Bull. Chem. Soc. Jpn., 61, 3807—3812 (1988)

Surface Activity of Complexes Formed with *N*-Dodecyl-*β*-alanine and Copper(II) Ion in Aqueous Solution

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(Received April 21, 1988)

The surface activity of the equimolar mixed solutions of *N*-dodecyl-*β*-alanine (NDA) and inorganic salts was studied at 30 °C. The surface tension of the NDA–$CuCl_2$ solution decreased more than that of the single NDA solution, whereas the surface tensions of the NDA–NaCl, NDA–$CaCl_2$, and NDA–$MgCl_2$ solutions were almost the same as that of the single NDA solution in the concentration region studied. The experiments with the bulk solution have shown that the 1:1-complex ion formed with NDA and the copper(II) ion is soluble and more surface-active than NDA alone, but the 1:2-complex is not effective in the surface activity because of its extremely low solubility. The formation constant of the 1:1-complex ion was determined, by potentiometry with both copper(II) and hydrogen ion-selective electrodes, to be 5.5×10^{-5}, while the standard free energy of the complex formation was found to be 24.7 kJ mol^{-1}. The composition and structure of the 1:2-complex were studied by means of X-ray diffractometry, IR spectroscopy, and elemental analyses for the precipitate. The total amounts of NDA adsorbed at the air/aqueous solution interface were determined by radiometry using tritium-labeled NDA, and the amount of the 1:1-complex adsorbed was calculated by the Gibbs adsorption isotherm. Thus, the compositions were determined in both the adsorbed and bulk phases. It was seen that the relative adsorbability of the 1:1-complex was larger than that of NDA by a factor of about 1.5×10^2 and, further, was larger than that of a 1:1-complex formed with NDA and sodium dodecylsulfate by a factor of about 3.7.

Ampholytic surfactants of the amino-acid type have been used in various fields because of their excellent characteristics (e.g., high detergency, bactericidal effect, low irritating to the skin, definite effect of pH on the solution properties, high biodegradability, and wide compatibility with other types of surfactants).[1] In spite of such characteristics of ampholytic surfactants, however, reports of their basic surface-chemical properties seem to be rather rare compared to the cases of anionic, cationic, and nonionic surfactants.

We have investigated some of the properties of *N*-dodecyl-*β*-alanine (NDA), which is one of most simple surfactants of the amino-acid type (e.g., the adsorption isotherms and the interfacial tensions at the air/aqueous solution[2] and oil/aqueous solution[3] interfaces, the pH effects on the surface activity,[4] and the interactions with anionic surfactants[5,6] and with insoluble monolayers).[7]

On the other hand, it is well-known that amino acids and the transition metal ions form a number of stable complexes in their aqueous solutions, and some of their structural properties have been investigated as models of metal complexes in biological systems.[8] Therefore, a similar interaction can be expected to occur between the transition metal ions and the ampholytic surfactants of the amino-acid type. However, little has been reported concerning the surface activity of such a complex in its aqueous solution.[9]

The purpose of the present study is to elucidate the surface activity of the complex formed in the mixed solution of the copper(II) ion and NDA.

Experimental

Materials. *N*-Dodecyl-*β*-alanine (NDA) (i.e., 3-(dodecylammonio)propionate) was synthesized from dodecylamine and *β*-propiolactone in acetonitrile; also, tritiated NDA was synthesized by the same procedure except that tritiated dodecylamine was used instead of dodecylamine. The details of the synthesis and purification of the materials have been reported elsewhere.[2] The salts of NaCl, $CaCl_2$, $MgCl_2$, and $CuCl_2$ were purified by recrystallization, repeated three times, from distilled water. Water was purified by distillation after it had been refluxed overnight with acidic permanganate and subsequently with alkaline permanganate.

Methods. The adsorption of NDA was measured by the same radiometry as that reported previously.[2,10] The surface tension was measured by the Wilhelmy plate method. The time dependence of the surface tension was self-recorded to obtain an equilibrium value.[11] The activities of the copper(II) and hydrogen ions in the solutions were measured with the ion-selective electrodes connected to the ion meter (Orion Research, U.S.A., model 920). To minimize the effect of the photo-sensitivity of the copper(II) ion-selective electrode on the output current, the apparatus was set up and operated in as dark a room as possible. All the measurements were made at 30±0.2 °C in the pH region of about 4.3—5.5, where the NDA molecules are mostly zwitterionic[4] and where copper(II) hydroxide is essentially absent.

Results and Discussion

Surface Activity of the Solution. Figure 1 shows the surface tension (γ) vs. concentration curves of the NDA solution (C) with and without an equimolar amount of $CuCl_2$. The abscissa of Fig. 1 shows the

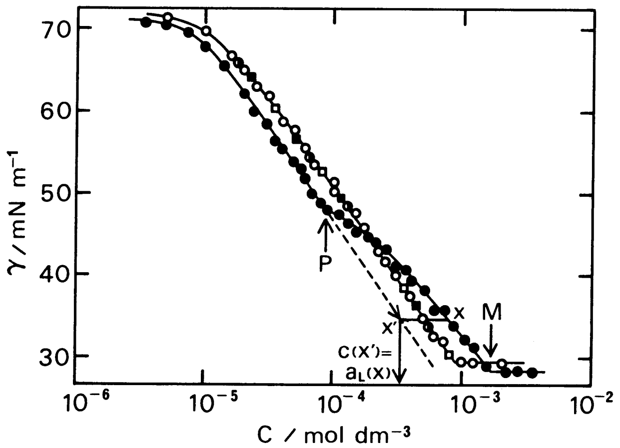

Fig. 1. Surface tension vs. concentration curves for NDA solutions alone (○), and with equimolar amount of $CuCl_2$ (●), $MgCl_2$ (□), $CaCl_2$ (■), and $NaCl_2$ (◑). Dashed line shows the extrapolation of the curve for NDA-$CuCl_2$ system above P point (see text).

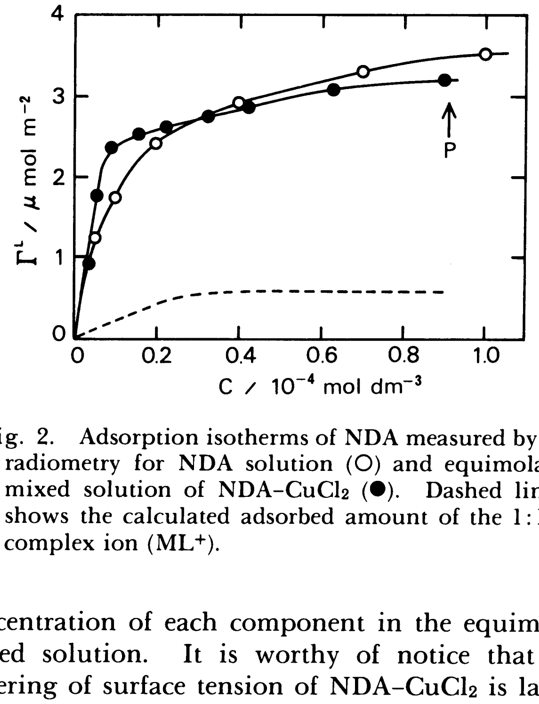

Fig. 2. Adsorption isotherms of NDA measured by a radiometry for NDA solution (○) and equimolar mixed solution of NDA-$CuCl_2$ (●). Dashed line shows the calculated adsorbed amount of the 1:1-complex ion (ML^+).

concentration of each component in the equimolar mixed solution. It is worthy of notice that the lowering of surface tension of NDA-$CuCl_2$ is larger than that of a single NDA solution and has a kink point at the concentration of 9.0×10^{-5} mol dm^{-3}. Here, we call this point P. Above the concentration of the P point, a flickering light was visible upon the irradiation of the He-Ne laser beam to the solution. This means that very fine crystalline particles would be generated, whereas a further lowering of the surface tension is observed until the micelle formation at 1.65×10^{-3} mol dm^{-3}. Here, we call this point M. On the other hand, the surface tensions of the other solutions, which had been prepared by an equimolar mixing of NDA-NaCl, NDA-$CaCl_2$, and NDA-$MgCl_2$, were almost the same as that of the single NDA solution in the corresponding concentration region. This finding indicates that the addition of such amounts of these salts caused no enhancement of the surface activity of the NDA solution. In other words, the salting-out effects were not observed in these systems. Therefore, the results obviously suggest the occurrence of a favorable and specific interaction of NDA with the copper(II) ion in the solution.

Figure 2 shows the adsorbed amounts of NDA (Γ^L) observed by radiometry at the air/solution interface with and without an equimolar amount of $CuCl_2$ in the concentration region below the P point in Fig. 1. The presence of $CuCl_2$ obviously enhanced the adsorption in the lower concentration region, but depressed it in the higher one, compared with that of the single NDA solution. This may be due to the formation of a surface-active complex, as may be expected from the results in Fig. 1. The depression of the adsorption isotherm in the higher concentration region is probably caused by both the ionic repulsion between the net charges of the adsorbed complexes and its geometrically large cross-section area due to the formation of a six-membered ring with NDA and the copper(II) ion, as will be shown later.

In general, it is well-known that the complexes of copper(II) ions and amino acids have the 1:2-composition and a planar structure, with the coordination number being 4.[8] Thus, in a dilute aqueous solution the complex-formation equilibria of NDA with the copper(II) ion are assumed to be described by the following two-step reactions:

$$M^{2+} + L^{\pm} \rightleftarrows ML^{+} + H^{+} \qquad (1)$$

$$ML^{+} + L^{\pm} \rightleftarrows ML_2 + H^{+}, \qquad (2)$$

where M^{2+}, ML^+, ML_2, $L^{\pm}$, and H^+ denote the copper(II) ion, the 1(copper(II)):1(NDA)-complex ion, the 1:2-complex, the zwitterionic NDA, and the hydrogen ion respectively. Thus, we have presumed that the enhanced surface activity of the solution at the concentrations below the P point, as seen in Fig. 1, is due mainly to the presence of the 1:1-complex ion (ML^+), while the depression above the P point is mainly attributable to the formation of the 1:2-complex (ML_2), which is essentially insoluble because of having two long chains in a molecule. In order to confirm this reasoning, the solution properties were studied precisely, as will be described in the following sections.

1:1-Complex (ML^+) Formation. In Fig. 3 the surface tension of the mixed solution of NDA with $CuCl_2$ is plotted against the concentration of NDA (C). The total concentrations of the mixed solutions were kept at 1.0×10^{-4} mol dm^{-3}. The maximum deviation of the surface tension of the mixed solution from that of the single NDA solution is found at the equimolar ratio of NDA/$CuCl_2$; this suggests the formation of the surface-active 1:1-complex ion (ML^+) in the solution.

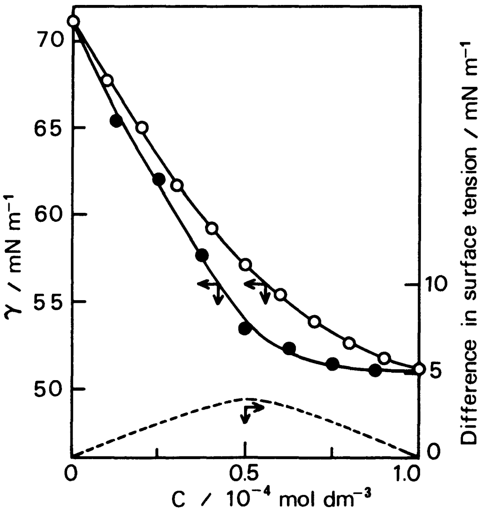

Fig. 3. Surface tensions of NDA (○) solution and NDA-CuCl$_2$ (●) solution (total concentration kept at 1.0×10^{-4} mol dm^{-3}) vs. NDA concentration curves. Dashed line shows the difference in surface tensions of NDA and NDA-CuCl$_2$ solutions.

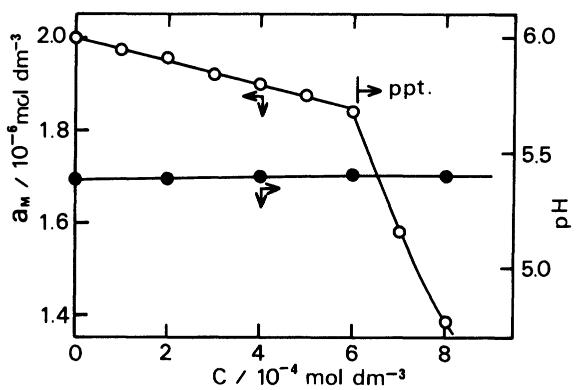

Fig. 4. Activities of copper(II) ion ($a_{\rm M}$) (○) and hydrogen ion (pH) (●) vs. the concentration of NDA.

In order to determine the formation constant of the 1:1-complex ion, the activity measurements of the copper(II) ion ($a_{\rm M}$) and the hydrogen ion ($a_{\rm H}$) in the mixed solution of NDA-CuCl$_2$ were made by means of potentiometry, but the results were not so reliable as to enable us to determine accurately the trace quantities of complexes formed in a dilute concentration region, as is shown in Fig. 2. Therefore, an alternative system was introduced. Pure NDA powder in a given amount was stirred into the CuCl$_2$ solution (2.0×10^{-6} mol dm^{-3}) in a thermostat. The values of $a_{\rm M}$ and $a_{\rm H}$ were measured as a function of the C value. The results are shown in Fig. 4. The $a_{\rm M}$ value gradually decreased with the increase in the C value and steeply decreased at about 5.8×10^{-4} mol dm^{-3} above which point the precipitate was observed in the solution as has been described in the surface tension measurements. On the other hand, the $a_{\rm H}$ value was almost invariable at pH 5.4, in spite of the increase in the C value due to the buffer action of the solution for a small amount of the released H$^+$ ion. Here, we obtain from Eqs. 1 and 2:

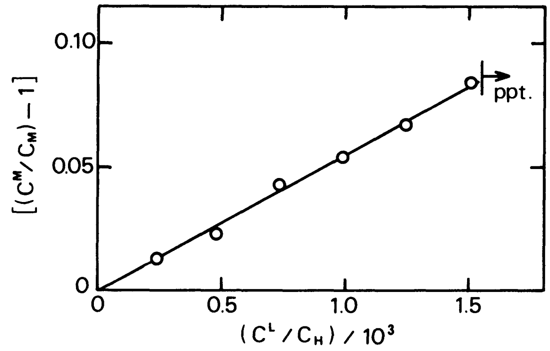

Fig. 5. $[(C^{\rm M}/C_{\rm M})-1]$ vs. $(C^{\rm L}/C_{\rm H})$ plot according to Eq. 5.

$$a_{\rm ML}\,a_{\rm H}/a_{\rm M}\,a_{\rm L} = K_1 \tag{3}$$

$$a_{\rm ML2}\,a_{\rm H}/a_{\rm ML}\,a_{\rm L} = K_2, \tag{4}$$

where K_1 and K_2 denote the successive formation constants of ML$^+$ and ML$_2$ and where $a_{\rm M}$, $a_{\rm L}$, $a_{\rm ML}$, $a_{\rm ML2}$, and $a_{\rm H}$ denote the activities of M^{2+}, L$^\pm$, ML$^+$, ML$_2$, and H$^+$ respectively. Further, since the concentration of each species is of the order of magnitude of 10^{-4}—10^{-6} mol dm^{-3}, the activities in Eqs. 3 and 4 can reasonably be replaced by these concentrations:

$$C_{\rm ML}\,C_{\rm H}/C_{\rm M}\,C_{\rm L} = K_1 \tag{3'}$$

$$C_{\rm ML2}\,C_{\rm H}/C_{\rm ML}\,C_{\rm L} = K_2 \tag{4'}$$

where $C_{\rm i}$ denotes the concentration of species i. Then, under the condition of $C^{\rm L}\gg C^{\rm M}$, as in the case of Fig. 4, the combination of Eqs. 3′ and 4′ gives:

$$(C^{\rm M}/C_{\rm M}) - 1 = K_1(C^{\rm L}/C_{\rm H}) + K_1K_2(C^{\rm L}/C_{\rm H})^2, \tag{5}$$

where $C^{\rm M}$ and $C^{\rm L}$ are the total concentrations defined as:

$$C^{\rm M} = C_{\rm M} + C_{\rm ML} + C_{\rm ML2} \tag{6}$$

$$C^{\rm L} = C_{\rm L} + C_{\rm ML} + 2C_{\rm ML2}. \tag{7}$$

If the ratio of K_2 to K_1 is assumed to be far less than unity, by analogy with the case of the β-alanine solution ($K_1 = 1.5\times10^{-3}$ and $K_2 = 5.9\times10^{-5}$),[12] the second term of R.H.S. in Eq. 5 is negligible. Therefore, the plot of $[(C^{\rm M}/C_{\rm M})-1]$ against $(C^{\rm L}/C_{\rm H})$ should be linear, and its slope should give us the K_1 value. Here, for the actual plot, the values of $a_{\rm M}$ and $a_{\rm H}$ were used as the values of $C_{\rm M}$ and $C_{\rm H}$ respectively. The results are shown in Fig. 5; the K_1 value was found to be 5.5×10^{-5}.

Then, the standard free energy change (ΔG°) in the 1:1-complex ion formation was calculated to be

24.7 kJ mol^{-1} according to this relation:

$$\Delta G^\circ = -RT\ln K_1. \tag{8}$$

This value is slightly larger than that of β-alanine (16.4 kJ mol^{-1}) calculated using the K_1 value obtained above, and fairly larger than those of some α-amino acids, for instance, glycine (7.1 kJ mol^{-1}) and α-alanine (7.7 kJ mol^{-1}).[13] This means that NDA is less reactive with the copper(II) ion than these amino acids. This result may reflect primarily the differences in the basicities of the nitrogen donors in these amino acids, and secondarily the differences in the structures of the chelate-rings of the 1:1-complexes.

Adsorbed Amount of the 1:1-Complex. In order to correlate the composition of the solution interior with that of the surface phase, the Gibbs adsorption isotherm was applied. The Gibbs adsorption isotherm is written generally[14] at a constant temperature and pressure as follows:

$$-\mathrm{d}\gamma/RT = \sum_i \Gamma_i\,\mathrm{d}(\ln a_i), \tag{9}$$

where γ denotes the surface tension, and Γ_i and a_i, the surface excess and the activity of the i-th species of solutes in the solution interior respectively. Here, since the formulation is limited to the concentration region below the P point in Fig. 1, the adsorbed species of solutes are assumed to be L$^\pm$, ML$^+$, and Cl$^-$; these species are related by Eq. 1, and the activity of each species can be replaced by the concentration for the reason described above. Thus, Eq. 9 can be rewritten as:

$$-\mathrm{d}\gamma/RT = \Gamma_\mathrm{L}\,\mathrm{d}(\ln C_\mathrm{L}) + \Gamma_\mathrm{ML}\,\mathrm{d}(\ln C_\mathrm{ML}) + \Gamma_\mathrm{Cl}\,\mathrm{d}(\ln C_\mathrm{Cl}), \tag{10}$$

where the subscript Cl denotes Cl$^-$.

The following relations are introduced to the total quantity (superscripts) of surface-active species in the surface phase and to the conditions of electrical neutrality in the surface and bulk phases:

$$\Gamma^\mathrm{L} = \Gamma_\mathrm{L} + \Gamma_\mathrm{ML} \tag{11}$$

$$\Gamma_\mathrm{ML} = \Gamma_\mathrm{Cl} \tag{12}$$

$$C^\mathrm{M} = (1/2)C_\mathrm{Cl}. \tag{13}$$

Under the condition of equimolar mixing, from Eqs. 6 and 7, and neglecting the third terms of R.H.S. for the reason described above, we obtain:

$$C^\mathrm{M} = C^\mathrm{L} = C \tag{14}$$

$$C_\mathrm{M} = C_\mathrm{L} = C_\mathrm{S}, \tag{15}$$

where C denotes the total concentrations of the respective solutes in the mixture (corresponding to the abscissa in Figs. 1 and 2) and where C_S denotes the single-ion concentrations of copper(II) and NDA. From Eqs. 10 and 12—15, we obtain:

$$-(\mathrm{d}\gamma/RT)_{1:1} = \Gamma_\mathrm{L}\,\mathrm{d}(\ln C_\mathrm{S}) + \Gamma_\mathrm{ML}\,\mathrm{d}(\ln C_\mathrm{ML}) + \Gamma_\mathrm{ML}\,\mathrm{d}(\ln C), \tag{16}$$

where the subscript 1:1 indicates the value for the equimolar mixed solution of NDA–CuCl$_2$. Since, under the present experimental conditions, the solution pH actually remains constant, as has been described previously and as shown in the case of Fig. 4, we obtain from Eq. 3′:

$$\mathrm{d}(\ln C_\mathrm{ML}) = 2\,\mathrm{d}(\ln C_\mathrm{S}). \tag{17}$$

By substituting Eqs. 11 and 17 into Eq. 16 we obtain:

$$-(\mathrm{d}\gamma/RT)_{1:1} = (\Gamma^\mathrm{L} + \Gamma_\mathrm{ML})\,\mathrm{d}(\ln C_\mathrm{S}) + \Gamma_\mathrm{ML}\,\mathrm{d}(\ln C). \tag{18}$$

By differentiating Eq. 18 with respect to ($\ln C$), we obtain:

$$\begin{aligned} -(1/RT)[\partial\gamma/\partial(\ln C)]_{1:1} &\equiv I_{1:1} \\ &= (\Gamma^\mathrm{L} + \Gamma_\mathrm{ML})[\partial(\ln C_\mathrm{S})/\partial(\ln C)]_{1:1} + \Gamma_\mathrm{ML}, \end{aligned} \tag{19}$$

Moreover, from Eq. 3′ we obtain:

$$[\partial(\ln C_\mathrm{S})/\partial(\ln C)]_{1:1} \equiv r = (q + q^{1/2})/2q, \tag{20}$$

where $q = [1 + 4K_1(C/C_\mathrm{H})]$.
By substituting Eq. 20 into Eq. 19, we obtain:

$$\Gamma_\mathrm{ML} = (I_{1:1} - r\Gamma^\mathrm{L})/(r+1). \tag{21}$$

Thus, we may calculate the adsorbed amount of the 1:1-complex ion (ML$^+$) from Eq. 21 by using the K_1 and Γ^L values determined by the potentiometry and radiometry respectively, and also the $I_{1:1}$ value given as the inclination of the surface tension vs. the equimolar concentration curve in Fig. 1. The amount of copper(II) in the adsorbed phase, estimated as ML$^+$, is shown with a dashed line in Fig. 2. While the molar ratio of ML$^+$ to the total NDA in the adsorbed phase, $\Gamma_\mathrm{ML}/\Gamma^\mathrm{L}$, is about 0.16 in the higher concentration region in Fig. 2, that in the solution interior, $C_\mathrm{ML}/C^\mathrm{L}$, as calculated using the K_1 value, is about 1.3×10^{-3} in the same concentration region. Consequently, it turns out that the surface activity of ML$^+$ is fairly larger than that of NDA alone.

Surface Activity of the 1:1-Complex. The surface activity of the 1:1-complex ion in this co-adsorption system was compared to that of NDA in terms of the relative adsorbability (α), which was defined as follows:[6]

Table 1. Relative Adsorbability of 1:1-Complexes and SDS to NDA

Adsorbate	$\lim_{C\to 0}(\Gamma/C)/\mathrm{m}$	α
NDA	3.1×10^{-4}	1
SDS	4.1×10^{-5}	0.13
NDA-SDS	1.0×10^{-2}	33[6]
NDA-Cu	3.7×10^{-2}	150

$$\alpha = \lim_{C \to 0} (\Gamma_{ML}/C_{ML})/(\Gamma_L/C_L). \tag{22}$$

The results are shown in Table 1, together with the values of the 1:1-complex ion formed between NDA and sodium dodecylsulfate (SDS).[6] It is worthy of notice that the surface activity of the 1:1-complex ion of copper(II) and NDA is larger than that of NDA by a factor of 1.5×10^2 and larger than that of the 1:1-complex of NDA and SDS by a factor of 3.6.

1:2-Complex Formation. In order to elucidate the effect of the precipitation on the surface tension of the solutions above the P point in Fig. 1, analyses of the precipitate were carried out. The precipitate which was generated in the equimolar mixed solution at 8.0×10^{-4} mol dm^{-3} was collected on a membrane filter (pore size, 3 μm) and dried in a desiccator for a week. The precipitate consisted of bluish and flaky microcrystals, and it was so hydrophobic as to repel its mother solution. The results of the elemental analyses of the precipitate are shown in Table 2.

In Table 3 the IR spectra of pure NDA and the precipitate obtained by the KBr disk method are compared. The precipitate lacks the absorption bands at 1650 cm^{-1} and 2330 cm^{-1} due to $=NH_2^+$. The absorption bands at 860 cm^{-1} due to $-(CH_2)_2-$ in the polar group of NDA, and also the absorption bands at 1400 cm^{-1} and 1570 cm^{-1} due to $-COO^-$ shift to higher frequencies. These results confirm that the precipitate is the hydrated 1:2-complex, $[Cu(NDA)_2]\cdot 2H_2O$, with a ring structure formed between the hydrophilic group of NDA and the copper(II) ion.

Further, in order to obtain information on the crystal structure of the 1:2-complex, the X-ray (Cu $K\alpha$ 0.154 nm) diffraction pattern was measured for the powdery precipitate. The main peaks, at the angles of 2θ=3.93° (1.00), 7.86° (0.24), 11.82° (0.16), and 15.44° (0.05), can all be assigned to a lattice space of 2.24 nm on the basis of the Bragg condition; here, the figures in parentheses indicate the relative intensity of each peak. This long lattice spacing may correspond to the distance between copper(II) ions aligned in a adjacent layers of the 1:2-complex with a multilayer structure. Since the total length of the single ML_2 molecule with the trans-form on a plane is about 3.35 nm, as estimated from the STS molecular model, the packing of ML_2 molecules in the crystal state represented schematically in Fig. 6 may explain the X-ray data. The crystallographic structure will be described more precisely elsewhere.

Solubility Product of the 1:2-Complex. The solubility product (K_{SP}) of the 1:2-complex described above is defined from Eqs. 3 and 4 as follows:

$$K_{SP} = a_M a_L^2 / a_H^2, \tag{23}$$

As the observed values of a_M and a_H, and the calculated value of a_L from Eq. 3 have been given at the P point in Fig. 1, the value of K_{SP} is calculated to be 3.9×10^{-2} mol dm^{-3}. Figure 7 shows the activities of copper(II) and hydrogen ions in $CuCl_2$ solutions with and without equimolar NDA, whose concentration region corresponds to that below the M point in Fig. 1. When we put the data of a_M and a_H in Fig. 7 into Eq. 23, it turns out that the calculated values of a_L still increased until the M point. Consequently, the a_L value calculated at a given surface tension (e.g., X point) between P and M points in Fig. 1 nearly coincides with the C value obtained by the extrapolation of the γ vs. log C curve smoothly over the P point to the given surface tension (X′ point). The extrapolated curve is shown by a dashed line in Fig. 1. Thus, this finding explains why the surface tension lowers continuously above the P point, even after forming the precipitate of the 1:2-complex, until the

Table 2. Elemental Analyses of Precipitate

	Found (%)	Calcd (%)[a)]
C	57.8	58.7
H	11.4	11.1
N	4.50	4.56
Cu	10.3	10.3
Cl	—	—
Molar ratio of N/Cu	1.98	2.00

a) For $Cu(NDA)_2\cdot 2H_2O$.

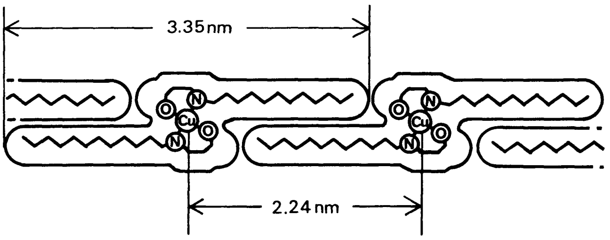

Fig. 6. A model for the molecular arrangement of the 1:2-complex in the precipitate.

Table 3. IR Spectra of the 1:2-Complex

Group	NDA (cm^{-1})	$Cu(NDA)_2\cdot 2H_2O$ (cm^{-1})	Assignment
$-(CH_2)_2-$[a)]	860	890	gauche
$-COO^-$	1410	1430	sym. str.
	1560	1580	asym. str.
$-NH_2^+$	1650	—	asym. deg. def.
	2330	—	asym. deg. def. +twisting

a) In the ammonio-propionate group.

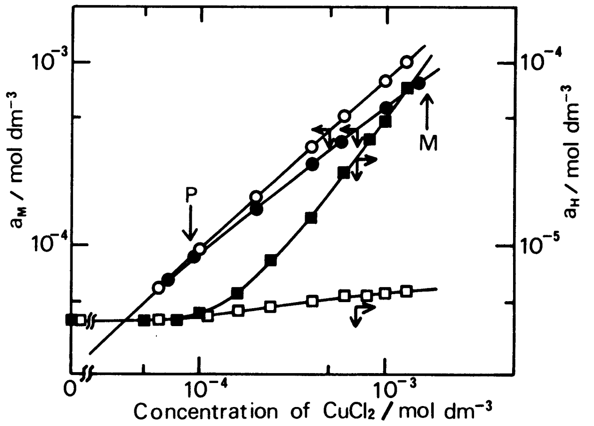

Fig. 7. Activities of copper(II) ion (a_M) and hydrogen ion (a_H) vs. the concentration of $CuCl_2$ with and without of equimolar amount of NDA: Copper(II) ion; (●) with and (○) without NDA. Hydrogen ion; (■) with and (□) without NDA.

micelle is formed at the M point.

Though, the 1:2-complex can be expected to be essentially highly surface-active, the complex has been considered in the present study as if it were surface-inactive. This was because the complex is not soluble at all as a result of its large hydrophobic moiety, as is shown in Fig. 6. However, it is conceivable that apparently the same composition may be observed at the co-adsorbing surface or in the mixed micelle formed with NDA and the 1:1-complex. The discrimination of such an ambiguous effect should be made in mixed solutions of the copper(II) ion and the short-chain compounds of *N*-alkyl-*β*-alanine, where the 1:2-complex may become soluble as one of the surface-active species. The study performed for this purpose will be presented elsewhere.

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12) These values could be determined for *β*-alanine using Eq. 5 by means of a procedure similar to that described in the text, since the values of a_M and a_H could be measured in a sufficiently high concentration region without precipitation.

13) The K_1 values used in the calculation of $\Delta G°$ for these amino acids were obtained according to this relation: $K_1 = K_1^* K_A$, where K_1^* denotes the formation constant of the 1:1-complex between the copper(II) ion and anionic amino acid ($M^{2+} + L^- \rightleftarrows ML^+$) and where K_A denotes the second dissociation constant of amino acid ($L^\pm \rightleftarrows L^- + H^+$). The K_1^* and K_A values are cited from: A. É. Martell and R. M. Smith, "Critical Stability Constants," Plenum Press, New York (1974), Vol. 1.

14) E. A. Guggenheim, "Thermodynamics," North Holland Publishing Co., Amsterdam (1957), p. 50.