Anomalous Salting-Out Effect of Sodium Perchlorate on *fac*-Tris(glycinato)cobalt(III)

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The effect of $NaClO_4$ on *fac*- and *mer*-isomers of tris(amino acidato)cobalt(III) ([Co(aa)$_3$]) was examined by determining their solubilities in aqueous $NaClO_4$ solutions. An addition of $NaClO_4$ increased the solubilities of both the isomers of [Co(aa)$_3$] except for tris(glycinato)cobalt(III) ([Co(gly)$_3$]). While the solubility of *mer*-[Co(gly)$_3$] was also increased by the addition of $NaClO_4$, $NaClO_4$ brought about abnormally large decrease in the solubility of *fac*-[Co(gly)$_3$]. The addition of $NaClO_4$ also produced a decrease in the solubility of tris(acetylacetonato)cobalt(III) ([Co(acac)$_3$]). The salting-out effect of $NaClO_4$ on *fac*-[Co(gly)$_3$] was compared with that on [Co(acac)$_3$]. While both the enthalpy ($\Delta_{tr}H^o$) and entropy of transfer ($\Delta_{tr}S^o$) from water to aqueous $NaClO_4$ solutions for [Co(acac)$_3$] were positive, those for *fac*-[Co(gly)$_3$] were generally negative. On the basis of these results, an origin for the salting-out effect of $NaClO_4$ on *fac*-[Co(gly)$_3$] is discussed.

I have investigated dissolution behaviors of tris(amino acidato)cobalt(III) ([Co(aa)$_3$]) in water and in ethanol. In these studies, the following anomalous effect of NaI on the solubility of *fac*-tris(glycinato)cobalt(III) (*fac*-[Co(gly)$_3$]) was found.[1] An addition of sodium halides increased the solubility of *mer*-(+)-tris(L-alaninato)cobalt(III) (*mer*-(+)-[Co(L-ala)$_3$]) (salting-in effect) and this salting-in effect increased in the order of NaF < NaCl < NaBr < NaI. The symbol (+) represents the dextrorotatory at 589 nm. The solubility of *fac*-[Co(gly)$_3$] was also increased by the addition of NaF, NaCl, or NaBr. The salting-in effect of each salt on *fac*-[Co(gly)$_3$] was larger than that on *mer*-(+)-[Co(L-ala)$_3$]. In contrast to these findings, the solubility of *fac*-[Co(gly)$_3$] was anomalously decreased by the addition of NaI (salting-out effect).

It is noteworthy to confirm whether the above-mentioned anomalous salting-out effect of NaI is characteristic of the *fac*-isomers of [Co(aa)$_3$] or not. It has been reported that I^- ion has a breaking effect on the three-dimensional network structure of water due to the hydrogen bonding among water molecules[2] and forms ion pairs with hydrophobic cations such as tetraalkylammonium ions.[3] The structure-breaking effect and the trend for ion pair formation of ClO_4^- ion are larger than those of I^-.[2,3] Thus, it is also interesting to examine the effect of ClO_4^- ion on the solubilities of [Co(aa)$_3$].

In this work, in order to investigate the origin of the salting-out effect of NaI on *fac*-[Co(gly)$_3$], the solubilities of both the *mer*- and *fac*-isomers of some [Co(aa)$_3$] in aqueous $NaClO_4$ solutions were determined over the temperature range of 5 to 50 °C. Furthermore, for comparison, the solubility of tris(2,4-pentanedionato)cobalt(III) (tris(acetylacetonato)cobalt(III), [Co(acac)$_3$]), which was regarded as typical nonpolar non-electrolyte, was also determined in aqueous $NaClO_4$ solutions. From these data the free energy ($\Delta_{tr}G^o$), enthalpy ($\Delta_{tr}H^o$), and entropy of transfer ($\Delta_{tr}S^o$) from water to aqueous $NaClO_4$ solutions for both the chelates were estimated and these values are compared with each other.

Experimental

The syntheses, separations, and characterizations of the *mer*- and *fac*-isomers of [Co(gly)$_3$],[4,5] (+)-[Co(L-ala)$_3$],[5,6] (+)-tris(L-serinato)cobalt(III) ((+)-[Co(L-ser)$_3$]),[7] and tris(2-amino-2-methylpropionato)cobalt(III) (tris(2-aminoisobutyrato)cobalt(III), [Co(aiba)$_3$])[8] have been reported in a series of investigations. The solubility measurements of these chelates were also carried out in the same manner as reported.[4,9] In the solubility determination, the temperature in a thermostat was maintained within 0.05 °C of the desired temperature. The stock solution of $NaClO_4$ was prepared by neutralizing reagent grade perchloric acid (70%) with anhydrous sodium carbonate; its concentration was determined gravimetrically by evaporating a definite aliquot of the stock solution to dryness at 120 °C. Analytical reagent grade sodium tetraphenylborate ($NaBPh_4$) and [Co(acac)$_3$] were used without further purification.

Results and Discussion

Estimation of Standard Thermodynamic Functions of Dissolution in Aqueous $NaClO_4$ Solutions at 25 °C. The solubility values in mol kg^{-1} (m) in aqueous $NaClO_4$ solutions for the *fac*- and *mer*-isomers of [Co(gly)$_3$], (+)-[Co(L-ala)$_3$], (+)-[Co(L-ser)$_3$], and [Co(aiba)$_3$] are listed in Tables 1 and 2, respectively. Furthermore, the solubilities of *fac*-[Co(gly)$_3$] in aqueous $NaBPh_4$ solutions and of [Co(acac)$_3$] in $NaClO_4$ solutions are tabulated in Table 3. The solubility measurements were repeated at least four times at each temperature and the errors given in parentheses in these tables were defined as the deviations at the 95% confidence levels. The deviations for *mer*-[Co(aa)$_3$] and [Co(acac)$_3$] were less than 2%, with a few exceptions for *mer*-(+)-[Co(L-ser)$_3$]. In contrast to *mer*-[Co(aa)$_3$], the deviations for the *fac*-isomers, whose solubilities are considerably smaller than those of the corresponding *mer*-isomers, were fairly large, especially for *fac*-[Co(gly)$_3$] and *fac*-(+)-[Co(L-ser)$_3$].

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Table 1. Solubilities (m) of *fac*-Isomers of $[Co(gly)_3]$, $[Co(L\text{-}ala)_3]$, $[Co(L\text{-}ser)_3]$, and $[Co(aiba)_3]$ in Aqueous $NaClO_4$ Solutions[a)]

$\theta/°C$	*fac*-$[Co(gly)_3]$						*fac*-(+)-$[Co(L\text{-}ala)_3]$			
	$m_s/mol\,kg^{-1}$						$m_s/mol\,kg^{-1}$			
	0.020	0.174	0.523	1.046	1.629	2.205	0.491	0.998	1.530	2.085
	$m/10^{-5}\ mol\,kg^{-1}$						$m/10^{-5}\ mol\,kg^{-1}$			
5	4.22 (0.08)									3.69 (0.03)
10	5.67 (0.07)						1.91 (0.06)	2.70 (0.05)	3.04 (0.02)	3.71 (0.04)
15	7.72 (0.05)	2.5 (0.1)		2.30 (0.07)	2.57 (0.07)	1.38 (0.02)	1.97 (0.04)	2.78 (0.02)	3.07 (0.05)	3.77 (0.03)
20	10.5 (0.1)	2.9 (0.1)	2.08 (0.04)	2.3 (0.1)	2.62 (0.05)	1.50 (0.07)	2.05 (0.03)	2.86 (0.03)	3.17 (0.03)	3.89 (0.02)
25	14.3 (0.3)	3.4 (0.1)	2.5 (0.1)	2.59 (0.06)	2.8 (0.2)	1.74 (0.08)	2.19 (0.04)	2.96 (0.03)	3.24 (0.02)	3.95 (0.03)
30	18.7 (0.2)	4.1 (0.1)	2.87 (0.07)	2.9 (0.1)	3.16 (0.05)	1.86 (0.08)	2.30 (0.02)	3.05 (0.06)	3.34 (0.02)	4.07 (0.03)
35	25.2 (0.3)	5.1 (0.2)	3.49 (0.04)	3.3 (0.1)	3.4 (0.1)	2.33 (0.06)	2.36 (0.02)	3.20 (0.07)	3.47 (0.03)	4.24 (0.04)
40	34.1 (0.4)	6.4 (0.1)	4.27 (0.08)	3.9 (0.1)	3.8 (0.1)	2.68 (0.07)	2.50 (0.03)	3.50 (0.07)	3.62 (0.05)	4.47 (0.04)
45	44.4 (0.7)	8.2 (0.2)	5.2 (0.2)	4.8 (0.1)	4.4 (0.3)	3.10 (0.04)	2.72 (0.03)	3.72 (0.07)	3.81 (0.07)	4.70 (0.02)
50	56.9 (0.5)	10.1 (0.2)		5.4 (0.2)	5.0 (0.1)	3.8 (0.1)	2.93 (0.08)	4.0 (0.1)	4.00 (0.07)	4.97 (0.06)

$\theta/°C$	*fac*-(+)-$[Co(L\text{-}ser)_3]$				*fac*-$[Co(aiba)_3]$			
	$m_s/mol\,kg^{-1}$				$m_s/mol\,kg^{-1}$			
	0.206	1.055	1.582	2.280	0.202	0.515	0.777	1.085
	$m/10^{-4}\ mol\,kg^{-1}$				$m/10^{-3}\ mol\,kg^{-1}$			
5	1.32 (0.01)	6.87 (0.04)	3.37 (0.01)	4.91 (0.03)	2.77 (0.02)	3.45 (0.01)	3.72 (0.05)	3.87 (0.01)
10	1.45 (0.02)	7.20 (0.09)	3.76 (0.02)	5.30 (0.03)	2.41 (0.02)	2.96 (0.04)	3.20 (0.02)	3.38 (0.01)
15	1.64 (0.02)	7.48 (0.06)	4.16 (0.03)	5.86 (0.05)	2.12 (0.02)	2.62 (0.02)	2.90 (0.03)	2.98 (0.02)
20	1.80 (0.01)	8.01 (0.04)	4.60 (0.02)	6.46 (0.07)	1.89 (0.01)	2.33 (0.03)	2.56 (0.01)	2.70 (0.03)
25	2.08 (0.03)	8.5 (0.1)	5.19 (0.04)	7.15 (0.07)	1.71 (0.01)	2.11 (0.01)	2.34 (0.02)	2.46 (0.02)
30	2.40 (0.03)	9.28 (0.05)	5.70 (0.07)	8.26 (0.05)	1.56 (0.01)	1.94 (0.01)	2.16 (0.02)	2.29 (0.02)
35	2.9 (0.1)	10.4 (0.3)	6.54 (0.09)	9.4 (0.2)	1.44 (0.01)	1.82 (0.01)	2.03 (0.02)	2.15 (0.01)
40	3.60 (0.08)	12.4 (0.4)	7.7 (0.2)	11.4 (0.5)	1.35 (0.03)	1.71 (0.01)	1.93 (0.02)	2.06 (0.02)

a) Errors defined as 95% confidence levels are given in parentheses. Solubilities in water (m^0) at 25 °C for *fac*-$[Co(gly)_3]$, *fac*-(+)-$[Co(L\text{-}ala)_3]$, *fac*-(+)-$[Co(L\text{-}ser)_3]$, and *fac*-$[Co(aiba)_3]$ ($6.56\ (0.09) \times 10^{-4}$, $1.03\ (0.02) \times 10^{-5}$, $8.0\ (0.2) \times 10^{-5}$, and $1.30\ (0.01) \times 10^{-3}$ $mol\,kg^{-1}$, respectively) have been reported in Refs. 4, 6, 7, and 8, respectively.

In the solubility measurement at high temperatures for *mer*-$[Co(gly)_3]$ in $NaClO_4$ solutions, repeated determination resulted in a progressive decrease in experimental values for the solubility. Especially, in the course of the solubility determination at 30 °C in 2.290 $mol\,kg^{-1}$ $NaClO_4$ solution, red crystal grains developed. These were identified as the *fac*-isomer by measuring their absorption spectrum. Thus, the solubility determination for *mer*-$[Co(gly)_3]$ in $NaClO_4$ solutions was restricted in the narrow temperature ranges, as shown in Table 2.

As typical examples for the temperature dependence of the solubilities, the values of $\ln m$ in 1.0 $mol\,kg^{-1}$ $NaClO_4$ solution for the *fac*- and *mer*-isomers of $[Co(gly)_3]$, (+)-$[Co(L\text{-}ala)_3]$, and $[Co(aiba)_3]$ are plotted against $1/T$ in Fig. 1. The standard state for the chelates in solutions is 1 $mol\,kg^{-1}$. The rather small solubilities for the chelates examined may permit one to regard the saturated solutions as ideal dilute solutions with respect to the chelates. Thus, the standard free energy ($\Delta_{dis}G^o$), enthalpy ($\Delta_{dis}H^o$), and entropy of dissolution ($\Delta_{dis}S^o$) in aqueous $NaClO_4$ and $NaBPh_4$ solutions at 25 °C were estimated by applying a least-squares analysis to the temperature dependence of the solubilities without any activity correction. The results are tabulated in Table 4. The method to estimate these thermodynamic functions, which has been described in detail in previous work,[10] is equivalent to fitting the solubility data to

$$R \ln m = \mathrm{A} + \mathrm{B}/T + \mathrm{C} \ln T + \mathrm{D}T + \mathrm{E}T^2 + \cdots, \qquad (1)$$

where R is the gas constant and A, B, C, D, and E ... are constants.

In Table 4, the values for $\Delta_{dis}G^o$, $\Delta_{dis}H^o$, and $T\Delta_{dis}S^o$ in water taken from the previous works are also referred to as $m_s = 0$ $mol\,kg^{-1}$. The estimation of $\Delta_{dis}H^o$ and $T\Delta_{dis}S^o$ from the temperature dependence of the solubilities for *mer*-$[Co(gly)_3]$ in 2.290 $mol\,kg^{-1}$ $NaClO_4$ solution was not applied because of the limited temperature range of 5 to 25 °C for the solubility determination.

Effect of $NaClO_4$ on Solubilities of *fac*- and *mer*-Isomers of $[Co(gly)_3]$, (+)-$[Co(L\text{-}ala)_3]$, (+)-$[Co(L\text{-}ser)_3]$, and $[Co(aiba)_3]$. In order to manifest the effect of $NaClO_4$ on the solubilities for the *fac*- and *mer*-isomers of $[Co(gly)_3]$, (+)-$[Co(L\text{-}ala)_3]$, (+)-$[Co(L\text{-}ser)_3]$, and $[Co(aiba)_3]$, I plotted the values for $\log(m^0/m)$ at 25 °C against $NaClO_4$ concentration (m_s) in Figs. 2 and 3, respectively. In these figures, the data for *fac*-$[Co(gly)_3]$ and *mer*-(+)-$[Co(L\text{-}ala)_3]$ in aqueous NaI solutions,[1] for *fac*-$[Co(gly)_3]$ in aqueous $NaBPh_4$ solutions, and for $[Co(acac)_3]$ in aqueous $NaClO_4$ solutions are also illustrated for comparison. The values at 25 °C for m^0, which represents the solubility in water, are given in the footnotes of Tables 1, 2, and 3.

The addition of $NaClO_4$ brings about a remarkable decrease in the solubility of *fac*-$[Co(gly)_3]$ in a manner similar to NaI, but increases the solubility of *mer*-$[Co(gly)_3]$. The salting-out effect of $NaClO_4$ is large even at the low salt concentration of 0.0199 $mol\,kg^{-1}$ and a smooth curve could not be drawn by

Table 2. Solubilities (m) of *mer*-Isomers of [Co(gly)$_3$], (+)-[Co(L-ala)$_3$], (+)-[Co(L-ser)$_3$], and [Co(aiba)$_3$] in Aqueous NaClO$_4$ Solutions[a)]

θ/°C	*mer*-[Co(gly)$_3$]				*mer*-(+)-[Co(L-ala)$_3$]			
	m_s/mol kg^{-1}				m_s/mol kg^{-1}			
	0.507	1.071	1.630	2.290	0.502	1.028	1.548	2.123
	m/10^{-2} mol kg^{-1}				m/10^{-3} mol kg^{-1}			
5	2.15 (0.01)	3.40 (0.01)	5.20 (0.06)	4.09 (0.06)	4.16 (0.04)	5.12 (0.04)	5.96 (0.04)	6.82 (0.03)
10	2.59 (0.02)	4.03 (0.05)	5.83 (0.05)	5.30 (0.04)	4.30 (0.04)	5.25 (0.01)	6.01 (0.04)	6.82 (0.05)
15	3.14 (0.03)	4.70 (0.02)	6.7 (0.1)	7.05 (0.04)	4.45 (0.06)	5.39 (0.04)	6.13 (0.09)	6.98 (0.04)
20	3.78 (0.03)	5.52 (0.02)	7.69 (0.04)	9.18 (0.07)	4.69 (0.04)	5.55 (0.05)	6.27 (0.06)	7.09 (0.05)
25	4.49 (0.03)	6.47 (0.04)	8.9 (0.1)	12.1 (0.1)	4.87 (0.03)	5.78 (0.03)	6.54 (0.02)	7.30 (0.08)
30	5.38 (0.09)	7.68 (0.06)	10.3 (0.1)		5.19 (0.07)	6.11 (0.02)	6.85 (0.02)	7.65 (0.03)
35	6.54 (0.05)	9.08 (0.08)			5.61 (0.03)	6.44 (0.06)	7.19 (0.02)	8.01 (0.05)
40					5.93 (0.07)	6.78 (0.09)	7.59 (0.03)	8.43 (0.04)
45					6.35 (0.09)	7.19 (0.04)	8.07 (0.07)	8.9 (0.1)
50					6.85 (0.05)	7.78 (0.08)	8.72 (0.06)	9.61 (0.05)
θ/°C	*mer*-(+)-[Co(L-ser)$_3$]				*mer*-[Co(aiba)$_3$]			
	m_s/mol kg^{-1}				m_s/mol kg^{-1}			
	0.501	1.051	1.630	2.407	0.209	0.516	0.778	1.047
	m/10^{-2} mol kg^{-1}				m/10^{-3} mol kg^{-1}			
5	0.729 (0.003)	1.00 (0.01)	1.44 (0.02)	1.85 (0.01)	5.01 (0.03)	4.96 (0.03)	4.78 (0.03)	4.66 (0.04)
10	0.876 (0.002)	1.16 (0.01)	1.65 (0.02)	2.16 (0.02)	4.79 (0.05)	4.72 (0.04)	4.57 (0.01)	4.46 (0.03)
15	1.07 (0.01)	1.40 (0.01)	1.96 (0.01)	2.51 (0.03)	4.53 (0.01)	4.54 (0.02)	4.44 (0.03)	4.31 (0.04)
20	1.33 (0.01)	1.70 (0.01)	2.34 (0.01)	2.93 (0.02)	4.39 (0.02)	4.43 (0.02)	4.33 (0.02)	4.25 (0.02)
25	1.64 (0.02)	2.11 (0.01)	2.54 (0.03)	3.08 (0.02)	4.33 (0.05)	4.37 (0.03)	4.27 (0.02)	4.20 (0.04)
30	1.81 (0.01)	2.26 (0.01)	2.64 (0.04)	3.16 (0.03)	4.31 (0.01)	4.37 (0.02)	4.29 (0.02)	4.22 (0.03)
35	1.98 (0.01)	2.44 (0.03)	2.83 (0.04)	3.34 (0.02)	4.31 (0.02)	4.41 (0.02)	4.38 (0.04)	4.35 (0.02)
40	2.16 (0.02)	2.66 (0.02)	3.07 (0.07)	3.53 (0.04)	4.41 (0.03)	4.54 (0.03)	4.50 (0.01)	4.44 (0.02)
45	2.41 (0.05)	2.90 (0.07)	3.37 (0.02)	3.73 (0.02)				
50	2.82 (0.02)	3.23 (0.03)	3.61 (0.01)	3.99 (0.04)				

a) Errors defined as 95% confidence levels are given in parentheses. Solubilities in water (m^0) at 25 °C for *mer*-[Co(gly)$_3$], *mer*-(+)-[Co(L-ala)$_3$], *mer*-(+)-[Co(L-ser)$_3$], and *mer*-[Co(aiba)$_3$] ($3.14\ (0.01) \times 10^{-2}$, $3.97\ (0.01) \times 10^{-3}$, $1.16\ (0.01) \times 10^{-2}$, and $4.32\ (0.02) \times 10^{-3}$ mol kg^{-1}, respectively) have been reported in Refs. 5, 1, 5, and 8, respectively.

Table 3. Solubilities (m) of *fac*-[Co(gly)$_3$] in Aqueous NaBPh$_4$ Solutions and of [Co(acac)$_3$] in Aqueous NaClO$_4$ Solutions[a)]

θ/°C	NaBPh$_4$ concentration m_s/mol kg^{-1}		NaClO$_4$ concentration m_s/mol kg^{-1}			
	0.270	0.569	0.209	0.713	1.520	2.520
	m/10^{-4} mol kg^{-1}		m/10^{-3} mol kg^{-1}			
5	3.6 (0.2)	4.5 (0.1)	6.66 (0.09)	4.47 (0.04)	2.49 (0.02)	1.67 (0.01)
10	4.3 (0.2)	5.1 (0.1)	5.42 (0.04)	3.76 (0.04)	2.31 (0.03)	1.58 (0.01)
15	5.0 (0.2)	5.87 (0.08)	4.77 (0.03)	3.41 (0.02)	2.17 (0.02)	1.52 (0.01)
20	6.0 (0.1)	7.5 (0.1)	4.32 (0.02)	3.11 (0.01)	2.09 (0.01)	1.47 (0.01)
25	7.1 (0.2)	8.6 (0.1)	4.02 (0.02)	2.91 (0.01)	2.01 (0.01)	1.44 (0.01)
30	8.7 (0.2)	10.1 (0.5)	3.78 (0.02)	2.76 (0.01)	1.95 (0.01)	1.41 (0.01)
35	10.5 (0.2)	12.1 (0.3)	3.61 (0.02)	2.66 (0.02)	1.91 (0.01)	1.41 (0.01)
40	13.1 (0.5)	15.2 (0.5)	3.47 (0.02)	2.59 (0.01)	1.88 (0.01)	1.48 (0.01)
45		20 (1)	3.34 (0.03)	2.54 (0.01)	1.87 (0.01)	
50			3.29 (0.02)	2.48 (0.01)	1.84 (0.04)	

a) Errors defined as 95% confidence levels are given in parentheses. Solubility of [Co(acac)$_3$] in water at 25 °C ($m^0 = 3.83\ (0.01) \times 10^{-3}$ mol kg^{-1}) has been reported in Ref. 9.

using a power series of m_s. The solubility of [Co(acac)$_3$] is also decreased by the addition of NaClO$_4$, but the plot of $\log(m^0/m)$ against m_s gives a straight line. The salting-out effect on [Co(acac)$_3$] has been also found for the addition of NaCl and Na$_2$SO$_4$[13] and linear relations between $\log(m^0/m)$ and m_s are popular for nonpolar non-electrolytes.[11] As shown in Figs. 2 and 3, the addition of NaClO$_4$ results in the salting-in effect on both the *fac*- and *mer*-isomers of [Co(aa)$_3$] other than [Co(gly)$_3$]. In these cases, the salting-in effect of NaClO$_4$ on the *fac*-isomer is larger than the effect on the corresponding *mer*-isomer of each chelate.

In general, it is well-known that inorganic salts such as so-

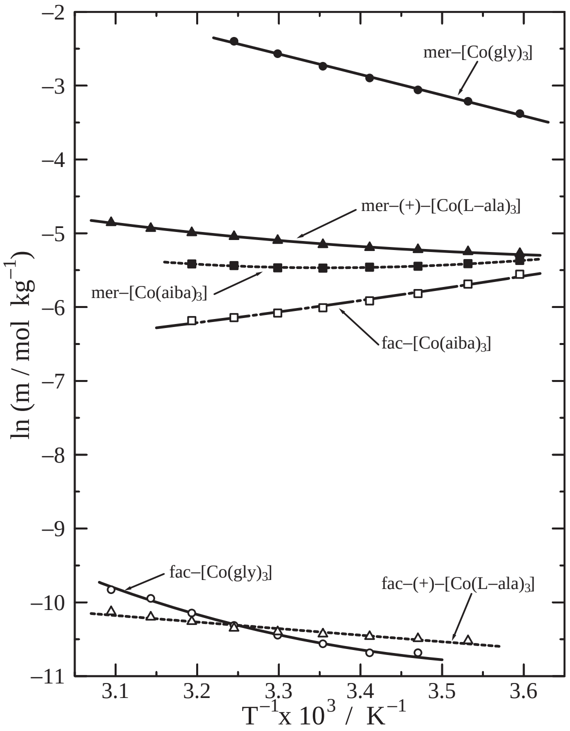

Fig. 1. Solubility curves for the *fac*- and *mer*-isomers of $[Co(gly)_3]$, (+)-[Co(L-ala)$_3$], and $[Co(aiba)_3]$ in 1.0 mol kg^{-1} $NaClO_4$ solutions depicted by plotting $\ln m$ against $1/T$. The curves are drawn by fitting the solubility data to $\ln m = a + b/T + c \ln T + dT$.

dium halides decrease the solubilities of nonpolar non-electrolytes and that the salting-out effect of each salt becomes small for polar non-electrolytes.[11,12] The salting-out effect of NaCl[13] and $NaClO_4$ (see Fig. 2) on $[Co(acac)_3]$ may be regarded as the usual result for nonpolar non-electrolytes. On the other hand, it has been previously discussed that the salting-in effect of sodium halides on $[Co(aa)_3]$ may be attributed to some specific interaction of activated α-carbon atom hydrogen in $[Co(aa)_3]$ with the surroundings.[8] The fact that the *fac*-isomers of $[Co(aa)_3]$ are adsorbed on an alumina column more strongly than the *mer*-isomers indicates that the *fac*-isomers are more polar than the *mer*-isomers. Thus, the results for $[Co(aa)_3]$ other than *fac*-$[Co(gly)_3]$ that the salting-in effect on the *fac*-isomers is larger than that on the *mer*-isomers (see Figs. 2 and 3) seems to be consistent with the general trend for the salt effect on non-electrolytes.

Perchlorate and I^- ions show the breaking effect on the threedimensional network structure of water.[2] It has been reported that the effect of tetrabutylammonium ion (Bu_4N^+), which shows a promoting effect on the network structure of water,[2] on the solubility of *fac*-$[Co(gly)_3]$ can be interpreted in the manner common to various $[Co(aa)_3]$ from the standpoint of hydrophobic interaction between the Bu_4N^+ ion and *fac*-$[Co(gly)_3]$.[8,14] This finding indicates that the Bu_4N^+ ion gives no specific effect on *fac*-$[Co(gly)_3]$. In order to examine the effect of a typical hydrophobic anion, the solubilities of *fac*-$[Co(gly)_3]$ were also determined in aqueous $NaBPh_4$ solutions. While the solubilities of *fac*-$[Co(gly)_3]$ in $NaBPh_4$ solutions are determined in the limited m_s range because of low solubility of $NaBPh_4$ in water, the BPh_4^- ion also seems not to produce any abnormal effect on *fac*-$[Co(gly)_3]$ (see Fig. 2).

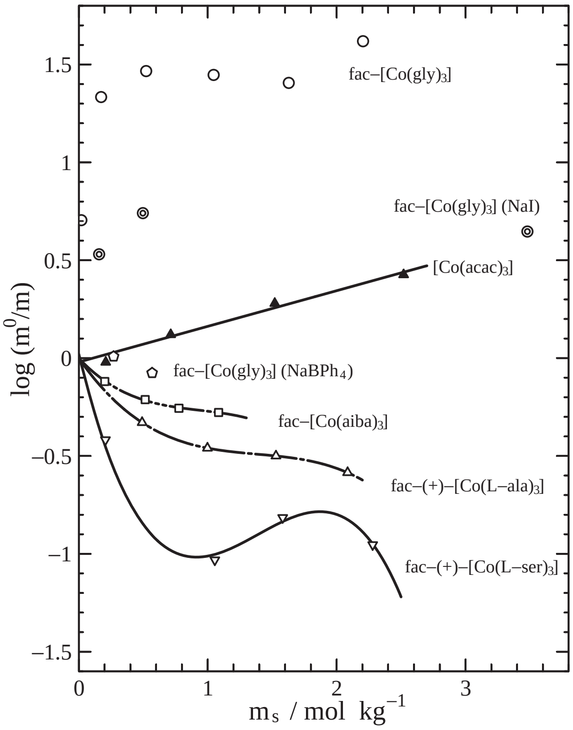

Fig. 2. Effect of $NaClO_4$ on *fac*-isomers of $[Co(gly)_3]$, (+)-[Co(L-ala)$_3$], (+)-[Co(L-ser)$_3$], and $[Co(aiba)_3]$, and on $[Co(acac)_3]$, and effect of $NaBPh_4$ on *fac*-$[Co(gly)_3]$ depicted by plotting $\log(m^0/m)$ against m_s. The lines are tentatively drawn by fitting the $\log(m^0/m)$ values to power series of m_s. The data for *fac*-$[Co(gly)_3]$ in aqueous NaI solutions were taken from Ref. 1.

Transfer Thermodynamic Functions from Water to $NaClO_4$ Solutions. In order to consider the cause of the salting-out effect of $NaClO_4$ on *fac*-$[Co(gly)_3]$, the thermodynamic functions of transfer ($\Delta_{tr}Y^o$) from water to the aqueous $NaClO_4$ solutions at 25 °C for $[Co(aa)_3]$ and $[Co(acac)_3]$ were calculated by using

$$\Delta_{tr}Y^o = \Delta_{dis}Y^o\ (\mathrm{NaClO_4\ soln}) - \Delta_{dis}Y^o\ (\mathrm{water}), \qquad (2)$$

where ($NaClO_4$ soln) and (water) denote the values for the thermodynamic functions of dissolution in the aqueous $NaClO_4$ solutions and in water, respectively. The values for $\Delta_{dis}G^o$, $\Delta_{dis}H^o$, and $T\Delta_{dis}S^o$ in water are also listed in Table 4. In Fig. 4, for the transfer process of $[Co(aa)_3]$ examined in the present study, $\Delta_{tr}H^o$ is plotted against $T\Delta_{tr}S^o$. In this figure, the data for the transfer of *mer*-(+)-[Co(L-ala)$_3$] from water to NaI solutions[1] or for the transfer of *fac*-$[Co(gly)_3]$ to $NaBPh_4$ solutions are also illustrated for comparison. The data for the transfer of *fac*-$[Co(gly)_3]$ to NaI solutions, which were estimated from the solubility data in the limited temperature range of 20 to 35 °C,[1] are given in parentheses and were excluded from a strict discussion because of rather large errors.

For the transfer processes other than the transfer of *fac*-$[Co(gly)_3]$ to $NaClO_4$ and NaI solutions, the plot of $\Delta_{tr}H^o$ against $T\Delta_{tr}S^o$ gives the correlation expressed by

Table 4. Standard Free Energy ($\Delta_{\rm dis}G^{\rm o}$), Enthalpy ($\Delta_{\rm dis}H^{\rm o}$), and Entropy of Dissolution ($\Delta_{\rm dis}S^{\rm o}$) in Aqueous NaClO$_4$ Solutions at 25 °C for *fac*- and *mer*-Isomers of [Co(gly)$_3$], (+)-[Co(L-ala)$_3$], (+)-[Co(L-ser)$_3$], and [Co(aiba)$_3$], and for [Co(acac)$_3$]$^{\rm a)}$

$m_{\rm s}$/mol kg^{-1}	$\Delta_{\rm dis}G^{\rm o}$	$\Delta_{\rm dis}H^{\rm o}$	$T\Delta_{\rm dis}S^{\rm o}$	$m_{\rm s}$/mol kg^{-1}	$\Delta_{\rm dis}G^{\rm o}$	$\Delta_{\rm dis}H^{\rm o}$	$T\Delta_{\rm dis}S^{\rm o}$
	fac-[Co(gly)$_3$]				*mer*-[Co(gly)$_3$]		
0	18.18 (0.01)$^{\rm b)}$	24.2 (0.1)$^{\rm b)}$	6.0$^{\rm b)}$	0	8.59 (0.02)$^{\rm c)}$	29.8 (0.1)$^{\rm c)}$	21.2$^{\rm c)}$
0.020	21.97 (0.02)	44.2 (0.4)	22.2				
0.174	25.52 (0.02)	28.2 (0.3)	2.7				
0.523	26.32 (0.03)	24 (1)	−2	0.507	7.69 (0.02)	26.7 (0.4)	19.0
1.046	26.23 (0.05)	16.1 (0.9)	−9.9	1.071	6.78 (0.01)	24.1 (0.3)	17.4
1.629	25.94 (0.03)	11.0 (0.5)	−14.9	1.630	6.00 (0.02)	21.8 (0.5)	15.8
2.205	27.22 (0.06)	18 (1)	−9	2.290	5.24 (0.04)	—$^{\rm d)}$	—$^{\rm d)}$
0.270$^{\rm e)}$	17.95 (0.02)	27.8 (0.2)	9.9				
0.569$^{\rm e)}$	17.53 (0.07)	27.1 (0.5)	9.6				
	fac-(+)-[Co(L-ala)$_3$]				*mer*-(+)-[Co(L-ala)$_3$]		
0	28.52 (0.03)$^{\rm f)}$	2.3 (0.2)$^{\rm f)}$	−26.2$^{\rm f)}$	0	13.70 (0.01)$^{\rm g)}$	9.1 (0.1)$^{\rm g)}$	−4.6$^{\rm g)}$
0.491	26.64 (0.03)	7.1 (0.3)	−19.5	0.502	13.17 (0.01)	8.0 (0.1)	−5.1
0.998	25.89 (0.02)	6.1 (0.2)	−19.7	1.028	12.77 (0.01)	6.5 (0.1)	−6.2
1.530	25.63 (0.01)	4.5 (0.1)	−21.1	1.548	12.47 (0.01)	5.9 (0.1)	−6.5
2.085	25.13 (0.01)	4.6 (0.1)	−20.5	2.123	12.19 (0.01)	5.3 (0.1)	−6.8
	fac-(+)-[Co(L-ser)$_3$]				*mer*-(+)-[Co(L-ser)$_3$]		
0	23.43 (0.01)$^{\rm h)}$	27.7 (0.3)$^{\rm h)}$	4.3$^{\rm h)}$	0	11.14 (0.05)$^{\rm c)}$	26.1 (0.4)$^{\rm c)}$	15.0$^{\rm c)}$
0.206	21.03 (0.02)	20.8 (0.5)	−0.2	0.501	10.34 (0.07)	22.5 (0.5)	12.2
1.055	17.53 (0.02)	11.4 (0.5)	−6.1	1.051	9.74 (0.07)	20.1 (0.5)	10.4
1.582	18.78 (0.02)	16.2 (0.5)	−2.5	1.630	9.16 (0.06)	12.7 (0.9)	3.6
2.280	17.94 (0.02)	17.7 (0.5)	−0.2	2.407	8.66 (0.04)	9.2 (0.7)	0.6
	fac-[Co(aiba)$_3$]				*mer*-[Co(aiba)$_3$]		
0	16.47 (0.02)$^{\rm i)}$	−15.1 (0.1)$^{\rm i)}$	−31.6$^{\rm i)}$	0	13.48 (0.01)$^{\rm i)}$	−2.3 (0.1)$^{\rm i)}$	−15.8$^{\rm i)}$
0.202	15.80 (0.01)	−14.1 (0.1)	−29.9	0.209	13.49 (0.01)	−1.7 (0.1)	−15.1
0.515	15.27 (0.01)	−13.4 (0.1)	−28.6	0.516	13.47 (0.01)	−1.0 (0.1)	−14.4
0.777	15.01 (0.02)	−12.6 (0.2)	−27.6	0.778	13.52 (0.01)	−0.7 (0.1)	−14.2
1.085	14.89 (0.01)	−11.9 (0.1)	−26.7	1.047	13.56 (0.01)	0.2 (0.1)	−13.3
	[Co(acac)$_3$]						
0	13.80 (0.01)$^{\rm j)}$	−14.3 (0.1)$^{\rm j)}$	−28.1$^{\rm j)}$				
0.209	13.70 (0.02)	−9.7 (0.3)	−23.4				
0.713	14.48 (0.01)	−8.3 (0.3)	−22.8				
1.520	15.40 (0.01)	−4.6 (0.1)	−20.0				
2.520	16.24 (0.01)	−2.8 (0.2)	−19.0				

a) Unit of $\Delta_{\rm dis}G^{\rm o}$, $\Delta_{\rm dis}H^{\rm o}$, and $T\Delta_{\rm dis}S^{\rm o}$ is kJ mol^{-1}. Errors estimated from the standard deviations of least-squares analysis are given in parentheses. b) Calculated from the data reported in Ref. 4. c) Taken from Ref. 5. d) Estimation from the temperature dependence of the solubilities seems to be unreasonable because of the limited temperature range (see text). e) Data in NaBPh$_4$ solutions. f) Calculated from the data reported in Ref. 6. g) Calculated from the data reported in Ref. 1. h) Calculated from the data reported in Ref. 7. i) Taken from Ref. 8. j) Calculated from the data reported in Ref. 9.

$$\Delta_{\rm tr}H^{\rm o} = 1.1 \times T\Delta_{\rm tr}S^{\rm o} - 1.7 \quad (\gamma = 0.9699), \tag{3}$$

where γ is the correlation coefficient. The chelates expressed by Eq. 3 are subject to the salting-in effect of NaClO$_4$ except for *mer*-[Co(aiba)$_3$]. For *mer*-[Co(aiba)$_3$] an excellent compensation relation between $\Delta_{\rm tr}H^{\rm o}$ and $T\Delta_{\rm tr}S^{\rm o}$ is found and its solubility is little affected by the addition of NaClO$_4$, as shown in Fig. 3. For the *mer*-isomers other than *mer*-[Co(aiba)$_3$], the salting-in effect is governed by $\Delta_{\rm tr}H^{\rm o}$ being more negative than $T\Delta_{\rm tr}S^{\rm o}$. The negative $\Delta_{\rm tr}H^{\rm o}$ suggests that an interaction of the *mer*-isomers with their surroundings in NaClO$_4$ solutions is stronger than that in water. At the analogous NaClO$_4$ concentration, $\Delta_{\rm tr}H^{\rm o}$ increases in the order of *mer*-(+)-[Co(L-ser)$_3$] < *mer*-[Co(gly)$_3$] < *mer*-(+)-[Co(L-ala)$_3$] (compare the symbols characterized by the same numbers in Fig. 4). The negative values of $\Delta_{\rm tr}H^{\rm o}$ for *mer*-(+)-[Co(L-ser)$_3$] suggests that the introduction of a polar OH group into the side chain of alanine produces a stronger interaction with the surroundings in NaClO$_4$ solution than in water. Equation 3 implies that a decrease in $T\Delta_{\rm tr}S^{\rm o}$ results in a decrease in $\Delta_{\rm tr}G^{\rm o}$ (Eq. 3 leads to $\Delta_{\rm tr}G^{\rm o} = 0.1 \times T\Delta_{\rm tr}S^{\rm o} - 1.7$). This implication of Eq. 3 is confirmed within each individual *mer*-isomer. Furthermore, the increasing sequence of $\Delta_{\rm tr}G^{\rm o}$ (decreasing sequence of the salting-in effect) for the *mer*-isomer shown in Fig. 4 corresponds to the decreasing sequence of $m_{\rm s}$ (compare Fig. 4 with Fig. 3). In other words, $T\Delta_{\rm tr}S^{\rm o}$ and $\Delta_{\rm tr}H^{\rm o}$ decrease with the increase in $m_{\rm s}$ and the increasing $m_{\rm s}$ results in the pronounced salting-in phenomenon.

For the *fac*-isomers, the above-mentioned implication of Eq. 3 is not necessarily valid. For example, $\Delta_{\rm tr}G^{\rm o}$ for *fac*-[Co(aiba)$_3$] decreases with increasing $T\Delta_{\rm tr}S^{\rm o}$. Furthermore, $\Delta_{\rm tr}H^{\rm o}$ and $T\Delta_{\rm tr}S^{\rm o}$ for *fac*-(+)-[Co(L-ala)$_3$] and *fac*-[Co(aiba)$_3$] are positive. The salting-in effect on these chelates is governed by $T\Delta_{\rm tr}S^{\rm o}$ being more positive than $\Delta_{\rm tr}H^{\rm o}$.

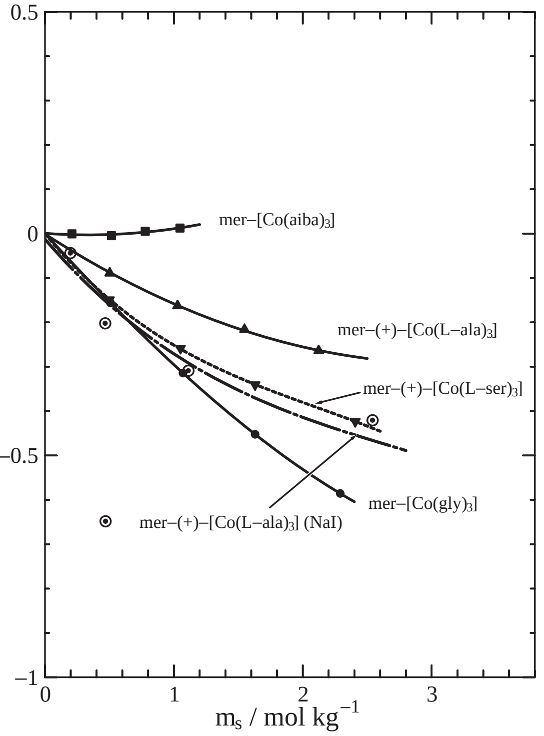

Fig. 3. Effect of $NaClO_4$ on *mer*-isomers of $[Co(gly)_3]$, (+)-[Co(L-ala)$_3$], (+)-[Co(L-ser)$_3$], and $[Co(aiba)_3]$ depicted by plotting $\log(m^0/m)$ against m_s. The lines are tentatively drawn by fitting the $\log(m^0/m)$ values to power series of m_s. The data for *mer*-(+)-[Co(L-ala)$_3$] in aqueous NaI solutions were taken from Ref. 1.

It has been found that NaCl and NaBr bring about the salting-in effect on some $[Co(aa)_3]$.[1] In order to compare the effect of these salts with that of $NaClO_4$, I illustrate the relation between $\Delta_{tr}H^o$ and $T\Delta_{tr}S^o$ for the transfer of some $[Co(aa)_3]$ to these salt solutions in Fig. 5. For comparison, the broken line corresponding to Eq. 3 shown in Fig. 4 is drawn in Fig. 5 as well. While the salting-in effect of NaCl, NaBr, and $NaNO_3$ on *mer*-(+)-[Co(L-ala)$_3$] can be also described by Eq. 3, the experimental points for the *fac*-isomers considerably deviate from Eq. 3. These results suggest that the salting-in effect on the *mer*-isomers of $[Co(aa)_3]$ is brought about by a common origin, which is not connected to the kind of salts, and that sources of the salting-in effect on the *fac*-isomers are dependent on the kind of salts and the kind of side chains in the amino acids of $[Co(aa)_3]$. This diversity of the salting-in effect on *fac*-$[Co(aa)_3]$ may be associated with the large polarity of *fac*-$[Co(aa)_3]$.

On the other hand, for the transfer of *fac*-$[Co(gly)_3]$ to aqueous $NaClO_4$ solutions, the $\Delta_{tr}H^o$ vs $T\Delta_{tr}S^o$ plot gives a separate correlation expressed by

$$\Delta_{tr}H^o = 0.9 \times T\Delta_{tr}S^o + 6.4 \quad (\gamma = 0.9975). \qquad (4)$$

While the large errors in the solubility determination of *fac*-$[Co(gly)_3]$ in $NaClO_4$ solutions make a detailed discussion on Eq. 4 ambiguous, Fig. 4 clearly shows that the salting-out phenomenon of $NaClO_4$ is brought about by an origin characteristic of *fac*-$[Co(gly)_3]$ alone.

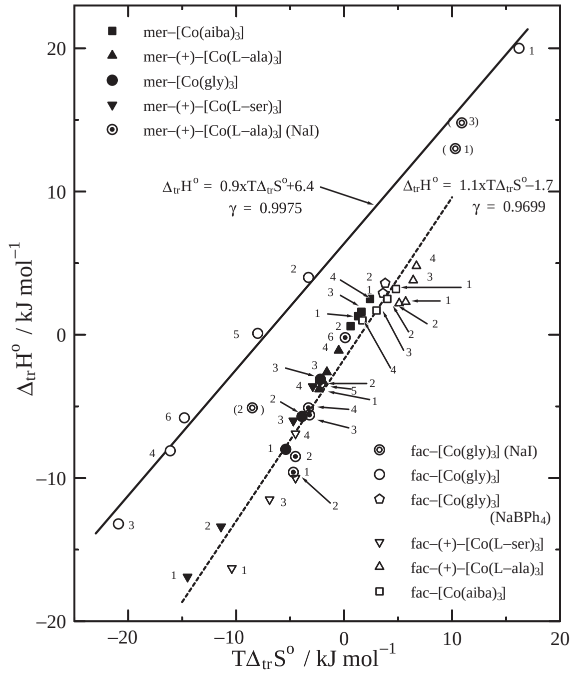

Fig. 4. Correlation between $\Delta_{tr}H^o$ and $T\Delta_{tr}S^o$ for the transfer process of the *fac*- and *mer*-isomers of $[Co(gly)_3]$, (+)-[Co(L-ala)$_3$], (+)-[Co(L-ser)$_3$], and $[Co(aiba)_3]$ from water to aqueous $NaClO_4$ solutions, and for the transfer of *fac*-$[Co(gly)_3]$ from water to aquous $NaBPh_4$ solutions. The data for the transfer of *fac*-$[Co(gly)_3]$ and *mer*-(+)-[Co(L-ala)$_3$] to aqueous NaI solutions, which were taken from Ref. 1, are also illustrated. The data for the transfer to NaI solutions of *fac*-$[Co(gly)_3]$ in the parentheses were excluded from the discussion because of large errors (see text). The numbers given beside the respective marks represent increasing sequence of $\Delta_{tr}G^o$. The broken and solid lines correspond to Eq. 3 and Eq. 4, respectively (see text).

As mentioned in the preceding section, the popular inorganic salts such as NaCl generally produce the salting-out effect on nonpolar non-electrolytes. Long and McDevit have explained that an increase in the energy to produce a cavity required to accommodate the non-electrolyte in water due to the addition of the salt results in the salting-out effect.[11] In order to compare the salting-out phenomenon for *fac*-$[Co(gly)_3]$ with that for $[Co(acac)_3]$, $\Delta_{tr}H^o$ for the transfer of $[Co(acac)_3]$ from water to aqueous $NaClO_4$ solutions is plotted against $T\Delta_{tr}S^o$ in Fig. 6, where the data for the transfer of $[Co(acac)_3]$ to aqueous NaCl and tetraethylammonium bromide (Et_4NBr) solutions are also plotted and the solid line corresponding to Eq. 4 in Fig. 4 is also drawn. For the transfer process of $[Co(acac)_3]$, both $\Delta_{tr}H^o$ and $T\Delta_{tr}S^o$ are positive and increase with increasing m_s. The salting-out effect is governed by $\Delta_{tr}H^o$ being more positive than $T\Delta_{tr}S^o$. This result seems to be consistent with the above-mentioned explanation of Long and McDevit.

On the other hand, for the transfer of *fac*-$[Co(gly)_3]$ to the $NaClO_4$ solutions, $\Delta_{tr}H^o$ and $T\Delta_{tr}S^o$ are positive in the low m_s regions but become negative at m_s higher than 0.5 mol kg^{-1} (see Figs. 2 and 4). This finding indicates that the salting-out effect of $NaClO_4$ on *fac*-$[Co(gly)_3]$ cannot be explained by

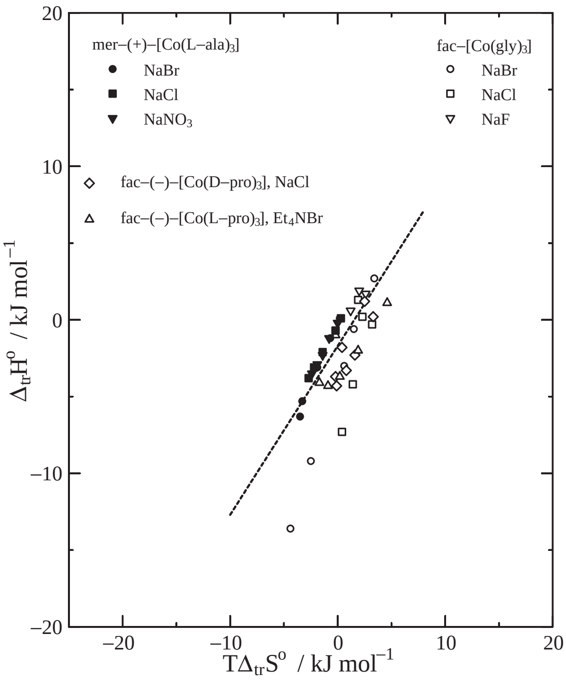

Fig. 5. Correlation between $\Delta_{tr}H^o$ and $T\Delta_{tr}S^o$ for some [Co(aa)$_3$]-salt systems where the salting-in effect has been observed. The data for *fac*-(−)-[Co(D-pro)$_3$] and *fac*-(−)-[Co(L-pro)$_3$], and for the transfer of *fac*-[Co(gly)$_3$] to aqueous NaCl solutions were calculated from the data reported in Ref. 13. The data for *mer*-(+)-[Co(L-ala)$_3$] and for the transfer of *fac*-[Co(gly)$_3$] to aqueous NaBr and NaF solutions were calculated from the data reported in Ref. 1. The broken line is identical with the broken line in Fig. 4.

the idea of Long and McDevit. The salting-out effect of NaClO$_4$ on *fac*-[Co(gly)$_3$] is so intense that the isomerization of *mer*-[Co(gly)$_3$] to the *fac*-isomer is observed at 30 °C in 2.290 mol kg^{-1} NaClO$_4$ solution. Thus, the salting-out of *fac*-[Co(gly)$_3$] by NaClO$_4$ is an extremely peculiar phenomenon and such peculiarity makes it necessary to employ another means in order to clarify the origin of the salting-out effect.

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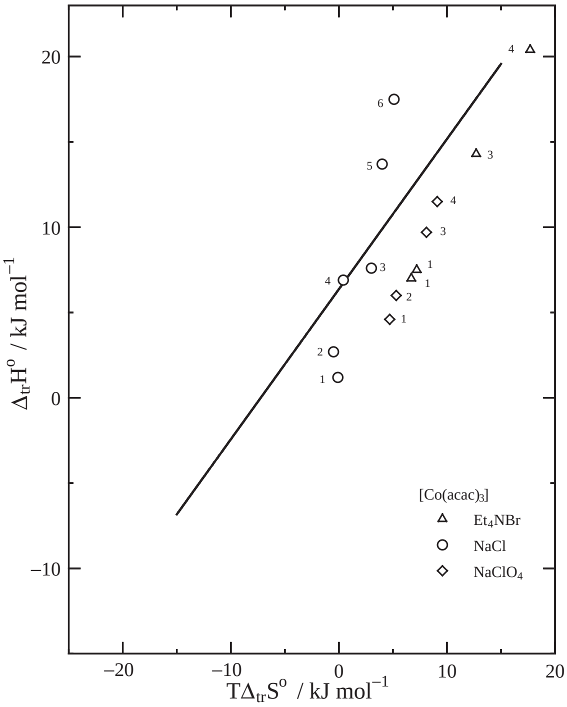

Fig. 6. Correlation between $\Delta_{tr}H^o$ and $T\Delta_{tr}S^o$ for the salting-out phenomenon of [Co(acac)$_3$]. The data for the transfer to aqueous NaCl and Et$_4$NBr solutions were calculated from the data reported in Ref. 13. The numbers given beside the respective marks represent increasing sequence of $\Delta_{tr}G^o$. The solid line is identical with the solid line in Fig. 4.

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