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Studies of Polymeric Flocculants. IX.[1] The Formation of Poly(methacrylohydrazide)-Copper(II) Complexes

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Formation constants for the complexes of poly(methacrylohydrazide) (PMH) with the copper(II) ion were measured by using a modification of Bjerrum's method proposed by Gregor and his coworkers. The pK_{a1} and pK_{a2} values of PMH determined in an aqueous solution with an ionic strength of 0.1 (KNO_3) at 25 °C were 3.20 and 10.61 respectively. Therefore, when the PMH–copper(II) complexes were formed above pH 7, the average number of ligands combined with one metal ion could be calculated approximately without using the first acid dissociation constant. The pK_{a2} value decreased with an increase in the ionic strength and temperature. The formation curves of the complexes showed that one copper(II) ion formed a coordination compound with six hydrazide groups in a high pH region (about pH 9). The formation constants increased with an increase in T_{Cu}/T_{HL} (the ratio of the total concentration of the copper(II) ion to the total concentration of the ligand) in the range higher than 0.1. The formation constants were unaffected by the degree of polymerization of PMH in the range from 64.1 to 5470, but the formation constants were affected by the kind of anion in copper(II) salts and neutral salts added and they increased in the order of $NO_3^- < SO_4^{2-} < Cl^-$. The thermodynamic parameters for the above reaction were determined by Ringbom's method.

The formation constants for polyelectrolytes–copper(II) complexes have been studied by many investigators.[2–7] However, the formation constants for poly(methacrylohydrazide)–metal(II) complexes had not been studied. In our preceding papers[1,8] we reported that poly(methacrylohydrazide) (PMH) could easily form water-insoluble complexes with heavy metals, especially with mercury(II), over a wide pH region and that mercury(II) could be removed from the solutions containing mercury(II) only or together with other metals. We also reported the formation constants for the complexes of PMH with bivalent transition metal ions and the average number of ligand combined with each metal ion, obtained by using a modification of Bjerrum's method. The formation curves for PMH–copper(II) complexes showed that one copper(II) ion formed a coordination compound with six hydrazide groups in a high pH region. In the present paper, in order to study in detail the formation of PMH–copper(II) complexes, the effect of T_{Cu}/T_{HL} ratio, the degree of polymerization of PMH, and the kind of anion in copper(II) salts and neutral salts added on the formation constants were investigated in an aqueous solution with an ionic strength of 0.1 at 25 °C. The changes in entropy, enthalpy, and free energy for the above reaction were also determined by Ringbom's method.

Experimental

Poly(methyl methacrylate) was prepared by solution polymerization initiated by benzoyl peroxide or α,α'-azobisisobutyronitrile in carbon tetrachloride, 1-dodecanol, and 1-dodecanethiol. Poly(methyl methacrylate) was purified by the conventional method, using acetone and methanol as solvent and precipitant respectively. The number average molecular weight of polymers was calculated by means of the following equation: $[\eta]=K\, M_n^a$.[9] The intrinsic viscosity was measured in benzene at 30 °C.

PMH was prepared by the hydrazinolysis of poly(methyl methacrylate) (1 g) with hydrazine hydrate (20 ml) at 175 °C for 7 h. The reaction mixture was poured into an excess of methanol in order to precipitate PMH. The PMH was purified by Soxhlet extraction with methanol for 80—100 h. The conversion was calculated on the basis of the nitrogen content of the PMH, itself determined by elemental analysis. Isobutyrohydrazide was selected as a monomeric model of PMH. Isobutyrohydrazide was prepared by treating ethyl isobutylate with anhydrous hydrazine at 90 °C for 6 h. It was purified by recrystallization from benzene. Found: C, 47.43; H, 9.63; N, 26.71%. Calcd for $C_4H_{10}N_2O$: C, 47.06; H, 9.80; N, 27.45%. All the other reagents were of a special reagent grade, and they were used without further purification.

Potentiometric Titration. In spite of the good solubility of PMH in water, the PMH–copper(II) complexes were apparently insoluble in water. Gregor *et al.*[2,3] showed that the binding phenomena are essentially the same whether the polymeric chelates precipitate or not, if the system is in equilibrium. Therefore, potentiometric titration was carried out by a batch method. The procedure was as follows: 5 ml of a 1 g/l PMH solution, 25 ml of a 0.2 mol/l neutral salt solution, and the desired amounts of a 0.005 mol/l potassium hydroxide solution were added into 100 ml stoppered flasks. Water was finally added to each flask until the total volume amounted to 50 ml. After nitrogen had been fully introduced into each flask in order to remove the CO_2, each flask was shaken by means of an incubator at 25 °C for 24 h. After shaking, the pH values of the solutions were measured by means of a Hitachi-Horiba F-7 pH meter at 25 °C under a nitrogen atmosphere. In the case of the complex formation from PMH and the copper(II) ion, a solution of copper(II) nitrate was added to each solution containing PMH and potassium nitrate. Then, the procedure described above was carried out.

Results and Discussion

PMH. The results of the synthesis of PMH are shown in Table 1. When Kern *et al.*[10] reported the synthesis and structure of poly(acrylohydrazide), they considered that each hydrazide group in the polymers contained 2/3 H_2O, even after the polymers had been dried *in vacuo*. It was found by thermo-balance analysis that PMH also contained about 1/3 H_2O per hydrazide group. It was recognized from the IR spectra (C=O, 1720 cm^{-1}) of the polymers obtained that the hydrazino-

TABLE 1. POLY(METHACRYLOHYDRAZIDE)

PMH	$\bar{P}_n$		Elemental analyses				H_2O Content		Conv.
			C(%)	H(%)	N(%)	O(%)	(wt %)	($x \cdot H_2O$)	(%)
PMH-1	5470	Found	47.3	7.5	24.2	21.0	6.3	1/3	91.2
		Calcd	46.5	8.2	24.2	21.1			
PMH-2	991	Found	48.5	8.0	22.4	21.1	5.5	1/3	84.1
		Calcd	47.5	8.2	22.4	21.9			
PMH-3	456	Found	46.6	8.0	22.4	23.0	6.9	1/3	84.1
		Calcd	47.5	8.2	22.4	21.9			
PMH-4	64.1	Found	46.9	8.1	22.0	23.0	6.5	1/3	82.5
		Calcd	47.7	8.1	22.0	22.2			

lysis of poly(methyl methacrylate) did not proceed completely under the present conditions. The calculated values of the elements in PMH shown in Table 1 were determined on the basis of the conversion and water content of PMH.

Acid Dissociation Constants of PMH. Albert *et al.*[11] and Nagano *et al.*[12] reported in detail the acid dissociation constants of hydrazide compound, they reported that the hydrazide compounds had two acid dissociation constants, *i.e.*, K_{a_1} in a low pH region and K_{a_2} in a high pH region. When the acid dissociation constants of PMH were measured in an aqueous solution with an ionic strength of 0.1(KNO_3) at 25 °C, the pK_{a_1} and pK_{a_2} values became 3.20 and 10.61 respectively.

It was proposed by Bjerrum that the average number of ligands combined with one metal ion can be calculated by means of Eq. 1, when the compounds with two acid dissociation constants such as hydrazide compounds form complexes with metal ions:

$$\bar{n} = \frac{[A_t] - ([H^+]^2/K_{a_1}K_{a_2} + [H^+]/K_{a_2} + 1)[A^-]}{[M_t]}, \qquad (1)$$

where $[A^-]$, which represents the concentration of the free hydrazide groups in the polymers not combined with metal ions, can be calculated using the following equation:

$$[A^-] = \frac{(2-\alpha)[A_t] - [H^+] + [OH^-]}{2[H^+]^2/K_{a_1}K_{a_2} + [H^+]/K_{a_2}}. \qquad (2)$$

$[A_t]$ is the total concentration of hydrazide groups in the polymers added, $[M_t]$ is the total concentration of the metal ions added, and K_{a_1} and K_{a_2} are the first and second acid dissociation constants respectively. α is the degree of neutralization. When the acid dissociation constants of isobutyrohydrazide were measured in an aqueous solution with an ionic strength of 0.1(KNO_3) at 25 °C, the pK_{a_1} and pK_{a_2} values became 3.27 and 10.74 respectively. It was found that the hydrogen ion due to the formation of complexes were released above pH 6.3. Therefore, in a higher pH region than 6.3, Eq. 1 can be approximated by

$$\bar{n} = \frac{[A_t] - ([H^+]/K_{a_2} + 1)[A^-]}{[M_t]}, \qquad (3)$$

where

$$[A^-] = \frac{(1-\alpha)[A_t] - [H^+] + [OH^-]}{[H^+]/K_{a_2}}. \qquad (4)$$

Thus, it is considered that the average number of ligands combined with one metal ion can be calculated by means of Eq. 3 without using pK_{a_1}. Consequently, the second acid dissociation constant, pK_{a_2}, of PMH was determined in detail.

Katchalsky and many other investigators have studied the potentiometric titration of polyelectrolytes,[13–15] they have shown that the experimental results for titra-

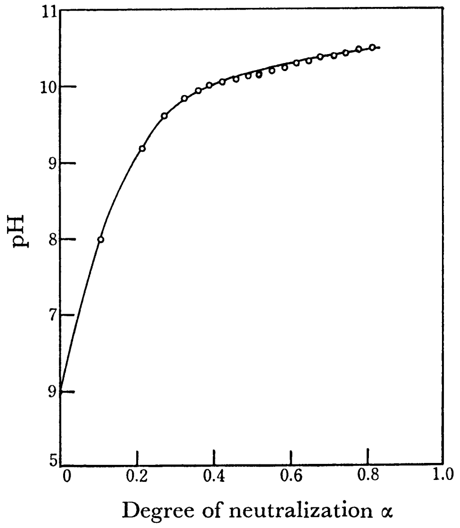


Fig. 1. The pH titration curve of PMH.
PMH ($\bar{P}_n$=5470): 8.64×10^{-4} unit mol/l, 25 °C, μ=0.10(KNO_3).

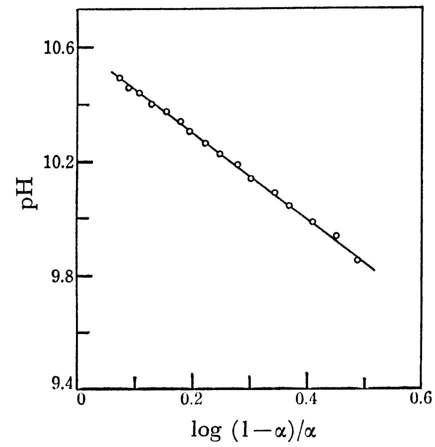


Fig. 2. Henderson-Hassebalch plots of PMH.
PMH ($\bar{P}_n$=5470): 8.64×10^{-4} unit mol/l, 25 °C, μ=0.10(KNO_3).

Table 2. pK_{a_2} and n (25 °C, $\mu=0.10$)

Polymer	Neutral salt	pK_{a_2}	n
Poly(methacrylohydrazide)	KNO_3	10.61	1.54
	K_2SO_4	10.58	1.48
	KCl	10.45	1.08

tion can be expressed by a modification of the Henderson-Hasselbach equation, $pH=pK_{a_2}-n\log(1-\alpha)$, where n is a constant. The pH titration curve of PMH with KOH in the solution with an ionic strength of $0.1(KNO_3)$ is shown in Fig. 1, while the Henderson-Hasselbach plots are shown in Fig. 2. The plots of pH *vs.* $\log(1-\alpha)/\alpha$ are linear in the range of the degree of neutralization from 0.3 to 0.8. The pK_{a_2} and n values of PMH were determined in solutions containing different neutral salts at 25 °C; the results are shown in Table 2. In a KCl aqueous solution, the pK_{a_2} and n values determined were smaller than those in the solutions of other neutral salts. Similar phenomena have been observed by Gregor *et al.*[2] for poly(acrylic acid). These pK_{a_2} values show that PMH behaves as a very weak acid, similarly to poly(vinyl alcohol),[4] poly(propenehydraxamic acid),[5] and poly(acrylaldehyde oxime)[6] under the present conditions. Machida *et al.*[16] reported that poly(acrylohydrazide) (conversion *ca.* 50%), which had been prepared by the hydrazinolysis of polyacrylamide with hydrazine hydrate, had a pK_{a_2} value of 10.64 and an n value of 1.36 at the ionic strength of 0.01(KCl) at 25 °C.

Table 3. Effect of the degree of polymerization of poly(methacrylohydrazide) on pK_{a_2} and n

Polymer	$\bar{P}_n$	pK_{a_2}	n
PMH-1	5470	10.61	1.54
PMH-2	991	10.64	1.55
PMH-3	456	10.60	1.53
PMH-4	64.1	10.61	1.49

Polymer concentration: *ca.* 8×10^{-4} unit mol/l, 25 °C, $\mu=0.1(KNO_3)$.

The pK_{a_2} and n values of PMH with different degrees of polymerization were determined at the ionic strength of $0.1(KNO_3)$; the results are shown in Table 3. Those results show that the degree of polymerization of PMH, ranging from 64.1 to 5470, did not affect the pK_{a_2} and n values.

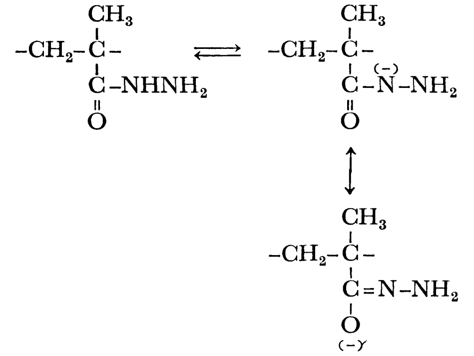
The pK_{a_2} and n values of PMH were determined at different temperatures (20—35 °C) and at different ionic strengths (0.01—0.1). The results are shown in Table 4. At the same temperature, the pK_{a_2} values decreased with an increase in the ionic strength, and at the same ionic strength, the pK_{a_2} values decreased with an increase in the temperature. These results suggest that the hydrazide groups of PMH in an aqueous solution are liable to dissociate with increases in the temperature and ionic strength. The n values were unaffected by either the temperature or the ionic strength under the present conditions. The plots of pK_{a_2} *vs.* $\sqrt[3]{\mu}$ at each temperature gave straight lines.[1] The thermodynamic acid dissociation constants, which were determined by an extrapolation of the linear pK_{a_2} *vs.* $\sqrt[3]{\mu}$ plots to the intercept, are shown in Table 5.

Table 5. pK°_{a2} of poly(methacrylohydrazide)

Temp (°C)	20	25	30	35
pK°_{a2}	10.90	10.76	10.62	10.46

Polymer ($\bar{P}_n=5470$): 8.64×10^{-4} unit mol/l.

Calculation of the Formation Constants. The formation constants for PMH-metal(II) complexes were calculated by a modification of Bjerrum's method proposed by Gregor *et al.*[2] It is considered that the hydrazide groups of PMH dissociate as follows in a pH region higher than pH 7:



$$\begin{array}{c} CH_3 \\ | \\ -CH_2-C- \\ | \\ C-NHNH_2 \\ \| \\ O \end{array} \rightleftarrows \begin{array}{c} CH_3 \\ | \\ -CH_2-C- \\ | \\ C-\overset{(-)}{N}-NH_2 \\ \| \\ O \end{array} \updownarrow \begin{array}{c} CH_3 \\ | \\ -CH_2-C- \\ | \\ C=N-NH_2 \\ | \\ O^{(-)} \end{array} \qquad (5)$$

If the hydrazide groups of PMH are represented by HA, the above equilibrium can be represented by the following simplified equation:

$$HA \rightleftarrows A^- + H^+ \qquad (6)$$

and the second acid dissociation constant, K_{a_2} can be represented by the following equation:

$$K_{a_2} = \frac{[A^-][H^+]}{[HA]}. \qquad (7)$$

Table 4. Effect of temperature and ionic strength on pK_{a2} and n

Ionic strength	20 °C		25 °C		30 °C		35 °C	
	pK_{a2}	n	pK_{a2}	n	pK_{a2}	n	pK_{a2}	n
0.01	10.83	1.49	10.69	1.56	10.55	1.51	10.39	1.48
0.02	10.80	1.51	10.67	1.53	10.52	1.51	10.36	1.50
0.05	10.77	1.51	10.63	1.52	10.48	1.48	10.33	1.50
0.10	10.74	1.48	10.61	1.54	10.46	1.51	10.30	1.50

Poly(methacrylohydrazide): $\bar{P}_n=5470$, 8.64×10^{-4} unit mol/l.
Neutral salt: KNO_3.

In the case under discussion, the formation of the complexes can be represented by the following equation:

$$\mathrm{HA} + \mathrm{MA}_{j-1} \rightleftarrows \mathrm{MA}_j + \mathrm{H}^+. \qquad (8)$$

The equilibrium constants, b_j, pertaining to the above equation are represented as:

$$b_j = \frac{[\mathrm{MA}_j][\mathrm{H}^+]}{[\mathrm{MA}_{j-1}][\mathrm{HA}]}, \qquad (9)$$

$$b_j = K_{a_2} k_j, \qquad (10)$$

where K_{a_2} is the second acid dissociation constant of PMH and k_j is the successive formation constant of the complexes. By simple manipulations, Bjerrum formation function can be expressed in terms of the b_j's:

$$\bar{n} = \frac{\sum_{i=1}^{N} iB_i\left(\frac{[\mathrm{HA}]}{[\mathrm{H}^+]}\right)^i}{1+\sum_{i=1}^{N} B_i\left(\frac{[\mathrm{HA}]}{[\mathrm{H}^+]}\right)^i}, \qquad (11)$$

$$B_i = \prod_{i=1}^{i} B_j. \qquad (12)$$

The average number of ligands combined with one copper(II) ion, $\bar{n}$, is given by its definition as:

$$\bar{n} = \frac{[\mathrm{A_t}] - [\mathrm{HA}] - [\mathrm{A}^-]}{[\mathrm{M_t}]}. \qquad (13)$$

The only unknown $[\mathrm{A}^-]$ was calculated from the following equation, Eq. 14, by an iterative procedure for the PMH–copper(II) complexes:

$$K_{a_2} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}\left(\frac{[\mathrm{A}^-]}{[\mathrm{A_t}]-[\mathrm{A}^-]}\right)^{n-1} \qquad (14)$$

where n is the value calculated from the modified Henderson-Hasselbach plots.

From the conservation equations and electroneutrality relation [HA], the concentration of undissociated PMH is found to be:

$$[\mathrm{HA}] = [\mathrm{A_t}](1-\alpha) + [\mathrm{OH}^-] - [\mathrm{H}^+] \qquad (15)$$

where α is the degree of neutralization. $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$ are calculated from the measured pH values and the ionization constant of water, with a correction for the activity coefficients.[17)]

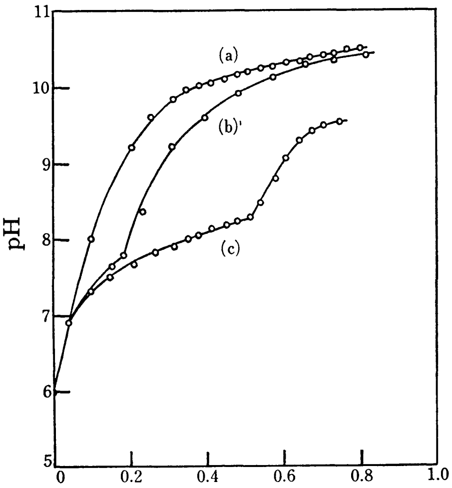


Fig. 3. The pH titration curves.
(a): PMH($\bar{P}_n$=5470) 8.64×10^{-4} unit mol/l, (b): $\mathrm{Cu(NO_3)_2}$ 8.00×10^{-5} mol/l, (c): (a)+(b). 25 °C, μ=0.10($\mathrm{KNO_3}$).

Chelate Formation. Figure 3 shows the titration curves for PMH in the absence and in the presence of copper(II) ions at the ionic strength of 0.1($\mathrm{KNO_3}$) at 25 °C. PMH–copper(II) complexes precipitated throughout the pH range below about pH 8.5. Above pH 8.5, it was found that the precipitates redissolved into the solution. This shows that the precipitates were not copper(II) hydroxides. It is not always obvious why the precipitates became soluble in water above about pH 8.5. However, it is probably the result of the reversal of the charge of the complexes. From Fig. 3, it may be seen that the release of hydrogen ions caused by the formation of PMH–copper(II) complexes began at about pH 7 and continued up to pH 9, and that the six hydrogen ions per copper(II) ion were released.

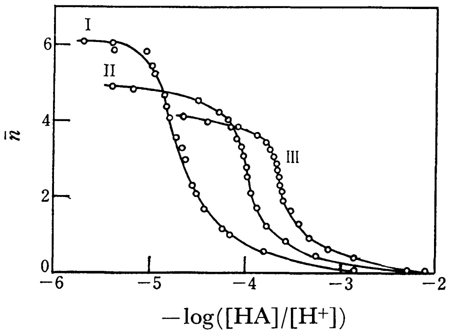


Fig. 4. Effect of $T_{\mathrm{Cu}}/T_{\mathrm{HL}}$ on modified Bjerrum plots.
PMH($\bar{P}_n$=5470): 8.28×10^{-4} unit mol/l, 25 °C, μ=0.10($\mathrm{KNO_3}$).
$T_{\mathrm{Cu}}/T_{\mathrm{HL}}$; I: 0.024—0.097, II: 0.145, III: 0.193.

The Effect of the $T_{\mathrm{Cu}}/T_{\mathrm{HL}}$ Ratio on the Modified Bjerrum Plots. The formation of PMH–copper(II) complexes was investigated in the range of the $T_{\mathrm{Cu}}/T_{\mathrm{HL}}$ values from 0.024 to 0.193. The modified formation curves are shown in Fig. 4. From Fig. 4, it may be seen that the modified Bjerrum plots obtained in the range from 0.024 to 0.097 of the $T_{\mathrm{Cu}}/T_{\mathrm{HL}}$ values fell on nearly the same curve. The plots show a definite tendency to flatten out toward a value of $\bar{n}=6$ as $-\log([\mathrm{HA}]/[\mathrm{H}^+])$ becomes more negative. This result suggests that one copper(II) ion forms a coordination compound with six hydrazide groups. However, when the $T_{\mathrm{Cu}}/T_{\mathrm{HL}}$ values increased above 0.145, the modified formation curves moved to a less negative value of $-\log([\mathrm{HA}]/[\mathrm{H}^+])$. It was also found that $\bar{n}$ decreased from 6 to 4 with an increase in the $T_{\mathrm{Cu}}/T_{\mathrm{HL}}$ values. In a previous paper,[1)] we also reported that a copper(II) ion formed a coordination compound with six hydrazide groups of isobutyrohydrazide when the formation of isobutyrohydrazide–copper(II) complexes was investigated in the $T_{\mathrm{Cu}}/T_{\mathrm{HL}}$ value of 0.1. Figure 5 shows the relationship between the successive formation constants and $\log(T_{\mathrm{Cu}}/T_{\mathrm{HL}})$. The successive formation constants had nearly the same values in the region below $\log(T_{\mathrm{Cu}}/T_{\mathrm{HL}})$ value of −1, but they increased remarkably in the region above $\log(T_{\mathrm{Cu}}/T_{\mathrm{HL}})$ value of −1. This suggests that the formation of PMH–copper(II) complexes is favored when the $T_{\mathrm{Cu}}/T_{\mathrm{HL}}$ values become larger than 0.1.

The Effect of the Degree of Polymerization on the Modified Bjerrum Plots. The formation of PMH–copper(II)

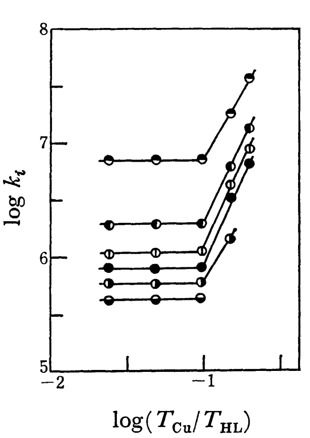


Fig. 5. Relation between formation constants and log(T_{Cu}/T_{HL}). PMH($\bar{P}_n$=5470): 8.28×10^{-4} unit mol/l, 25 °C, μ=0.10(KNO$_3$).
◓: log k_1, ◐: lo k_2, ⦶: log k_3, ●: log k_4, ◑: log k_5, ◒: log k_6.

complexes was investigated for PMH with different degrees of polymerization. The modified Bjerrum plots all fell on nearly the same curve irrespective of the degree of polymerization of PMH. That is, the formation constants for PMH–copper(II) complexes were unaffected by the degrees of polymerization ranging from 64.1 to 5470.

The Effect of the Kind of Anion on the Modified Bjerrum Plots. The formation of PMH–copper(II) complexes was investigated in a solution with the ionic strength of 0.1 by varying the anion (NO_3^-, Cl^-, SO_4^{2-}) in the copper(II) salts and neutral salts added. The modified Bjerrum plots are shown in Fig. 6, while the formation constants are listed in Table 6. It may be seen that the formation constants increased in this order: $NO_3^- < SO_4^{2-} < Cl^-$. As is already known, a complexation reaction in an aqueous solution is a replacement reaction between the ligands in the polymers and aqua-complexes of metals. Therefore, it is considered that the change in the structure of aqua-complexes of metals caused by counter anions and surrounding anions in the solution affected the formation constants. Hojo *et al.*[4] reported analogous phenomena for poly(vinyl alcohol)–copper(II) complexes, but they reported that the formation constants increased in the order of: $SO_4^{2-} < Cl^- < NO_3^-$. The difference in the order of formation constants between poly(vinyl alcohol)–copper(II) complexes and PMH–copper(II) complexes can not be explained at present.

Table 6 also lists the formation constants for isobutyrohydrazide determined in a solution with the ionic strength of 0.1(KNO$_3$); the data for isobutyrohydrazide were determined in a manner exactly analogous to that used for PMH described above. The data show that the isobutyrohydrazide–copper(II) complexes were more stable than PMH–copper(II) complexes. Such phenomena as that a monomeric analogue forms more stable complexes than its polymer have been observed for poly(acrylaldehyde oxime)[6] or poly(4-pentene-2,3-dione dioxime).[18]

Entropy and Enthalpy for Complexation for PMH–Copper(II). Entropy and enthalpy changes for the complexation reaction between PMH and copper(II) ions were studied by using Ringbom's method.[19] The formation of PMH–copper(II) complexes was inves-

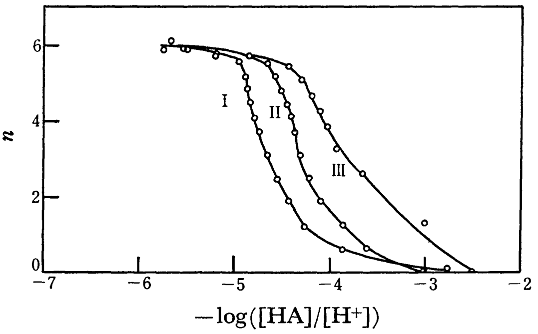


Fig. 6. Effect of the kind of anion on modified Bjerrum plots.
PMH($\bar{P}_n$=5470: 8.28×10^{-4} unit mol/l, Cu(NO$_3$)$_2$, CuSO$_4$, CuCl$_2$: 8.00×10^{-5} mol/l.
Anion; I: NO_3^-, II: SO_4^{2-}, III: Cl^-.

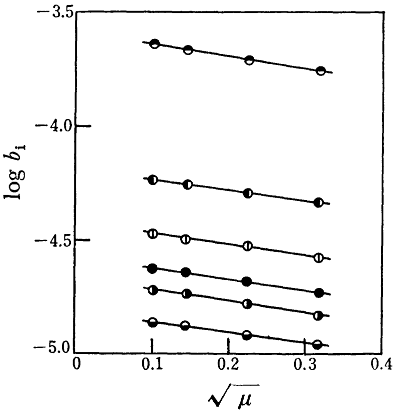


Fig. 7. Relation between log b_i and $\sqrt{\mu}$.
PMH($\bar{P}_n$=5470): 8.64×10^{-4} unit mol/l, Cu(NO$_3$)$_2$: 8.00×10^{-5} mol/l, 25 °C.
◓: log b_1, ◐: log b_2, ⦶: log b_3, ●: log b_4, ◑: log b_5, ◒: log b_6.

Table 6. Effect of the kind of anion on the formation constants

Ligand	Anion	log k_1	log k_2	log k_3	log k_4	log k_5	log k_6	log K
PMH[a]	NO_3^-	6.84	6.26	6.04	5.89	5.79	5.67	36.49
	SO_4^{2-}	7.10	6.61	6.38	6.25	6.15	5.71	38.20
	Cl^-	7.73	7.30	6.86	6.52	6.29	5.84	40.54
IBH[b]	NO_3^-	8.52	8.24	8.10	8.04	7.89	7.04	47.83

a) Poly(methacrylohydrazide). b) Isobutyrohydrazide. PMH($\bar{P}_n$=5470): 8.28×10^{-4} unit mol/l, Cu(NO$_3$)$_2$, CuSO$_4$, CuCl$_2$: 8.00×10^{-5} mol/l, IBH: 1×10^{-3} mol/l, Cu(NO$_3$)$_2$: 1×10^{-4} mol/l, 25 °C, μ=0.10.

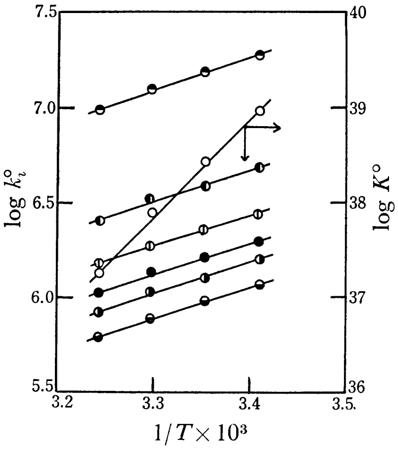


Fig. 8. Formation constants *vs.* $1/T$ plots PMH($\bar{P}_n$=5470): 8.64×10^{-4} unit mol/l, $Cu(NO_3)_2$: 8.00×10^{-5} mol/l. ◓: $\log k_1^\circ$, ◐: $\log k_2^\circ$, ⦶: $\log k_3^\circ$, ●: $\log k_4^\circ$, ◑: $\log k_5^\circ$, ◒: $\log k_6^\circ$, ○: $\log K^\circ$.

tigated at an ionic strength of 0.01—0.1 and a temperature of 20—35 °C. The relationship between the equilibrium constants, b_j, determined from the modified Bjerrum plots and $\sqrt{\mu}$ are shown in Fig. 7. It is found that the plots of $\log b_j$ *vs.* $\sqrt{\mu}$ are linear in the range from 0.01 to 0.1 of the ionic strength. The $\log b_i^\circ$ was determined by the extrapolation of the linear $\log b_i$ *vs.* $\sqrt{\mu}$ plots to the intercept. The plots of $\log k_i^\circ$ calculated from Eq. 10 *vs.* $1/T$ are shown in Fig. 8. In all cases, the plots of $\log k_i^\circ$ *vs.* $1/T$ gave straight lines.

ΔH°, ΔG°, and ΔS° have the following equations:

$$\Delta G^\circ = -RT \ln K^\circ, \tag{16}$$

$$\ln K^\circ = \frac{-\Delta H^\circ}{RT} + C, \tag{17}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \tag{18}$$

Here, from the slope of the plots of $\log K_i^\circ$ *vs.* $1/T$, ΔH° for the reaction was obtained, ΔG° was obtained from the value of $\ln k_i^\circ$ at 25 °C, and ΔS° was calculated from the difference between ΔH° and ΔG°. The results are shown in Table 7. All the ΔH° values are negative; this suggests that the formation reaction of PMH–copper(II) complexes is an exothermic reaction. Moreover, these values were five times as large as those for poly(vinyl alcohol)–copper(II) complexes.[4] This suggests that the PMH–copper(II) complexes are more stable than the poly(vinyl alcohol)–copper(II) complexes. The ΔS° values are positive, and they decrease as follows: $\Delta S_1^\circ > \Delta S_2^\circ > \cdots > \Delta S_6^\circ$. Generally, entropy increases because of the release of water, which is coordinated with copper(II) ions and polymeric ligands, as a result of the formation of PMH–copper(II) complexes. On the other hand, the degree of freedom of copper(II) ions and polymeric ligands decreases because of the coordination of copper(II) ions with hydrazide groups. Therefore, it is considered that the entropy changes for PMH–copper(II) complexes finally decreased in the order presented above. These phenomena have also been reported for poly(vinyl alcohol)–copper(II) complexes.[4]

TABLE 7. THE THERMODYNAMIC PARAMETERS OF PMH–COPPER(II) COMPLEXES

i	$\log k_i^\circ$	$-\Delta G_i^\circ$ (kcal/mol)	$-\Delta H_i^\circ$ (kcal/mol)	ΔS_i° (cal/deg·mol)
1	7.19	9.81	7.58	7.48
2	6.59	8.99	7.26	5.81
3	6.36	8.67	7.67	3.36
4	6.21	8.47	7.56	3.05
5	6.11	8.33	7.50	2.79
6	5.97	8.14	7.35	2.65
$\sum_{i=1}^{6} i$	38.43	52.41	44.63	26.11

PMH($\bar{P}_n$=5470): 8.64×10^{-4} unit mol/l, $Cu(NO_3)_2$: 8.00×10^{-5} mol/l. 1) $HA + Cu^{2+} \rightleftarrows CuA^+ + H^+$ 2) $HA + CuA^+ \rightleftarrows CuA_2 + H^+$ ……6) $HA + CuA_5^{3-} \rightleftarrows CuA_6^{4-} + H^+$.

From the results described above, it can be seen that one copper(II) ion formed a coordination compound with six hydrazide groups of PMH in a high pH region (about pH 9) when the T_{Cu}/T_{HL} values became less than 0.1. The formation constants were unaffected by the degree of polymerization of PMH, but were affected by the kind of anion of copper(II) salts and neutral salts added. From the thermodynamic data, it was recognized that the formation reaction of PMH–copper(II) was an exothermic reaction.

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