

Thermodynamics studies of cetyltrimethylammonium bromide (CTAB) in N, N-dimethyl acetamide-water mixtures

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ABSTRACT

The variations of molar conductivity of Cetyltrimethyl ammonium bromide (CTAB) in mixtures of varying concentrations of N, N-dimethyl acetamide in water at constant temperature of 22 ± 0.2 °C were studied. The critical micelle concentration (CMC) for each surfactant is measured. It is found that the CMC values in mixtures of N, N-dimethyl acetamide and water solutions of various surfactants are lower than the CMC values in water, and the driving force for micelle formation correlates with solvophobicity. The surfactant-solvent interactions that drive amphiphilic self-organization in N, N-dimethyl acetamide in water are discussed. Thermodynamic parameters were evaluated for micellar system to explain the results.

Key words: N, N-dimethyl acetamide; Conductivity; Critical micelle concentration; hydrophobic interactions; Micelle

INTRODUCTION

Recently, micelle formation in non-aqueous solvents has attracted little attention as compared to the vast number of extensive studies that have been reported in the literature dealing with the formation of micelles in aqueous surfactant solutions. To differentiate them from "inverted" micelles which are formed in non-polar organic solvents, the term "solvophobic" has been applied by various researchers¹⁻³ to organic solvents, in analogy with the "hydrophobic interactions" causing micellization in aqueous media.

Hydrophobic interactions are important in maintaining conformation of proteins and various macromolecules. The free energies of the enthalpy changes actually unfavorable at low temperature, $\Delta H > 0$. It is generally believed that around the non-polar parts of the surfactants in contact with water there is an increased ordering of water molecules as the result of hydrogen bonding and that on the formation of the hydrophobic bond this order is

diminished, so there is a positive entropy change⁴⁻⁶. The micelles formed due to "solvophobic interaction" in polar non-aqueous solvents are similar in many respects to the micelles that are formed in aqueous media, although, in general, micelle formation is not as favored in non-aqueous solvents (of low dielectric constants) as in water for a given surfactant^{1,2,7}. In spite of the recognition of the importance of water structure in micelle formation in aqueous surfactant solutions, no significant attempt seems to have been made to investigate the role of the structure^{1,2,7-11} which may exist in many polar organic solvents due to the presence of one or more potential hydrogen bonding centers in their molecules.

The critical micelle concentration (CMC) of several salts of fatty acids and other long hydrocarbon chains terminating in a group capable of ionization in water has been studied by several workers, with hundreds of references in the literature, which cannot all be cited. However, important work¹²⁻¹⁵ on colloidal electrolytes is

relevant to the present work. Relatively fewer papers on solutions of surfactants in non-polar solvents have been published¹⁶⁻¹⁷. Almost no work has been done on the properties of sodium salts of fatty acids in polar solvents other than water. Recently some work has been done in this laboratory on micelle formation in molten acetamide¹⁸⁻¹⁹ which acts as good solvents for both ionic inorganic and covalent organic compounds¹⁹⁻²³.

In continuation of the work on micelle formation in non-aqueous solvents²⁴⁻²⁸, an effort has been made to study the effects of N,N-dimethyl acetamide on the CMC of aqueous solutions of Cetyltrimethyl ammonium bromide (CTAB) which fall into the soaps are studied. Some of the physical properties which determine the CMC are comparable for N,N-dimethyl acetamide and water. The dielectric constant of water is higher than that of N,N-dimethyl acetamide whereas the dipole moment of N, N-dimethyl acetamide is more than double that of water. Some of the physical properties of N, N-dimethyl acetamide and water are given in Table 1.

EXPERIMENTAL

N,N-dimethyl acetamide after drying for 72 hours on freshly ignited quick lime, was repeatedly vacuum distilled and the middle fraction of N,N-dimethyl acetamide having a specific conductivity (κ) in the range of $2 \times 10^{-6} \text{ S cm}^{-1}$ was collected²⁹⁻³⁰. Cetyltrimethyl ammonium bromide (CTAB) used in the present work was obtained from Fluka (purity > 99%), and was used without further purification. Specific conductivities of the solutions were measured at a constant temperature at $22.0 \pm 0.2^\circ\text{C}$ using a Crison model 255 Conductivity meter and a dipping cell with platinum electrodes (cell constant, 0.12cm^{-1}). The reproducibility of the instrument was

better than 0.2%. Doubly distilled deionized water of conductivity $1 \times 10^{-6} \text{ S cm}^{-1}$ was used throughout the work.

RESULTS AND DISCUSSION

Molar conductivities of Cetyltrimethyl ammonium bromide (CTAB) have been plotted against the concentrations of the Cetyltrimethyl ammonium bromide (CTAB) in N, N-dimethyl acetamide-water mixture of various concentrations. A drop in the molar conductivity is observed at a certain concentration. In order to find the CMC, tangents are drawn on the portions of the plots as described elsewhere¹⁸⁻¹⁹. The point of intersection of these gives the CMC³¹⁻³⁵ which are reported in Table 2.

It is observed that the CMC of N, N-dimethyl acetamide-water mixture is lower than the CMC of CTAB in water. Similar behavior has been observed by some workers for aqueous solutions of some surfactants³⁶⁻³⁸. It is also evident from Fig.1 that the CMC of CTAB decreases as the concentration of N, N-dimethyl acetamide in water increases, suggesting that such a mixture will have a higher dielectric constant than water because of the presence of N, N-dimethyl acetamide. It can be generalized that the CMC values of CTAB in N, N-dimethyl acetamide-water mixtures are lower than the CMC values of these CTAB in pure N, N-dimethyl acetamide. In this respect, N,N-dimethyl acetamide behaves as normal alcohols¹⁶. Similar effects have been observed by the addition of a hydrocarbon, which lowers the CMC. This is opposite to the behavior of dioxane and urea, which have small and complex effects. At higher concentration they markedly increase CMC or even inhibit micelle formation^{16,20}.

Table 1: Physical properties of N,N-dimethyl acetamide and water

Properties	N, N-dimethyl acetamide	Water
Dipole moment	3.72 D	1.87 D
Dielectric constant	37.78 (25°C)	78.45 (25°C)
Surface tension	32.43 dyn cm ⁻¹ (30°C)	62.60 dyn cm ⁻¹ (80°C)
Viscosity	2.141 cp (20.4°C)	0.3547 cp (80°C)
Specific conductance	$2 \times 10^{-6} \text{ S cm}^{-1}$ (25°C)	$10^{-6} \text{ S cm}^{-1}$ (25°C)

It could be suggested that the addition of N,N-dimethyl acetamide to aqueous solutions of Cetyltrimethyl ammonium bromide (CTAB) perturbs the interface of surfactant micellar solutions by intercalation of the N, N-dimethyl acetamide into the head group region and opening up the head group region to stronger water interaction. The intensity of this effect depends on the concentration of N, N-dimethyl acetamide in the N, N-dimethyl acetamide-water mixture.

Although the dielectric constant of water and N,N-dimethyl acetamide mixtures have not been determined, one can say that such mixtures will have lower dielectric constants than water because of the presence of N,N-dimethyl acetamide, since the dielectric constant partly governs the ionization of surfactants and thus helps

in the formation of micelles.

The result shown in Fig. 1 permits the calculation of standard free energies of micellization, ΔG_m° , for Cetyltrimethyl ammonium bromide (CTAB) in N, N-dimethyl acetamide-water mixtures. The ΔG_m° values are calculated using the relationship

$$\Delta G_m^\circ = -RT \ln \text{CMC}$$

Even though the size of the micelle is not known at present. Also, the low CMC values in N,N-dimethyl acetamide may invalidate the use of the above mentioned equation because the monomer activity would be similar to the monomer concentration. Such ΔG values should therefore, be taken only as an approximation. The results for CTAB in NMA are mentioned in Table 3.

Table 2: The CMC values of CTAB in mixtures of various concentrations in N, N-dimethyl acetamide in water mixtures at different temperatures

Conc. of N, N-dimethyl acetamide in water (M)	CMC (x 10 ⁻⁴ M)			
	295 K	300 K	305 K	308 K
0.00	1.66	1.71	1.75	1.79
0.25	1.62	1.68	1.72	1.76
0.50	1.58	1.64	1.68	1.72
0.75	1.54	1.60	1.64	1.68
1.00	1.50	1.58	1.62	1.64
1.25	1.47	1.55	1.59	1.62
1.50	1.44	1.51	1.56	1.58
1.75	1.40	1.48	1.52	1.54
2.00	1.35	1.44	1.48	1.50

Table 3: Thermodynamic parameters of CTAB in N,N-dimethyl acetamide-water mixtures of various concentrations

Concentration (M)	ΔG° (kJ/mole)	ΔH° (kJ/mole)	ΔS° (J/mol.K)
0.00	-21.35	-0.511	70.63
0.25	-21.41	-0.560	70.67
0.50	-21.47	-0.574	70.83
0.75	-21.53	-0.588	70.99
1.00	-21.60	-0.615	71.12
1.25	-21.64	-0.662	71.13
1.50	-21.70	-0.652	71.33
1.75	-21.76	-0.657	71.55
2.00	-21.85	-0.724	61.63

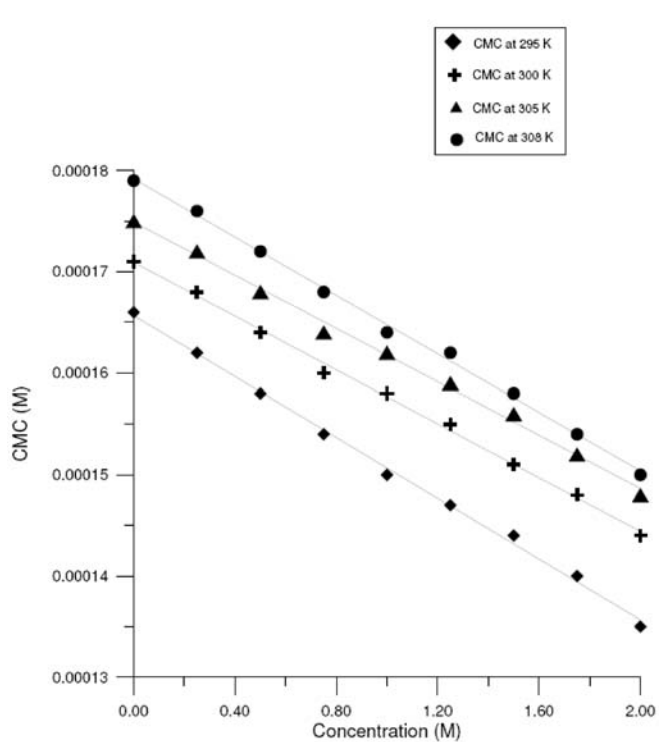


Fig. 1

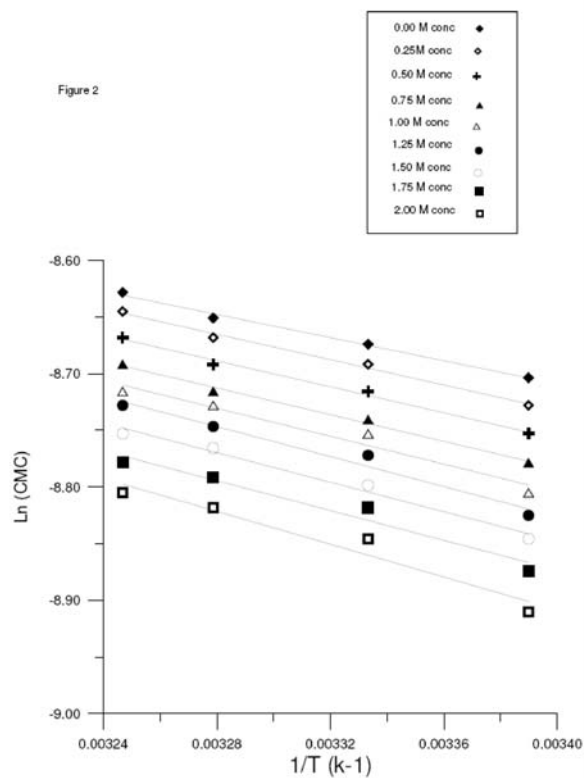


Fig. 2

Table 3 shows a decrease in Gibbs energy in N, N-dimethyl acetamide-water mixtures of various concentrations. It suggests that a strong solvophobic interaction takes place for longer alkyl chain in N, N-dimethyl acetamide-water mixtures of various concentrations.

The CMC values of Cetyltrimethyl ammonium bromide (CTAB) in N,N-dimethyl acetamide-water mixtures of various concentrations at different temperatures are reported in Table 2 as shown in fig.2. The plot in \ln CMC of CTAB against $1/T$ gives a good straight line with a negative slope. This shows that the micelle size does not change within the temperature range studied. In the present work the van's Hoff equation $d \ln(\text{CMC})/dt = \Delta H^\circ / RT^2$, is applicable. The value of ΔH° , enthalpy of

micellization, has been calculated from the slope of the line and are included in Table 3.

These values are in the range of the hydrogen bond energy. N,N-dimethyl acetamide has a strong tendency to form hydrogen bonding³⁸⁻⁴⁰. The standard entropies of micellization were calculated from the values of ΔH°_m and ΔG°_m using $\Delta G = \Delta H^\circ_m - T\Delta S^\circ_m$ and are also included in Table 3.

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