

# Equilibrium and Kinetic Studies of Ligand-Exchange Reaction of Aluminum(III)-5-Sulfoquinoline-8-ol Complex with Phosphate Ion by Reversed-Phase Ion-Pair Liquid Chromatography

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## Abstract

The reversed-phase ion-pair liquid chromatographic behavior of complexes of aluminum(III) with 5-sulfoquinoline-8-ol (HQS) on a column packed with a polystyrene-divinylbenzene copolymer is investigated with eluents that contain phosphate buffer. The aluminum(III)-HQS complex results in two peaks on the chromatograms; the heights of the peaks strongly depend on the pH of the eluent, the concentrations of HQS and phosphate buffer in the eluent, and the column temperature. The results obtained are interpreted according to the ligand-exchange reaction of aluminum(III)-HQS with  $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$  in the eluent. The compositions of the mixed ligand complexes are determined, and the equilibrium and rate constants for the ligand-exchange reaction are estimated.

## Introduction

High-performance liquid chromatography (HPLC) is an excellent method for the separation and determination of metal complexes. However, broad, tailing, or split peaks are often observed on the chromatograms for some metal complexes (1-7). This phenomena has been ascribed to ligand-exchange reactions of the metal complexes with some components of the eluents (4,5), to coordination reactions of central metal ions with active sites on the column packing materials (6,7), or to *mer-fac* isomerization reactions (2,3). Distorted or split peaks can indicate serious problems such as incomplete separation and inaccurate determination, but they provide information about the mechanism of the reactions of the metal complexes that occur in solution.

5-Sulfoquinoline-8-ol (HQS) is known for its ability to form highly stable and aqueous soluble anionic complexes with a variety of metal ions (8). We investigated the reversed-phase ion-pair liquid chromatographic (LC) behavior of HQS complexes of Zn(II), Cu(II), Al(III), Ga(III), and In(III) on octadecyl-modified silica (ODS) by using a fluorescence detector. We found that the chromatogram of the Al(III)-HQS complex has two peaks when eluents that contain a phosphate buffer were used

but there is only a single peak when eluents that contain acetate buffer or bis-tris (bis-[2-hydroxyethyl]iminotris[hydroxyethyl]methane) buffer are used (9). The chromatograms of other metal-HQS complexes exhibited single peaks even when the eluents contained a phosphate buffer.

We have shown that this anomalous behavior of the aluminum complex can be explained according to the ligand-exchange reaction of Al(III)-HQS with  $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$  in the eluent. We have also determined that the mixed ligand complex has a metal-to-HQS molar ratio of 1:1 at pH 6.5. However, the dependence of the composition of the mixed ligand complex on pH and on the concentrations of HQS and phosphate ions has not been determined, and the equilibrium and kinetics of the ligand-exchange reaction have not yet been investigated.

Spectrophotometric methods generally have been used to study the equilibrium and kinetics of chemical reactions in solution. The progress of the reaction is followed by directly monitoring the entire reaction mixture. HPLC provides an alternative technique for the analysis of the reaction of metal complexes; it enables not only the determination of equilibrium and rate constants but also the separation and direct visualization of the species under study (3,10).

In the present work, we measured the heights of the peaks that were obtained for the two Al(III) complexes as a function of reaction time, pH, and HQS and phosphate concentrations in the eluent. We used reversed-phase ion-pair LC conditions and a phosphate buffer system. The column was packed with a polystyrene-divinylbenzene copolymer (PS-DVB) instead of ODS to investigate the reaction of the Al(III) complexes in both alkaline and acidic media. The composition of the complex (mixed ligand Al(III), HQS, and phosphate) and the equilibrium and rate constants for the interconversion reaction between the two Al(III) complexes were estimated.

## Experimental

### Apparatus

The solvent delivery system consisted of a Senshu Kagaku SSC-3100B pump (Tokyo, Japan) and an SSC-3110 micropro-

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cessor control unit. The sample injector was a Senshu Kagaku SSC-EiE-005 injector equipped with a 20- $\mu$ L loop. The detector was an S-3350 spectrofluorescence detector from Soma Kogaku (Tokyo, Japan). The excitation and detection wavelengths were set at 364 and 500 nm, respectively. TSKgel Styrene-250 (polystyrene-divinylbenzene copolymer, 5  $\mu$ m) purchased from Tosoh (Tokyo, Japan) was slurry-packed into an 150- $\times$ 6-mm i.d. titanium column. The column temperature was controlled by a Yamato BH-71 constant temperature water circulator (Tokyo, Japan) through a column jacket. A Model F-13 pH meter (Horiba, Tokyo, Japan) equipped with a Model 6366-10D glass electrode was used for pH measurements.

### Reagents

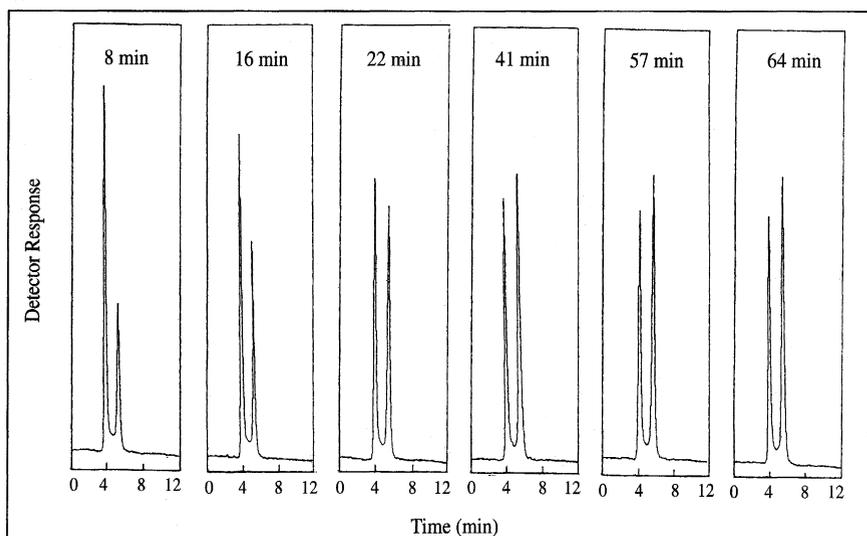
All reagents used in this study were of analytical-reagent grade unless otherwise stated. HPLC-grade acetonitrile was obtained from Kanto Chemicals (Tokyo, Japan). Distilled and deionized water was further purified via passage through an Organo Puric-Z water purification unit (Tokyo, Japan). 5-Sulfoquinoline-8-ol, which was purchased from Wako Chemicals (Osaka, Japan), was recrystallized twice from large volumes of hot water in a polypropylene container. Tetrabutylammonium bromide (TBABr) obtained from Tokyo Kasei (Tokyo, Japan) was used as an ion-pairing reagent as received.

A standard stock solution of Al(III) (for atomic absorption use, 1000 ppm) was purchased from Kanto Chemicals. A stock solution of Ga(III) (1000 ppm) was prepared by dissolving gallium oxide in 0.1M nitric acid.

Acetonitrile-water (20:80, w/w) was used as the eluent. It contained 10mM TBABr, 0.5–4.0mM HQS, and 0.1M phosphate buffer ( $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$ ) unless otherwise stated. The eluents were filtered through a 0.45- $\mu$ m membrane filter and degassed ultrasonically before use.

### Procedure

Sample solutions were prepared by appropriate dilution of



**Figure 1.** Dependence of the chromatographic profile of the Al(III)-HQS complex on incubation time of the sample solution. The eluent was acetonitrile-water (2:8, w/w) that contained 4.0mM HQS, 10mM TBABr, and 0.10M phosphate buffer (pH 7.5). The concentration of Al(III) solution injected was 1.0 ppm. The temperature was 25°C.

the metal stock solutions with the eluent to be used. The final concentration of each metal ion in sample solutions was 1.0 ppm unless otherwise mentioned. The sample solutions thus prepared were immediately transferred to polyethylene or polypropylene bottles and maintained at 25°C  $\pm$  1°C. Elutions were carried out at 1.0 mL/min.

## Results and Discussion

### Chromatographic behavior of Al(III)-HQS complexes

When Al(III) was injected onto the PS-DVB column, two peaks were eluted in a similar manner as observed on the ODS column (9). Figure 1 shows the dependence of the peak profiles for Al(III)-HQS on the incubation time after preparation of the sample solution. The chromatogram was obtained at pH 6.5. The height or area of the first peak (at 3.7 min) decreased, and that of the second peak (at 5.1 min) showed the opposite tendency. This result can be explained in terms of the formation of two different species of Al(III) complexes and the interconversion reaction between them (9). The formation of the species that results in the first peak, Al(1), appears to be much faster than that of the other species, Al(2), which results in the second peak. It can be seen from Figure 1 that the interconversion reaction reaches equilibrium within 50 min. Subsequent experiments were performed by using sample solutions permitted to stand for more than 50 min after preparation unless otherwise stated.

Figure 2 shows the effect of HQS concentration in the eluent on the chromatographic profile of the Al(III) complexes. The height of the peak for Al(1) decreased while that for Al(2) increased with an increase in the HQS concentration. This indicates that the increase in HQS concentration in the eluent shifts the equilibrium of the interconversion reaction between Al(1) and Al(2) in the direction favorable for the formation of the latter species.

An increase in the phosphate concentration, on the other hand, increased the height of the Al(1) peak but decreased that of the Al(2) peak. Figure 3 shows the chromatogram obtained for an injection of Al(III) ion at pH 9.0 with the increased concentration of phosphate in the eluent; the ionic strength of the eluent was kept constant at 0.3M by the addition of KBr. This result suggests that Al(1) is a mixed ligand complex that consists of Al(III) ion with HQS and phosphate ion; the increase in phosphate concentration in the eluent converts Al(2) to Al(1).

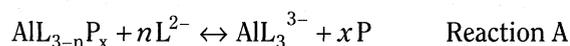
The chromatographic behavior of the Ga(III)-HQS complex was also investigated under the same conditions as described for Al(III)-HQS. The Ga(III) complex resulted in only one peak, which had the same retention time as that of the Al(2) peak in all the eluent systems studied. Based on these

observations, we assumed that the Al(2) and the Ga(III)-HQS complexes have the same charge and the same metal-to-ligand molar ratio. The chemical formula of these metal-HQS complexes can be expressed as  $ML_3^{3-}$  by analogy to the complexation of these metal ions with quinoline-8-ol (11–13), where  $M^{3+}$  and  $L^{2-}$  denote a trivalent metal ion and the deprotonated HQS ion, respectively.

The chromatogram obtained for Al(III) also was dependent on column temperature. The peaks for Al(1) and Al(2) began to overlap with an increase in temperature, and eventually only one broad peak was observed at 60°C (chromatograms not shown). This result can be explained on the basis of the acceleration of the interconversion reaction between Al(1) and Al(2) as described in a previous paper (9). The effect of temperature on the chromatographic behavior on the PS-DVB column was almost the same as that observed on the ODS column (9).

#### Equilibrium of the ligand-exchange reaction of the Al(III)-HQS complex with phosphate ion

Based on the results previously described, the chemical formulas of Al(1) and Al(2) should be  $AlL_{3-n}P_x$  and  $AlL_3^{3-}$ , respectively, where P is  $H_2PO_4^-$  or  $HPO_4^{2-}$ . Accordingly, the interconversion reaction between these Al(III) species is expressed as



The charges of P and  $AlL_{3-n}P_x$  are not presented since the phosphate species that coordinates the Al(III) ion is not identified.

The equilibrium constant,  $K$ , of reaction A is given by the following equation:

$$K = \frac{[AlL_3^{3-}][P]^x}{[AlL_{3-n}P_x][L^{2-}]^n} \quad \text{Eq 1}$$

If the concentration of Al(III) ion is negligibly smaller than

those of HQS and phosphate in the eluent, the ratio of the peak height of Al(2) to that of Al(1) at equilibrium,  $h_{2e}/h_{1e}$ , can be represented as

$$\frac{h_{2e}}{h_{1e}} = \frac{\epsilon_2 K K_a^n C_{HQS}^n}{\epsilon_1 [P]^x ([H^+] + K_a)^n} \quad \text{Eq 2}$$

where  $K_a$  is the acid dissociation constant for the hydroxyl group of HQS,  $C_{HQS}$  is the total HQS concentration in the eluent, and  $\epsilon_1$  and  $\epsilon_2$  are the molar fluorescence intensities for Al(1) and Al(2), respectively.  $K_a$  and  $C_{HQS}$  are given by the following equations:

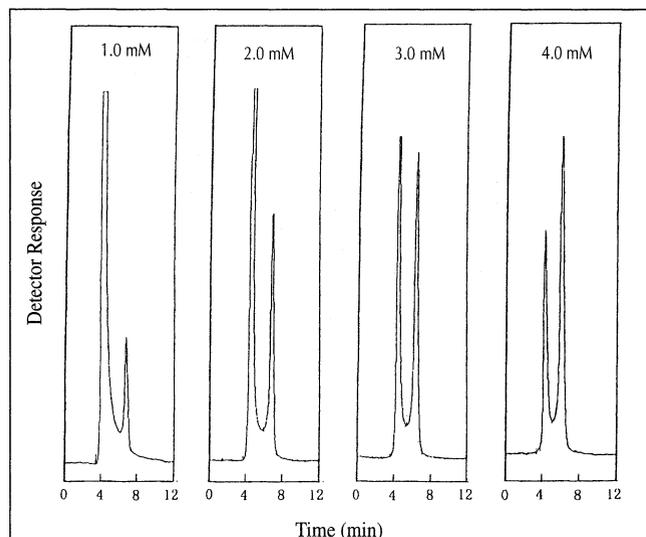
$$K_a = \frac{[L^{2-}][H^+]}{[HL^-]} \quad \text{Eq 3}$$

$$C_{HQS} = [HL^-] + [L^{2-}] \quad \text{Eq 4}$$

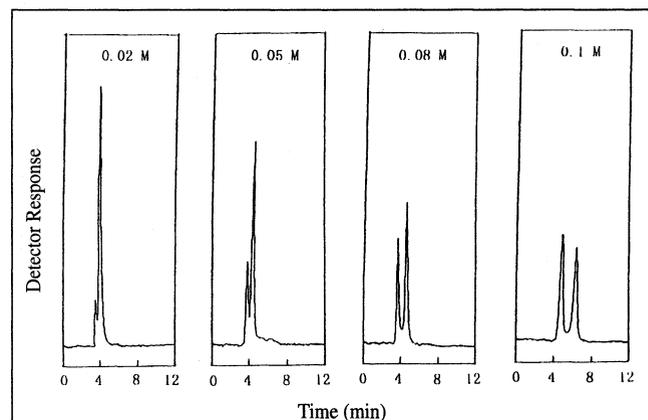
As shown in Figure 4, the ratio of  $h_{2e}$  to  $h_{1e}$  is independent of the Al(III) concentration in the sample solution over the range examined. This means that the concentrations of HQS and phosphate in the mobile phase are virtually unaffected by the Al(III) concentration, and Equation 2 holds true for the system.

Equation 2 indicates that the plot of  $\log(h_{2e}/h_{1e})$  versus  $\log C_{HQS}$  should give a straight line with a slope of  $n$  provided that the pH and the phosphate concentration in the eluent are kept constant.

Figure 5 shows plots of  $\log(h_{2e}/h_{1e})$  versus  $\log C_{HQS}$  for the systems in which the pH of the eluents were 6.5, 7.5, and 9.0. All the plots yielded straight lines, and the slopes of the plots were 1.9, 1.2, and 1.2, for pH 6.5, 7.5, and 9.0, respectively. This result reveals that the composition of Al(1) depends on the pH; the species in which the molar ratio of Al(III) to HQS is 1:1 is dominant at pH 6.5, while the complex of molar ratio 1:2 is the main species at pH values of 7.5 and 9.0. These two species cannot be separated chromatographically, probably because the interconversion reaction between them proceeds very quickly.



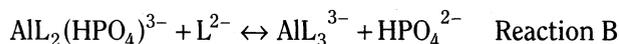
**Figure 2.** Dependence of the chromatographic profile of the Al(III)-HQS complex on the HQS concentration in the eluent. The eluent was acetonitrile–water (2:8, w/w). It contained 1.0–4.0 mM HQS, 10 mM TBABr, and 0.10 M phosphate buffer (pH 6.5). The concentration of Al(1) solution injected was 1.0 ppm. The temperature was 25°C.



**Figure 3.** Dependence of the chromatographic profile of the Al(III)-HQS complex on the phosphate concentration in the eluent. The eluent was acetonitrile–water (2:8, w/w). It contained 1.0 mM HQS, 10 mM TBABr, and 0.02–0.10 M phosphate, and KBr (ionic strength, 0.30 M, pH 9.0). The concentration of Al(III) solution injected was 1.0 ppm. The temperature was 25°C.

Similarly, the molar ratio of Al(III) to P can also be estimated according to Equation 2. It is expected that the plot of  $\log(h_{2e}/h_{1e})$  versus  $\log [P]$  should give a straight line with a slope of  $-x$  if the HQS concentration and the pH of the eluent are kept constant. Figure 6 shows the  $\log(h_{2e}/h_{1e})$  versus  $\log [P]$  plot obtained at pH 9.0, where  $\text{HPO}_4^{2-}$  can be regarded as only one phosphate species in the eluent. As shown in Figure 6, the plot gives a straight line with a slope of  $-1.1$ , which suggests that the molar ratio of Al(III) to  $\text{HPO}_4^{2-}$  for Al(1) is 1:1.

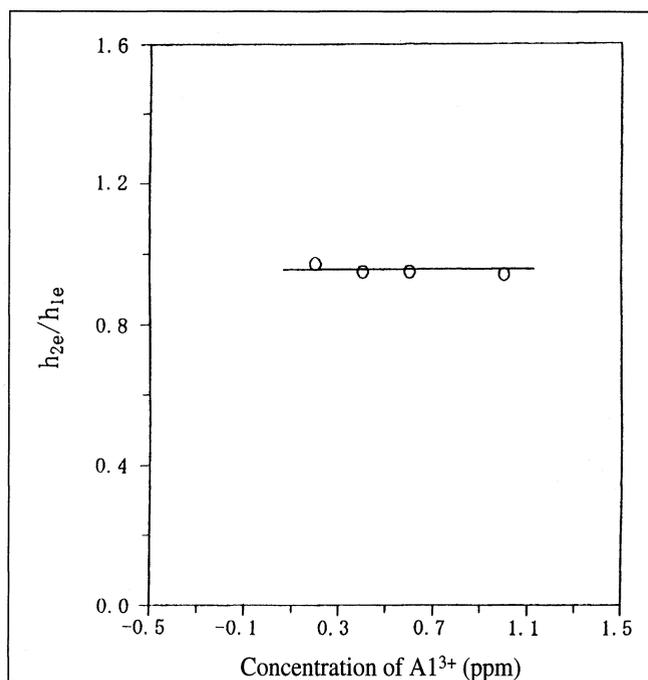
Based on these results, the ligand-exchange reaction of  $\text{AlL}_3^{3-}$  with  $\text{HPO}_4^{2-}$  at pH 9.0 can be expressed as



It should be noted that  $\text{H}_2\text{O}$  or  $\text{OH}^-$  might also coordinate  $\text{AlL}_2(\text{HPO}_4)^{3-}$ . The equilibrium constant for reaction B can be estimated from Equation 2 provided the ratio of the molar fluorescence intensities of Al(1) and Al(2),  $\epsilon_1/\epsilon_2$ , are known. As shown in Figure 1, the peak height of Al(1) decreases while that of Al(2) increases with increasing time of incubation of the sample solution until the interconversion reaction reaches equilibrium. Consequently,  $\epsilon_1/\epsilon_2$  can be obtained according to the following equation

$$\frac{\epsilon_1}{\epsilon_2} = \frac{(h_{1t} - h_{1e})}{(h_{2e} - h_{2t})} \quad \text{Eq 5}$$

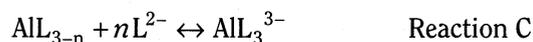
where  $h_{1t}$  and  $h_{2t}$  are the peak heights of Al(1) and Al(2), respectively, at incubation time  $t$ . Here we assumed that the decrease in moles of Al(1) equals the increase in moles of Al(2). The  $\epsilon_1/\epsilon_2$  ratio was estimated to be  $1.03 \pm 0.04$  from the results shown in Figure 1. By substitution of the  $K_a$  value ( $10^{-8.42}$ )



**Figure 4.** Effect of the Al(III) concentration on peak height at equilibrium ( $h_{2e}/h_{1e}$ ). The eluent was acetonitrile-water (2:8, w/w). It contained 3.0mM HQS, 10mM TBABr, and 0.10M phosphate buffer (pH 6.50). The temperature was 25°C.

obtained from the literature (14,15) and the  $\epsilon_1/\epsilon_2$  value as well as the other experimentally obtained values (i.e.,  $h_{2e}/h_{1e}$ ,  $[P]$ ,  $[\text{H}^+]$ , and  $C_{\text{HQS}}$ ) into Equation 2, we obtain the equilibrium constant for reaction B:  $\log K = 1.58$ .

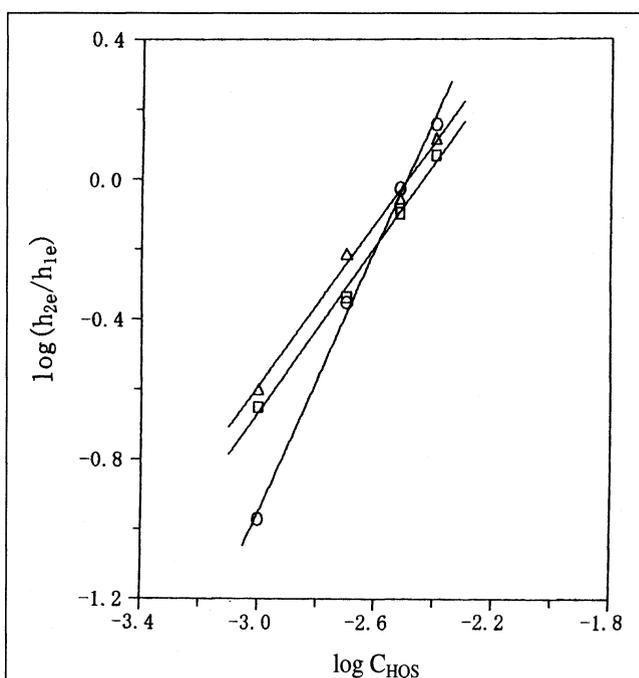
We evaluated the apparent equilibrium constants,  $K'$  ( $= K/[P]^x$ ), instead of  $K$ , for the interconversion reactions at pH 6.5 and 7.5 because two species of phosphate,  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ , exist at comparable concentrations at these pH values and because  $\text{H}_2\text{PO}_4^-$  might coordinate Al(III) ion as well as  $\text{HPO}_4^{2-}$ . The  $K'$  value corresponds to the equilibrium constant for the following reaction in the solutions containing phosphate buffer



where  $n = 2$  at pH 6.5 and  $n = 1$  at pH 7.5, respectively. The  $\log K'$  values obtained are 8.87 at pH 6.5 and 3.38 at pH 7.5, respectively. The  $\log K'$  value obtained at pH 6.5 in this work is compatible with that obtained using the ODS column at the same pH ( $\log K' = 8.72$ ) (9). This means that there is no significant difference between PS-DVB and ODS when equilibrium constants are evaluated.

#### Kinetics of the ligand-exchange reaction of Al(III)-HQS complex with phosphate ions

The kinetics of the ligand-exchange reaction at pH 7.5 were investigated on the basis of the dependence of the peak height on the reaction time shown in Figure 1. Since the concentrations of the Al(III) complexes are negligibly smaller than those of HQS and phosphate ions in the sample and eluent solutions, the HQS and phosphate concentrations are considered to be constant throughout the experiment. If the kinetics of the



**Figure 5.** Plots of the log of the peak height at equilibrium ( $h_{2e}/h_{1e}$ ) versus the log of the concentration of HQS ( $C_{\text{HQS}}$ ).  $\circ$  = pH 6.5,  $\square$  = pH 7.5,  $\triangle$  = pH 9.0.

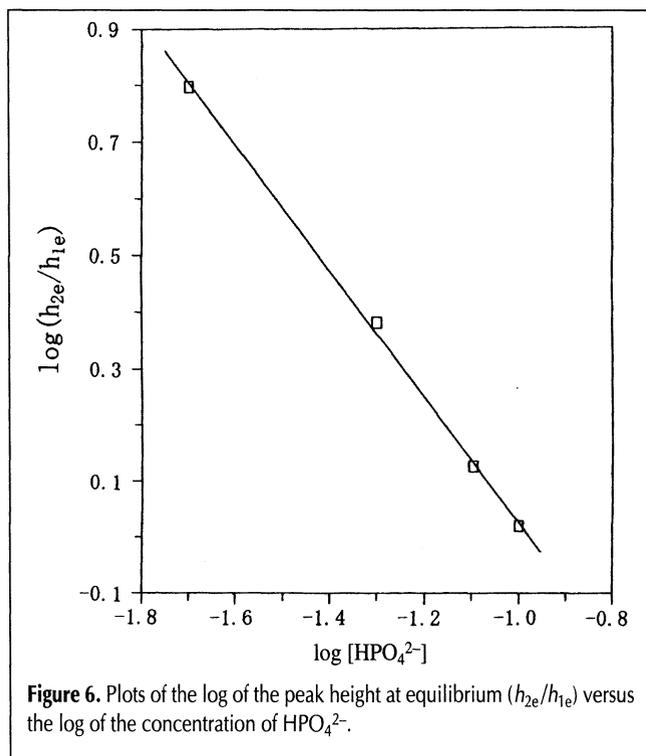
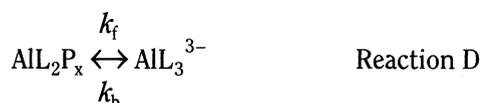


Figure 6. Plots of the log of the peak height at equilibrium ( $h_{2e}/h_{1e}$ ) versus the log of the concentration of  $\text{HPO}_4^{2-}$ .

ligand-exchange reaction are reversible and the forward and backward reactions are first order in  $\text{AlL}_2\text{P}_x$  and  $\text{AlL}_3^{3-}$  respectively, the reaction can be represented in a simplified form as



It is reasonable to assume that  $\text{AlL}_2\text{P}_x$  is formed instantaneously just after mixing the Al(III) stock solution with the eluent solution, and then it is gradually converted to  $\text{AlL}_3^{3-}$  because the  $(h_{1t}-h_{1e})$  to  $(h_{2t}-h_{2e})$  ratio does not depend on the incubation time as described above. Therefore the rate of the formation of  $\text{AlL}_3^{3-}$  is described by the following equation:

$$\frac{d[\text{AlL}_3^{3-}]}{dt} = k_f(C_{\text{Al}} - [\text{AlL}_3^{3-}]_t) - k_b[\text{AlL}_3^{3-}]_t \quad \text{Eq 6}$$

where  $C_{\text{Al}}$  denotes the total concentration of the Al(III) complexes and  $[\text{AlL}_3^{3-}]_t$  is the concentration of  $\text{AlL}_3^{3-}$  at a given time  $t$ . At equilibrium

$$K'' = \frac{[\text{AlL}_3^{3-}]_e}{C_{\text{Al}} - [\text{AlL}_3^{3-}]_e} = \frac{K [\text{L}^{2-}]^n}{[\text{P}]^x} = \frac{k_f}{k_b} \quad \text{Eq 7}$$

where  $K''$  is the equilibrium constant of reaction D and  $[\text{AlL}_3^{3-}]_e$  is the equilibrium concentration of  $\text{AlL}_3^{3-}$ . The value of  $K''$  is experimentally obtained by using the following equation:

$$K'' = \frac{h_{2e} \varepsilon_1}{h_{1e} \varepsilon_2} \quad \text{Eq 8}$$

Assuming that peak height is proportional to the concentra-

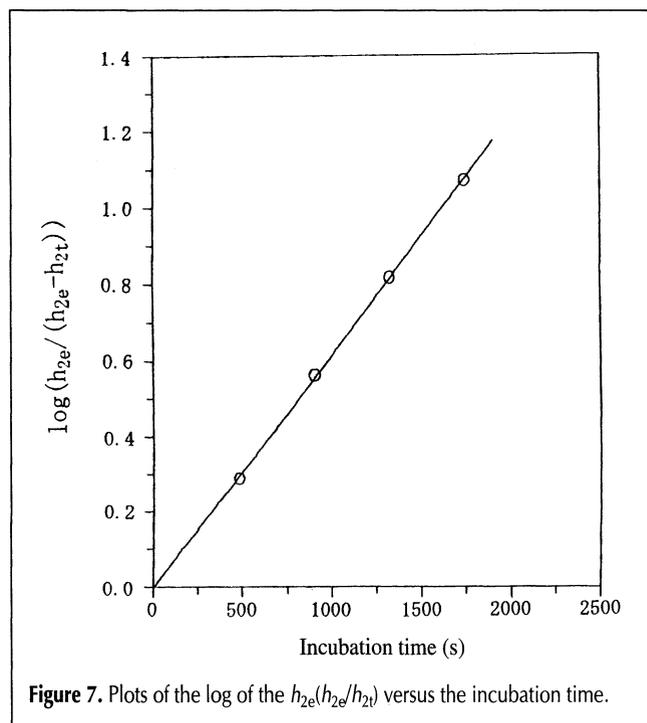


Figure 7. Plots of the log of the  $h_{2e}(h_{2e}/h_{2t})$  versus the incubation time.

tion of each corresponding species, the following relationship can be obtained based on Equations 6 and 7:

$$2.303 \log \frac{h_{2e}}{h_{2e} - h_{2t}} = \frac{K'' + 1}{K''} k_f t \quad \text{Eq 9}$$

The plots of data according to Equation 9 are shown in Figure 7 for data obtained with solutions that contain 4.0mM HQS and 0.1M phosphate buffer at pH 7.5. Here the incubation time of the sample solution prior to the injection is taken as  $t$ . As can be seen from Figure 7, a good straight line, which went through the origin, was obtained. This corroborates the validity of the simple reaction model described in reaction D and indicates that the interconversion during the chromatographic process is negligible. The rate constants,  $k_f$  and  $k_b$ , which were determined from the slope of the plot, were  $7.78 \times 10^{-4} \text{ s}^{-1}$  and  $6.48 \times 10^{-4} \text{ s}^{-1}$ , respectively.

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