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Polarographic Studies of the Associated Ion-pairs of Polyphosphate with the Hexaamminecobalt(III) Ion

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The polarographic behavior of the hexaamminecobalt(III) ion was studied in solutions of polyphosphate with different numbers of chains. The decrease in the diffusion current, i_d, with an increase in the phosphate (C_p)-to-hexaamminecobalt(III) (C_{Co}) mole ratio was found to be proportional to 1/4 the power of the molecular weight, M, of the $Co(NH_3)_6^{3+}$-polyphosphate. This fact shows the associated ions between $Co(NH_3)_6^{3+}$ ions and polyphosphate anions are transported to the electrode by diffusion at a rate depending on the square root of the molecular weight of the diffusion depolarizer. From the shift of the half-wave potential in the presence of excess polyphosphate, the chemical compositions of the associated ion-pairs were determined as a function of log C_p/C_{Co}.

The association of hexaamminecobalt(III) ions with sulfate, iodide, and several other halide ions has been evidenced by the spectrophotometric studies in aqueous media.[1-4] Hexaamminecobalt(III) ($Co(NH_3)_6^{3+}$) cations form precipitates with pyrophosphate and polyphosphate anions, but the precipitate of $Co(NH_3)_6^{3+}$-polyphosphate dissolves in an excess of polyphosphate. Laitinen *et al.*[5,6] reported the amperometric determination of pyrophosphate and triphosphate, with hexaamminecobalt(III) or tris-ethylenediamminecobalt(III) as the titrant. For completing the precipitation of $Co(NH_3)_6^{3+}$-triphosphate, the addition of some alcohol is indispensable. Since $Co(NH_3)_6^{3+}$ is highly stable and inert to ligand substitution, it is interesting to study in detail the type and the strength of the interaction exerted between $Co(NH_3)_6^{3+}$ ions and polyphosphate ions. The present work will deal with the diffusion currents and the half-wave potentials of $Co(NH_3)_6^{3+}$ in solutions of the polyphosphate with different numbers of chains.

Experimental

Apparatus. A Yanagimoto polarograph of the P8-D was employed for recording the DC polarograms. The potential was calibrated by means of potentiometer to within 1 mV. For the measurement, an H-type cell was used, the SCE being isolated from the solution by a bridge of saturated KCl with ultrafine sintered-glass membranes. The internal resistance was about 3 kΩ. The capillary used had an m value of 2.355 mg/s and a drop time of 3.57 s at a mercury height of 78.8 cm in distilled water at open circuit and at 25 °C.

Reagents. For obtaining sodium triphosphate of a high purity, a commercial triphosphate product containing more than 80% of triphosphate was used as the starting material. The purification was carried out by recrystallization, and the recrystallization was carried out by the use of 20% ethanol. When recrystallization was repeated five times, the product was the hydrate crystal of $Na_5P_3O_{10} \cdot 6H_2O$ (99.9% purity, according to our anion-exchange chromatographic analysis).[7] For preparing polyphosphate, the sodium dihydrogenphosphate (NaH_2PO_4) of the guaranteed reagent was dehydrated and melted at 800 °C for 3 hr. Vitreous oligomer phosphate with an average number of 100 chains was obtained by pouring the molten salt on a cold brass plate. The hexaaminecobalt(III) chloride was prepared according to the method described in the literature,[8] recrystallization from 60% alcohol and a 0.5 M hydrochloric acid solution was repeated two times. For the polarographic measurements, polyacrylamide was used as the maximum suppressor. All the other reagents used were guaranteed reagents. Triply-distilled water was used for test solutions throughout the experiments.

Results and Discussion

Precipitation. Hexaamminecobalt(III)-oligomer phosphate, including pyrophosphate, was precipitated either from a 0.1 M $NaClO_4$ solution of pH 5.95 or from a 0.1 M $NH_3 \cdot NH_4Cl$ buffer solution of pH 9.98. The precipitate of hexaamminecobalt(III) pyrophosphate was not dissolved by increasing the pyrophosphate concentration. The precipitate of hexaamminecobalt(III) polyphosphate was formed within a C_p/C_{Co} mole ratio of about 10; the precipitate dissolved again in excess of polyphosphate. Polarograms of $Co(NH_3)_6^{3+}$ upon the addition of polyphosphate are shown in Fig. 1. The precipitate formation of hexaamminecobalt(III) polyphosphate results in a sharp decrease in the diffusion currents, as is shown in Fig. 2. Curves a and b in Fig. 2 correspond to the precipitations

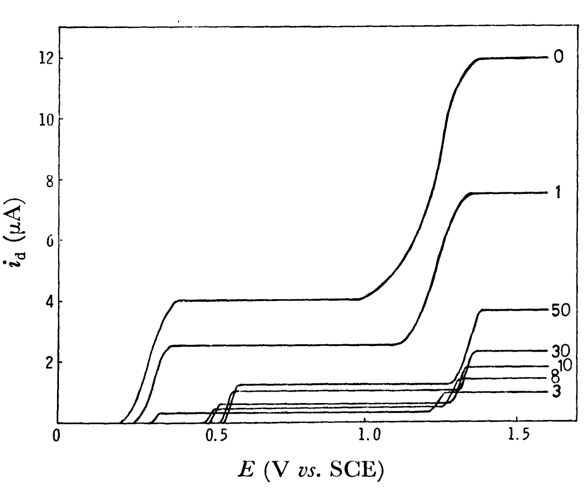

Fig. 1. Polarograms of $Co(NH_3)_6^{3+}$ with addition of polyphosphate. The numerical values show the C_p/C_{Co} mole ratio.

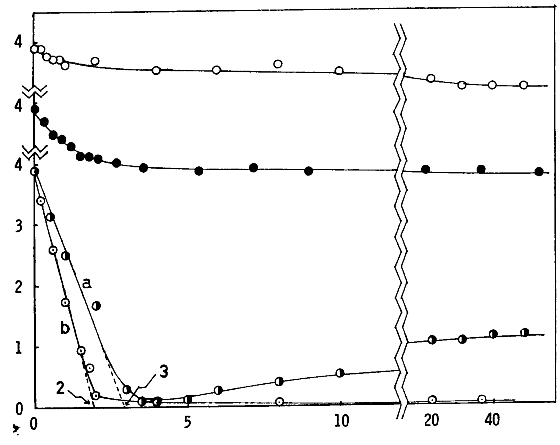

Fig. 2. Diffusion currents for reduction of 1×10^{-3} M $Co(NH_3)_6^{3+}$ ion (first wave) in 0.1 M $NaClO_4$ with 0.007% polyacrylamide.

(○) orthophosphate (◉) pyrophosphate
(●) triphosphate (◑) polyphosphate

of polyphosphate and pyrophosphate respectively. Curve a has a minimum at a C_p/C_{Co} mole ratio of about 3, which could be estimated by the extrapolation of the straight line a to the intercept on the abscissa. The diffusion current attains a constant value at a polyphosphate concentration of about 2×10^{-2} M, equal to a C_p/C_{Co} ratio of about 20. Curve b in Fig. 2 show an equivalent point, C_p/C_{Co}, equal to 2 on the abscissa, which agrees with the precipitation of hexaamminecobalt(III) pyrophosphate in a one-to-one mole ratio with respect to the concentrations of pyrophosphate and hexaamminecobalt(III). If one mole of $Co(NH_3)_6^{3+}$ and one mole of $P_2O_7^{4-}$ precipitate, then one mole of the univalent cation is required to neutralize the excess charge. From flame photometric analysis of the sodium content in the precipitate of hexaamminecobalt(III) pyrophosphate, the C_{Na}/C_{Co} mole ratio was found to be unity. From these finding, the composition of the hexaamminecobalt(III) pyrophosphate precipitate is shown to be $Na[Co(NH_3)_6]P_2O_7$, in agreement with the formula proposed by Laitinen and McCune.[5,6] Curve a in Fig. 3 shows the decrease in the diffusion current for $Co(NH_3)_6^{3+}$ in presence of polyphosphate at various C_p/C_{Co} mole ratio. Curve b in Fig. 3 is the result of the unprecipitated phosphate concentration obtained by the molybdenum-blue method of colorimetric analysis for the phosphate after the polyphosphate form has been converted into the monomer form by acid hydrolysis.[9] Curves a and b in Fig. 3 show the equivalent point at C_p/C_{Co} mole ratio of 3 corresponding to the concentrations of 7.78×10^{-4} M and 2×10^{-4} M for $Co(NH_3)_6^{3+}$ and phosphate respectively. From these data, the apparent solubility product, K'_{sp}, can be calculated by:

$$K'_{sp} = (7.78\times10^{-4}) \times (2\times10^{-4})^3 = 6.22 \times 10^{-15}$$

for the precipitation reaction expressed by (1):

$$Co(NH_3)_6^{3+} + 3(PO_3^-) = Co(NH_3)_6(PO_3)_3 \qquad (1)$$

The polyphosphate anion, $(PO_3^-)_n$, is a linear-chain oligomer with an average number of chains of about 100 and has a single negative charge per chain-like molecule, PO_3. A single PO_3^- unit produces an ionic bond with one-third of the trivalent hexaamminecobalt(III) ion. The precipitation reaction (1) is a reasonable assumption when the PO_3^- unit in the polymer chain behaves like a monomer free ion.

Diffusion Current. The curves in Fig. 2 show that the diffusion currents due to the reduction of Co(III) to Co(II) for a fixed $Co(NH_3)_6^{3+}$ concentration of 1×10^{-3} M in a concentration range of a large C_p/C_{Co} ratio such as 20: 1 are 3.35, 2.85, and 1.05 μA for orthophosphate, triphosphate, and oligomer phosphate with an average number of chains of 100 respectively. It appears likely that the diffusion current depends on the polyphosphate species. In this respect, synthetic oligomer phosphates with numbers of chains of 6, 10, and 20 are employed for measuring the diffusion currents at the C_p/C_{Co} ratio of 50. The results are represented in Fig. 4 by plotting $\log i_d$ against $\log M$

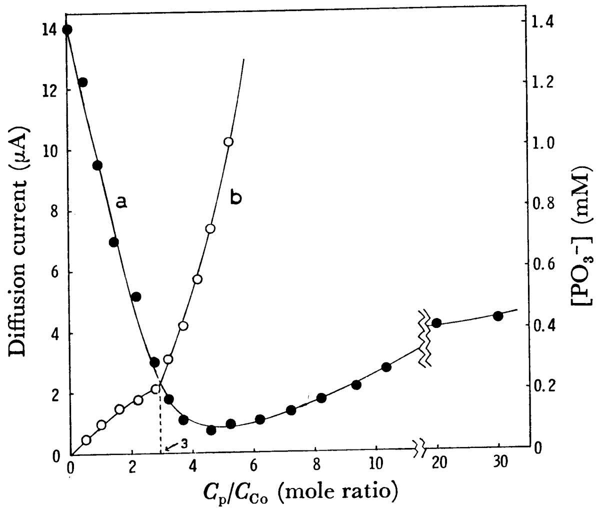

Fig. 3. Variation of diffusion current with $Co(NH_3)_6^{3+}$ concentration of 3.6×10^{-3} M (curve a) and phosphate ion concentration (curve b) with increasing C_p/C_{Co} mole ratio.

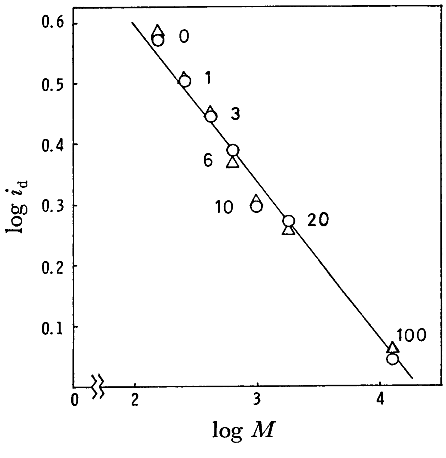

Fig. 4. The relationship between $\log i_d$ for the first wave and $\log M$. The numerical values show the number of chains.

(○) 0.1 M NH_3—0.1 M NH_4Cl
(△) 0.1 M $NaClO_4$

Table 1. Variation of diffusion currents of hexaamminecobalt(III) with polyphosphate of different number of chains

Electrochemically active species[a]	Molecular weight, M	Current (μA) at $C_p/C_{Co}=50$ First wave $i_d(1)\cdot M^{1/4}$ NH_3[b]	Current (μA) at $C_p/C_{Co}=50$ First wave $i_d(1)\cdot M^{1/4}$ $NaClO_4$[c]	Current (μA) at $C_p/C_{Co}=50$ Second wave $i_d(2)\cdot M^{1/4}$ NH_3[b]	Current (μA) at $C_p/C_{Co}=50$ Second wave $i_d(2)\cdot M^{1/4}$ $NaClO_4$[c]
Co(III) alone	161	13.46	13.96	25.95	27.06
Co(III)-monomer	257	12.95	12.97	25.38	25.94
Co(III)-trimer	416	12.55	12.73	23.21	23.71
Co(III)-polymer $n=6$	651	12.42	11.72	23.44	21.67
Co(III)-polymer $n=10$	967	11.17	11.49	21.30	22.14
Co(III)-polymer $n=20$	1757	12.04	12.04	24.41	23.43
Co(III)-polymer $n=100$	13034	11.75	12.06	29.06	26.82
Mean		12.33	12.50	24.69	24.39
Deviation: ± (%)		5.74	6.34	9.24	8.38

a) Co(III): $Co(NH_3)_6^{3+}$, n: number of chains. b) 0.1 M NH_3—0.1 M NH_4Cl(pH: 9.98).
c) 0.1 M $NaClO_4$ (pH: 5.95).

in order to establish a quantitative relation between the diffusion current, i_d, and the molecular weight, M, of the $Co(NH_3)_6^{3+}$-oligomer phosphate. Since the influence of the viscosity was observed only when there were 100 chains, the corrected value of i_d was used for that. The straight line drawn for $\log i_d-\log M$ plots in Fig. 4 has a slope approximately equal to $-1/4$. This fact can be explained as follows. Since the diffusion current, i_d, is proportional to the square root of the diffusion coefficient, D, in the relation known as the Ilkovic equation, and since the diffusion coefficient, D, is inversely proportional to the square root of the molecular weight, M, of the diffusion species,[10] the diffusion current, i_d, is inversely proportional to 1/4 the power of the molecular weight, M, of $Co(NH_3)_6^{3+}$ polyphosphate. This is a reasonable assumption for associated ion-pairs with respect to $Co(NH_3)_6^{3+}$ polyphosphate when the decrease in the diffusion current is due to the diffusion coefficient. The constancy of $i_d\times M^{1/4}$ holds well for all the oligomer phosphates with different numbers of chains, as is shown in Table 1. It is worthwhile noting this application of the $i_d\times M^{1/4}$ rule that the molecular weight of an oligomer phosphate can be determined by measuring the diffusion current of the reduction containing an excess amount of the oligomer phosphate in question.

Half-wave Potential. The variation in the half-wave potentials with the increasing C_p/C_{Co} ratio is illustrated in Fig. 5 for the hexaamminecobalt(III)

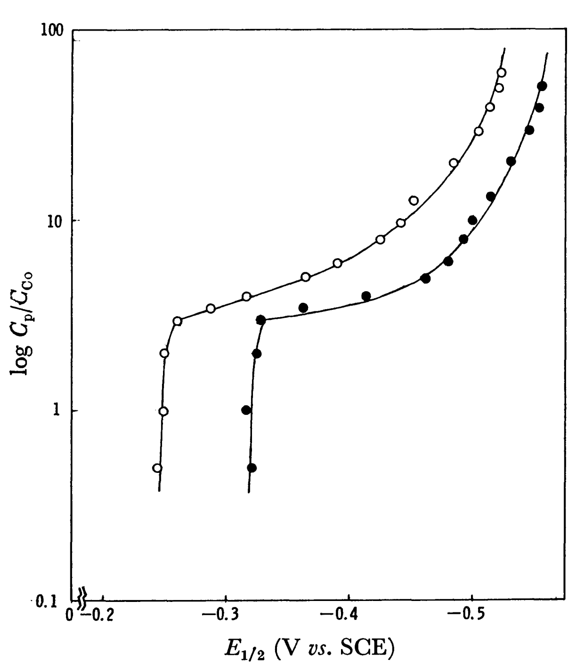

Fig. 5. Variation of half-wave potentials for polyphosphate with increasing the logarithmic function of C_p/C_{Co} ratio for the first wave.
(○) 0.1 M NH_3—0.1 M NH_4Cl
(●) 0.1 M $NaClO_4$

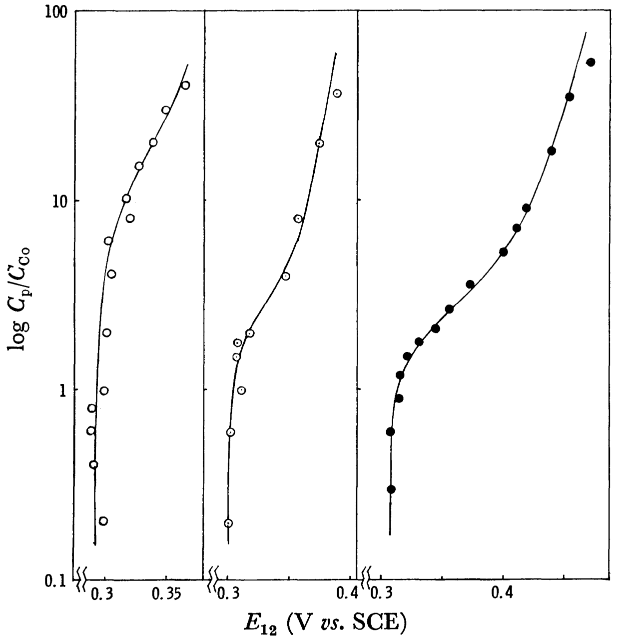

Fig. 6. Variation of half-wave potentials for orthophosphate, pyrophosphate and triphosphate with increasing the logarithmic function of C_p/C_{Co} ratio for the first wave in 0.1 M $NaClO_4$.
(○) orthophosphate (⊙) pyrophosphate
(●) triphosphate

Table 2. THE HALF-WAVE POTENTIALS OF THE ASSOCIATED ION-PAIRS OF HEXAAMMINECOBALT(III) IN PRESENCE OF EXCESS PHOSPHATE AT 25 °C.

First wave half-wave potentials $E_{1/2}$ in absence of phosphate are -0.251_7 V (*vs.* SCE) in 0.1 M NH_3—0.1 M NH_4Cl at pH 9.98 and -0.301_4 V (*vs.* SCE) in 0.1 M $NaClO_4$ at pH 5.95. $\Delta E_{1/2}$ is the difference in half-wave potentials between free $Co(NH_3)_6{}^{3+}$ and ion-pairs of $Co(NH_3)_6{}^{3+}$-phosphate.

Hexaamminecobalt(III) 10^{-3} M
Phosphate 5×10^{-2} M

Phosphate	$-E_{1/2}$		$-\Delta E_{1/2}$		α	
	NH_3[a)]	$NaClO_4$[b)]	NH_3[a)]	$NaClO_4$[b)]	NH_3[a)]	$NaClO_4$[b)]
Orthophosphate	0.344_9	0.354_3	0.093_2	0.052_9	0.48	0.66
Pyrophosphate	0.369_6	0.386_9	0.117_9	0.085_5	0.58	0.67
Triphosphate	0.418_5	0.474_5	0.166_8	0.173_1	0.54	0.80
Polyphosphate	0.522_3	0.556_2	0.270_7	0.254_8	0.97	0.85

a) 0.1 M NH_3—0.1 M NH_4Cl. b) 0.1 M $NaClO_4$.

polyphosphate system in two media with different pH values. The influence of the adsorption on the electrode surface of polyphosphate was checked by measuring the electrocapillary curve; this influence is rarely observed. The negative shifts of the half-wave potentials observed in the range of C_p/C_{Co} ratios from 3 to 6 are larger than the shifts observed at C_p/C_{Co} ratios beyond 6. This fact indicates that the soluble and stable ion-pairs were formed in the vicinity of C_p/C_{Co} ratios of about 6. The maximum value of the potential shift amounts to some hundred millivolts on the negative side at the C_p/C_{Co} ratio of 50. In Fig. 6 similar curves for the variation in half-wave potentials are illustrated for orthophosphate, pyrophosphate, and triphosphate respectively. The negative shifts of their potentials are not so large as compared with the shifts caused by the higher-oligomer phosphate. It can be seen that the larger the number of chains of phosphate, the more the negative shifts of the half-wave potentials. The final values of the half-wave potentials at the C_p/C_{Co} ratio of 50 are represented in Table 2, where all the electrochemically active species of hexaamminecobalt(III) are presented in the form of ion-pairs produced between $Co(NH_3)_6{}^{3+}$ and oligomer phosphate anions. The transfer coefficients, α, shown in the third column of Table 2 were obtained from the plots of $\log[i/(i_d-i)]$ against E at the C_p/C_{Co} ratio of 50.

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