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SOLUBILITY PHASE DIAGRAM OF BIS(ETHYLENEDIAMINE)OXALATOCOBALT(III) (1*R*,3*S*,4*S*,7*R*)-3-BROMOCAMPHOR-9-SULFONATE

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The solubility isotherm of a ternary system, Λ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)$ – Δ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)$ – H_2O, was determined between 5 and 25 °C. It was found 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, in spite of the formation of a pseudo racemic compound Λ-$[Co(ox)(en)_2]\cdot$Δ-$[Co(ox)(en)_2](d\text{-}C_{10}H_{14}OBrSO_3)_2\cdot 2H_2O$.

In a previous paper,$^{1)}$ it has been shown that the resolving agent (1*R*,3*S*,4*S*,7*R*)-3-bromocamphor-9-sulfonate 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 a pseudo racemate rac-$[Co(ox)(en)_2]$(*d*-bcs)$\cdot H_2O$. Continued efforts to determine the isotherms at other temperatures revealed that the optical resolution becomes possible below 19 °C and the results are presented here briefly.

Figure shows the solubility isotherm of a ternary system, Λ-$[Co(ox)(en)_2]$-(*d*-bcs) – Δ-$[Co(ox)(en)_2]$(*d*-bcs) – H_2O, at 5 and 25 °C. The solubilities are given in molality in a way previously reported.$^{2)}$ The isotherm at 25 °C has somewhat changed from the reported one,$^{1)}$ but the principal feature has not altered and two invariant points G_1 and G_2 appear on both sides of the " racemic line " OS. On the contrary, at 5 °C, both invariant points appear at the left hand side of the " racemic line ". If an aqueous solution of rac-$[Co(ox)(en)_2]$(*d*-bcs) is concentrated at the constant temperature 5 °C, the less soluble diastereomer Δ-$[Co(ox)(en)_2]$(*d*-bcs)$\cdot 4H_2O$ will appear in the solid phase, and the point of saturated solution will move along the curve R_1G_2. When the liquid phase composition reaches the point G_2, the diastereomer will disappear with precipitating the pseudo racemate and the liquid phase composition will remain unaltered. Finally, only the solid pseudo racemate will remain. When the less soluble diastereomer is removed just before reaching G_2, the yield 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)$\cdot H_2O$, will precipitate till the solution composition reaches the point G_1. By separating and redissolving this pseudo racemate, successive optical resolution becomes possible.

Metastable states were observed at 5 °C (see Figure). In the region $G_4R_2G_2$,

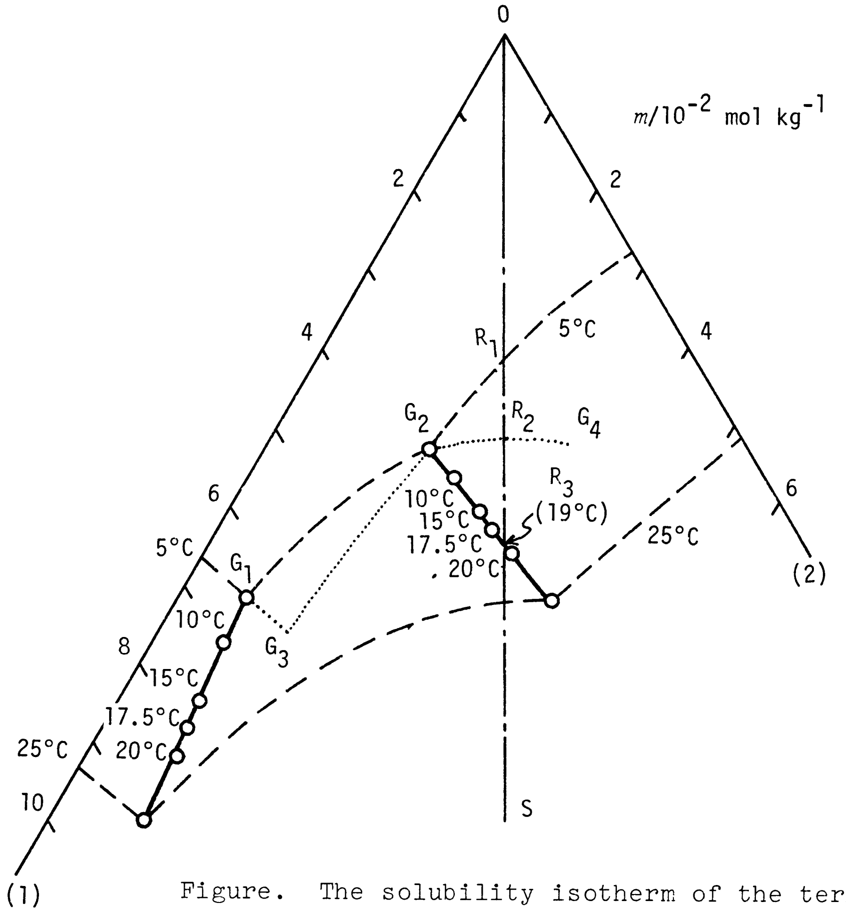

Figure. The solubility isotherm of the ternary system, Λ-$[Co(ox)(en)_2](d\text{-bcs})$ – Δ-$[Co(ox)(en)_2](d\text{-bcs})$ – H_2O, at 5 (……, metastable states) and 25 °C, and the temperature dependence of the two invariant points, G_1 and G_2, in this system at 5-25 °C. Solubility is presented in molality m of anhydrous salts, Λ-$[Co(ox)(en)_2](d\text{-bcs})$ (1) and Δ-$[Co(ox)(en)_2](d\text{-bcs})$ (2).

the solution is in metastable equilibrium with the solid phase, Λ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(ox)(en)_2](d\text{-bcs})_2\cdot 2H_2O$, and the point G_3 corresponds to the metastable invariant point, where both solids, Λ-$[Co(ox)(en)_2](d\text{-bcs})\cdot H_2O$ and Δ-$[Co(ox)(en)_2](d\text{-bcs})\cdot 4H_2O$, coexist. If the solution composition moves along the curve $R_1G_2G_3$ in an optical resolution, the yield of Δ-diastereomer will increase.

Figure also presents the temperature dependence (5 - 25 °C) of the two invariant points G_1 and G_2. The present results show that the solubility data reported previously for rac-$[Co(ox)(en)_2](d\text{-bcs})\cdot H_2O$ at 5, 10, and 15 °C[1] are of metastable states. It is noteworthy that the curve of temperature dependence of G_2 intersects the " racemic line " OS at 19 °C (point R_3). In this ternary system, therefore, optical resolution is possible at temperatures lower than 19 °C.

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