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Solubility Isotherms of Reciprocal Salt-Pairs of Optically Active Cobalt(III) Complexes

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Two kinds of four-component solubility isotherms consisting of (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)–(Cl$^-$, X$^-$)–H$_2$O, where X$^-$ stands for Δ-[Co(edta)]$^-$ or (R,R)-C$_4$H$_5$O$_6$$^-$, have been determined experimentally at 25 °C. It has been found that neither double salt nor solid solution exists and no configurational activity is observed in these systems. The applications of these phase diagrams to the practical optical resolutions are discussed.

Several solubility isotherms of reciprocal salt-pairs which have two cations and two anions such as (Na$^+$, NH$_4$$^+$)–(Cl$^-$, HCO$_3$$^-$)–H$_2$O and (K$^+$, Mg^{2+})–(Cl$^-$, SO$_4$$^{2-}$)–H$_2$O have been reported[1–3] and applied to the alkali industry. However no such isotherm has been reported for the system of metal complexes. The four-component solubility isotherms of reciprocal salt-pairs containing a pair of diastereomers are especially interesting in a viewpoint of optical resolution.

In this connection, some of the three-component solubility isotherms of chiral cobalt(III) complexes have already been reported from our laboratory.[4]

The present paper deals with the solubility isotherms (at 25 °C) of two kinds of reciprocal salt-pairs, (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)–(Cl$^-$, X$^-$)–H$_2$O, where X$^-$ stands for Δ-[Co(edta)]$^-$ or (+)$_{589}$-(R,R)-C$_4$H$_5$O$_6$$^-$ (abbreviated to d-H$_3$tart$^-$). These four-component systems provide the model cases of the optical resolutions of *rac*-[Co(ox)(en)$_2$]Cl with resolving agents containing the chiral anion X$^-$.

Experimental

Materials. [*Co(ox)(en)*$_2$]*X, X*=*Cl*·*H*$_2$*O and* d-*H*$_3$*tart*·n*H*$_2$*O*: Racemic chloride monohydrate and racemic acetate were prepared and optically resolved by the methods of Dwyer *et al.*[5] and Jordan *et al.*,[6] and that improved by Koine.[7] The Δ-[Co(ox)(en)$_2$]Cl·H$_2$O complex was obtained from the filtrate from the less soluble diastereomer Λ-[Co(ox)(en)$_2$](d-H$_3$tart)·H$_2$O in these procedures by adding 12 M HCl, and was optically purified by repeated crystallizations from warm water. The more soluble diastereomer Δ-[Co(ox)(en)$_2$](d-H$_3$tart)·2H$_2$O was prepared from Δ-[Co(ox)(en)$_2$]Cl·H$_2$O, d-H$_4$tart, and Ag$_2$(d-H$_2$tart) in the mole ratio of 2 : 1 : 1, and recrystallized from warm water. Found: C, 26.42; H, 5.56; N, 12.40%. Calcd for Δ-[Co(ox)(en)$_2$](d-H$_3$tart)·2H$_2$O: C, 26.56; H, 5.57; N, 12.39%. The Λ-[Co(ox)(en)$_2$]Cl·H$_2$O complex was obtained by adding 12 M HCl to a warm solution of the less soluble diastereomer.

Δ-*K*[*Co(edta)*]·*2H*$_2$*O*: This complex was resolved by the method of Jordan *et al.*[6] and optically purified by fractional crystallization after treating with a cation exchange resin K$^+$ form.

[*Co(ox)(en)*$_2$]Δ-[*Co(edta)*]·n*H*$_2$*O*: The less soluble diastereomer Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·H$_2$O was obtained by the method of Dwyer *et al.*[5] The more soluble diastereomer was prepared from Λ-[Co(ox)(en)$_2$](CH$_3$COO) and Δ-K[Co(edta)]·2H$_2$O and recrystallized from warm water. Found: C, 28.97; H, 5.11; N, 12.70%. Calcd for Λ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·3H$_2$O: C, 28.75; H, 5.13; N, 12.57%.

Measurements. Solubility was measured at 25 °C as follows: a mixed aqueous solution containing an excess of one, two, or three solid complex salt(s) in a conical flask was stirred mechanically for *ca.* 1.5 h at 25 °C in a thermostat regulated within ±0.1 °C. After the resulting saturated solution had been left to stand for a while, a portion of the supernatant solution was sucked into a weighing bottle through a cotton plug and then weighed. The amount of each ion in the saturated solution was determined as follows. The sample was diluted with water to a known volume, and its optical density and CD were measured. In the cases of containing Δ-[Co(edta)]$^-$ ion, optical densities were measured at 470.0 and 580.0 nm, and CD at 540.5 and 590.0 nm. The concentrations of {Λ-[Co(ox)(en)$_2$]$^+$+Δ-[Co(ox)(en)$_2$]$^+$} and Δ-[Co(edta)]$^-$ were derived from the observed optical densities, referring to the established values for the molar absorption coefficients of the component ions: ε(470.0 nm)=89.1 and ε(580.0 nm)=11.7 for Λ- and Δ-[Co(ox)(en)$_2$]$^+$, and ε(470.0 nm)=93.2 and ε(580.0 nm)=199 for Δ-[Co(edta)]$^-$. The concentrations of {Λ-[Co(ox)(en)$_2$]$^+$−Δ-[Co(ox)(en)$_2$]$^+$} and Δ-[Co(edta)]$^-$ were also derived from the observed CD values, referring to the data: $\Delta\varepsilon$(540.5 nm)=±2.31 and $\Delta\varepsilon$(590.0 nm)=±0.255 for Λ- and Δ-[Co(ox)(en)$_2$]$^+$ (+ and − for Λ and Δ, respectively), and $\Delta\varepsilon$(540.5 nm)=0 and $\Delta\varepsilon$(590.0 nm)=−1.66 for Δ-[Co(edta)]$^-$. The concentrations of Λ- and Δ-[Co(ox)(en)$_2$]$^+$ were separately calculated from those of {Λ-[Co(ox)(en)$_2$]$^+$+Δ-[Co(ox)(en)$_2$]$^+$} and {Λ-[Co(ox)(en)$_2$]$^+$−Δ-[Co(ox)(en)$_2$]$^+$}. The concentration of Δ-[Co(edta)]$^-$ was obtained from the mean values through the absorption and CD measurements. In the cases of not containing Δ-[Co(edta)]$^-$, optical densities and CD of the diluted sample solutions were measured at 497.0 and 523.0 nm, respectively, and the concentrations of Λ- and Δ-[Co(ox)(en)$_2$]$^+$ were separately derived, referring to the data: ε(497.0 nm)=119 and $\Delta\varepsilon$(523.0 nm)=±27.5 for Λ- and Δ-[Co(ox)(en)$_2$]$^+$ (+ and − for Λ and Δ, respectively). In the cases of containing d-H$_3$tart$^-$ and Cl$^-$ ions, a titration method was combined with the spectral one in order to determine the amount of d-H$_3$tart$^-$: the sample solution, which was sucked up and then weighed, was diluted to an appropriate volume and titrated with a 0.01 mol dm^{-3} NaOH solution to the end point of pH jump of the second step dissociation of the dicarboxylic acid.

In these ways, the amounts of all the cations and anions and then the amount of water in the saturated solution were obtained. Thus the concentrations of all the complex salts were calculated in molality. From a few reference experiments, it was confirmed that the optical densities and CD of the present cobalt(III) complex ions were not influenced by the coexistence of the counter ions, and that the absorption or CD value obtained for a mixed solution of several complex ions at a given wavelength was equal to the sum of those measured for the individual complex ions.

The solid phases were identified from the elemental analyses, the absorption and CD spectra, and so on. Optical densities were measured with a JASCO UVIDEC-1 spectrophotometer and CD with a JASCO MOE-1 spectropolarimeter.

Results and Discussion

Definition of Solubility Diagrams of Reciprocal Salt-Pairs. Solubility isotherms of reciprocal salt-pairs, (A^+, B^+)–(X^-, Y^-)–solvent, can be drawn in space as shown in Fig. 1.[1] Four vectors along four axes starting from an origin O show the solubilities of AX, AY, BX, and BY in a solvent. In this definition, the mutual nearest neighbor axes are situated at an angle of 60° and have a common-ion. The angle between an axis and the opposite one becomes 90°. Any saturated solution can be expressed as a point defined by summing up the position vectors of the solubilities of the salts contained. So the points of the solubilities of the binary and ternary systems are situated on the axes and the side faces of the tetragonal pyramid, respectively, except for the two ternary systems such as AX–BY–solvent and AY–BX–solvent which have only the solid phases of $A_pB_{1-p}X_pY_{1-p}\cdot n$(solvent) and $A_qB_{1-q}X_{1-q}Y_q\cdot n'$(solvent), respectively ($0 \leqq p \leqq 1$ and $0 \leqq q \leqq 1$). In the four-component system, there are two ways to attribute a solution to three salts and the solvent, assuming the concentrations of all the salts to be positive; for example, the choice is possible between the sets AX+BX+AY+solvent and AX+BX+BY+solvent. However, the points of these two systems are the same in space, when each axis is graduated in molality.

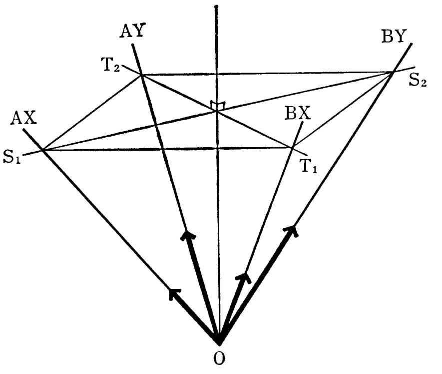

Fig. 1. Solubility diagram of reciprocal salt-pairs (A^+, B^+)-(X^-, Y^-)-solvent.

In this way, the phase diagram of reciprocal salt-pairs is strictly determined,[8] and the isotherms can be drawn by three kinds of plane figures: they are the plane projection on the horizontal base, the side elevation projected by parallel light along S_1S_2 or T_1T_2, and the clinographic projection with a light source at the origin O in Fig. 1. The clinographic projection has the property that the abscissa and ordinate indicate the mole fractions of B^+ and Y^-, respectively, to all the cations or anions (see Figs. 3 and 5).

Solubility Isotherms of (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$–(Cl^-, X^-)–H_2O; X^-=Δ-[Co(edta)]$^-$ and d-*H_3tart$^-$.* The solubility data obtained are given in Tables 1 and 2, and in Figs. 2—5. Neither double salt including racemic compound nor solid solution

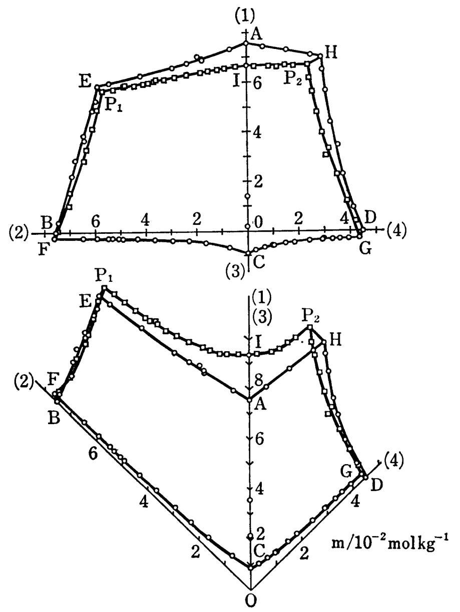

Fig. 2. The plane projection (upper) and the side elevation of the solubility isotherm of the reciprocal salt-pairs (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)-(Cl^-, Δ-[Co(edta)]$^-$)-H_2O at 25 °C: solubility is presented in molality m of anhydrous salt; (1) Λ-[Co(ox)(en)$_2$]Cl, (2) Δ-[Co(ox)(en)$_2$]Cl, (3) Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)], (4) Λ-[Co(ox)(en)$_2$]Δ-[Co(edta)]; □, solubility of four-components; ○, solubility of two- or three-components.

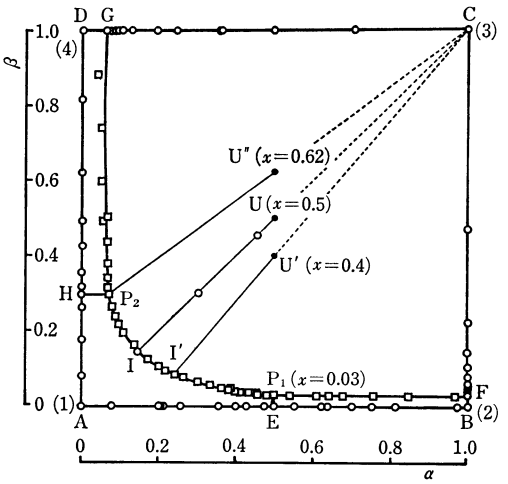

Fig. 3. The clinographic projection of the solubility isotherm of the reciprocal salt-pairs (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$) - (Cl^-, Δ-[Co(edta)]$^-$) - H_2O at 25 °C: α, mole fraction of Δ-[Co(ox)(en)$_2$]$^+$ to all the cations; β, mole fraction of Δ-[Co(edta)]$^-$ to all the anions; (1) Λ-[Co(ox)(en)$_2$]Cl, (2) Δ-[Co(ox)(en)$_2$]Cl, (3) Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)], (4) Λ-[Co(ox)(en)$_2$]Δ-[Co(edta)]; □, solubility of four-components; ○, solubility of two- or three-components.

TABLE 1. EQUILIBRIUM OF (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)-(Cl$^-$, Δ-[Co(edta)]$^-$)-H$_2$O SYSTEM AT 25 °C
In liquid phases, solubility is presented in molality m of anhydrous salt. Abbreviations are as follows: Λ-[Co(ox)(en)$_2$]Cl·H$_2$O = ΛCl, Δ-[Co(ox)(en)$_2$]Cl·H$_2$O = ΔCl, Λ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·3H$_2$O = ΛR$_1$, Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·H$_2$O = ΔR$_1$.

a)	b)	Liquid phase$^{c)}$ $m/10^{-2}$ mol kg^{-1}				Solid phase
		ΛCl	ΔCl	ΛR$_1$	ΔR$_1$	
A	2	7.57 (±0.09)				ΛCl
A↕E	3	7.32	0.63			ΛCl
		6.90	1.75			
		6.96	1.79			
		7.04	1.93			
		6.77	2.34			
		6.58	2.92			
		6.29	4.19			
		6.00	5.44			
B	2		7.57 (±0.09)			ΛCl
B↕E	3	0.41	7.45			ΔC
		1.60	6.98			
		2.24	6.92			
		2.88	6.78			
		3.69	6.42			
		3.90	6.44			
		4.91	6.08			
		5.30	5.96			
E	3	5.89 (±0.10)	5.89 (±0.10)			ΛCl +ΔCl
P$_1$	4	6.06 (±0.11)	5.68 (±0.12)		0.37 (±0.06)	ΛCl +ΔCl +ΔR$_1$
C	2				0.89 (±0.02)	ΔR$_1$
C↕G	3			0.31	0.75	ΔR$_1$
				0.65	0.65	
				0.96	0.55	
				1.02	0.57	
				1.47	0.48	
				1.82	0.44	
				2.42	0.36	
				2.92	0.34	
				2.96	0.32	
				3.31	0.33	
				3.59	0.32	
				3.93	0.30	
D	2			4.49 (±0.04)		ΛR$_1$
G	3			4.33 (±0.01)	0.28 (±0.01)	ΛR$_1$ +ΔR$_1$
G↕P$_2$	4	0.58		4.23	0.20	ΛR$_1$ +ΔR$_1$
		1.46		3.90	0.27	
		2.58		3.51	0.32	
		3.69		3.20	0.38	
		3.48		3.07	0.45	
		4.46		2.93	0.51	
		5.35		2.74	0.58	
		6.21		2.56	0.62	
		6.79		2.45	0.66	
P$_2$	4	7.38 (±0.32)		2.39 (±0.15)	0.72 (±0.15)	ΛCl +ΛR$_1$ +ΔR$_1$
D↕H	3	0.93		4.13		ΛR$_1$
		2.26		3.71		
		3.55		3.43		
		4.38		3.26		
		5.63		3.08		
		6.47		2.97		
A↕H	3	7.44		0.65		ΛCl
		7.28		1.56		
		7.06		2.50		
H	3	6.96 (±0.13)		2.92 (±0.04)		ΛCl +ΛR$_1$
C↕F	3		0.74		0.65	ΔR$_1$
			1.65		0.47	
			2.31		0.39	
			2.94		0.34	
			3.67		0.31	
			4.34		0.27	
			4.93		0.26	
			5.08		0.25	
			5.34		0.24	
			5.49		0.26	
			5.93		0.24	
			6.49		0.23	
F	3		7.65 (±0.07)		0.22 (±0.02)	ΔCl +ΔR$_1$
F↕P$_1$	4	0.27	7.49		0.21	ΔCl +ΔR$_1$
		1.31	7.04		0.23	
		2.25	6.78		0.26	
		3.18	6.44		0.28	
		3.64	6.33		0.29	
		4.50	6.08		0.31	
		5.30	5.94		0.33	
P$_1$↕I	4	6.13	5.27		0.37	ΛCl +ΔR$_1$
		6.25	4.88		0.38	
		6.33	4.80		0.42	
		6.33	4.44		0.42	
		6.39	4.06		0.44	
		6.46	3.86		0.45	
		6.57	3.65		0.54	
		6.59	3.58		0.48	
		6.63	3.25		0.51	
		6.80	2.82		0.57	
		6.95	2.35		0.64	
		7.15	1.80		0.76	
		7.26	1.51		0.81	
		7.40	1.14		0.91	
		7.57	0.86		1.02	
		7.82	0.42		1.20	
I	3	8.02 (±0.08)			1.36 (±0.02)	ΛCl +ΔR$_1$
I↕P$_2$	4	7.89		0.30	1.26	ΛCl +ΔR$_1$
		7.65		0.87	1.01	
		7.54		1.19	0.92	
		7.53		1.51	0.86	
		7.45		1.83	0.80	
C↕I	3	1.18			0.99	ΔR$_1$
		2.49			1.08	

a) Positions of the points in Figs. 2 and 3. In these expressions A↔E, for example, does not contain the points A and E. b) Number of components. c) The values in parentheses are estimated errors and were calculated from twice the standard deviations of the experimental measurements, which were repeated 3—25 times.

TABLE 2. EQUILIBRIUM OF (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)-(Cl$^-$, *d*-H$_3$tart$^-$)-H$_2$O SYSTEM at 25 °C
In liquid phases, solubility is presented in molality *m* of anhydrous salt. Abbreviations are as follows: Λ-[Co(ox)(en)$_2$]Cl·H$_2$O=ΛCl, Δ-[Co(ox)(en)$_2$]Cl·H$_2$O=ΔCl, Λ-[Co(ox)(en)$_2$](*d*-H$_3$tart)·H$_2$O=ΛR$_2$, Δ-[Co(ox)(en)$_2$](*d*-H$_3$tart)·2H$_2$O=ΔR$_2$. The data for A, B, E, A↔E, and B↔E are listed in Table 1.

a)	b)	Liquid phase[c)] m/10^{-2} mol kg^{-1} ΛCl	ΔCl	ΛR$_2$	ΔR$_2$	Solid phase
C	2				10.52	ΔR$_2$
					(±0.11)	
C↔G	3			1.13	10.19	ΔR$_2$
D	2			4.67		ΛR$_2$
D↔G	3			4.26	1.03	ΛR$_2$
				3.84	2.89	
				3.34	4.99	
				3.08	7.00	
				2.85	8.58	
G	3			2.89	9.85	ΛR$_2$ +ΔR$_2$
				(±0.10)	(±0.33)	
G↔P_2	4		0.82	2.91	9.06	ΛR$_2$ +ΔR$_2$
			0.84	2.98	9.16	
			1.73	3.07	8.63	
			2.63	3.25	8.25	
			3.30	3.33	7.98	
			3.99	3.44	7.70	
			5.03	3.48	7.51	
			5.51	3.56	7.21	
			5.90	3.71	7.05	
P_2	4		6.78	3.89	6.69	ΔCl +ΛR$_2$ +ΔR$_2$
			(±0.18)	(±0.14)	(±0.28)	
B↔F	3		7.22		1.10	ΔCl
			6.94		2.16	
			6.58		3.12	
			6.46		4.16	
			6.10		5.57	
			5.78		7.15	
C↔F	3		1.39		9.98	ΔR$_2$
			3.66		9.26	
F	3		5.70		8.84	ΔCl +ΔR$_2$
			(±0.20)		(±0.08)	
F↔P_2	4		6.03	0.93	8.15	ΔCl +ΔR$_2$
			6.07	1.79	7.80	
			6.39	2.77	7.26	
			6.75	3.44	6.84	
E↔P_1	4	5.49	6.23	0.74		ΛCl +ΔCl
		4.98	6.57	1.59		
		4.50	6.78	2.28		
		3.71	7.20	3.48		
		3.17	7.58	4.41		
P_1	4	2.97	7.76	4.78		ΛCl +ΔCl +ΛR$_2$
		(±0.06)	(±0.09)	(±0.05)		
A↔H	3	7.30		0.78		ΛCl
		7.10		1.62		
		7.02		1.96		
		6.80		2.44		
		6.80		2.65		
D↔H	3	1.55		4.12		ΛR$_2$
		2.75		3.74		
		3.41		3.56		
		4.45		3.33		
		5.14		3.23		
H	3	6.72		2.98		ΛCl +ΛR$_2$
		(±0.28)		(±0.04)		
H↔P_1	4	6.27	0.82	3.10		ΛCl +ΛR$_2$
		5.87	1.54	3.27		
		5.55	1.90	3.37		
		5.41	2.35	3.44		
		4.85	3.43	3.73		
		4.61	4.01	3.82		
		4.48	4.38	3.94		
		4.01	5.46	4.17		
		3.44	6.61	4.50		
P_1↔P_2	4[d)]	0.68	8.69	5.72		ΔCl +ΛR$_2$
		0.65	8.74	5.73		
			8.92	5.98	0.14	
			8.84	5.89	0.28	
			8.96	5.92	0.28	
			8.79	5.79	0.46	
			8.61	5.62	0.88	
			8.60	5.66	0.89	
			8.57	5.55	1.17	
			8.49	5.48	1.27	
			8.16	5.24	1.83	
			8.17	5.13	2.10	
			8.10	5.08	2.18	
			8.06	4.99	2.49	
			7.70	4.84	3.06	
			7.62	4.71	3.25	
			7.63	4.64	3.72	
			7.39	4.42	4.48	
			6.83	4.12	5.97	

a) Positions of the points in Figs. 4 and 5. A↔E, for example, does not contain the points A and E. b) Number of components. c) The values in parentheses mean the same in Table 1. d) The point I, where P_1↔P_2 intersects the OBD plane, has exceptionally number of components 3.

exists in these systems. In the areas of AEP$_1$P$_2$H, BFP$_1$E, CGP$_2$P$_1$F, and DHP$_2$G in Figs. 2 and 3, the saturated solutions are in equilibrium with the solids, Λ-[Co(ox)(en)$_2$]Cl·H$_2$O, Δ-[Co(ox)(en)$_2$]Cl·H$_2$O, Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·H$_2$O, and Λ-[Co(ox)(en)$_2$]-Δ-[Co(edta)]·3H$_2$O, respectively. In the areas of AEP$_1$H, BFP$_2$P$_1$E, CGP$_2$F, and DHP$_1$P$_2$G in Figs. 4 and 5, the saturated solutions are in equilibrium with the solids, Λ-[Co(ox)(en)$_2$]Cl·H$_2$O, Δ-[Co(ox)(en)$_2$]-Cl·H$_2$O, Δ-[Co(ox)(en)$_2$](*d*-H$_3$tart)·2H$_2$O, and Λ-[Co-(ox)(en)$_2$](*d*-H$_3$tart)·H$_2$O, respectively.

In the region along the G↔P_2 line (Figs. 3 and 5) which has four-components containing ΛX and ΔX as solid phases (X=R$_1$ or R$_2$, and the abbreviations are the same as those in Tables 1 and 2), it was observed experimentally that the mole ratio of Λ^+ to Δ^+ in

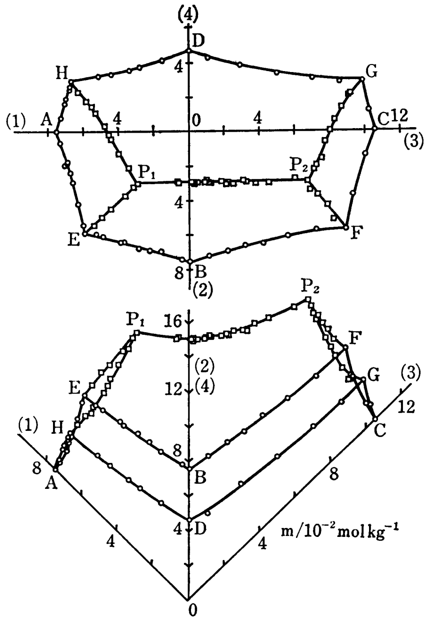

Fig. 4. The plane projection (upper) and the side elevation of the solubility isotherm of the reciprocal salt-pairs (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)-(Cl$^-$, d-H$_3$tart$^-$)-H$_2$O at 25 °C: solubility is presented in molality m of anhydrous salt; (1) Λ-[Co(ox)(en)$_2$]Cl, (2) Δ-[Co(ox)(en)$_2$]Cl, (3) Δ-[Co(ox)(en)$_2$](d-H$_3$tart), (4) Λ-[Co(ox)(en)$_2$](d-H$_3$tart); □, solubility of four-components; ○, solubility of two- or three-components.

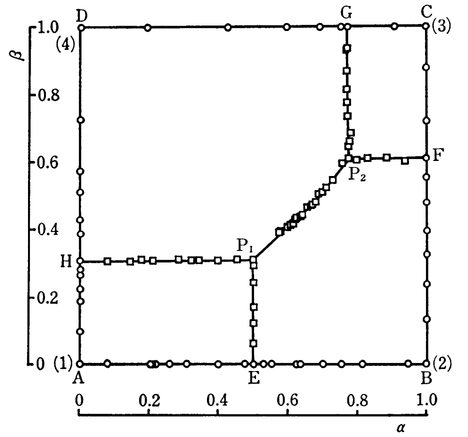

Fig. 5. The clinographic projection of the solubility isotherm of the reciprocal salt-pairs (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)-(Cl$^-$, d-H$_3$tart$^-$)-H$_2$O at 25 °C: α, mole fraction of Δ-[Co(ox)(en)$_2$]$^+$ to all the cations; β, mole fraction of d-H$_3$tart$^-$ to all the anions; (1) Λ-[Co(ox)(en)$_2$]Cl, (2) Δ-[Co(ox)(en)$_2$]Cl, (3) Δ-[Co(ox)(en)$_2$](d-H$_3$tart), (4) Λ-[Co(ox)(en)$_2$](d-H$_3$tart); □, solubility of four-components; ○, solubility of two- or three-components.

the liquid phase was almost constant. The analogous situations exist in the regions of E↔P$_1$, F↔P$_1$ and H↔P$_2$ (X=R$_1$), and E↔P$_1$, H↔P$_1$ and F↔P$_2$ (X=R$_2$). In other words, when two solids having a common-ion are in equilibrium with a solution, the mole ratio between the counter ions in its solution does not change by adding the fourth ion; thus no configurational activity[9–11] was observed in the present systems.

Applications to Optical Resolution. (1) (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)-(Cl$^-$, Δ-[Co(edta)]$^-$)-H$_2$O System: The Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·H$_2$O diastereomer is predominant in the solid phases (Figs. 2 and 3), and this system can be applied successfully to the practical optical resolution. One mole of *rac*-[Co(ox)(en)$_2$]Cl·H$_2$O is dissolved in an excess of water and x mol of Δ-Ag[Co(edta)] is added to it ($0 \leqq x \leqq 1$). After the resulting precipitate AgCl has been filtered off, the filtrate is concentrated at 25 °C. Ignoring the dissolved AgCl, this operation produces just the same condition as that of the above solubility isotherm (Figs. 2 and 3).

There are several cases about the values of x: in the case of $0 \leqq x < 0.03$, the situation corresponds to the region of E↔P$_1$ in Figs. 2 and 3, giving no success in the optical resolution because of the precipitation of the racemic mixture [Co(ox)(en)$_2$]Cl·H$_2$O. The value, $x=0.03$, corresponds to the point P$_1$; the optical resolution is also unsuccessful because of the simultaneous precipitations of the $\Delta+\Lambda$ mixture of [Co(ox)(en)$_2$]Cl·H$_2$O and the diastereomer Δ-[Co(ox)(en)$_2$]Δ-Co[(edta)]·H$_2$O. In the case of $0.03 < x < 0.62$, which relates to the region of P$_1$↔P$_2$, the optical resolution is possible since the precipitation of the diastereomer Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·H$_2$O occurs firstly and that of Λ-[Co(ox)(en)$_2$]Cl·H$_2$O later, but the yield of the pure less soluble diastereomer is not maximum. If an unsaturated solution having the composition U′ ($x=0.4$) in Fig. 3 is concentrated at the constant temperature 25 °C, the composition of the solution will remain at the point U′ so long as the solution is unsaturated. When the solution becomes saturated, the precipitation of the less soluble diastereomer will appear in this system and the point will move along the line U′→I′. At the point I′ the second precipitation Λ-[Co(ox)(en)$_2$]Cl·H$_2$O will begin to appear, and the trace of the point will proceed along I′→P$_1$. Finally at the invariant point P$_1$ the third solid Δ-[Co(ox)(en)$_2$]Cl·H$_2$O will appear. If we start from the point U ($x=0.5$), the solution composition will finally reach the point I (the invariant point in the ternary system, Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)]-Λ-[Co(ox)(en)$_2$]Cl-H$_2$O), and then the composition of the liquid phase will never change. And if we start from U″ ($x=0.62$), the solution composition will finally reach the invariant point P$_2$, where the solids, Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·H$_2$O, Λ-[Co(ox)(en)$_2$]Cl·H$_2$O, and Λ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·3H$_2$O, coexist. The yield of the pure less soluble diastereomer will become maximum in the range $0.62 \leqq x \leqq 1$. From the viewpoint of saving the resolving agent, the condition, $x=0.62$, which relates to the point P$_2$ is the most desirable. The calculated yield of the pure diastereomer is 93% of Δ-[Co(ox)(en)$_2$]$^+$ (47% of the racemic one).

It has been reported that the solubility ratio of Λ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·3H$_2$O to Δ-[Co(ox)(en)$_2$]Δ-[Co(edta)]·H$_2$O in the ternary system becomes larger with increasing temperature.[4] Therefore, more desirable conditions of the optical resolution may be found at higher temperatures.

(2) (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)–(Cl$^-$, d-H$_3$tart$^-$)–H$_2$O System: In this system (Figs. 4 and 5), all the complex salts have comparable solubilities in contrast to the case (1) containing Δ-[Co(edta)]$^-$ ion. This system can be also applied in the same manner as mentioned above; the resolving agents practically used are $x/2$ mol of d-H$_4$tart and $x/2$ mol of Ag$_2$(d-H$_2$tart). The optical resolution will be successful in the range $0.31 < x \leqq 1$ which correlates to the regions of $P_1 \leftrightarrow P_2$ and $P_2 \leftrightarrow G$ in Figs. 4 and 5. The yield of the pure less soluble diastereomer becomes maximum in the range $0.75 \leqq x \leqq 1$ and reaches 71% of Λ-[Co(ox)(en)$_2$]$^+$ (35% of the racemic one).

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