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Effects of Chain Length of Chemically Modified Silica Gels on Adsorption of Acetylacetone and Its Copper Complex from Aqueous Phase

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Distributions of acetylacetone and its copper complex between an aqueous phase and a chemically modified silica gel were measured. The modified silica gels were synthesized, and four different alkyl chains from butyl to octadecyl groups were introduced into the surface. The observed distributions were interpreted by a solubility parameter theory as in a liquid–liquid partition experiment. It is found that the solubility parameter theory can be used as a tool for interpretation of the distribution of acetylacetone and its complex between aqueous and gel phases.

Surface-modified silica gels are useful as collectors of metal cations from aqueous solution by formation of metal complexes and as a stationary phase in liquid chromatography of the complexes. However, only a few systematic studies concerning the adsorption behavior of the metal complexes between aqueous phase and the gel phase have been done.(1,2) Thus it is unknown how the adsorption equilibria of chemical species such as organic compounds or metal complexes between the phases can be described systematically.

In the field of solvent extraction, the solubility parameter proposed by Hildebrand(3) is a powerful tool for interpretation, and its solvent effect has been analyzed.(4) After this, Saito and Suzuki(5) expanded this concept to gel chromatography, and investigated the contribution of a partition effect of normal alkanes and metal complexes with acetylacetone using a poly(vinyl acetate) gel. However they used only one gel, and so they could not interpret the gel effect like the solvent effect in a liquid–liquid partition system, since a series of gels the properties of which are controlled was not available. This approach has not been applied to the adsorption system using surface-modified silica gels in spite of its analytical importance.

In this study, we synthesized a series of surface-modified silica gels, and examined the adsorption behavior of acetylacetone and its copper complex onto the silica gels. The silica gels had four different alkyl chains from butyl to octadecyl group introduced. Using these controlled silica gels, we investigated the effects of alkyl chain length bonded to surface of the gel, the gel effect, as a function of solubility parameter as done in the liquid–liquid partition experiments.(3,4)

Experimental

Microbead-type silica gel (Fuji Devison, surface area 523 $\mathrm{m^2\,g^{-1}}$, particle size 30—50 µm, and average pore size 6 nm) was used. Four kinds of alkyl chains were introduced into the silica gel surface by reaction in cyclohexane with the following silane coupling reagents: butyldimethylchlorosilane (abbreviated C4 hereafter), octylmethyldichlorosilane (C8), dodecylmethyldichlorosilane (C12), and octadecyldimethylchlorosilane (C18). Specific surface areas were measured by the Cranston–Inkley method. Heats of immersion of the gels to water were obtained by a conduction-type microcalorimeter, and amounts of the loaded alkane were measured by elemental analysis.(6) The values obtained are summarized in Table 1.

Reagent grade materials were used without further purification.

The procedure of measurement of the adsorption ratio was described elsewhere.(1)

Results and Discussion

Chemically Modified Silica Gel. Concentrations of the alkyl groups were almost constant at 0.57 mequiv $\mathrm{g^{-1}}$ irrespective to the chain length as shown in Table 1. Specific surface area, however, decreased with increments of the chain length of alkyl groups connected to the surface. The heat of immersion decreased with the increase of length of the alkyl chain. The relationship of the concentration of the alkyl chain and the specific surface area shows that the alkyl groups bond vertically to the surface. The tendency of the heat of immersion shows that the hydrophobicity of the surfaces increases with increments of chain length.

Adsorption of Acetylacetone. Figure 1 illustrates the adsorption behavior of acetylacetone onto the gels. Maximum concentration of acetylacetone at an initial state before adsorption was 1.0×10^{-2} $\mathrm{mol\,dm^{-3}}$. The adsorption isotherms are linear except for the C18 gel. It is evident that the adsorption behavior obeyed Henry's law in this concentration range for the C4 to C12 gel systems, and that the adsorption isotherm in C18 gel shows the Langmuir type.

The dependence of the adsorption ratio upon the chain length is summarized in Fig. 2 along with the adsorption onto the bare silica gel, which is unmodified. The adsorption ratio decreases with decrease of the chain length bonding to the silica gel surface, and the minimum adsorption is observed at the C4 gel. The dependence of the chain length from C18 to C4 gels seems to shown the hydrophobicity of the gel surface and the thickness of the phase composed of alkyl chain. It is

Table 1. Chemically Modified Silica Gels and Its Characterization

Loaded substituents	Surface area	Amounts of Loaded alkanes	Heat of immersion
	$m^2\ g^{-1}$	$mequiv\ g^{-1}$	$J\ g^{-1}$
Unmodified silica gel	522.5	—	78.2
C_4H_9– (C4)	490.1	0.60	63.6
C_8H_{17}– (C8)	446.6	0.65	47.0
$C_{12}H_{25}$– (C12)	412.6	0.51	48.9
$C_{18}H_{37}$– (C18)	295.5	0.55	24.3

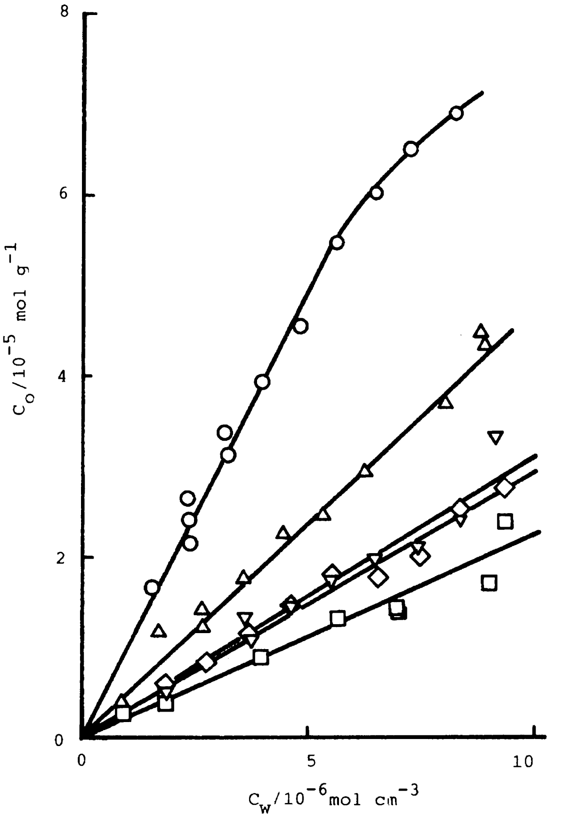

Fig. 1. Adsorption of acetylacetone onto the silica gels modified by the different alkyl groups. ○: C18, △: C12, ▽: C8, □: C4, and ◇: bare silica gel. (pH 5.75, T=298.15±0.1 K).

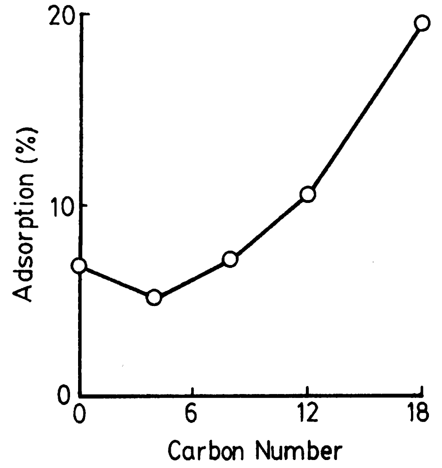

Fig. 2. Dependence of adsorption ratio of acetylacetone on the chain length of alkyl groups bonded to the surface of silica gel (pH 5.75, T=298.15±0.1 K).

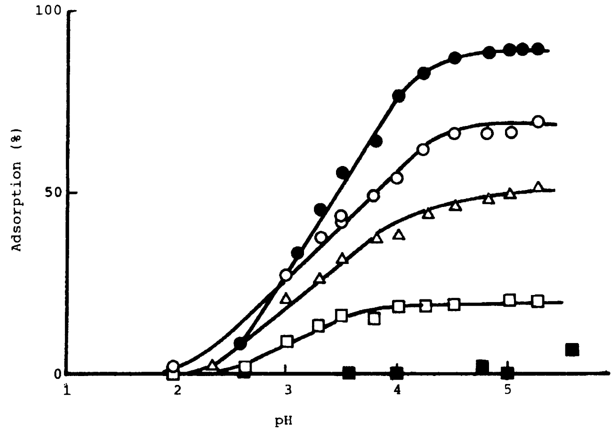

Fig. 3. Adsorption of copper(II) onto the silica gels modified by different alkyl groups in the presence of acetylacetone. ●: C18, ○: C12, △: C8, □: C4, and ■: bare silica gel. ([acac]=1.0×10^{-2} mol dm^{-3}, and [Cu]=3.14×10^{-6} mol dm^{-3} at an initial state in the aqueous phase. T=298.15±0.1 K).

considered that the hydrophobic nature and the thickness, that is volume, of the phase increases with the increase of chain length, and that both of these properties serve as an adequate situation for the adsorption process. The adsorption ratio of the bare silica gel is larger than that of C4 gel. The increase of adsorption ratio in the bare silica gel may have another reason, that is the interaction between acetylacetone and silanol groups of the silica gel surface via hydrogen bonding.

Adsorption of Copper(II) Ion in the Presence of Acetylacetone onto the Gels. Adsorption of copper(II) complex with acetylacetone onto the silica gels is illustrated in Fig. 3. In the whole pH region measured, copper was not adsorbed without acetylacetone, when surface-modified silica gels were used as the adsorbent.

In Fig. 3, both the pH at which the adsorption occurs (about 2.5) and the adsorption becomes nearly constant (about 4.5) are almost the same in all the gels. This shows that the chemical species concerned in the adsorption is the same in all the gels, but has a different adsorption constant.

The adsorption ratio of copper increases with the length of the alkyl chain. The correlation between alkyl chain length and the adsorption ratio of copper at pH 5 is illustrated in Fig. 4. Although it has been reported that copper ion is adsorbed onto the bare silica gel surface by an ion exchange mechanism with the surface silanol group,[7] copper did not adsorb on a bare silica gel in the presence of acetylacetone. It is considered that the ion exchange of copper ion is inhibited by the formation of their metal complex. In the gels modified by alkyl chains, the adsorption ratios of copper are increased with the length of alkyl chains as shown in acetylacetone alone. Also, this means that the adsorption obeys the surface hydrophobicity.

The desorption curve of copper in the presence of acetylacetone is shown in Fig. 5. The curve shows a reverse shape against the adsorption curve. This means that the system studied is a reversible process, and no additional reaction occurs on the surface.

Applicability of Solubility Parameter to the Adsorption System. Solubility Parameters of the Chemically Modified Gel Phase: The results mentioned above shows that the system studied can be described as a reversible process. Therefore, it is expected that the system can be analyzed by the concept of the solubility parameter. We used this process on the adsorption system of acetylacetone and its copper complex from a liquid phase to gel phases modified by alkyl groups. That is, we regarded the gel phase as a phase similar to a liquid phase, since it is expected that the alkyl chains bonded to the gel surface have sufficient freedom of motion in a limited space.

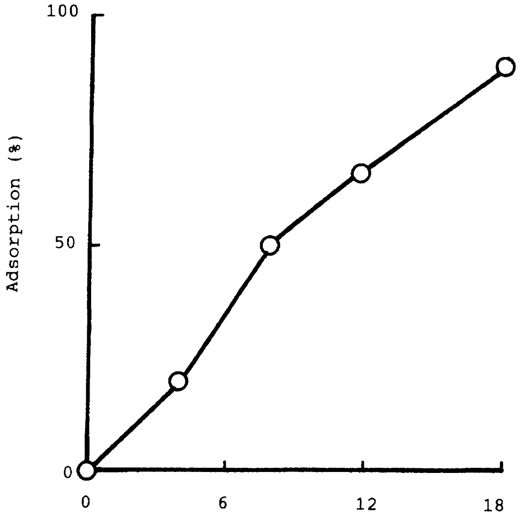

Fig. 4. Dependence of adsorption ratio of copper(II) on the chain length of alkyl groups bonded to the surface of silica gel in the presence of acetylacetone. (pH 5.0, T=298.15±0.1 K).

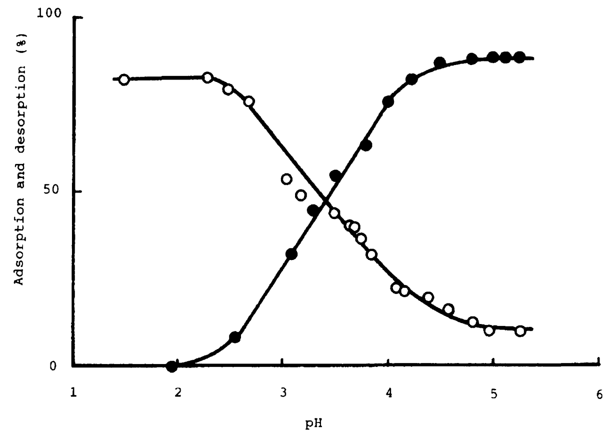

Fig. 5. Adsorption and desorption of copper(II) in the presence of acetylacetone in the system containing C18. (●: adsorption curve, ○: desorption curve).

Table 2. Solubility Parameters of Chemically Modified Silica Gels, δ_o, and Corresponding n-Alkanes, δ_{alkane}

Modified silica gels	$\ln D_{\text{acac}}$	δ_o $(\text{cal cm}^{-3})^{1/2}$	δ_{alkane}[7] $(\text{cal cm}^{-3})^{1/2}$
C4	0.89	5.96	6.8
C8	1.16	6.08	7.6
C12	1.56	6.53	7.9
C18	2.32	7.07	N.a.[a]

a) not available. b) 1 cal=4.184 J.

Table 2 summarized the estimated values of solubility parameter of the gel phase, δ_o, from the adsorption ratio of acetylacetone, D_{acac}, using the following equations:[4]

$$RT\ln D_{\text{acac}} = V_{\text{acac}}(\delta_w + \delta_o - 2\delta_{\text{acac}})(\delta_w - \delta_o), \quad (1)$$

$$D_{\text{acac}} = x_o/x_w = (C_o/n_o)/(C_w/n_w), \quad (2)$$

where R denotes the gas constant, T temperature, δ solubility parameter, x mole fraction of acetylacetone, n number of moles per gram of solvent or alkyl group bonded to the gel surface, and V molar volume. The subscripts w, o, and acac denote aqueous and gel phase, and acetylacetone, respectively. We used 17.5 and 10.5 as the values of solubility parameters for aqueous phase and acetylacetone, respectively, reported by Wakahayashi et al.[4] The values of adsorption ratio of acetylacetone, D_{acac}, were obtained by Eq. 2 using final concentrations of acetylacetone in aqueous phase, $C_w/\text{mol cm}^{-3}$ ($=C_w/\text{mol g}^{-1}$ within experimental error), and that of gel phase, $C_o/\text{mol g}^{-1}$, and number of moles of alkanes put on are listed in Table 1. The values of solubility parameter of the gels calculated from these values are listed in Table 2.

The solubility parameters of the gels estimated in this study show that the longer the chain length, the larger the value. The absolute values are in the range of normal alkanes listed in the same table, and the tendency of variation is consistent with the normal alkanes.[8] The

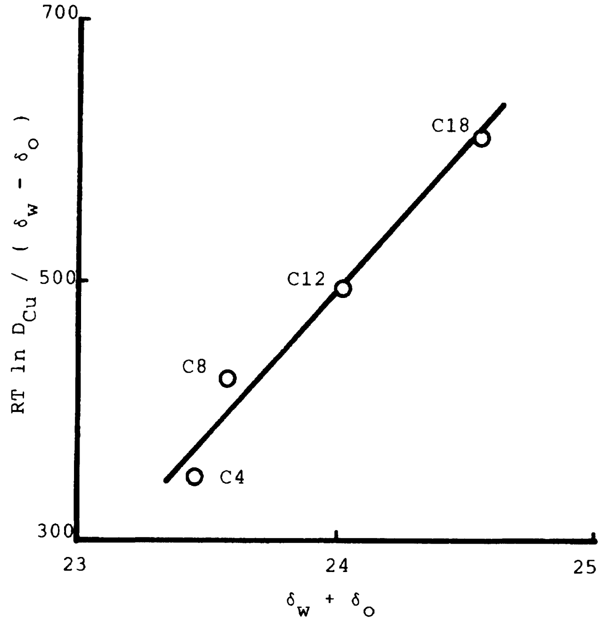

Fig. 6. Correlation between adsorption coefficients of copper(II) in the presence of acetylacetone and solubility parameters of gels .

gel phases seem to be fairly nonpolar in the adsorption equilibria of acetylacetone.

Adsorption Behavior of Complex Molecule: Using the solubility parameters for the gel phases obtained above, we attempted to describe the adsorption of complex molecule in terms of the solubility parameter. The unknown parameters are the solubility parameter of the adsorbing species and its molar volume. They can be obtained from the slope and intercept of a plot of $RT\ln D_{Cu}/(\delta_w-\delta_o)$ vs. $(\delta_w+\delta_o)$ based on Eq. 1, where D_{Cu} denotes the adsorption ratio of copper with acetylacetone. The results is shown in Fig. 6, in which a linear relationship is obtained. This means that the adsorption system can be described by the solubility parameter as well as the system of liquid–liquid partition systems. The estimated solubility parameter of copper complex with acetylacetone was 10.8 from the figure, and almost equal to the value of acetylacetone. That is, the magnitude of the solubility parameter is set by that of the ligand molecule. This phenomenon is consistent with the case of a liquid–liquid partition system.[4] The volume of adsorbate was 199 $cm^3 mol^{-1}$ and is almost twice that of the acetylacetone molecule (104.3 $cm^3 mol^{-1}$ calculated from their density). This means that two acetylacetone molecules are contained in the adsorption species. At pH 5.0 and in the case of a large excess of concentration of acetylacetone to copper, it is considered that a 1 : 2 complex of copper with acetylacetone is the dominant adsorbate under these conditions, contrary to the lower pH region where 1 : 1 complex adsorbs.[1]

Concluding Remarks. The adsorption behavior of acetylacetone can be described by the surface hydrophobicity of the gels modified by alkyl chains from butyl to octadecyl groups. Also, that of copper ion in the presence of acetylacetone can be interpreted in the same manner with acetylacetone alone. Since the adsorption reaction of copper with acetylacetone can be regarded as a reversible process, we examined whether the adsorption process can be described by the concept of the solubility parameter. Consequently the linear relation between the terms including solubility parameters and the adsorption ratio were obtained as shown in the liquid–liquid partition systems. This seems to shown that we can regard the silica gels with chemically modified surfaces as a phase like a liquid phase in the liquid–liquid partition systems in this method. The gel surface is not rigorously the same as a liquid phase, since the thermodynamic definition of the solubility parameter cannot be given.[8] The concept of the solubility parameter derived from the regular solution theory, however, was useful to describe the adsorption process of metal complex with acetylacetone. This results shows the versatility of the concept, and this method seems to be a powerful tool to outline the adsorption process between liquid and solid phases as well as a liquid–liquid partition system.

Acetylacetone usually exists as a mixture of keto and enol forms because of its tautomerism. In the liquid phase, concentrations of two tautomers can be estimated by a NMR measurement. However, in the adsorption process studied here, it is difficult to obtain their values, because the adsorption process occurs at an interface between two phases. Although we regarded acetylacetone as one phase, and ignored the tautomerism in this study, the analysis gave a good results. For this reason, it is considered that the concept of solubility parameter may be insensitive to the effect of tautomerism.

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