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Studies on Inclusion Behaviors of β -Cyclodextrin-Starch Composite Gel by Spin Probe Method

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ABSTRACT

A composite gel prepared from β -cyclodextrin and starch in a 1:2 ratio and cross-linked by epichlorohydrin was used as a host compound for inclusions. The competitive inclusion between 4-hydroxy-2,2,6,6-tetramethylpiperidiny-1-oxyl and chloro-substituted acetic acids was monitored by ESR spectroscopy. The triplet signals enabled us to estimate the rotational correlation frequencies of the

radical by employing Kivelson's equation. The unusual temperature dependence of the frequencies suggests that gradual loosening of the gel link occurs with an increase of temperature from 30 to 60°C, resulting in increased amounts of the inclusion which cancels the increments of the correlation frequencies. The gel is found to be a better host than β -cyclodextrin for dichloro, monochloro, and unsubstituted acetic acids, at least below 50°C. Trichloroacetic acid is included in the gel as much as is dichloroacetic acid, but much more than monochloroacetic acid and acetic acid, which still compete comparably with radical inclusion.

INTRODUCTION

Current topics on cyclodextrins related to reaction models of enzymatic functions have been abundant. However, studies on immobilized cyclodextrins as a host molecule or catalyst are few in spite of the great demand for immobilized enzymes.

A potential means of investigating the inclusion behavior of cyclodextrins is the spin probe method with electron spin resonance (ESR) spectroscopy. Kinetic studies on the deacylation reaction assisted by cyclodextrins using spin-labeled acyl compounds have promoted the methods [1-3].

We have also studied the kinetics of the base-catalyzed decarboxylation of trichloroacetic acid in the presence of β -cyclodextrin (β -CD) or cycloheptaamylose [4], and the inclusion mechanism by the new spin probe method in which the inclusion of chloroacetic acid is determined in the same system by the inclusion of the nitroxyl radical whose rotational correlation frequencies are measured by means of ESR [5]. The new method is free from the care required for spin-labeled substrates which may change in size and polarity and may not reflect real degree of inclusion or the mechanism of the substrates.

In the present study the method is applied to competitive inclusions of chloroacetic acids and a spin probe in the presence of a β -CD-starch composite gel as an immobilized host.

EXPERIMENTAL

A β -cyclodextrin-starch composite gel was prepared as follows. Commercially available β -CD (2 g) and soluble corn starch (4 g) were dissolved in 3 N NaOH solution (16.7 mL). A mixed solution of liquid paraffin (15 mL), kerosene (35 mL), a surface-active agent, solbitan fatty acid ester (2 g), and epichlorohydrin (25 mL) was prepared. The former aqueous solution was added gradually to the prepared mixture solution. The suspended solution was stirred for 3 h at 60°C. The

resulting composite gel was washed repeatedly with a nonionic detergent and water. The water content was removed by using acetone, and then dried in vacuo at 30°C.

Another type of β -CD gel which did not contain starch was prepared according to the literature [6]. All other chemicals and ESR measurements were the same as those employed in the previous work [5]. The gel (100 mg) was added to a solution (3 mL) of 4-hydroxy-2,2,6,6-tetramethyl piperidiny-1-oxyl (I) (3×10^{-4} M) and acetic acids (3.75×10^{-5} to 3.0×10^{-3} M).

RESULTS AND DISCUSSION

An aqueous solution of (I) was kept at 60°C for 3 h after addition of the composite gel. The swelling mixture was placed in an ESR sample tube of 1 ϕ mm.

The average hyperfine splitting constant (a^N) of the triplet signals was 16.8 gauss, which was nearly equal to the a^N in the presence of β -CD instead of the gel. However, the unsymmetric triplet peaks were further broadened, indicating anisotropic rotation of (I) (see Fig. 1).

The rotational correlation time (τ_c) of the spin can be calculated by Kivelson's equation [7]:

$$\tau_c = \left\{ (h_0/h_{+1})^{1/2} + (h_0/h_{-1})^{1/2} - 2 \right\} (4\pi\sqrt{3}/b^2) W_0 \quad (1)$$

where h and W are peak height and peak width, respectively; subscripts +1, 0, and -1 correspond to magnetic spin quantum number $M = +1, 0, \text{ and } -1$, respectively; and the term $(4\pi\sqrt{3}/b^2)$ equals 5.96626×10^{-10} . When the temperature is elevated from 30 to 60°C, as shown in Fig. 2(f), $\log \tau_c^{-1}$ remained constant; from 60 to 80°C it increased moderately. Upon replacement of the composite gel with another gel which did not contain starch, a very similar curve of the temperature dependence of $\log \tau_c^{-1}$ was observed (Fig. 2g).

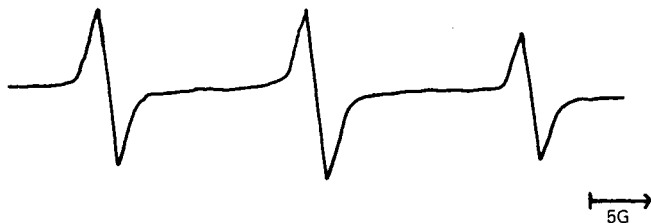


FIG. 1. ESR spectrum of nitroxyl radical (I) in the presence of the β -cyclodextrin-starch composite gel at 30°C.

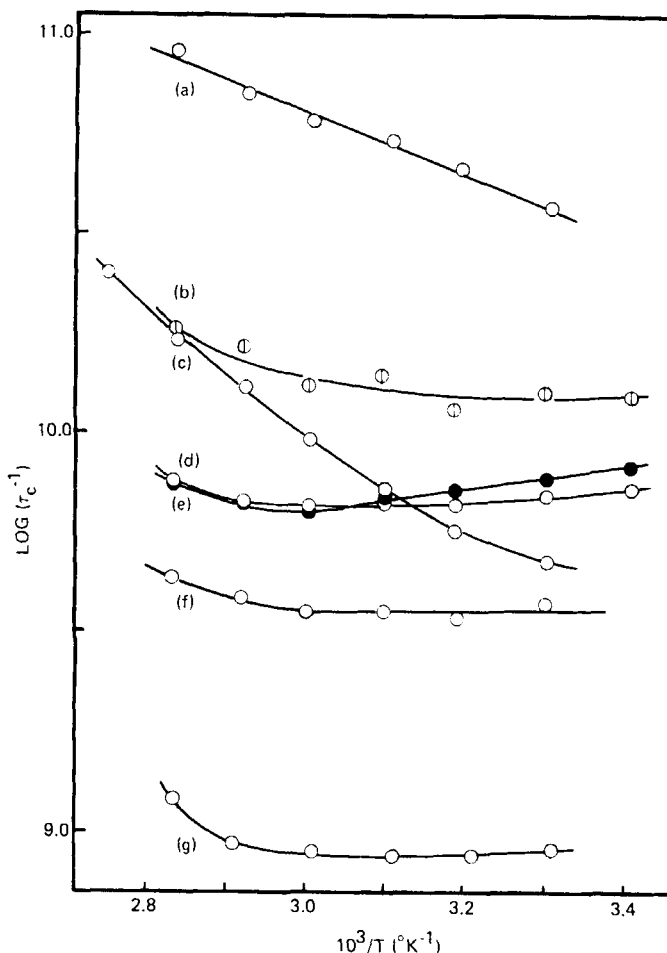


FIG. 2. Relationship between rotational correlation frequency (τ_c) of nitroxy radical (I) and temperature (T) in the presence or absence of various hosts: (a), (I) only; (b), (I) and DCAA with the composite gel; (c), (I) with β -CD; (d), (I) and MCAA with the composite gel; (e), (I) and AA with the composite gel; (f), (I) with the composite gel; (g), (I) with the β -CD gel free of starch.

Such a temperature dependence is quite unusual. In the case of β -CD (Fig. 2c), $\log \tau_c^{-1}$ increases normally with an elevation of temperature except below 30°C where the status of water molecules in the β -CD cavity is supposedly unchanged [5]. The abnormality of the present case may be explained by the loosening of gel linkages with an

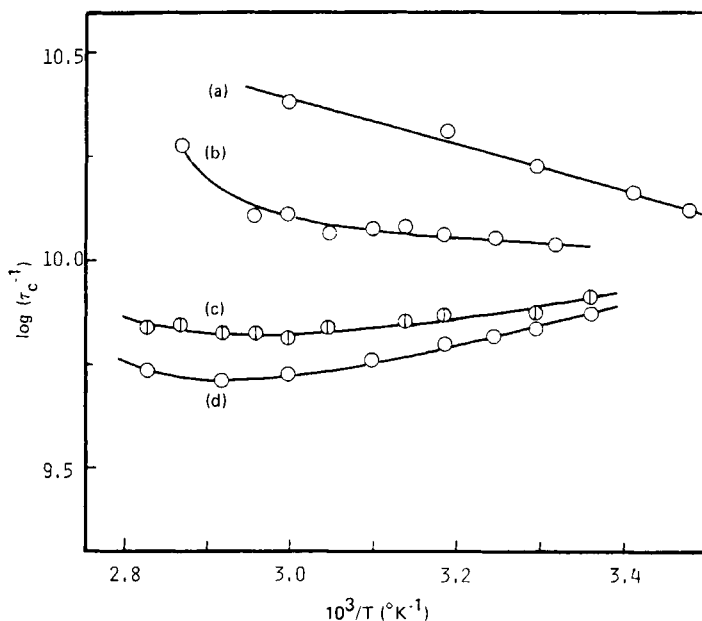


FIG. 3. Effect of concentration of trichloroacetic acid (TCAA) on the inclusion of (I) in the β -CD-starch composite gel. The ratios of $[TCAA]/[(I)]$ are (a) 10, (b) 2, (c) $1/4$, and (d) $1/8$.

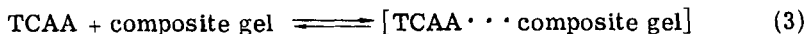
increase in temperature. The increment of the free rotation of (I) was canceled by the increased amount of (I) trapped in the loosened gel. This compensation gradually becomes out of balance over 60°C , resulting in an increase of $\log \tau_c^{-1}$. The rotation of (I) in the composite gel was about 18 times or 3 times slower than that without any host molecules (Fig. 2a) or in β -CD (Fig. 2c) at 60°C . However, the equilibration shown by Eq. (2) is still fast enough on an ESR time scale to be observed in weight-averaged signals:



In order to examine the competitive inclusion into the gel, a mixed solution of (I) and a chloro-substituted acetic acid was used. First admixed was trichloroacetic acid (TCAA) because it is among the best acetic acids for inclusion in β -CD [5]. As shown in Fig. 3(b), the τ_c value of (I) decreased as much as in competitive inclusion into β -CD under the same conditions. $\log \tau_c^{-1}$ did not essentially change up to 60°C ; here the compensation effect also appeared to be operating.

The amount of (I) removed from the gel was increased by increasing the concentration of TCAA added (Fig. 3a). On the other hand,

when the ratio of TCAA to (I) was decreased to 1/4 or 1/8, the predominant inclusion of (I) was deduced from correlation curves (Fig. 3c and 3d). These experiments confirmed the competitive inclusion of Eqs. (2) and (3):



When dichloroacetic acid (DCAA) was used in place of TCAA, the $\log \tau_c^{-1}$ values and the temperature-dependence curve were virtually equal to those of TCAA (Fig. 2b). This fact indicates that the gel is a better host for DCAA than for β -CD.

Monochloroacetic acid (MCAA) and acetic acid (AA) were also included to a greater extent in the gel, at least below 50°C (Fig. 2d and 2e). These two curves of temperature dependence almost overlapped in Fig. 3(c), and were parallel to that of (I) in the gel but free of these competitive substrates (cf. Fig. 2f).

It is remarkable that the inclusion of AA, which has not been recognized in β -CD, is comparable with that of (I) in the gel at 60°C.

It is concluded that the gel is less selective for a number of chloro-substituents, but is a better host for acetic acids.

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