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Optical Resolution and Ternary System Solubility Isotherms of Cobalt(III) Complex Salts

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The characteristics of three-component phase diagrams consisting of water and a pair of enantiomeric or diastereomeric cobalt(III) complex salts have been clarified experimentally by constructing the solubility isotherms of the following 6 ternary systems at 25 °C: H_2O–Δ-$[Co(ox)(en)_2]X$–Λ-$[Co(ox)(en)_2]X$, where X stands for Cl^-, I^-, (R,R)-$C_4H_5O_6^-$, Δ-$[Co(edta)]^-$, $^1/_2[Sb_2\{(R,R)\text{-}C_4H_2O_6\}_2]^{2-}$ or d-$C_{10}H_{14}OBrSO_3^-$. It has been found that the latter two anions form an active racemate, *rac*-$[Co(ox)(en)_2]_2[Sb_2\{(R,R)\text{-}C_4H_2O_6\}_2]\cdot 5H_2O$ and *rac*-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot H_2O$, respectively. Solubility of the $[Co(ox)(en)_2]^+$ salts containing optically active counterions was determined at 5—60 °C in water.

The solubility isotherm for a multi-component system consisting of an optically inactive solvent and a pair of enantiomers or diastereomers seems to give useful information on optical resolution.[1,2] However, no such isotherm seems to have been reported for the system of metal complexes and water. The present paper deals with some solubility isotherms for the ternary systems, H_2O–Δ-$[Co(ox)(en)_2]X$–Λ-$[Co(ox)(en)_2]X$, where X stands for univalent anions such as (a) Cl^-, (b) I^-, (c) (R,R)-$C_4H_5O_6^-$, (d) Δ-$[Co(edta)]^-$, (e) $^1/_2[Sb_2\{(R,R)\text{-}C_4H_2O_6\}_2]^{2-}$ or (f) d-$C_{10}H_{14}OBrSO_3^-$. The monohydrate and tetrahydrate of the chloride (a) are spontaneously resolved,[3-5] but the iodide (b) forms a solid racemic compound.[4] Anions (c) and (d) represent the successful cases of optical resolution, and (e) and (f) the unsuccessful ones.

Experimental

Materials. *$[Co(ox)(en)_2]I$*: Racemic chloride monohydrate was prepared by the method of Dwyer *et al.*[6] and was optically resolved by two kinds of resolving agents: $(+)_{589}$-(R,R)-tartrate(1−) ion (abbreviated to d-$C_4H_5O_6^-$), which gave the $\Lambda(+)_{589}$ iodide through the less soluble diastereomer Λ-$[Co(ox)(en)_2](d\text{-}C_4H_5O_6)\cdot H_2O$,[7] and $\Delta(+)_{546}$-$[Co(edta)]^-$, which gave the $\Delta(-)_{589}$ iodide through the less soluble diastereomer Δ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]\cdot H_2O$. The Λ-$(+)_{589}$ iodide showed $\Delta\varepsilon_{523} = +2.55$ (lit,[7] $\Delta\varepsilon_{520} = +2.64$), and the $\Delta(-)_{589}$ iodide −2.53.

$[Co(ox)(en)_2]Cl\cdot H_2O$: The recemic complex was also prepared by the method of Dwyer *et al.* The $\Lambda(+)_{589}$ and $\Delta(-)_{589}$ isomers were obtained from the corresponding iodides by treating with AgCl; $\Delta\varepsilon_{523} = +2.57$ and −2.60, respectively.

$[Co(ox)(en)_2]$(d-$C_4H_5O_6$)$\cdot nH_2O$: The Λ-complex salt monohydrate was obtained by the method of Jordan *et al.*,[7] and recrystallized from water; $\Delta\varepsilon_{523} = +2.60$ (lit,[7] $\Delta\varepsilon_{520} = +2.65$). Found: C, 27.46; H, 5.36; N, 12.89%. Calcd for Λ-$[Co(ox)(en)_2](d\text{-}C_4H_5O_6)\cdot H_2O$: C, 27.65; H, 5.35; N, 12.90%. The Δ-complex salt 2.5-hydrate was separated by the method of Froebe[8] from the filtrate from the Λ-complex diastereomer in the procedure of Jordan *et al.*[7] and purified by repeated recrystallizations from hot water; $\Delta\varepsilon_{523} = -2.67$, the yield was almost 1/10 of the corresponding Λ-complex diastereomer. Found: C, 26.20; H, 5.67; N, 11.95%. Calcd for Δ-$[Co(ox)(en)_2](d\text{-}C_4H_5O_6)\cdot 2.5H_2O$: C, 26.03; H. 5.69; N, 12.15%.

$[Co(ox)(en)_2]_2[Sb_2$(d-$C_4H_2O_6)_2]\cdot nH_2O$: The diastereomers were obtained by the reaction of an aqueous suspension (0.1 mol, 50 °C) of $\Lambda(+)_{589}$- or $\Delta(-)_{589}$-$[Co(ox)(en)_2]I$, or *rac*-$[Co(ox)(en)_2]Cl\cdot H_2O$ with freshly prepared silver antimony(III) $(+)_{589}$-tartrate, which was precipitated in advance from a cold aqueous solution of tatar emetic $K_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 3H_2O$ (0.05 mol) by adding the equivalent amount of silver nitrate solution. Recrystallization was carried out from warm water; $\Delta\varepsilon_{523}$ per the complex cation was +2.59, −2.48, and 0 for the Λ-, Δ-, and *rac*-complex diastereomers, respectively. Found: C, 19.82; H, 4.04; N, 9.58%. Calcd for Λ-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 6H_2O$: C, 20.39; H, 4.12; N, 9.51%. Found: C, 20.56; H, 3.85; N, 9.56%. Calcd for Δ-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 4H_2O$: C, 21.03; H, 3.89; N, 9.81%. Found: C, 20.21; H, 4.02; N, 9.76%. Calcd for *rac*-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 5H_2O$: C, 20.71; H, 4.00; N, 9.66%.

$[Co(ox)(en)_2]$(d-$C_{10}H_{14}OBrSO_3)\cdot nH_2O$: Ammonium $(+)_{589}$-$(1R,3S,4S,7R)$-3-bromocamphor-9-sulfonate (the anion is abbreviated to d-$C_{10}H_{14}OBrSO_3^-$) was converted into silver salt by treatment with silver nitrate in a cold aqueous solution. The $\Lambda(+)_{589}$- or $\Delta(-)_{589}$-$[Co(ox)(en)_2]I$, or *rac*-$[Co(ox)(en)_2]Cl\cdot H_2O$ was suspended in warm water and treated with Ag(d-$C_{10}H_{14}OBrSO_3$). The diastereomers obtained were recrystallized from warm water; $\Delta\varepsilon_{523} = +2.54$, −2.58, and 0 for the Λ-, Δ-, and *rac*-complex diastereomers, respectively. Anal. Found: C, 31.56; H, 5.42; N, 9.83%. Calcd for Λ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot H_2O$: C, 32.27; H, 5.43; N, 9.41%. Found: C, 30.74; H, 5.66; N, 9.01%. Calcd for Δ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot 2.5H_2O$: C, 30.87; H, 5.68; N, 9.00%. Found: C, 32.00; H, 5.46; N, 9.52%. Calcd for *rac*-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot H_2O$: C, 32.27, H, 5.43; N, 9.41%.

$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]\cdot nH_2O$: The less soluble diastereomer was obtained by the method of Dwyer *et al.*;[6] $[\alpha]_{589} = -550°$ (lit,[6] +550° for the enantiomer trihydrate). Found: C, 30.30; H, 4.77; N, 13.35%. Calcd for Δ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]\cdot H_2O$: C, 30.39; H, 4.78; N, 13.29%.

The more soluble diastereomer was prepared from Λ-[Co-

TABLE 1. ABSORPTION AND CIRCULAR DICHROISM MAXIMUM VALUES OF $[Co(ox)(en)_2]X$ SALTS USED FOR CALCULATION OF SOLUBILITY

X	ε at 497 nm	$\Delta\varepsilon$ at 523 nm
Cl^-	117	±2.60
I^-	122	±2.55
d-$C_4H_5O_6^-$	123	±2.67
$1/2[Sb_2(d\text{-}C_4H_2O_6)_2]^{2-}$	116	±2.59
d-$C_{10}H_{14}OBrSO_3^-$	119	±2.58
Δ-$[Co(edta)]^-$	398[a]	—

a) at 524 nm.

TABLE 2. SOLUBILITY OF THE $[Co(ox)(en)_2]^+$ SALTS CONTAINING OPTICALLY ACTIVE COUNTER-IONS (grams of anhydrous salt in 100 grams of water)

Temp (°C)	No. of salt[a)]										
	1	2	3	4	5	6	7	8	9	10	11
5	0.98	2.93	1.21	0.291	3.59	2.58	0.907	3.88	—		3.00
10	1.14	3.46	1.46	0.341	4.12	2.73	1.04	4.25	1.76[b)]		3.20
15	1.37	4.10	1.86	0.403	4.80	3.00	1.20	4.67	2.13		3.52
20	1.62	4.79	2.21	0.475	5.43	3.30	1.35	5.09	2.49		3.78
25	1.87	5.60	2.79	0.556	6.25	3.67	1.53	5.53	2.97		4.23
30	2.16	6.57	3.47	0.657	7.15	3.92	1.75	6.09	3.50		4.58
35	2.54	7.74	4.24	0.766	8.21	4.40	2.03	6.86	4.02		5.09
40	3.05	8.92	5.26	0.864	9.50	4.76	2.30	7.54		4.39	5.57
45	3.47	10.5	6.38	1.01	10.98	5.27	2.57	8.33		4.83	6.10
50	4.01	—	7.97	1.14	12.66	5.85	2.94	9.19		5.31	6.82
55	4.59	13.5	9.58	1.26	14.54	6.50	3.35	10.3		5.76	7.59
60	5.21	15.5	11.2	1.35	16.78	7.17	3.79	11.7		6.42	8.36

a) 1: Λ-$[Co(ox)(en)_2](d\text{-}C_4H_5O_6)\cdot H_2O$, 2: Δ-$[Co(ox)(en)_2](d\text{-}C_4H_5O_6)\cdot 2.5H_2O$, 3: Λ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]\cdot 2.5H_2O$, 4: Δ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]\cdot H_2O$, 5: Λ-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 6H_2O$, 6: Δ-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 4H_2O$, 7: *rac*-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 5H_2O$, 8: Λ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot H_2O$, 9: Δ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot 4H_2O$, 10: Δ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot 2.5H_2O$, 11: *rac*-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot H_2O$. b) At 8 °C.

$(ox)(en)_2]I$ and Δ-$Ag[Co(edta)]$, the latter being obtained by the method given by Maricondi and Douglas.[9)] Recrystallization was carried out from warm water; $\Delta\varepsilon_{538}=+2.25$. Found: C, 28.42; H, 5.07; N, 12.53%. Calcd for Δ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]\cdot 3H_2O$: C, 28.75; H, 5.13; N, 12.57%.

Measurements. Mutual solubility of the Δ and Λ complex salts in water was measured at 25 °C as follows: A mixed aqueous solution of the Δ and Λ complex salts containing an excess of the solid complex salt(s) in a conical flask was stirred mechanically for about 2 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. This was diluted to a known volume, and its optical density and CD were measured at the wave lengths 497 and 523 nm, respectively, except for the case of $X=\Delta$-$[Co(edta)]^-$. The optical density value is related to the total amount of enantiomers (or diastereomers) and the CD value the difference in amounts of Δ and Λ complexes, since no counter ions influence the absorption or CD spectra in the visible region regardless of whether they are optically active or not. Thus, the absorption and CD maximum values of the complex salts (Table 1) enable us to calculate the amounts of both Δ and Λ complexes separately.

In the case of $X=\Delta$-$[Co(edta)]^-$, the total amount of diastereomers was calculated from the observed optical density at 524 nm, where the absorption maximum of $[Co(ox)(en)_2]$-$[Co(edta)]$ salt lies, and the difference in the amount of diastereomers from the observed CD at 538 nm, where the CD curve of Δ-$[Co(edta)]^-$ ion intersects the zero line; the complex salt has a value of $\Delta\varepsilon=\pm 2.25$ at this wavelength. The observed CD value at 561 nm, where the CD curve of Λ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]$ diastereomer intersects the zero line, was also used for calculation of the dissolved amount of the Δ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]$ diastereomer.

The solid phases were identified from the elemental analyses and measurements of CD or optical rotation (solvent: H_2O). The solubility of complexes in water at 5—60 °C (Table 2) was determined in the same way as previously reported.[4)] Optical densities were measured with a Jasco UVIDEC-1 spectrophotometer, CD with a Jasco MOE-1 spectropolarimeter, and optical rotation with a Jasco DIP-4 digital polarimeter.

Results and Discussion

The ternary system data obtained are given in Table 3 and Figs. 1—6. In the triangular isotherms the top part (H_2O corner) is enlarged for the sake of convenience and the tie lines omitted.

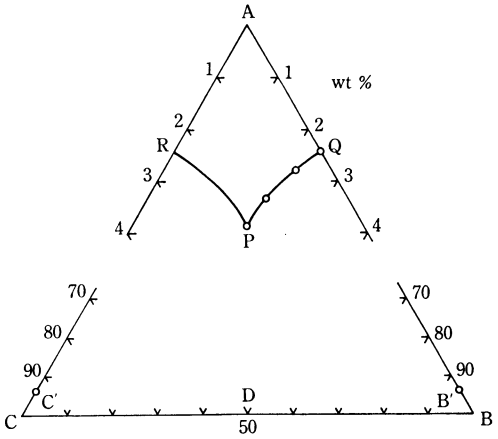

Fig. 1. Solubility isotherm of the ternary system H_2O-(A)-Δ-$[Co(ox)(en)_2]Cl$(B)-Λ-$[Co(ox)(en)_2]Cl$(C) at 25 °C. The solid phase B′ or C′ is monohydrate of B or C, respectively.

Spontaneous Resolution. $[Co(ox)(en)_2]Cl$: Figure 1 shows the ternary phase diagram at 25 °C for the system consisting of Δ and Λ isomers of chloride and water. One invariant point P is found. The triangular area PB′C′ represents the compositions consisting of Δ chloride monohydrate, Λ chloride monohydrate and a saturated solution of composition P, which is identical to a saturated solution of the racemic complex. This is the case of spontaneous resolution. The molar solubility in point P should be identical to or larger than $\sqrt{2}/2$ of that in point Q or R.[4)]

Table 3. Solubility in the ternary systems, H_2O-Δ-[Co(ox)(en)$_2$]X-Λ-[Co(ox)(en)$_2$]X, at 25 °C

X	Liquid phase composition (wt %)		Solid phase
	Δ-salt	Λ-salt	
Cl⁻	2.43	0	Δ-[ ]X·H_2O
	2.17	0.62	Δ-[ ]X·H_2O
	1.99	1.36	Δ-[ ]X·H_2O
	1.91	1.91	Δ-[ ]X·H_2O+Λ-[ ]X·H_2O
I⁻	0.41	0	Δ-[ ]X
	0.40	0.01	Δ-[ ]X+*rac*-[ ]X
	0.21	0.02	*rac*-[ ]X
	0.13	0.06	*rac*-[ ]X
	0.08	0.10	*rac*-[ ]X
	0.05	0.15	*rac*-[ ]X
	0.02	0.24	*rac*-[ ]X
	0.01	0.34	*rac*-[ ]X
	0.01	0.40	Λ-[ ]X+*rac*-[ ]X
	0	0.41	Λ-[ ]X
d-$C_4H_5O_6^-$	5.29	0	Δ-[ ]X·2.5H_2O
	5.07	0.64	Δ-[ ]X·2.5H_2O
	4.99	1.06	Δ-[ ]X·2.5H_2O+ Λ-[ ]·H_2O
	3.79	1.09	Λ-[ ]X·H_2O
	2.73	1.23	Λ-[ ]X·H_2O
	1.43	1.48	Λ-[ ]X·H_2O
	0.03	1.92	Λ-[ ]X·H_2O
Δ-[Co-(edta)]⁻	0.52	0.04	Δ-[ ]X·H_2O
	0.41	0.39	Δ-[ ]X·H_2O
	0.36	0.67	Δ-[ ]X·H_2O
	0.29	1.26	Δ-[ ]X·H_2O
	0.26	1.70	Δ-[ ]X·H_2O
	0.20	2.68	Δ-[ ]X·H_2O+ Λ-[ ]X·2.5H_2O
	0	2.72	Λ-[ ]X·2.5H_2O
1/2[Sb_2(*d*-$C_4H_2O_6$)$_2$]$^{2-}$	3.51	0.04	Δ-[ ]X·2H_2O
	3.51	0.20	Δ-[ ]X·2H_2O+ *rac*-[ ]X·2.5H_2O
	2.46	0.24	*rac*-[ ]X·2.5H_2O
	1.45	0.39	*rac*-[ ]X·2.5H_2O
	0.89	0.68	*rac*-[ ]X·2.5H_2O
	0.61	0.90	*rac*-[ ]X·2.5H_2O
	0.48	1.25	*rac*-[ ]X·2.5H_2O
	0.17	3.51	*rac*-[ ]X·2.5H_2O
	0.12	5.08	*rac*-[ ]X·2.5H_2O
	0.12	5.73	Λ-[ ]X·3H_2O+ *rac*-[ ]X·2.5H_2O
	0	5.75	Λ-[ ]X·3H_2O
d-$C_{10}H_{14}$-$OBrSO_3^-$	2.88	0	Δ-[ ]X·4H_2O
	2.78	1.18	Δ-[ ]X·4H_2O
	2.70	1.48	Δ-[ ]X·4H_2O+ *rac*-[ ]X·H_2O
	2.35	1.81	*rac*-[ ]X·H_2O
	1.90	2.33	*rac*-[ ]X·H_2O
	1.40	2.98	*rac*-[ ]X·H_2O
	1.10	3.65	*rac*-[ ]X·H_2O
	0.88	4.35	*rac*-[ ]X·H_2O
	0.92	4.70	Λ-[ ]X·H_2O+ *rac*-[ ]X·H_2O
	0.06	5.12	Λ-[ ]X·H_2O

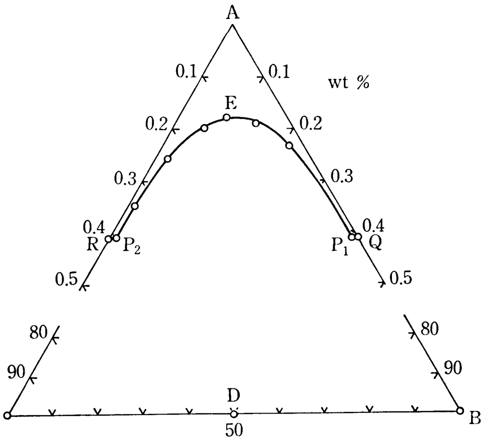

Fig. 2. Solubility isotherm of the ternary system H_2O-(A)-Δ-[Co(ox)(en)$_2$]I(B)-Λ-[Co(ox)(en)$_2$]I(C) at 25 °C.

Formation of Racemic Compound. [*Co*(*ox*)(*en*)$_2$]*I*: Figure 2 shows the case of Δ and Λ isomers of iodide and water. Two invariant points P_1 and P_2 appear, the curve P_1EP_2 representing the solubility of the racemic compound Δ-[Co(ox)(en)$_2$]I·Λ-[Co(ox)(en)$_2$]I (D). The solubility curve of the Δ or Λ complex, QP_1 or RP_2, is greatly suppressed in the diagram.

Optical Resolution by Solubility Difference between Diastereomers. [*Co*(*ox*)(*en*)$_2$]*X*(*X*=d-$C_4H_5O_6^-$ *and* Δ-[*Co*(*edta*)]⁻): The optically active [Co(ox)(en)$_2$]⁺ ion was first obtained by the substitution reaction[10] of optically active *cis*-[$CoCl_2$(en)$_2$]⁺ with oxalate ion, or by preferential crystallization by seeding[11] some optically active complex salts into a concentrated aqueous solution of the racemic bromide [Co(ox)(en)$_2$]Br. The optical resolution through its diastereomer was first performed by Dwyer *et al.*[6] with the use of optically active [Co(edta)]⁻ ion as the resolving agent. Later, Jordan *et al.*[7] reported a fine procedure of resolution through the (+)$_{589}$-tartrate(1−) diastereomer, [Co(ox)(en)$_2$](*d*-$C_4H_5O_6$).

Figure 3 shows the isotherm for the complex of X= *d*-$C_4H_5O_6^-$. Invariant point P appears near the right

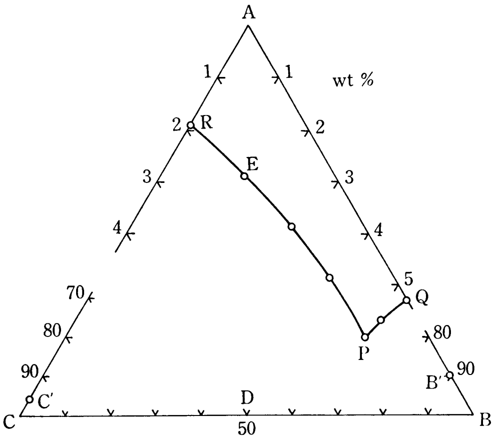

Fig. 3. Solubility isotherm of the ternary system H_2O-(A)-Δ-[Co(ox)(en)$_2$](*d*-$C_4H_5O_6$)(B)-Λ-[Co(ox)(en)$_2$](*d*-$C_4H_5O_6$) (C) at 25 °C. The solid phase B′ is 2.5 hydrate of B, and C′ monohydrate of C.

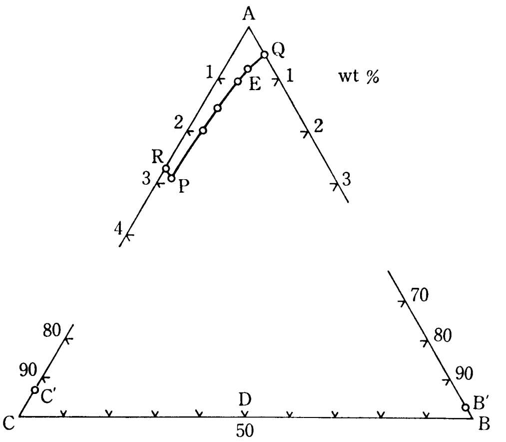

Fig. 4. Solubility isotherm of the ternary system H_2O(A)-Δ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]$(B)-$\Lambda$-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(edta)]$(C) at 25 °C. The solid phase B′ is monohydrate of B, and C′ 2.5 hydrate of C.

hand side. If an aqueous solution of equimolar mixture of the two diastereomers is concentrated at this temperature, the less soluble diastereomer Λ-$[Co(ox)(en)_2](d\text{-}C_4H_5O_6)\cdot H_2O$ would crystallize out first and the solution composition would change along the solubility curve EP. The solid phase consists of both the diastereomers at P. Figure 4 shows the case of $X=\Delta$-$[Co(edta)]^-$, the invariant point P appearing near the left hand side. It is expected that the nearer the invariant point to the right or left hand side, the higher the relative yield of the less soluble diastereomer. The relative composition of the saturated solution at point P is $\Delta:\Lambda=3.75:50$ and $50:10.6$ for the $X=\Delta$-$[Co(edta)]^-$ and $X=d\text{-}C_4H_5O_6^-$, respectively.

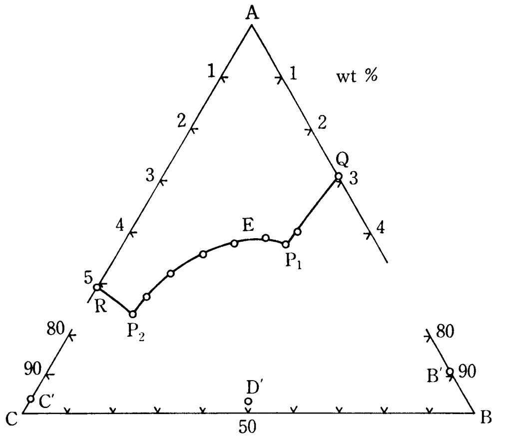

Fig. 5. Solubility isotherm of the ternary system H_2O(A)-Δ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)$(B)-$\Lambda$-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)$(C) at 25 °C. The solid phase B′ is tetrahydrate of B, C′ monohydrate of C, and D′ *rac*-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot H_2O$.

Optically Active Racemate Formed between Diastereomers. $[Co(ox)(en)_2]X$ $(X={}^1/_2[Sb_2(d\text{-}C_4H_2O_6)_2]^{2-}$ and $d\text{-}C_{10}H_{14}OBrSO_3^-)$: Figure 5 shows the isotherm for the system consisting of Δ and Λ diastereomers of the $(+)_{589}$-$(1R,3S,4S,7R)$-3-bromocamphor-9-sulfonate salt and water. Two invariant points P_1 and P_2 appear, the curve P_1EP_2 representing the solubility of a new solid compound formed between the two diastereomers. This solid compound was isolated from the system and characterized by elemental analysis, visible and ultraviolet absorption, CD, ORD, and IR spectra. It was confirmed that the compound is an optically active racemate, Δ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot\Lambda$-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot 2H_2O=$ *rac*-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)\cdot H_2O$. The same compound was obtained by treating *rac*-$[Co(ox)(en)_2]Cl\cdot H_2O$ with silver *d*-bromocamphorsulfonate (see Experimental). If an aqueous solution of this active racemate is concentrated at 25 °C, its composition would change along AE (Fig. 5) and the racemate monohydrate (D′) would crystallize out at point E. Thus the separation of Δ and Λ diastereomers by fractional crystallization is impossible, though the solubility of the two diastereomers in water differs greatly (Table 2).

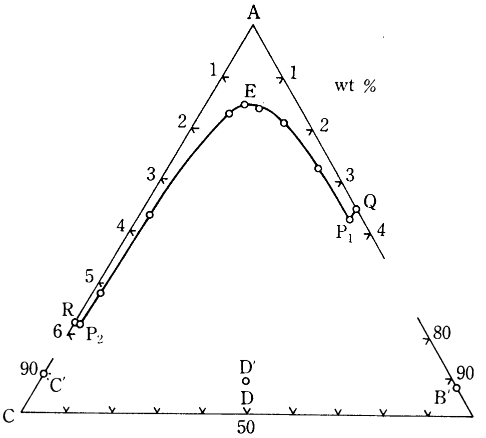

Fig. 6. Solubility isotherm of the ternary system H_2O(A)-Δ-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]$(B)-$\Lambda$-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]$(C) at 25 °C. The solid phase B′ is tetrahydrate of B, C′ hexahydrate of C, and D′ *rac*-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 5H_2O$.

Figure 6 shows the case of $X={}^1/_2[Sb_2(d\text{-}C_4H_2O_6)_2]^{2-}$. Here, the solubility curve of the active racemate is spread over a wide region and those of the pure Δ and Λ diastereomers are much suppressed. The racemate has the composition Δ-$[Co(ox)(en)_2]\cdot\Lambda$-$[Co(ox)(en)_2]\cdot[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 5H_2O=$ *rac*-$[Co(ox)(en)_2]_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 5H_2O$.

It is generally thought that the so-called inadequate resolving agent is the one which gives a pair of diastereomers with a smaller difference in solubility. The present solubility data, however, show that the formation of an optically active racemate is also an important cause for unsuccessful optical resolution. A few such active racemates have been reported: a *d*-tartrate(2−) racemate, *rac*-$[Co(en)_2(1,10\text{-phenanthroline})]_2(d\text{-}C_4H_4O_6)_3\cdot 9H_2O$, which has been named by Jaeger[12] a "partial racemoid."

Temperature Dependence of Solubility in Water. Table 2 shows temperature dependence of solubility of the $[Co(ox)(en)_2]^+$ salts containing optically active counter ions in water. Most of the salts show a temperature dependence similar to that of the halide salts.[4] Thus the solubility at 25 and 60 °C is 1.5—2 and 3—5 times larger than that at 5 °C, respectively. An exceptional case is found in Λ-[Co(ox)(en)$_2$]$\cdot\Delta$-[Co(edta)]$\cdot$2.5H$_2$O, its solubility at 60 °C being about 9 times greater than that at 5 °C. The solubility difference between the Δ and Λ diastereomers of Δ-[Co(edta)]$^-$ salt becomes very large at higher temperatures.

The solubility curve of Δ-[Co(ox)(en)$_2$](*d*-C$_{10}$H$_{14}$-OBrSO$_3$) has an inflection point at about 35 °C, where the solid phase changes from 4-hydrate (below 35 °C) to 2.5-hydrate (above 35 °C). However, no such inflection was found in the corresponding Λ diastereomer or the active racemate. The solid phases of both salts consist of the monohydrate in 5—60 °C.

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