報 文

Surface Properties and Micelle Formation of a Series of Alkyl Octakis(oxyethylene) Ethers in the Aqueous Solutions and Their Temperature Dependences

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The values of cmc, area per molecule and equilibrium surface tension at cmc of a homologous series of alkyl octakis (oxyethylene) ethers (C_nE_8 : $n=10$ to 15) were determined from the concentration dependence of surface tension in the temperature range 15.0°C to 40.0°C. The areas per molecule and equilibrium surface tension values at the cmc decreased with an increasing carbon number and they showed zigzag curves by the difference in even and odd carbon numbers. These findings may be attributed to the difference in the molecular orientation between the molecules with even carbon number and ones with odd carbon number on the air-water interface.

On the other hand, the plots of log cmc *vs.* the number of carbon atoms (N) in the alkyl chain exhibited a linear relationship, and the difference between even and odd carbon numbers was not observed on the bulk properties. The free energy change relating to micelle formation, ΔG_m , was calculated from the temperature dependence of the cmc. ΔH_m and ΔS_m values were estimated from the slopes and the intercepts of the log cmc versus the reciprocal of temperature plots, respectively. This result indicates that ΔS_m dominates over the micellization. Furthermore, the values of $\Delta G_m(-CH_2-)$, $\Delta H_m(-CH_2-)$, $\Delta S_m(-CH_2-)$ and $T\Delta S_m(-CH_2-)$ per methylene group calculated from the slope of each thermodynamic parameter against the carbon number were -0.68 kcal/mol, -0.33 kcal/mol, 1.16 cal/(mol·deg), and 0.35 kcal/mol, respectively. It was concluded that the summation of $\Delta H_m(-CH_2-)$ and $T\Delta S_m(-CH_2-)$ contributed to the micellization.

1 Introduction

Although many investigations^{1)~5)} have so far been reported with respect of surface and micellar properties of alkyl poly(oxyethylene) ethers having a Poisson distribution of the ethylene oxide chain and further with an alkyl chain comprising even carbon numbers, relatively^{6)~8)} few studies have been carried out for a series of alkyl poly(oxyethylene) ethers with an alkyl chain comprising even and odd carbon numbers and in addition with a homogeneous ethylene oxide chain.

In this work, surface tensions for such a

series of alkyl octakis(oxyethylene) ethers (C_nE_8 : $n=10$ to 15) with a homogeneous octa-ethylene oxide chains and further with an alkyl chain consisting of either even or odd carbon numbers are measured in aqueous solutions in the temperature range from 15.0°C to 40.0°C. The effects of the temperature and of the difference in even and odd carbon numbers among their surfactant molecules on the surface area per molecule at air-water interface and on the micellization will be discussed on the basis of the experimentally obtained data and also the thermodynamic parameters calculated from the surface tension measurements.

2 Experimental procedures

2.1 Materials

Alkyl octakis (oxyethylene) ethers $C_nH_{2n+1}O(CH_2CH_2O)_8H$ (C_nE_8 ; $n=10$ to 15) were supplied by Nikko Chemicals Co., Tokyo, Japan. The homogeneity of the octakis(oxyethylene) chain was confirmed by TLC. The purity was found by GLC to be in excess of 99.0%. Traces of impurity nondetectable by TLC and GLC were removed by repeated passage through a gel permeation chromatographic column until the minimum in the surface tension curves and the corresponding peak in the GPC chromatogram disappeared. The identical process was used to purify all samples.

Water was purified by passing through a Milli-Q system (Nihon Millipore Co.) until its specific conductivity fell below $10^{-7} \cdot \Omega^{-1} \cdot \text{cm}^{-1}$.

2.2 Measurements

Surface tensions of the surfactant solutions prepared by dilution of the mother liquor were measured with a modified Wilhelmy type surface tensiometer SHIMADZU ST-1. Measurements were performed at 15.0, 20.0, 25.0, 30.0 and $40.0 \pm 0.1^\circ\text{C}$. Equilibrium reachings were taken between 1 and 2 h. This time interval was acceptable even for the lowest concentration of surfactant solutions. The establishment of equilibrium was checked by repeated measurements in 5 min intervals after reaching 1 h.

3 Results and discussion

Surface tensions as a function of solute concentrations of C_nE_8 ($n=10$ to 15) were measured in the temperature range from 15.0°C to 40.0°C . The typical curves are given for $C_{10}E_8$ and $C_{13}E_8$ in Figs.-1 (a) and (b), respectively. Some surface properties and cmc of C_nE_8 obtained from their curves are summarized in Table-1.

The molecular area values in Table-1 calculated by using the Gibbs adsorption isotherm equation from the slopes of the curves below the sharp breaks at their cmc in the temperature range 15.0°C to 40.0°C are plotted in Fig.-2 against the number of carbon atoms (N) in the alkyl chain.

These plots are zigzag in the difference of

Fig.-1 (a) Plots of surface tension against the logarithm of the solute concentrations for $C_{10}E_8$ at given temperatures.

Fig.-1 (b) Plots of surface tension against the logarithm of the solute concentrations for $C_{13}E_8$ at given temperatures.

the even-odd numbered carbon atoms, and the molecular area values decrease with an increase of the alkyl chain length. The zigzag line can be shown by two separate dashed lines among the surfactants with even carbon number and those with odd number in Fig.-2. The upper

Table-1 Some surface properties and cmc obtained from surface tension curves in the temperature range from 15.0°C to 40.0°C.

Temp. (°C)	cmc (M)	γ_{cmc} (dyn/cm)	$-\partial\gamma/\partial \log C$	$\Gamma'(\text{mol}/\text{cm}^2) \times 10^{10}$	A (Å ²)
C₁₀E₈					
15	1.4×10^{-3}	37.3	12.49	2.26	73.5
20	1.2×10^{-3}	36.5	13.35	2.38	69.8
25	1.0×10^{-3}	35.5	13.80	2.42	68.6
30	9.3×10^{-4}	34.4	14.42	2.48	66.9
40	7.6×10^{-4}	33.5	15.15	2.53	65.6
C₁₁E₈					
15	4.0×10^{-4}	36.8	13.00	2.36	70.4
20	3.5×10^{-4}	36.0	13.82	2.46	67.5
25	3.0×10^{-4}	35.3	14.36	2.50	66.4
30	2.7×10^{-4}	34.0	14.88	2.56	64.9
40	2.3×10^{-4}	33.3	15.63	2.61	63.6
C₁₂E₈					
15	9.7×10^{-5}	36.0	14.52	2.63	63.1
20	8.3×10^{-5}	35.0	15.06	2.68	62.0
25	7.1×10^{-5}	34.3	15.50	2.72	61.1
30	6.9×10^{-5}	33.4	16.14	2.78	59.7
40	5.8×10^{-5}	32.7	16.88	2.82	58.9
C₁₃E₈					
15	3.2×10^{-5}	36.5	15.62	2.83	58.7
20	2.8×10^{-5}	35.8	16.14	2.87	57.9
25	2.7×10^{-5}	34.9	16.40	2.87	57.9
30	2.5×10^{-5}	33.8	16.86	2.90	57.3
40	2.0×10^{-5}	32.8	17.52	2.92	56.9
C₁₄E₈					
15	1.1×10^{-5}	35.7	18.36	3.33	49.9
20	9.8×10^{-6}	35.0	18.75	3.34	49.7
25	9.0×10^{-6}	34.0	19.00	3.33	49.9
30	8.0×10^{-6}	33.2	19.48	3.35	49.6
40	7.2×10^{-6}	32.3	20.10	3.35	49.6
C₁₅E₈					
15	4.1×10^{-6}	36.0	20.35	3.69	45.0
20	3.7×10^{-6}	35.2	20.66	3.68	45.1
25	3.5×10^{-6}	34.3	20.95	3.67	45.2
30	3.2×10^{-6}	33.5	21.37	3.68	45.1
40	3.0×10^{-6}	32.6	22.01	3.67	45.2

line is for the surfactants with odd carbon number and the lower one for those with even carbon number. It is evident from these findings in **Fig.-2** that the molecular orientation of the former with odd carbon number on the air-water interface is a little different from that of the latter with the even carbon number. This suggests that the packing for the former on the air-water interface is more loosely than that for the latter.

Temperature dependences of their molecular areas decreased with the increase of hydrocarbon chain length, but were not observed for

Fig.-2 Plots of area per molecule at the air-water interface at the cmc against the number of carbon atoms (N) in the alkyl chain of C_nE_8 .

$C_{14}E_8$ and $C_{15}E_8$ as shown in **Fig.-2** and molecular areas for the two surfactants showed almost the same value in all temperature range from 15.0°C to 40.0°C. This suggests that, whereas the increase of the molecular motion caused by rising temperature decreases the amount of the adsorption on the water surface, it increases due to dehydration of ethylene oxide chain in the molecule with rising temperature, and in the case of $C_{14}E_8$ and $C_{15}E_8$, two opposite effects^(2), 9), 10) are compensated each other.

In a similar manner as in the case of the molecular area data, the plots of the equilibrium surface tension at the cmc vs. carbon number (N) at the given temperatures, as shown in **Fig.-3**, exhibited a zigzag line and the surface tension values decreased with the increase of the carbon number (N) and temperature.

This zigzag line is also represented by two different curves as shown in **Fig.-3**. The upper line is for the surfactants with odd carbon number, and the lower line for even carbon number. This gives a stronger support to the findings obtained from the molecular area data that the adsorption amount is larger for the surfactant with even carbon number than that

Fig.-3 Plots of surface tension at the cmc against the number of carbon atoms (N) in the alkyl chain of C_nE_3 in the temperature range from 15.0°C to 40.0°C.

for one with odd number.

Plots of $\log \text{cmc}$ vs. the number of carbon atoms (N) in the alkyl chain exhibit a linear relationship^{(10),(11)} as shown in **Fig.-4**.

The linear relationships in the temperature

Fig.-4 Plots of $\log \text{cmc}$ at given temperatures against the number of carbon atoms (N) in the alkyl chain of C_nE_3 .

range from 15.0°C to 40.0°C are given by the following general equation.

$$\log \text{cmc} = A_1 N + B_1 \quad (1)$$

The constants of A_1 and B_1 are summarized in **Table-2**.

Table-2 The constants corresponding to Eq. (1) and Eq. (3).

Temp. (°C)	A_1	B_1	$A_2 \times 10^{-3}$	$B_2 \times 10^{-3}$
15.0	-0.51	2.18	-0.67	0.58
20.0	-0.51	2.07	-0.68	0.44
25.0	-0.50	1.89	-0.68	0.21
30.0	-0.50	1.86	-0.69	0.17
40.0	-0.48	1.66	-0.69	-0.12

Table-3 Thermodynamic parameters for micellization of C_nE_3 .

Temp. (°C)	ΔG_m (kcal·mol ⁻¹)	ΔH_m (kcal·mol ⁻¹)	$T\Delta S_m$ (kcal·mol ⁻¹)	ΔS_m (cal·mol ⁻¹ ·deg ⁻¹)
$C_{10}E_3$				
15	-6.06	4.41	10.49	36.4
20	-6.25	4.41	10.66	36.4
25	-6.46	4.41	10.85	36.4
30	-6.62	4.41	11.03	36.4
40	-6.96	4.41	11.37	36.4
$C_{11}E_3$				
15	-6.77	3.99	10.76	37.4
20	-6.97	3.99	10.96	37.4
25	-7.18	3.99	11.15	37.4
30	-7.36	3.99	11.35	37.4
40	-7.71	3.99	11.70	37.4
$C_{12}E_3$				
15	-7.59	3.66	11.25	39.1
20	-7.81	3.66	11.47	39.1
25	-8.04	3.66	11.66	39.1
30	-8.19	3.66	11.85	39.1
40	-8.56	3.66	12.22	39.1
$C_{13}E_3$				
15	-8.22	3.28	11.50	39.9
20	-8.44	3.28	11.72	39.9
25	-8.61	3.28	11.90	39.9
30	-8.80	3.28	12.08	39.9
40	-9.23	3.28	12.51	39.9
$C_{14}E_3$				
15	-8.83	3.02	11.85	41.2
20	-9.05	3.02	12.07	41.2
25	-9.26	3.02	12.28	41.2
30	-9.48	3.02	12.50	41.2
40	-9.86	3.02	12.88	41.2
$C_{15}E_3$				
15	-9.40	2.73	12.13	42.1
20	-9.62	2.73	12.35	42.1
25	-9.82	2.73	12.55	42.1
30	-10.04	2.73	12.77	42.1
40	-10.41	2.73	13.14	42.1

Their linear relationships were not affected by the difference between even and odd carbon numbers differing from the results for the surface properties.

The standard free energy of micelle formation (ΔG_m) is calculated according to P. Malyneux¹²⁾ by the following equation.

$$\Delta G_m = 2.303 RT (\log \text{cmc} - \log w) \quad (2)$$

where w is the molar concentration of water at the given temperature. ΔG_m values calculated by Eq. (2) are listed in **Table-3**.

These ΔG_m values decrease with increasing number of carbon atoms from C_{10} to C_{15} in the alkyl chain of alkyl octakis (oxyethylene) ethers and further with increasing temperature as listed up in **Table-3**.

By combining Eq. (2) with Eq. (1), Eq. (3) is obtained.

$$\Delta G_m = A_2 N + B_2 \quad (3)$$

The constants of A_2 and B_2 in the temperature range from 15.0°C to 40.0°C are summarized in **Table-2**.

The free energy changes for micelle formation per methylene group, $\Delta G_m(-CH_2-)$, are given from the slopes (A_2) of Eq. (3). These values (A_2) were constant for each given temperature and agreed with data^{13)~15)} published previously.

For the interpretation of the negative sign before the constant term, 0.12 at temperature of 40.0°C in **Table-2**, Eq. (3) is divided into independent additive contributions of the components in the amphiphile molecule according to Eq. (4)¹⁶⁾.

$$\Delta G_m = \Delta G_m(CH_3-) + (N-1)\Delta G_m(-CH_2-) + \Delta G_m(-W) \quad (4)$$

where $\Delta G_m(CH_3-)$ and $\Delta G_m(-W)$ are the free energy changes for micellization of methyl group and hydrophilic group, respectively. Furthermore, Eq. (3) at temperature of 40.0°C is represented by

$$\Delta G_m = N\Delta G_m(-CH_2-) - 0.12 \quad (5)$$

The difference between Eqs. (4) and (5) is as follows;

$$\Delta G_m(CH_3-) - \Delta G_m(-CH_2-) + \Delta G_m(-W) = -0.12 \quad (6)$$

Here, $\Delta G_m(CH_3-)$ may be eliminated by the use of available data^{17), 18)} from the solubility of liquid n -alkanes in water at 25°C.

Thus, the free energy of the process

can be represented within ± 0.04 kcal/mol for $n=5$ to 8 by the contributions

$$\begin{aligned} \Delta G(-CH_2-) &= -0.85 \text{ kcal/mol;} \\ \Delta G(CH_3-) &= -2.18 \text{ kcal/mol} \end{aligned} \quad (8)$$

Therefore, if we apply these parameters to micellization, it follows from Eq. (6) that

$$\Delta G_m(-W) = 1.21 \frac{\text{kcal}}{\text{mol}} \quad (9)$$

It is evident that the positive value of $\Delta G_m(-W)$ means the opposition to micellization. Consequently, as the constant term of -0.12 in Eq. (3) at temperature of 40.0°C includes the contributions of $\Delta G_m(-W)$ and of the difference between $\Delta G_m(CH_3-)$ and $\Delta G_m(-CH_2-)$, the sign before the constant term becomes negative due to larger contribution of methyl group than one of hydrophilic group.

The log cmc for each homolog in the series was plotted versus the reciprocal of temperatures as shown in **Fig-5**.

Fig-5 Plot of log cmc against the reciprocal of temperature ($1/T$).

As these log cmc versus $1/T$ curves are nearly linear, they can be expressed by the following equation.

$$\log \text{cmc} = \frac{A_3}{T} + B_3 \quad (10)$$

The constants of A_3 and B_3 of $C_n E_8$ are given in **Table-4**.

The corresponding ΔH_m and ΔS_m values may

Table-4 The constnat of each C_nE_8 corresponding to Eq. (10).

	$A_3 \times 10^{-3}$	B_3
$C_{10}E_8$	0.963	-6.21
$C_{11}E_8$	0.872	-6.44
$C_{12}E_8$	0.800	-6.80
$C_{13}E_8$	0.717	-6.98
$C_{14}E_8$	0.660	-7.26
$C_{15}E_8$	0.597	-7.46

be expressed by the following¹²⁾ Eq. (11).

$$\log \text{cmc} = \frac{\Delta H_m}{2.303 RT} - \frac{\Delta S_m}{2.303 R} + \log W \quad (11)$$

By combining Eq. (10) corresponding to C_nE_8 with Eq. (11), ΔH_m and ΔS_m for micelle formation are calculated and are listed up together with $T\Delta S_m$ and ΔG_m in **Table-3**. As shown in **Table-3**, negative value for ΔG_m is given by the larger $T\Delta S_m$ value than ΔH_m . This indicates that $T\Delta S_m$ value becomes a dominant factor for the micellization. In order to estimate the contribution of the increase of alkyl chain to the micellization, ΔH_m , $T\Delta S_m$ and ΔG_m at 25.0 °C are plotted against the number of carbon atoms (N) in the alkyl chain as shown in **Fig.-6**.

Fig.-6 Thermodynamic parameters of micellization at temperature of 25.0°C as a function of alkyl chain length for C_nE_8 .

ΔG_m and ΔH_m values decrease with increasing carbon number, while the corresponding $T\Delta S_m$

Table-5 Thermodynamic parameters per methylene group for micellization at each temperature.

Temp. (°C)	$\Delta G_m(-CH_2-)$ (kcal·mol ⁻¹)	$\Delta H_m(-CH_2-)$ (kcal·mol ⁻¹)	$T\Delta S_m(-CH_2-)$ (kcal·mol ⁻¹)	$\Delta S_m(-CH_2-)$ (cal·mol ⁻¹ ·deg ⁻¹)
15.0	-0.67	-0.33	0.34	1.18
20.0	-0.68	-0.33	0.35	1.19
25.0	-0.68	-0.33	0.35	1.17
30.0	-0.69	-0.33	0.36	1.19
40.0	-0.69	-0.33	0.36	1.15

values increase. From the slopes of each curve in **Fig.-6**, their parameters per methylene group [$\Delta G_m(-CH_2-)$, $\Delta H_m(-CH_2-)$ and $T\Delta S_m(-CH_2-)$] are obtained as listed up in **Table-5**. From these results, it is evident that the summation of $\Delta H_m(-CH_2-)$ and $T\Delta S_m(-CH_2-)$ contributes to the micellization. (Received Jan. 5, 1981)

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アルキル=オクタキス(オキシエチレン)= エーテル同族体の水溶液表面とミセルの 性質及びそれらの温度依存性

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アルキル=オクタキス(オキシエチレン)=エーテル同族体 (C_nE_8 : $n=10\sim15$) の cmc, 一分子当たりの面積及び cmc での平衡表面張力値を, 15.0 から 40.0°C の温度範囲で, 表面張力の濃度曲線から求めた。一分子当たりの面積及び cmc での平衡表面張力は, 炭素数の増加とともに減少し, 偶数と奇数の炭素数の違いでジグザグ曲線となった。このことは, 偶数と奇数のお互いに異なった炭素数を持つ界面活性剤分子間の気-液界面における分子配向性の違いによるものであると思われる。

一方, アルキル鎖長中の炭素数に対する $\log \text{cmc}$ のプロットは, 直線関係を示し, 偶数と奇数の炭素数の差異は, バルクの性質に対しては観察されなかった。ミセル形成に関する自由エネルギー変化 (ΔG_m) は, cmc の温度依存性から計算された。また ΔH_m と ΔS_m の値は, $\log \text{cmc}$ に対する温度の逆数のプロットから得られた直線の傾きと切片とから, それぞれ求められた。これらの結果から, C_nE_8 系列のミセル形成に伴う ΔS_m は, ΔG_m に対して支配的に寄与することがわかる。さらに, メチレン基 1 個当たりの $\Delta G_m(-CH_2-)$, $\Delta H_m(-CH_2-)$, $\Delta S_m(-CH_2-)$ 及び $T\Delta S_m(-CH_2-)$ の値は, 炭素数に対する各熱力学的関数の傾きから, それぞれ -0.68 kcal/mol , -0.33 kcal/mol , $1.16 \text{ cal/mol}\cdot\text{deg}$, 0.35 kcal/mol と計算された。

この結果として, メチレン基 1 個当たりの $\Delta H_m(-CH_2-)$ と $T\Delta S_m(-CH_2-)$ は, とくにミセル形成に寄与すると結論された。