

수용액상 계면활성제의 임계 미셀 농도에 대한 N-methyl acetamide의 영향

Sadeq M. Alawi* and M. Salim Akhter

Department of Chemistry, University of Bahrain, P.O.Box 32038, Kingdom of Bahrain
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Effect of N-Methyl Acetamide on the Critical Micelle Concentration of Aqueous Solutions of Some Surfactants

Sadeq M. Alawi* and M. Salim Akhter

Department of Chemistry, University of Bahrain, P.O.Box 32038, Kingdom of Bahrain
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요 약. 다양한 농도의 N-methyl acetamide 수용액에서 계면 활성제의 농도에 따른 계면활성제들 (sodium caprylate, sodium laurate, sodium palmitate, sodium stearate, sodium oleate, sodium dodecyl sulphate, lithium dodecyl sulphate)의 몰 전도도 변화를 30±0.2 °C의 일정온도에서 연구하였다. 각각의 계면활성제에 대한 임계 미셀 농도 (CMC)를 측정하였다. 수용액에 N-methyl acetamide이 공존할 때에는 여러 계면 활성제의 CMC 값이 수용액에서의 CMC 값보다 더 낮고, 미셀 형성에 대한 추진력은 소용매성과 관련되었다. N-methyl acetamide 수용액에서 양쪽성 자기-조직화를 추진하는 계면활성제-용매의 상호작용에 대해 논의하였다. 이 결과들을 설명하기 위하여 미셀 시스템에 대한 열역학적 매개변수들을 추정하였다.

주제어: N-methyl acetamide, 전도도, 임계 미셀 농도, 소수성 상호작용, 미셀

ABSTRACT. The variations of molar conductivity of various surfactants such as sodium caprylate, sodium laurate, sodium palmitate, sodium stearate, sodium oleate, sodium dodecyl sulphate, and lithium dodecyl sulphate with concentrations of the surfactants for each of the solutions consisting of mixtures of varying concentrations of N-methyl acetamide in water at constant temperature of 30±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-methyl 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-methyl acetamide in water are discussed. Thermodynamic parameters were evaluated for micellar system to explain the results.

Keywords: N-methyl 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 surfactants 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, analogous to 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 are 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 change.⁴⁻⁶ 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 which may exist in many polar organic solvents due to the presence of one or more potential hydrogen bonding centers in their molecules.^{1,2,7-11}

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 researchers, with hundreds of references in the literature, which cannot all be cited. However, important work on colloidal electrolytes is relevant to the present work.¹²⁻¹⁵ Relatively fewer papers on solutions of surfactants in non-polar solvents have been published.¹⁶ 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 acetamide which acts as a good solvent for both ionic inorganic and covalent organic compounds.¹⁷⁻²³

In continuation of our work on micelle formation in non-aqueous solvents, an effort has been made to study the effects of N-methyl acetamide on the CMC of aqueous solutions of sodium salts of saturated fatty acids which fall into the soaps are investigated.²⁴⁻²⁸ In this work it has also been investigated to find out how the CMC values compare with those of saturated fatty acid soaps, especially with respect to unsaturated fatty acid soaps and other type of surfactants like sodium dodecyl sulphate and lithium

dodecyl sulphate. Some of the physical properties which determine the CMC are comparable for N-methyl acetamide and water. The dielectric constant of water is lower than that of N-methyl acetamide whereas the dipole moment of N-methyl acetamide is more than double that of water. In this laboratory the CMC of several surfactants in N-methyl acetamide has been determined by the conductivity method. Some of the physical properties of N-methyl acetamide and water are given in *Table 1*.

EXPERIMENTAL

N-methyl acetamide (NMA), after drying for 72 hours on freshly ignited quick lime, was repeatedly vacuum distilled and the middle fraction of NMA having a specific conductivity (k) in the range of 2×10^{-6} S cm^{-1} was collected.^{24,25} All the surfactants used in the present work were obtained from Fluka (purity > 99%), and were used without further purification. Specific conductivities of the solutions were measured at a constant temperature at 30.0 ± 0.2 °C using a Crison model 255 Conductivity meter and a dipping cell with platinum electrodes (cell constant, 0.12 cm^{-1}). The reproducibility of the instrument was better than 0.2%. Doubly distilled deionized water of conductivity 1×10^{-6} S cm^{-1} was used throughout the work.

RESULTS AND DISCUSSION

Molar conductivities of surfactants have been plotted against the concentrations of the surfactants. For each of the surfactants a drop in the molar conductivity is observed at a certain concentration. In order to find the CMC, tan-

Table 1. A comparison of some of the physical properties of N-methyl acetamide and water

Properties	N-methyl acetamide	Water
Dipole moment	4.39 D	1.87 D
Dielectric constant	191.3 (32°C)	78.45 (25°C)
Surface tension	33.67 dyn cm^{-1} (30°C)	62.60 dyn cm^{-1} (80°C)
Viscosity	3.23 cp (35°C)	0.3547 cp (80°C)
Specific Conductance	2×10^{-7} S cm^{-1} (40°C)	10^{-6} S cm^{-1} (25°C)

Table 2. The CMC values of NaDS, LiDS, NaO, NaS, NaPalm, NaL, NaCap, for various concentrations of N-methyl acetamide in water at 30 ± 0.2 °C

Conc. Of acetamide in water (M)	CMC (10^{-3} M)						
	NaDS (12) ^b	LiDS (12)	NaO (17) ^c	NaS (17)	Na Palm (15)	NaL (11)	Na Cap (7)
0.00 ^a	7.0	7.8	1.8	1.0	1.7	2.4	3.2
0.25	6.8	7.6	1.6	0.7	1.5	2.0	2.7
0.50	6.6	7.3	1.4	0.6	1.2	1.6	2.2
0.75	6.4	7.0	1.3	0.7	1.1	1.3	1.9
1.00	6.1	6.8	1.1	0.8	0.9	1.0	1.4
1.25	5.9	6.3	0.7	0.6	0.6	0.7	1.2
1.50	5.6	5.8	0.5	0.4	0.4	0.4	0.9
1.75	5.2	5.3	0.3	0.2	0.2	0.3	0.5
2.00	4.9	5.0	0.2	0.1	0.1	0.3	0.4

^aNaDS, sodium dodecyl sulphate; LiDS, lithium dodecyl sulphate; NaO, sodium oleate; NaS, sodium stearate; Na Palm, sodium palmitate; NaL, sodium laurate; NaCap, sodium caprylate.

^bNumber of Carbons in alkyl chain.

^cWith a double bond.

gents are drawn on the portions of the plots as described elsewhere.^{17,18} The point of intersection of these gives the CMC³¹⁻³⁵ which are reported in *Table 2*.

It is observed that the CMC of surfactants in N-methyl acetamide-water mixture is lower than the CMC of surfactants in water.¹²⁻¹⁴ *Fig. 1* shows the plot of log cmc of Sodium Caprylate, Sodium Laurate, Sodium Palmitate and Sodium Stearate against the number of carbon atoms in the alkyl chain in the surfactants. A straight line is obtained showing that as the number of carbon atoms in the alkyl chain increases the CMC decreases. Similar behavior has been observed by some researchers for aqueous solutions of some surfactants.³⁶⁻³⁹ It is also evident from *Fig. 1* that the CMC of the surfactant decreases as the concentration of N-methyl acetamide in water increases, suggesting that such a mixture will have higher a dielectric constant than water because of the presence of N-methyl acetamide. It can be concluded that the CMC values of sodium salts of saturated fatty acids, sodium salts of unsaturated fatty acids, lithium dodecyl sulphate and sodium dodecyl sulphate in N-methyl acetamide-water mixtures are lower than the CMC values of these surfactants in pure N-methyl acetamide. In this respect, N-methyl acetamide behaves like normal alcohols.¹⁶ 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}

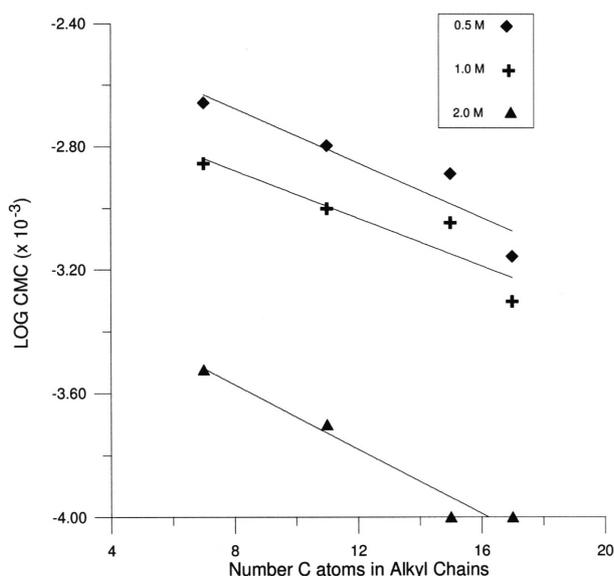


Fig. 1. Plot of log cmc of surfactants against the number of carbon atoms in the alkyl chain of the surfactants at various concentration of N-methyl acetamide in the mixtures at 30 ± 0.2 °C.

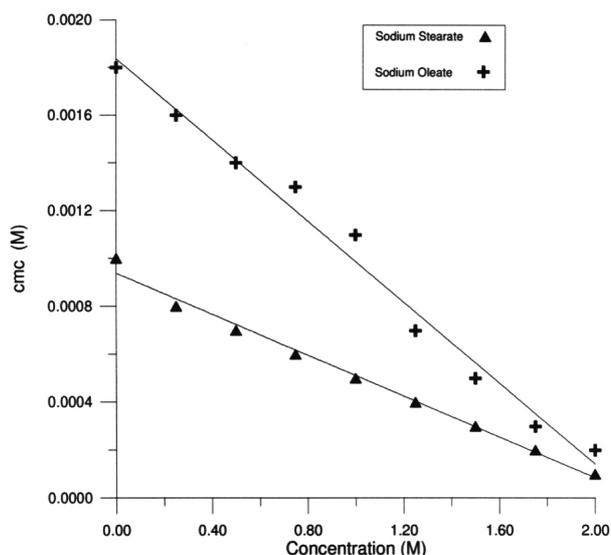


Fig. 2. Plot of cmc of sodium oleate and sodium stearate in N-methyl acetamide-water mixtures against the concentration of N-methyl acetamide in aqueous solutions at 30 ± 0.2 °C.

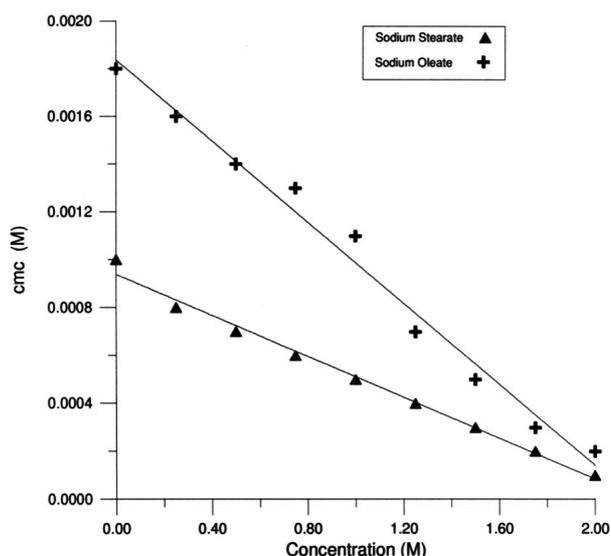


Fig. 3. Plot of cmc of sodium dodecyl sulphate and lithium dodecyl sulphate in N-methyl acetamide-water mixtures against the concentration of N-methyl acetamide in aqueous solutions at 30 ± 0.2 °C.

It may be pointed out that there is a general trend that the CMC of surfactants decreases constantly with increase in the concentration of N-methyl acetamide as shown in *Figs. 2-4*. It could be suggested that the addition of N-methyl acetamide to aqueous solutions of various surfactants perturbs the interface of surfactant micellar solutions by intercalation of the N-methyl acetamide into the head group region and opening up the head group region to stronger water interaction. The intensity of this effect

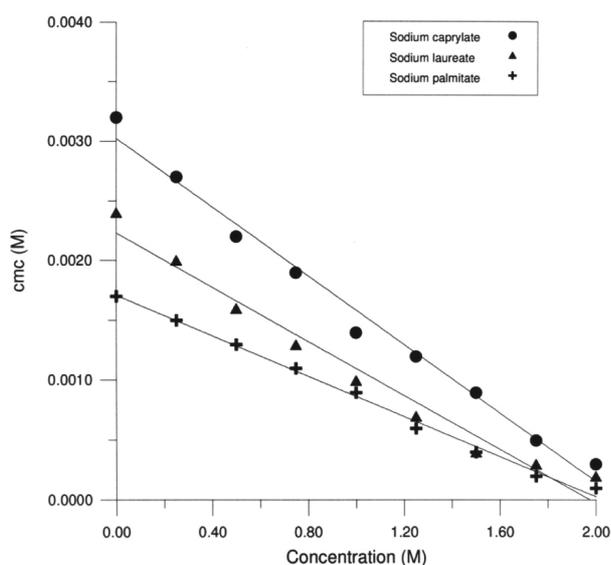


Fig. 4. Plot of cmc of sodium caprylate, sodium laureate and sodium palmitate in N-methyl acetamide-water mixtures against the concentration of N-methyl acetamide in aqueous solutions at 30 ± 0.2 °C.

depends on the concentration of N-methyl acetamide in the acetamide-water mixture.

It is observed from *Table 2* that the CMC of sodium oleate, which has a double bond, is higher than that for sodium stearate in N-methyl acetamide-water mixtures. Both surfactants have eighteen carbon atoms. A similar behavior has been observed for these two surfactants in aqueous solutions by other workers.³⁵ The introduction of a double bond in a surfactant leads to increased CMC in comparison with the corresponding surfactants without double bonds as shown in *Fig. 2*.

LiDS have a higher CMC than NaDS in acetamide-water mixtures as shown in *Fig. 3*. It appears that the CMC of alkali dodecyl sulphates increases with decreasing counter ion atomic number. Various researchers have reported that the increasing ionic radius of the alkali metal ions causes a decrease in the CMC. The smaller the hydrated radii, the greater will be the action on charged groups of the micelle and the greater the lowering of the CMC.³⁶⁻³⁸

Although the dielectric constant of water and N-methyl 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-methyl acetamide, since the dielectric constant partly governs the ionization of surfactants and thus helps in the formation of micelles.

To elucidate more clearly the effect of N-methyl acetamide on the CMC of aqueous solution of surfactants

(NaDS, LiDS, NaO, NaS, NaPalm, NaL and NaCap), the ratio (β) of the number of counterion to that of the surfactant ion in micelles in varying concentrations of N-methyl acetamide-water mixtures is determined.

The ratio (β) is calculated from the slopes of pre-micellar region to post-micellar region. The values are used for the free energy change for the micellization (ΔG_m°) and for the enthalpy of micellization (ΔH_m°).

The result shown in *Fig. 1* permits the calculation of standard free energies of micellization, ΔG_m° , for various surfactants in N-methyl acetamide-water mixtures. The ΔG_m° values are calculated using the relationship.

$$\Delta G_m^\circ = (1+\beta) RT \ln \text{CMC}$$

even though the size of the micelle is not known at present. Also, the low CMC values in N-methyl acetamide may invalidate the use of the above mentioned equation because the monomer activity would be quite different from the monomer concentration. Such DG values should, therefore, be taken only as an approximation.³⁹ The results for various surfactants in NMA are mentioned in *Table 3*.

Table 3 shows a decrease in Gibbs energy as the number of carbon atoms in alkyl chain of various surfactant increases. It suggests that a strong solvophobic interaction takes place for longer alkyl chains of Sodium surfactants in N-methylacetamide-water mixtures.

The decrease in the effect of ΔG_m° may be explained by saying that N-methyl acetamide behaves as a co-solvent with water. N-methyl acetamide may reduce the hydration of micelle surface through hydrogen bonding with water hydrated to micelle surface, and increase the repulsive force between ionic head groups because of the increase of the charge density of micelle surfaces. Therefore, the ratio of counter ion binding to micelles in N-methyl acetamide-water mixtures is important in the calculation of thermodynamic parameters.

The CMC values of NaDS, LiDS, NaO, NaS, NaPalm, NaL and NaCap, in N-methyl acetamide-water mixture at different temperatures were determined. The plot of $\ln \text{CMC}$ of four surfactants 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 modified form of van's Hoff equation, is applicable. The value of ΔH_m° , enthalpy of micellization, has been calculated from the slope of the line and is included in *Table 3*.

These values are in the range of the hydrogen bond energy. N-methyl acetamide has a strong tendency to form hydrogen bonding. Negative values of ΔH_m° were obtained

Table 3. Values of thermodynamic parameters (ΔG_m^o , ΔH_m^o (kJ mol⁻¹), ΔS_m^o (JK⁻¹) for NaDS, LiDS, NaO, NaS, Na Palm, NaL and NaCap in N-methyl acetamide-water mixture of various concentrations

Conc. of N-methyl acetamide in water (M)	NaDS			LiDS			NaO			NaS			Na Palm			NaL			NaCap		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
0.00	12.1	72.4	200	11.9	84.0	238	15.5	96.0	266	18.9	111	304	16.2	56.7	134	15.4	38.3	75.6	14.6	35.5	69.0
0.25	12.3	71.7	196	12.2	82.4	232	15.8	94.2	259	19.2	106	286	16.4	50.5	127	15.7	38.0	73.6	15.0	35.0	66
0.50	12.5	71.0	193	12.3	81.6	229	16.1	93.6	256	19.4	101	269	16.9	54.2	123	16.3	37.2	69	15.6	34.2	61
0.75	12.7	70.7	191	12.5	81.0	226	16.6	91.6	248	19.8	98.0	258	17.2	53.4	120	16.7	36.8	66	15.9	33.7	59
1.00	12.9	70.2	189	12.6	80.6	224	17.4	89.8	239	20.1	95	247	17.4	52.8	117	17.6	36.0	61	16.2	33.0	55
1.25	13.1	69.8	187	12.8	80.2	222	17.9	89.0	235	20.5	93	239	18.0	51.4	110	18.0	35.0	56	16.6	32.0	51
1.50	13.3	69.6	186	13.0	79.6	220	18.7	88.0	229	20.9	91	231	18.2	51.0	108	18.4	34.0	52	17.1	31.0	46
1.75	13.5	69.2	184	13.2	79.0	217	20.4	86.4	218	21.4	90	226	18.8	50.0	103	18.6	33.0	48	17.7	30.0	41
2.00	13.8	68.7	181	13.5	78.0	213	23.4	85.2	204	24.1	88	211	19.8	48.4	94	19.0	31.0	40	18.8	29.0	34

- ΔG_m^o , Standard Gibbs energy of micellization.

- ΔH_m^o , Standard Enthalpy of micellization.

- ΔS_m^o , Standard Entropy of micellization.

from the micelle formation of the surfactant tetradecyl-trimethyl-ammonium bromide (C₁₄ TAB) in water and hydrazine.⁴⁰ The standard entropies of micellization were calculated from the values of ΔH_m^o and ΔG_m^o using $\Delta G_m^o = \Delta H_m^o - T\Delta S_m^o$ and are also included in Table 3.

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