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Solubility Isotherm of Reciprocal Salt-Pairs Containing Bis(ethylenediamine)oxalatocobalt(III) (1*R*,3*S*,4*S*,7*R*)-3-Bromocamphor-9-sulfonate

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Four-component solubility isotherm of reciprocal salt-pairs consisting of (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)–(Cl$^-$, *d*-$C_{10}H_{14}OBrSO_3^-$)–H_2O has been determined experimentally at 25 °C. It was found that a pseudoracemate, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-$C_{10}H_{14}OBrSO_3$)$_2$·$2H_2O$, is present as the only double salt, optical resolution of the bis(ethylenediamine)oxalatocobalt(III) ion in this system at 25 °C being impossible as in the case of the ternary system, Λ-[Co(ox)(en)$_2$](*d*-$C_{10}H_{14}OBrSO_3$)–Δ-[Co(ox)(en)$_2$](*d*-$C_{10}H_{14}OBrSO_3$)–H_2O, at 25 °C.

The (1*R*,3*S*,4*S*,7*R*)-3-bromocamphor-9-sulfonate(1−) anion, *d*-$C_{10}H_{14}OBrSO_3^-$ (abbreviated to *d*-bcs$^-$) is known as one of the most effective resolving agents for metal complexes. It was concluded from a study on the solubility isotherm of a ternary system, Λ-[Co(ox)(en)$_2$](*d*-bcs)–Δ-[Co(ox)(en)$_2$](*d*-bcs)–H_2O, that the resolving agent is unsuitable to the optical resolution of bis(ethylenediamine)oxalatocobalt(III) complex, [Co(ox)(en)$_2$]$^+$, at 25 °C because of the formation of a pseudoracemate, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·$2H_2O$.[1] Recently, we have found that the optical resolution is possible at temperatures lower than 19 °C, in spite of the existence of the pseudoracemate in the ternary system.[2] Nevertheless, it is interesting to see in which way the pseudoracemate behaves to prevent the optical resolution in a four-component system, since no four component system containing a pseudoracemate has been studied in view of solubility phase diagrams and their application to a practical optical resolution.

This paper deals with the determination of the solubility isotherm of the reciprocal salt-pairs, (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)–(Cl$^-$, *d*-bcs$^-$)–H_2O, at 25 °C. Discussion is given on the possibility of the optical resolution of the bis(ethylenediamine)oxalatocobalt(III) ion as compared with two other successful cases of optical resolution of the complex.[3]

Experimental

Materials. *[Co(ox)(en)$_2$]Cl·H_2O*: The Λ- and Δ-complex chloride monohydrates were the same as reported.[3]

[Co(ox)(en)$_2$](d-bcs)·nH_2O: The Λ-diastereomeric salt monohydrate, Δ-diastereomeric salt 1.5-hydrate, and the pseudoracemate dihydrate, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·$2H_2O$, were the same as reported.[2]

Measurements. Solubility in water at 25 °C was determined in molality.[3] Optical densities were measured at 497 nm, and CD at 523 and 310 nm. The concentrations of {Λ-[Co(ox)(en)$_2$]$^+$+Δ-[Co(ox)(en)$_2$]$^+$} were determined from the observed optical densities, referring to the established molar absorption coefficients of the component ions; ε(497 nm) = 120 for Λ- and Δ-[Co(ox)(en)$_2$]$^+$, and ε(497 nm) = 0 for *d*-bcs$^-$. The concentrations of {Λ-[Co(ox)(en)$_2$]$^+$−Δ-[Co(ox)(en)$_2$]$^+$} were determined from the observed CD values in 523 nm, referring to the following data; $\Delta\varepsilon$(523 nm) = +2.71, −2.71, and 0 for Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$, and *d*-bcs$^-$, respectively. The concentrations of Λ- and Δ-[Co(ox)(en)$_2$]$^+$ were separately calculated from the concentrations of {Λ-[Co(ox)(en)$_2$]$^+$+Δ-[Co(ox)(en)$_2$]$^+$} and {Λ-[Co(ox)(en)$_2$]$^+$−Δ-[Co(ox)(en)$_2$]$^+$}. The concentrations of *d*-bcs$^-$ were determined from the observed CD values in 310 nm; $\Delta\varepsilon$(310 nm) = +3.23 for *d*-bcs$^-$ and $\Delta\varepsilon$(310 nm) = 0 for Λ- and Δ-[Co(ox)(en)$_2$]$^+$.

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

Results and Discussion

The solubility data are given in Table 1, and Figs. 1 and 2. Solubility is expressed in molalities of component ions and are attributed to the molalities of

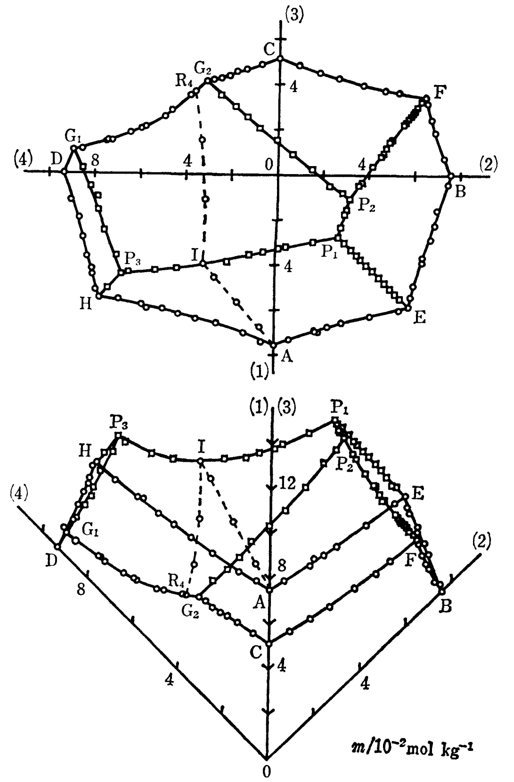

Fig. 1. The plane projection (upper) and the side elevation of the solubility isotherm of the system, (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)–(Cl$^-$, *d*-bcs$^-$)–H_2O, at 25 °C. Solubility is presented in molality *m* of anhydrous salt: (1) Λ-[Co(ox)(en)$_2$]Cl, (2) Δ-[Co(ox)(en)$_2$]Cl, (3) Δ-[Co(ox)(en)$_2$](*d*-bcs), and (4) Λ-[Co(ox)(en)$_2$](*d*-bcs); □, 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$^-$, *d*-bcs$^-$)-H$_2$O SYSTEM AT 25 °C
In liquid phases, solubility is presented in molalities *m* of the component ions. Abbreviations are as follows:
Λ-[Co(ox)(en)$_2$]$^+$=Λ^+, Δ-[Co(ox)(en)$_2$]$^+$=Δ^+, Λ-[Co(ox)(en)$_2$]Cl·H$_2$O=ΛCl, Δ-[Co(ox)(en)$_2$]Cl·H$_2$O=ΔCl, Δ-[Co(ox)(en)$_2$](*d*-bcs)·4H$_2$O=Δ(*d*-bcs), Λ-[Co(ox)(en)$_2$](*d*-bcs)·H$_2$O=Λ(*d*-bcs), and Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·2H$_2$O=$\Lambda\Delta$(d-bcs)$_2$.

a)	b)	Liquid phase[c)] m/10^{-2} mol kg^{-1}			Solid phase
		Λ^+	Δ^+	*d*-bcs$^-$	
$G_1\updownarrow P_3$	4	9.49	1.18	9.71	Λ(*d*-bcs) +$\Lambda\Delta$(*d*-bcs)$_2$
		9.97	1.26	9.44	
		10.26	1.36	9.25	
		10.77	1.31	9.16	
		11.43	1.39	8.94	
		12.10	1.52	8.50	
P_3	4	12.76 (±0.20)	1.57 (±0.10)	8.33 (±0.16)	ΛCl +Λ(*d*-bcs) +$\Lambda\Delta$(*d*-bcs)$_2$
$G_2\updownarrow P_2$	4	3.50	4.48	6.99	Δ(*d*-bcs) +$\Lambda\Delta$(*d*-bcs)$_2$
		3.68	4.80	6.68	
		3.90	5.10	6.44	
		4.25	5.46	6.29	
		4.47	5.92	5.98	
		4.76	6.32	5.65	
		5.20	6.93	5.43	
		5.73	7.53	5.24	
		5.88	7.94	5.09	
P_2	4	6.14 (±0.17)	8.19 (±0.10)	5.05 (±0.08)	ΔCl +Δ(*d*-bcs) +$\Lambda\Delta$(*d*-bcs)$_2$
$A\updownarrow H$	3	7.95		0.56	ΛCl
		8.35		1.34	
		9.14		2.55	
		9.82		3.44	
		10.39		4.22	
		10.88		4.92	
		11.57		5.61	
		11.61		5.82	
		12.38		6.85	
$D\updownarrow H$	3	10.22		9.03	Λ(*d*-bcs)
		10.60		8.65	
		11.25		8.45	
		11.84		8.22	
		12.21		8.01	
		12.45		7.99	
		12.99		7.84	
H	3	13.16 (±0.10)		7.68 (±0.04)	ΛCl +Λ(*d*-bcs)
$H\updownarrow P_3$	4	12.95	0.57	7.91	ΛCl +Λ(*d*-bcs)
$B\updownarrow F$	3		7.99	0.73	ΔCl
			8.72	1.89	
			9.12	2.43	
			9.63	3.18	
$C\updownarrow F$	3		5.71	4.83	Δ(*d*-bcs)
			6.30	4.50	
			6.85	4.23	
			7.66	3.96	
			8.33	3.71	
			8.89	3.65	
F	3		9.83 (±0.04)	3.41 (±0.03)	ΔCl +Δ(*d*-bcs)
$F\updownarrow P_2$	4	0.27	9.80	3.52	ΔCl +Δ(*d*-bcs)
		0.57	9.64	3.57	
		0.78	9.59	3.62	
		0.92	9.57	3.68	
		1.04	9.48	3.69	
		1.19	9.39	3.71	
		1.37	9.38	3.77	
		1.43	9.35	3.76	
		1.58	9.33	3.84	
		2.55	9.07	4.08	
		2.62	8.93	4.05	
		2.98	8.88	4.14	
		3.31	8.83	4.22	
		3.46	8.77	4.27	
		4.15	8.60	4.48	
		5.02	8.36	4.67	
		5.23	8.36	4.79	
$E\updownarrow P_1$	4	6.10	6.10	0.61	ΛCl +ΔCl
		6.12	6.12	0.84	
		6.30	6.30	1.24	
		6.46	6.46	1.65	
		6.59	6.59	2.05	
		6.75	6.75	2.49	
		6.87	6.87	2.89	
		7.00	7.00	3.26	
		7.10	7.10	3.54	
		7.23	7.23	3.92	
		7.40	7.40	4.39	
P_1	4	7.58 (±0.03)	7.58 (±0.03)	4.86 (±0.09)	ΛCl +ΔCl +$\Lambda\Delta$(*d*-bcs)$_2$
$P_1\updownarrow P_2$	4	7.17	7.77	4.96	ΔCl +$\Lambda\Delta$(*d*-bcs)$_2$
		6.73	7.93	5.00	
		6.55	7.99	4.98	
$P_3\updownarrow I$	4	12.42	1.59	8.07	ΛCl +$\Lambda\Delta$(*d*-bcs)$_2$
		11.51	1.98	7.26	
		10.91	2.42	6.74	
I	3	10.17 (±0.12)	3.07 (±0.02)	6.20 (±0.07)	ΛCl +$\Lambda\Delta$(*d*-bcs)$_2$
$I\updownarrow P_1$	4	9.63	3.71	5.80	ΛCl +$\Lambda\Delta$(*d*-bcs)$_2$
		9.05	4.41	5.53	
		8.78	4.86	5.39	
		8.47	5.36	5.25	
		8.39	5.66	5.23	
		7.92	6.59	4.97	
$R_4\updownarrow I$	3	5.25	3.40	6.74	$\Lambda\Delta$(*d*-bcs)$_2$
		7.45	3.18	6.35	
$A\updownarrow I$	3	8.05	0.66	1.32	ΛCl
		8.89	1.62	3.26	
		9.80	2.68	5.35	

a) Positions of points shown in Figs. 1 and 2. G_1↔P_3, for example, does not contain points G_1 and P_3. Reported data for A, B, E, A↔E, and B↔E[3)] and for C, C↔G_2, R_4, R_4↔G_1, G_1, and D[2)] not shown. b) Number of components. c) Values in parentheses are estimated errors and calculated from twice the standard deviations of experimental measurements repeated 4—7 times. At a point in A↔I, I, and R_4↔I, the molality of *d*-bcs$^-$ ideally becomes twice those of Δ^+.

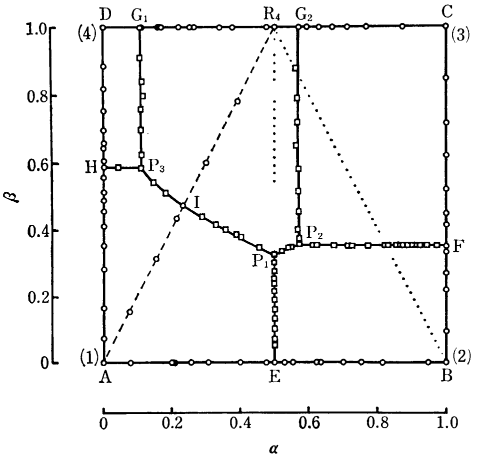

Fig. 2. The clinographic projection of the solubility isotherm of the system, (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$–(Cl$^-$, *d*-bcs$^-$)–H$_2$O, at 25 °C: α, mole fraction of Δ-[Co(ox)(en)$_2$]$^+$ to all the cations; β, mole fraction of *d*-bcs$^-$ to all the anions; (1) Λ-[Co(ox)(en)$_2$]Cl,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

three salts.[3] Thus the solubility isotherm can be drawn in a space according to the definition of solubility diagrams of reciprocal salt-pairs; Figure 1 represents the plane projection and the side elevation, and Fig. 2 the clinographic projection.[3]

The isotherm shows that the pseudoracemic compound, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·2H$_2$O, is present as the only double salt, no solid solution existing in this system. In the areas of AEP$_1$IP$_3$H, EBFP$_2$P$_1$, CG$_2$P$_2$F, G$_2$R$_4$G$_1$P$_3$IP$_1$P$_2$, and DHP$_3$G$_1$ in Figs. 1 and 2, which contain their boundaries, 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*-bcs)·4H$_2$O, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·2H$_2$O, and Λ-[Co(ox)(en)$_2$](*d*-bcs)·H$_2$O, respectively. Points A, B, C, R$_4$, and D denote the solubility of binary systems, and the faces AEB, BFC, CG$_2$R$_4$G$_1$D, DHA, and AIR$_4$ that of ternary systems. The lines of EP$_1$, FP$_2$, G$_2$P$_2$, G$_1$P$_3$, and HP$_3$ in Fig. 2 are almost parallel to the abscissa or ordinate. This shows that the mole ratio of Λ-[Co(ox)(en)$_2$]$^+$ to Δ-[Co(ox)(en)$_2$]$^+$ or Cl$^-$ to *d*-bcs$^-$ is constant on these lines.[3]

On the "racemic line" ER$_4$ (Fig. 2) where the amounts of Λ- and Δ-[Co(ox)(en)$_2$]$^+$ ions are equal, the saturated solution is in equilibrium with the pseudoracemate, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·2H$_2$O (on P$_1$R$_4$), or the racemic mixture, [Co(ox)(en)$_2$]Cl·H$_2$O (on EP$_1$). Thus, the system at 25 °C can not be applied successfully to practical optical resolution. One mole of *rac*-[Co(ox)(en)$_2$]Cl is dissolved in an excess of water and x mol of Ag(*d*-bcs) is added ($0<x<1$). The resulting precipitate AgCl is filtered off and the filtrate then concentrated at 25 °C. If we ignore the dissolved AgCl, this operation gives just the same conditions as the isotherm, (Λ-[Co(ox)(en)$_2$]$^+$, Δ-[Co(ox)(en)$_2$]$^+$)–(Cl$^-$, *d*-bcs$^-$)–H$_2$O, at 25 °C. In the case of $0<x<0.32$, the situation corresponds to the region of E↔P$_1$, giving the first precipitation of the racemic mixture, [Co(ox)(en)$_2$]Cl·H$_2$O, on concentrating at 25 °C. In the case of $x=0.32$ which corresponds to point P$_1$, the racemic mixture, [Co(ox)(en)$_2$]Cl·H$_2$O, and the pseudoracemate, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·2H$_2$O, will precipitate simultaneously. In the case of $0.32<x<1$ which is related to the region of P$_1$↔R$_4$, the pseudoracemate deposits at first. The final liquid phase composition in this operation corresponds to point P$_1$ regardless of the value of x. Thus, optical resolution is impossible in this isotherm because of the formation of the racemic mixture or the pseudoracemic compound. No tie-line intersects the "racemic line".

There are three invariant points, P$_1$, P$_2$, and P$_3$, in the four-component system at 25 °C. When the unsaturated solution composition is in the region of AR$_4$D except for its boundary in Fig. 2, the concentration of this solution would bring the solution composition to point P$_3$. Thus, point P$_3$ represents the final liquid phase composition for the region AR$_4$D. Both points P$_1$ and P$_2$ also represent the final liquid phase compositions for the regions ABR$_4$ and BCR$_4$, respectively. Point P$_2$ is a kind of "pseudo invariant point,"[2] since the composition of P$_2$ exists not in the region BCR$_4$ but in ABR$_4$.

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