# 琉球大学学術リポジトリ

# Spectrophotometric and Calorimetric Studies of the Thermodynamics for the Interaction of Sodium p-Toluenesulfonate with Dodecyltrimethylammonium Bromide Micelles

# Spectrophotometric and Calorimetric Studies of the Thermodynamics for the Interaction of Sodium p-Toluenesulfonate with Dodecyltrimethylammonium Bromide Micelles

Toshio UCHIHARA*, Kazuya NAKASONE*,
Akira ARAKAKI*, and Akio KINJO*

## Abstract

The thermodynamic properties for the interaction of sodium p-toluenesulfonate with dodecyltrimethylammonium bromide micelles were studied by spectrophotometric and calorimetric techniques to compare these two methods with each other as a means for the study of such an interaction. Thermodynamic parameters of $K = (2.5 \pm 0.7) \times 10^3$ M$^{-1}$, $\Delta G° = -4.6 \pm 0.4$ kcal mol$^{-1}$, $\Delta H° = -2.1 \pm 0.2$ kcal mol$^{-1}$ and $\Delta S° = 8.4 \pm 0.7$ cal deg$^{-1}$ mol$^{-1}$ were obtained by the spectrophotometric method at 25℃. Calorimetric method gave $K = (2.0 \pm 1.5) \times 10^3$ M$^{-1}$, $\Delta G° = -4.5 \pm 1.0$ kcal mol$^{-1}$, $\Delta H° = -1.40 \pm 0.09$ kcal mol$^{-1}$ and $\Delta S° = 10 \pm 3$ kcal mol$^{-1}$ at the same temperature. The results suggest that the spectrophotometric method is recommended for the determination of equilibrium constant and standard free energy change and calorimetric method for the measurement of standard enthalpy change. Entropy change had better be evaluated by the combination of two methods. Though the calorimetric method produced larger errors in the present study because of the small heat of the interaction, it would be useful for the study of the interactions of the systems which evolve the appreciable heat and to which the spectrophotometric method is not applicable.

## Introduction

Recently there has developed an increasing interest in surfactant micellar solutions as media for the chemical and photochemical reactions owing to the similarity of the micelles to biological membranes.[1-3] In order to obtain better understanding of reactions in micellar solutions, the knowledges of the interactions between substrates and micelles are important.

Such interactions have been investigated mainly by the spectrophotometric[4-8] and fluorimetric[9-12] techniques. However, the spectrophotometric technique requires that the solute molecule has an appropriate chromophor and its molar absorption coefficient varies with going from water to micelles. Applications of the fluorimetric method also suffers from the same kind of restrictions such as that the solute must be fluorescent and the spectra should be different in two phases or the fluorescence

* Dept. of Chemistry, College of Science, Univ. of the Ryukyus

has to be quenched selectively in aqueous phase with quencher molecules. And further, some uncertainties seem inevitable when these methods are employed to determine the enthalpy and entropy change, since the methods require the values of equilibrium constant at various different temperatures which may affect micelles.

There have been a few calorimetric studies of the interactions of the molecules with micelles [13, 14], in which calorimetry was used only to determine transfer enthalpy from aqueous to micellar phase. It seems that the calorimetric method have not been employed to determine the equilibrium constant for the interactions described. If the method could be used for the study of such interactions, it would be versatile since it does not suffer from the restrictions mentioned above.

In the present study the thermodynamic parameters such as K, $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the interaction of sodium p–toluenesulfonate (STS) with dodecyltrimethylammonium bromide (DTAB) micelles were determined by both spectrophotometric and calorimetric methods to compare these two methods with each other as a means for the study of such an interaction. Sodium p–toluenesulfonate was employed as the probe molecule for the reason that the molecule was easily soluble in two phases and was known to suit for the spectrophotometric experiment.

## Experimental

*Materials.* The reagent grade DTAB of Tokyo Kasei kogyo Co. was recrystallized twice from acetone containing small amount of ethanol and dried in vacuo for 10 hours at room temperature. [15] Gravimetric analysis of DTAB in the form of silver bromide using silver nitrate gave 99.7 % purity. The extra pure STS also from Tokyo Kasei Kogyo Co. was purified by three times recrystallization from water-ethanol (1:3) and dried in vacuo for 1 hour at 80–90 ℃. The purity of STS was determined to be 99.0 % by ion exchange and acid–base titration using Amberlite IR–120B (H) cation exchange resin. Deionized water was distilled from alkaline permanganate and subsequently twice from a pyrex glass still.

*Apparatus and procedures.* Absorption spectra were recorded on a Hitachi EPS–3T recording spectrophotometer using 10 mm quartz cells. Calorimetric experiments were carried out with a twin conduction type microcalorimeter CM–204S2 of Leska Co. connected to a Rikadenki recorder CR–101 through a nanovolt meter／amplifier TR–8513B of Takeda Riken Kogyo Co.. A typical calorimetric procedure was conducted in the following way. Twin calorimeter cells of stainless steel were each filled with 50 ml DTAB solutions, delivered by volumetric pipet. 2 ml of STS solutions was sealed in a pyrex glass ampoule. Another ampoule containing 2 ml of water was used as reference. Both ampoules were soaked in DTAB solutions of twin cells, respectively. After the cells and ampoules were allowed overnight to equilibrate thermally at 25 ℃, the ampoules were broken and two solutions were mixed. The heat evolved then was recorded as a function of time. From the area under the curve, the heat for the interaction between STS and DTAB micelles was

calculated by comparing with the area obtained when the known amount   of heat was electrically generated. The calorimeter was calibrated against the literature value of molar heat of solution of KCl, 4.115 kcal/mol[16]

## Results and Discussion

*Spectrophotometric study.* A series of solutions of STS at 2.50 x $10^{-3}$ M   were prepared with varying the concentration of DTAB from 0 to 0.1 M. The absorbance of the solutions at the wavelength of 261 nm were then measured at several   different temperatures. The results at 25℃ were plotted as a function of the concentration of DTAB in Fig. 1. The data at other temperatures are tabulated in Table 1.
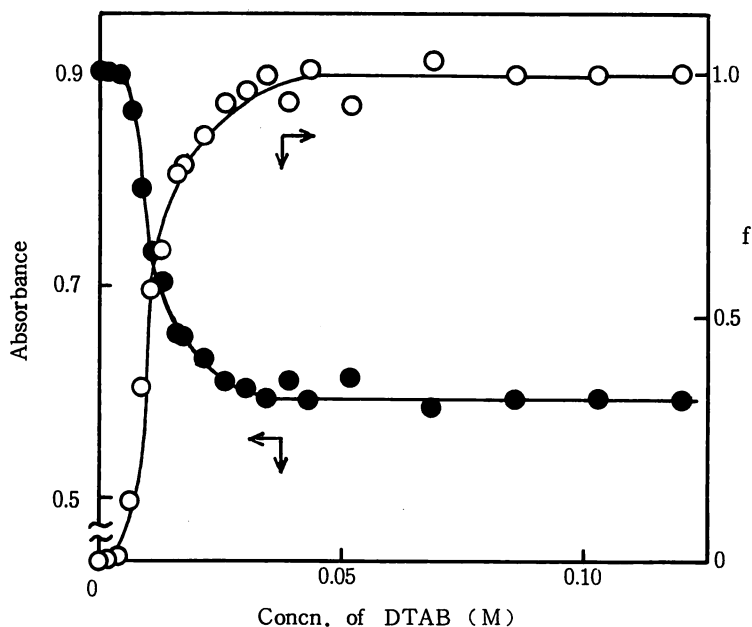


Fig. 1   Absorbance of sodium p‐toluenesulfonate (STS) solution at 261 nm and   fraction f of STS associated to micelles as a function of concn. of dodecyltrimethylammonium   bromide (DTAB) at 25℃. Concn. of STS : 2.5 x $10^{-3}$M.

As seen from Fig. 1, in the absence and at the low   concentration   region of DTAB below the critical micelle concentration (cmc), the absorbances of  STS   remained unchanged. However, when DTAB was increased above cmc,   the   absorbances decreased drastically until they reached a constant value, which suggested the complete solubilization of STS in the micelles. At DTAB concentrations lower than the plateau, the absorbance of the solution would be the sum   of the contributions from STS in aqueous phase and that associated with micelles.

Therefore, the fraction f of STS associated with micelles can be calculated from the absorbance using the equation[5],

Table. 1 Absorbance of sodium p-toluenesulfonate (STS) as a function of concentration of dodecyltrimethylammonium bromide (DTAB) at various temperatures. Concn. of STS: 2.50 x $10^{-3}$ M.

| Concn. of DTAB(M) | Absorbance (at 261 nm) | | | | |
|---|---|---|---|---|---|
| | 15.3℃ | 20.5℃ | 23.5℃ | 31.5℃ | 35.8℃ |
| 0.0000 | 0.903 | 0.898 | 0.893 | 0.893 | 0.868 |
| 0.0025 | 0.902 | 0.897 | 0.892 | 0.892 | 0.868 |
| 0.0050 | 0.897 | 0.892 | 0.889 | 0.887 | 0.863 |
| 0.0075 | 0.821 | 0.816 | 0.817 | 0.823 | 0.814 |
| 0.0100 | 0.741 | 0.742 | 0.744 | 0.749 | 0.741 |
| 0.0125 | 0.687 | 0.691 | 0.693 | 0.695 | 0.690 |
| 0.0150 | 0.654 | 0.658 | 0.660 | 0.659 | 0.657 |
| 0.0175 | 0.630 | 0.636 | 0.639 | 0.635 | 0.633 |
| 0.0200 | 0.613 | 0.621 | 0.623 | 0.618 | 0.614 |
| 0.0250 | 0.594 | 0.605 | 0 607 | 0.598 | 0.598 |
| 0.0300 | 0.589 | 0.599 | 0.601 | 0.592 | 0.590 |
| 0.0350 | 0.582 | 0.592 | 0.595 | 0.583 | 0.582 |
| 0.0400 | 0.580 | 0.589 | 0.591 | 0.578 | 0.579 |
| 0.0500 | 0.577 | 0.586 | 0.589 | 0.575 | 0.573 |
| 0.0600 | 0.572 | 0.585 | 0.587 | 0.574 | 0.574 |
| 0.0700 | 0.572 | 0.584 | 0.585 | 0.572 | 0.571 |
| 0.0800 | 0.572 | 0.582 | 0.584 | 0.568 | 0.567 |
| 0.1000 | 0.569 | 0.584 | 0.582 | 0.565 | 0.566 |

$$f = \frac{C_m}{C_m + C_a} = \frac{C_m}{C_t} = \frac{A - C_t \varepsilon_a}{C_t (\varepsilon_m - \varepsilon_a)} \tag{1}$$

where $C_m$ is the concentration of STS bound to micelles, $C_a$ the concentration in aqueous phase, $C_t$ the total concentration, A the absorbance, $\varepsilon_a$ the absorptivity in aqueous phase and $\varepsilon_m$ the absorptivity of micellar bound STS. $\varepsilon_a$ was determined to be 362 $mol^{-1}$ $cm^{-1}$ for the STS solution in the absence of DTAB. The plateau region of the absorbance in Fig. 1 gave $\varepsilon_m = 238$ $mol^{-1}$ $cm^{-1}$ assuming that $C_a = 0$ and $C_t = C_m$ in the region.

The fraction f calculated from the absorbance data in Fig. 1 is also plotted as a function of the concentration of DTAB in the same figure. $C_m$ and $C_a$ can be now easily calculated from the total concentration using f.

Several equations have been proposed for the experimental determination of the equilibrium constant of the interaction between the solute molecule and micelles.

They are classified into four categories, equation based on the complex formation between the solute molecules and surfactant molecules[5, 6], that for the partitioning of the solute between micellar and aqueous phase[12, 17, 18], Freundlich adsorption isotherm[6] and Langmuir adsorption isotherm[6]. These four equations were tried to treat the present data. The best straight line was obtained with Langmuir adsorption isotherm,

$$\frac{B}{C_m} = \frac{N}{KL}\frac{1}{C_a} + \frac{N}{L} \tag{2}$$

where B=concn. of DTAB−cmc, N the aggregation number of DTAB, L the number of adsorption sites, K the equilibrium constant, $C_m$ and $C_a$ are the same notations as before. The equlibrium constant K is obtained from the slope and intercept of a straight line drawn by plotting the left side of Equation (2) against $1/C_a$.

In applying Equation (2) to the experimental values of $C_m$ and $C_a$, we excluded values which corresponded to value of f greater than 0.9 or smaller than 0.2 to minimize errors. That is, Equation (2) was applied to the rising region of the fraction f shown in Fig. 1. The data from Fig. 1 and Table 1 are plotted in Fig. 2
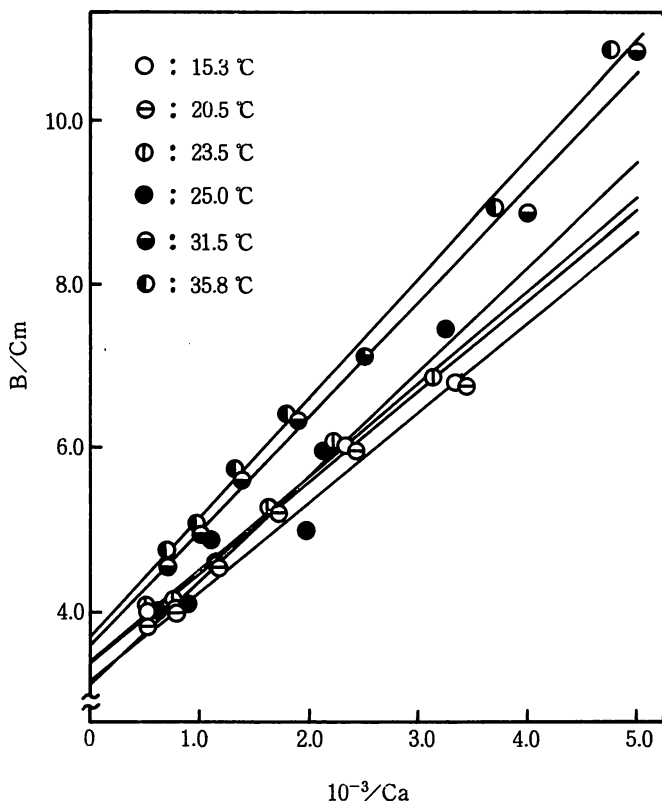


Fig. 2 Plot of Langmuir adsorption isotherm for the spectrophotometric data at various temperatures.

and the least square lines were drawn through experimental points. From the plots
the equilibrium constants were determined to be 3.1, 2.9, 3.0, 2.5 and 2.5 x $10^3$ $M^{-1}$
at 15.3, 20.5, 23.5, 31.5 and 35.8 ℃, respectively. The equilibrium constant at 25℃ is
presented in Table 2 for the comparison with the value obtained by calorimetric
method.

The standard free energy change for the interaction was calculated using Equa-
tion (3). The result at 25℃ is also presented in Table 2 as a typical example. For
the determination of the standard enthalpy change and entropy change, Equation (4)
and (5) were used, respectively, as usual way. The left hand side of Equation (4)
was plotted against 1／T and the best straight line was drawn through plotted points
in Fig.3. The standard enthalpy change was obtained from the slope. The entropy
change was calculated from $\Delta G°$ and $\Delta H°$ using Equation (5). The results are tabu-
lated in Table 2. Errors of the parameters in Table 2 were evaluated on the basis of
reproducibility of measurements.

$$\Delta G° = -RT \ln K \tag{3}$$

$$R \ln K = -\Delta H°／T + \Delta S° \tag{4}$$

$$\Delta S° = (\Delta H° - \Delta G°)／T \tag{5}$$
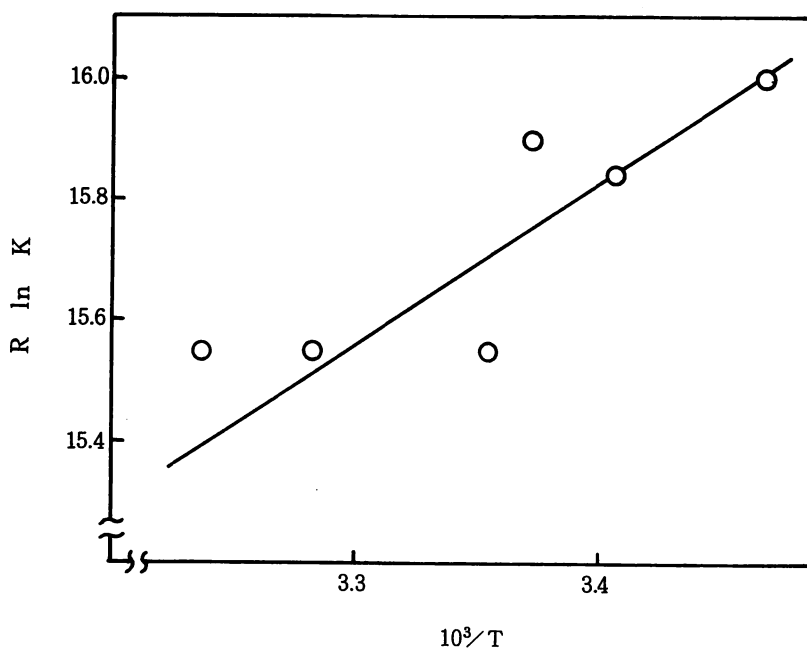


Fig. 3  Plot of R ln K vs 1／T for the spectrophotometric data.

Table 2   Thermodynamic parameters for the interaction of sodium p- toluenesulfonate with do-
decyltrimethylammonium bromide micelles at 25℃.

| Method | K $(10^3/M)$ | $\varDelta G°$ ( kcal/mol) | $\varDelta H°$ ( kcal/mol) | $\varDelta S°$ (cal deg$^{-1}$ mol$^{-1}$) |
|:---:|:---:|:---:|:---:|:---:|
| A | $2.5 \pm 0.7$ | $-4.6 \pm 0.4$ | $-2.1 \pm 0.2$ | $8.4 \pm 0.7$ |
| B | $2.0 \pm 1.5$ | $-4.5 \pm 1.0$ | $-1.5 \pm 0.1$ | $10 \pm 3$ |
|  |  |  | $-1.40 \pm 0.09*$ |  |

* obtained  from  the  slope  of  Fig. 6.

A : Spectrophotometric  method

B : Calorimetric  method

*Calorimetric study A.*   In this study, the concentration of DTAB  solutions  in
the twin calorimeter cells was varied from 0 to 0.12 M. The concentration  of  STS
sealed in the ampoule was maintained at constant value of 6.51 x$10^{-2}$ M  which cor-
responded to 2.50 x $10^{-3}$ M in the final form of the solutions upon being mixed with
DTAB solutions.   With the concentration of STS used in the present study,  heat of
dilution was negligible, which was measured by filling each of the twin  cells  with
50 ml of water instead of DTAB solutions.

Heat evolved by the interaction of STS with DTAB micelles is   plotted  as  a
function of the concentration of DTAB in Fig. 4. The solid curve is  drawn  to  re-
present the average value of the experimental points. Heat of  the  interaction was
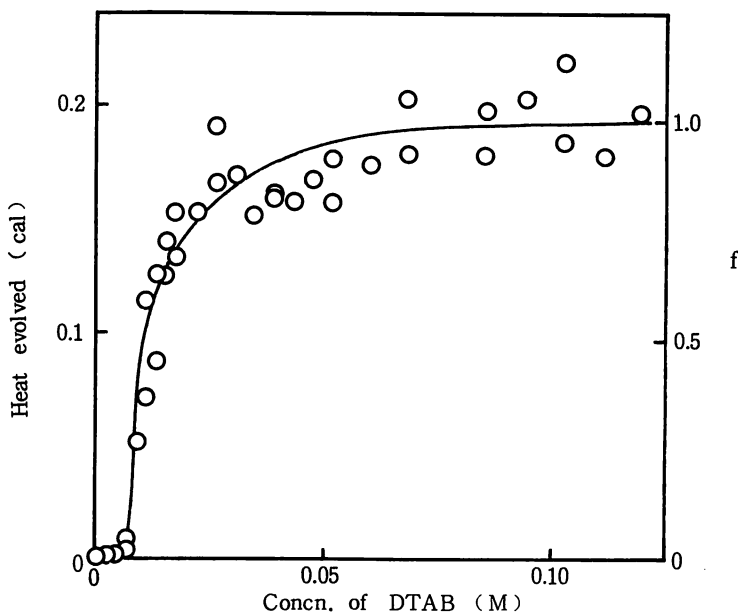


Fig. 4   Heat evolved and fraction f of sodium p - toluenesulfonate (STS) associated to micelles as a
function of concn. of dodecyltrimethylammonium bromide (DTAB) at 25℃. Plot for f  coin-
cides  with  that for heat. Concn. of STS:2.50 x 10$^{-3}$   M.

negligible in the absence and at the low concentration region of DTAB below cmc. When DTAB was increased above cmc, the heat drastically increased and finally reached a plateau again. Though the experimental points are rather scattered, the present heat–DTAB concentration profile suggests that the calorimetric method could be used also for the determination of the equilibrium constant.

The fraction f was calculated using the equation,

$$f = q / Q \qquad (6)$$

where q is the heat evolved at any concentration of DTAB and Q the average heat evolved in the plateau region. Fig. 4 represents also the plot for f which coincides with that for the heat evolved.

$C_m$ and $C_a$ were calculated from f assuming that STS was completely associated to the micelles at the concentrations of DTAB corresponding to the plateau. They were used for the plot of Langmuir adsorption isotherm shown in Fig. 5. The equilibrium constant was obtained from the least square line in the figure and presented in Table 2.
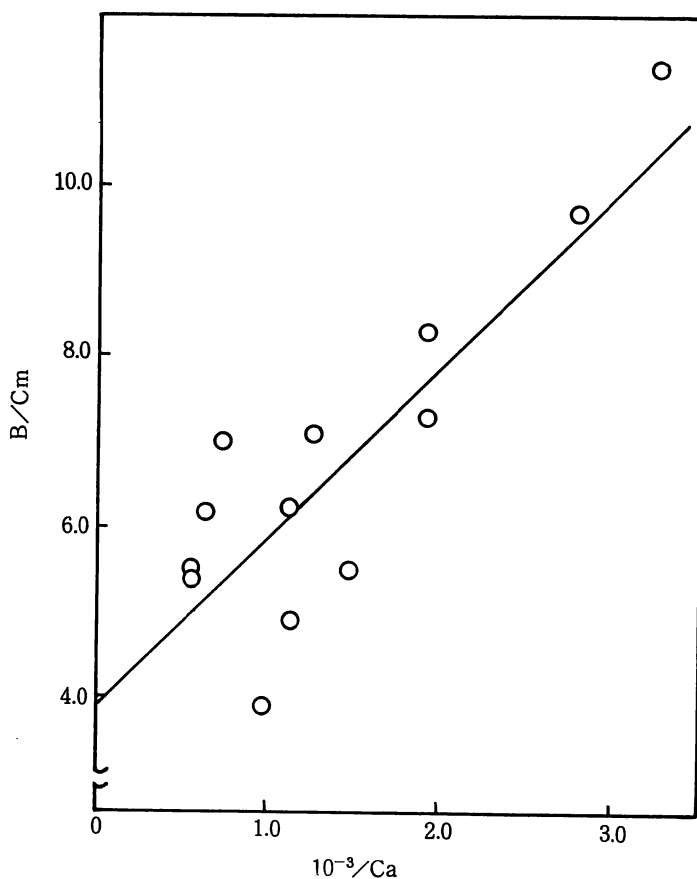


Fig. 5 Plot of Langmuir adsorption isotherm for the calorimetric data at 25℃.

The standard free energy change  was calculated from the equilibrium  constant using Equation (3) as in the case of the spectrophotometric study. The value of the standard enthalpy change without asterisk in Table 2 was obtained from  the average value of the heat evolved in the plateau region of the plot in Fig.4. The standard entropy change was also calculated using Equation (5).

As seen from Table 2, the calorimetric method gives rather large errors to the equilibrium constant and consequently to the standard free energy change and  entropy change in comparison with the spectrophotometric method though two  methods give comparable values within experimental errors. The reason may  be due to the fact that the heat evolved is too small for the system studied in the present investigation.

Therefore, the spectrophotometric method is recommended for the determination of the equilibrium constant and consequently the standard free energy change if the method is applicable to the system studied.   However,  the calorimetric  method would be useful for the system which evolves the appreciable amount of heat  and for which the spectrophotometric method can not be used,  for  example,  systems such as aliphatic alcohols, esters and so on.

The value of the standard enthalpy change determined by the calorimetric method is smaller than that obtained by the spectrophotometric method.  The difference is beyond the experimental errors. Another set of calorimetric  experiments  were run to confirm the result.

*Calorimetric study B.*    The following procedures were followed in this series of experiments. The concentration of STS in the ampoule was varied in the way so that it would be from 0 to $10.8 \times 10^{-3}$ M in the  final  form  of  the  concentration upon being mixed, while the concentration of both solutions of DTAB  in the twin cells was maintained at the constant value of 0.065 M in contrast with  the procedure employed in Calorimetric study A. The heat evolved was corrected  for  the heat of dilution with the higher concentrations of the STS solutions.   The heat of dilution was as much as 0.089 cal for the STS concentration of $8.64 \times 10^{-3}$  M  in the final form of the solution. The heat of dilution was measured by the way described in the previous section.

The heat thus measured is plotted as a function of the concentration of STS in Fig. 6. The standard enthalpy change was obtained from the slope  of the straight line. The result is presented in Table 2 as the value with asterisk.   It is in good agreement with the result obtained in the previous calorimetric study.

According to Fendler[1], micellization of the surfactant molecules  themselves is dependent on the temperature. This effect is supposed to be reflected to the  larger values of the standard enthalpy change measured by the spectrophotometric method. The calorimetric method is, therefore, recommended for the  determination  of  the standard enthalpy change.
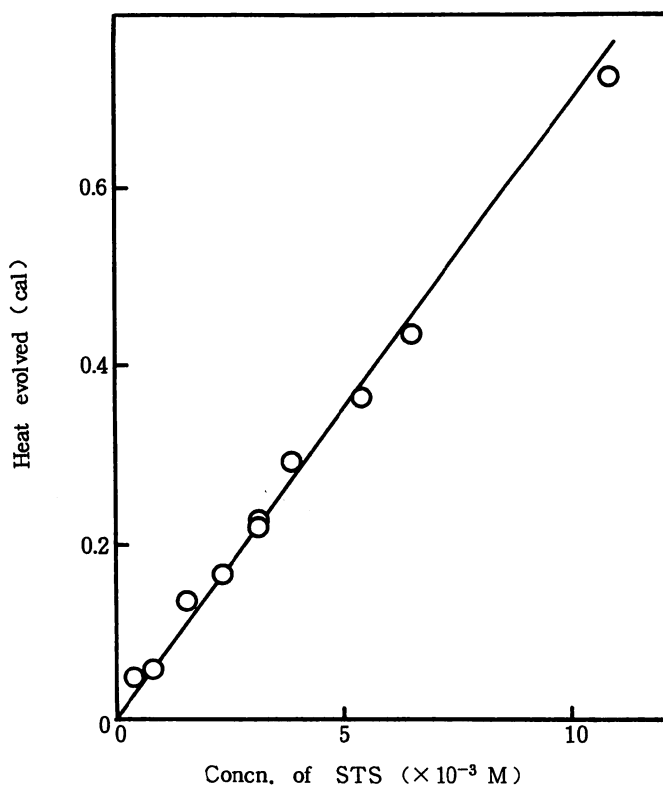
Fig. 6  Heat evolved as a function of sodiun p-toluenesulfonate
(STS) at 25℃. Concn. of dodecyltrimethylammonium
bromide:0.065 M.

# References

1) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975.

2) M. Grätzel and J. K. Thomas, "Modern Fluorescence Spectroscopy, Vol. 2", ed. by E. L. Wehry, Plenum Press, New York, 1976, p. 169.

3) J. K. Thomas, Chem. Rev., *80*, 283 (1980).

4) N. A. Riegelman, M. K. Allawala, M. K. Hrenoff, and L. A. Strait, J. Colloid Sci., *13*, 208 (1958).

5) L. Sepulveda, J. Colloid Interface Sci., *46*, 372 (1974).

6) Y. Nemoto and H. Funahashi, Hyomen, *15*, 625 (1977).

7) C. A. Bunton and L. Sepulveda, J. Phys. Chem., *83*, 680 (1979).

8) C. Hirose and L. Sepulveda, J. Phys. Chem., *85*, 3689 (1981).

9) R. R. Hautala, N. E. Schore, and N. J. Turro, J. Am. Chem. Soc., *95*, 5508 (1973).

10) M. Van Bochstaele, J. Gelan, H. Martens, J. Put, J. C. Deberen,  N. Boens, and F. C. de Schrijver, Chem. Phys. Lett., *58*, 211 (1978).

11) M. Algrem, F. Grieser, and J. K. Thomas, J. Am. Chem. Soc., *101*, 279 (1979).

12) E. Lissi, E. Abuin, and A. M. Rocha, J. Phys. Chem., *84*, 2406 (1980).

13) J. W. Larsen and L. J. Magid, J. Phys. Chem., *78*, 834 (1974).

14) S. Abe and K. Ogino, Abstracts of the 32th Symposium on Colloid and Interface Chemistry, Kochi, Japan, 1979, p. 182.

15) R. D. Geer, E. D. Eylar, and E. W. Anacker, J. Phys. Chem., *75*, 369 (1971).

16) R. C. Weast ed.,"Handbook of Chemistry and Physics, 57th ed.", CRC Press, Cleveland, Ohio, 1976.

17) D. G. Herries, W. Bishop, and F. M. Richards, J. Phys. Chem., *68*, 1842 (1964).

18) A. M. Mankowich, J. Am. Oil Chem. Soc., *42*, 185 (1965).