Original Papers

Aggregation of *N*-Octanoyl-*N*-phenylhydroxylamine in Carbon Tetrachloride

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The aggregation number of *N*-octanoyl-*N*-phenylhydroxylamine (C8-PHA) in carbon tetrachloride was determined on the basis of the extraction equilibria of copper(II) chelate with C8-PHA between aqueous and carbon tetrachloride phases. According to the relation of the distribution ratio of copper(II) with its concentration in the organic phase, the formation of a reversed micelle consisting of approximately 13 C8-PHA molecules was deduced when C8-PHA concentration was greater than 0.1 mol dm^{-3}. The Karl Fisher titration results showed that one water molecule was included in the reversed micelle. The polar parameter ($E_T(1)$) of the reversed micelle was determined to be 250 kJ mol^{-1} by measuring absorption spectra of 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine (HPTPP) as a function of C8-PHA concentration in carbon tetrachloride. The $E_T(1)$ value was different from that in carbon tetrachloride, indicating the incorporation of HPTPP into the polar core region where the hydrophilic chelating groups are oriented inward in the reversed micelle. On the basis of the $E_T(1)$ values in organic solvents, the polar core region could be regarded as being an alcoholic medium.

Keywords Aggregation, *N*-octanoyl-*N*-phenylhydroxylamine, reversed micelle, polar parameter

The aggregation of chelating extractants with long-chain alkyl groups in organic solvents has attracted interest because of their formation of reversed micelles and their use for extraction of metal ions.[1-3] We reported previously the extraction equilibria of *N*-alkylcarbonyl-*N*-phenylhydroxylamines (R-PHAs) and their metal chelates between carbon tetrachloride and aqueous phases.[4] R-PHAs react with metal ions as bidentate ligands through the carbonyl and hydroxyl oxygens. We tested a series of R-PHAs for elucidating the effect of alkyl substituents at the position of the carbonyl group on the selectivity in the extraction of metal ions. For this purpose, the distribution ratio of metal ions was measured as functions of R-PHA concentration and pH.

In the course of these studies, we noticed that the slope of the plots of logarithmic distribution ratio *vs.* logarithmic R-PHA concentration decreased above a certain concentration of R-PHA. The decrease in the slope was probably due to the aggregation of R-PHAs and thus the formation of a reversed micelle. This induced us to start a study on the aggregation of R-PHAs in carbon tetrachloride. In this paper, the aggregation numbers of *N*-octanoyl-*N*-phenylhydroxylamine (C8-PHA) are determined and the properties of a polar core region in the reversed micelle are evaluated. The former is based on the distribution equilibrium of copper(II), and the latter on the extraction of water and 4-nitrophenol and on the measurement of a polar parameter ($E_T(1)$)[5,6] of 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine as a spectroscopic probe.

Experimental

Reagents

Preparation of C8-PHA comprised the addition of the acid chloride of octanoic acid into an ether solution containing phenylhydroxylamine and sodium hydrogencarbonate and the purification of the product by recrystallization.[4] The acid chloride was prepared by refluxing the octanoic acid with thionyl chloride and distilling out the acid chloride produced.

A standard solution (0.1 mol dm^{-3}) of copper(II) was prepared by dissolving an appropriate amount of copper(II) nitrate hexahydrate in 0.01 mol dm^{-3} nitric acid. The solution was standardized by EDTA titration.

Apparatus

A Hitachi 170-30 atomic absorption spectrometer was employed for the determination of copper(II) in the aqueous phase. A Toa HM-60S pH meter was used for measuring pH values in the aqueous phase. An Iwaki KM-VS shaker was used for mixing the two phases.

Absorbance and absorption spectra were measured by a Hitachi U2000 double-beam spectrophotometer with 1-cm cells. Water concentration in the organic phase was measured by the Karl Fisher method, for which a Mitsubishi CA-02 moisture meter was used.

Procedure

In the experiments for the distribution equilibria of copper(II), a 20.0-cm^3 portion of an aqueous solution containing an appropriate amount of copper(II) was placed in a glass vial. The initial copper(II) concentration was 1.00×10^{-4} mol dm^{-3}. Then a 4.00-cm^3 portion of carbon tetrachloride containing a definite amount of C8-PHA was placed in the vial. The two phases were equilibrated for 15 min at 20±1°C. The pH of the aqueous phase was adjusted with an acetate buffer and nitric acid. The total concentration of acetate component in the aqueous phase was 0.001 mol dm^{-3}. The ionic strength was adjusted at 0.1 with sodium nitrate and nitric acid. After phase separation, the copper(II) concentration in the aqueous phase was determined by the atomic absorption method. The concentration of copper(II) in the organic phase was calculated by the material balance of copper(II).

In the experiment for the determination of the aggregation number of C8-PHA, a 5.00 cm^3 portion of an aqueous solution containing copper(II) (5.00×10^{-4} – 5.00×10^{-2} mol dm^{-3}) was equilibrated with a 5.00 cm^3 portion of carbon tetrachloride containing C8-PHA (0.300 mol dm^{-3}). An appropriate amount of nitric acid had been added into the aqueous solution so as to reach pH 1.50 after the equilibrium. Other experimental procedures were the same as those for the distribution equilibrium of copper(II).

Results and Discussion

Distribution equilibrium of copper(II)

In general, we can describe the extraction of copper(II) with C8-PHA by Eq. (1)[4],

$$Cu^{2+} + 2HL_o \rightleftharpoons CuL_{2,o} + 2H^+. \quad (1)$$

Here, we have assumed that the aggregation of C8-PHA in the organic phase is negligible, that copper(II) ion is present in the agueous phase largely as a free ion (Cu^{2+}), and that the extracted species in the organic phase is the uncharged copper(II) chelates ($CuL_{2,o}$). In Eq.(1), species having a subscript (o) mean those present in the organic phase. The extraction constant, K_{ex}, for the equilibrium reaction (Eq.(1)) will be given by Eq.(2):

$$K_{ex} = [CuL_2]_o[H^+]^2/[Cu^{2+}][HL]_o^2. \quad (2)$$

The distribution ratio (D), which is defined by a ratio of total copper(II) concentrations between the two phases, is written as

$$D = [CuL_2]_o/[Cu^{2+}]. \quad (3)$$

Combining Eq.(3) with Eq.(2), we obtain Eq.(4):

$$\log D = 2pH + 2\log[HL]_o + \log K_{ex}. \quad (4)$$

Accordingly, if the experimental values of log D are plotted as a function of pH (at constant log[HL]$_o$) or log[HL]$_o$ (at constant pH), the plots should be a straight line with a slope of 2. The plots of log D against pH at various fixed concentrations of C8-PHA are presented in Fig. 1. The slopes of the straight lines were 2 and were independent of the C8-PHA concentration. Hence, the uncharged chelate, $CuL_{2,o}$, is likely to be exclusively extracted. For further elucidation of the extracted copper(II) species, the values of (log D − 2pH) were plotted as a function of log[HL]$_o$, as shown in Fig. 2. The term of [HL]$_o$ can be equated to the initial, total

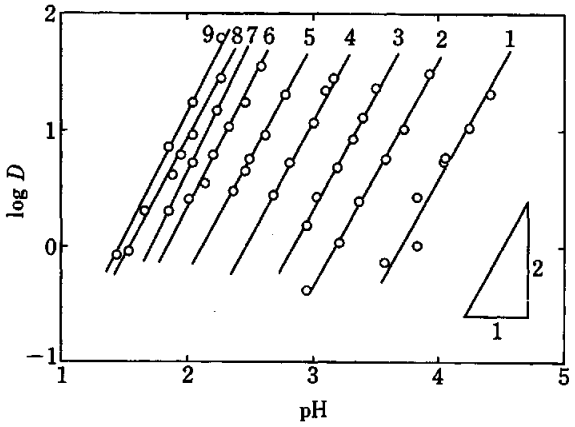

Fig. 1 Plots of log D against pH in the extraction of copper(II) with C8-PHA. Aqueous phase: [Cu^{2+}]=1.00×10^{-4} mol dm^{-3}, [(H,Na)NO_3]=0.1 mol dm^{-3}, [acetate]=0.001 mol dm^{-3}, organic phase: [HL_o]/mol dm^{-3}: 1) 2.02×10^{-3}; 2) 5.01×10^{-3}; 3) 0.998×10^{-2}; 4) 2.00×10^{-2}; 5) 5.00×10^{-2}; 6) 1.00×10^{-1}; 7) 2.00×10^{-1}; 8) 3.00×10^{-1}; 9) 5.00×10^{-1}; 20°C.

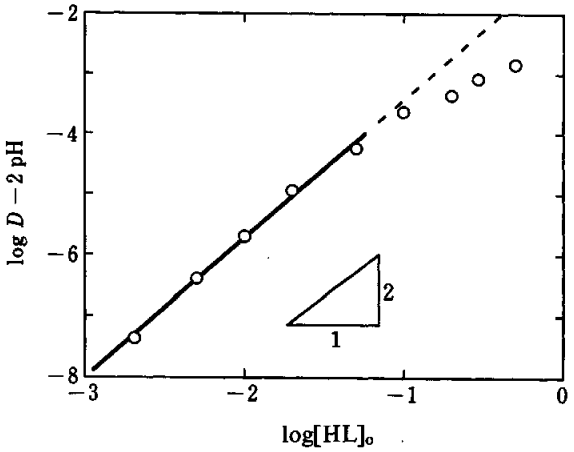

Fig. 2 Plot of (log D−2 pH) against log[HL]$_o$. The plot was obtained from the data of Fig. 1 at log$D$=0.07.

concentration of C8-PHA, $[HL]_{o,int}$, under the present experimental conditions. C8-PHA bound to copper(II) is practically negligible. The slope of the plot was 2 at C8-PHA concentrations lower than 0.07 mol dm^{-3}. Thus, the copper(II) species extracted in the organic phase was concluded to be $CuL_{2,o}$ below 0.07 mol dm^{-3} C8-PHA.

Determination of aggregation number

The slope of the plots in Fig. 2 was less than 2 at C8-PHA concentration greater than 0.1 mol dm^{-3}. This fact indicates that the assumptions are inappropriate above 0.1 mol dm^{-3}. The aggregation of C8-PHA must be taken into account. Then, we determined the association number of C8-PHA on the basis of the distribution equilibrium of copper(II), as discussed below.

We have first assumed that C8-PHA molecules form an aggregate like a reversed micelle, consisting of a fixed number of C8-PHA molecules (n), and that a copper(II) ion is complexed with a reversed micelle. Therefore, the equilibrium expression for the extraction of copper(II) with the reversed micelle and the distribution ratio (D') can be given by Eqs.(5) and (6), respectively:

$$Cu^{2+} + (HL)_{n,o} \rightleftharpoons CuL_2(HL)_{(n-2),o} + 2H^+, \quad (5)$$

$$D' = [CuL_2(HL)_{(n-2)}]_o / [Cu^{2+}]. \quad (6)$$

For the equilibrium reaction expressed by Eq.(5), we can define the extraction constant, K'_{ex}, as Eq.(7):

$$K'_{ex} = [CuL_2(HL)_{(n-2)}]_o[H^+]^2/[Cu^{2+}][(HL)_n]_o. \quad (7)$$

Combining Eqs.(6) and (7), we obtain

$$\log D' = 2pH + \log[(HL)_n]_o + \log K'_{ex}. \quad (8)$$

The concentration of the reversed micelle, $[(HL)_n]_o$, can be expressed as equal to $[HL']_o/n$, where $[HL']_o$ is the total concentration of C8-PHA uncomplexed with copper(II). Thus, Eq.(8) is rewritten as

$$\log D' = 2pH + \log[HL']_o - \log n + \log K'_{ex}. \quad (9)$$

According to Eq.(9), we plotted the relation between (log D'−2pH) and $\log[HL']_o$ in Fig. 3. Under the present experimental conditions $[HL']_o$ approximates to $[HL]_{o,int}$. In Fig. 3, the slope of the plot was approximately 1. This fact suggests the presence of an aggregate such as the reversed micelle consisting of a fixed number of C8-PHA molecules.

In order to estimate the aggregation number (n), we combine Eqs.(6) and (7) to obtain Eq.(10) which is expressed in terms of copper(II) concentration in the organic phase:[1]

$$D' = (K'_{ex}/[H^+]^2)([HL]_{o,int}/n - [CuL_2(HL)_{(n-2)}]_o). \quad (10)$$

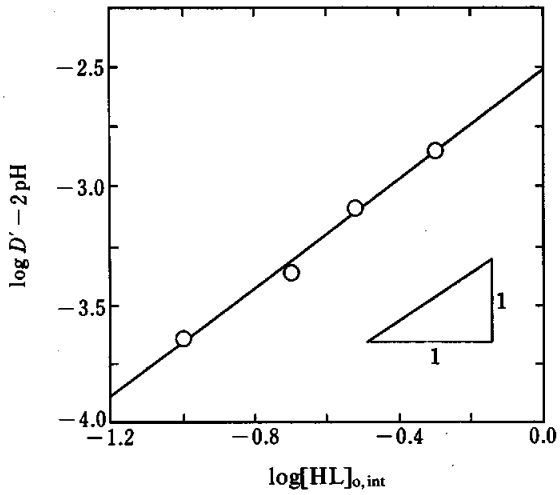

Fig. 3 Plot of (log D'−2 pH) against $\log[HL]_{o,int}$.

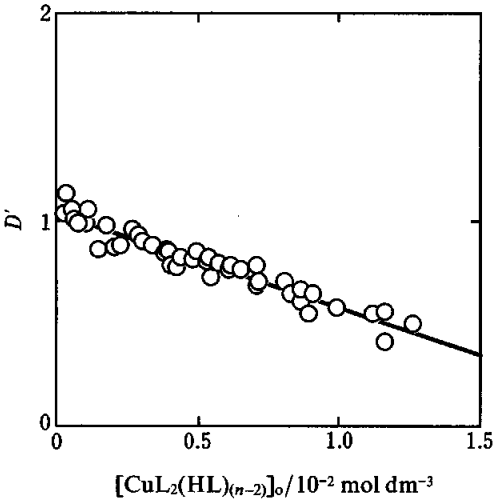

Fig. 4 Plot of D' against $[CuL_2(HL)_{(n-2)}]_o$: $[HL]_{o,int}$=0.300 mol dm^{-3}, pH=1.50.

When H^+ concentration is kept constant, we can obtain Eq.(11),

$$D' = K([HL]_{o,int}/n - [CuL_2(HL)_{(n-2)}]_o). \quad (11)$$

where $K = K'_{ex}/[H^+]^2$.

In Eq.(11), a plot of D' *versus* $[CuL_2(HL)_{(n-2)}]_o$ at a fixed value of $[H^+]$ should have a straight line with a slope of $-K$ and an intercept of $K[HL]_{o,int}/n$. Thus it is possible to evaluate the values of K'_{ex} and n. In Fig. 4, the data indicates that the plot at pH 1.50 is linear. From the slope and the intercept, we obtained the values of n and K'_{ex} to be 13.4±0.2 and (4.64±0.06)×10^{-2}, respectively. By using these values, we calculated the term ($-\log n + \log K'_{ex}$) in Eq.(9) to be −2.46±0.01, which agreed with that of the intercept (*ca.* −2.5) in Fig. 3. This is well consistent with the assumption on the formation of an aggregate, which can be regarded as

being a reversed micelle composed of 13 C8-PHA molecules. It appears that in the reversed micelle the hydrophilic chelating groups are oriented inward, forming a polar core region and the hydrophilic tails are directed toward and in contact with the bulk carbon tetrachloride.

Extraction of water

As water molecules are generally incorporated into a reversed micelle in an organic solvent[2,3,7], it is to be expected that the reversed micelle of C8-PHA can also extract water into the polar core region. To confirm this prediction, the concentration of water extracted into carbon tetrachloride was determined by the Karl Fisher method, as a function of C8-PHA concentration. For this purpose, a 5.00-cm^3 portion of carbon tetrachloride containing C8-PHA at various concentrations from 0 to 0.5 mol dm^{-3} was equilibrated by shaking with an equivolume of an aqueous solution in which the pH was kept at 7.0 with a phosphate buffer (total phosphate concentration; 0.001 mol dm^{-3}) and the ionic strength was maintained at 0.1 ($NaNO_3$).

The results obtained are given in Fig. 5. Up to 0.07 mol dm^{-3} of C8-PHA, the water concentrations in the organic phase remained constant at a level corresponding to the solubility in pure carbon tetrachloride. Meanwhile, the water concentrations were increased with an increase in C8-PHA concentration in the range greater than 0.1 mol dm^{-3}. In the concentration range higher than 0.1 mol dm^{-3}, the slope of the straight line in Fig. 5 was 1/(12.5±0.7). This indicates the incorporation of a water molecule into the reversed micelle composed of approximately 13 C8-PHA molecules.

Extraction of 4-nitrophenol

In order to obtain further insight into the reversed micelle of C8-PHA, we examined the properties of the polar core region in the reversed micelle on the basis of two methods discussed below. The first is on the extraction of 4-nitrophenol which is not extracted into carbon tetrachloride ($\log K_d$=−0.99)[8] without the presence of reversed micelles. An aqueous solution containing 4-nitrophenol and a phosphate buffer of pH 7.0 was equilibrated with an equivolume of carbon tetrachloride at various concentrations of C8-PHA. We determined the distribution ratio of 4-nitrophenol, $D_{(4\text{-np})}$, by measuring absorbances in the aqueous phase and then using the material balance of 4-nitrophenol.

Figure 6 shows that 4-nitrophenol is extracted into the organic phase. This indicates that 4-nitrophenol is in the reversed micelle. The linear relation between $D_{(4\text{-np})}$ and C8-PHA concentration means that the distribution ratio per a C8-PHA reversed micelle is constant, which also supports the formation of the reversed micelle.

Polar parameters in reversed micelle

Next, we evaluated the polar parameters of the

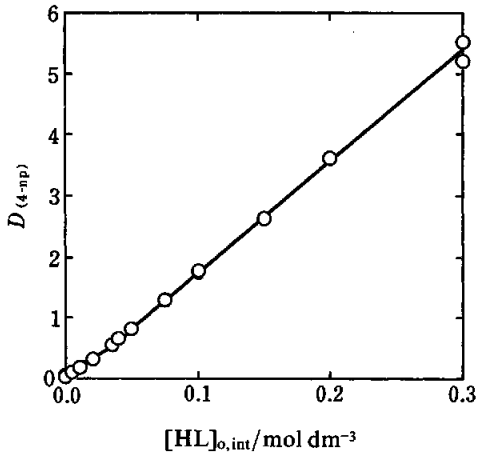

Fig. 6 Distribution ratio of 4-nitrophenol between aqueous and carbon tetrachloride phases as a function of C8-PHA. [(H,Na)NO_3]=0.1 mol dm^{-3}, pH=2.0, 20°C.

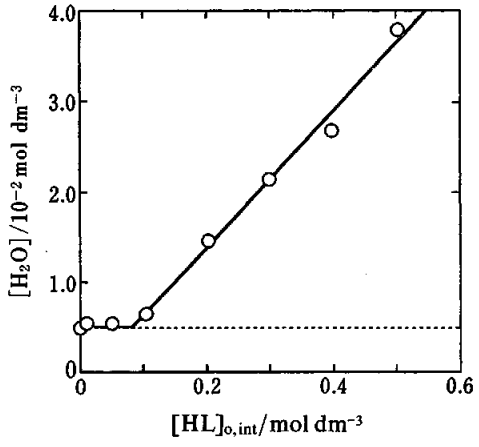

Fig. 5 Concentration of water in carbon tetrachloride solution of C8-PHA. Aqueous phase: 5.0 cm^3, [$NaNO_3$]=0.1 mol dm^{-3}, [phosphate]=0.001 mol dm^{-3} (pH=7.0), organic phase: 5.0 cm^3.

Table 1 The polar parameter ($E_T(1)$) values in C8-PHA solution of carbon tetrachloride and in organic solvents

Solvent	λ_{max}/nm	$E_T(1)$/kJ mol^{-1}
Water[a]	412	290
Ethanol[a]	467	258
1-Propanol[a]	477	250
2-Propanol[a]	501	239
1-Butanol[a]	484	247
2-Octanol[a]	544	220
Carbon tetrachloride	—	171[b]
[C8-PHA]/mol dm^{-3}		
0.1	498	240
0.2	480	249
0.3	475	252

a. Ref. 5.

b. Calculated from the equation ($E_T(1)$=1.00$E_T(30)$+35.0 kJ mol^{-1})[5], E_T was quoted from ref. 6.

reversed micelle. For this purpose, 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine was employed as a spectroscopic probe. The compound was dissolved in water-saturated carbon tetrachloride containing C8-PHA, and the solution thus prepared was subjected to measurements of the absorption spectrum of the compound as a function of C8-PHA concentration. From the spectral data, we calculated the polar parameter ($E_T(1)$) according to the method of Hormadaly and Marcus.[5,6] The $E_T(1)$ values in C8-PHA solutions of carbon tetrachloride are presented in Table 1 together with literature values in different pure organic solvents. The $E_T(1)$ value (about 250 kJ mol^{-1}) thus obtained is different from that in pure carbon tetrachloride and is very close to those in alcoholic solvents. The polar core region in the reversed micelle was similar to alcoholic media. These results will be added evidence for the formation of the reversed micelle of C8-PHA.

In conclusion, further studies on the aggregation of other R-PHAs should be fruitful in regard to the use of their reversed micelles for extraction of metal ions. Branching of the alkylcarbonyl groups transmitted R-PHAs different selectivity with respect to C8-PHA.[4] The formation of reversed micelles thus appears to be an additional factor for enhancing the selectivity in the extraction of metal ions with R-PHAs.

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