The Effect of Temperature on the 2nd C.M.C. of Dodecylpyridinium Chloride.

Dodecylpyridinium Chloride수용액의 제 2 임계농도에서의 온도 효과

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ABSTRACT

The variation of 2nd CMC with temperature for Dodecylpyridinium Chloride over the range 5° to 50° has been measured by electrical conductivity methods.

The values of the change in heat content, ΔHm and other thermodyamic parameters have been estimated for the same temperature range from the equations which are expressed as a power series in T. The segnificance of these thermodynamic values has been discussed.

INTRODUCTION

The physical and chemical properties of the lst critical micelle concentration have been studied for a number of surface-active agents(1-7), but apparently less extensively for the 2nd CMC of the cationic agents(8-12, 17-20 25 26). Professor Lee suggested the mechanism attributed to the reaction in 2nd micelle formation of the D.P.C. solution(17)

$$M2 \rightleftharpoons M1 + 1.2Cl^-$$

Where Mland M2 are two types of micelle. And he suggested the strucural change in the state of 2nd critical mecelle concentration(for example, spherical structure in lst c.m.c changes into capsule or rod-like mode in 2nd c.m.c)

In this paper, the relations between the claculated thermodynamic values and the model of the different state were studied.

In the course of investigations into the properties of systemes containing dodecylpyridinium chloride it was found necessary to determine the C.M.C at several temperature

and it was decided to undertake a complete study of the effect of temperature within the range 5°C to 50°C

EXPERIMENTAL MATERIALS

Dodecan-1-ol (WACO) was chlorinated in benzene solvent by using thionyl chloride (13, 14), and purified product was heated with pyridine (15) to give crude dodecylpyridinium chloride.

This was purified by solution in acetone, filtrations and recrystallisation was performed five times from a mixture of acetone-ether (2 : 1) at 2°C to give a white solid. This crystal was stored over phosphorus pentoxide.

The compound exhibited two melting points at 68°C and 146°C (reported, 68°C and 146°C)

Chlorine content found 13.5%, required 12.5% (By titration withe $AgNO_3$ in fluorescein as indicator). No minimum was found in the surface tension-concentration curve. It was considered that the product was essentially pure, free from unchanged alcohol or alkyl halide and from appreciabie amounts of homologous compound (16).

Water was prepared by passage through an ion exchange column and then distillized three times with $KMnO_4$. Such water had a specific conductance of 1.6×10^{-6} mho. cm^{-1} at 20°C.

One sample of water was used throughout the determinations for with results are listed.

EXPERIMENTAL PROCEDURE

Solutions of weighed sample of dodecylpyridinium chloride were prepared and ajusted to volume in calibrated flask at 20°C. The solution was then bubbled with N_2 gas for 14 hrs.

Throughout the measurement, the space over the solution was filled with N_2 gas lest CO_2 gas should be solubilized to sample solution.

Conductivities were measured using a Industrial Instrument. Inc. (Model R.C. 16B₂) Conductivity Bridge with a Fisher Sc. Co. Conductivity cell containing the solution under test immersed in an insulated water bath.

The eledtrode systems had cell constants of about 0.1013, the exact values being determined from conductance measurement with standard potassium chloide solutions.

The conductivity being measured after each dilution until a constant value was obtained,

2nd C.M.C. values were obtained from the point of intersection of the two extrapolated straight-line portions of the specific conductance versus concentration graph(Fig. 1). The values listed in table 1.

Fig. 2 was obtained from the relationship between temperature and 2nd C.M.C. of dodecylpyridium chloride in aqueous solution.
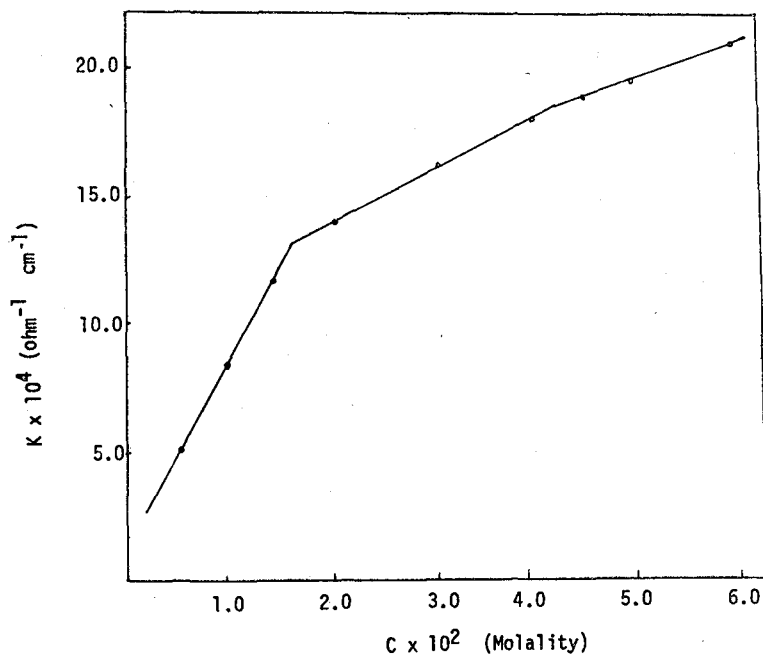

Fig. 1. Plot of Specific Conductance vs. Concentration of D.P.C. in water at 20°C.

Table 1 1st CMC and 2nd C.M.C. of Dodecylpyridium Chloride in Water.

Temperature (°K)	2nd C.M.C of D.P.C (Molality × 10⁻³)	2nd C.M.C of D.P.C (Molality × 10⁻³)
278.2	17.60	43.80
283.2	17.30	43.20
288.2	17.00	43.10
293.2	17.20	43.20
298.2	17.40	43.70
303.2	17.80	44.20
308.2	18.20	44.80
313.2	19.00	45.10
318.2	19.80	45.60
323.2	20.60	46.30

Rdsult and Discussions

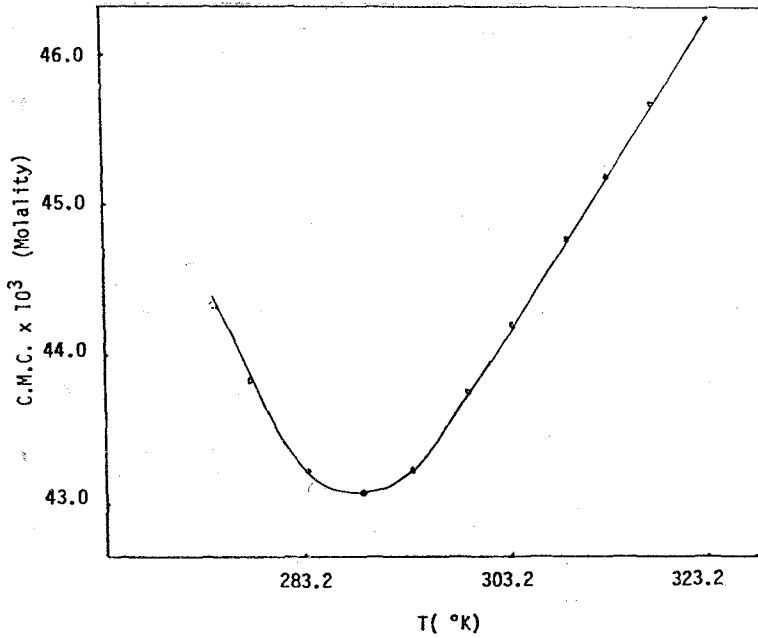From the Table 1, a series of polynomials was obtained by using Gaussian least square

Fig. 2. Effect of Temperature on the 2nd *C.M.C.* of *D.P.C.* in water.
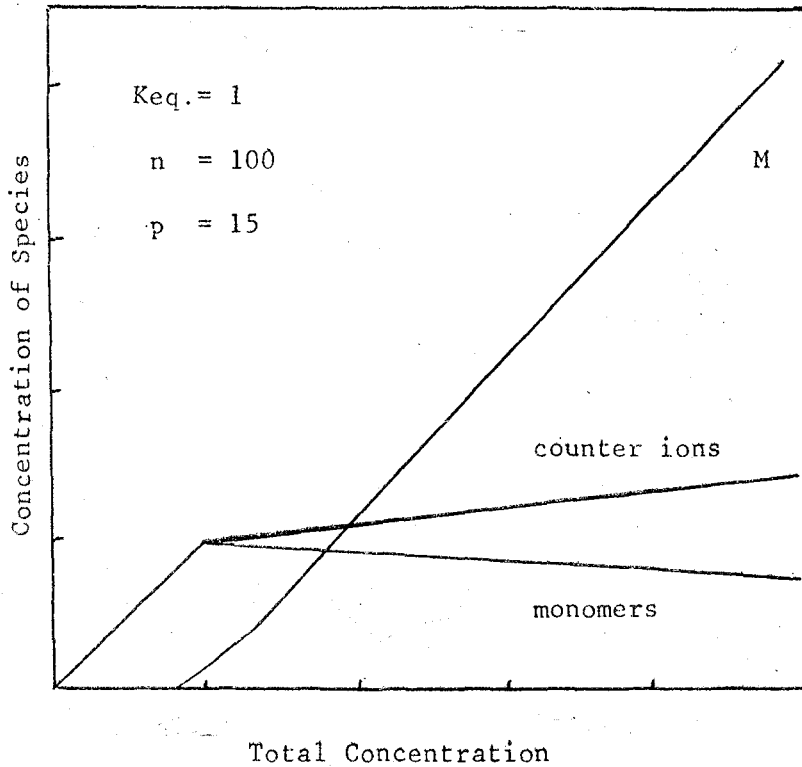
Fig. 3. Concentration of unaggregated surfactant or micelle(and counterion) VS. total concentration of surfactant.

method. All the calculated point fell within the limit of error of the measurement.

$$\log(\text{제}1CMC) = -25.17445074 + 0.4231382587\,T$$
$$-2.613024384 \times 10^{-3}T^2 + 6.764479792 \times 10^{-6}T^3$$
$$-6.295415289 \times 10^{-9}T^4$$

$$\log(\text{제}2CMC) = 305.2089658 - 4.001016759\,T + 1.956801864 \times 10^{-2}T^2$$
$$-4.251412188 \times 10^{-5}T^3 + 3.462938237 \times 10^{-8}T^4$$

The mechanism for the 2nd *C.M.C.* of *D.P.C.* was studied by using the method of ultrasonic techinque in aqueous solution(17-20)

$$M_1 + 1.2\ Cl^- \rightleftharpoons M_2 \tag{1}$$

where M_1 and M_2 are two types of micelle

The standard free energy of mice-lization is given by

$$\Delta G m^0 = -nRT \ln \frac{(M_2)}{M_1(Cl^-)^{1.2}} \tag{2}$$

where (M_1), (M_2), (Cl^-) are equilibrium concentrations

For the standard equilibrium state in micellar phase, (M_1) and (M_2) are equal to unity The concentration of Cl^- maintains constant values approximately between 1st *C.M.C* and 2nd *C.M.C.*(Fig. 3)

Above 2nd *CMC*, its values are 1st *CMC* in given temperature.

Therefore eq.(2) reduces to

$$\Delta G m^0 = nRT \ln(Cl^-)^{1.2} \tag{3}$$

Combining eq. (3) with the Gibbs-Helmholtz equation,

$$\frac{\partial}{\partial T}\ \frac{\Delta G}{T} = -\frac{\Delta H}{T^2} \tag{4}$$

the standard enthalpy of micellization can be obtained

$$\Delta H m^0 = -nRT^2 \frac{\partial}{\partial T}(\ln(Cl^-)^{1.2}) \tag{5}$$

The standard entropy of micellization can be obtaine from

$$\Delta S_m^0 = (\Delta H^0 - \Delta G^0)/T \tag{6}$$

Also since the free energy of micellization under equilibrium conditions at constant temperature and pressure is 0, the entropy change will be given by

$$\Delta Sm = \Delta Hm/T \tag{7}$$

From the above equations, the values of the thermodynamic parameters were calculated as following.

$$\Delta G m^0 = nRT \ln(\text{제}1C.M.C)^{1.2} \text{(From eq. (3))}$$

Here, n is equal to 2 by the Taylor[27]

Therefore

$$\Delta Gm^0 = 9.152 \times 1.2 \times \log 1 (제 1 CMC)$$

$$= 9.125 \times 1.2 (-25.17445074 + 0.4231382587\,T$$

$$-2.613024384 \times 10^{-3}T^2 + 6.764479792 \times 10^{-6}T^3$$

$$-6.295415289 \times 10^{-9} + 4)$$

$$\Delta Hm^0 = \Delta Hm = -2RT^2 \frac{\partial}{\partial T}\ \ln(제 1 CMC)^{1\cdot2}$$

$$= 9.152 \times 1.2 (0.42313825875\,T^2$$

$$-2 \times 2.613024384 \times 10^{-3}T^3$$

$$+3 \times 6.764479792 \times 10^{-6}T^4$$

$$-4 \times 6.295415289 \times 10^{-9}T^5$$

$$\Delta Sm = \Delta Hm / T \text{(from eq. (7))}$$

$$\Delta Sm^0 = (\Delta H^0 - \Delta G^0) / T \text{ (from eq. (6))}$$

The values are listed in Table 2.

Table 2. Thermodynamic Quantities for Micellization of *D.P.C* in water on 2nd *C.M.C.*

Temperature(°K)	ΔGm^0(kcal/mole)	ΔHm°(kcal/mole)	ΔSm(cal/deg/mole)	ΔSm^0(cal/deg/mole)
278.2	−5.36	1.98	7.25	26.38
283.2	−5.48	1.11	3.92	23.27
288.2	−5.60	0.22	0.76	20.19
293.2	−5.64	−0.66	− 2.25	16.98
298.2	−5.76	−1.51	− 5.06	14.25
303.2	−5.82	−2.30	− 7.59	11.61
308.2	−5.89	−3.01	−10.24	9.34
313.2	−5.92	−3.61	−11.53	7.38
318.2	−5.95	−4.04	−12.70	6.00
323.2	−5.99	−4.30	−13.30	5.23

When the standard free energy of micellization is negative, spontaneous aggregation of surfactant ion or micelles(over 1st *cmc*) under standard state conditions is possible.

However, it is shown that although addition(or dissociation-recombination reaction) between micelles under standard state conditions is favorble(negative ΔGm^0) at all temperatures, ΔHm^0 is positive below about 15°C and does not contributed to the process feasibility, these behaviors were reported by Taylor[27] in 1st *C.M.C* of Dodocypyridium Bromide solution in aqueous media. Positive heats of micellization have also been inferred from calorimetric measurements of heats of dilution and solution.[24]

In 1st *C.M.C* it is well explained by the suggestion of "icebergs" [28].—It centers on the structural changes that occur in water when nonpolar solutes enter solution. Water molecules are thought to form ordered regions referred to as "icebergs", around the surfactant ions. When such an ion becomes part of a micelle its frozen mantle thaws to the bulk water state. This makes ΔHm more positive than it would otherwise be and increased the randomness of the system. As the temperature increases, the icebergs deminish in size and/or become less rigid. As a result, their melting provides a progressively smaller positive contribution to the entropy change. At some elivated temperature, micellization becomes primarilly an enthalpic process with neagative ΔHm values arising from the loss of translational energy on the part of single ions and the liberation of heat when the paraffin chains condense.

However in 2nd *C.M.C*, it is thought that counter ion effect is more participated in micelle formation(or structural change). It is well known that the *cmc* and micelle size are strongly influenced by the nature of the counter ion [29]. It is thought that the increased concentration of counter ion from dissociation in 2nd *cmc* has an effect in disrupting the structure of bulk water.

The positiveness of ΔSm^0 is solely responsible for the favorabilty of the reaction.

From the above values, it is suggested that reactions(as aggregation reaction or dissociation-recombination reaction between micelles and conter ions) are spontaneous and effected by concentration of counter ion.

It is believed that continuous study for the provement of the structure in 2nd *cmc* should be performed all the more.

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요　약

Dodecylpyridinium Chloride수용액의 제 2 임계농도의 온도효과를 5°C에서 50°C의 온도범위에서 전기 전도도 방법으로 측정하였다. 열용량 및 다른 열역학 변수들이 값을 온도 T에 대한 멱합수로 부터 구하고 이들이 갖는 의의와 상호간의 관계를 미셀형성시의 용매효과 등의 일반적인 여러가지 학설로 비교 논의하였다.