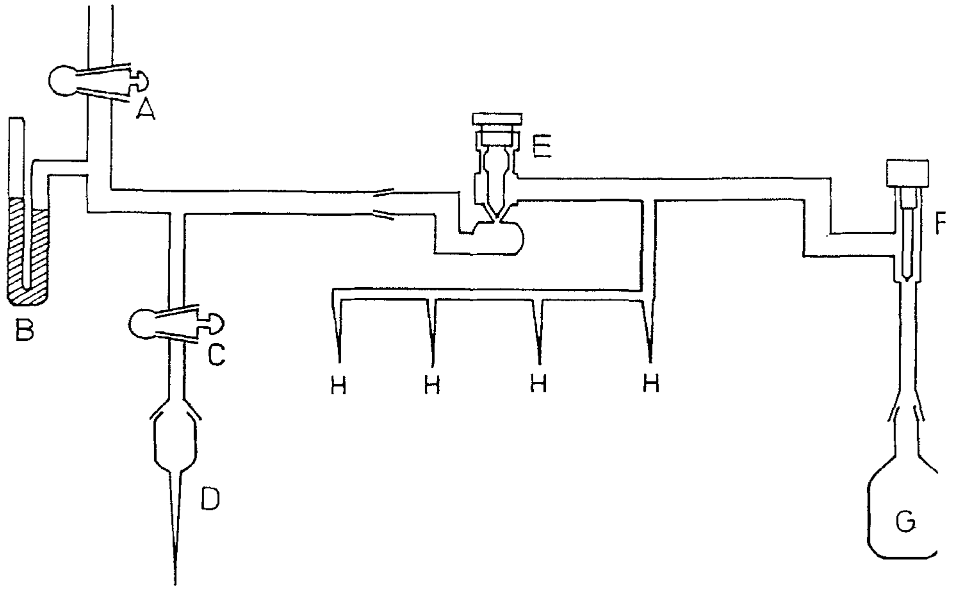

Figure 3 The apparatus used to determine the vapor composition of solutions of benzene and cyclohexane, or cyclohexene and cyclohexane in SiPh in the absence of presence of Agtac. A, C, E, and F stopcocks, B mercury manometer, D ligand reservoir, G reaction vessel and H capillary to condense vapor phase.

$$\Delta E\ (\mathrm{mV}) = 32.51 \pm 0.19\ [C_8H_2Cl_6] \qquad (1)$$

as where the error limits are a standard deviation.

A suspension of Agtac in $CHCl_3$ gave $\Delta E = 0$ referred to the pure solvent. Therefore, no measurable solubility of Agtac in $CHCl_3$ was observed. This was supported by filtering a suspension of powdered Agtac in $CHCl_3$, and evaporating the filtrate carefully; but no residual solid was observed.

A chloroform solution of PhSi, 1.000 molal based on the monomer unit, gave ΔE 5.56 mV in the vvpo measurement. Therefore, the solution contained (5.56 mV)/(32.5 mV/molal) = 0.172 molal of the polymer. Then, 1.00/0.172 = 5.85 is the degree of polymerization of the siloxane.

An excess of Agtac was suspended in the same $CHCl_3$ solution of PhSi and the resultant solution was assayed by vvpo: 5.62 mV, 0.173 molal. Subsequently, the dissolved Agtac concentration was determined to be 0.0530 molal based on silver ion. Therefore, the presence of PhSi in $CHCl_3$ made Agac soluble.

Vapor Pressure Measurements

Table 1 summarizes the vapor pressures of C_6H_6 and C_6H_{10} dissolved in PhSi for various concentrations at 40°C.

When Agtac is introduced to a ligand solution, the vapor pressure of the ligand decreases by coordination to the silver ion. Thus, a benzene solution in PhSi, $[C_6H_6] = 0.19$ molal, displays a vapor pressure of 20 mmHg. The vapor pressure

Table 1 Vapor pressures of C_6H_6 and C_6H_{10} dissolved in PhSi at 40.0 °C

C_6H_6		C_6H_{10}	
$[C_6H_6]_f$	P, mmHg	$[C_6H_{10}]_f$	P, mmHg
0.190	20.4	0.238	25.5
0.287	29.4	0.431	40.5
0.576	51.2	0.672	58.9
0.964	75.7	0.964	76.1
1.260	89.7	1.360	94.0

decreases to 15 mmHg in the presence of [Agtac] = 0.73 molal. We assume the decrease is attributed to the reaction, SiPh·Agtac + L = Agtac·L + SiPh.

The total benzene or cyclohexene concentrations, $[C_6H_6]_t$ and $[C_6H_{10}]_t$, respectively, are expressed as (mole of ligand)/(kg of the siloxane). The decrease of the vapor pressure in the presence of Agtac as attributed to formation of the nonvolatile complex Agtac·L. Therefore, the free benzene $[C_6H_6]_f$ concentration in the presence of Agtac was estimated based on the vapor pressures of the ligand in pure PhSi. The vapor pressure of benzene in the absence of Agtac was observed as $P = 0$ at $[C_6H_6] = 0$ and $P = 0.190$ mmHg at $[C_6H_6] = 20.4$ mmHg as seen in Table 1: the free benzene concentration was approximated as $[C_6H_6]_f = 0.00931P$ if P fell in the range of $0 < P$ (mmHg) < 0.190. Similarly the following expressions were employed: $[C_6H_6]_f = 0.190 + 0.0108(P - 20.4)$ for $20.4 < P < 29.4$,; $[C_6H_6]_f = 0.287 + 0.0132(P - 29.4)$ for $29.4 < P < 51.2$,; $[C_6H_6]_f = 0.576 + 0.0158$ $(P = 51.2)$ for $51.2 < P < 75.8$.

It was assumed that the concentration of the silver-benzene complex was given as $[Ag \cdot C_6H_6] = [C_6H_6]_t - [C_6H_6]_f$, and $[Ag \cdot C_6H_6] = [Ag]_t - [Ag]_f$. Thus the free silver concentration $[Ag]_f$ was evaluated. The formation and equilibrium constants, $K_f = [Ag \cdot C_6H_6] \times [Ag]_f^{-1} \times [C_6H_6]_f^{-1}$ and $K_e = [Ag \cdot C_6H_6] \times [PhSi] \times [Ag]_f^{-1} \times [C_6H_6]_f^{-1}$, respectively, were assumed, where [PhSi] refers to the monomer-based concentration, thus, 1000 kg/(136 g/mole) = 7.34 molal.

The free cyclohexene concentrations are evaluated as: for $0<P<23.8$, $[C_6H_{10}]_f = 0.00933P$; for $23.8<P<40.5$, $[C_6H_{10}]_f = 0.238 + 0.0129(P - 23.8)$.

Table 2 summarizes the results.

Vapor Compositions

As shown in Figure 4, the ligand, L, and cyclohexane in PhSi form the gas phase. Their ratio in the gas phase is expected to be proportional to their ratio in the liquid phase while the gas-liquid partition coefficient of each species is effected. Therefore,

	PhSi	Agtac + PhSi
gas phase	$L + C_6H_{12}$ $r_o = [C_6H_{12}]^g/[L]^g$ $= p_o[C_6H_{12}]/L]_t$	$L + C_6H_{12}$ $r_{Ag} = [C_6H_{12}]^g/[L]^g{}_{Ag}$ $= p_{Ag}]C_6H_{12}]_{Ag}/[L]_f$
liquid phase	$L + C_6H_{12} +$ PhSi	$L + C_6H_{12} +$ PhSi + Agtac + Agtac.L

Figure 4 Summary of the gas phase composition determination.

Table 2 Vapor pressures of C_6H_6 and C_6H_{10} dissolved in PhSi in the presence of Agtac (0.743 m) at 40.0°C: Evaluation of the chemical species concentrations and the formation and equilibrium constants, K_f and K_e, respectively

C_6H_6

$[C_6H_6]_t$	pmmHg	$[C_6H_6]_f$	$[Ag \cdot C_6H_6]$	$[Ag]_f$	K_f	K_e
0.193	15.1	0.141	0.052	0.795	0.463	3.40
0.338	25.0	0.240	0.0981	0.645	0.632	4.64
0.533	36.1	0.375	0.158	0.585	0.500	3.67
0.679	43.9	0.478	0.201	0.542	0.775	5.69
0.972	58.3	0.688	0.284	0.459	0.899	6.60
1.360	74.2	0.941	0.419	0.324	1.38	10.1

C_6H_{10}

$[C_6H_{10}]_t$	PmmHg	$[C_6H_{10}]_f$	$[Ag \cdot C_6H_{10}]$	$[Ag]_f$	K_f	K_e
0.245	10.6	0.099	0.146	0.597	2.47	18.1
0.441	18.1	0.169	0.272	0.471	3.42	25.1
0.687	27.9	0.269	0.418	0.325	4.79	35.1
0.981	40.0	0.425	0.556	0.187	6.99	51.3

$$r_o = [C_6H_{12}]^g/[L]^g = p_o[C_6H_{12}]/[L]_t \qquad (1)$$

where the superscript g shows the gas phase concentration and those without a superscript show the liquid phase concentration; p_o is a constant.

Dissolving Agtac in the same solution, the free ligand concentration must be altered because of the formation of the complex, Agtac·L. Then, the ratio in the gas phase is

$$r_{Ag} = [C_6H_{12}]^g_{Ag} / [L]^g_{Ag} = p_{Ag}[C_6H_{12}]_{Ag} / [L]_f \qquad (2)$$

On the other hand, the cyclohexane concentration in the liquid phase is not altered by the presence of the silver salt: $[C_6H_{12}]^g_{Ag} = [C_6H_{12}]^g$ and $[C_6H_{12}]_{Ag} = [C_6H_{12}]$. Thus, eq. (**2**) is written as:

$$r_{Ag} = [C_6H_{12}]^g / [L]^g_{Ag} = p_{Ag}[C_6H_{12}] / [L]_f \qquad (3)$$

Since p_o and p_{Ag} are obtained by combining the gas-liquid partition coefficients of these chemical species, they might be the same: $p_o = p_{Ag}$. Then, $r_o / r_{Ag} = [L]_f / [L]_t$ is obtained from eqs. (**1**) and (**3**). Thus,

$$[L]_f = [L]_t \times r_o / r_{Ag}) \qquad (4)$$

The values of r_o and r_{Ag} were determined by gas chromatography and are summarized in Table 3.

DISCUSSION

The K_f and K_e values in Table 2 apparently increase as the ligand concentration increases. This could be attributed to the formation of larger coordination number

Table 3 Determination of the vapor composition ratio of the ligand *vs.* C_6H_{12} and subsequent estimate of the chemical species concentration in the solution in order to obtain the formation and equilibrium constants

C_6H_6

$[C_6H_6]_t$	r_o/r_{Ag}	$[C_6H_6]_f$	$[Ag \cdot C_6H_6]$	$[Ag]_f$	K_f	K_e
0.619	0.758	0.469	0.150	0.593	0.538	3.95
1.237	0.749	0.926	0.311	0.432	0.777	5.70
1.856	0.850	1.578	0.278	0.456	0.387	2.84

C_6H_{10}

$[C_6H_{10}]_t$	r_o/r_{Ag}	$[C_6H_{10}]_f$	$[AgC_6H_{10}]$	$[Ag]_f$	K_f	K_e
0.723	0.559	0.404	0.319	0.424	1.88	13.8
1.503	0.693	1.042	0.461	0.282	1.57	11.5
2.168	0.736	1.595	0.573	0.170	2.11	15.5
2.891	0.786	2.274	0.617	0.126	2.15	15.8

such as Agtac$\cdot L_2$. On the other hand, Table 3 does not show such increases. Instead, the K_f and K_e values evaluated in both methods are similar.

We have assumed that the vapor pressure of the ligands in PhSi is not altered by the presence of Agtac. However, the importance of the salt-out effect is well documented.[11] The free ligand concentration would be overestimated by the vapor pressure in the presence of the salt-out effect. Assuming Agtac exercises a bigger salt-out effect than Agtac$\cdot$L, a ligand suffers the bigger effect at the lower ligand concentration as for $[Ag \cdot L]$ and $[Ag]_f$ in Table 2.

We employed C_6H_{12} as the internal standard,[12] which is inert in the system. The cyclohexane might feel to a similar degree the effect.

Therefore, the ratio, r_o/r_{Ag} might cancel the effect, consequently the formation constants estimated in Table 3 are more accurate than those in Table 2.

This paper explains the vapor pressures of benzene and cyclohexene based on ligand exchange reactions in the high concentration regions of the constituents: Agtac 0.1–0.8, benzene 0.2–1.9, PhSi 7.4 molal. Usually these are expressed as phase diagrams. We met severe difficulties (large salt-out effects, *etc.*) such that the measured values were not sufficiently sensitive to evaluate the formation constans accurately. Since thermodynamic expression of the reactions at high concentration is not exploited well, the accumulation of experimental data is indispensable to understand reactions and to predict numerically the behavior of the reactants.

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References

1. A.E. Hill, *J. Am. Chem. Soc.*, **43**, 254 (1920).
2. A.E. Hill, *J. Am. Chem. Soc.*, **44**, 1163 (1921).
3. A.E. Hill, and F.W. Miller, *J. Am. Chem. Soc.*, **47**, 2702 (1925).
4. W.F. Eberz, H.J. Wilge, D.M. Yost and H.J. Lucas, *J. Am. Chem. Soc.*, **59**, 45 (1937).
5. D.J. Haase and D.G. Walker, *Chem. Eng. Prog.*, **70**, 74 (1974).
6. D.J. Haase, *Chem. Eng., Aug.* **4**, 52 (1975).
7. B.W. Branford, D. Harvey and D.E. Chalkley, *J. Inst. Pet.*, **41**, 80 (1955).
8. A.M. soto, N. Yanagihara and T. Ogura, *Anal. Chem.* **63**, 1178 (1991).
9. N. Yanagihara, J.A. Sampedro, R. Casillas, Q. Fernando and T. Ogura, *Inorg. Chem.* **21**, 475 (1982).
10. T. Ogura and R. Casillas, *Anal. Chem.*, **52**, 1372 (1980).
11. F.R. Hartley, C. Burgess and R.M. Alcock, *Solution Equilibria*, (Ellis Horwood, Chichester, 1980) p. 163.
12. N. Yanagihara, R. Casillas, V.F. Rodriguez, L.R. Hurtado, H. and T. Ogura, *Rev. Soc. Quim. Mex.* **29**, 329 (1985).