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Conductometric and Potentiometric Studies of the Association of α-Cyclodextrin with Ionic Surfactants and Their Homologs

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The conductometric determination was made of the association constants of α-cyclodextrin (αCD) with ionic surfactants and their homologs. For 1-alkanesulfonate ions with carbon atoms (n) of 5—12, the association constant was found to increase regularly with n and become abruptly constant at $n=10$. The association constants for sodium 1-dodecanesulfonate, dodecylammonium chloride, dodecyltrimethylammonium chloride, and 1-dodecylpyridinium chloride were all similar in their magnitude. The effect of complexation on the micellar properties of sodium dodecyl sulfate and dodecyltrimethylammonium chloride were also studied potentiometrically by determining the counterion activities. In both cases, the critical micelle concentration increased regularly, while the degree of counterion association to the micelle decreased almost linearly with increasing αCD concentrations. It was suggested that the αCD–surfactant ion complex is solubilized in the hydrophilic surface region of surfactant micelle to give rise to a decrease in the surface charge density.

Cyclodextrins have been well known to form inclusion compounds with a variety of small molecules by several kinds of driving forces.[1] In the complexation of bulky hydrophobic molecule such as 1-adamantanecarboxylate, the hydrophobic interaction has been found to play an important role.[2] It is thus interesting to study the interactions of cyclodextrins with the surfactant ion which has an ionic head group as well as a large hydrocarbon chain of varying hydrophobicity. In this connection, Okubo *et al.*[3] made the conductometric study of the complexations of α- and β-cyclodextrins (αCD and βCD) with sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB) in water and mixed solvents. They found that in all cases an apparent critical micelle concentration increases regularly with increasing cyclodextrin concentration. In conformity with the difference of the hydrophobicities of the surfactant ion and cyclodextrin, the association constant, K, was found to increase in the order of SDS–αCD<SDS–βCD <CTAB–αCD<CTAB–βCD. They also pointed out that the decrease in K in mixed solvents comes partly from the decrease in hydrophobic attractive interaction between cyclodextrin and surfactant ion.

These observations prompted us to study the cyclodextrin–surfactant ion interactions both from thermodynamic and colloid chemical standpoints. In this paper is described the conductometric determination of the association constants of α-cyclodextrin with various ionic surfactants and their homologs. The potentiometric study was also undertaken to obtain information about the effect of complexation on the micellar properties of sodium dodecyl sulfate and dodecyltrimethylammonium chloride.

Experimental

Materials. Sodium dodecyl sulfate (SDS, Nakarai Chemicals Ltd.) and 1-dodecylpyridinium chloride (DPC, Tokyo Kasei Kogyo Co. Ltd.) were dissolved in hot ethanol and refluxed with active carbon for 10 h, respectively. After cooling the filtrate, the precipitate was further recrystallized twice from ethanol. The purification of dodecyltrimethylammonium chloride (DTAC, Tokyo Kasei Kogyo Co. Ltd.) was the same as that described above, except that acetone was used. Dodecylammonium chloride (DAC) was prepared from dodecylamine (purity>99%, Nakarai Chemicals Ltd.).[4] Sodium p-dodecylbenzenesulfonate (SDBS, purity>99%, Wako Pure Chemical Industry Co. Ltd.), sodium 1-alkanesulfonates with carbon atoms (n) of 5—8, 11, and 12 (Tokyo Kasei Kogyo Co. Ltd., guaranteed grade), and α-cyclodextrin (αCD, purity>98%, Seikagaku Kogyo Co. Ltd.) were used without further purifications. Sodium 1-alkanesulfonates with n of 9 and 10 were synthesized from the alkyl bromides purified by vacuum distillation.[5]

Conductivity Measurements. The conductivity was measured with an accuracy of ±0.1 μS by using a TOA Electronics Ltd. Conductivity Meter model CM-50AT. The cell constant of the conductivity cell was estimated to be 1.005 cm^{-1} at 25 °C. In order to remove trace amounts of conducting impurities, the aqueous solution of αCD was passed through the mixed ion bed (Bio-Rad AG501-X8). The concentration of αCD was determined gravimetrically by drying aliquots of the stock solution over phosphorus pentaoxide under reduced pressure and estimating the water content of the resulting powder from elementary analysis. The conductivity was measured as a function of αCD concentration, C_h, at a constant amphiphile concentration of around 2.5 mmol dm^{-3}.

Electromotive Force Measurements. The counterion activities in SDS and DTAC solutions were measured at 25 °C by using a TOKO Ion Electrode type 1100 Na^+ and a chloride ion selective ceramic electrode, National IE-510103, respectively. The electromotive forces (EMF) of the following cells were measured with an accuracy of ±0.1 mV by using a Corning Digital 112 Research pH Meter.

Sodium ion electrode (or Chloride ion electrode)|
Sample solution|1 mol dm^{-3} NH_4NO_3 Agar bridge|
Reference electrode (Ag-AgCl)

Prior to the measurements with surfactant solutions, these electrodes were calibrated with a sodium chloride solution of known activity.[6] In both cases, the electrode showed an ideal response of 59.2 mV per decade change in measuring ion activity in the concentration range between 5×10^{-3} and 0.1 mol dm^{-3}. The counterion activity was determined as a

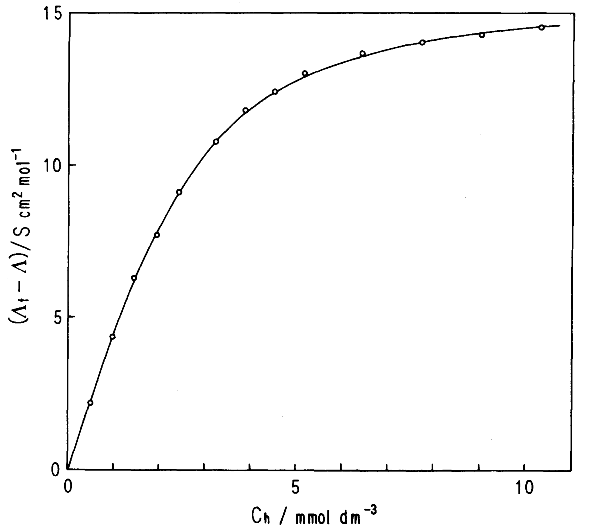

Fig. 1. Plots of $\Lambda_f - \Lambda$ vs. αCD concentration (C_h) for sodium 1-nonanesulfonate solution at 25 °C. C= 2.496 mmol dm^{-3}.
O, observed; solid line, calculated from Eq. 4 with $K = 1.49 \times 10^3$ dm^3 mol^{-1} and $\lambda_f - \lambda_a = 15.8$ S cm^2 mol^{-1}.

function of the surfactant concentration, C, under the conditions where the molar ratio of αCD to surfactant, R ($=C_h/C$), was kept constant.

Results and Discussion

Association Constant. Figure 1 shows the typical plots of $\Lambda_f - \Lambda$ vs. αCD concentration for sodium 1-nonanesulfonate at 25 °C, where Λ_f and Λ represent the equivalent conductivity in the absence and presence of αCD respectively. It has been found that neither Na$^+$ nor Cl$^-$ interacts appreciably with αCD.[7] Thus the successive decrease in Λ can reasonably be ascribed to the increase in the concentration of the associated 1-nonanesulfonate ion which has considerably smaller ionic equivalent conductivity than that of unassociated one. Similar results were also obtained for all of the amphiphiles studied.

In dilute electrolyte solution, which is the case for the present experiments, the activity coefficient ratio of associated and unassociated ions can safely be set equal to unity. Moreover, the activity coefficient of αCD is negligible under our experimental conditions.[8] Therefore, assuming a 1:1 reaction scheme,[3]

$$\mathrm{R}^{\pm} + \alpha\mathrm{CD} \rightleftharpoons \alpha\mathrm{CD}\cdot\mathrm{R}^{\pm}, \tag{1}$$

the association constant, K, can be written as

$$K = f/(1-f)(C_h - fC), \tag{2}$$

where R$^{\pm}$ refers to the amphiphilic ion and f to the fraction of R$^{\pm}$ associated with αCD, respectively. If we denote the ionic equivalent conductivities of R$^{\pm}$ and αCD·R$^{\pm}$ by λ_f and λ_a, we may write

$$\Lambda_f - \Lambda = f(\lambda_f - \lambda_a). \tag{3}$$

The use of Eqs. 2 and 3 for the evaluation of K requires a knowledge of λ_a. Unfortunately, however, the value of λ_a is somewhat difficult to estimate, since Λ decreases slightly but continuously even at higher αCD concentrations (see Fig. 1). This is especially true for 1-alkanesulfonate ion with shorter alkyl chain length. It follows immediately from Eqs. 2 and 3 that

$$\Lambda_f - \Lambda = \frac{\lambda_f - \lambda_a}{2KC}[K(C+C_h) + 1 - \sqrt{\{K(C+C_h)+1\}^2 - 4K^2CC_h}]. \tag{4}$$

Table 1. The conductometric and thermodynamic parameters of αCD–amphiphile systems

Amphiphile	C	Temp	Λ_f	$\lambda_f - \lambda_a$	K	$-\Delta G^\circ$
	mmol dm^{-3}	°C	S cm^2 mol^{-1}	S cm^2 mol^{-1}	dm^3 mol^{-1}	kJ mol^{-1}
$C_nH_{2n+1}SO_3Na$						
n=5	2.485	25	76.9	19.6	1.57×10^2	22.5
n=6	2.503	10	50.7	11.6	5.38×10^2	25.6
	2.526	25	74.2	17.9	3.79×10^2	24.7[a]
	2.503	40	99.5	24.1	2.81×10^2	23.9
n=7	2.552	10	50.2	11.6	8.70×10^2	26.7
	3.143	25	73.3	16.7	6.76×10^2	26.1[b]
	2.552	40	98.4	21.6	5.59×10^2	25.7
n=8	2.540	25	72.9	16.3	1.08×10^3	27.3
n=9	2.496	25	71.5	15.8	1.49×10^3	28.1
n=10	2.500	25	71.3	14.5	2.02×10^3	28.8
n=11	2.520	25	69.9	13.8	2.07×10^3	28.9
n=12	2.503	25	69.8	13.1	2.14×10^3	29.0
SDS	2.687	25	69.0	14.5	1.12×10^3	27.4
SDBS	0.869	25	67.5	8.2	5.73×10^3	31.4
DAC	2.544	25	99.1	14.9	2.27×10^3	29.1
DTAC	2.536	25	98.8	13.1	2.48×10^3	29.3
DPC	2.712	25	91.1	11.5	2.80×10^3	30.1

a) $\Delta H^\circ = -15.8$ kJ mol^{-1}, $\Delta S^\circ = 29.9$ J K^{-1} mol^{-1}.
b) $\Delta H^\circ = -10.7$ kJ mol^{-1}, $\Delta S^\circ = 51.7$ J K^{-1} mol^{-1}.

On the basis of Eq. 4, therefore, the values of K and $\lambda_f - \lambda_a$ were all evaluated from the plots of $\Lambda_f - \Lambda$ *vs.* C_h by using the non-linear least squares method (Gauss-Newton algorithm). The results are summarized in Table 1 together with the standard free energy change of complex formation, ΔG°, estimated from K_x (=55.5 K). The solid line in Fig. 1 shows the calculated conductivity curve from Eq. 4 with parameters thus determined for sodium 1-nonanesulfonate. The agreement between experimental and calculated curves is quite satisfactory over whole range of C_h, indicating the validity of a 1:1 reaction scheme. Similar agreements were also observed for all amphiphiles studied.

The most remarkable feature of Table 1 is the regular increase in K with the number of carbon atoms (n) and the leveling-off phenomenon above $n=10$ for 1-alkanesulfonate ions. The corresponding chain length dependence of ΔG° is shown in Fig. 2. These results suggest that αCD cavity accomodates succesively the methylene groups of hydrocarbon tail presumably by hydrophobic interaction. It is worth noting here that αCD molecule can accommodate at most 5 methylene groups of a fully extended alkyl chain in its hydrophobic cavity of 0.67 nm[9] long. According to the geometric consideration, therefore, the leveling-off phenomenon of K or ΔG° appears to occur at $n \approx 6$ even if we take into account the fact that the methylene group closest to the ionic head group shows little or no hydrophobicity.[10] As is clearly shown in Fig. 2, however, this is not the case for the present result. In an inclusion process of long hydrocarbon chain, it seems thus highly probable that the additional 4 methylene groups can still interact with other part of αCD molecule than hydrophobic cavity, presumably with the lateral hydrophilic surfaces. A similar interaction was reported by Komiyama and Bender[2] for a complexation of bulky 1-adamantanecarboxylate with αCD. In this case, the complexation was found not only to accompany large positive entropy change but to occur in such a way that the guest molecule sits on top of the cavity. In Table 1 are also given the standard enthalpy and entropy changes estimated for 1-hexane- and 1-heptanesulfonate ions from temperature dependence of K_x. In the case of 1-hexanesulfonate ion, the contribution of enthalpy term to ΔG° is larger than that of entropy term ($-T\Delta S^\circ$), while the reverse is found for 1-heptanesulfonate ion. Although the detailed mechanism remains unclear, the observed decrease in the magnitude of ΔH° and the drastic increase in ΔS° for 1-heptanesulfonate ion are supposed to arise partly from the partial breakdown of the water structure around OH groups due to the penetration of hydrocarbon tail into lateral hydrophilic surface and partly from the change in the water structure around hydrocarbon tail associated with the transfer process from bulk phase to hydrophilic surface region.

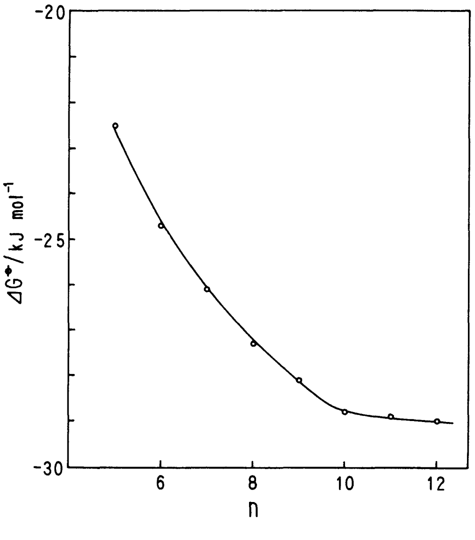

Fig. 2. The chain length dependence of ΔG° for sodium 1-alkanesulfonate at 25 °C.

The inspection of Table 1 also reveals another interesting feature that the association constants for surfactants with dodecyl chain, *i. e.*, sodium 1-dodecanesulfonate, DAC, DTAC, and DPC, are all similar in their magnitude in spite of the differences in the chemical and electrical properties of ionic head group. This fact suggests that the interaction between ionic head group and αCD molecule plays a minor role in the inclusion process of surfactant ion. An exceptional increase in K for SDBS can reasonably be ascribed to the presence of the additional aromatic ring, since a number of aromatic compounds have been found to interact strongly with αCD.[1] It should be noted that the value of K for sodium 1-dodecanesulfonate is about twice as large as that for SDS. In micelle formation of SDS, the extra oxygen atom in the sulfate group has been known to behave as an extra CH_2 group.[11] The presence of this anomalous oxygen atom may be responsible for the observed decrease in K for SDS.

Micellar Properties. In the complexation of the surfactant ion, the resulting complex is still supposed to behave like an amphiphilic ion with apparently shorter chain length. One might thus expect that the addition of αCD to surfactant solutions would affect not only the critical micelle concentration (cmc, C_0) but the micellar properties such as the degree (β) of counterion association to the micelle. Thus, we made the potentiometric determinations of β in solutions of SDS and DTAC in the presence of αCD. Figure 3 shows the typical semilogarithmic plots of the EMF (E_-) of the chloride ion electrode *vs.* DTAC concentration at varying values of R. The break point in this figure corresponds to the cmc at a given value of R. Similar behaviors were also observed for SDS solutions. In Fig. 4 are plotted the critical micelle concentrations thus determined for DTAC and SDS as a function of R. It should be noted that the cmc

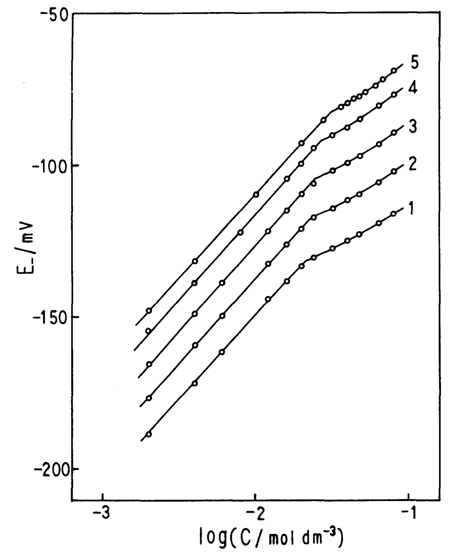

Fig. 3. The semilogarithmic plots of E_- *vs.* C for DTAC solution at 25 °C. 1, $R=0$; 2, $R=0.091$; 3, $R=0.185$; 4, $R=0.275$; 5, $R=0.366$. The curves 2, 3, 4, and 5 are displaced upward by 10, 20, 30, and 40 mV, respectively.

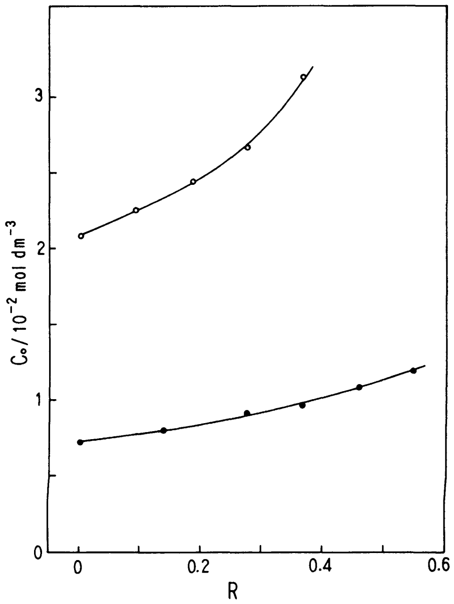

Fig. 4. Plots of C_o *vs.* R at 25 °C. ●, SDS; ○, DTAC.

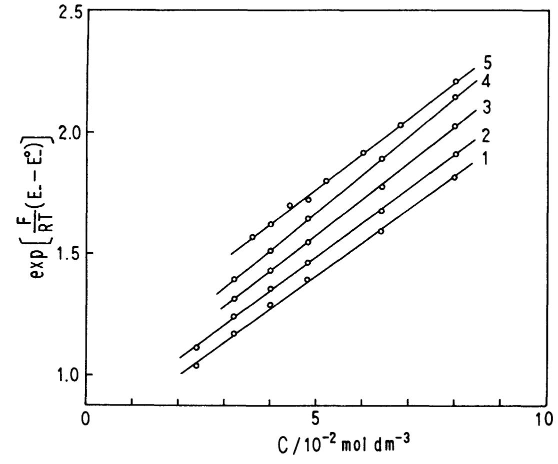

Fig. 5. Plots of the right-hand side of Eq. 6 *vs.* C for DTAC solution at 25 °C. 1, $R=0$; 2, $R=0.091$; 3, $R=0.185$; 4, $R=0.275$; 5, $R=0.366$. The straight lines 2, 3, 4, and 5 are displaced upward by 0.1, 0.2, 0.3, and 0.5, respectively.

becomes progressively higher as R increases and eventually disappears at R larger than 0.4 for DTAC and 0.6 for SDS respectively. Okubo *et al.*[3] assumed implicitly that the increase in an apparent cmc comes only from the increase in the concentration of the associated surfactant ion, *i.e.*, the concentration (C_m) of the monomeric surfactant ion available for the micellization process remains constant even in the presence of cyclodextrins. From the thermodynamical standpoint, however, other factors than that described above, *e.g.* the effect of the electrical potential at the micellar surface (ψ_s) on C_m can not be ignored even at the cmc, since an increase in the cmc is necessarily accompanied by the regular decrease in the magnitude of ψ_s by virtue of the increase in total counterion concentration. In fact the value of C_m calculated from Eq. 2 with K in Table 1 is not constant but decreases appreciably as R increases. For example with SDS, the value of C_m at the cmc decreases down to 6.20×10^{-3} mol dm^{-3} at $R=0.548$ (*cf.* $C_m=7.18\times10^{-3}$ mol dm^{-3} at $R=0$). If the associated surfactant ions are solubilized in the hydrophilic surface region of the micelle, the resulting depression in surface charge density will play an additional role in determining the value of ψ_s.

The EMF of the chloride ion electrode can be described as

$$E_- = E_-^\ominus + (RT/F)\ln a_-, \qquad (5)$$

where $E_-^\ominus$ refers to the standard electrode potential and a_- to the chloride ion activity; other symbols have their usual meanings. Denoting the values of E_- and a_- at the cmc by E_-° and a_-° respectively, we immediately have

$$a_-/a_-^\circ = \exp\left[(F/RT)(E_- - E_-^\circ)\right]. \qquad (6)$$

Figure 5 shows the plots of the right-hand side of Eq. 6 *vs.* DTAC concentration at higher concentrations than cmc. In agreement with the results[12–15] reported for counterion activities in various ionic surfactant solutions without host molecule, the chloride ion activity increases linearly with increasing DTAC concentration regardless of the value of R. This is also the case for SDS solutions containing αCD. These results allow us to estimate the degree of counterion association to the micellle at the cmc, β_o, as a function of R. If we denote the total intermicellar concentration of the associated and unassociated surfactant ions in bulk phase by C_b, and the counterion activity

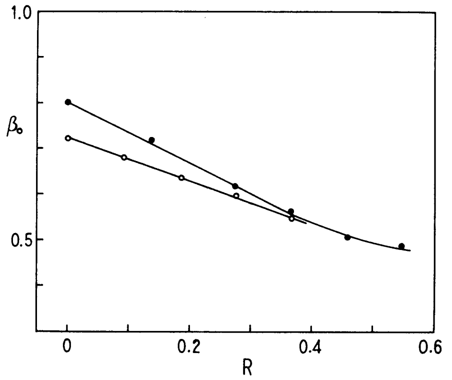

Fig. 6. Plots of β_o *vs.* R at 25 °C. ●, SDS; ○, DTAC.

coefficient by γ_-, Eq. 6 can be rewritten as

$$a_-/a_-^\circ = \gamma_-[C_b+(1-\beta)(C-C_b)]/\gamma_-^\circ C_o. \qquad (7)$$

In solution of ionic surfactant alone, it is usually assumed that the values of γ_-, β, and C_b which in such case represents the concentration of the monomeric surfactant ion remain constant in the concentration range above cmc.[12–14,16] Because of the complications arising from the presence of the associated surfactant ions, it is somewhat doubtful whether the same assumption can be applicable for the present systems. Apart from the concentration dependences of γ_-, β, and C_b, however, we can easily estimate the value of β_o from the slope of the straight line in Fig. 5, since the changes in these parameters can safely be ignored at least in quite narrow concentration range above cmc. The results are shown in Fig. 6. An important feature of Fig. 6 is the regular decrease in β_o with respect to R. In their theoretical study of the counterion condensation on charged planar surface, Engström and Wennerström[17] have derived the following expression for the fraction, P_c, of counterions bound to the surface region of thickness Δ which is the order of the diameter of a hydrated counterion.

$$P_c = 1 - [1-(\sigma Ze\Delta/2\varepsilon_r\varepsilon_0 kT)]^{-1} \qquad (8)$$

Here, σ is the surface charge density, Ze the charge of the counterion, ε_r the relative permittivity, and ε_0 the permittivity of a vacuum, respectively. In view of the fact that most of the micellar properties of ionic surfactant solutions can be interpreted in terms of the lamellar model,[18] P_c in Eq. 8 is supposed to be closely related to β_o. This in turn suggests that the observed decrease in β_o arises virtually from a decrease in the magnitude of surface charge density. It seems therefore most likely that the surfactant ion associated with bulky cyclodextrin molecule is solubilized in the hydrophilic surface region of surfactant micelle to give rise to a decrease in surface charge density.

As mentioned previously, the break point in EMF *vs.* log C plots became undetectable at R higher than 0.4 for DTAC and 0.6 for SDS, respectively. Therefore, the limiting value of β_o appears to correspond to the critical surface charge density, σ_{crit}, below which the counterion fixation no longer takes place. For example with SDS, the tentative estimation based on Eq. 8 with Δ=0.45 nm[6] leads to σ_{crit} of one unit charge per 2.1 nm^2 at R=0.548. On account of the definite size of the micellar aggregate, however, the actual value of σ_{crit} will probably be larger than that estimated above.

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