

Complexation of Co-contaminant Mixtures between Silver(I) and Polycyclic Aromatic Hydrocarbons

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The complexation of co-contaminant mixtures between Ag(I) and polycyclic aromatic hydrocarbon (PAH) molecules (naphthalene, pyrene, and perylene) were investigated to quantify the equilibrium constants of their complexes and elucidate the interactions between Ag(I) and PAH molecules. The apparent solubilities of PAHs in aqueous solutions increased with increasing Ag(I) ion concentration. The values, K_1 and K_2 of equilibrium constants of complexes of Ag(I)-PAHs, were 2.990 and 0.378, 3.615 and 1.261, and 4.034 and 1.255, for naphthalene, pyrene, and perylene, respectively. The K_1 and K_2 values of PAHs for Ag(I) increased in the order of naphthalene < pyrene < perylene and naphthalene < pyrene \cong perylene, respectively, indicating that a larger size of PAH molecule is likely to have more a richer concentration of electrons on the plane surfaces which can lead to stronger complexes with the Ag(I) ion. For the species of Ag(I)-PAH complexes, a 1:1 Ag(I) : the aromatic complex, $AgAr^+$, was found to be a predominant species over a 2:1 Ag(I) : aromatic complex, Ag_2Ar^{++} . The PAH molecules with four or more aromatic rings and/or bay regions were observed to have slightly less affinity with the Ag(I) ion than expected, which might result from inhibiting forces such as the spread of aromatic π electrons over a wide molecular surface area and the intermolecular electronic repulsion in bay regions.

Key Words : Silver(I), Polycyclic Aromatic Hydrocarbons, Complexation, Cation- π Interaction, Co-contaminant Mixtures

1. Introduction

Multicomponent contaminant mixtures, including binary, ternary, quaternary, and higher order contaminant mixtures, occur widely at many waste sites.¹⁾ Individual contaminants can interact with each other and alter each other's subsurface biogeochemical behavior by geochemical processes and reactions. Hence, a comprehensive understanding of co-contaminant interactions will be useful in elucidating the fate and transport of co-contaminant mixtures in subsurface environments and enhancing fundamental concepts for in-situ remediation by mixed co-contaminants. Examples of complex contamination problems involving both organic and inorganic chemicals

are numerous; often, these contaminated sites include the presence of polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs), pesticides and toxic metals/metalloids.¹⁾ Among possible binary co-contaminant mixtures, the pair of PAHs and silver (Ag(I)) have received much attention because Ag(I) is known to be a metal species that can have interactions with PAH molecules.^{2,3)} When PAHs and Ag(I) co-exist in contaminated geo-environmental systems, they can form co-contaminant mixtures, which are likely to cause more complex environmental contamination.

PAHs are a group of ubiquitous organic contaminants that continue to receive considerable attention because of their widespread occurrence, toxicity, and persistence in the environment.⁴⁻⁷⁾ In particular, naphthalene, pyrene, and perylene among PAHs are known or

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suspected to be mutagenic, carcinogenic and/or co-carcinogen.^{6,7)} They have been found widely distributed in freshwater, sediments, soils, and leachates.^{4,5)} Pyrene and perylene are of much concern in environments due to their reluctance to biodegradation. They are classified as persistent compounds, whose degradation occurs so slowly as to make biological treatment inefficient.⁸⁾ Ag(I) has received much concern because of its toxic effects and widespread presence at many contaminated environments.^{9,10)} Relatively high concentration of Ag(I) can be often found in the tailings and stream sediments near mining and industrial sites, which might contribute to production of highly concentrated co-contaminants with PAHs.⁹⁾ Ag(I) is presently regulated and guided in the United States as a toxic material as a result of requirements by the Safe Drinking Water Act, the Clean Water Act, and the Resources Conservation and Recovery Act.¹⁰⁾

Recently, reactions of aromatic rings with polar and charged species in aqueous systems have become an increasingly active area of research. Studies of the interactions between aromatic rings and cations have shown that an appreciable attraction exists between the two species.^{11,12)} In the case of benzene, the six π -electrons form diffuse electron clouds above and below the plane and create a substantial negative charge on the ring faces that is counterbalanced by an equal band of positive charge along the edge of the plane. The electrostatic attraction between cations and negatively-charged benzene faces has been termed the "cation- π interaction".¹¹⁾ The energy of the interaction can be relatively strong, approximately one-fifth that of typical covalent bonds and about five times stronger than a hydrogen bond.^{12,13)}

Several researchers have shown spectroscopic evidence of cation- π bonding between silver(I) ion and PAHs in solid and gaseous phases.¹⁴⁻¹⁸⁾ However, very little research has been presented to show spectroscopic evidence of the complexation of Ag(I) with aromatic hydrocarbons in the aqueous phase. In fact, only a few older studies exist that show Ag(I) complexation of PAHs in water based on the macroscopic observation of solubility enhancement.^{2,3)} Andrews and Keefer²⁾ presented macro-

scopic evidence for the formation of Ag(I) cation complexes with PAHs in the aqueous phase and reported equilibrium constants for the argentation of the PAHs in aqueous solution. Kofahl and Lucas³⁾ also demonstrated the formation of cation complexes with PAHs. However, their evidence of Ag(I)-PAH complexes was provided only for limited PAH solutes such as naphthalene, phenanthrene or benzo(c)phenanthrene. Little to no information is available for equilibrium constants of Ag(I) with more persistent PAHs, such as pyrene and perylene, which are of more significance in subsurface environments due to their persistence and toxicity. The physicochemical and steric properties of PAH molecules can play a pivotal role in affecting the interactions of Ag(I) with PAH molecules. For example, PAH molecules with larger size and without bay regions are expected to have stronger interaction with Ag(I) ions because they contain richer electron clouds and less inhibiting forces on the PAH surfaces. Hence, the information on the physicochemical and steric characteristics of PAH molecules influencing the Ag(I)-PAH complexes can be of much importance in understanding the interplay between Ag(I) and PAH molecules. Nevertheless there is little to no research on the physicochemical and steric properties of PAH molecules to be able in determining the magnitude of interaction between Ag(I) and PAH molecules.

This study quantified and provided the equilibrium constants of co-contaminant mixtures between Ag(I) and three PAH molecules (naphthalene, pyrene, and perylene). The correlation of Ag(I)-PAH equilibrium constants with physicochemical and steric characteristics of PAH molecules was investigated to properly understand the interaction of co-contaminant mixtures between PAHs and Ag(I). In addition, we also explored the feasible species of co-contaminant mixtures between Ag(I) and PAHs.

2. Experimental Section

2.1. Materials

Three PAHs, naphthalene (99%, Aldrich Chemical), pyrene (99%, Aldrich Chemical), and perylene (99%, Aldrich Chemical) were used as organic contaminants. Silver perchlorate (AgClO_4 ,

crystals, Aldrich Chemical) was used as a representative inorganic contaminant. Perchlorate salt was employed in this study because the perchlorate anion has a low affinity with other cations. All aqueous solutions were prepared using distilled deionized water (DDW) (Mega-Pure System MP-6A). PAH stock solutions were obtained by serial dilution of naphthalene, pyrene, and perylene in methanol (HPLC Grade, Fisher Scientific), resulting in six preparations with concentrations ranging from 0.013 to 0.157 mol/L (1.7 to 20.1 g/L), 0.059 to 0.321 mmol/L (12.0 to 65.0 mg/L), and 0.080 to 0.333 μ mol/L (0.020 to 0.084 mg/L), respectively.

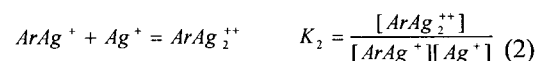
2.2 Ag(I)-PAH complexation experiments

Experiments for equilibrium constants of complexation of Ag(I) ions and PAH molecules were conducted in twenty-five milliliter glass centrifuge tubes with teflon-lined screw caps. For naphthalene, lead foil was placed onto the inner face of the teflon-lined screw caps to minimize volatilization losses. The glass centrifuge tubes were prepared for use by soaking in methanol (HPLC Grade, Fisher Scientific) overnight, soaking in nitric acid at least overnight, and then rinsing with DDW. Silver-salt solutions were prepared at more than three different concentrations, and then twenty milliliters of each solution was added to a centrifuge tube. Replicate samples with different concentrations of silver salt solutions were spiked with 20 μ L of a particular PAH stock solution, which resulted in initial aqueous PAH concentrations (i.e., 98.8 mg/L, 364.0 μ g/L, and 288.0 ng/L for naphthalene, pyrene, and perylene, respectively) of four times higher than the determined PAH solubility at 20 °C, even after accounting for sorption to the centrifuge tube walls and teflon liners. In a blank test, the average sorbed concentrations of naphthalene, pyrene, and perylene to the centrifuge tube walls and teflon liners was 7.6%, 9.5%, and 33.7% for the spiked initial PAH concentrations of 98.8 mg/L, 364.0 μ g/L, and 288.0 ng/L for naphthalene, pyrene, and perylene, respectively. The small volume of methanol added (volume fraction of 0.001) had no effect on PAH solubilities.¹⁹ All samples were then agitated on a temperature-controlled (20 \pm 0.1°C) orbital shaker at 375 rpm for 24 hours. After equi-

libration, the batch reactors were centrifuged at 7000 rpm in a temperature-controlled centrifuge for 1 hour to separate the over-saturated solids. Hexane extraction of the PAHs was used to avoid fluorescent quenching by Ag(I).²⁰ For these samples, 7-mL aliquots of the supernatants were transferred to 40 mL glass amber vials before adding an equal volume of hexane. The vials were shaken vigorously by hand for three minutes, and then mixed for a minimum of three hours on a temperature-controlled shaker at 20 °C before determining PAH concentrations. PAH concentrations in hexane were measured using fluorescent spectroscopy (Photon Technology International, Inc.). Pyrene and perylene in the hexane extracts were quantified by fluorescence at the excitation/emission wavelengths of 336/ 374 and 433/469 nm, respectively, whereas naphthalene concentrations in hexane were quantified with a diode array spectrophotometer (Hewlett Packard, 8452A) via absorbance at 276 nm. Ag(I) concentrations were analyzed by flame atomic absorption spectrometry using a Varian Spectra AA 20 Plus spectrometer at the wavelength of 328.1 nm.

2.3. Calculation of equilibrium constants for Ag(I)-PAH complexes

Andrews and Keefer proposed a possible method to obtain the equilibrium constants for complexes of Ag(I) with PAHs from solubility data.²⁾ Based on the assumption that a 2:1 Ag(I) : aromatic complex (i.e., Ag_2Ar^{++}) as well as a 1:1 Ag(I) : aromatic complex (i.e., $AgAr^+$) could form, they established the following equilibrium equations:



$$[Ar]_t = [Ar] + [ArAg^+] + [ArAg_2^{++}] \\ = [Ar] \{ 1 + K_1[Ag^+] + K_1K_2[Ag^+]^2 \} \quad (3)$$

Where [Ar] is the aqueous molar concentration of uncomplexed/free aromatic hydrocarbon, $[Ag^+]$ is the molar concentration of the silver ion in free form, $[Ar]_t$ is the aqueous molar concentration of all aromatic hydrocarbon containing species, and K_1 and K_2 are the equilibrium constants for the $ArAg^+$ and $ArAg_2^{++}$

complexes.

As shown in equation 3, the best values of $[Ar]$, K_1 , and K_2 can be obtained by using a graph-fitting method. In this study, the equilibrium constants (K_1 and K_2 values) for Ag(I)-PAH complexes were quantified by fitting a second-order polynomial curve to the experimental solubility data. For example, the K_1 and K_2 values can be derived through the manner in which the coefficient values of the x^2 and x variables in the second-order polynomial curve are divided by the constant value in the curve, respectively. The x axis in the second-order polynomial curve represents the molar concentration of the silver ion in free form, corresponding to $[Ag^+]$ in equation 3.

3. Results and Discussion

3.1. Complexation of Ag(I) with PAH molecules

Solubilities of naphthalene, pyrene, and perylene in DDW were determined at 20 °C, and these values are shown in Table 1 along with their physicochemical properties taken from the literature. The information on the solubilities in DDW and physicochemical properties of PAHs was used for determining the initial spiking PAH concentrations in PAH solubility experiments in the presence of silver salt solutions and examining the correlation between equilibrium constants of complexes and molar volume of PAHs, respectively. PAH solubility experiments in the presence of silver perchlorate were conducted to investigate the complexation of Ag(I) with PAH molecules and determine the equilibrium constants of complexes of PAHs with Ag(I) cation. The experimental results for naphthalene, pyrene, and

perylene are shown in Fig. 1. The apparent solubilities of naphthalene, pyrene, and perylene in aqueous solution increased with increasing Ag(I) ion concentration. This result suggests that the Ag(I) ion can interact with PAH molecules, possibly through the manner that the relatively strong complex may form between Ag(I) and the electron clouds present on the electron-rich PAH faces.

The equilibrium constants, K_1 and K_2 , of $ArAg^+$ and $ArAg_2^{++}$ complexes, were obtained by fitting second-order polynomial curves to the solubility data. Table 2 represents equilibrium constants of complexes between Ag(I) and aromatic hydrocarbons as measured by this study as well as previous studies.^{2,3)} The K_1 and K_2 for the formation of the complexes of Ag(I)-PAHs, were 2.990 and 0.378, 3.615 and 1.261, and 4.034 and 1.255, for naphthalene, pyrene, and perylene, respectively. The K_1 value (2.990) of this study for naphthalene was in good agreement with the values (3.080 and 2.937) determined by Andrews and Keefer²⁾ and Kofahl and Lucas.³⁾ In Table 2, the K_1 values of PAHs for the Ag(I) ion increase in the order of naphthalene < pyrene < perylene. The trend of increasing K_1 with increasing molecular size of PAHs may be attributed to the fact that PAHs with more aromatic rings can have larger area or higher positions for aromatic rings to be able to interact with the Ag(I) ion. As shown in Table 2, the magnitude of K_2 values for three PAHs was observed in the order of naphthalene < pyrene \approx perylene. The similar K_2 value of perylene to that of pyrene might result from inhibiting forces such as intermolecular electric repulsion or steric repulsion in bay regions, which will be more widely discussed in the latter part of this

Table 1. Physicochemical properties of PAHs and aqueous solubilities of PAHs in distilled water

PAH	MW ^a (g/mol)	MV ^b (mL)	HSA ^c (Å ²)	Aqueous Solubility		N ^e
Naphthalene	128.2	125.0	155.8	24.7 ± 1.2 mg/L	193 ± 9.1 μM	22
Pyrene	202.3	171.5	213.0	90.6 ± 1.8 μg/L	447.8 ± 9.1 μM	10
Perylene	252.3	202	251.5	72.1 ± 2.1 μg/L	286 ± 8 pM	14

^a Molecular weight values from ref. 21. ^b Molar volume values from ref. 22. ^c Hydrophobic surface area values from ref. 23. ^d Measured at 20 °C in distilled, deionized water (DDW). Values shown are ± standard error. ^e Number of data point used

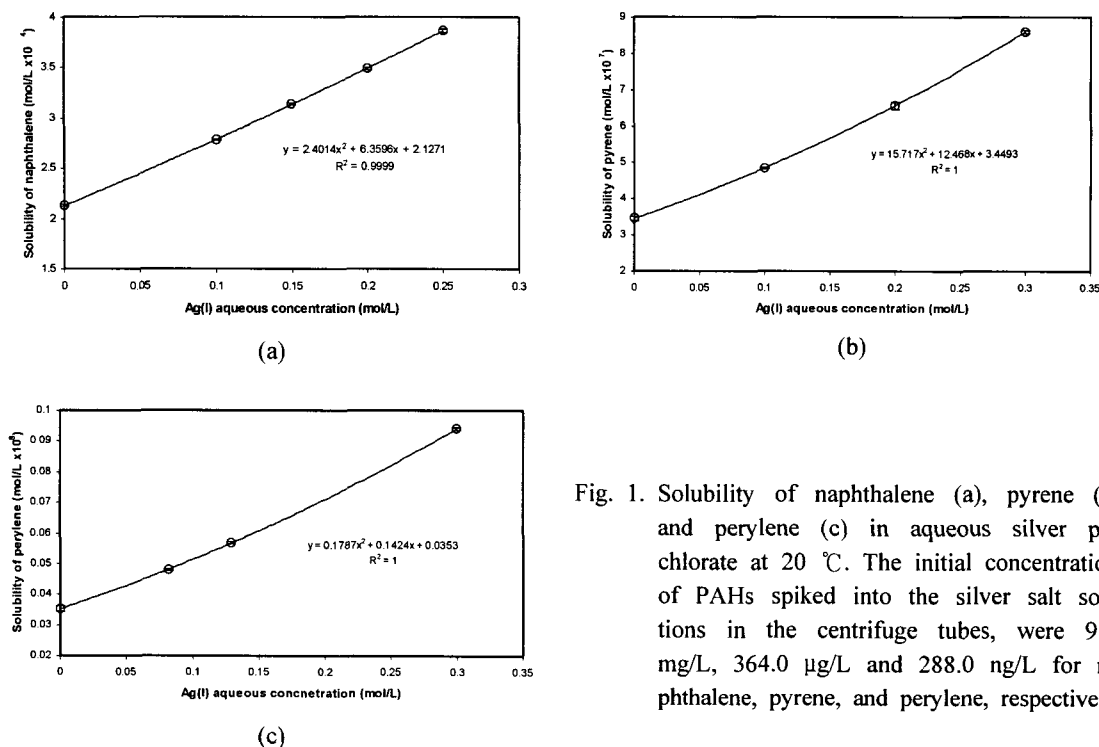


Fig. 1. Solubility of naphthalene (a), pyrene (b), and perylene (c) in aqueous silver perchlorate at 20 °C. The initial concentrations of PAHs spiked into the silver salt solutions in the centrifuge tubes, were 98.8 mg/L, 364.0 µg/L and 288.0 ng/L for naphthalene, pyrene, and perylene, respectively.

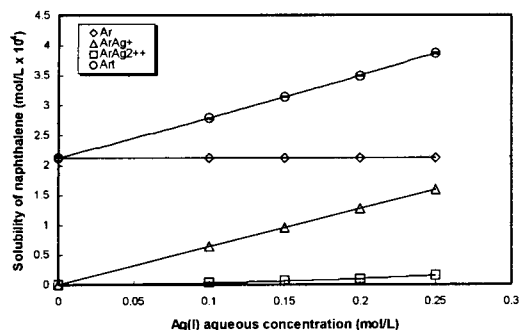
Table 2. Equilibrium constants of complexes between PAHs and Ag(I) ion

PAHs	K_1	K_2	K_3	References
Benzene	2.410	0.212		Andrews and Keefer ²⁾
Naphthalene	3.080	0.909		Andrews and Keefer ²⁾
	2.937	0.909		Kofahl and Lucas ³⁾
	2.990±0.062	0.378±0.070		This Study
Phenanthrene	3.670	1.800		Andrews and Keefer ²⁾
	3.550	0.990	0.470	Kofahl and Lucas ³⁾
Pyrene	3.615±0.061	1.261±0.038		This Study
Perylene	4.034±0.040	1.255±0.032		This Study

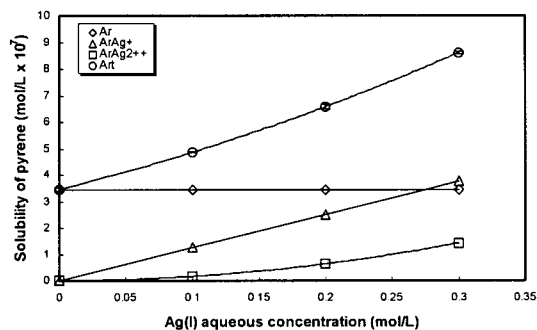
report. The K_1 values for three PAHs are observed to be greater than the K_2 values, suggesting that the $AgAr^+$ complex relating to the K_1 value could be a precedent and predominant form over Ag_2Ar^{++} complex relating to the K_2 value because the presence of Ag(I) ions as a form of $AgAr^+$ ahead of Ag_2Ar^{++} on the planes or position of the PAH molecules may reduce the possibility that the second Ag(I) ion is added into the existing bonding form of $AgAr^+$.

3.2. Speciation of Ag(I)-PAH complexes

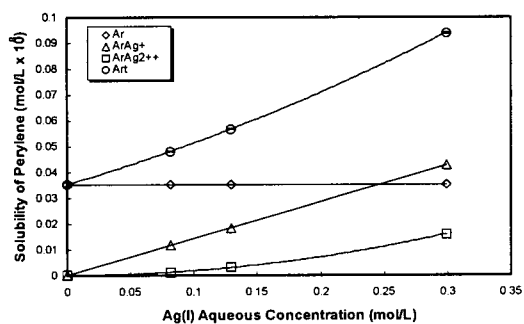
Speciation diagrams for naphthalene, pyrene, and perylene using equilibrium constants from Table 2 are represented in Fig. 2. The speciation diagrams for naphthalene, pyrene, and perylene show how the concentrations of Ar , $ArAg^+$, and $ArAg_2^{++}$ are changing with Ag^+ concentration. The concentrations of $ArAg^+$ and $ArAg_2^{++}$ species were increased with increasing Ag^+ concentration in solution. Additionally, it was observed in the speciation diagram for



(a)



(b)



(c)

Fig. 2. Speciation diagrams for naphthalene (a), pyrene (b), and perylene (c) using constants from Table 2. The symbols \diamond , \triangle , \square , \circ indicate the molar concentration of free PAH(Ar), complexed form of PAH molecule with Ag(I) ion (ArAg^+), complexed form of PAH molecule with Ag(I) ion (ArAg^{2++}), and PAH containing all species (Ar_I), respectively. The initial concentration of each PAH spiked into the silver salt solution in the centrifuge tube, was the same as that shown in Fig. 1.

three PAHs that a 1:1 Ag(I) : aromatic complex, AgAr^+ was the predominant species over a 2:1 Ag(I) : aromatic complex, $\text{Ag}_2\text{Ar}^{2+}$, indicating that the AgAr^+ species can play an important role in complexation of Ag(I) and PAH molecules.

3.3. Correlations of complexation constants with molar volumes of PAHs

As shown in previous researches in Table 2, it can be found that the K_1 and K_2 values increased with increasing PAH molecular size. Their findings provide a clue to verify the hypothesis that the magnitude of K_1 values of a series of PAHs may have some correlation with molar volumes of PAHs to represent the molecular size of PAH molecules, because PAHs with a larger molar volume can have richer electrons that can interact with cations. Hence, the relationship between the PAH molar volume and equilibrium constants of PAH was examined in this study. Molar volume of organic compounds can be obtained by dividing the organic molecular mass (g/mol) by liquid density of organic compound (g/cm³ or g/mL).

The information on the molar volume for naphthalene, pyrene, and perylene were retrieved from literature as shown in Table 1. Fig. 3 depicts the correlation of K_1 and K_2 values of the complexes between three PAHs (i.e., naphthalene, pyrene, and perylene) and Ag(I). It was found that there was a proportional correlation between molar volume and K_1 values of naphthalene, pyrene, and perylene. The K_2 values of PAH molecules for naphthalene and pyrene showed a proportional relation with their molar volumes but not for perylene. The deviation of K_2 value of perylene from the proportional correlation line between molar volume and K_2 values, contrary to the expectation that perylene would have larger K_2 value than pyrene, like in the case of the K_1 value, might result from the steric effect of perylene with two bay regions (unlike pyrene with no bay region, which will be discussed in latter part of this report).

Fig. 4 represents the comparison of correlations between K_1 values and PAH molar volumes measured by several researches. The K_1 values of previous studies for PAHs also

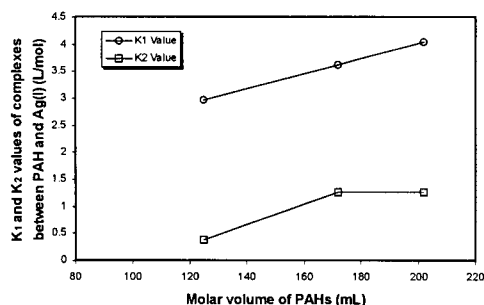


Fig. 3. Correlation of K_1 and K_2 values of complexes between three PAHs (naphthalene, pyrene, and perylene) and Ag(I) with molar volume of PAHs.

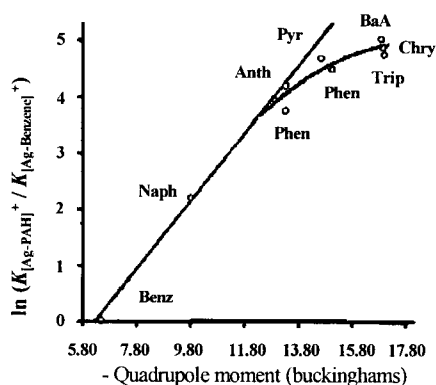


Fig. 5. Correlation of relative Ag(I) affinities of PAHs and quadruple moment. Relative Ag(I) affinities of PAHs are calculated using ion intensity ratio of Ag(I)-benzene ($K_{[Ag-Benzene]}$) to Ag(I)-PAHs ($K_{[Ag-PAH]}$). (Benz : benzene, Nap : naphthalene, Phen : phenanthrene, Anth : anthracene, Fluo : fluoranthene, Pyr : pyrene, Trip : triphenylene, BaA : baenz[a]anthracene, and Chry : chrysene) The data are retrieved from the study of Ng *et. al.*¹⁸⁾

exhibited a strong proportional correlation with PAH molar volumes. However, their slopes were slightly different from those of this study. The PAHs with relatively large surface areas (i.e., pyrene and perylene) and/or bay regions (i.e., perylene) showed slightly lower K_1 values deviated from the proportional correlation trend line of other researches. This result can be explained by the finding of Ng *et. al.*¹⁴⁾ They explored the binding energy of Ag^+ -PAH complexes in the gas phase according to the

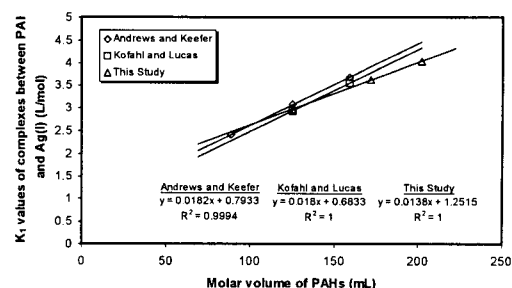


Fig. 4. Comparison of correlations of K_1 values of complexes between PAH and Ag(I) with molar volume of PAHs.

size of PAH molecules. Their experimental result for the correlation between relative Ag(I) ion affinities for PAHs and their quadrupole moment is represented in Fig. 5. They observed that PAHs with four or more aromatic rings (i.e., pyrene, triphenylene, chrysene or benz[a]-anthracene) and/or bay regions (i.e., phenanthrene, triphenylene, chrysene, benz[a]anthracene) exhibited inadequate trends off the correlation line of Ag(I) ion affinity with quadruple moment of PAHs. They speculate that their results might be attributed to the weakened cation-quadruple moment due to surface area effects such as : the spread of aromatic π electrons over a wide molecular surface area, and/or the steric effect such as intermolecular electronic repulsion in bay regions. In other words, the Ag(I) affinity for PAHs with high number of aromatic rings (four or more rings) and/or bay regions might be to some extent reduced due to the surface area and/or steric effects. The trend of unexpected slightly lower K_1 values of pyrene and perylene in Fig. 4 seems to coincide well with the mass spectrometric kinetic experimental results for Ag(I) affinities of nine common PAHs of Ng *et. al.* in Fig. 5.¹⁸⁾ The inhibiting forces on Ag(I) ion affinity of PAHs due to the surface area and/or steric effects may account for the deviated lower K_2 value for perylene contrary to the general trend of increasing complexation constants with increasing PAH molecular size. Perylene with high surface areas and two bay regions may influence more significantly on the K_2 value relative to the K_1 value by the surface area and/or steric effects. Based on the above discussion, it seems that the proportional corre-

lation of molar volumes of PAH molecules with respect to their K_1 values in Fig. 5 can hold only for a limited series of PAHs, indicating that the trend of proportionally increasing Ag(I) affinity with increasing molecular size of PAHs may not be fully adequate in describing the interaction of Ag(I) with a whole series of PAHs.

4. Conclusions

The equilibrium constants of complexes between Ag(I) and PAHs (naphthalene, pyrene, and perylene) were determined and then the interactions of Ag(I) with PAH molecules were investigated using the solubility experiments of PAHs in the presence of a silver-salt solution. Based on the experimental results from this study, the following conclusions are offered.

- 1) The apparent solubilities of naphthalene, pyrene, and perylene in aqueous solutions increased with increasing Ag(I) ion concentration, providing evidence that the Ag(I) ion can interact with PAH molecules.
- 2) The values, K_1 and K_2 of equilibrium constants of complexes of Ag(I)-PAHs, were 2.990 and 0.378, 3.615 and 1.261, and 4.034 and 1.255, for naphthalene, pyrene, and perylene, respectively.
- 3) A general trend of increasing K_1 and K_2 values of Ag(I)-PAH complexes with increasing PAH solute size was observed for three different sizes of PAH molecules, indicating that a larger size of PAH molecule is likely to have richer electrons on the plane surfaces which can lead to stronger complexes with Ag(I) ion.
- 4) Based on the speciation diagram for Ag(I)-PAH complexes, it was found that a 1:1 Ag(I) : Aromatic complex, $AgAr_+$ was the predominant species over a 2:1 Ag(I) : Aromatic complex, Ag_2Ar^{++} .
- 5) The PAH molecules with four or more aromatic rings and/or bay regions were observed to have slightly less affinity with the Ag(I) ion than expected, which may be due to inhibiting forces such as spread of aromatic π electrons over a wide molecular surface area and intermolecular electronic repulsion in bay regions.

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