Adsorption Behavior of Some Metal Ions onto Octadecylsilica Gel in the Presence of Acetylacetone

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(Received December 11, 1989)

Adsorption of 11 metal acetylacetonate complexes onto an octadecylsilica(ODS) gel from an aqueous solution was measured as a function of pH. It was found that the pH dependencies regarding adsorption are almost consistent with those of a solvent-extraction system, except for Zn(II) which is unextracted into benzene. Plots of the adsorption ratio against pH indicates the 1 : 1 complexes are adsorbed onto ODS gel, except for Al(III) whose composition is 1 : 2.

Recently, several methods for the preconcentration of metal ions dissolved in water have been attempted using octadecylsilica gel as an adsorbent. Elements are adsorbed on the gel as a complex with a ligand.[1-5] This concentration method has some advantages: the procedure is very simple and gives a large concentration rate; also, the matrix components can be easily removed.

On the other hand, a liquid chromatographic behavior of metal complexes has also been studied by many workers using ODS gel as a stationary phase.[6]

However, we have acquired some basic data concerning the partition of the complex between the gel and aqueous solution, except for the copper acetylacetonate complex.[7] No systematic investigation of the partition behavior of metal complexes between aqueous and gel phases has been carried out. We therefore have no criteria concerning the selection of the conditions for the separation and concentration of metal complexes from the aqueous phase.

In this study we investigated the adsorption behavior of eleven metal ions (Al(III), Be(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II)) by a batch method. Acetylacetone (2,4-pentanedione) was employed as a ligand. Since it has been widely used as an extractant in solvent extraction systems, the extraction behavior of its metal complexes has been studied in detail.[8]

Experimental

Materials. The ODS gel used in this study was Unisil PC-18 purchased from Gasukuro Kogyo (particle size 27—47 μm). Chromatographic grade acetylacetone (Kishida Kagaku) was used without further purification. Perchloric acid and its sodium salt were guaranteed reagent of Kanto Kagaku. Hydrochloric acid of trace analysis grade was used.

The aqueous solutions containing Co(II), Fe(III), Ni(II), or Pb(II) were prepared from $CoCl_2\cdot 2H_2O$, $FeCl_3\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, or $Pb(NO_3)_2$, of guaranteed reagent from Kanto Kagaku, respectively. Solutions containing Cd(II), Cr(III), Mn(II), and Zn(II) were prepared from the commercially available stock solutions for atomic absorption spectrometry (Nakarai Kagaku). That containing Al(III) was prepared by the procedure described in JIS. Be(II) solution was obtained from $BeCO_3\cdot Be(OH)_2$ offered from Tokyo Kogyo Shikenjo.

Procedure. Solutions containing 3.71×10^{-5} M metal ion and 5.00×10^{-3} M acetylacetone were prepared. The ionic strength and pH of the solutions were adjusted by $NaClO_4$ and $HClO_4$ or NaOH. The ionic strength of the solutions was 0.1.

The measurement procedure of the adsorption equilibria was reported previously.[7] The temperature during measurements was 298±0.3K. The concentrations of metal ions on the gel phase were calculated from the concentration change in the aqueous phase before and after equilibration.

Results and Discussion

In Fig. 1 the pH dependence of the adsorption of the metal ions in the presence of acetylacetone is summarized. As shown, the pH region which shows an adsorption rate above 80 per cent is found in Al(III) at pH>4.5, Be(II) at pH>4, Cu(II) at pH>4, Fe(III) at pH>3, Pb(II) at pH>6, and Zn(II) at pH>8.5. A hundred per cent adsorption was not achieved. The phase concerning adsorption is a very thin film consisting of an alkyl chain bound to a silica surface. Since the gel surface is rather polar, it is considered that metal complexes could be distributed between aqueous and gel phase in a higher pH region.

Co(II) ions show maximum adsorption at pH 7.2; and the adsorption rate at the pH value was about 30 per cent. Mn(II) has a maximum adsorption of about 35 per cent at pH 9.5. This pH value is almost the upper limit for an investigation, due to the destruction of ODS gel at higher pH values. Ni(II), Cd(II) and Cr(III) show no appreciable adsorption in the pH region investigated. These pH dependencies agree with those of solvent extraction, except for Zn(II). Although it is reported that Zn ion is scarcely extracted by acetylacetone in a solvent extraction system,[8] it is quantitatively adsorbed in this system.

If more than 80 per cent of ions are adsorbed, it is found that the adsorption curves of all the ions are similar except for Al, of which it is more steep than the others. This seems to mean that the composition of the adsorbed complex of Al differs from those of the other complexes.

Analogous to solvent extraction, we define equimo-

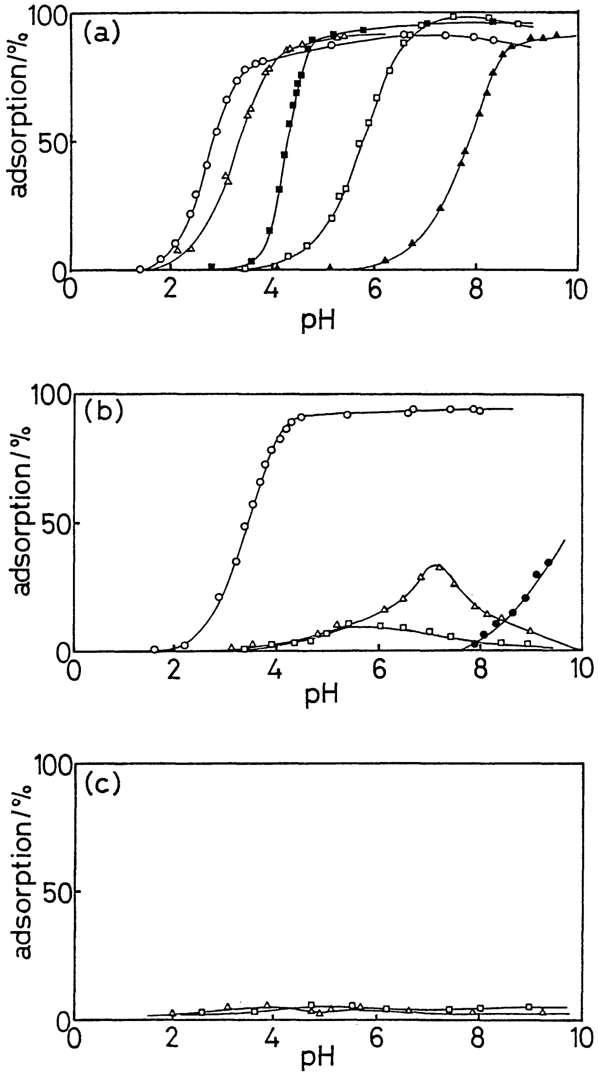

Fig. 1. pH dependence of adsorption of metal ions onto ODS gel in the presence of acetylacetone at 298+0.3K. Initial concentration of metal ions are 3.51×10^{-5} M, and of acetylacetone , 5.00×10^{-3} M. Ionic strength is 0.1. (a) ○; Fe(III), △; Cu(II), ■; Al(III), □; Pb(II), ▲; Zn(II). (b) ○; Be(II), △; Co(II), □; Ni(II), ●; Mn(II). (c) □; Cr(III), △; Cd(II).

lar adsorption $\mathrm{pH_{eq}}$ as the pH value at which the concentrations of metal ions in both phases are equal. This value corresponds to $\mathrm{pH_{1/2}}$ in solvent extraction. Data are summarized in Table 1 regarding ions which have adsorption rates above 80 per cent, along with the values obtained in a solvent extraction system using benzene as an organic phase.[8] As shown, The $\mathrm{pH_{eq}}$ of Al(III), Be(II), Cu(II), and Fe(III) to ODS gel were slightly smaller than $\mathrm{pH_{1/2}}$ of the solvent extraction. The $\mathrm{pH_{eq}}$ value of Pb(II) ion is 2 pH unit smaller than $\mathrm{pH_{1/2}}$ of the extraction system. Though the value of Zn(II) was 6.13, no $\mathrm{pH_{1/2}}$ value for half extraction has been reported.

In a previous paper[7] it was described the perchlorate anion does not affect the adsorption of Cu(II) in the presence of acetylacetone. Accordingly, we suppose that the adsorption equilibria of the present system are the same as the distribution equilibria of complex molecules between two liquid phases as follows:

$$\mathrm{Hacac_g} \overset{K_\mathrm{D}}{\rightleftarrows} \mathrm{Hacac_a}, \tag{1a}$$

$$\mathrm{Hacac_g} \overset{K_\mathrm{a}}{\rightleftarrows} \mathrm{H^+{}_a} + \mathrm{acac^-{}_a}, \tag{1b}$$

$$\mathrm{M}^{m+}{}_\mathrm{a} + n\ \mathrm{acac^-{}_a} \overset{\beta_n}{\rightleftarrows} \mathrm{Macac}_{n,\mathrm{a}}, \tag{1c}$$

and

$$\mathrm{Macac}_{n,\mathrm{a}} \overset{K'_\mathrm{D}}{\rightleftarrows} \mathrm{Macac}_{n,\mathrm{g}}, \tag{1d}$$

where subscripts g and a denote the gel and aqueous phase, respectively. K_D, K'_D, K_a, and β_n are distribution constant of acetylacetone between two phases for adsorption, that of complex for adsorption, dissociation constant of acetylacetone and overall formation constant of complex, respectively. The pH dependence of adsorption of metal complex with acetylacetone can thus be decribed in similar form to that of the liquid-liquid extraction equilibria, that is, when the adsorption ratio, D, is defined as

$$D/\mathrm{cm^3\,g^{-1}} = C_\mathrm{g}/C_\mathrm{a}. \tag{2}$$

Here, C_g and C_a are the concentrations of metal ion in the gel and aqueous phases, respectively. The pH dependence of the adsorption ratio is represented as

$$\log D = \log K_\mathrm{ad} + n\ \log[\mathrm{Hacac}]_\mathrm{g} + n\ \mathrm{pH} \tag{3}$$

where K_ad is defined as the adsorption constant after notation in liquid-liquid partition equilibria. Coefficient n in the equation denotes the number of ligand molecules included in the adsorbed complex molecule. Eq. 3 shows that the slope of a plot of $\log D$ vs. pH represents the number of acetylacetone in the adsorbed molecule, if concentration of acetylacetone on the gel phase can be regarded as constant.

The concentration of acetylacetone on the gel was calculated from the adsorption data of acetylacetone previously reported as $D_\mathrm{acac}=22.4$.[7] The concentration of acetylacetone on gel was estimated to be 7.16×10^{-5} mol g^{-1}. Since the concentration of metal ions is 1.33×10^{-6} mol g^{-1} and is much smaller than that of acetylacetone, we can regard the concentration of acetylacetone on the gel as being constant in all adsorption steps.

Figure 2 shows a plot based on Eq. 3; linear relationships between pH and $\log D$ were obtained. This fact indicates that the adsorption mechanism is valid. The obtained slopes are summarized in Table 1. All of the slopes are nearly unity, except for Al, whose value is nearly two. For Cu, the adsorption equilibria was thoroughly discussed in a previous report.[7] We have shown that Cu(II) is adsorbed onto ODS gel in the presence of acetylacetone as a 1 : 1 complex.

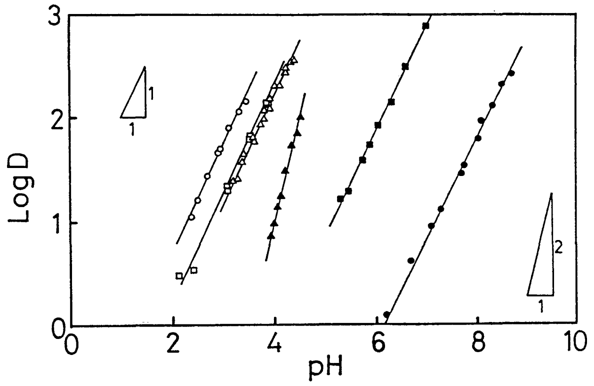

Fig. 2. Plot of log D vs. pH of metal ions in the presence of acetylacetone. ○; Fe(III), □; Cu(II), △; Be(II), ▲; Al(III), ■; Pb(II), ●; Zn(II).

The other metal ions whose slopes are unity are also considered to be adsorbed on ODS gel as 1 : 1 complexes with acetylacetone. On the other hand, Al ions seem to be adsorbed as a 1 : 2 complex; the reason for this is not clear at present. These results show that metal ions are adsorbed on ODS gel as charged complexes, contrary to solvent extraction in which they are extracted as noncharged metal complexes. It is considered that the charged complex is stable on the gel surface, and that a surface can be regarded as an interface corresponding to a liquid-liquid interface, since it is reported in extraction kinetics that charged 1 : 1 complexes are in the interface.[9)]

The adsorption constants are listed in Table 1 along with the extraction constant, K_{ex}, of which the dimension is converted to $\mathrm{cm^3\,g^{-1}}$. All of the obtained K_{ad} values were larger than that of solvent extraction. Especially, the value of Pb is 7 units larger than the extraction system; no value of Zn has been reported in an extraction system. This phenomenon is due to a difference in the compositions between adsorbed and extracted complexes. From the adsorption or extraction mechanism, K_{ad} and K_{ex} are represented as follows:

$$K_{\mathrm{ad}} = K'_{\mathrm{Dad}}\,\beta_{n_{\mathrm{ad}}}\,K_{\mathrm{a}}^{n_{\mathrm{ad}}}/K_{\mathrm{D,ad}}^{n_{\mathrm{ad}}} \qquad (4)$$

and

$$K_{\mathrm{ex}} = K'_{\mathrm{Dex}}\,\beta_{n_{\mathrm{ex}}}\,K_{\mathrm{a}}^{n_{\mathrm{ex}}}/K_{\mathrm{D,ex}}^{n_{\mathrm{ex}}}, \qquad (4')$$

where subscripts ad and ex denote adsorption and extraction systems, respectively. The number of ligands contained in adsorbed and extracted complex are denoted by n_{ad} and n_{ex}, respectively. The difference between $\log K_{\mathrm{ad}}$ and $\log K_{\mathrm{ex}}$ is represented as

$$\log(K_{\mathrm{ad}}/K_{\mathrm{ex}}) = \log(K'_{\mathrm{Dad}}/K'_{\mathrm{Dex}}) + \log(\beta_{n_{\mathrm{ad}}}/\beta_{n_{\mathrm{ex}}}) + (n_{\mathrm{ex}} - n_{\mathrm{ad}})\mathrm{p}K_{\mathrm{a}} + (n_{\mathrm{ex}}\log K_{\mathrm{D,ex}} - n_{\mathrm{ad}}\log K_{\mathrm{D,ad}}). \qquad (5)$$

Table 1. Composition of Adsorbed Complex, n, Equimolar $\mathrm{pH_{eq}}$ and Adsorption Constant K_{ad} of ODS-Aqueous Solution Systems, and Corresponding Values in Solvent Extraction

Ions	Adsorption			Extraction*	
	n	$\mathrm{pH_{eq}}$	$-\log K_{\mathrm{ad}}$	$\mathrm{pH}_{1/2}$	$-\log K_{\mathrm{ex}}$
Al(III)	2.00	3.47	4.65	3.30	6.48
Be(II)	1.05	1.85	0.73	2.45	2.79
Cu(II)	0.98	1.90	0.81	2.90	3.97
Fe(III)	0.99	1.30	0.16	1.60	1.39
Pb(II)	1.01	4.15	3.02	6.20	10.15
Zn(II)	0.95	6.13	4.73	ne	ne

ne: Not extracted.
*: Benzene is used as organic solvent.[8)]

It is reported that $\log K_{\mathrm{D,ex}}$ is 0.71 for the liquid-liquid distribution between the aqueous phase and benzene, $\mathrm{p}K_{\mathrm{a}}$ is 8.84,[10)] and that $\log K_{\mathrm{D,ad}}$ is 1.35 for adsorption to ODS gel.[7)] The β_n values can be obtained from the literature,[11,12)] as listed in Table 2. Using these values, the values of K_{ad} obtained in this work and K_{ex} from the literature,[8)] we can calculate K'_{Dad} and K'_{Dex} from Eq. 4 and 4′. The calculated values are summarized in Table 2. It is shown in the seventh and eighth column of the table that the differences between $\log K'_{\mathrm{Dad}}$ and $\log K'_{\mathrm{Dex}}$ are small, comparable to the differences between $\log K_{\mathrm{D,ad}}$ and $\log K_{\mathrm{D,ex}}$. If the first and the fourth terms of the right-hand side of Eq. 5 are ignored, we can estimate the difference between $\log K_{\mathrm{ad}}$ and $\log K_{\mathrm{ex}}$ from the second and the third terms in the equation. The estimated values of the differences are listed in the sixth column in Table 2, along with the observed values in the fifth column. The calculated values are in good agreement with the observed ones. It is shown from this calculation that the predominant terms over the difference between $\log K_{\mathrm{ad}}$ and $\log K_{\mathrm{ex}}$ are those containing $K_{\mathrm{a}}{}^n$ and β_n that is, the difference of composition of complexes between adsorption and extraction system, n_{ad} and n_{ex}.

Table 2. Comparison between Adsorption Constant and Extraction Constant

Ions	$\log\beta_1$*	$\log\beta_2$*	$\log\beta_3$*	$\log K_{\mathrm{ad}}-\log K_{\mathrm{ex}}$		$\log K_{\mathrm{D}}'{}_{\mathrm{ad}}$	$\log K_{\mathrm{D}}'{}_{\mathrm{ex}}$
				obsd	calcd		
Al(III)	8.60	16.5	22.3	1.83	3.04	−0.77	−0.13
Be(II)	7.90	14.59	—	2.06	2.15	1.56	1.72
Cu(II)	8.16	14.76	—	3.16	2.24	1.22	0.37
Fe(III)	9.80	18.8	26.2	1.23	1.28	0.23	1.06
Pb(II)	4.2**	6.32	—	7.13	6.72	2.97	2.63

* Ref. 11.
** Ref. 12.

Consequently, it is predicted that a larger adsorption constant than the extraction constant can be obtained in the metal ions of which the difference between the overall formation constants is small, for example β_1 and β_2 for Pb(II).

We thanks Prof. Hitoshi Watarai of Akita University for his helpful advice and encouragement to this work.

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