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# Effect of Ethanol on the Outer-sphere Association of $\Lambda$- or $\Delta$-Tris(ethylenediamine)cobalt(III) with *d*-Tartrate Ions in Aqueous Solutions

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The effect of ethanol on the outer-sphere association of $\Lambda$- or $\Delta$-[Coen$_3$]$^{3+}$ ion (en=ethylenediamine) with *d*-tartrate ion was investigated in aqueous solutions containing 0, 1, 3, and 5 wt% of ethanol at 25 °C by measuring the change in optical density of the charge-transfer spectra at 265 nm. It was found that the association constant of $\Lambda$-[Coen$_3$]$^{3+}$ ion with *d*-tartrate ion $K_{A(\Lambda)}$ was a little larger than that of $\Delta$-[Coen$_3$]$^{3+}$ ion $K_{A(\Delta)}$, and that the addition of ethanol increased both $K_{A(\Lambda)}$ and $K_{A(\Delta)}$ but decreased the ratio $K_{A(\Lambda)}/K_{A(\Delta)}$. The diminished discrimination between $\Lambda$- and $\Delta$-[Coen$_3$]$^{3+}$ ions by *d*-tartrate ion was discussed in terms of the solubility of these diastereoisomers in aqueous ethanol and was attributed to the increased electrostatic interaction between the complex and *d*-tartrate ions arising from the decrease in the dielectric constant of the medium.

It is well-known that the racemic [Coen$_3$]$^{3+}$ ion is resolved from the fact that the $\Lambda$-form precipitates as $\Lambda$-[Coen$_3$]X*d*-tart (X=halide anion and *d*-tart=*d*-tartrate dianion), while the corresponding $\Delta$-form remains gelatinous when evaporated in aqueous solution. The discrimination of $\Lambda$- from $\Delta$-forms by *d*-tart ion is expected to take place also in solution, *viz.*, the differential outer-sphere association with *d*-tart ion is anticipated for $\Lambda$- and $\Delta$-[Coen$_3$]$^{3+}$ ions. Addition of alcohol decreases solubility of many inorganic salts. This is the case with this system. Thus, it seems of interest to examine the effect of alcohol on the outer-sphere association of $\Lambda$- or $\Delta$-[Coen$_3$]$^{3+}$ ion with *d*-tart ion in aqueous solution. The purpose of this investigation is to find optimum conditions for the discrimination between $\Lambda$- and $\Delta$-forms. As the first step, the association constants were determined by spectrophotometry in aqueous ethanol.

Ogino and Saito[1] and Nordén[2] reported from the measurements of charge-transfer (CT) and the corresponding circular dichroism (CD) spectra that *d*-tart ion associates to a greater extent with $\Lambda$-[Coen$_3$]$^{3+}$ than with $\Delta$-[Coen$_3$]$^{3+}$ ion in aqueous solution. They neglected the association of [Coen$_3$]$^{3+}$ ion with perchlorate ion added to adjust ionic strength constant, on the ground that the spectra are not altered by its addition. However, it is not plausible from both electrostatic[3] and experimental[4] viewpoints that [Coen$_3$]$^{3+}$ ion does not associate at all with $ClO_4^-$ ion even in aqueous solution. Addition of alcohol is expected to promote ionic association of the complex cation not only with *d*-tart ion but also with $ClO_4^-$ ion owing to the accompanying decrease in the dielectric constant of the medium. Therefore, measurements should be carried out on a system which contains no anions other than *d*-tart ion.[5]

## Experimental

*Materials.* $\Lambda$-[Coen$_3$](*d*-tart)$_{3/2}$·6$H_2O$(or 5.5$H_2O$) was prepared by the double decomposition of $\Lambda$-[Coen$_3$]Br*d*-tart·5$H_2O$ with an equivalent amount of $Ag_2$*d*-tart. Found: C, 25.32; H, 6.99; N, 15.15%. Calcd for $C_{12}H_{42}N_6O_{15}Co$(or $C_{12}H_{41}N_6O_{14.5}Co$): C, 25.31(25.72); H, 7.43(7.37); N, 14.76 (15.00)%. Similar procedures gave $\Delta$-[Coen$_3$](*d*-tart)$_{3/2}$·6$H_2O$(or 6.5$H_2O$) when $\Delta$-[Coen$_3$]$Br_3$·2$H_2O$ was used in place of $\Lambda$-[Coen$_3$]Br*d*-tart·5$H_2O$. Found: C, 24.73; H, 7.18; N, 14.46%. Calcd for $C_{12}H_{42}N_6O_{15}Co$(or $C_{12}H_{43}N_6O_{15.5}Co$): C, 25.31(24.92); H, 7.43(7.49); N, 14.76(14.53)%. Since the number of molecules of the water of crystallization in these complex salts was not definite, the concentration of the stock solutions was determined spectrophotometrically by using the absorption band at 465 nm, the magnitude and the shape of which do not change on the addition of *d*-tart ion. Its molar extinction coefficients are listed in Table 1. Molar rotation at 589 nm was +620 and −380° for $\Lambda$- and $\Delta$-form, respectively.[6] Their optical purity is thus satisfactory, taking the contribution from 3/2 *d*-tart ion (+126°) into consideration.

The starting materials $\Lambda$-[Coen$_3$]Br*d*-tart·5$H_2O$ and $\Delta$-[Coen$_3$]$Br_3$·2$H_2O$ were prepared by the usual method,[7] their specific rotations being in good agreement with those given in the literature.[7] [Coen$_3$]($ClO_4$)$_3$ was prepared by the usual method[7] starting with $CoSO_4$·7$H_2O$ and $HClO_4$ in place of $CoCl_2$·6$H_2O$ and HCl, respectively. Found: C, 13.41; H, 4.53; N, 15.86%. Calcd for $C_6H_{24}O_{12}Cl_3Co$: C, 13.41; H, 4.50; N, 15.63%.

Ion-exchanged water was purified by distillation. Ethanol was refluxed over calcium oxide and then over magnesium ethoxide, and then fractionated. Mixed solvents were prepared by weight. KNa*d*-tartrate·4$H_2O$ of reagent grade was used without further purification.

*Apparatus.* A Shimadzu double beam spectrophotometer UV-200 with 1 cm quartz cells was used for the measurement of CT absorption spectra. Its cell compartment was kept at 25±0.2 °C with a Komatsu-Yamato Coolnics CTR-120.

*Procedure.* Sample solutions used for measurements were prepared with appropriate amounts of stock solutions of $\Lambda$- and $\Delta$-[Coen$_3$](*d*-tart)$_{3/2}$ (0.01 mol/l) and of KNa*d*-tart (0.05 mol/l). Reference solutions prepared from the stock solutions of [Coen$_3$]($ClO_4$)$_3$ (0.01 mol/l) had strictly the same total concentration of [Coen$_3$]$^{3+}$ ion as in the corresponding sample solutions so that the spectrophotometer could allow us to measure directly the absorption at 265 nm due to the ion-pair formation between $\Lambda$- or $\Delta$-[Coen$_3$]$^{3+}$ and *d*-tart ions. The concentration of [Coen$_3$]$^{3+}$ ion was $(1.0—6.0)\times10^{-3}$ mol/l and that of *d*-tart ion was $(1.0—1.2)\times10^{-2}$ mol/l, giving the final ionic strength 0.033 taking the decrease by ion-pair formation into consideration. Since pH of the sample solutions was around 7, the formation of H*d*-tart$^-$ ion or $H_2$*d*-tart was negligible.

Solubility was measured at 25 °C by a conventional method in the mixed solvents with ethanol, the concentration of the saturated solutions being determined by spectrophotometry.

## Results and Discussion

Let $M^{3+}$ and $A^{2-}$ denote $[\mathrm{Coen}_3]^{3+}$ and $d$-tart$^{2-}$ ions, respectively. Then the outer-sphere association equilibrium is

$$M^{3+} + A^{2-} \rightleftarrows MA^{+}$$

if only the first step association is assumed. The outer-sphere association constant $K_A$ is given by

$$K_A = [MA^+]/[M^{3+}][A^{2-}] = x/(C_M - x)(C_A - x) \quad (1)$$

where $C_M$ and $C_A$ refer to the total concentration of $M^{3+}$ and $A^{2-}$, respectively, and $x$ refers to the concentration of $MA^+$ at equilibrium. Since no other species than $M^{3+}$ and $M^+$ present in solution contributes to the absorbance at the wavelength employed for the measurement (265 nm), the difference of the absorbance $\Delta D$ between a sample solution and its reference solution can be given by

$$\Delta D = x(\varepsilon_{MA} - \varepsilon_M) \quad (2)$$

if both sample and reference solutions have the same total concentration of $M^{3+}$ and the cell length is 1 cm. $\varepsilon$ denotes the molar extinction coefficient of the species indicated by the subscript. Combining Eqs. (1) and (2) we have

$$C_M(C_A - x)/\Delta D = (C_A - x)/(\varepsilon_{MA} - \varepsilon_M) + 1/K_A(\varepsilon_{MA} - \varepsilon_M) \quad (3)$$

which is valid at a constant ionic strength and constant temperature.

Firstly an appropriate value of $K_A$ is assumed and $x$'s obtained from Eq. (1) are substituted into Eq. (3). The plot of the quantity on the left-hand side of Eq. (3) *vs.* $(C_A - x)$ gives a refined association constant as (slope)/(intercept), which is again substituted into Eq. (1). The same procedures are continued until a constant $K_A$ is attained. Calculation should be carried out with the data having the same final ionic strength $I$, which is given by

$$I = 3C_M + 3C_A - 6x.$$

Details of analysis have been given by Tanaka *et al.*[5]

Typical examples of the plot of $\Delta D$ *vs.* $C_M$ are shown in Fig. 1, where for any value of $C_M$, the amount of A added to $\Lambda$-solution is equal to that to $\Delta$-solution. Thus we see in Fig. 1 that $\Delta D$ of $\Lambda$-solution is larger than that of $\Delta$-solution and that the addition of ethanol increases $\Delta D$ of both solutions but decreases the difference in $\Delta D$ between them. Figure 2 shows some of the final plots of Eq. (3) obtained along the line described above. The linearity in Fig. 2 supports the assumption that only the first step association occurs under these experimental conditions.

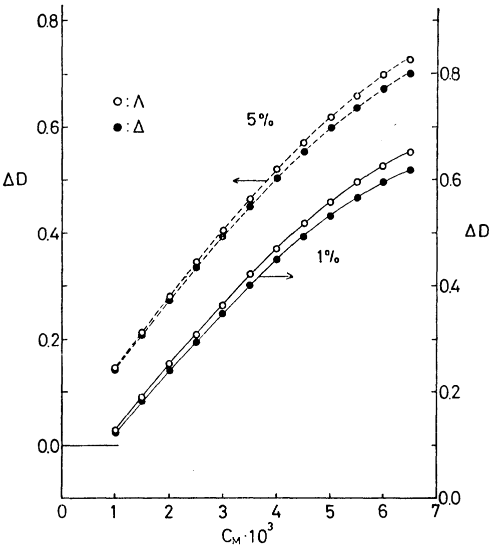

Fig. 1. Plot of $\Delta D$ *vs.* $C_M$.
5% (----) and 1% (——) solutions correspond to the left- and right-hand scales, respectively. Open and closed circles for $\Lambda$- and $\Delta$-solutions, respectively.

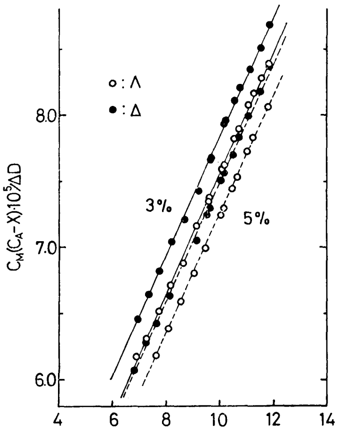

Fig. 2. Some final plots of Eq. (3).
3% (——), 5% (----). Open and closed circles for $\Lambda$- and $\Delta$-solutions, respectively.

Derived parameters along with the values of $\varepsilon_M$ (at 265 nm) are summarized in Table 1, where $K_{A(\Lambda)}$ and $K_{A(\Delta)}$ refer to the association constant of $d$-tart ion with $\Lambda$- and $\Delta$-$[\mathrm{Coen}_3]^{3+}$ ions, respectively, the final ionic strength being 0.033 in all cases. These para-

TABLE 1. ASSOCIATION CONSTANT AT 25 °C ($I$=0.033)

| | 0 % | 1 % | 3 % | 5 % | 0 % |
|---|---|---|---|---|---|
| $K_A$ ($\Lambda$) | 131.7±3.2 | 139.8±3.6 | 156.9±3.1 | 170.9±3.5 | |
| $K_A$ ($\Delta$) | 118.9±4.3 | 125.6±4.4 | 143.7±2.6 | 159.3±3.7 | |
| $\varepsilon_{MA}$-$\varepsilon_M$ ($\Lambda$) | 210.5±3.2 | 213.5±3.3 | 216.4±2.3 | 219.3±2.2 | 366[a)], 350[b)] |
| $\varepsilon_{MA}$-$\varepsilon_M$ ($\Delta$) | 211.3±5.4 | 212.5±4.9 | 216.2±2.3 | 217.6±2.7 | 415[a)], 390[b)] |
| $K_{A(\Lambda)}/K_{A(\Delta)}$ | 1.11 | 1.11 | 1.09 | 1.07 | 1.30[c)], 1.18[b)] |
| $\varepsilon_M$ (at 465 nm) | 88.9 | 89.0 | 89.2 | 89.3 | |
| $\varepsilon_M$ (at 265 nm) | 165 | 167 | 170 | 172 | 158[a)], 165[b)] |

a) Ref. 1. b) Ref. 2. c) recalculated value. 1.24 is reported in Ref. 1.

Table 2. Association constant extrapolated to $I$=0.1 in water at 25 °C

| $a$[a] | $K_{A(\Lambda)}$ |  | $K_{A(\Delta)}$ |  | Theoretical |  |
|---|---|---|---|---|---|---|
|  | This work | Literature | This work | Literature | Fuoss | Bjerrum |
| 5 Å | 50.7±1.2 | 23.4±1.0[b] | 45.7±1.7 | 18.0±0.7[b] | 89 | 77 |
| 6 Å | 55.8±1.4 | 26±2[c] | 50.4±1.8 | 22±2[c] | 44 | 56 |

a) $\log f_z = -AZ^2I^{1/2}/(1+BaI)$. b) Recalculated in Ref. 1. c) Ref. 2.

meters indicate that $K_{A(\Lambda)}$ is a little larger than $K_{A(\Delta)}$ and that the addition of a small amount of ethanol promotes ionic association. The promotion might be interpreted in terms of the decrease in the dielectric constant of the medium. It should be noted that $(\varepsilon_{MA}-\varepsilon_M)$ as well as $\varepsilon_M$ increases with the increase of ethanol content, but the values for $\Lambda$-form are equal to those for $\Delta$-form in every case investigated within experimental error. On the other hand, Ogino and Saito[1] obtained 366±15, 415±16, and 365±13[8] as the value of $(\varepsilon_{MA}-\varepsilon_M)$ for $\Lambda$-, $\Delta$-, and racemic forms, respectively, in aqueous solutions at $I$=0.1 (NaClO$_4$).[2] $\varepsilon_M$ (at 265 nm) we obtained in water differs somewhat from the value 158 reported by Ogino and Saito but agrees well with that by Nordén. Though the origins of the differences are not known, it is certain that the value of $(\varepsilon_{MA}-\varepsilon_M)$ for the racemate should lie between the corresponding values for $\Lambda$- and $\Delta$-forms if they are different.

The ratio $K_{A(\Lambda)}/K_{A(\Delta)}$, a measure of the discrimination between $\Lambda$- and $\Delta$-forms by $d$-tart ion in solution and defined to be a *discrimination factor*, is diminished on the addition of ethanol. Ogino and Saito,[1] and Nordén[2] reported 1.30 and 1.18, respectively, for the value of the factor in water, both of which are considerably larger than the value 1.11 we obtained. In order to compare our results with theirs in detail, our association constants in water were extrapolated to $I$=0.1 with the aid of the extended Debye-Hückel equation for activity coefficients with $a$=5 and 6 Å. The results are listed in Table 2 together with the values estimated by means of Fuoss[9] and Bjerrum[3] equations derived on the basis of pure electrostatics. We see that our association constant is about twice as large as theirs and that 6 Å[10] substituted as $a$ into the theoretical equations reproduces our association constants satisfactorily. The interionic distance seems reasonable from molecular models though $d$-tart$^{2-}$ ion is not an ideal rigid-sphere with its charge uniformly distributed. Thus it may be concluded that the neglect of the association of [Coen$_3$]$^{3+}$ ion with ClO$_4^-$ ion is responsible for the smaller $K_A$ values obtained by Ogino and Saito, and Nordén and that outer-sphere association of $d$-tart ion with $\Lambda$- or $\Delta$-[Coen$_3$]$^{3+}$ ion is described almost completely by pure electrostatic theories; the contribution from non-electrostatic interaction which is thought to discriminate $\Lambda$- from $\Delta$-forms, is much smaller than that from the electrostatic one.

In order to explain the large discrimination factors obtained by Ogino and Saito, and Nordén, it is assumed that the electrostatic field of [Coen$_3$]$^{3+}$ ion is reduced by the ion-pair formation with ClO$_4^-$ ion, and the electrostatic interaction between the complex ion and $d$-tart ion is weakened, *viz.*, non-electrostatic interaction is enhanced as compared with an electrostatic one when a large amount of NaClO$_4$ is added. Thus it follows that presence of some univalent anions such as ClO$_4^-$ or Br$^-$ ion in solution seems more effective in the discrimination between $\Lambda$- and $\Delta$-forms by $d$-tart ion than the addition of alcohol which causes increase in the electrostatic interaction between $\Lambda$- or $\Delta$-[Coen$_3$]$^{3+}$ and $d$-tart ions. In fact Br$^-$ ion in crystalline $\Lambda$-[Coen$_3$]-Br$d$-tart·5H$_2$O is attached closely to [Coen$_3$]$^{3+}$ ion from the direction of its three-fold axis and is considered to play an important role in the crystal formation.[11]

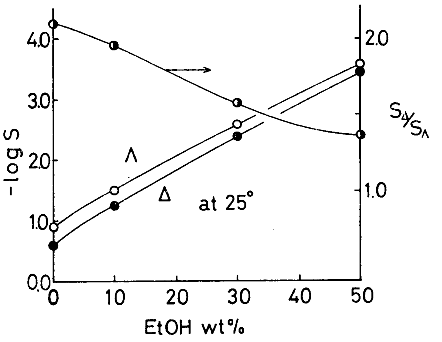

Fig. 3. Variation of solubilities of $\Lambda$- and $\Delta$-[Coen$_3$](d-tart)$_{3/2}$ with the content of ethanol at 25 °C. Solubility ratio $S_\Delta/S_\Lambda$ (◐) corresponds to the right-hand scale. Open and closed circles for $\Lambda$- and $\Delta$-forms, respectively.

The discrimination factor is very close to unity in solution and is therefore regarded at most as a part of the causes that precipitate only $\Lambda$-form as $\Lambda$-[Coen$_3$]-Br$d$-tart·5H$_2$O. In this connection, the effect of ethanol on the solubility of $\Lambda$- and $\Delta$-[Coen$_3$]($d$-tart)$_{3/2}$ was examined at 25 °C. The results are given in Fig. 3, where $S$ denotes the concentration of the saturated solution in mol/l. The solubility difference between $\Lambda$- and $\Delta$-forms decreases with the increase in ethanol content just like the discrimination factor in solution, but the solubility ratio $S_\Delta/S_\Lambda$ is considerably larger than the factor. Thus it might be concluded that the addition of alcohol is unfavourable to the discrimination of $\Lambda$- from $\Delta$-forms by $d$-tart ion, since it only leads to increased electrostatic interaction between the complex and $d$-tart ions.

## Reference and Notes

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