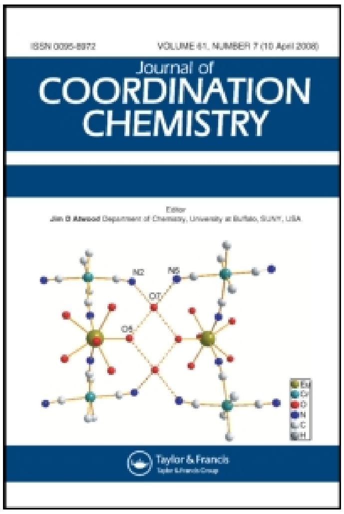

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SILVER COMPLEXES OF POLY(METHYLPHENYLSILOXANE) FOR SEPARATION OF ALIPHATIC, OLEFINIC AND AROMATIC HYDROCARBONS BY GAS CHROMATOGRAPHY AND DETERMINATION OF THE π-COMPLEX FORMATION CONSTANTS

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SILVER COMPLEXES OF POLY(METHYLPHENYLSILOXANE) FOR SEPARATION OF ALIPHATIC, OLEFINIC AND AROMATIC HYDROCARBONS BY GAS CHROMATOGRAPHY AND DETERMINATION OF THE π-COMPLEX FORMATION CONSTANTS

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Silver trifluoroacetate and trifluoromethanesulfonate become highly soluble to poly(methylphenylsiloxane) because of the ion's coordination to the phenyl group: the resulting solution is highly stable. The silver trifluoroacetate or trifluoromethanesulfonate solution has been employed as the liquid phase in gas-liquid chromatography in order to study the separation of mixtures of cyclohexane, cylcohexene and benzene in the temperature range from 50 to 170°C. Use of an internal standard, such as cyclohexane, enables one to evaluate the complex formation constants as well as the salting-out effect merely by measuring the retention time in the presence or absence of Ag^+. The complex formation constants of some aromatic and gaseous olefinic compounds have been determined.

KEYWORDS: poly(methyphenylsiloxane), silver(I), gas chromatography, benzene, cyclohexene

INTRODUCTION

Silver(I) nitrate dissolved in ethylene glycol has been widely used as the liquid phase in gas chromatographic separation of unsaturated hydrocarbons such as aromatic and olefinic compounds.[1-4] Cvetanovic *et al.* succeeded in separating deuterated olefinic isomers with the aid of the same liquid phase[2] but because of the solution's

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thermal instability, the column temperature had to be maintained below 50°C. Obviously, the increased retention times for unsaturated compounds are caused by their weak coordination to the silver ion: therefore, the higher the formation constant of the silver-olefin complex, the greater the retention time. Muhs and Weise[3] and Gil-Av and Herling[4] independently developed almost the same analytical method to evaluate complex formation constants by gas chromatography. The method is based on determination of the retention time of a ligand with and without the Ag^+ ion and determination of the pressures at the sample inlet and outlet, retention volumes, and the flow rates of the carrier gas in the presence and the absence of Ag^+ ion. The complexity of the mathematical treatment described by these investigators obscures the relationship between the retention time and the formation constant of a silver-olefin complex.

In this paper, we show the complex formation constant is determined in a straightforward manner by measuring the retention times of a ligand and an internal standard in the presence of silver ion in the liquid phase and in the absence of the ion. We have also shown that relative increases of retention time are directly proportional to the formation constant and to the $[Ag^+]$ in the liquid phase. The previous work showed the Ag^+ ion is coordinated to a phenyl group in the liquid phase, and is stable at temperature as high as 170°C.[5]

EXPERIMENTAL

Materials

$AgCF_3CO_2$ (Agtac)[6] and $AgCF_3SO_3$ (Agtms)[7] were prepared as reported previously, by reacting Ag_2O, freshly prepared from $AgNO_3$, and NaOH, with a methanol solution of CF_3CO_2H and CF_3SO_3H, respectively. Each compound was recrystallized from hot benzene and the coordinated benzene was removed at 70°C in *vacuo*. Poly(methylphensiloxane) (PhSi) (OV-17, Supelco), silylated diatomaceous earth (Neosorb NCS, Nishio Kogyo, Japan), cyclohexane (Aldrich), cyclohexene (Aldrich) and benzene (Aldrich) were used without further treatment.

Chromatography

An aliquot of Agtac or Agtms and 0.3870 g of PhSi were dissolved in 20.0 mL of benzene, and 2.640 g of the solid support was added to the solution. In order to attain equilibrium the mixture was kept in a rotary evaporator at 50 °C for 30 min with no vacuum applied. Later, the solvent was removed by reducing the pressure. The resultant solid was packed in a stainless steel column of 1/8 inch od. × 6 ft length.

Chromatograms were obtained with a Perkin-Elmer Model 990 Gas Chromatograph equipped with a thermal conductivity detector.

DESCRIPTION OF THE METHOD

It has been shown[3] that the retention time, t, of a component on a gas chromatography column is expressed as eq. (1),

$$H = C \times t \text{ and } C = \{3[(p_i/p_o)^2 - 1]F\}/\{2[(p_i/p_o\}^3 - 1]V\} \qquad (1)$$

where H is the partition coefficient between liquid and gas phase and V (mL), F (mL/min), p_i (atm) and p_o (atm) represent the volume of the liquid phase, flow rate, inlet pressure and outlet pressure, respectively.

Muhs and Weiss[3] and Gil-Av and Herling[4] independently developed eq. (**2**) for a silver(I) ion bearing liquid phase.

$$K[Ag^+] = (H - H_L)/H_L \qquad (2)$$

where K represents the complex formation constant of the silver(I) ion-unsaturated hydrocarbon complex, H_L and H represent the partition coefficients of the ligand between the liquid phase and the vapor phase, in the absence and in the presence of silver(I) ion, respectively.

Fig. 1 and Diagram 1 show the chromatographic patterns when a mixture of an internal standard R and a ligand L is chromatographed by the reference column (Re column) which has PhSi as the liquid phase. Two peaks with retention time t^R_{Re} and

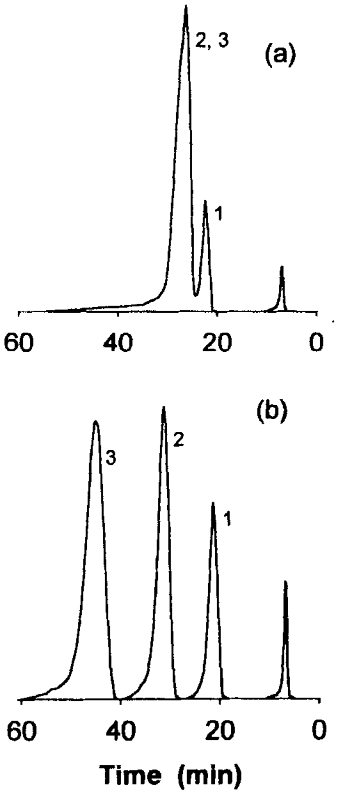

Figure 1 Chromatograms of C_6H_{12} (1), C_6H_6 (2), and C_6H_{10} (3) from a reference column (a) and Agtac column (b) at 101°C.

t^L_{Re} appear, and the corresponding partition coefficients H^R_{Re} and $H^L_{Re} = H_L$ are evaluated by eq. (**1**) which are given as eqs. (**3**) and (**4**).

$$H^R_{Re} = C_{Re}\, t^R_{Re} \qquad (3)$$

$$H^L_{Re} = H_L = C_{Re}\, t^L_{Re} \qquad (4)$$

The mixture is separated by a Ag column, which has Ag^+ ion dissolved in PhSi, into two peaks having the retention time t^R_{Ag} and t^L_{Ag}. The partition coefficients, H^R_{Ag} and H^L_{Ag}, are given as:

$$H^R_{Ag} = C_{Ag}\, t^R_{Ag} \qquad (5)$$

$$H^L_{Ag} = C_{Ag}\, t^L_{Ag} \qquad (6)$$

Cyclohexane employed as an inner standard invariably has a smaller partition coefficient in a silver column than a reference column, as shown in Diagram 1. Therefore, the ratio of the coefficients is defined to the salting-out coefficient σ as eq. (7). It is assumed that R and L in a Ag column are subjected to the same salting-out effect.

$$\sigma = H^R_{Ag}/H^R_{Re} \qquad (7)$$

An imaginary retention time, t_{imag}, can be postulated as the retention time of L in a Ag column that is not subjected to the salting-out effect. Then, the corresponding partition coefficient would become H in eq. (**2**), which is obtained from multiplying H^L_{Ag} by $1/\sigma$. Thus,

$$H = H^L_{Ag}/\sigma \qquad (8)$$

Equation (**9**) is obtained by substituting eqs. (**3**) – (**8**) to eq. (**2**).

$$K[Ag^+] = [(t^R_{Re}/t^L_{Re})\,(t^L_{Ag}/t^R_{Ag})] - 1 \qquad (9)$$

The formation constant, K, can be evaluated from eq. (**9**) merely by measuring the four retention time values, if the silver ion concentration in the liquid phase is available. The simplicity of eq. (**9**) is obvious when compared with eqs. (**1**) and (**2**).

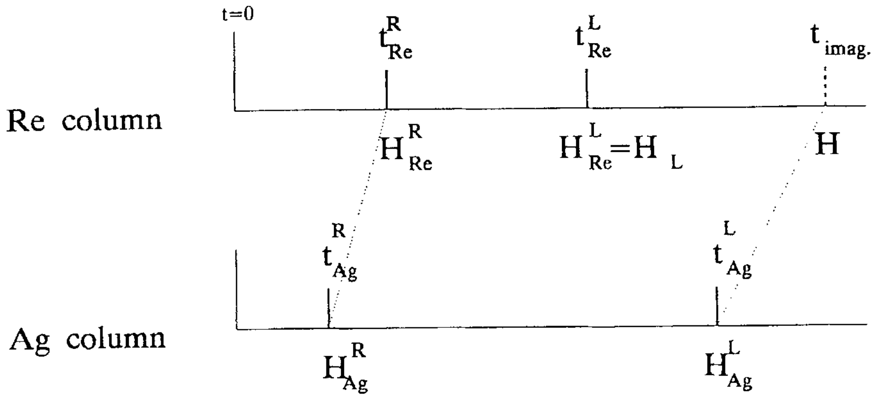

Diagram 1

In this work, cyclohexane was employed as the internal standard; and the complex formation constants for benzene and cyclohexene with Agtac and Agtms were determined by means of eq.(**9**).

RESULTS AND DISCUSSION

Figure 1 compares gas chromatograms of a mixture of cyclohexane, cyclohexene, and benzene, in reference and Agtac columns at 101°C. The silver column separated benzene and cyclohexene (b); in contrast they were not separated in the reference column. The silver column lowered the retention time of the internal standard.

Figure 2 (A) shows the plot of $[(t^{R}_{Re}/t^{L}_{Re})\,(t^{L}_{Ag}/t^{R}_{Ag})] - 1$ for C_6H_{10}, as ordinate on the left-hand side, *vs*, Agtac concentration. Since the former term corresponds to $K[Ag^+]$ in eq. (**9**), a linear relationship is expected; this is confirmed in the range of $[Agtac] \leq 1.4$.[8] However, the observed $[t^{R}_{Re}/t^{L}_{Re})\,(t^{L}_{Ag}/t^{R}_{Ag})] - 1$ value levels out at the higher concentrations.

Plots of $(H/H_L) - 1$ *vs.* $[Ag^+]$ in ethylene glycol presented by Muhs and Weiss[3] are similar to our plots (shown in Figures 2 (A), (B), (C) and (D)). They attributed the leveling out to the salting-out effect.

The lower half of Figure 2 (E) shows the salting-out coefficients σ and the partition coefficients of cyclohexane, H, in PhSi at various concentrations of Agtac obtained by use of eq. (**1**). The σ and H values decrease as the Agtac concentrations increase. Therefore, this effect must be superimposed on the Muhs-Weiss plots for C_6H_{10}, Figure 2 (B).

On the other hand, the $[(t^{R}_{Re}/t^{L}_{Re})\,(t^{L}_{Ag}/t^{R}_{Ag})] - 1$ values have been evaluated by using eq. (**9**), where it has been assumed that the partition coefficients of benzene and cyclohexene, in a certain concentration of the silver salt dissolved in PhSi, decrease in the same proportion as that of cyclohexane.

Since both ordinates of Figure 2, $[(t^{R}_{Re}/t^{L}_{Re})\,(t^{L}_{Ag}/t^{R}_{Ag})] - 1$ and (H/H_L) pm11, correspond to $K[Ag^+]$ as shown in eqs. (**2**) and (**9**), both plots are expected to be identical. However, the slope of the Muhs-Weiss plot at lower concentration is notably smaller than that for $[(t^{R}_{Re}/t^{L}_{Re})\,(t^{L}_{Ag}/t^{R}_{Ag})] - 1$ *vs.* $[Ag^+]$. This might be attributed to the fact that Muhs-Weiss and Gil-Av-Harling have not taken into account the salting-out effect in eq. (**2**) although they did demonstrate the importance of this effect.[3]

The cycolhexene plateau for $[(t^{R}_{Re}/t^{L}_{Re})\,(t^{L}_{Ag}/t^{R}_{Ag})] - 1$ reaches 1.7 and $(H/H_L) - 1$ reaches 1.2. The higher value of the former indicates that the salting-out effect has not been taken into account.

Figures 2 (C) and (D) show plots of $K[Ag^+]$ for benzene *vs.* $[Ag^+]$. Small positive values are obtained for $K[Ag^+]$ based on the absolute partition function of the ligand in PhSi containing various concentrations of Agtac as seen in Figure 2 (D). On the other hand, Figure 2 (C) exhibits $K[Ag^+]$ values obtained with the aid of the relative partition function of benzene to cyclohexane; the behavior of this value is analogous to its behavior in Figures 2 (A) and (B).

It is noteworthy that Figures 2 (A), (B), (C) and (D) consist of a sloping line and plateau, and the intersections of the lines fall within a narrow range of [Agtac]. Moreover, σ and H values attain minimum values in the same range. This is caused

Table 1 The temperature dependence of complex formation constants in *ln*K = A/T(K) + B ± s[a] and some thermodynamic constants.

Ligand	Agsalt	A	B	s[a]	ΔH KJ mol^{-1}	ΔS mJ deg^{-1}mol^{-1}
C_6H_{10}	Agtac	1277	-3.527	0.058	-10.6	-0.029
	Agtms	2932	-7.465	0.023	-24.4	-0.062
C_6H_6	Agtac	-0.266	-1.340	0.044	-0.002	-0.013
	Agtms	1477	-5.778	0.064	-12.3	--0.048

[a] standard deviation

by the limited solubility of the silver salt, and an estimate of the solubility of Agtac in PhSi is 1.4 molal at 71°C.

Muhs and Weiss[3] employed a H^{L}_{Ag} value for H in eq. (**1**). Therefore, $K^M[Ag^+]$ is given as eq. (**10**) substituting eqs. (**3**)–(**8**) to eq. (**2**),

$$K^M[Ag^+] = \sigma\,[(t^R_{Re}/t^t_{Re})\,(t^L{}_{Ag}/t^R_{Ag})] - 1 \qquad (10)$$

where K^M refers to the complex formation constant they obtained. Thus, the ordinate $(H/H_L) - 1$ in Fig. 2 displays $K^M[Ag^+]$ of eq. (**10**).

However, the salting-out constant σ cannot be evaluated by the retention time values alone but must be determined from all values in eq. (**1**). Fortunately, σ is cancelled and only four retention times remain in eq. (**8**).

Eq. (**9**) is applicable not only to silver complex formation but also to any interaction of a species with an active center in the liquid phase, if $[Ag^+]$ is substituted by the concentration of the nonvolatile active center. We believe that selection of a reference compound will play a key role in this method as seen previously.[6]

Fig. 3 shows the temperature dependence of the complex formation constants of Agtac and Agtms with benzene and cyclohexene in PhSi. Table 1 summarizes the Cladius-Clapeyron expression for the formation constants and the thermodynamic constants, and Table 2 compares the observed constants to those calculated by use of the A and B values shown in Table 1. As shown in Tables 1 and 2, the calculated

Table 2 A comparison of the observed π-complex formation constants at various temperatures *vs.* the calculated ones using the values presented in Table 1.

		Formation constant, K, molal^{-1}			
temp. °C		Agtac.C_6H_{10}	Agtms.C_6H_{10}	Agtac.C_6H_6	Agtms.C_6H_6
51	obs	1.52	-	0.206	-
	calc	1.51	-	0.201	-
58	obs	1.28	3.85	0.190	0.252
	calc	1.39	4.02	0.201	0.268
71	obs	1.20	3.01	0.194	0.240
	calc	1.20	2.88	0.201	0.227
81	obs	1.13	2.29	0.215	0.216
	calc	1.08	2.26	0.201	0.201
90	obs	1.04	1.90	0.223	0.169
	calc	1.01	1.84	0.201	0.181
101	obs	0.817	1.33	0.182	0.159
	calc	0.893	1.45	0.201	0.160

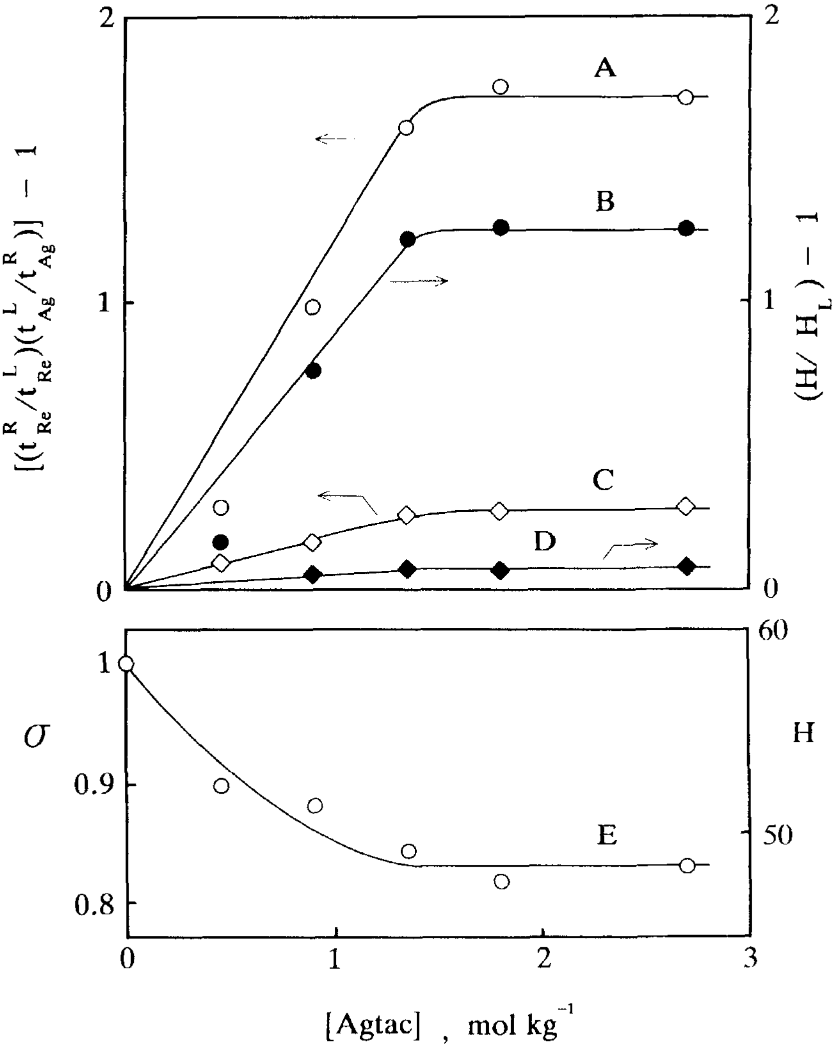

Figure 2 (1) upper half: Plots of $[(t_{Re}^{R}/t_{Re}^{L})(t_{Ag}^{L}/t_{Ag}^{R})] - 1$ *vs.* [Agtac] for cyclohexene (A) and benzene (C); and plots of $(H/H_L) - 1$ *vs.* [Agtac] for cyclohexene (B) and benzene (D). (2) lower half: Plots of σ and H *vs.* [Agtac] for cyclohexane at 71 °C (E).

formation constants deviate considerably from the experimental values obtained by least squares treatment. These relatively large errors may be attributed to channel formation in the column and diffusion of the sample gases into the column packing.

As the enthalpy change for the Agtac-benzene complex is very close to zero (Table 1), the complex formation constant, t_{Ag}^{L}/t_{Ag}^{R} in eq. (**9**), stays practically unchanged as the temperature changes. Therefore, it is possible to say which peak of a complex mixture of hydrocarbons, such as petroleum products, belongs

Table 3 Some complex formation constants of aromatic compounds with Agtac at 120°

Compound	K
toluene	1.1
o-xylene	0.81
m-xylene	0.58
p-xylene	0.56
ethylbenzene	0.51
styrene	1.2

to alkene or aromatic complex by comparing the relative retention times employing PhSi and Agtac dissolved into PhSi as the liquid phase and measuring the retention times at two temperatures for a silver column. Peaks

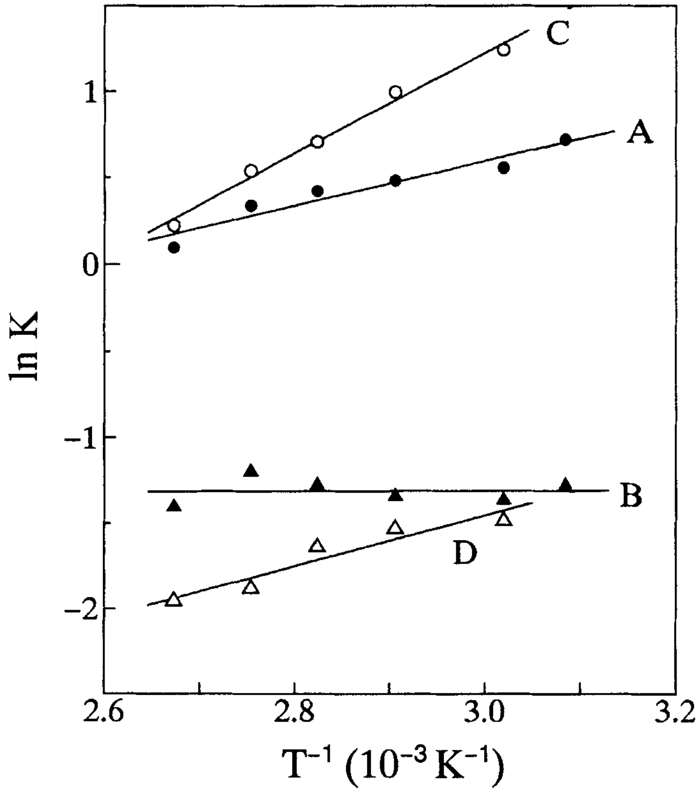

Figure 3 Plots of *ln*K *vs.* 1/T: (A) C_6H_{10}/Agtac; (B) C_6H_6/Agtac; (C) C_6H_{10}/Agtms; (D) C_6H_6/Agtms.

that increase the relative retention time might be aromatic or alkene. The aromatic hydrocarbons might not suffer temperature change, assuming that the enthalpy changes for complex formation is nearly zero as seen in benzene. However, it is indispensable to accumulate more experimental data.

Previously it was observed that the complex formation constant of Agtac with benzene falls in a range of 0.4–0.8 by vapor composition and 0.8–1.4 by vapor pressure analysis, and that with cyclohexene 1.6–2.2 and 2.5–7.0 by vapor composition and vapor pressure, respectively.[9] The similar values have been determined in this study as 0.3 and 2.3 for benzene and cyclohexene, respectively.

The two lines for cyclohexene as well as for benzene are located close together, but these pairs are located far apart from each other as reported previously.[10] This provides a simple basis for distinguishing between olefinic and aromatic compounds by gas chromatography.

Since the tms anion has poorer coordinating power than the tac anion,[11] Agtms might form a stronger complex than Agtac as seen in the cyclohexene plots shown Figs. 3 (A) and (C).

Contrary to this benzene coordinates more strongly with Agtac than with Agtms as shown in Figs. 3 (B) and (D). Therefore, the benzene complex of Agtac must be stabilized in a special manner. It is notable that Fig. 2 (B) is practically horizontal. Thus, the temperature dependent term, A or ΔH in Table 1, is almost zero. In addition, the entropy change is also very small. Since the exchange reaction requires little free energy change, it takes place evenly with PhSi and benzene. We believe the resultant benzene and PhSi complexes are very similar.

It is known that tac anion coordinates in diverse manners through the carboxylate group.[12] Our previous study showed that Agtac was a mixture of monomeric and dimeric forms in benzene as eq (**11**),

$$2\mathrm{Agtac}(C_6H_6)_x = (\mathrm{Agtac})_2(C_6H_6)_2 + (2x - 2)C_6H_6 \qquad (11)$$

where x indicates an unknown number.[6] The dimerization constant was determined to be 8×10^2 molal^{-1} at 34.8°C.[6]

A similar equilibrium might be attributed to the formation of chemical species in PhSi. Denoting Ph_n for PhSi in order to show the polymerization number by n, the following species are expected to be present in the liquid phase:

i. free ligand: Ph_n
    $(Agtac)_2/Ph_n = 0$

ii. monomer: $(Ph_n)_x$ -Agtac

iii. dimer: $Ph_n-(Agtac)_2-Ph_n$
    $(Agtac)_2/Ph_n = 0.5$

iv. olygomers: $Ph_n-(Agtac)_2-Ph_n-(Atrac)_2-Ph_n$, *etc.*
    $0.5 < (Agtac)_2/Ph_n < 1$

v. polymers: $-(Agtac)_2-Ph_n-(Agrac)_2-Ph_n$----
    $(Agtac)_2/Ph_n = 1$

vi. multimetalated ligands: $(Agtac)_2-Ph_n-(Agta)_2$, *etc.*
    $(Agtac)_2/Ph_n < 1$

The mole ratio, $(Agtac)_2/Ph_n$, is given in the second line of each species.

On the other hand, the concentration of Agtac was approximately 1.0 molal in the liquid phase and $n = 5.85$.[11] Then, the mole ratio, $(Agtac)_2/Ph_n = (1.0/2)/(1000/136 \times 5.85) = 0.37$. Therefore, the main species in the liquid phase may be a mixture of dimer and monomer as seen in benzene.

Table 3 shows the complex formation constants of some aromatic compounds that were determined gas chromatographically. The three isomers of xylene have very similar retention times in PhSi. However, *o*-xylene coordinates 40% more strongly than *m*- or *p*-isomers. Thus, by employing [Agtac] = 1 molal in a column, an approximately 40% greater retention time is expected for the *o*-isomer in comparison to other isomers by inspection of eq. (**9**). However, *m*- and p-isomers of xylene were not separated in this column.

The retention time of styrene is 30% greater than that of ethylbenzene at 120°C in PhSi. Since the complex formation constant of styrene is 2.35 times of ethylbenzene, the ratio of retention times of these compounds are approximated by use of eq. (9), assuming $\sigma = 1$; $1.3 \times 2.35 \approx 3$.

Some gaseous compounds were chromatographed at 27°C using a 0.90 molal Agtac column. However, the formation constants for ethylene and vinyl chloride could not be determined because the retention times were too small. The formation constants with propylene and butadiene are 0.2 and 0.3, respectively.

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References and notes

1. B.W. Bradford, D. Harvey and D.E. Chalkely, *J. Inst. Petro.* **41**, 80 (1955).
2. (a) R.J. Cretanovic, F.J. Duncan and W.E. Falconer, *Can. J. Chem.* **41**, 2095 (1963). (b) J.G. Atkinson, A.A. Russel and R.S. Stuart, *Can. J. Chem.* **45**, 1963 (1967). (c) S.P. Wasik and W. Tsang, *J. Phys. Chem.* **74**, 2970 (1970). (d) K.K. Lee and F.S. Rowland, *Anal. Chem.* **36**, 2181 (1962).
3. M.H. Muhs and F.T. Weiss, *J. Am. Chem. Soc.* **84**, 4697 (1962).
4. E. Gil-Av and J. Herling, *J. Phys. Chem.* **66**, 1208 (1962).
5. A.M. Soto, N. Yanagihara and T. Ogura, *Anal. Chem.* **63**, 1178 (1991).
6. N. Yanagihara, R. Casillas, V.F. Rodriguez, L.R. Hurtado, H. and T. Ogura, *Rev. Soc. Quim. Mex.* **29**, 329 (1985).
7. G.M Whitesides and F.D. Gutowski, *J. Org. Chem.* **41**, 2882 (1976).
8. A referee pointed out that the line would intercept the *x*-axis at [Agtac] = 0.2, which may be an indication of some other effect. We agree. In the near future we would like to further study the possibility that there exists special sites in the solid phase or even in PhSi, where the silver ion is selectively trapped to lose the coordination potential to benzene.
9. A.M. Soto, N. Yanagihara and T. Ogura, *the preceding paper.*
10. F.R. Hartly, *Chem. Rev.* **73**, 163 (1973).
11. P.J. Stang and M.R. White, *Aldrichimica Acta*, **16**, 15 (1983).
12. (a) R.G. Griffin, J.D. Ellett, Jr., M. Mehring, J.G. Bullitt and J.S. Waugh, *J. Chem. Phys.* **57**, 2147 (1972). (b) C.D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.* **17**, 1 (1975).