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CALORIMETRIC STUDIES ON THE STATE OF WATER IN AEROSOL OT REVERSED MICELLES.

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SUMMARY

The state of water in the Aerosol OT (AOT) / isooctane reversed micelle solutions was studied by a microcalorimeter of conduction type. The molar enthalpy changes of water were obtained by mixing AOT solutions of various R values with those at R of zero, where R means the molar ratio of water to surfactant, AOT. The observed enthalpy values at larger R were endothermic, whereas those at smaller R were exothermic. An enthalpy curve against R was drawn by adding consecutively the enthalpy changes, showing a maximum at R of 2. This feature was qualitatively discussed in terms of the state of water in reversed micelles.

INTRODUCTION

Reversed micelles mean aggregates of surfactants and polar solutes formed in organic media. Water is readily solubilized in the polar core of reversed micelles, forming a so-called water pool. Since the water pool is thought to resemble pockets of water in bioaggregates such as biomembranes(ref. 1) and mithocondria(ref. 2) etc, the water pool is an interesting subject from the viewpoint of their catalytic activities(ref. 3,4) and reactivities of enzymes(ref. 5) in nonaqueous solution environments.

The water molecules constituting the water pool can be usually classified into two categories, type I and type II(ref. 6). The type I water resides near the inner surface of the micelles and is bound to ionic head groups of surfactants. The type II water does not interact directly with the surfactant and exhibits properties similar to bulk water. The type I water mainly exists in a small water pool. As the size of the water pool expands, type II water becomes dominant, where two types of water would be in equilibrium. Such a description of the water pool is called as a two phase model.

In this study, the reversed micelle systems were provided by dissolving the surfactant, Aerosol OT [sodium 1,4-bis(2-ethyl- hexyl)sulfosuccinate,AOT] in

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isooctane because they are very stable and are known to solubilize a large contents of water(ref. 7).

Calorimetric investigation on the solubilization of water in reversed micelles may be useful for the purpose of clarifying their state of water, however, a few calorimetries have been carried out. In this study, the heats of solubilization of water in reversed micelles were measured with a microcalorimeter of conduction type

EXPERIMENTAL

Materials

The used solvents were dried over a type 4A Molecular Sieve which had been activated by heating at 200°C under reduced pressure for several hours and then cooled in vacuo over silica gel(ref. 4). The AOT was obtained from Nikko Chemicals. The AOT was dried at 50 °C in vacuo over P_2O_5 and used immediately(ref. 4).

Preparation of sample solutions

AOT reversed micelle solutions were prepared by dissolving AOT in isooctane. The used concentrations of AOT in isooctane solution were 0.31 and 0.15 mol kg^{-1}. The AOT /isooctane solutions of various R values were prepared by adding different contents of water to fixed quantities of AOT in isooctane, where R values mean the molar ratio of water to surfactant, AOT. Minute contents of water in AOT solution were determined by using a moisturemeter, CA-OC, Mitsubishi Chemical Ind..

The Calorimetric measurements

The microcalorimeter used was a twin conduction type (model MPL-III Tokyo Riko) equipped with an ampoule system. In order to assure rapidly the complete equilibration, the AOT solution of a certain R value in the vessel was mixed with that containing no added water in the ampoule. Ten mL of the AOT solution was put in a sample vessel and two mL of that containing no added water was sealed in a glass ampoule. The R value of AOT solution in a sample vessel was termed R_1 and the R value at equilibrium attained by mixing AOT solutions of $R=R_1$ and R=0 was termed R_2.

The same vessel without sample was used as the reference. Both of the AOT solutions in the ampoule and vessel were stood above 18 h in order to attain temperature equilibrium at 20 C. After the temperature equilibrium, the calorimetric measurements were started by crushing the ampoule. The solution in the ampoule was readily mixed with that in the vessel by stirrer magnetically connected to a rotating devise.

RESULTS AND DISCUSSION

Figure 1 shows typical time courses of the heat effects in mixing of AOT solutions of R_1 and R=0, where AOT concentrations are 0.31 mol Kg^{-1} and 0.15 mol Kg^{-1}. The remarkable endothermic curves at large R and exothermic curves at small R were observed. Table I shows the observed heats, ΔH_{obs}, and the molar enthalpy changes of water, ΔH, in the region of $0.2<R_1<30$. The endothermic values were observed in larger R, whereas the exothermic values were observed in smaller R at concentrations of AOT, 0.31 mol Kg^{-1} and 0.15 mol kg^{-1}.

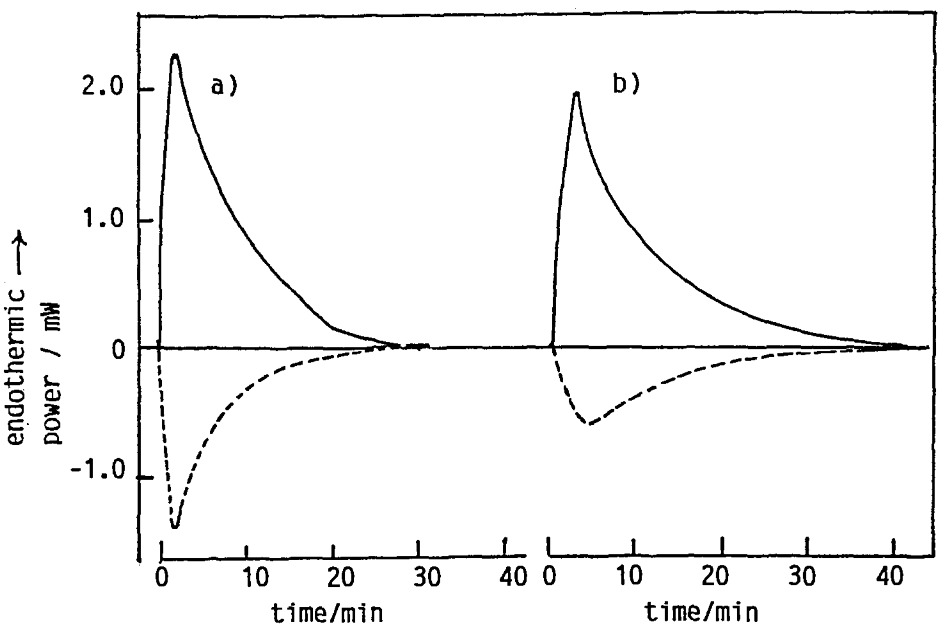


Fig. 1. Time courses of heat effects in mixing AOT solutions of R_1 and R=0 at 20 °C.
a), 0.31 mol Kg^{-1} AOT solution; b), 0.15 mol Kg^{-1} AOT solution. Solid lines were obtained in the case of $R_1=20$ and $R_2=16$, and broken lines were obtained in the case of $R_1=1.0$ and $R_2=0.8$ (R_1 and R_2, see Experimental).

Aprano et al. (Ref. 8) measured the heat of mixing water with AOT/n-heptane solutions using a flow microcalorimeter. They observed that the heats are absorbed as the result of the dissolution of water into the empty reversed micelles which mean that the R is zero. They reported that the dependence of experimental data on R is mainly due to the water partitioning between two states in water pools. They also considered that the insertion of water in reversed micellles is mainly driven by a favourable change of entropy, showing the positive enthalpies of solution of water. It is shown in Scheme 1-A. In this model, the water in S phase is near the inner surface of the micelle and that in B phase exists in the center of the water pool, having similar properties to bulk water.

TABLE 1

The heat effects of mixing AOT/isooctane solutions accompanied with change in R value at 20°C.

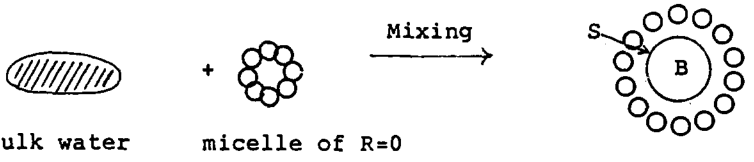
0.31 mol Kg^{-1} AOT solution				0.15 mol kg^{-1} AOT solution			
R_1	R_2	ΔH_{obs} mJ	ΔH J/H_2Omol	R_1	R_2	ΔH_{obs} mJ	ΔH J/H_2Omol
30.0	25.0	+1580	+26.2	30.0	25.0	+ 859	+28.6
24.0	20.0	+1090	+22.7	24.2	20.1	+1410	+58.4
20.0	16.7	+1030	+25.7	22.2	18.5	+1390	+62.7
16.0	13.3	+ 927	+29.0	19.6	16.3	+1350	+69.0
15.0	12.5	+1330	+44.3	16.0	13.3	+1320	+80.2
12.0	10.0	+1080	+45.0	12.1	10.0	+ 282	+22.9
10.0	8.33	+2510	+125	10.0	8.3	+ 248	+24.8
8.0	6.67	+ 965	+60.3	7.90	6.58	+ 638	+80.8
6.0	5.0	+1280	+107	4.85	4.04	+ 274	+56.5
5.0	4.17	+1020	+102	3.94	3.28	+ 194	+49.2
4.0	3.33	+ 408	+51.1	3.00	2.50	+ 125	+41.1
3.6	3.0	+ 360	+50.0	2.50	2.08	+ 110	+45.1
3.0	2.5	+ 408	+68.1	2.00	1.67	+ 57.8	+28.9
2.4	2.0	+ 105	+21.9	1.50	1.25	- 88.7	-59.1
2.0	1.67	- 52.7	-13.2	0.96	0.83	- 209	-219
1.77	1.48	- 136	-38.0	0.63	0.53	- 171	-270
1.40	1.17	- 464	-166	0.48	0.41	- 168	-401
1.30	1.08	- 450	-173	0.22	0.19	- 194	-754
1.0	0.83	- 345	-173				
0.80	0.67	- 209	-131				
0.50	0.42	- 271	-271				

R_1 and R_2, see Experimental; ΔH_{obs}, observed heat; ΔH, molar enthalpy change of water.

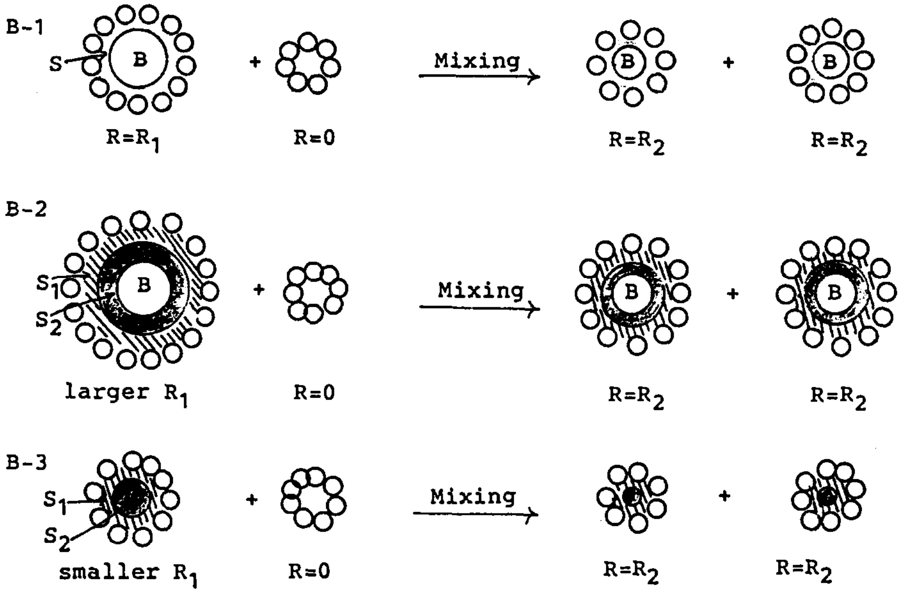
According to Aprano's assumption, the heats measured in our study are due to the change of the state of the water. The process is shown in Scheme 1-B. After the mixing , a certain amount of water is transferred from the micelles of R_1 to empty micelles, which forms the micelle of R_2. Consequently, the heat measured is due to the difference between the molar enthalpies of water in the micelles of R_1 and R_2. Therefore, we are able to make an enthalpy curve of water against R values by adding consecutively each value of the heat of mixing. Figure 1 was drawn by this way.

Scheme 1. Mixing of AOT reversed micelle solutions.

A Mixing of AOT solution of R=0 with bulk water.



B · Mixing of AOT reversed micelle solution of $R=R_1$ with that of R=0.



S phase consists of water near the inner surface of the reversed micelle; B phase consists of water in the center of the water pool; S_1 phase consists of water which has a strong interaction with the head groups of micelles. S_2 phase is located between S_1 and B phases.

Our enthalpy curve showed a characteristic feature, as shown in Fig.2. In the range of R greater than 4, the enthalpy values increase with decreasing R, similar to the results of Aprano et al., whereas in the smaller range of R, enthalpy values show a maximum at R of 2 and rapidly decrease.

If we adopted the two phase model, the process of the mixing means that the water is transferred from the B phase to the S phase as shown in Scheme 1-B-1. Consequently, the fractions of the water in two phases were varied by the mixing, resulting in the change of the averaged molar enthalpy of the water. In the case that the water in S phase is enthalpically more unstable than in B phase, the process of the mixing must always be endothermic and enthalpy curve increases monotonously with decreasing R value.

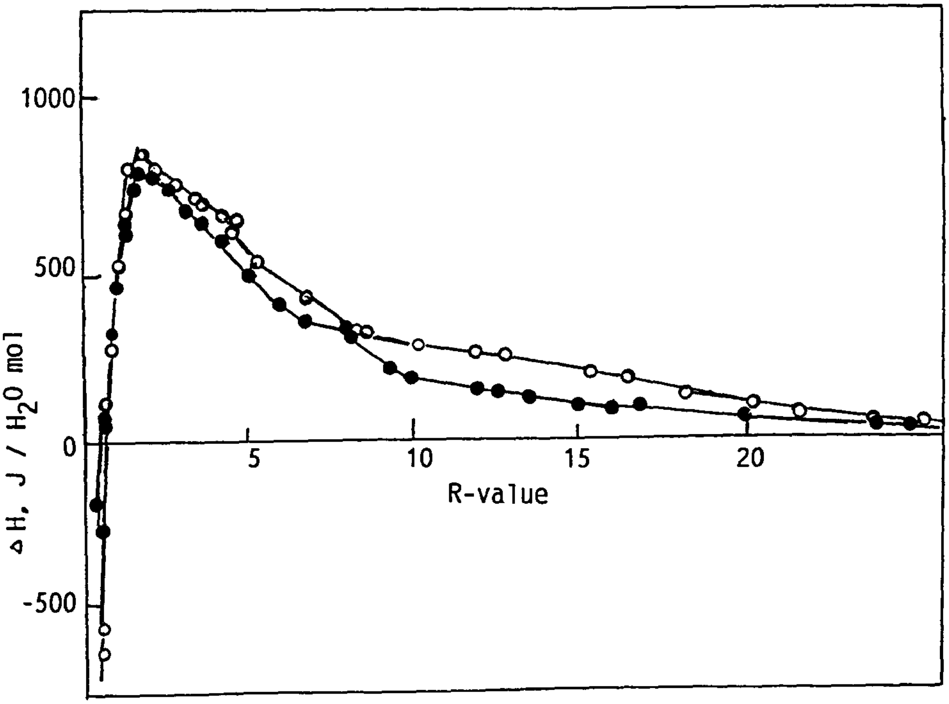


Fig. 2. Averaged molar enthalpies of solution of water as a function of R value.

Observed curves for 0.31 mol Kg^{-1} AOT solution(●) and 0.15 mol Kg^{-1} AOT solution(○) were obtained by adding consecutively the heat of mixing (see text). We assumed that H is asymptotic to zero at large R.

Accordingly, our feature of enthalpy curve cann't be explained by the two phase model. Therefore, we assumed "three phase model", similar to the Frank-

Wen's model(ref. 9) with regard to the hydration of electrolyte ion, as shown in Scheme 1-B-2. In this model, the water in S_1 phase has a strong interaction with the head groups of micelles and is very stable. The structure of the water near the S_1 phase is destroyed due to this interaction. The phase formed by this type of water is called S_2. The water in B phase exists in the core of the water pool and has the same properties as those in B phase of the two phases model. When the R_1 value of the initial state is large enough, the water in the B phase is transferred into S_2 and S_1 phases as the result of mixing as shown in Scheme 1-B-2. If the size of S_1 phase is smaller than that of S_2 phase, the evolution of the heat due to the movement into S_1 phase is hidden by the absorption of the heat due to the movement into the S_2 phase. Consequently, we can observe the dependence of the enthalpy curve on the R value, similar to that of the two phase model in the large R region. However, if the R_1 value is small and no water exists in B phase as shown in Scheme 1-B-3, enthalpically unstable water in S_2 phase is transferred into S_1

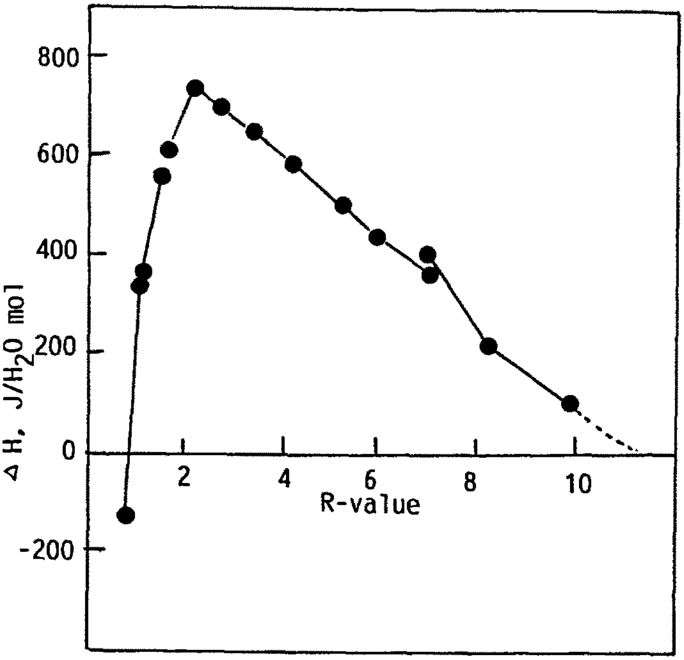


Fig. 3. The enthalpy curves of solution of water in AOT/chloroform solution as a function of R value.
The curve was obtained by the same way as Fig.2.

phase and the heat is evolved. As the result, the maximum is observed in the enthalpy curve. According to three phase model, calorimetric results were qualitatively explained. Kon-no et al.(ref. 10) estimated the negative enthalpy values of solution of AOT micelles at smaller R from the temperature dependence of the vapor pressure, supporting our interpretation.

In this report, we propose a possible interpretation based on the model appeared in the literatures(ref. 8-10), however, a few obvious facts to prove the properties of water in S_1 and S_2 have been obtained. We are trying to measure directly the heat of sorption of water vapour in the empty micelle(ref. 11).

We also found that the shape of the enthalpy curve depends on the kind of the solvents. For example, Fig.3 shows the enthalpy curve of AOT/chloroform solution. As it is known that the size of the reversed micelle depends on solvent(ref. 12), concomitantly, the properties and/or size of S_1 and S_2 phases are changed. In that case, the heat of mixing might be dependent on the kind of the solvent. In addition, we need to pay attention to the facts that the size of the reversed micelle become large with increase in R value(ref. 13), which causes conformational change(ref. 14) on the surfactant molecules accompanying the heat effect. The theoretical treatment will be carried out by considering these problems.

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