© 1998 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 71, 149—153 (1998)

Adsorption Equilibria of 1,10-Phenanthroline and Its Fe(II) Complex on Octadecyl-Bonded Silica Gel

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(Received June 26, 1997)

Adsorption of 1,10-phenanthroline (phen) and its iron(II) complex (Fe(II)-phen) on octadecyl-bonded silica (ODS) gel from aqueous solution was studied by a batch method. The adsorption isotherms of phen and Fe(II)-phen were Langmiur type. Equilibrium constants for the adsorption reaction were estimated from the adsorption data in the system containing a small amount of adsorbates, in which the adsorption isotherm obeyed *Henry's law*. It was clear that the adsorbed species of phen was not only the basic type but also the acidic type: protonated phen. The adsorption behavior in trace amounts (1.79×10^{-5} mol dm^{-3}; 1 ppm) of Fe(II)-phen was analyzed by their equilibrium parameters. The distribution constants of Fe(II)-phen between ODS gel and aqueous solution were determined. The effect of co-existent anions on the adsorption of Fe(II)-phen was discussed from the obtained constants.

Due to the present ecological situation, some attempts to limit the use of harmful organic solvents have been made. The extraction of metal ions into an appropriate solvent using a ligand is also replaced by a process using a solvent-free solid adsorbent. Many determination methods of metal ions using solid phase extraction have been reported.[1] But there has been only a little systematic analysis of the adsorption on solid adsorbents,[2] in comparison with that of liquid–liquid extraction. Based on the liquid chromatographic method, numerous investigations on the distribution of metal ions and complexes have been also reported.[3,4] Although several adsorption parameters of hydrophobic substances from water–methanol mixed solvent were obtained by a moment analysis with pulse response experiment,[5—7] there are few reports about the adsorption equilibrium parameters of metal complexes from aqueous solution.

We have been systematically studying the adsorption equilibria of some β-diketon complexes on ODS gel by a batch-wise procedure.[8—11] ODS gel has been adopted as the model solid adsorbent, on account of its stability, possibility of recycling, well characterized properties and commercial availability. Several features of the adsorption on ODS gel have been displayed in comparison with those of the liquid–liquid extraction. It was found that charged complexes were also adsorbed on ODS gel[8,9,11], while charged complexes were hard to distribute into organic solvent on a liquid–liquid extraction. The solubility parameter theory can be used in the adsorption investigation on the effect of alkyl-chain-length of chemically modified silica gels such as in a liquid–liquid extraction.[11]

In the previous reports, only β-diketones and its metal complexes have been used. In this research we studied the adsorption behavior of Fe(II)-phen as a stable charged complex with a neutral ligand in order to disclose ODS gel adsorption. It was considered that bulky charged ligands and complexes may be adsorbed on the solid absorbent, in particular, which would be an important feature of the adsorption on the solid adsorbent from aqueous solution.

Experimental

Materials. The ODS gel used in this study was Unisil PC18 purchased from GL Sciences. The preparation of ODS gel was described in our previous paper.[8] An Fe(II) stock solution (1.79×10^{-3} mol dm^{-3}) was prepared by dissolving $FeCl_2$, which was donated from Alfa Products, and adding a small amount of hydrochloric acid (final pH 2). 1,10-Phenanthlorine was a guaranteed reagent from Kanto Kagaku.

Adsorption Procedure. The procedures for investigating adsorption equilibria were the same as those described in our previous paper.[8] In the batch-wise study, the total volume of aqueous solution and the amount of ODS gel were 25 cm^3 and 0.5 g, respectively. The temperature during the examination was maintained at 298 ± 1 K. The concentration of iron in aqueous solution after filtration was measured by a furnace atomic adsorption spectrometer (Shimadzu AA-640-12). The aqueous concentration of phen was determined by spectrophotometry (Hitachi 330 spectrophotometer).

Results and Discussion

Adsorption of phen. Figure 1 shows the adsorption isotherms of phen in 0.1 mol dm^{-3} of KCl aqueous solution at pH 3 and pH 4. According to a category of the liquid phase adsorption from the diluted aqueous solution by Giles et al.,[12] the curves of the adsorption isotherm belongs to *Langmuir* type, in which the apparent saturated concentration of phen on the gel are 1.2×10^{-4} mol $g_{gel}{}^{-1}$ (mole of adsorptive molecules per 1 g of ODS gel) at pH 3 and 2.4×10^{-4} mol $g_{gel}{}^{-1}$ at pH 4. Since none of particular sites for the adsorption may exist on ODS gels, the analysis of equilibrium parameters based on the fixed sites can not be applied.[13]

Figure 2 shows the dependence of adsorptive ratios of phen

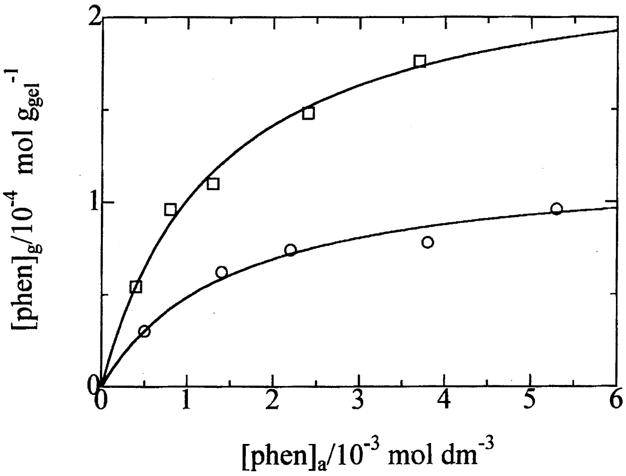

Fig. 1. Adsorption Isotherms of phen onto ODS gel. ○: at pH 3.0, □: at pH 4.0.

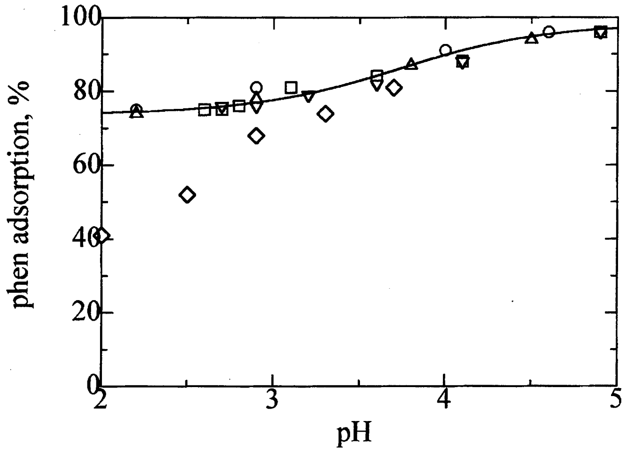

Fig. 2. pH dependence of adsorption of phen onto ODS gel in 0.1 mol dm^{-3} KCl solution. Initial concentration of phen; ○: 1.79×10^{-5} mol dm^{-3}, △: 3.58×10^{-5} mol dm^{-3}, □: 8.95×10^{-5} mol dm^{-3}, ▽: 1.79×10^{-4} mol dm^{-3}, ◇: 4.47×10^{-4} mol dm^{-3}. Solid lines is calculated from $\log K_{\mathrm{dphen}}=3.5$ and $\log K_{\mathrm{dphenH^+}}=2.2$.

on pH in 0.1 mol dm^{-3} KCl aqueous solution. In the case that the initial concentration of phen is below 1.79×10^{-4} mol dm^{-3}, the adsorptive ratio of phen is independent of the concentration of phen. Moreover, the quite similar curves were observed in the results from aqueous solution containing K_2SO_4, KNO_3, and KBr as reagents for adjusting ionic strengths ($\mu=0.1$). When the adsorptive amount of phen is far smaller than the saturated amount at each pH, the adsorption isotherm of phen can be described by *Henry's law*. In the experimental pH region, a basic type (*phen*) and an acidic type: protonated phen (*phenH*$^+$) were found in aqueous solution. Therefore the adsorption equilibria of phen between aqueous solution and ODS gel can be shown as follows:

$$phen_{\mathrm{a}} \xrightleftharpoons{Kd_{phen}} phen_{\mathrm{g}} \tag{1a}$$

$$phenH^+_{\mathrm{a}} \xrightleftharpoons{Kd_{phenH^+}} phenH^+_{\mathrm{g}} \tag{1b}$$

where

$$Kd_{phen} = [phen]_{\mathrm{g}}/[phen]_{\mathrm{a}} \tag{2a}$$

$$Kd_{phenH^+} = [phenH^+]_{\mathrm{g}}/[phenH^+]_{\mathrm{a}} \tag{2b}$$

The adsorption ratio of phen, D_{phen}, is represented as follows:

$$D_{\mathrm{phen}} = ([phen]_{\mathrm{g}} + [phenH^+]_{\mathrm{g}})/([phen]_{\mathrm{a}} + [phenH^+]_{\mathrm{a}}) \tag{3}$$

where $[phen]_{\mathrm{g}}$ and $[phenH^+]_{\mathrm{g}}$ are the concentrations of the basic type and acidic type on ODS gel, respectively while $[phen]_{\mathrm{a}}$ and $[phenH^+]_{\mathrm{a}}$ are those in the aqueous solution.

In order to calculate the two distribution constants, Eq. 3 is converted into Eq. 4, by taking account of the acid dissociation constant, $K_{\mathrm{a}}=([phen]_{\mathrm{a}}[\mathrm{H}^+])/[phenH^+]_{\mathrm{a}}$ and Eq. 2.

$$(1+[\mathrm{H}^+]/K_{\mathrm{a}})D_{phen} = K_{\mathrm{d}phen} + K_{\mathrm{d}phenH^+}[\mathrm{H}^+]/K_{\mathrm{a}} \tag{4}$$

The plots of $(1+[\mathrm{H}^+]/K_{\mathrm{a}})D_{phen}$ vs. $[\mathrm{H}^+]$ are shown in Fig. 3. $K_{\mathrm{d}phenH^+}/K_{\mathrm{a}}$ and $K_{\mathrm{d}phen}$ are obtained from the slope and the intercept, respectively. Since pK_{a} was 4.93 from the literature,[14] the values obtained for $\log K_{\mathrm{d}phen}$ and $\log K_{\mathrm{d}phenH^+}$ were 3.5 and 2.2, respectively. The calculated curve based upon these constants was in good agreement with the experimental data shown in Fig. 2. It was interesting that a considerable amount of *phenH*$^+$ was adsorbed in the ODS gel. The value of the distribution constant for *phenH*$^+$ was comparable to that of heptanedione, one of the β-diketones previously reported.[11] It can be pointed out that, in the case of a bulky ligand such as phen, the charged ligand was easy to be adsorbed on the solid absorbent.

Park et al.[15] reported the adsorption of phen and Fe(II)-complex onto silica gel. According their article, phen was well adsorbed onto silica gel, and the percentage of adsorbed phen was independent of pH. From the independence of pH, they concluded that the adsorption of *phen* and *phenH*$^+$ occurred due to hydrophobic expulsion. The percentage (30%) of adsorption of phen onto 1 g of silica gel is smaller than that onto 0.5 g of ODS gel, since most of 4.47×10^{-4} mol dm^{-3} phen was adsorbed onto ODS gel at pH 5. Although it is necessary to consider the surface areas of the silica gel and

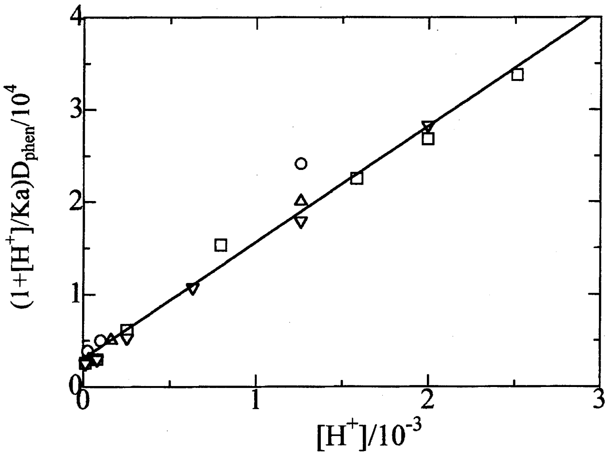

Fig. 3. Plots of $(1+[\mathrm{H}^+]/K_{\mathrm{a}})D_{\mathrm{phen}}$ vs. $[\mathrm{H}^+]$ of phen. Dot signs are same as shown in Fig. 2.

the ODS in order to estimate the adsorptivity strictly, from the low adsorption percentage, it follows that the interaction between phen and silica gel is not so large. Thus, in the present ODS gel adsorption of phen, the effect of residual silanol groups may be ignored.

Adsorption of Fe(II) Ion. Figure 4 shows the adsorption ratios of Fe(II) ion on ODS gel at various pH values. Although no adsorption occurs below 4.1, the amount of the adsorption increased beyond pH 4.1. When the pH of the aqueous solution increased, Fe(II) ion forms into its hydroxide complex. The region of the precipitation of $Fe(OH)_2$ for 1.79×10^{-5} mol dm^{-3} of Fe(II) ion was more than about pH 8 according to the ion product.[16] The region of forming the significant amount of $FeOH^+$ was also close to pH 8 according to the acid dissociation constant of Fe(II) ion for the hydrolysis.[16] Since the pH 4.1 was far smaller than pH 8, some side reaction such as the oxidation of Fe(II) ion into Fe(III) ion was assumed. However, it has been reported that the effective oxidation did not occur even in weak acidic solution.[17,18] Moreover, when we examined the adsorption of Fe(II) ion onto ODS gel in presence of hydroxylamine as a reducing agent, the adsorption of Fe(II) ion also began to occur near pH 4. It was concluded that no oxidation of Fe(II) ion into Fe(III) ion occurred in the present experimental condition. On the other hand, it was also reported that Fe(II) ion adsorbed into a silica gel beyond pH 4.[15] Therefore, the residual silanols in ODS gel can be related with the adsorption of Fe(II) ion. As the other possibility, the adsorption of Fe(II) ion onto ODS gel may result from an ion pair and/or complex between Fe(II) ion and a co-existent inorganic anion. Although the reason for the adsorption of Fe(II) ion can not be specified, the adsorption of Fe(II) ion did not occur below pH 4.1.

Adsorption of Fe(II)-phen Complex. The adsorption isotherm of Fe(II)-phen is shown in Fig. 5. In the isotherm examination, the amount of phen was always fifth times the number of Fe(II) ion ($n_{\mathrm{phen}}/n_{\mathrm{Fe(II)}}=5$). The curve belongs to *Langmuir* type, and the saturated concentration was 2.9×10^{-5} mol g_{gel}^{-1}, which was smaller than that of phen.

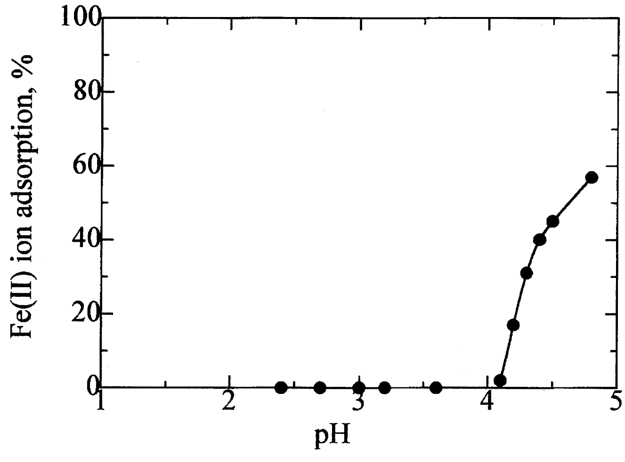

Fig. 4. pH dependence of adsorption of Fe(II) ion in absence of phen.

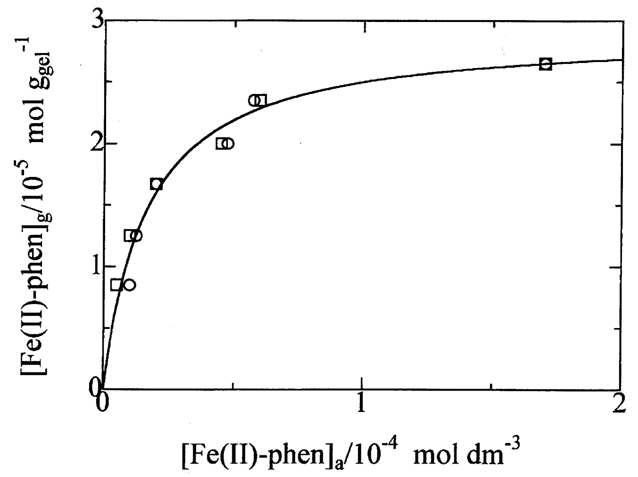

Fig. 5. Adsorption Isotherms of Fe(II)-phen onto ODS gel. ○: at pH 3.0, □: at pH 4.0.

The adsorption isotherm is complicated, so a few species of Fe(II)-phen complexes, *phen* and $phenH^+$ must exist. When $n_{\mathrm{phen}}/n_{\mathrm{Fe(II)}}=5$, however, most of Fe(II) ion is converted into $[Fe(phen)_3]^{2+}$ except for very low pH because of the large stability constant[14] of $[Fe(phen)_3]^{2+}$. In fact, the observed results at pH=3.0 and pH=4.0 were nearly identical, as shown in Fig. 5. Therefore the observed isotherm may be regarded as the isotherm of only $[Fe(phen)_3]^{2+}$, except that a superfluous amount of phen was simultaneously adsorbed.

Figure 6 shows the dependence of adsorption ratios of Fe(II) on pH in the presence of a constant amount of phen in 0.1 mol dm^{-3} KNO_3 aqueous solution. The concentration of Fe(II) ion in initial aqueous solution was 1.79×10^{-5} mol dm^{-3}. Even if all of Fe(II) ion was adsorbed, the amount (4.47×10^{-7} mol) is one twenty-eighth of the saturated amount of $[Fe(phen)_3]^{2+}$. Therefore, in this case such as

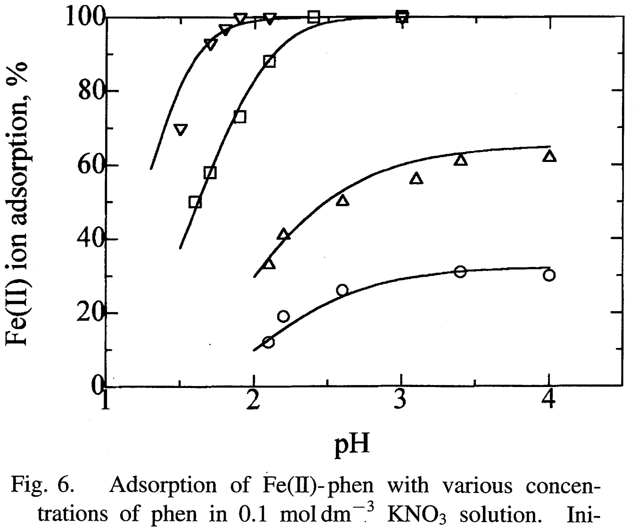

Fig. 6. Adsorption of Fe(II)-phen with various concentrations of phen in 0.1 mol dm^{-3} KNO_3 solution. Initial concentration of Fe(II) ion is 1.79×10^{-5} mol dm^{-3}. Initial concentration of phen; ○: 1.79×10^{-5} mol dm^{-3}, △: 3.58×10^{-5} mol dm^{-3}, □: 8.95×10^{-5} mol dm^{-3}, ▽: 1.79×10^{-4} mol dm^{-3}. Solid lines are calculated from $\log K_{\mathrm{dFe(phen)_3}^{2+}}=5.0$.

quite low concentration of Fe(II) ion, the adsorption equilibria may be independent of the restriction on adsorptive area, so the adsorption behavior of Fe(II)-phen was dominated by their equilibrium constants. The adsorption equilibria of Fe(II)-phen were displayed as shown below:

$$\mathrm{Fe(phen)^{2+}}_{\mathrm{a}} \xrightleftharpoons{K_{\mathrm{dFe(phen)^{2+}}}} \mathrm{Fe(phen)^{2+}}_{\mathrm{g}} \tag{5a}$$

$$\mathrm{Fe(phen)_2{}^{2+}}_{\mathrm{a}} \xrightleftharpoons{K_{\mathrm{dFe(phen)_2{}^{2+}}}} \mathrm{Fe(phen)_2{}^{2+}}_{\mathrm{g}} \tag{5b}$$

$$\mathrm{Fe(phen)_3{}^{2+}}_{\mathrm{a}} \xrightleftharpoons{K_{\mathrm{dFe(phen)_3{}^{2+}}}} \mathrm{Fe(phen)_3{}^{2+}}_{\mathrm{g}} \tag{5c}$$

Thus, pH dependence of the adsorption (Fig. 6) can be described by three distribution constants of Fe(II)-phen. Since it was hard to determine the three distribution constants simultaneously, their adsorption curves was interpreted as follows. When $n_{\mathrm{phen}}/n_{\mathrm{Fe(II)}}=1$, as shown in Fig. 6, the adsorption ratios did not exceed 33%. Also, when $n_{\mathrm{phen}}/n_{\mathrm{Fe(II)}}=2$, their values did not exceed 66%. The limitation of the adsorption amount indicated that adsorbed Fe(II) ion always required the triple moles of phen. Therefore, by taking account of the distribution constant of only $[\mathrm{Fe(phen)_3}]^{2+}$, the data of the adsorption ratios were simulated. The solid lines as shown in Fig. 6 were drawn by the calculation in which $\log K_{\mathrm{dFe(phen)_3{}^{2+}}}=5.0$. The curves were in good agreement with the observed adsorption ratios of Fe(II) ion.

It has reported that the adsorption of Fe(II)-phen onto silica gel also occurred.[15] However, the percentage of adsorption of Fe(II)-phen onto 1 g of silica gel is smaller than that onto 0.5 g of ODS gel. Since the interaction between Fe(II)-phen and silica gel was not so large, the effect of residual silanol groups on the adsorption of Fe(II)-phen may also be ignored.

Effect of Co-existent Anion on Adsorption of Fe(II)-phen. Although no effect of the co-existent anion on the adsorption of phen has been observed, the adsorption of Fe(II)-phen was affected by co-existent anions. Figure 7 shows the dependence of adsorption ratios of Fe(II) ion with phen on pH in 0.1 mol dm^{-3} KCl aqueous solution. The adsorption ratios on the high concentration region of phen ($n_{\mathrm{phen}}/n_{\mathrm{Fe(II)}}=$ 5 and 10) were smaller than those in 0.1 mol dm^{-3} $\mathrm{KNO_3}$ aqueous solution. The adsorption ratios for $\mathrm{phen_{total}}/\mathrm{Fe(II)_{total}}=1$ and 2 were higher than 33 and 66% at the high pH region, respectively. Therefore, the adsorption of the lower order complexes can not be neglected. When only $[\mathrm{Fe(phen)_3}]^{2+}$ is taken into account, the calculated curve does not fit with the observed values as shown in the dashed lines of Fig. 7. When $\mathrm{Fe(phen)^{2+}}$ is also taken as an adsorbate, however, the calculated curves fit with the observed values as shown in the solid lines. Then the distribution constants for $\mathrm{Fe(phen)^{2+}}$ and $[\mathrm{Fe(phen)_3}]^{2+}$ were $\log K_{\mathrm{dFe(phen)^{2+}}}=3.0$ and $\log K_{\mathrm{dFe(phen)_3{}^{2+}}}=4.1$, respectively. The presence of a low order complex such as $\mathrm{Fe(phen)^{2+}}$ may indicate that chloride ion combined with $\mathrm{Fe(phen)^{2+}}$ because chloride ion can become a ligand.

On the other hand, it is possible that $\mathrm{Fe(phen)_2{}^{2+}}$ also adsorbs onto ODS gel. However, the stability constant of $\mathrm{Fe(phen)_2{}^{2+}}$ is smaller than those of $[\mathrm{Fe(phen)_3}]^{2+}$ and $\mathrm{Fe(phen)^{2+}}$. No significant amount of $\mathrm{Fe(phen)_2{}^{2+}}$ was present even in aqueous solution. Therefore, the adsorption of $\mathrm{Fe(phen)_2{}^{2+}}$ may be neglected.

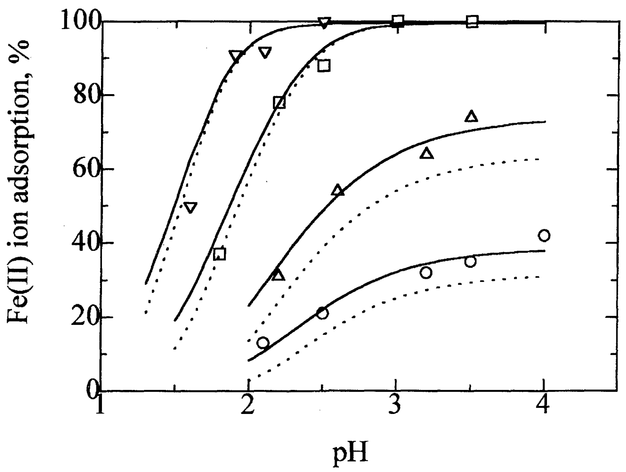

Fig. 7. Adsorption of Fe(II)-phen with various concentrations of phen in 0.1 mol dm^{-3} KCl solution. Initial concentration of Fe(II) ion is 1.79×10^{-5} mol dm^{-3}. Initial concentration of phen; ○: 1.79×10^{-5} mol dm^{-3}, △: 3.58×10^{-5} mol dm^{-3}, □: 8.95×10^{-5} mol dm^{-3}, ▽: 1.79×10^{-4} mol dm^{-3}. Dashed lines are calculated from $\log K_{\mathrm{dFe(phen)_3{}^{2+}}}=4.1$. Solid lines are calculated from $\log K_{\mathrm{dFe(phen)^{2+}}}=3.0$ and $\log K_{\mathrm{dFe(phen)_3{}^{2+}}}=4.1$.

Several co-existent anions were also examined, such as $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{ClO_4^-}$, and $\mathrm{SO_4{}^{2-}}$. When 0.1 mol dm^{-3} of KI and $\mathrm{NaClO_4}$ aqueous solution were used, however, $[\mathrm{Fe(phen)_3}]^{2+}$ were precipitated in the solution. So the adsorption examination was not made. In 0.1 mol dm^{-3} KBr and 0.033 mol dm^{-3} $\mathrm{K_2SO_4}$ aqueous solution the adsorption curves of Fe(II) ion were the same as the dashed lines of Fig. 7. That is, the adsorption from the solution containing $\mathrm{Br^-}$ or $\mathrm{SO_4{}^{2-}}$ should be interpreted by taking account of only $[\mathrm{Fe(phen)_3}]^{2+}$. Their obtained distribution constants are listed in Table 1. In the presence of $\mathrm{Br^-}$, $\mathrm{Cl^-}$, and $\mathrm{SO_4{}^{2-}}$, the distribution constants of $[\mathrm{Fe(phen)_3}]^{2+}$ were exactly the same, while the constant for $\mathrm{NO_3{}^-}$ was larger. The large distribution constant seems to be related to the lyotropic series: $\mathrm{SO_4{}^{2-}}>\mathrm{Cl^-}>\mathrm{Br^-}>\mathrm{NO_3{}^-}>\mathrm{I^-}>\mathrm{ClO_4{}^-}$, which represents the capability for salting out of an electrolyte. The series was almost proportional to the force of the hydration for ions. Since a hydrophobic interaction may be the driving force for the adsorption of $[\mathrm{Fe(phen)_3}]^{2+}$, it was reasonable that the adsorption of $[\mathrm{Fe(phen)_3}]^{2+}$ was accelerated by the

Table 1. Distribution Constants of Fe(II)-phen between the Aqueous Solution and ODS Gel

Co-existent salt	$\log K_{\mathrm{Fe(phen)_3{}^{2+}}}$	$\log K_{\mathrm{Fe(phen)^{2+}}}$
$\mathrm{KNO_3}$	5.0	a)
KBr	4.1	a)
KCl	4.1	3.0
$\mathrm{K_2SO_4}$	4.1	a)

a) The value may be too small, and it can not be determined.

ion association with an anion of a low rank in the lyotropic series. It was already reported that $[Fe(phen)_3]^{2+}$ strongly adsorbed with a bulky anion such an anionic surfactant onto an octadecyl-bonded glass beads.[19)]

Conclusion. Similar to the adsorption of hydrophobic matters onto activated charcoal from aqueous solution,[13)] the adsorption isotherms of phen and Fe(II)-phen onto ODS gel were Langmiur type. Adsorption constants for phen and distribution constants for Fe(II)-phen were determined from the results in the low concentrations of their adsorbates. It was found that the adsorbed species of phen was not only the basic type but also the acidic type; protonated phen. Thus, it was defined that an important character was the adsorption of charged bulky ligands. Moreover, it was clear that the main species of Fe(II)-phen complexes related to the adsorption was $[Fe(phen)_3]^{2+}$. In KCl aqueous solution, however, the low order complexes such as $Fe(phen)^{2+}$ must also be considered because Cl^- became a ligand. The distribution constant of $[Fe(phen)_3]^{2+}$ for KNO_3 aqueous solution was larger than those for KCl, KBr, and K_2SO_4 aqueous solutions. Therefore, it was pointed out that $[Fe(phen)_3]^{2+}$ had a tendency to adsorb more easily with a co-existence anion of a low rank in the lyotropic series.

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