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A Study of Vitamin A as a Probe in Critical Micelle Concentration Determinations of Surfactants

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Abstract. The critical micelle concentrations (CMC) of some sodium alkyl sulfates (SNS, SdS, SDS, STS, and SHS), sodium dodecyl sulfonate (SDSO), CTAB and Triton X–100 were determined by measuring both the absorbance and the absorption wavelength of vitamin A in aqueous solutions of surfactants of various concentrations. The results are in agreement with those obtained by other methods in the literature. The influence of micelles upon the absorption spectra of vitamin A have been investigated. The effects of the temperature and the incubation time on the measurements have been discussed.

Key words: CMC, inclusion, micelle, probe, vitamin A.

1. Introduction

Surfactants play an important role in biological studies of membranes. They can extract membrane proteins when their concentrations are above the critical micelle concentration (CMC) [1]. The CMC is the concentration at which surfactant molecules begin to self-associate in solution to form stable aggregates called micelles [2]. Many methods have been developed for determining the CMC [3, 4]. The application of UV-VIS absorption to determining CMC has been reported. The measurements were based on the changes in the absorption wavelength or absorbance at the CMC [5–7].

Retinol (vitamin A) is a lipophilic compound which regulates and controls diverse physiological functions, e.g. fetal vision development, cell proliferation and differentiation throughout life [8, 9]. Although the solubility of vitamin A in water is poor, it is soluble in micelles. Moreover, when vitamin A is added to a solution of surfactant at a concentration above the CMC, its λ_{max} approaches that measured in n-octane (328 nm). Below the CMC, however, λ_{max} of vitamin A approaches that in water (295 nm). The change of absorption wavelength of vitamin A is sensitive to the concentration of the surfactant. It led us to explore the possibility of utilizing vitamin A for determining the CMC of surfactants.

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In this work, vitamin A was used as a probe compound for determining the CMC of the anionic surfactants sodium alkyl sulfates and sodium dodecyl sulfonate (SDSO), the cationic surfactant cetyl trimethylammonium bromide (CTAB) and the neutral surfactant Triton X-100 (TX-100) by following changes of both the UV-VIS absorption wavelength and the absorbance.

2. Experimental

2.1. Materials

All-*trans*-retinol (Fluka) was used without further purification. Sodium alkyl sulfates, $ROSO_3Na$ [R = Nonyl (SNS), decyl (SdS), tetradecyl (STS), hexadecyl (SHS)] were synthesized by the procedure described in the literature [10], and recrystallized three times from ethanol. Sodium dodecyl sulfate (SDS) and sodium dodecyl sulfonate (SDSO) were purchased from Merck, and recrystallized twice from ethanol before use. CTAB (Tokyo Kasei) and Triton X-100 (Aldrich) were used as received. Triply distilled water was employed.

2.2. Preparation of samples

Stock aqueous solutions of surfactants were prepared in advance. 7.10 mg retinol was dissolved in 10.0 mL methanol. 5.0 μL of the solution was transferred to a 5.0 mL volumetric flask. The solvent was evaporated under vacuum at room temperature. 5.0 mL of stock aqueous solution of surfactant was added to the flask, the resulting solution contained 2.5×10^{-6} mol L^{-1} of vitamin A. After degassing by an argon stream, it was ultrasonicated for 30 min at 35°C for STS, 45°C for SHS and SDSO, and 25°C for the other surfactants, and allowed to stand for several hours. All operations were carried out in the dark.

2.3. Spectral measurements

The absorption spectra of vitamin A in the aqueous solutions of surfactants were measured with a Hitachi 557 UV-VIS spectrophotometer. The measurements were carried out at 25 to 65°C.

3. Results and Discussion

Vitamin A is a retinoid polyene which exhibits a strong UV-VIS absorption. The absorption is observed at 328 nm in n-octane and at 295 nm in water. When vitamin A is included in micelles, its close range solvation should be similar to that in n-octane solvent. Table I lists the λ_{max} values in different micelles. The λ_{max} of vitamin A is around 330 nm in the micelles, which is different from that measured in water. Therefore, vitamin A can be chosen as a probe compound for CMC determination by the UV-VIS absorption method.

TABLE I. λ_{max} of vitamin A in the different media

Medium	Concentration (mol L^{-1})	T/°C	λ_{max}/nm
H_2O		35	295
n-octane		25	328
SNS	6.0×10^{-2}	25	328
SdS	3.0×10^{-2}	25	329
SDS	8.3×10^{-3}	25	330
STS	2.5×10^{-3}	35	332
SHS	7.5×10^{-3}	45	332
SDSO	1.2×10^{-2}	45	332
CTAB	1.0×10^{-3}	25	330
TX-100	2.0×10^{-4}	25	328

The shift of the absorption wavelength of vitamin A is dependent on the concentration of surfactants. When the concentration of a surfactant is below its CMC, the surfactant molecule may not interact with vitamin A strongly. When the concentration of surfactant is above the CMC, the micelle is formed. The number of micelles increases with increasing concentration of surfactant, hence, more vitamin A molecules can enter the micelles to dissolve in the micellar solution. As it obeys Beer's law, the absorbance of vitamin A is also dependent on the concentration of the surfactant. Figure 1 shows the change of the absorption band of vitamin A at concentrations below, near and above the CMC. Both the intensity and the absorption wavelength vary with the concentration of surfactant.

Temperature may influence the CMC determination using absorbance measurements. The solubility of vitamin A in aqueous bulk solution increases and the difference in absorbance of vitamin A at λ_{max} between the aqueous bulk solution and in micelles decreases with increasing temperature. When the temperature was increased from 25 to 45°C, the absorbance of vitamin A in the SDS micelle ($\lambda_{max} = 330$ nm) decreased (Figure 2), whilst the absorbance of vitamin A in aqueous bulk solution ($\lambda_{max} = 295$ nm) increased. A further increase of absorbance at 295 nm and a decrease at 330 nm were observed at 55°C. A decrease in the absorbance of vitamin A in micelle aqueous solution was observed at 65°C (Figure 2), the decrease in aqueous solution resulting from the decomposition of vitamin A. It is note worthy that the temperature did not influence the position of λ_{max} of vitamin A in aqueous solutions of surfactants. CMC determination by the absorption wavelength measurement is thus applicable for surfactants with high Krafft points.

The solubility equilibrium of vitamin A in aqueous solutions of surfactants was complete in 16 h of incubation time after ultrasonicating for 30 min (Figure 3). Figure 3 shows that with a short incubation time, e.g. 30 min, the difference in absorbance of vitamin A in the micelle and in the aqueous bulk solution is much smaller than the corresponding value when the equilibrium is attained. This

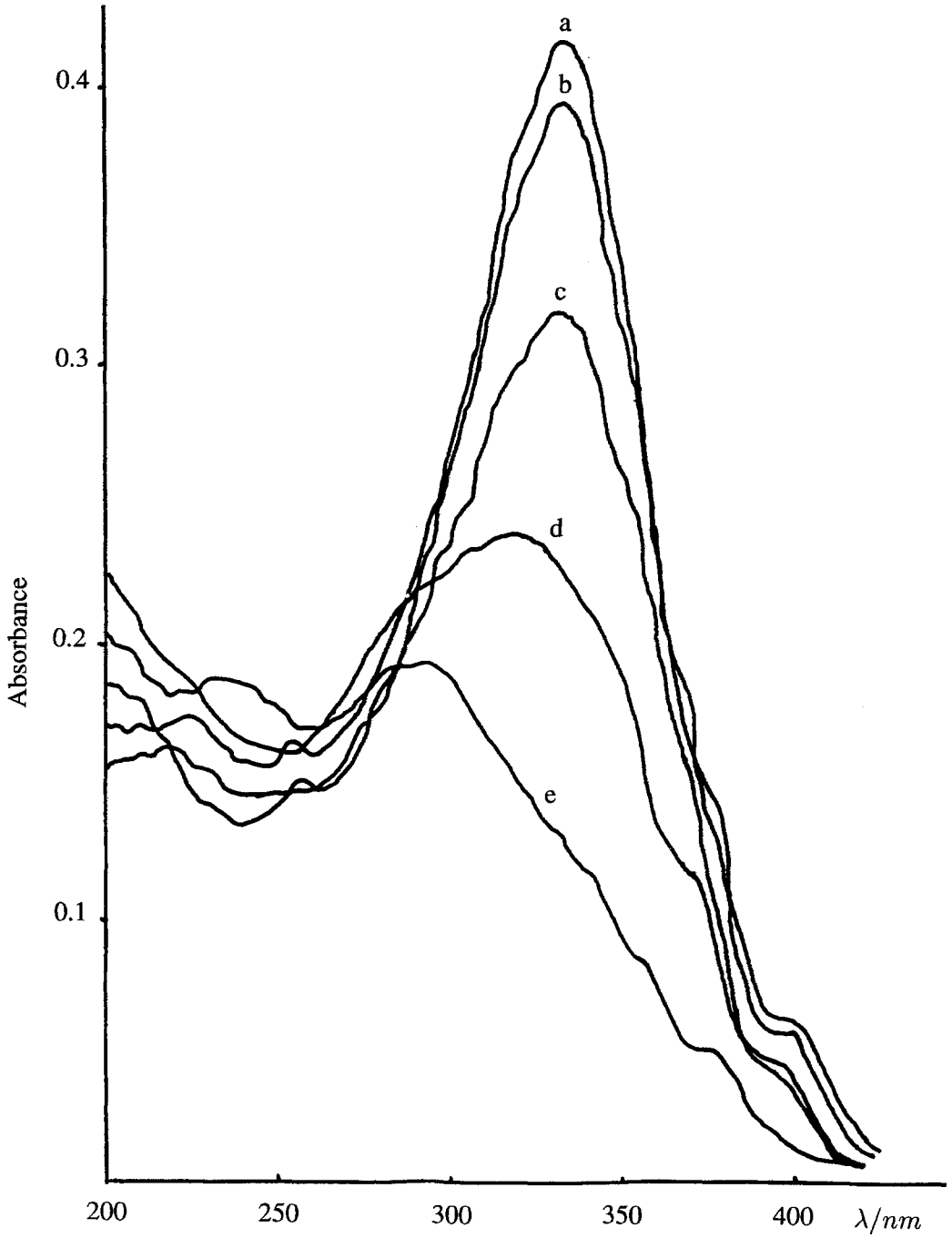

Fig. 1. Absorption spectra of vitamin A (2.5×10^{-6} mol L^{-1}) in the vicinity of the CMC for SDS recorded at 25°C. The concentration of SDS: 1.0×10^{-2} (a), 8.5×10^{-3} (b), 8.0×10^{-3} (c), 7.5×10^{-3} (d) and 4.0×10^{-3} (e) mol L^{-1}.

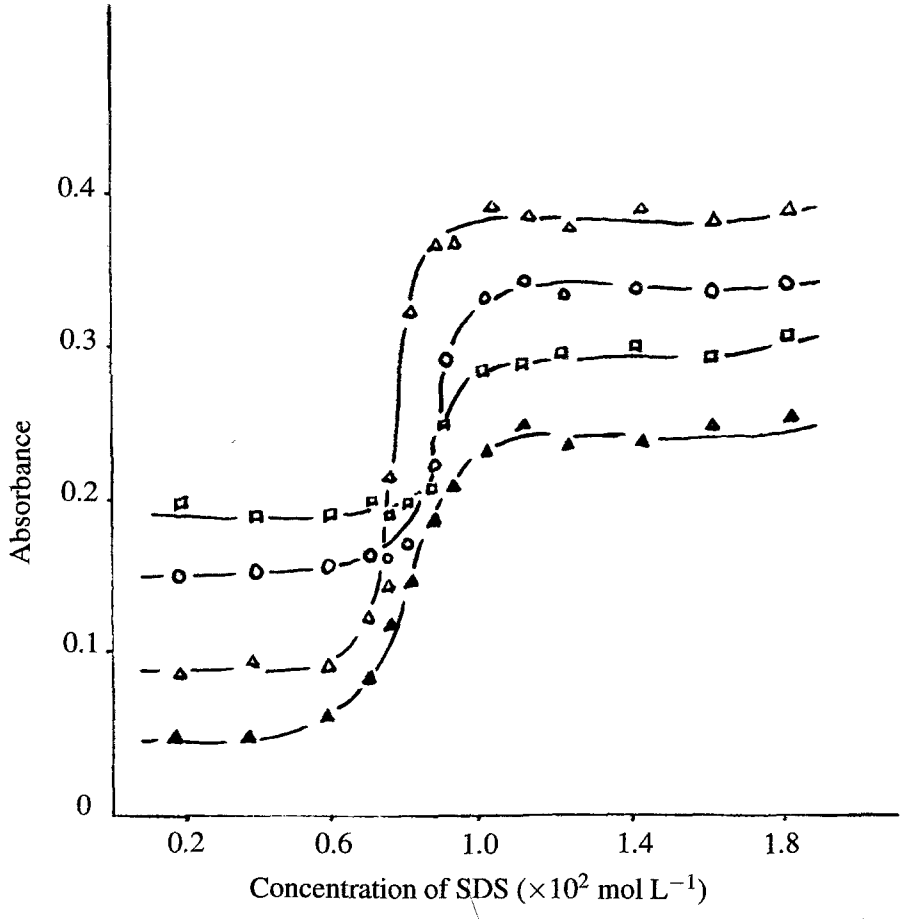

Fig. 2. Effect of temperature upon the absorbance of vitamin A (2.5×10^{-6} mol L^{-1}) in an aqueous solution of SDS (incubation time 10 h). 25°C (△), 45°C (○), 55°C (□) and 65°C (▲).

difference increases with increasing incubation time. However, no changes in the curves of absorbance vs. surfactant concentration were observed for incubation times longer than 16 h. The same results were obtained in the measurement of the absorption wavelength with various incubation times. These results suggest that an incubation time of 4.5–7 h is long enough for the CMC determination.

A low concentration of probe compound is needed for CMC determination. This requirement was fulfilled as the concentration of vitamin A in aqueous solution of surfactants used in this work was 2.5×10^{-6} mol L^{-1}.

4. Conclusions

The CMC of surfactants were obtained from the curves of absorbance as well as wavelength of vitamin A in aqueous solutions of micelles vs the concentrations

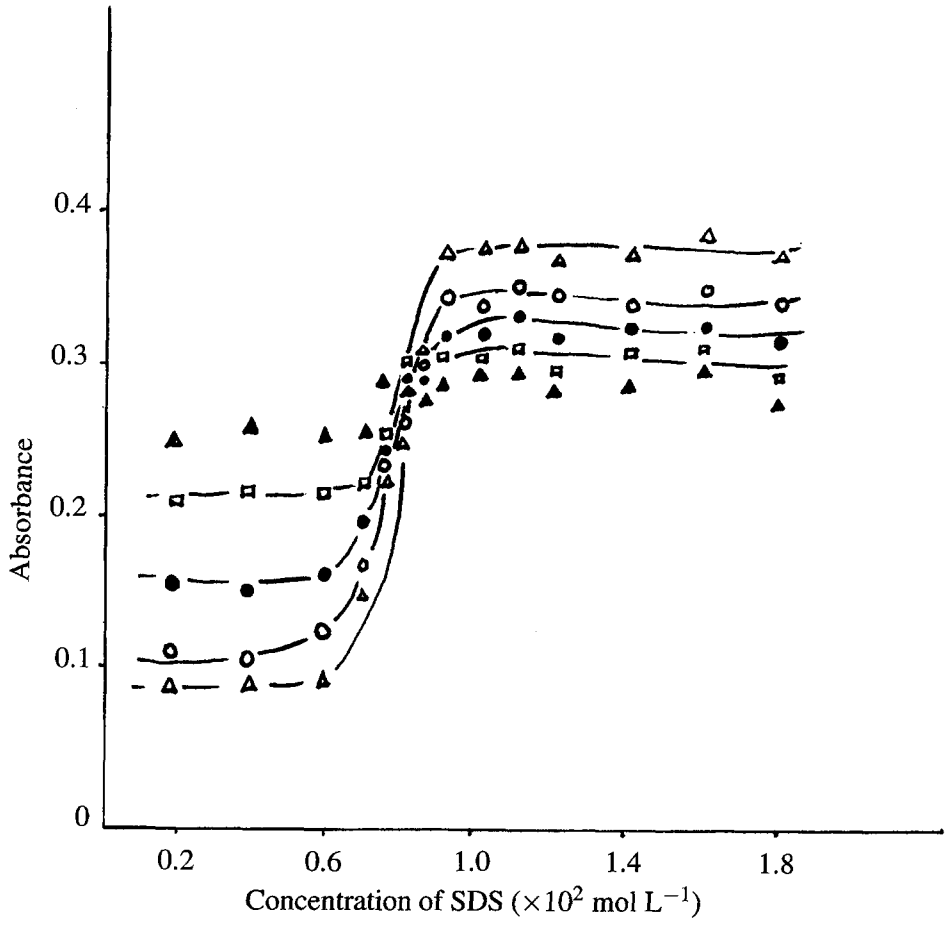

Fig. 3. Effect of incubation time on the absorbance of vitamin A (2.5×10^{-6} mol L^{-1}) in an aqueous solution of SDS at 25°C: 0.5 (▲), 1.5 (□), 4.5 (•), 7.0 (o) and 16 (△) h.

TABLE II. The CMC of the surfactants

Surfactant	CMC[a] (mol L^{-1})	CMC[b] (mol L^{-1})	Lit data (mol L^{-1})	Ref.
SNS	6.0×10^{-2}	5.7×10^{-2}		
SdS	2.3×10^{-2}	2.3×10^{-2}	2.3×10^{-2}	[11]
SDS	8.3×10^{-3}	8.0×10^{-3}	8.2×10^{-3}	[12]
STS	2.4×10^{-3}	2.4×10^{-3}	2.4×10^{-3}	[13]
SHS	7.5×10^{-4}	–	5.8×10^{-4}	[13]
SDSO	1.2×10^{-2}	1.2×10^{-2}	9.2×10^{-3}	[14]
CTAB	9.2×10^{-4}	9.0×10^{-4}	9.2×10^{-4}	[15]
TX-100	2.2×10^{-4}	1.5×10^{-4}	2.0×10^{-4}	[16]

[a] Based on wavelength.

[b] Based on absorbance.

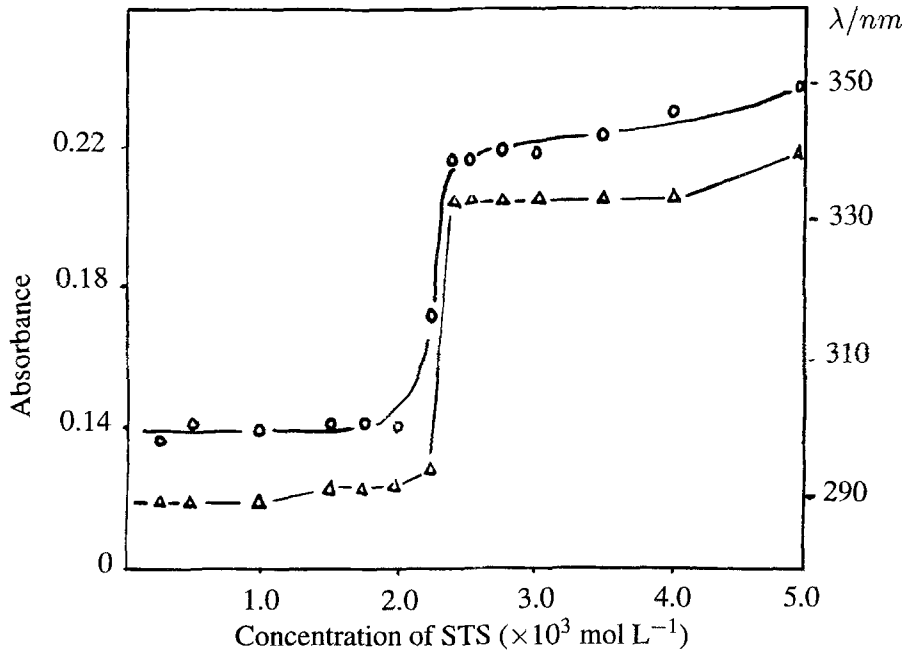

Fig. 4. Plots of λ_{max} (Δ) and absorbance (o) of vitamin A vs. the concentration of STS.

of the surfactants (Table II, Figure 4). The data are in good accordance to those reported in the literature [11–16] by other methods. The method described in this paper is convenient and accurate. In summary, vitamin A is a sensitive probe which can be used in CMC determination for the surfactants satisfactorily by UV-VIS measurements.

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