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Thermodynamic Study of Brij 35 in Aquo-Polyethylene Glycol Solvents

Leena Koshy and Animesh Kumar Rakshit*
Department of Chemistry, Faculty of Science, M. S. University of Baroda, Baroda 390002, India

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Synopsis. The critical micelle concentrations of Brij 35 in aquo PEG 200 solutions were determined by the iodine solubilization method at five different temperatures at various PEG percents. The thermodynamic quantities of micellization as well as the free energies of micellization at infinite dilution were computed and rationalized.

As a part of our interest on the thermodynamics of micellization of nonionic surfactant, Brij 35, in aqueous solution in the presence of various solutes, it was decided to study the effect of polyethylene glycol 200 (PEG 200) on the micellization process of this surfactant in water. Effect of sucrose[1] was studied earlier. PEG 200 is an oligomer and its effect on micellization of Brij 35 was expected to be more chemical than electrochemical in nature. We choose PEG 200 because a literature survey did not show any study with this oligomer. This paper deals with PEG 200 at concentration of 2 to 10% w/v. Due to the importance of nonionic surfactants in industry, e.g., detergency,[2] in the formation of microemulsion[3] which may be useful in tertiary oil recovery and so on, the importance of detailed knowledge of thermodynamics of micellization of nonionic surfactants in presence of other components has become topical. Though there are reasonably large number of studies of the nonionic surfactant Triton X100,[4,5] we have not found detailed systematic study of Brij 35 in literature. Therefore a systematic thermodynamic study of the effect of PEG 200 on the micellization of Brij 35 is reported here.

PEG 200 (Merck, India) was used without any further treatment. Brij 35 (BDH, England) was also used as received. Its chemical formula is $C_mH_{2m+1}(OCH_2CH_2)_nOH$ where m=12 and n=23 with molar mass 1198. Iodine (Sarabhai, India) was sublimed before use and water was doubly distilled from $KMnO_4$. The iodine solubilization method[1,6] was used for determining critical micelle concentration (cmc). The experimental procedure adopted was explained in an earlier publication.[1] There was always a possibility of PEG interacting with iodine and thereby affecting the result. Hence direct surface tension determination by the Wilhelmy plate method was done for a few systems in absence of iodine to determine the critical micelle concentration. The results were comparable with each other as can be seen from Table 1.

Table 1. Critical Micelle Concentration, cmc (μmol dm^{-3}) of Brij 35 in Various Aquo-PEG Solutions at Different Temperatures

Solvent (% PEG 200)	cmc at				
	30 °C	35 °C	40 °C	45 °C	50 °C
0.0	46	43	40	37	34
2.0	31	33(33)[a]	35	37(36)[a]	39
4.0	27	30	33	36	38
6.0	26	29(29)[a]	33	36	38
8.0	25	28	30	35	37
10.0	23	25	28	30	35

a) By direct surface tension determination by Wilhelmy plate method in absence of iodine.

In Table 1 the cmc in water as well as in 2,4,6,8, and 10% PEG 200-water solution at the experimental temperatures of 30,35,40,45, and 50 °C are reported. The maximum error in these values was estimated to be 1.0 μmol from at least three separate measurements and then the standard deviation of the mean was computed. In Fig. 1 we plot the variation of cmc (mole fraction scale) as a function of concentration of PEG at different temperatures. It seems that the effect of increase in temperature and that of increase in PEG amount is similar. It is well known that increase in temperature effects the three dimensional water matrix by breaking it. It seems that the addition of PEG has similar effect. When PEG is added to water, by virtue of its very presence, it breaks the water matrix and then interacts with water to form a different three dimensional structure. The variation of cmc seems to be dependent on the water structure to a very large extent and not to be so much on the water–PEG matrix. Formation of structured solvent should probably have increased the

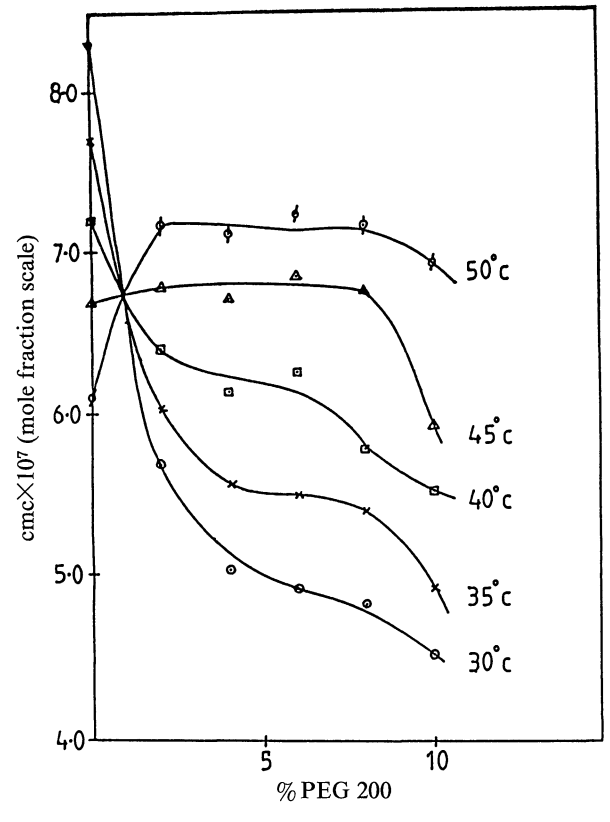

Fig. 1. Plot of cmc vs. % PEG 200 in aquo-PEG 200 solutions at various temperatures.

Table 2. Free Energy, Enthalpy, and Entropy of Micellization of Brij 35 in Aquo–PEG 200 Solutions

Solvent	ΔG_m/kJ mol^{-1}					ΔH_m/kJ mol^{-1}					ΔS_m/J mol^{-1} K^{-1}				
(% PEG)	30 °C	35 °C	40 °C	45 °C	50 °C	30 °C	35 °C	40 °C	45 °C	50 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.0	35.3	35.9	36.7	37.5	38.3	11.4	11.8	12.2	12.6	13.0	154	155	156	157	159
2.0	36.2	36.7	37.1	37.5	38.0	−8.8	−9.1	−9.4	−9.7	−10.1	90.4	89.3	88.4	87.4	86.5
4.0	36.5	36.9	37.2	37.6	38.0	−13.3	−13.7	−14.2	−14.6	−15.1	76.7	75.2	73.6	72.1	71.0
6.0	36.6	36.9	37.2	37.5	38.0	−14.9	−15.5	−15.9	−16.5	−17.0	71.5	69.6	67.7	66.2	64.9
8.0	36.6	36.9	37.4	37.6	38.0	−15.3	−15.8	−16.3	−16.8	−17.3	70.5	68.8	67.3	65.2	63.9
10.0	36.8	37.2	37.5	37.9	38.1	−15.9	−16.4	−16.9	−17.5	−18.0	69.1	67.4	65.7	64.2	62.0

cmc. Now in Table 1 we find that there is increase in the cmc values at 50 °C with the addition of PEG (2%). That is why we believe that the water–PEG structure has also some effect on cmc values. Two opposing effects are present in the system. These are (1) water structure break down and (2) water–PEG structured matrix formation. The cmc values depend on the effect of these two factors on micelle formation. The quantitative effect of each of these factors is difficult to estimate at this moment. From Fig. 1 it is observed that at about 1% PEG all cmc-concentration of PEG isotherms intersect. This fact indicates that probably at this concentration of PEG the processes of micellization of Brij 35 at all temperatures are similar.

In Table 2 the thermodynamic quantities calculated for these systems are given. The free energy, enthalpy, and entropy of micellization were computed by using the following well known relations

$$\Delta G_m = RT \ln(\text{cmc}),$$
$$\Delta H_m = -RT^2 \, d \ln(\text{cmc})/dT,$$
$$\Delta S_m = (\Delta H_m - \Delta G_m)/T,$$

where cmc was taken in mole fraction scale. The transfer process here means the formation of the micelle in the corresponding solvent from solvated free monomer surfactant whose mole fraction was unity. To calculate ΔH_m, ln(cmc) was plotted against T and a linear plot was obtained. The slope of the line was taken as $d \ln(\text{cmc})/dT$. This value was found to be positive for all PEG containing systems. Therefore the micellization process was exothermic for all of them. Only for pure aqueous solution the micellization was endothermic in nature. The maximum error in ΔG_m was estimated to be ±0.3%. The error in ΔH_m was ±3.0% which was determined from the standard deviation of the slope of ln(cmc)–T plot by regression analysis. The error in ΔS_m values was ±1.0%.

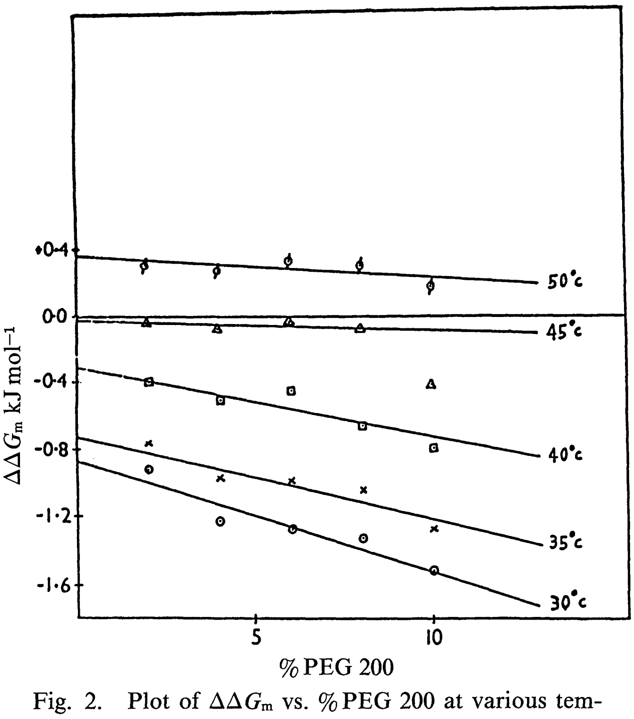

Fig. 2. Plot of $\Delta\Delta G_m$ vs. % PEG 200 at various temperatures.

From Table 2 we find that the ΔS_m is of the order of 70 J mol^{-1} K^{-1}. This type of high entropy change is generally associated with phase changes. Hence it can be assumed that the micelle behaves as a new phase here. It has also been suggested7) that the positive values of ΔS_m can be attributed to the increase in entropy due to water structure breakdown on micellization as well as due to release of water molecules associated with hydrocarbon chains8,9) which overshadows the decrease in entropy due to micelle formation. Shaw10) suggests that it might be due to the freedom of movement of the hydrocarbon chain in the core of the micelle.

It is possible to calculate $\Delta\Delta G_m$ for these systems. This quantity is the free energy of transfer of micelle from pure aqueous environment to PEG containing solution environment plus the medium effect i.e. the free energy of transfer of free monomer surfactant from water to the particular solvent. Pure solvent at atmospheric pressure was taken as the standard state. In Fig. 2 such $\Delta\Delta G_m$ is plotted against % PEG at all temperatures. It is observed that at the highest temperature of study i.e. at 50 °C these processes of transfer together is nonspontaneous one whereas at 45 °C the transfer free energy change is around zero. At other temperatures of 30, 35, and the 40 °C the Brij 35, in monomeric form and also as micelle, prefers the PEG containing solvent rather than the aqueous one (for example at 2% PEG Δcmc in comparison with aqueous solution at 30 °C is 15 units whereas at 50 °C it is −5 units, Table 1). Also

Table 3. $\Delta\Delta G_m$ and $\Delta G_m^{s,0}$ in Aquo–PEG Solvent Systems

Temperature/°C	$\lim_{c\to 0} \Delta\Delta G_m$ / kJ mol^{-1}	$\Delta G_m^{s,0}$ / kJ mol^{-1}
30	−0.87	−36.2
35	−0.73	−36.6
40	−0.32	−37.0
45	−0.03	−37.5
50	0.36	−37.9

this linear plot can be extrapolated to $c=0$ where c is the concentration of PEG. On can then write

$$\lim_{c\to 0} \Delta\Delta G_{\mathrm{m}} = \Delta G_{\mathrm{m}}^{\mathrm{s},0} - \Delta G_{\mathrm{m}}^{\mathrm{w}}$$

where s is solvent, w is water and 0 indicates that the solvent is infinitely diluted in terms of PEG. This quantity signifies whether the micelle prefers an infinitely dilute PEG containing aqueous environment to a purely aqueous surrounding or not.

The data so calculated for $\Delta G_{\mathrm{m}}^{\mathrm{s},0}$ range between −36.2 to −37.9 kJ mol^{-1} at between 30 and 50 °C respectively which are quite similar to that in a sucrose system[1] suggesting similar effect by these two solutes on overall water matrix.

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