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Temperature Dependence of the Optical Resolution and Solubility Isotherm of Bis(ethylenediamine)oxalatocobalt(III) (1*R*,3*S*,4*S*,7*R*)-3-Bromocamphor-9-sulfonate

Akira Fuyuhiro,* Kazuaki Yamanari, and Yoichi Shimura
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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The determination of solubility isotherm of a 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, between 5 and 25 °C, revealed that the resolving agent (1*R*,3*S*,4*S*,7*R*)-3-bromocamphor-9-sulfonate ion is applicable to the optical resolution of the [Co(ox)(en)$_2$]$^+$ ion below 19 °C from the viewpoint of solubility in water, in spite of the formation of a pseudo racemic compound, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](d-$C_{10}H_{14}OBrSO_3$)$_2$·2H_2O.

Some useful informations on optical resolutions have been given from the studies of solubility isotherms for a multi-component system containing a pair of diastereomeric salts of metal complexes[1,2] or organic substances.[3] The previous investigations showed that the formation of a pseudo racemate[1] or solid solutions[3] causes an unsuccessful or difficult optical resolution; for example, the resolving agent, (1*R*,3*S*,4*S*,7*R*)-3-bromocamphor-9-sulfonate(1−) ion (abbreviated to *d*-bcs$^-$), is not applicable to the optical resolution of [Co(ox)(en)$_2$]$^+$ ion at 25 °C because of the formation of the pseudo racemate, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](d-bcs)$_2$·2H_2O.[1] Successive study to determine the isotherms of the *d*-bcs salts at other temperatures revealed that the optical resolution becomes possible below 19 °C in spite of the formation of the pseudo racemate. Thus the solubility isotherm of the ternary system, Λ-[Co(ox)(en)$_2$](d-bcs)–Δ-[Co(ox)(en)$_2$](d-bcs)–H_2O, at 5 °C and the temperature dependence of two invariant points in a region of 5—25 °C are presented here; a short letter of the results was presented elsewhere.[4]

Experimental

Materials. *[Co(ox)(en)$_2$](*d*-bcs)*: The Λ- and Δ-diastereomers, and the pseudo racemate were prepared by the method previously reported[1]; ε(497 nm) = 120 for each complex, and $\Delta\varepsilon$(523 nm) = +2.71, −2.71, and 0 for the Λ- and Δ-diastereomers, and the pseudo racemate, respectively. Found: C, 32.47; H, 5.48; N, 9.41%. Calcd for Λ-[Co(ox)(en)$_2$](d-bcs)·H_2O: C, 32.29; H, 5.42; N, 9.41%. Found: C, 31.93; H, 5.56; N, 9.35%. Calcd for Δ-[Co(ox)(en)$_2$](d-bcs)·1.5H_2O: C, 31.80; H, 5.50; N, 9.27%. Found: C, 32.30; H, 5.42; N, 9.40%. Calcd for *rac*-[Co(ox)(en)$_2$](d-bcs)·H_2O: C, 32.29; H, 5.42; N, 9.41%. The analytical values of the Δ-diastereomer corresponded to those of neither tetrahydrate nor 2.5-hydrate[1] but 1.5-hydrate.

Measurements. The solubilities of complexes in water were determined in molality in the same way as previously reported.[2] 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

The solubility data obtained are given in Table 1, and Figs. 1 and 2, where any saturated solution is expressed as a point defined by summing up the position vectors of the solubilities of the one or two component salt(s) contained.[2]

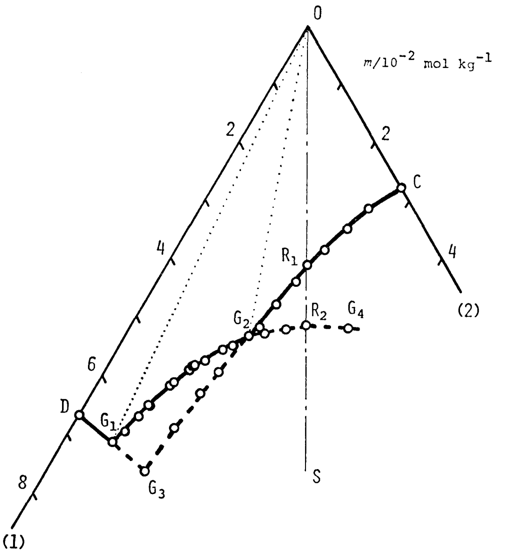

Fig. 1. Solubility isotherm of the ternary system, Λ-[Co(ox)(en)$_2$](d-bcs)–Δ-[Co(ox)(en)$_2$](d-bcs)–H_2O, at 5 °C. Solubility is presented in molality *m* of anhydrous salt; Λ-[Co(ox)(en)$_2$](d-bcs) (1) and Δ-[Co(ox)(en)$_2$](d-bcs) (2).

Solubility Isotherm of Λ-*[Co(ox)(en)$_2$](*d*-bcs)*–Δ-*[Co(ox)(en)$_2$](*d*-bcs)–H_2O at 5 °C.* Figure 1 shows the solubility isotherm of the ternary system, Λ-[Co(ox)(en)$_2$](d-bcs)–Δ-[Co(ox)(en)$_2$](d-bcs)–H_2O, at 5 °C. The pseudo racemate, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](d-bcs)$_2$·2H_2O, exists in the region G_1G_2 at 5 °C as in the case of 25 °C.[1] At 25 °C the invariant points, G_1 and G_2, appear on the left and the right hand sides of the "racemic line" OS, respectively (see Fig. 2). On the contrary, at 5 °C, both points appear on the left hand side of the "racemic line". Therefore, the isotherms at 5 °C represents the first case that the optical resolution becomes possible in spite of existence of the pseudo racemic compound.

If an aqueous solution of *rac*-[Co(ox)(en)$_2$](d-bcs) is concentrated at the constant temperature 5 °C, in other words, if the solution whose composition is on the line OR_1 in Fig. 1 is concentrated, the less soluble diastereomer Δ-[Co(ox)(en)$_2$](d-bcs)·4H_2O will appear in the solid phase at the point R_1, and then

Table 1. Equilibrium of the system, Λ-[Co(ox)(en)$_2$](*d*-bcs)-Δ-[Co(ox)(en)$_2$](*d*-bcs)-H_2O, at 5 and 25 °C, and the temperature dependence of the two invariant points, G_1 and G_2

In liquid phase, solubility is presented in molality *m* of anhydrous salt. Abbreviations are as follows: Λ-[Co(ox)(en)$_2$](*d*-bcs)·H_2O=Λ, Δ-[Co(ox)(en)$_2$](*d*-bcs)·$4H_2O$=Δ, and Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·$2H_2O$=*rac*; *, metastable state.

T/°C	a)	Liquid phase[b] $m/10^{-2}$ mol kg^{-1}		Solid phase
		Λ	Δ	
5	C		2.78 (±0.06)	Δ
	C↕G_2	0.66	2.46	Δ
		1.14	2.33	
		1.66	2.18	
		2.04	2.05	
		2.03	2.04	
		2.35	2.04	
		2.84	1.93	
		2.83	1.94	
		3.27	1.89	
	G_2	3.51 (±0.10)	1.79 (±0.08)	Δ +*rac*
	G_4*	1.97*	3.22*	*rac**
	R_2*	2.57*	2.57*	*rac**
	R_2*↕G_2	2.89*	2.29*	*rac**
		3.25*	2.02*	
	G_2↕G_1	3.82	1.64	*rac*
		3.83	1.66	
		4.00	1.53	
		4.36	1.36	
		4.53	1.23	
		4.55	1.26	
		4.56	1.24	
		4.66	1.21	
		5.00	1.10	
		5.10	1.06	
		5.53	0.96	
		5.56	0.91	
		5.80	0.86	
		6·11	0.82	
	G_1	6.41 (±0.13)	0.73 (±0.08)	Λ +*rac*
	D	6.65 (±0.03)		Λ
	G_2↕G_3*	4.26*	1.68*	Δ*
		4.69*	1.59*	
		5.38*	1.51*	
	G_3*	6.19* (±0.08)	1.45* (±0.02)	Λ* +Δ*

T/°C	a)	Liquid phase[b] $m/10^{-2}$ mol kg^{-1}		Solid phase
		Λ	Δ	
25	C		5.15 (±0.02)	Δ
	C↕G_2	0.72	4.89	Δ
		1.41	4.68	
		1.83	4.55	
		2.18	4.36	
		2.51	4.27	
		2.85	4.19	
	G_2	3.13 (±0.11)	4.13 (±0.06)	Δ +*rac*
	R_4	3.65 (±0.02)	3.65 (±0.02)	*rac*
	R_4↕G_1	3.83	3.50	*rac*
		4.67	2.83	
		4.97	2.57	
		5.81	2.10	
		5.99	2.02	
		6.42	1.81	
		7.27	1.48	
		7.41	1.52	
		7.49	1.48	
		7.54	1.43	
		8.56	1.09	
		8.84	1.11	
	G_1	8.96 (±0.10)	1.06 (±0.08)	Λ +*rac*
	D	9.32 (±0.03)		Λ
10	G_1	6.93	0.78	Λ+*rac*
15	G_1	7.55	0.90	Λ+*rac*
17.5	G_1	7.87	0.93	Λ+*rac*
20	G_1	8.17	0.99	Λ+*rac*
10	G_2	3.39	2.26	Δ+*rac*
15	G_2	3.34	2.75	Δ+*rac*
17.5	G_2	3.31	3.00	Δ+*rac*
20	G_2	3.25	3.39	Δ+*rac*

a) Positions of the points in Figs. 1 and 2. In these expressions, G_1↔G_2, for example, does not contain the points G_1 and G_2. b) The values in parentheses are estimated errors and were calculated from twice the standard deviations of the experimental measurements, which were repeated 3—11 times.

the point of the saturated solution will move along the curve R_1G_2. After the liquid phase composition reaches the point G_2, the less soluble diastereomer will gradually disappear with precipitating the pseudo racemate, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·$2H_2O$, while the liquid phase composition will remain unaltered. Finally, only the solid pseudo racemate will remain. When the solid less soluble diastereomer is removed from the system just before reaching G_2 on the curve R_1G_2, the yield of the diastereomer will be 49% of Δ-[Co(ox)(en)$_2$]$^+$ (25% of the racemic one). Further evaporation will change the composition of the liquid phase from G_2 to G_1 and the second solid, *rac*-[Co(ox)(en)$_2$](*d*-bcs)·H_2O, will precipitate till the solution composition reaches the point G_1. By separating and re-dissolving this pseudo racemate, successive optical resolution will become possible.

If the initial solution composition is in the region OR_1C in Fig. 1, the isothermal concentration of this solution will also cause the first precipitation of Δ-[Co(ox)(en)$_2$](*d*-bcs)·$4H_2O$. When the solution composition reaches the point G_2, the second solid,

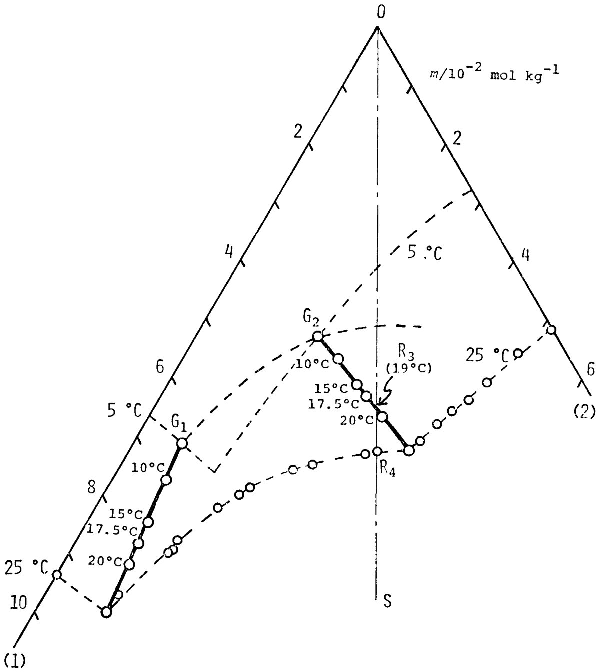

Fig. 2. Temperature dependence of the two invariant points, G_1 and G_2, of the ternary system, Λ-[Co(ox)(en)$_2$](*d*-bcs)–Δ-[Co(ox)(en)$_2$](*d*-bcs)–H_2O, at 5—25 °C. Solubility is presented in molality *m* of anhydrous salt; Λ-[Co(ox)(en)$_2$](*d*-bcs) (1) and Δ-[Co(ox)(en)$_2$](*d*-bcs) (2).

Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·$2H_2O$, will begin to precipitate, but the first solid will not completely disappear and both solids will remain to the last. If the initial solution composition is in the region OG_2R_1, the first and the second solids will deposit similarly, and then the solution composition will begin to move along the curve G_2G_1 as soon as all the first solid dissolve in the liquid phase. When the solution composition reaches G_1, the third solid, Λ-[Co(ox)(en)$_2$](*d*-bcs)·H_2O, will appear in the system. At last, only the second and the third solids will remain.

Therefore the point G_2 is a kind of "pseudo invariant point", and corresponds to the final liquid phase composition of the right hand region in Fig. 1. Only when the liquid phase composition is in the region OG_1G_2 or on the line OG_2, the pseudo racemic compound, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·$2H_2O$, deposits as the first precipitation in this system at 5 °C. Thus the pseudo recemate shows the incongruent solubility in water at 5 °C and can be recrystallized at this temperature without decomposition only from an aqueous solution containing an appropriate amount of Λ-[Co(ox)(en)$_2$](*d*-bcs) salt.

Certain metastable states which were maintained at least for several hours were observed at 5 °C. On the curve $G_2R_2G_4$ in Fig. 1, the solution is in metastable equilibrium with the solid phase, Λ-[Co(ox)(en)$_2$]·Δ-[Co(ox)(en)$_2$](*d*-bcs)$_2$·$2H_2O$, and the point R_2 represents the metastable solubility of the pseudo racemate. The point G_3 corresponds to the metastable invariant point, where both solids, Λ-[Co(ox)(en)$_2$](*d*-bcs)·H_2O and Δ-[Co(ox)(en)$_2$](*d*-bcs)·$4H_2O$, coexist. If the solution composition moves along the curve $R_1G_2G_3$ in an optical resolution, the yield of the Δ-diastereomer will increase.

Solubilities of Λ-*[Co(ox)(en)$_2$](*d*-bcs)–*Δ*-[Co(ox)(en)$_2$](*d*-bcs)–H_2O between 5 and 25 °C.* Figure 2 represents the temperature dependence (5—25 °C) of the two invariant points, G_1 and G_2. The curve of the temperature dependence of G_2 intersects the "racemic line" OS at 19 °C (point R_3). Therefore, the optical resolution using this ternary system becomes possible at temperatures lower than 19 °C. Futhermore, it was found that the solubility data reported previously for *rac*-[Co(ox)(en)$_2$](*d*-bcs)·H_2O at 5, 10, and 15 °C[1] are of metastable states and its value at 5 °C corresponds to the point R_2 in Fig. 1.

The solubility isotherm of the present system at 25 °C has somewhat changed from that previously reported,[1] in which some errors are included with regard to the solubilities of Δ-[Co(ox)(en)$_2$](*d*-bcs)·$4H_2O$, though the principal feature has not altered. Since the phase change in crystals of the Δ-diastereomer from the 1.5- or 2.5-hydrate to the tetrahydrate required about half a day with considerable deviations, it seems that the true tetrahydrate was not realized in some determinations of the previous experiment.[1] The corrected data are also given in Table 1.

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