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Gel Filtration of Solubilized Systems. VII.¹⁾ Temperature Effect on the Solubilization of Ethylparaben in Hexaoxyethylene Lauryl Ether Micelles

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The effect of temperature on the solubilization of ethyl *p*-hydroxybenzoate(ethylparaben) in hexaoxyethylene lauryl ether (C₁₂E₆) micelles was examined by the gel filtration method using Sephadex G-200.

The values of standard Gibbs energy (ΔG^\ominus), enthalpy (ΔH^\ominus) and entropy (ΔS^\ominus) changes for the micellar solubilization of ethylparaben were calculated, together with the interaction energy parameter (ω). The negative values of ΔH^\ominus and ω showed that there is an interaction between the phenolic OH group in ethylparaben and the polyoxyethylene groups in the C₁₂E₆ micellar phase. The positive values of ΔS^\ominus suggest that the alkane moiety of ethylparaben is incorporated into the hydrocarbon core of C₁₂E₆ micelles. These results showed that both enthalpy and entropy effects control the micellar solubilization of ethylparaben.

Keywords—ethyl *p*-hydroxybenzoate; nonionic surfactant; micelle; gel filtration; solubilization; temperature effect; entropy change; enthalpy change; interaction energy parameter

In the previous paper,¹⁾ we reported that thermodynamic parameters such as the distribution coefficient (K), mole fractions of a solubilize in the micellar (X_s^m) and in aqueous phases (X_s^w), activity coefficient of a solubilize (γ_s^{*m}), critical micellar concentration (cmc), and interaction energy parameter (ω) could be estimated by the gel filtration method for methyl *p*-hydroxybenzoate(methylparaben) solubilized in micellar hexaoxyethylene lauryl ether (C₁₂E₆) solution,¹⁾ and the solubilization (dissolution into the micellar phase) depends on both the entropy of mixing and the interaction of methylparaben with C₁₂E₆ in the mixed micelles. The present paper deals with the effect of temperature on the solubilization of ethyl *p*-hydroxybenzoate(ethylparaben) in aqueous C₁₂E₆ micelles by the gel filtration method.

Experimental

C₁₂E₆ was obtained from Nikko Chemicals Co., Ltd. Ethylparaben was of reagent grade. Distilled water was used after degassing *in vacuo*. Gel filtration on Sephadex G-200 in a jacketed column (1.6 × 4 cm, Pharmacia, Sweden) was carried out in the same way as described previously.¹⁾ The total volume of the gel bed was in the range of 60—62 ml and the void volume was in the range of 24.5—25.3 ml.

The concentrations of ethylparaben and C₁₂E₆ in each fraction were determined as previously described for the methylparaben-C₁₂E₆ system.^{1,2)} The values of K , X_s^m , X_s^w , γ_s^{*m} , ω and cmc in the solubilized system of ethylparaben in aqueous C₁₂E₆ were calculated as previously reported.¹⁾

Results and Discussion

Gel filtration on Sephadex G-200 was carried out with aqueous C₁₂E₆ micellar solutions solubilizing ethylparaben at various concentrations in the range of temperature of 5 to 30 °C. In dilute solutions of a surfactant there is less probability that micelles interact with each other,^{1,3)} so the concentration of C₁₂E₆ was held constant at 2 mM (0.1%) in all runs. This

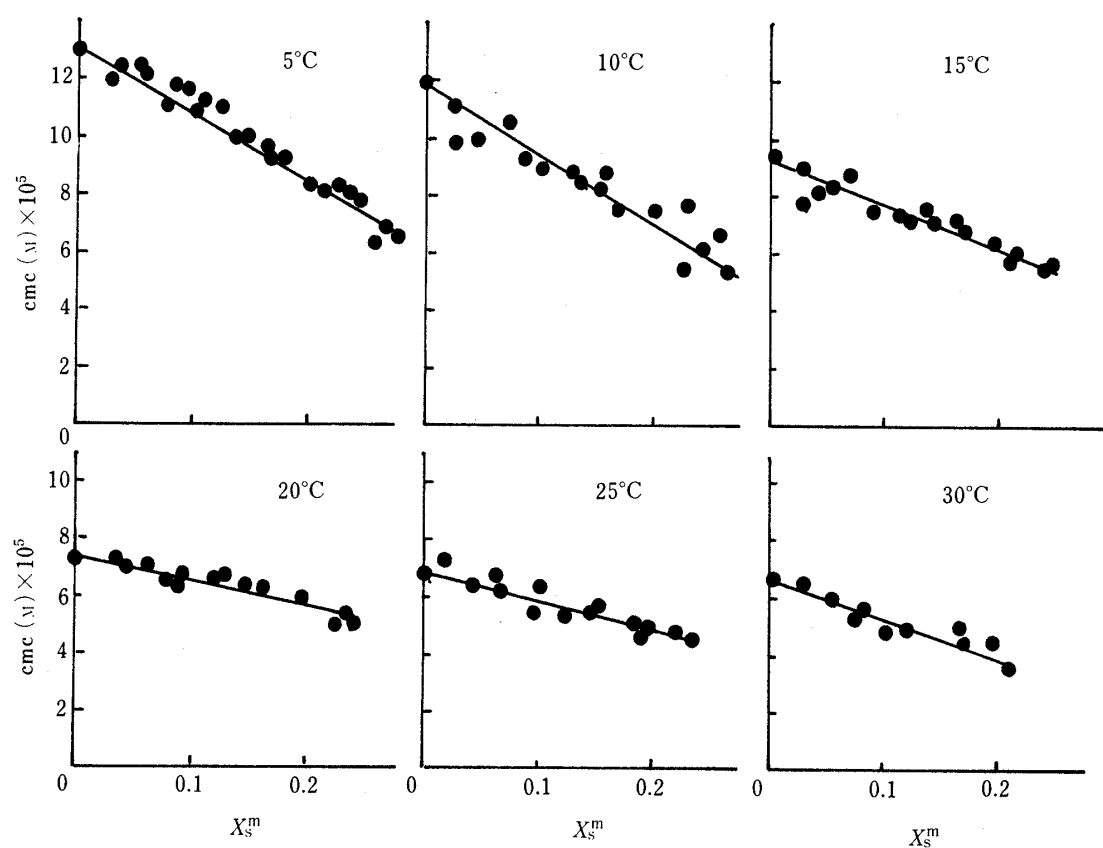


Fig. 1. The cmc of Aqueous $C_{12}E_6$ in the Presence of Ethylparaben

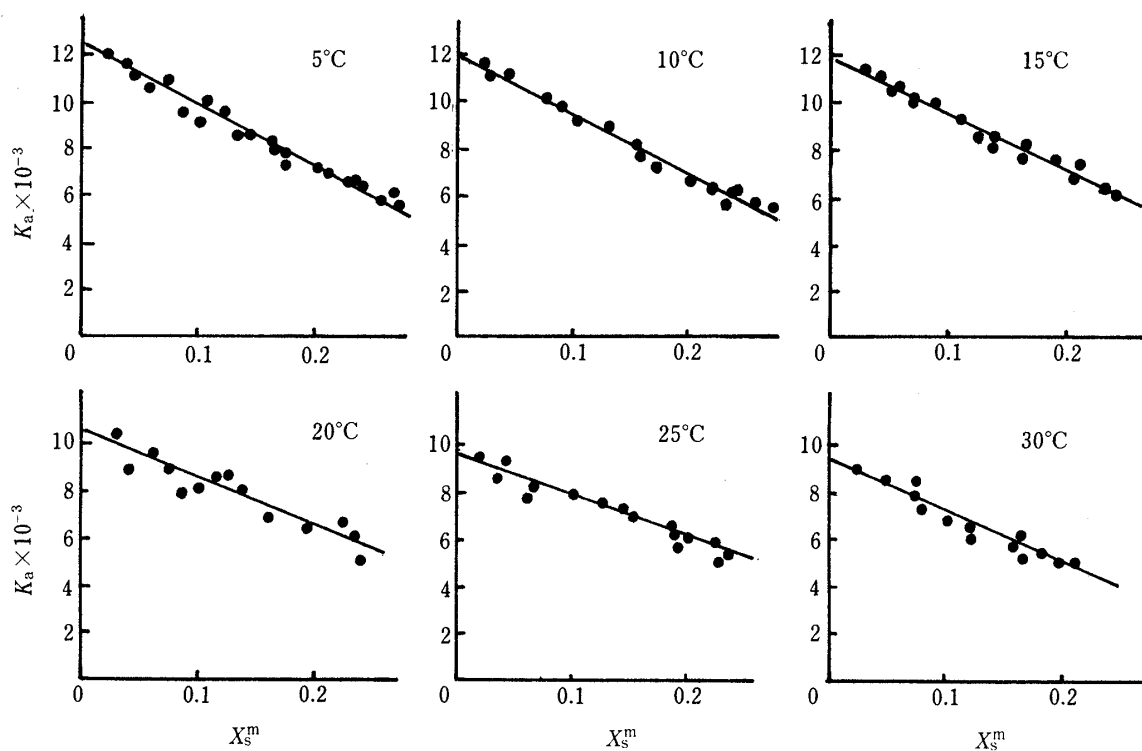


Fig. 2. Plot of the K_a Values of Ethylparaben against the X_s^m Values

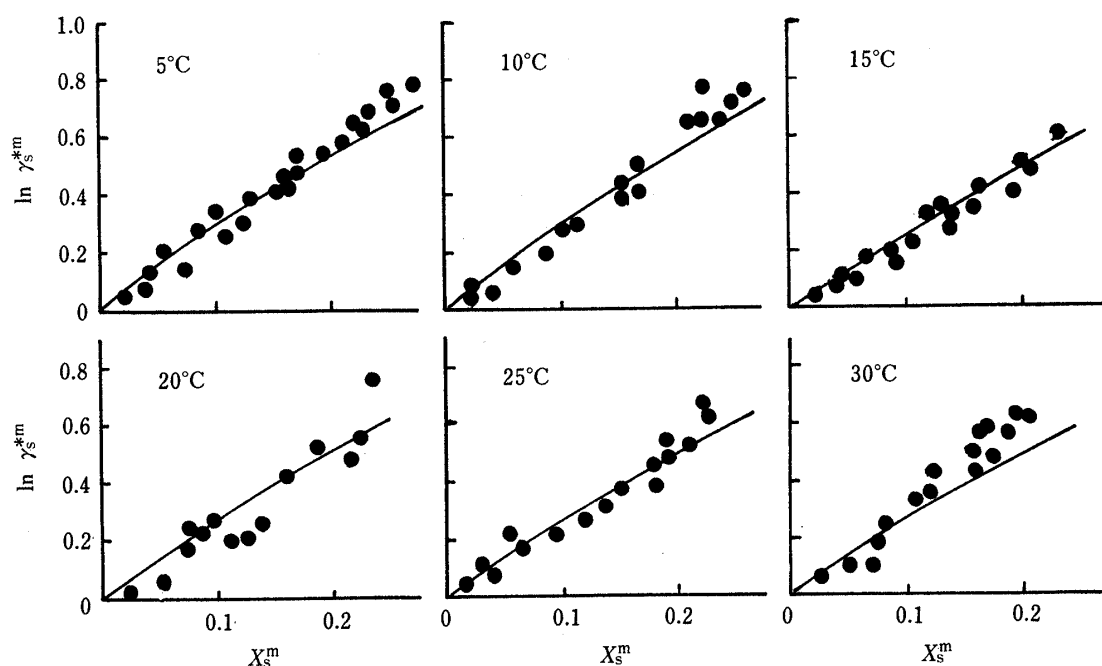


Fig. 3. Plot of the $\ln \gamma_s^{*m}$ Values of Ethylparaben against the X_s^m Values

The solid curves at various temperatures were calculated from Eq. (1), taking $\omega = -810$ cal/mol.

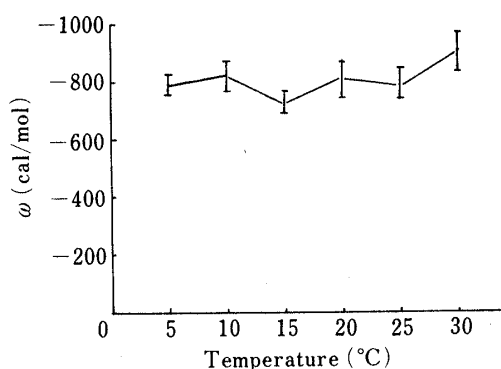


Fig. 4. Plot of the Interaction Energy Parameter (ω) Values against Temperature

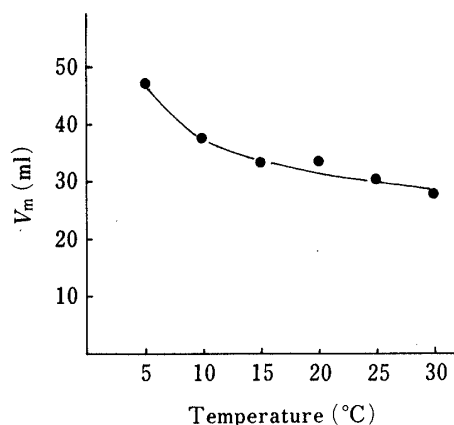


Fig. 5. Plot of Retention Volume of $C_{12}E_6$ Micelles against Temperature

concentration is higher than the cmc's in the temperature range (5 to 30 °C), as shown in Fig. 1.

Figure 2 is a plot of the apparent distribution coefficient (K_a) against X_s^m at temperatures of 5 to 30 °C. Since each K_a value is a linearly decreasing function of X_s^m , the value obtained by extrapolation to zero X_s^m corresponds to the K value.⁴⁾

Figure 3 shows a plot of $\ln \gamma_s^{*m}$ values against X_s^m . It can be seen that $\ln \gamma_s^{*m}$ becomes larger than zero with an increase of X_s^m , indicating that the solution state of ethylparaben in $C_{12}E_6$ micelles is nonideal.⁵⁾

Figure 4 shows the ω values calculated by Eq. (1), in which R is the gas constant and T is absolute temperature; this figure shows that the ω values in the range of 5 to 30 °C are almost independent of temperature. Thus, it is reasonable to apply Eq. (1) to the solubilized system. It is considered that in a solubilized system of ethylparaben- $C_{12}E_6$, there is an interaction, *i.e.* a

hydrogen bonding in the mixed micelles, on the basis of the ω value.¹⁾ This is in accordance with the conclusion based on the cmc data already reported¹⁾ and furthermore supports the conclusion based on data on the molar volumes.⁶⁾

$$\ln \gamma_s^{*m} = X_s^m(X_s^m - 2)\omega/RT \quad (1)$$

It is known that the retention volume (V_m) of surfactant micelles is a function of micellar size.⁷⁻⁹⁾ As shown in Fig. 5, a plot of V_m of $C_{12}E_6$ micelles against temperature shows that the micellar size increases with increase in temperature. However, it is considered that this micellar size change with temperature does not lead to a marked variation in the solvent properties of the micelles because the ω value is almost independent of temperature.

Next, let us discuss the effects of temperature on the thermodynamic parameters for the distribution of ethylparaben between the $C_{12}E_6$ micellar and aqueous phases.

Many attempts have been made to estimate the solubilization process for a solubilize by using thermodynamic parameters such as K_a obtained by the solubility method,¹⁰⁻¹²⁾ but the attempts failed because the solubility method determined only the K_a value but not the K value which is a thermodynamic equilibrium constant.¹³⁾ The K value, which can be obtained by the gel filtration method described above,¹⁾ can provide a value for the standard Gibbs energy change (ΔG^\ominus) of micellar solubilization, based on Eq. (2).

$$\Delta G^\ominus = -RT \ln K \quad (2)$$

Furthermore, the values of enthalpy and entropy changes (ΔH^\ominus and ΔS^\ominus) of the micellar solubilization can be obtained from Eqs. (3) and (4), respectively.

$$\Delta H^\ominus = -Rd \ln K/d(1/T) \quad (3)$$

$$T\Delta S^\ominus = \Delta H^\ominus - \Delta G^\ominus \quad (4)$$

The values of $-R \ln K$ were plotted against $1/T$ and a least-squares treatment of this plot gives a ΔH^\ominus value of -2.00 kcal/mol. This negative value of ΔH^\ominus shows that ethylparaben dissolves in $C_{12}E_6$ micelles by an exothermic process. It can be assumed that there is an interaction between the phenolic OH group in ethylparaben and the polyoxyethylene groups in $C_{12}E_6$ micelles, and that this interaction exceeds that between phenolic OH group and water in the aqueous phase. The interaction in the micelles can be considered to correspond to the ω value. Since the ΔS^\ominus values are positive, as shown in Table I, it is likely that there is a hydrophobic interaction in this solubilization process^{12,14)} and that the alkane moiety of ethylparaben is incorporated into the hydrocarbon core of $C_{12}E_6$ micelles.

On the basis of these results, both enthalpy and entropy effects appear to control the solubilization of ethylparaben from the aqueous to the $C_{12}E_6$ micellar phase. This is interesting in view of the finding that the solubilization of alcohols from the aqueous to the micellar phase depends on the effect of entropy rather than that of enthalpy.¹⁴⁾

TABLE I. Thermodynamic Parameters

Temperature (°C)	K	ΔG^\ominus (cal/mol)	ΔH^\ominus (cal/mol)	ΔS^\ominus (cal/mol·degree)
5	12600	-5220	} -2000	+12
10	12000	-5280		+12
15	11600	-5360		+12
20	10500	-5400		+12
25	9870	-5450		+12
30	9540	-5520		+12

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