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Adsorption Equilibria of Copper on Octadecylsilica Gel in the Presence of Acetylacetone

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The solid-liquid adsorption equilibria of copper with acetylacetone between octadecyl-bonded silica (ODS) gel and aqueous solution were investigated by a batch method at 298±1 K. It is found that a 1:1 complex of copper with acetylacetone is adsorbed on the gel surface.

Some types of chemically modified silica gels have been widely used as stationary phases for high-performance liquid chromatography. Among them, octadecylsilica (ODS) gel has been adopted for reversed phase chromatography, and the chromatographic behavior of various kinds of solute species has been studied in the system using ODS gel. They include studies using metal complexes as solute.[1–7] In these studies, it is well-known that the labile complexes introduced into the column give long tailing on the chromatograms. The phenomena have been explained as the degradation of complex molecules in the separation process; they were supressed by an addition of ligand to the eluent.

The ODS gel has also been used as a solid adsorbent for the preconcentration of trace metals in water.[8–14] In these studies, various complexing agents have been added to the sample solution as a coadsorbent. Metal ions in the samples form complexes with ligand molecules; these were considered to be adsorbed on the gel surface by a hydrophobic interaction with the long alkyl chains on the gel surface.

In these studies, however, the adsorption mechanisms underlying the separation or concentration process were not investigated for the systems containing metal complexes. They have simply been regarded as similar to those involved in the solvent extraction.

It was reported by some workers that an active site on the gel surface behaves as a cation exchanger.[15–17] Although it seems likely that the long alkyl chain on the gel surface plays an important role in the adsorption of metal complexes, these studies indicate that the roles played by the active site can not be neglected. Indeed, Mackey[16] pointed out that iron, copper, manganese, and zinc ions were adsorbed without complexing agent on the ODS gel (Waters) of low coverage.

It is also reported in the kinetic studies of liquid–liquid extraction that the 1:1 complex of copper with several kinds of ligands may be adsorbed at the liquid–liquid interface.[18–19] These studies suggest that the species adsorbed onto ODS gel follow a different mechanism from that involved in liquid–liquid extraction equilibria between two bulk phases, because the octadecyl monolayer on the ODS gel surface may behave as an interface similar to that involved in the solvent extraction or partition systems. Recently, Fardy *et al.*[14] pointed out from the calculation of the concentration of some complexes in the solution containing 8-quinolinol and some metal ions that the 1:1 complexes play dominant roles in the adsorption of copper, manganese and zinc ions on Sep-Pak C_{18} (Waters) which, according to Mackey,[16] adsorbs no metal cation except for iron.

From the above consideration, it can be supposed that the adsorbed species of metal ions on the ODS gel in the presence of some ligands would be much different from that extracted in solvent extraction or liquid–liquid partition of metal complexes. In this study, the adsorption equilibria of copper between the ODS gel and the aqueous phase were investigated in the presence of acetylacetone (2,4-pentanedione). Acetylacetone was chosen for the reasons: (1) the behavior of the ligand and its metal complexes in liquid–liquid partition has been thoroughly investigated; (2) its concentration in the adsorption systems can be changed over a wide range, since its solubility in water is relatively high; and (3) it is stable in water. The second reason aids in making the systems relatively simple, because other solvents like methanol are not required in order to dissolve the insoluble ligands such as 8-quinolinol.

Experimental

Materials. ODS gel (Unisil P-C18, Gasukuro Kogyo) was washed with diluted hydrochloric acid (Special Reagent for Trace Analysis, Kishida Chem.), ultra-pure water (obtained from Milli-Q system, Milipore Corp.), and methanol (Guaranteed reagent, Kanto Kagaku) successively, and then dried.

Acetylacetone (Guaranteed reagent, Kanto Kagaku) was used after distillation. All other reagents were commercially available guaranteed reagents, and were used without further purification.

Apparatus. The pH of the initial and final solutions were measured by a Toyo Kagaku TD-4 pH meter. The copper concentrations in solutions were determined by atomic absorption spectrometry with a Shimadzu AA-640-12 atomic adsorption spectrometer equipped with GFA-2 graphite furnace atomizer. The concentration of acetylacetone was determined by UV absorbance at 274 nm using a Shimadzu UV-140-02 spectrometer. All the measurements were carried out in a thermostated room at 298±1 K. A box shaker (Itagaki Rika) was employed for equilibration of the adsorption mixtures.

Procedures. Twenty-five cm^3 buffer solutions of 1/15 mol dm^{-3} (CH_3COOH-CH_3COONa-NaOH or $HClO_4$-$NaClO_4$) were introduced into a 100 cm^3 vials, to which stock solution of 1.57×10^{-4} mol dm^{-3} of copper(II) sulfate, and 9.6×10^{-1} mol dm^{-3} of acetylacetone were added. They were filled up to 100 cm^3 with ultra-pure water, and the pH measured.

For the measurements of the adsorption equilibria, 20 cm^3 aliquots were introduced into 50 cm^3 glass centrifuge tubes containing 0.5 g ODS gel. The mixtures were shaken for 10 min at a shaking rate of *ca.* 300 min^{-1}. The equilibrated mixtures were allowed to stand for about 30 min in order to separate the gel from the aqueous phase. The solutions were filtered through a membrane filter of 10 μm pore to remove the gel. The pH and copper concentration of the filtrates were measured.

The ODS gels were washed with a 1 per cent solution of acetylacetone in chloroform in order to elute the adsorbed copper from the gel. Next the gel was rinsed with chloroform until no uv absorption of acetylacetone was observed in the chloroform. After the gel was successively washed with methanol, water, diluted hydrochloric acid (pH 2), and again water; it could then be reused.

The concentration of copper, C, adsorbed on the gel was calculated from the following equation

$$C_{\mathrm{ad}} = (C_{\mathrm{in}} - C_{\mathrm{f}})V/m, \qquad (1)$$

where subscripts ad, in, and f denote the adsorbed, initial, and filtrate, respectively. V represents the volume of the aqueous phase and m is the mass of the ODS gel.

The distribution ratio, D, was defined by the following equation

$$D = C_{\mathrm{ad}}/C_{\mathrm{f}} \qquad (2)$$

where the concentration of copper(II) cation in the filtrates are expressed in unit of mol cm^{-3}.

Results and Discussion

The equilibria of adsorption of copper between aqueous phase and ODS gel were attained within 5 min under these experimental conditions of the present investigation. In the measurements, the shaking time was fixed at 30 min, above which the distribution ratios were constant within experimental error.

The adsorption behavior of acetylacetone on the gel is shown in Fig. 1 as a function of initial concentration. The concentration of adsorbed acetylacetone increases linearly with the increasing concentration in the filtrates up to 0.5×10^{-2} mol dm^{-3}. In more concentrated solutions, however, another linearity appears. The distribution ratio tends to decrease with increase of acetylacetone concentration. At low concentrations, it decreases more steeply. The typical concentration of acetylacetone used in the adsorption experiments of copper(II) cation was 1×10^{-2} mol dm^{-3} and the volume of the solutions was 20 cm^3. Under these conditions, the concentration of acetylacetone on the gel is proportional to the initial concentration, and the adsorptive ability of the gel can be regarded as undersaturated.

The adsorption isotherms of acetylacetone obey the Freundlich equation (Fig. 2), but not the Langmuir equation. According to the theoretical consideration,[20] the surface of the ODS gels is not homogeneous, and it has more than two kinds of sites available

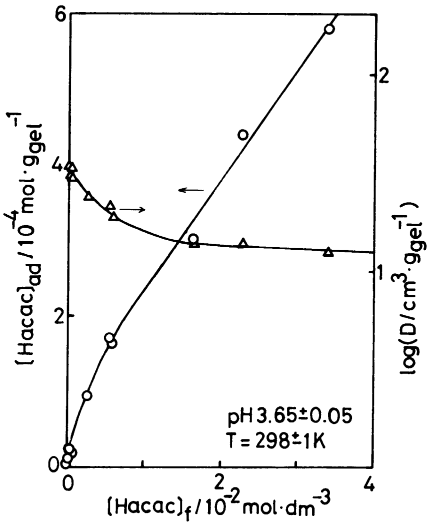

Fig. 1. Adsorption of acetylacetone onto ODS gel. ○ denotes concentration of acetylacetone on ODS gel, and △ is the distribution ratio.

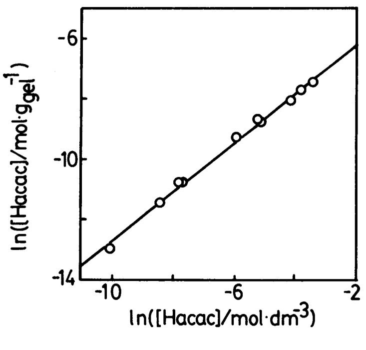

Fig. 2. Analysis of adsorption of acetylacetone by means of Freundlich equation.
$\ln[Hacac]_{ad} = 0.810 \ln[Hacac]_f - 4.60$

for adsorption of acetylacetone. This phenomenon agrees with the results that the gel has a second active site in addition to the hydrophobic site.15–17) It is expected that these would be the remaining silanols on the surface which can interact *via* hydrogen bonding with acetylacetone, hydrophobic alkyl chains of octadecyl groups bonded on the surface, and the intermediate site among them. According to the information from the manufacturer, the gel used in the present study has uncovered surface silanols.

In Fig. 3, the pH dependence of the adsorption of acetylacetone is illustrated. The adsorption is independent of pH in the region studied. This indicates that acetylacetone is adsorbed on the gel surface as an electrically neutral species.

The dependence of adsorption of copper(II) cation upon the initial concentration is shown in Fig. 4, where the ratios of copper(II) cation concentration to that of acetylacetone are constant. The concentration of copper(II) cation on the gel increased linearly with its initial concentration in the aqueous phase up to 2×10^{-4} mol dm^{-3}, and its adsorption ratio was constant below a copper(II) cation concentration of 1.0×10^{-4} mol dm^{-3}. The ODS gel used in this study has a large ability to adsorb the copper complex, enough to permit experiments at very low copper concentrations of 1.57×10^{-5} mol dm^{-3} (this corresponds to 1 ppm Cu), or up to 3.14×10^{-5} mol dm^{-3} in the experiments of Job's continuous variation method. In this concentration range, 95 per cent of the copper(II) cation was adsorbed.

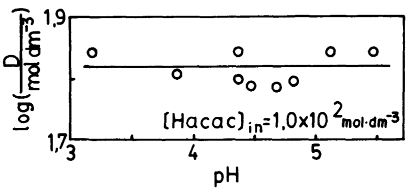

Fig. 3. pH Dependence of adsorption of aceylacetone onto ODS gel. Acetate buffer used.

Now, consider the concentration of copper(II) cation, acetylacetone, and silanol group on the gel surface. The copper concentration on the gel is 6.3×10^{-7} mol g_{gel}^{-1} when the initial concentration is 1.57×10^{-5} mol dm^{-3} and the volume of solution is 20 cm^3, if the copper were completely adsorbed. The concentration of acetylacetone adsorbed is about 3.6×10^{-4} mol g_{gel}^{-1}, when its initial concentration in the aqueous phase is 1.0×10^{-2} mol dm^{-3} and the volume is 20 cm^3, since the adsorption rate is 90 per cent under these experimental conditions. Moreover the total concentration of residual silanol groups on the gel surface is estimated as 1.1×10^{-3} mol g_{gel}^{-1} on the basis of surface silanol concentration21) and the information from the manufacturer. It is found from the above estimation that the concentration of copper on the gel is much smaller than those of the others, and the concentration change of acetylacetone and surface silanol caused by the adsorption of copper can be neglected. However, the concentration change of acetylacetone in solution or on the gel may significantly influence the adsorption of copper, since the concentration is comparable to that of the surface silanol.

The dependence of the distribution ratio of copper(II) cation upon the acetylacetone concentration and pH are shown in Fig 5. The pH range, in which the distribution ratio regularly increased, shifted to high pH with decrease of ligand concentration. This phenomenon is consistent with that observed in solvent extraction. However, the apparent values of the so-called extraction coefficients,

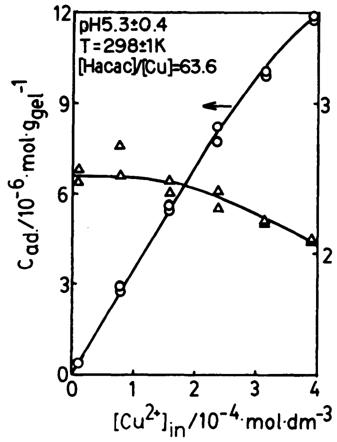

Fig. 4. Concentration dependence of adsorption of copper(II) cation with acetylacetone onto ODS gel. Concentrations of copper on gel are represented by ○, and its distribution ratio, △, respectively.

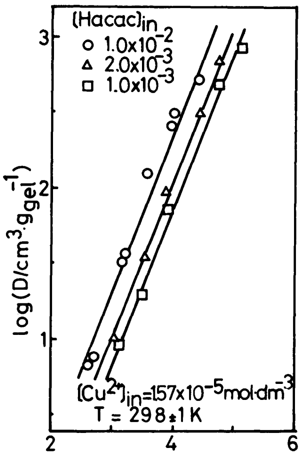

Fig. 5. pH Dependence of adsorption of copper(II) cation with acetylacetone onto ODS gel.

K_{ex}, calculated on the assumption that the ODS gel behaves as one of the phases, were not constant as tabulated in Table 1. K_{ex} is represented as the terms reciprocal to the distribution coefficient of ligand species between two phases, K_L, in the partition mechanism. As shown in Fig. 1, the apparent K_L values also decrease with increase of concentration of acetylacetone. For this reason, it is considered that the activity of the acetylacetone adsorbed on the surface is lowered in the diluted region by the adsorption to the surface silanol groups.[16]

The salt effect on the adsorption was investigated using acetic acid buffer solutions and perchlorate solution at constant pH and ionic strength in order to clarify whether the acetate anion is contained in the adsorbed species. The adsorption ratio was independent of the change of the composition of salts as shown in Fig. 6. Perchlorate anion is well known as one of the weakest ligands and forms no complexes in aqueous solution. The results in this figure suggests that acetate anion is not involved in the adsorption of copper. This fact is supported by the calculation of the degree of complex formation in these mixtures, where the concentration of acetate complex is negligibly small.

In order to determine the chemical composition of the adsorbed species, both the Job's continuous variation method and the molar ratio method were applied. In the Job's continuous varation study, the maximum adsorption was obtained for an equimolar solution. In the molar ratio study, the constant adsorptions were obtained over the equimolar solution. These results suggest that the adsorbed species are composed of one copper(II) cation and one ligand molecule.

TABLE 1. ADSORPTION EQUILIBRIA OF COPPER(II) CATION WITH ACETYLACETONE ONTO ODS GEL IN PRESENCE OF ACETATE BUFFER

$C_{\mathrm{acac,in}}/10^{-3}$ mol dm^{-3}	Slope	Log K_{ex}
1.0	1.09	0.935
2.0	1.09	0.739
10.0	1.12	0.226

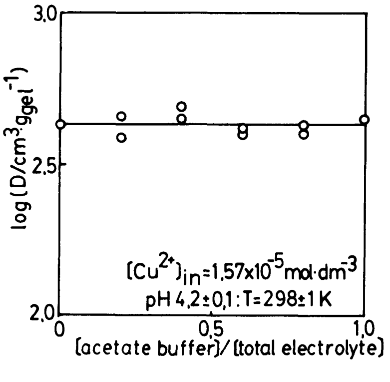

Fig. 6. Dependence of adsorption ratio of copper(II) cation by acetylacetone upon compositions of buffer solution.

The main driving force for the adsorption of the copper(II) cation with acetylacetone onto ODS gel from aqueous media is considered to be the hydrophobic interaction of the acetylacetonato complexes with the alkyl chain bonded on the gel. However, as mentioned above, the adsorption behavior cannot be completely interpreted only by the hydrophobic interaction. That is, it is found in this study that copper(II) cation in the aqueous media is adsorbed on the gel as the charged 1:1 complex of copper(II) cation and acetylacetone. To account for the neutralization of the electric charge of the gel adsorbing copper(II) cation, we may include another interaction of the charged complex with the ODS gel surface, *e. g.*, with residual silanol groups on it, as pointed out by Mackey.[16] At this stage it seems unlikely that the adsorbed 1:1 complexes would immediately exchange with the proton of the surface silanol groups buried under the alkyl chain. If the cation exchange occurs between the charged complex and the surface silanol, the distribution ratio is expressed as follows:

$$D = \frac{K_{\mathrm{ch}}\beta_{\mathrm{n-1}}K_{\mathrm{a}}{}^{n-1}}{K_{\mathrm{L}}{}^{n-1}}[\mathrm{HOSi}]_{\mathrm{s}}\frac{[\mathrm{Hacac}]_{\mathrm{gel}}^{n-1}}{[\mathrm{H}^+]^n}, \tag{3}$$

were K_{ch}, β_{n}, and K_{a} denote the exchange coefficient between complex and surface silanol, the formation constant of the charged complex, and the dissociation constant of acetylacetone, respectively. s and n indicate the surface and the charge on the copper(II) cation. As the concentration of copper on the gel is much smaller than that of the surface silanol, the concentration of silanol can be regarded as remaining constant. From the equation, it is concluded that if the cation exchange occurs the slope of log D *vs.* pH plot must have a value of nearly two. However, the slope obtained in the present study is close to unity. Therefore, it is reasonable to assume that the adsorption of the copper(II) cation onto the ODS gel can be explained by the partition of a 1:1 complex of copper(II) cation and acetylacetonate anion between the bulk aqueous phase and the alkyl chain layer on the ODS gel as one of the interface. The charge neutralization may be attained between ODS gel adsorbing complexes and anion in the aqueous phase in equilibrated mixtures.

The results obtained in this study may afford basic information essential to an understanding of the mechanism of separation of complexes in liquid chromatography with ODS gel and the concentration of the metal with acetylacetone onto the gel. As mentioned above, this behavior is different from the partition mechanisms in bulk phase for liquid-liquid partition, but similar to the mechanism proposed in explaining the kinetics of partition of metal complex in the interface between two liquid phases.[18,19]

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References

1) E. Gaetani, C. F. Laureri, A. Mangia, and G. Paolari, *Anal. Chem.*, **48**, 1725 (1976).

2) A. Mangia, G. Paolari, E. Gaetani, and C. F. Laureri, *Anal. Chim. Acta*, **92**, 111 (1977).

3) G. Schwedt, *Chromatographia*, **12**, 289 (1979).

4) S. Ichinoki and M. Yamazaki, *Bunseki Kagaku*, **31**, E319 (1982).

5) R. C. Gurira and P. W. Carr, *J. Chromatogr.*, **252**, 185 (1982).

6) S. R. Huchins, P. R. Haddad, and S. Dilli, *J. Chromatogr.*, **252**, 185 (1982)

7) J. S. Huber, J. C. Kraak, and H. Veening, *Anal. Chem.*, **44**, 1554 (1972).

8) S. Taguchi and K. Goto, *Talanta*, **27**, 819 (1980).

9) H. Watanabe, K. Goto, S. Taguchi, J. W. McLaren, S. S. Berman, and D. S. Russel, *Anal. Chem.*, **53**, 738 (1981).

10) S. Taguchi, K. Goto, and H. Watanabe, *Talanta*, **28**, 613 (1981).

11) G. L. Mills and J. G. Quinn, *Mar. Chem.*, **10**, 93 (1981).

12) S. Taguchi, C. Yoshikura, and K. Goto, *Bunseki Kagaku*, **31**, 32 (1982).

13) R. E. Sturgeon, S. S. Berman, and S. N. Willie, *Talanta*, **29**, 167 (1982).

14) J. J. Fardy, G. D. McOrist, and T. M. Florence, *Anal. Chim. Acta*, **159**, 199 (1984).

15) O. A. G. J. van der Houwen, R. H. A. Sorel, A. Halshoff, J. Teeuwsen, and A. W. M. Indemans, *J. Chromatogr.*, **242**, 275 (1981).

16) D. J. Mackey, *J. Chromatogr.*, **242**, 275 (1982).

17) S. G. Weber and W. G. Tramposch, *Anal. Chem.*, **55**, 1771 (1983).

18) I. Komasawa, *J. Chem. Eng. Jpn.*, **13**, 204 (1980).

19) M. Cox *Proceedings ISEC '80 paper* 80—118 (1980).

20) T. Kei, "Kyuchaku," Kyoritsu Shuppan, Tokyo (1965), Chapter 3.

21) R. G. Gilpin and M. F. Burke, *Anal. Chem.*, **45**, 1383 (1973).