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A Conductometric Study on the Phenylglyoxylic Acid-Strychnine Complex

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In order to elucidate the mechanism by which phenylglyoxylic acid (PGA) is reduced electrochemically in the presence of strychnine (SC) to form mandelic acid (MA), which exhibits an optically active property, conductometric studies were carried out. The formation of a 1 : 1 complex between PGA (or MA) and SC was suggested from the results that equimolar mixture of PGA (or MA) and SC showed a maximum decrease of conductivity. Equilibrium constants of the 1 : 1 complex of PGA-SC or MA-SC were determined from the results of conductivity measurements at various temperatures. The thermodynamic data were calculated. ΔH and ΔS were found to be $+22\ \mathrm{kJ\,mol^{-1}}$ and $+1.1\times10^{2}\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for both the PGA-SC complex and MA-SC complex.

There have been many papers concerning asymmetric electrochemical reaction occurring in the presence of optically active substances such as alkaloids used as inductors.[1-6] It is known that phenylglyoxylic acid (PGA) is reduced electrochemically under the influence of strychnine (SC) to form mandelic acid (MA), which exhibits a dextrorotatory property.[1,2] However, the reaction mechanism remains unclear at present. Therefore, we presumed that PGA might combine with SC to form a complex, which was adsorbed onto the surface of the electrode,[7] and reduced to form the MA-SC complex. For the first step towards verifying our presumption, in this paper, we present the results of conductometric studies to determine equilibrium constants, and then calculate thermodynamic data for complexes of PGA-SC and MA-SC. On the basis of these results, we speculate about a possible formation of the complex for the asymmetric electrochemical reduction.

Theoretical

Let K be an equilibrium constant, if PGA or MA reacts with SC to form a 1 : 1 complex. Also let concentrations of free PGA (or MA), free SC and 1 : 1 complex be [P], [S], and [PS], and total concentrations of PGA (or MA) and SC be P_T and S_T, then,

$$\mathrm{P} + \mathrm{S} \rightleftarrows \mathrm{PS}, \tag{1}$$

$$K = \frac{[\mathrm{PS}]}{[\mathrm{P}]\,[\mathrm{S}]}, \tag{2}$$

$$P_T = [\mathrm{P}] + [\mathrm{PS}], \tag{3}$$

$$S_T = [\mathrm{S}] + [\mathrm{PS}], \tag{4}$$

In the case of an equimolar mixture, we define a ratio of [PS] to C as α,

$$\alpha = \frac{[\mathrm{PS}]}{C}, \tag{5}$$

where

$$P_T = S_T = C. \tag{6}$$

From Eqs. 2—6, the following equation was derived.

$$\frac{\alpha}{(1-\alpha)^2} = KC. \tag{7}$$

From plots of $\alpha/(1-\alpha)^2$ against C, we may obtain a straight line, the slope of which is equal to K.

The value of α will be obtained by the measurement of conductivity as follows:

Let the conductivity of each individual solution of PGA (or MA) and SC, and the conductivity of mixture of PGA (or MA) and SC be κ_P, κ_S, κ_{PS}, and their molar conductivities be Λ_P, Λ_S, Λ_{PS}, then

$$\kappa_P = P_T\Lambda_P, \tag{8}$$

$$\kappa_S = S_T\Lambda_S, \tag{9}$$

$$\kappa_{PS} = [\mathrm{P}]\Lambda_P + [\mathrm{S}]\Lambda_S + [\mathrm{PS}]\Lambda_{PS}. \tag{10}$$

Eq. 10 is acceptable at very low concentrations of PGA (or MA) and SC, unless other species of complex may exist in the solution. The difference of conductivity, $\Delta\kappa$, is

$$\Delta\kappa = (\kappa_P + \kappa_S) - \kappa_{PS}. \tag{11}$$

The 1 : 1 complex may exhibit less ionic property, because a carboxyl group of PGA (or MA) and a heterocyclic nitrogen (not an indolizine nitrogen) of SC are locked inside the complex by the formation of an ionic bond. Therefore, it is reasonable to assume that

$$\Lambda_{PS} \ll \Lambda_P \text{ or } \Lambda_{PS} \ll \Lambda_S. \tag{12}$$

If we neglect Λ_{PS}, then, the following equation is introduced from Eqs. 5 and 8—12.

$$\frac{\Delta\kappa}{\kappa_P + \kappa_S} = \alpha. \tag{13}$$

The values of α are determined at every concentration of equimolar mixtures of PGA (or MA) and SC by Eq. 13 from the measurement of conductivity. Then, we can obtain K from the slope at zero with respect to concentration on plots of $\alpha/(1-\alpha)^2$ against C according to Eq. 7. If a 1 : 1 complex exists in the mixture, a maximum difference of $\Delta\kappa$ must appear at $P_T = S_T$ in relation between the molar ratio and $\Delta\kappa$, when

P_T+S_T=constant. This can be demonstrated by the derivation in the same manner as Jop's consecutive variation method,[8] except that absorption is replaced by conductivity. This modified Jop's method is valuable for the determination of the equilibrium constants of molecular complexes, which is obtained by ionic bond formation with conductivity change and without absorption change.

Experimental

PGA, MA, and SC sulfate used were commercially available reagent grade. SC sulfate was used in place of free SC, which is less soluble in water. These compounds were dissolved in deionized water to prepare a 1—60 mol dm^{-3} solution.

The conductivities were measured with a TOA conductometer CM-30ET at 20—35 °C

Results and Discussion

The sample solutions were prepared with various concentrations of individual solution of PGA, MA, and SC, and those of equimolar mixture of PGA (or MA) and SC. The conductivities were measured at 20—35 °C. The results are shown in Figs. 1 and 2.

In order to verify the presence of a 1 : 1 complex, sample solutions were prepared with various molar

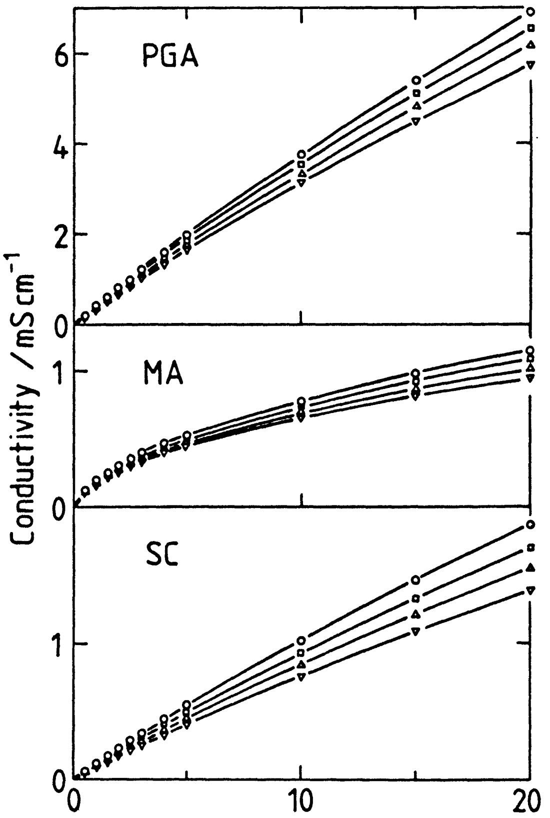

Fig. 1. The conductivities of individual solution of PGA, MA, or SC. —▽—: 20 °C, —△—: 25 °C, —□—: 30 °C, and —○—: 35 °C.

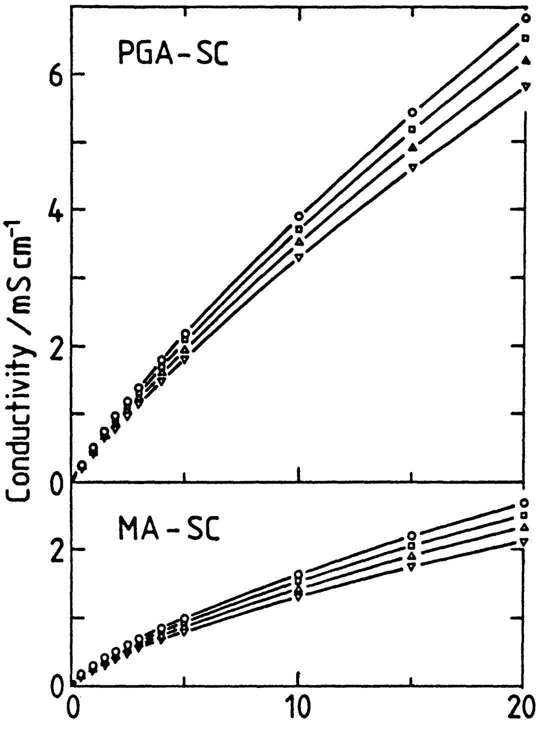

Fig. 2. The conductivities of equimolar mixture of PGA and SC, or MA and SC. The same symbols as those in Fig. 1 are used.

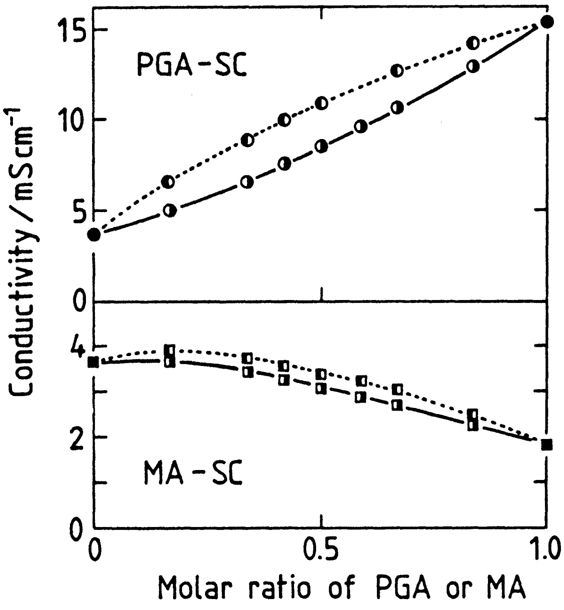

Fig. 3. Plots of conductivity against molar ratio on PGA-SC and MA-SC systems (25 °C). Total concentrations of PGA (or MA) and SC were maintained at 60 mmol dm^{-3}. Solid lines; conductivity of mixture of PGA (or MA) and SC at each molar ratio. Dotted lines; sum of conductivities of individual solution of PGA (or MA) and SC at corresponding concentration.

ratio of PGA (or MA) and SC under the conditions that the total concentration of the two components was kept constant, and these conductivites were measured at 25 °C. We have many data on the relation between conductivity and molar ratio. In order to avoid duplication we present here only two plots at 60 mmol dm^{-3} of total concentration as typical results in Fig. 3.

In Fig. 3, plots on solid lines show the conductivity of a mixture of PGA (or MA) and SC at each molar ratio, and plots on dotted lines show the sum of conductivities of individual solution of PGA (or MA) and SC at the corresponding concentration. The sum of conductivities was calculated from the data in Fig. 1. The gaps between the solid lines and dotted lines are equal to $\Delta\kappa$s. It was found that the maximum gap ($\Delta\kappa$) was obtained at a molar ratio of 0.5.

It must be considered that SC sulfate might be dissociated into SC and sulfate ion completely at infinite dilution in water. The same consideration is applied in the case of a mixture of PGA (or MA) and SC, when the conductivity of the sulfate portion may be offset by the subtraction of the mixture from the sum of indvidual solutions.

This consideration sustains our presumption of the presence of a 1 : 1 complex in the mixture of PGA (or MA) and SC. The conductivity of the mixture was smaller than the sum of the conductivities of the individual solution of PGA (or MA) and SC. This is because the concentrations of free carboxyl group and free base decrease on the formation of an ionic bond.

The values of α were calculated by Eq. 13 and in turn those of $\alpha/(1-\alpha)^2$ were obtained. Plots of $\alpha/(1-\alpha)^2$ against concentration of PGA (or MA) are shown in Fig. 4. This indicates that Eq. 7 is effective at very low the concentrations. The slopes, which should be equal to the equilibrium constant, K, were determined at zero extrapolation on every curve in Fig. 4. It was found, on the other hand, that plots according to Kohlrausch's equation, $\Lambda = \Lambda_\infty - A\sqrt{C}$, with the data in Figs. 1 and 2 fell on straight lines in lower regions of concentration of individuals and mixtrues of PGA and SC as shown in Fig. 5. The values of α in the case of the PGA-SC mixture in the region of very low concentration were recalculated by using values obtained from the straight lines in Fig. 5. The dotted lines in Fig. 4 in the case of the PGA-SC mixtures were obtained by using values, α from Fig. 5. Equilibrium constants, K, were determined from the slopes at every temperature. In the case of MA solutions, no straight line is obtained from the Kohlrausch plots (Fig. 6). This is because MA is a weak acid. Therefore, we made slopes in Fig. 4 in the case of MA-SC mixture by a rough estimate. The values of K are summarized in Table 1, larger error in the case of MA-SC than PGA-SC should be considered in Table 1.

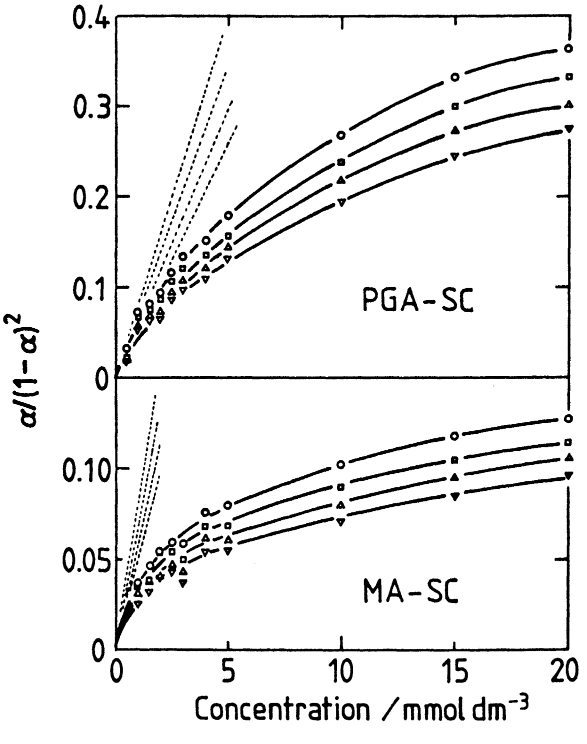

Fig. 4. Plots of $\alpha/(1-\alpha)^2$ against concentration of PGA (or MA). The same symbols as those in Fig. 1. are used. Dotted lines show the slopes of each curve at the zero concentration.

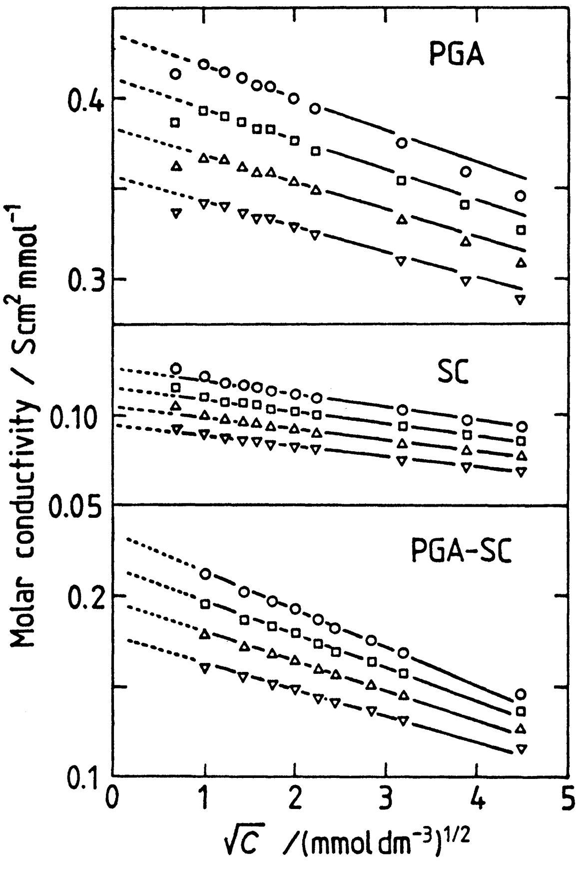

Fig. 5. Plots according to Kohlrausch's equation on PGA, SC, and PGA-SC solutions. The same symbols as those in Fig. 1 are used.

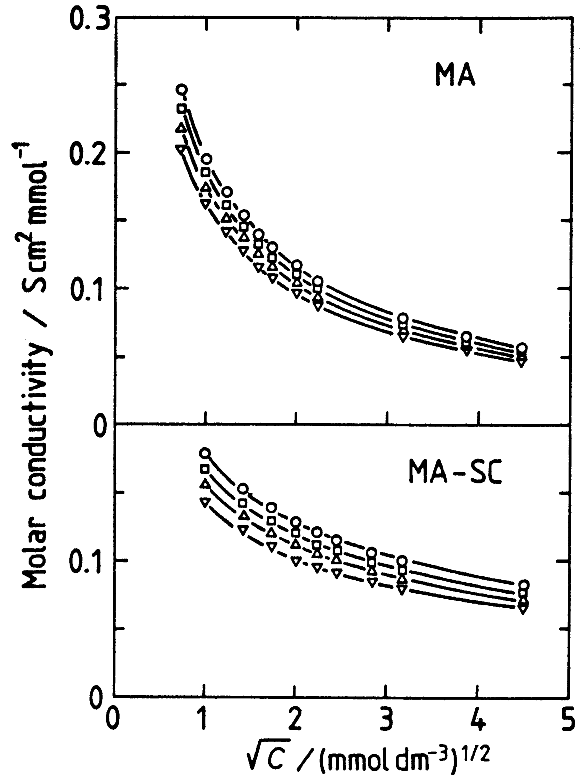

Fig. 6. Plots according to Kohlrausch's equation on MA and MA-SC solutions. The same symbols as those in Fig. 1 are used.

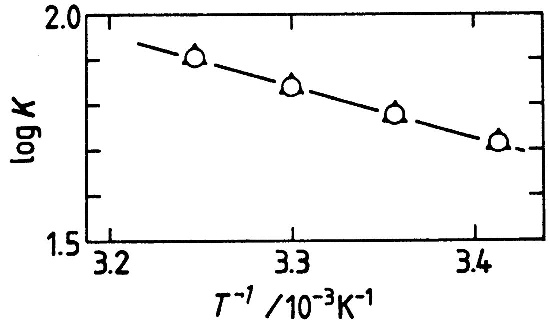

Fig. 7. Plots of $\log K$ against $1/T$ on PGA-SC and MA-SC systems. —O—: PGA-SC system and —Δ—: MA-SC system.

From plots of $\log K$ against $1/T$, we obtained straight lines as shown in Fig. 7. Thermodynamic data, ΔH and ΔS, were calculated with slopes in Fig. 7 by the equation, $\ln K = (-\Delta H/R)\ (1/T) + (\Delta S/R)$, as shown in Table 1.

Positive values of ΔH and ΔS suggest the existence of hydrophobic interaction in the process of 1 : 1 complex formation in aqueous solution. It is plausible that a phenyl group of PGA (or MA) may contact with a hydrophobic group supposed to be a benzene ring of SC by excluding water molecules from hydrated PGA (or MA) and hydrated SC.

Table 1. Equilibrium Constants and Thermodynamic Data for Both PGA-SC and MA-SC Systems. The Same Data Were Obtained on Both Systems as in Table 1

Equilibrium constant/dm^3 mol^{-1}	52±5 (293 k) 60±5 (298 K) 69±5 (303 K) 80±5 (308 K)
ΔH°/J mol^{-1}	$+2.2\times10^4$
ΔS°/J K^{-1} mol^{-1}	$+1.1\times10^2$

The values of ΔH and ΔS show almost no difference in both the PGA-SC complex and the MA-SC complex. It seems that the difference of molecular structure between PGA and MA may change little with the ratio of complex formation.

The equilibrium constant of the PGA-SC complex is consistent with that of the MA-SC complex in the region of 20—35 °C. Therefore, it is possible that the PGA in the PGA-SC complex is replaced by MA to form the MA-SC complex. As the PGA-SC complex is reduced to form the MA-SC complex on the surface of the electrode, the following process must be repeated:

$$\text{PGA} + \text{SC} \rightleftarrows \text{PGA-SC} \xrightarrow{2\text{H}^+,\ 2e} \text{MA-SC} \rightleftarrows \text{MA} + \text{SC}. \tag{14}$$

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