Study of Reverse Micellization of Span 60 in Toluene

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Synopsis. Critical reverse micelle concentration (crmc) of Span 60 in toluene was determined by iodine solubilization method at 20, 25, 30, and 35 °C. The corresponding thermodynamic quantities of reverse micellization process were computed and are discussed.

Nonionic surfactants are sometimes known to form reverse micelles in organic media. One of the suggested methods for the determination of reverse critical micelle concentration (crmc) is the iodine solubilization method.[1] This method has been found to be applicable in both aqueous and in nonaqueous solutions.[2] Among nonionic surfactants micellization of Triton X100 and Brij 35 in presence and in absence of different additives in aqueous solutions has been well studied.[3,4] Reverse micellization of these surfactants in organic media has also been studied.[2] However we failed to find any reverse micellization data of Span 60 in toluene. Hence in continuation of our interest[4—6] in the thermodynamics of micellization, we present in this paper the various thermodynamic quantities associated with reverse micellization of Span 60 (Sorbitan monostearate) in toluene.

Span 60 (Koch light laboratories Ltd., England) was without any further purification. Toluene (Merck, India) was kept with 4 Å molecular sieves and was freshly distilled from that before use. Iodine (AR, Sarabhai Chemicals, India) was resublimed before use. A solution of iodine in toluene was made. This solution was used as solvent in this study. The transmittance of this solution was determined by Spectronic 20 at room temperature and was found to be 80%. The concentration of iodine was 10 mg per 100 ml. The λ_{max} of this solution was found to be 410 nm (Fig. 1). A known weight of Span 60 was then taken in a volumetric flask and a solution of it was made with iodine–toluene solution as solvent. This was the stock solution. The λ_{max} of this solution was at 435 nm (Fig. 1), with iodine solution as standard for 100% transmittance. The iodine-reverse micelle complex gives rise to this new λ_{max}.[2] All absorbance readings were taken at 435 nm. The dilute solutions of Span 60 were made in various volumetric flasks by taking different quantities of stock solution and then diluting with the solvent. Hence all solutions had same concentration of iodine but various amounts i.e. concentration of Span 60. These flasks with solutions were kept in a temperature controlled bath (±0.1 °C) for an hour with intermittant shaking. The absorbance of these solutions was then read at 435 nm. We appreciate the fact that at the moment the readings were noted, the solutions were not in the thermostatic bath. Hence the readings were taken in the shortest possible time and each reading was repeated at least three times to check on its reproducibility. We did not observe any discrepancy and hence believe that the values are proper at the particular temperature.

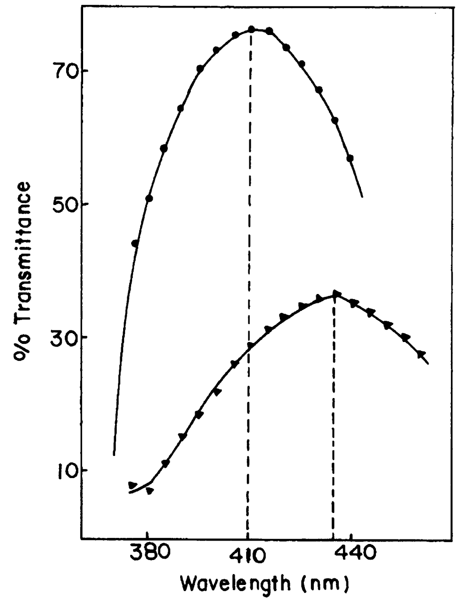

Fig. 1. Plot of % transmittance vs. wave length to determine λ_{max} of iodine toluene solution (▲ in presence and ● in absence of Span 60).

The absorbance values were then plotted against Span 60 concentration (Fig. 2) and break points in the plots, at all temperatures, were noted. These were taken as crmc of reverse micellization of Span 60 in toluene at corresponding temperatures. Iodine forms complex with reverse micelles. The higher the Span 60 concentration, more reverse micelles are formed and hence higher concentration of iodine-reverse micelle complex. This will increase the absorbance at 435 nm. Below crmc also such change in absorbance is noted though not to the extent as over crmc. This observation indicates that iodine has interaction with similar type of material over and below crmc. That is some type of reverse micelle formation occurs below crmc too.[2] In Table 1 the crmc s of Span 60 are tabulated at different experimental temperatures. The maximum error in these values was estimated to be less than 0.5%. The crmc values are not dependent on iodine concentration. Generally when dyes are used as spectroscopic probe, the reverse micelle structure gets effected by the size of

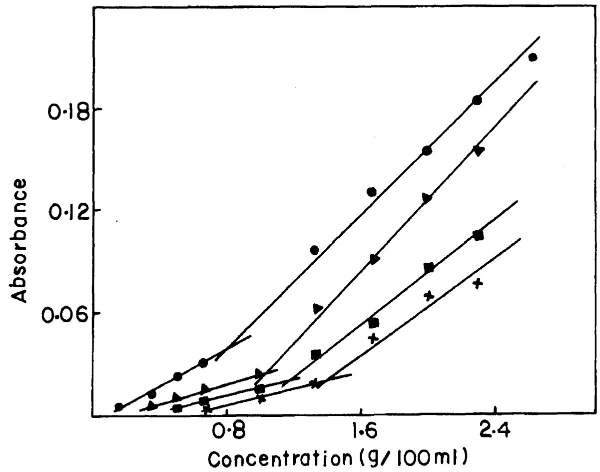

Fig. 2. Plot of absorbance vs concentration of Span 60 to determine critical reverse micelle concentration (●: 20 ; ▲: 25 ; ■: 30 ; and ×: 35 °C).

Table 1. Critical Reverse Micelle Concentration (crmc), Free Energy ($\Delta G^\circ_{\rm rm}$), Enthalpy ($\Delta H^\circ_{\rm rm}$), and Entropy ($\Delta S^\circ_{\rm rm}$) of Reverse Micellization of Span 60 in Toluene at Different Temperatures

Temperature	crmc	$-\Delta G^\circ_{\rm rm}$	$-\Delta H^\circ_{\rm rm}$	$-\Delta S^\circ_{\rm rm}$
°C	mmol dm^{-3}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
20	18.6	15.2	25.3	34.6
25	23.2	14.9	26.2	37.9
30	27.9	14.7	27.1	41.0
35	32.5	14.5	28.0	43.8

the probe. Hence all critical reverse micelle concentration data become suspect. Iodine is of small size and does not seem to effect the reverse micelle structure.[2] Moreover in our earlier studies[4—6] we reported critical micelle concentration (cmc) of various systems by iodine solubilization method as well as by direct surface tension measurement. The cmc values did not differ indicating no effect of concentration of iodine on cmc at least in this concentration of iodine.

The thermodynamic quantities calculated at different temperatures are presented in Table 1. The standard free energy, enthalpy and entropy of reverse micellization were calculated by the well known relations (valid for nonionic surfactants)

$$\Delta G^\circ_{\rm rm} = RT \ln ({\rm crmc})$$
$$\Delta H^\circ_{\rm rm} = -RT^2 \, d \ln ({\rm crmc})/dT$$
$$\Delta S^\circ_{\rm rm} = (\Delta H^\circ_{\rm rm} - \Delta G^\circ_{\rm rm})/T$$

where the reverse micelle concentration was in the mole fraction scale. The transfer process here indicates the formation of reverse micelle from the solvated free monomer surfactant whose mole fraction was unity. To calculate $\Delta H^\circ_{\rm rm}$, ln (crmc) was plotted against T. It was linear (corr. coeff. 0.996) and the slope was taken as $d \ln ({\rm crmc})/dT$. All thermodynamic quantities are negative. This shows that the process of reverse micellization is spontaneous, exothermic and associated with loss in degree of randomness.

The critical reverse micelle concentration (crmc) increases with temperature (Table 1). The increase in temperature increases the kinetic energy of the molecules forcing an increased state of motion. Therefore higher concentration of surfactants are required to bring the molecules sufficiently close for sufficiently long time to result in the reverse micelle formation. That is higher the temperature, higher the crmc. The crmc–T plot is also perfectly linear (corr. coeff. 0.996). A linear correlation is observed between enthalpy and entropy of reverse micellization. Such enthalpy–entropy compensation effect has been observed earlier in many physicochemical processes including micellization and monolayer formation.[4—8] The slope of this line was computed and was found to be 289 K. This indicates that at 289 K, the free energy of reverse micellization would be independent of entropic contribution. Hence we can conclude that the reverse micelle formation of Span 60 in toluene is enthalpy driven one.

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