DETERMINATION OF CRITICAL MICELLES CONCENTRATION OF AEROSOL OT/ ISOOCTANE REVERSE MICELLES BY FOURIER TRANSFORMED INFRARED SPECTROSCOPY (FTIR)

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Introduction:

Reverse micelles are spherical aggregates of surfactants in nonpolar media. Since reverse micelles can

accommodate a large amount of water and biological molecules in a nonpolar media, the mechanism of micelle formation has become a subject of detailed study. Among the different reverse micellar systems, the AOT/isooctane reverse micellar system is very commonly used.

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(a) AOT molecule

Fig. 1 (a) Chemical structure of AOT molecule; (b) Deconvoluted FTIR spectrum of carbonyl bond of AOT/isooctane solution: (■) experimental data, (····) individual Gaussian peak and (—) resultant of Gaussian peaks; $C_{\text{AOT}} = 10 \text{ mmol/dm}^3$

Determination of the CMC is very important to evaluate the total micellar concentration of a reverse micellar system; as from CMC, one can get an idea of the amount of free surfactant present in the solvent system. From IR spectra, one can see directly what change is occurring in the different bonds of surfactant molecule with the increase of surfactant concentration. So CMC determined by FTIR gives a more accurate result with a simple procedure than other physical methods; such as, measurement of conductivity (Eicke and Arnold, 1974), surface tension (Hsiao *et al.*, 1956), or adding additives (Jean and Ache, 1978).

AOT (**Fig. 1(a)**) is a diester derivative of succinic acid where the sulfonate and the two carbonyl groups remain within the skeleton of the succinic acid part of the AOT molecule. The two long hydrocarbon chains come from the ester groups. The polar groups of AOT molecule are stereochemically directed along the various bonds of the ethane skeleton of the succinic acid part of the molecule and can rotate about the ethanic C-C bond (Maitra and Eicke, 1981). The relative IR intensities and the frequencies of the two C=O bonds change with the change of environment (Jain *et al.*, 1989; MacDonald *et al.*, 1986). In this study the CMC was determined based on the ratios of the intensities of these two carbonyl bonds starting from a very low AOT concentration.

Fig. 2 Effect of AOT concentration on $I_{1739/1720}$ ratio (i.e. C=O bond): (a) $C_{\text{AOT}} = 0-15 \text{ mmol/dm}^3$, (b) $C_{\text{AOT}} = 0-300 \text{ mmol/dm}^3$

1. Experimental

1.1 Materials and sample preparation

Pure AOT was purchased from Wako Pure Chemical Industries Ltd. After dissolving in methanol, it was reprecipitated by drying in a vacuum drier. Spectral grade isooctane was purchased from Nacalai Tesque Inc. Ltd. and was used without further purification. At first, 300 (mmol/dm^3) AOT solution was prepared and then diluted to different degrees by adding isooctane. The solutions were then stored in a constant temperature box at 25°C for 24 hours before taking FTIR spectra.

1.2 FTIR spectra

FTIR spectra were taken using Horiba FT-210 Fourier Transformed Infrared Spectrometer using a Baseline HATR (Horizontal Attenuated Total Reflectance) cell. The data were recorded by a Horiba Spectradesk. The

Fig. 3 Different isomers of AOT in reverse micelles

Table 1. Literature value of CMC of selected AOT / solvent reverse micelles

solvent	CMC (mmol/dm ³)(method)	ref.
benzene	2.0 dye absorption	Muto and Meguro, 1973
	0.5 spec conduct	Eicke and Arnold, 1974
carbon tetrachloride	0.6 dye absorption	Muto and Meguro, 1973
chloroform	0.4 dye absorption	Muto and Meguro, 1973
cyclohexane	0.95-1.1 uv absorption	Fendler and Fendler, 1975
isooctane	0.6-0.9 positron annihilation	Jean and Ache, 1978

same sample volume was poured into the cell, though a change of sample volume had almost no effect on the FTIR spectra while using a HATR cell. FTIR spectra were recorded in the 600-4000 cm⁻¹ range. Fifty scans were taken of each sample at a resolution of 4 cm⁻¹. An empty cell was used as the blank cell. Due to the high clarity of the spectra, no smoothing was done. All the spectra were taken at room temperature (25°C). Individual peak position and intensity were determined by curve fitting of Gaussian bands applying a Marquardt - Levenberg algorithm.

3. Results and Discussion

The carbonyl bond of AOT gives a strong IR band in the 1700-1760 cm⁻¹ region (**Fig. 1(b)**). Curve fitting revealed that it is a fusion of two peaks, and for the pure AOT it was found that the position of the higher frequency peak was at 1739 cm⁻¹ and that of the lower one was at 1714 cm⁻¹. But when AOT was dissolved in isooctane it was found that the lower peak frequency increased slightly to 1720 ± 2 cm⁻¹ and the higher one remained at the same position. The ratio between the intensities of these two peaks changed sharply at a point as shown in the **Figs. 2(a) and 2(b)**.

As AOT is a diester derivative of succinic acid, its two carbonyl bonds gave strong FTIR band in the 1700-1760 cm⁻¹ region. Maitra *et al.* (1981) made a detailed study about the rotational isomerism of these two carbonyl bonds about the ethanic C-C bond by ¹H NMR spectroscopy. According to their study, these two carbonyl bonds do not share the same isomeric characteristics. Based on the environment in which the AOT molecule is located, these bonds distribute themselves into different conformers. The lower frequency corresponds to a *gauche* conformer and the higher frequency corresponds to a *trans* conformer (Jain *et al.*, 1989). If rotational isomerism exists in the molecule, it is seen that in the *gauche* conformation, all the polar groups are directed toward the polar side of the interface, while in the *trans* conformation, a carbonyl group moves

from the polar side to the hydrocarbon part of the monolayer. **Figure 3** shows the stereospecific positions of the polar parts of the AOT molecule. The proportions of these two bonds vary with temperature and nature of the solvent environment (Maitra and Eicke, 1981). In the pure state of AOT, the I_{1739/1720} ratio (ratio between the intensities of the higher frequency to the lower frequency peaks) was equal to almost unity, but when AOT was dissolved in isooctane, this ratio changed. It is seen from **Figs. 2(a) and 2(b)** that there is an abrupt change of this ratio at around C_{AOT} = 1 mmol/dm³. At a very low AOT concentration, every AOT molecule exists as a monomer in the isooctane solution and experiences a hydrocarbon (nonpolar) environment. In this region, I_{1739/1720} was higher, which indicates that the proportion of *trans* conformer is high and one carbonyl group is present in the hydrocarbon phase. But when AOT concentration was increased beyond 1 mmol/dm³, the value of I_{1739/1720} dropped suddenly, which indicates that the proportion of *gauche* conformer increased suddenly. This means some fraction of the polar part of the AOT molecule is directed toward the polar environment, and this could happen when reverse micelle is produced. So C_{AOT} = 1 mmol/dm³ could be taken as the CMC of the AOT/isooctane reverse micellar system.

The observed CMC value is in good agreement with that obtained by Jean and Ache (1978) via positron annihilation techniques (0.6 - 0.9 mmol/dm³). This CMC value coincides with the CMC's determined by UV absorbance in another solvent of similar polarity, cyclohexane, where the corresponding value was 0.95 - 1.2 mmol/dm³ (Fendler and Fendler, 1975). **Table 1** also shows some previously reported CMC values of AOT in different solvents. From **Table 1**, it is seen that the CMC found by FTIR agrees fairly with the previously reported values.

Conclusion

FTIR analysis of AOT/isooctane solution shows that the pattern of carbonyl spectra changes at the critical micelle concentration, i.e., when the reverse micelle is produced. This happens due to the rotational isomerism of two carbonyl bonds present in the AOT molecule. The CMC determination by this method is very simple and this method could be used to determine the CMC of other surfactant/solvent systems.

Nomenclature:

AOT	=	sodium bis(2-ethyl 1-hexyl) sulfosuccinate
CMC	=	critical micelle concentration expressed in terms of AOT concentration [mmol/dm ³]
C _{AOT}	=	AOT concentration [mmol/dm ³]
I _{1739/1720}	=	intensity ratio of peak at 1739 cm ⁻¹ to that at 1720 cm ⁻¹

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