Interaction between Surface Active Agents and Proteins. IV. Heat of Interaction of Sodium Dodecyl Sulfate and Egg Albumin

By Koichiro Aoki* and Yasushi Suzuki

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Introduction

As previously described[1], we studied electrophoretically the sodium dodecyl sulfate (SDS) and egg albumin system at points of higher pH's than that of the isoelectric point of egg albumin. In that study it was concluded that SDS-egg albumin complexes were formed in the following way at pH 6.8: When the weight mixing ratio albumin/SDS was between 100/0 and 80/20 the composition of the complex was AD_n (n=40), and when the mixing ratio albumin/SDS was between 80/20 and 35/65 the composition of the complex changed continuously from AD_n to the completion of AD_{8n}.

In the present study we measured the temperature change occurring when SDS

* Present temporary address: Department of Chemistry, Purdue University, Lafayette, Indiana, U. S. A.

1) K. Aoki, This bulletin **29**, 369 (1956).

and egg albumin solutions were mixed at the same condition as in the above electrophoretic study and calculated the heat of interaction.

Experimental

The apparatus is shown in Fig. 1[2]. Experiments were carried out in a thermostat at 25± 0.001°C. Because very slight temperature changes accompanied the reaction, 10-junction of copper-constantan thermocouple and a galvanometer of high sensitivity were used to trace the temperature change[3,4]. We found that the sensitivity of the apparatus we assembled was such that a 1 mm movement of the needle on the lamp scale corresponded to 0.0006°C. The reaction vessel was unsilvered Dewar flask, the volume of which was about 120 cc. and the water equivalent 93.0 cal.*

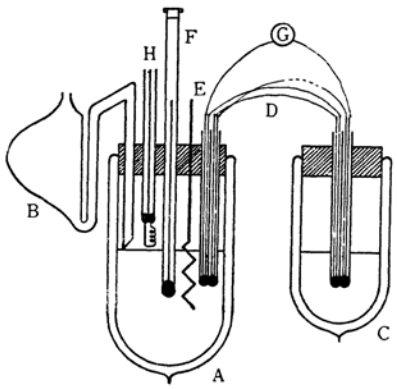

Fig. 1. Apparatus.

A. Reaction vessel.
B. Vessel for warming SDS solution.
C. Vessel for holding one end of thermocouple.
D. 10-junction of copper-constantan thermocouple.
E. Stirrer.
F. Beckmann thermometer.
G. Galvanometer.
H. Platinum wire.

The buffer solution used was pH 6.8 and ionic strength 0.10. Into a reaction vessel A, 50 cc. of 1.00% buffered albumin solution was put. Fifty cc. of buffered SDS solution varying in concentration were put into another vessel B. Then we let these two solutions stand in the thermostat for about ten hours to make them aquire the temperature of the thermostat. After that they were mixed, and at the same time we began to measure the temperature change which accompanied the reaction.

In addition, we measured the heat of dilution of albumin and of SDS. We put 50 cc. of buffered albumin solution or buffered SDS solution into reaction vessel A and put the same amount of buffer solution into vessel B. We measured the temperature change occurring when albumin or SDS solution was diluted to twice the original volume by pouring the solution in vessel B into vessel A.

Results

Heat was generated when SDS or albumin solution was diluted with the buffer. Fig. 2 shows a typical run of the temperature change occurring when albumin and SDS solutions were diluted. Considering the maximum value of this curve to be the amount of heat generated, the following values were obtained for the heats of dilution:

SDS	1.2 cal./g.
egg albumin	0.8 cal./g.

These are the values obtained when the solutions, the concentrations of which were less than 1.00%, were diluted to twice their original volumes.

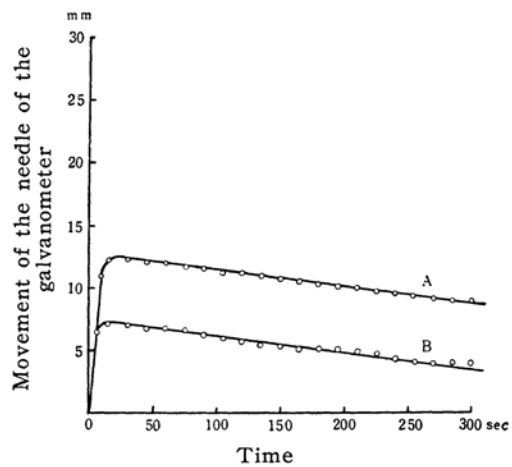

Fig. 2. Heat of dilution.

A: Heat generated when 1.00% buffered SDS solution was diluted to twice its original volume.
B: Heat generated when 1.00% buffered albumin solution was diluted to twice its original volume.

Hutchinson et. al.[5] measured accurately the heats of dissolution of sodium alkyl sulfates. Using their data, we can calculate the heat produced when 0.050M (1.30%) aqueous sodium decyl sulfate solution is diluted to 0.025 M (0.65%) at 25.00°C. The value is found to be 1.0 cal./g. Our values of the heat of dilution are considered reasonable when compared with this value.

Heat was instantly generated when SDS and egg albumin solutions were mixed. Fig. 3 shows

2) E. Suito, *Rev. Phys. Chem. Japan*, **13**, 74 (1939).
3) N. H. Ray. *Trans. Faraday Soc.*, **48**, 809 (1952).
4) J. Osugi and K. Hiromi, *Rev. Phys. Chem. Japan.* **22**, 76 (1952).
* The experimental procedure to find this value was the same as used by E. Suito[2].

5) E. Hutchinson, K. E. Manchester and L. Winslow, *J. Phys Chem.*, **58**, 1124 (1954).

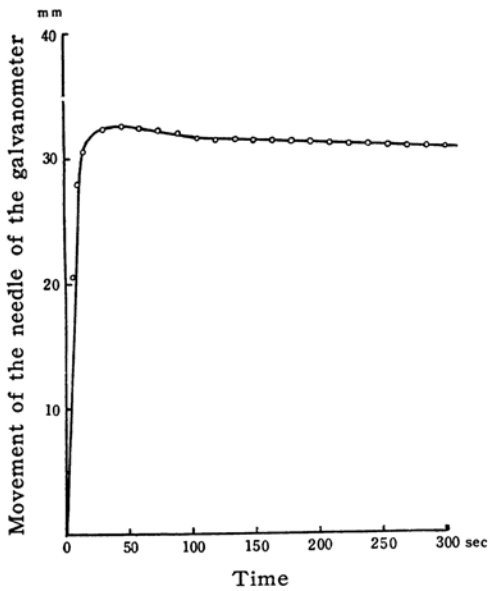

Fig. 3. Heat of reaction.
Heat produced when 1.00% SDS solution and 1.00% albumin solution were mixed.

one tracing of the temperature change with time. Taking the maximum value of this curve as the total heat produced, we deducted from this maximum value the heat of dilution of egg albumin and that of SDS, to obtain the value of the heat of the reaction itself. As the amount of SDS used was different in each experiment, the value of the heat of dilution of SDS to be deducted was calculated proportionally using the value of 1.2 cal./g.

In this study the concentration of egg albumin was kept constant at 1.00%. Each of the SDS solutions varying in concentration from 0.05% to 1.00% was mixed with this egg albumin solution. Thus we obtained the relation between the mixing ratio albumin/SDS and the heat evolved. The results are shown in Fig. 4. In these experiments any error in measuring the heat produced is within ±0.2 cal.

Discussion

It was concluded from the electrophoretic experiment that SDS and egg albumin did not combine in the same way above and below the mixing ratio albumin/SDS=80/20, that is, the composition of the complex was constant when the mixing ratio albumin/SDS was between 100/0 and 80/20, while it changed continuously in the region from 80/20 to 35/65[1]. Referring to the result, we assume that the curve *abc* in Fig. 4 consists of two straight lines *ab* and *bc*, which change the slope near the point albumin/SDS=80/20.

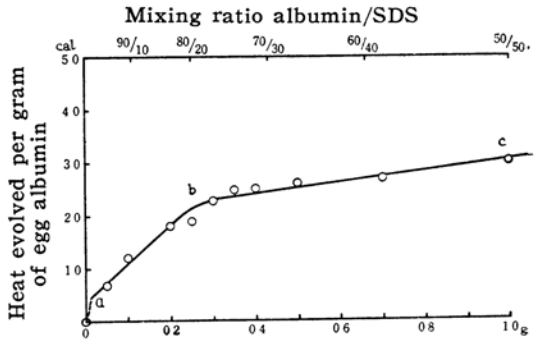

Fig. 4. Relation between mixing ratio albumin/SDS and heat of reaction.

Recently, Hill[6] observed by equilibrium dialysis that after one mole of anionic detergent* combined with one mole of egg albumin, another kind of interaction took place. Considering his results SDS and egg albumin may combine in a different way also above and below the mixing ratio albumin/SDS=99.4/0.6. Here the molecular weight of egg albumin and of SDS was assumed to be 46,000 and 288, respectively. When *ba* in Fig. 4 is extended to the left, it does not pass the origin. This may be fact which corresponds to the above Hill's observation.

In the region where the mixing ratio albumin/SDS is between 100/0, or more precisely 99.4/0.6, and 80/20, 40 molecules of SDS are bound to one egg albumin molecule. Using the molecular weights cited above, the following equation is obtained from the slope of the straight line *ab*.

$$\text{Egg albumin} + 40\,\text{SDS} = \text{Complex} + 92.1\,\text{kcal.}$$

or

$$-\Delta H = 92.1\ \text{kcal./mol. albumin} = 2.3\ \text{kcal./mol. SDS}$$

If we assume that one NH_3^+ radical on the egg albumin molecule reacts with one OSO_3^- radical of SDS within this mixing ratio, we can rewrite the above equation as

$$\cdots NH_3^+ + \cdots OSO_3^- = \text{Complex} + 2.3\,\text{kcal.}$$

This value of heat of reaction is far smaller than that of the heat of neutralization between strong acid and strong base, 13.7 kcal./mol. (at about 30°C).

In the range where the mixing ratio albumin/SDS is between 80/20 and 35/65,

6) R. M. Hill, Ph. D. Thesis, University of Minnesota, 1955.

* He used sodium-*n*-octylbenzene-*p*-sulfonate.

the following equation is obtained from the slope of the straight line *bc*.

$$\text{Complex}+\text{SDS}=\text{Complex}'+0.3\ \text{kcal.}$$

The values of the heat of interaction obtained in this study are of the same order as those found by Goddard and Pethica[7] in the bovine serum-albumin-SDS system.

The CMC (critical micelle concentration) of SDS is 0.04% (0.0013 mol./l.) in a buffer solution of ionic strength 0.10[8]. Thus when 1.00% albumin solution and 0.05% SDS solution are mixed, the concentration of SDS is above the CMC before mixing and below it after mixing. When they are mixed, there should be an adsorption of heat owing to the decomposition of the micelle. Goddard and Benson[9] calculated the heat of micelle formation of SDS to be ca. 0.1 kcal./mol. SDS at 25°C, using their data and the assumption of Hutchinson et. al.[5] The amount of SDS used at this mixing ratio was so small, 0.05 g. (0.002 mol.), that such a small quantity of heat could not be measured.

7) E. D. Goddard and B. A. Pethica, *J. Chem. Soc.*, **1951**, 2659.
8) K. Aoki and J. Hori, This bulletin, **29**. 104 (1956).
9) E. D. Goddard and G. C. Benson, *Trans. Faraday Soc.*, **52**, 409 (1956).

Summary

We measured the heat evolved when egg albumin and SDS solutions were mixed at pH 6.8 and at 25.00°C, and calculated the heat of interaction.

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Chemistry Laboratory, Nagoya City University, Nagoya