ENTHALPIES AND HEAT CAPACITIES OF MICELLIZATION OF SOME SURFACTANTS IN AQUEOUS SOLUTIONS

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by
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C E R T I F I C A T E

This is to certify that the thesis entitled " ENTHALPIES AND HEAT CAPACITIES OF MICELLIZATION OF SOME SURFACTANTS IN AQUEOUS SOLUTIONS" being submitted by Mr.Pramod Kumar Singh to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Pramod Kumar Singh has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

I.I.T.,Delhi

May 6, 1983

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(PRAMOD KUMAR SINGH)

A B S T R A C T

The thesis describes the thermodynamic investigation of micelle formation by surfactants in water, both in absence and in presence of cosolutes. For this, ΔH_m and $\Delta C_{p,m}$ have been determined from calorimetrically measured differential enthalpies ($\bar{H}_2 - H_2^o$) and heat capacities ($\bar{C}_{p,2} - C_{p,2}^o$) above and below the critical micellization concentration (c.m.c.). The surfactants studied are sodium dodecylsulfate (SDDS), hexadecyltrimethylammonium bromide (HTAB), hexadecylpyridinium bromide monohydrate ($HPB.H_2O$), and hexadecylpyridinium chloride monohydrate ($HPC.H_2O$).

The ΔH_m data in water are at 298.15 and 308.15 K for SDDS, 308.15 and 318.15 K for HTAB and $HPB.H_2O$, and 298.15, 308.15, 318.15, and 328.15 K for $HPC.H_2O$, with $\Delta C_{p,m}$ being evaluated as the mean value over a 10 K interval from these data. ΔH_m and $\Delta C_{p,m}$ are both negative, and in good agreement with other published data when such a comparison is possible. The magnitudes of $\Delta C_{p,m}$ in absence of cosolutes indicate that the alkyl groups in the micelle core may retain hydration upto two to four CH_2 groups from the polar end. Data for SDDS in 3M (aq.) urea, and for HTAB, $HPB.H_2O$ and $HPC.H_2O$ in 2M (aq.) urea show that the sign of change for ΔH_m due to urea is temperature dependent, as is also the case with sign of

enthalpies of transfer from water to urea solutions for the monomers and the micelles. ΔH_m become more exothermic for SDDS and HPC.H_2O and less exothermic for HTAB and HPB.H_2O in the presence of urea. For SDDS, a large exothermic transfer to urea solution for the micelles has been atttibuted to the urea mediated counter ion binding to micelle. In urea solutions, the infinite dilution values of ($\bar{C}^{o}_{p,2} - C^{o}_{p,2}$) are less positive and $\Delta C_{p,m}$ are less negative but there is a small positive change for the micellar state ($\bar{C}_{p,2} - C^{o}_{p,2}$). This has been interpreted as the evidence of slight enhancement of core hydration in urea solutions. The ($\bar{H}_2 - H^{o}_2$) for HPB.H_2O in 2 M (aq.) dioxane as a function of molality (from infinite dilution upto concentrations above the c.m.c.) has been measured at 308.15 and 318.15 K. The ($\bar{H}_2 - H^{o}_2$) decreases rapidly without discontinuity near the c.m.c., but becomes nearly constant at higher concentrations. This indicates polydispersity of micelles relativeto water, ΔH_m is more exothermic, while $\Delta C_{p,m}$ is less negative in aqueous dioxane. The transfer from water to 2 M (aq.) dioxane for the micelles is much less endothermic than for the monomers. This may be due to the solubilized dioxane. The heat capacity of transfer for the micellar surfactant is large and positive, indicating increased hydration of core in the aqueous dioxane medium upto about eight $-CH_2-$ groups from the polar end. The heat capacity of transfer for monomers is negative, so that $\Delta C_{p,m}$ is much less negative in this medium than that in water. While the heat capacity data can be understood on the basis of the Frank-Evans model of structural effects of hydration, the alkyl-alkyl van der Waals interactions, the polar head group repulsion, and possible specific interactions together with the structural effects are required for a satisfactory understanding of the enthalpy data obtained in this study. Our findings for the hydration of micelle core, specially in the aqueous dioxane medium, also point out the need for a detailed examination of the model of micelles proposed by Menger.

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