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FORMATION OF MICELLES OF CETYLTRIMETHYLAMMONIUM BROMIDE IN WATER-GLYCEROL SOLUTIONS

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ABSTRACT

The micellization of cetyltrimethylammonium bromide (CTAB), in glycerol and aqueous solutions of glycerol was studied by means of surface tensiometry. The critical micellar concentration (CMC) was determined at 25 °C and 40 °C and thermodynamic parameters such as the free energy of micellization (ΔG^o_{mic}), enthalpy (ΔH^o_{mic}) and entropy (ΔS^o_{mic}) of micellization were also measured. At 40 °C, CTAB forms micelles in pure glycerol and in the entire range of water-glycerol solutions. For 25 °C, the CMC ranged from 9.2×10^{-4} M in pure water to 8.5×10^{-3M} for solutions containing 90% glycerol by volume. The corresponding values obtained for ΔG^o_{mic} were -4.14 and -2.82 kcal/mole; for ΔH^o_{mic} were -1.03 kcal/mole and -3.73 kcal/mole and for ΔS^o_{mic} were +10.43 and -3.10 e.u. Addition of glycerol decreases the spontaneity of micelles formation of CTAB in water.

RESUMO:

O processo de micelização do brometo de cetiltrimetilamônio (CTAB) em glicerol e soluções aquosas de glicerol foi estudado por métodos de tensiometria superficial. A concentração micelar crítica (CMC) foi determinada a 25 °C e 40 °C e parâmetros termodinâmicos tais como a energia livre (ΔG^o_{mic}) de micelização, entalpia (ΔH^o_{mic}) e entropia (ΔS^o_{mic}) de micelização também foram medidos. A uma temperatura de 40 °C, CTAB forma micelas em glicerol puro e na faixa inteira de soluções aquosas de glicerol. Para 25 °C, a CMC variou de $9{,}2 \times 10^{-4}$ M em água pura até $8{,}50 \times 10^{-3}$ M para soluções aquosas contendo 90% de glicerol por volume. Os valores correspondentes obtidos para ΔG^o_{mic} foram -4,14 kcal/mole e -2,82 kcal/mole; com ΔH^o_{mic} = -1,03 kcal/mole e -3,73 kcal/mole e com ΔS^o_{mic} = +10,43 e -3,10 e.u., respectivamente. A adição de glicerol diminuiu a espontaneidade do processo de micelização de CTAB em água.

KEYWORDS: Micellization, Cetyltrimethylammonium Bromide (CTAB), Critical Micellar Concentration, Glycerol, Water-Glycerol Solutions.

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INTRODUCTION

As a part of our systematic study of the process of micellization in non-aqueous solvents and water solutions containing various cosolvent or additives[1-16], we have also investigated the formation of micelles of the surfactant cetyltrimethylammonium bromide (CTAB) in pure glycerol and water solutions containing glycerol.

The subject of the effect of cosolvents on micelle formation has been originally treated by Ray and Nemethy[17-19] and has been reviewed in the literature[11,20];

Glycerol and ethylene glycol form intra- and intermolecular hydrogen bonds. Experimental studies involving various techniques, including NMR, for aqueous solutions of glycerol and ethylene glycol have shown the existence of intra- and intermolecular hydrogen bonding and have indicated that the hydrogen bonds between either one of the two and water are stronger than those among themselves[21-23].

Both have been employed in protein conformation studies and as simple membrane simulators. Being dense liquids, they approximate portion of membranes in terms of their anhydrous environment. Glycerol has been used as a viscous agent in the construction of media close to the intracellular environment during the investigation of the allosteric enzyme glycogen phospharylase b[24]. Reactivation effects by glycerol and ethylene glycol of inactivated δ-aminolevulinic acid synthetase were reported. It was indicated that the protein conformation around the pyridoxal 5'-phosphate binding site of synthetase was stabilized by the two polyprotic alcohols[25].

EXPERIMENTAL PROCEDURE

The glycerol used was analytical reagent grade supplied by Merck do Brasil S.A., Rio de Janeiro. It was employed without any additional treatment or purification. Cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}N^+(CH_3)_3\ Br^-$ (CTAB), was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin, USA. It was recrystallized twice from ethyl alcohol and dried under vacuum for two days. Deionized distilled water was used for the preparation of all the solutions.

All solutions were prepared volumetrically at the following percentages by volume of glycerol: 0.00; 10.0; 20.0; 30.0; 40.0; 50.0; 60.0; 70.0; 80.0; 90.0 and 100%. All of them containing at least fifteen different concentrations of CTAB. The surface tension of the water-CTAB-glycerol solutions was measured at 25 °C, 40 °C and sometimes 32 °C by means of a Fisher Model 21, Semi-Automatic Tensiometer. Ten milliliters aliquots of the solutions were placed in a Petri dish with a diameter of 6 cm. The temperature of the solutions was brought to the chosen temperature using a water bath and the Petri dish was kept at the desired temperature by placing it in a container through which water was circulated from the constant temperature bath. The tensiometer was set a constant height. The final surface tension of any solution was the average of at least three independent measurements.

The critical micellar concentrations (CMC's) were determined from plots of the concentration of the surface tension of the solutions versus the concentration or the logarithm of the concentration of CTAB. The marked change in the plots was taken as an indication of micelle formation and the inflection point was considered to correspond to the CMC.

The thermodynamic parameters ΔG°_{mic}, ΔH°_{mic} and ΔS°_{mic} were determined using standard equations[26,27] derived on the basis of the assumption that the process of micellization involves the formation of a distinct micellar phase at the CMC and that the concentration of monomers in solution is constant, once micelles are formed. The experimental accuracy in the values determined for ΔG°_{mic} is about ± 100 cal/mole. On the other hand, ΔH°_{mic} and ΔS°_{mic} are more approximate since they were calculated on the basis of measurements at two or three temperatures only.

RESULTS AND DISCUSSION

Some typical experimental results obtained for the surface tension of CTAB in water-glycerol solutions at 25 °C are illustrated in Figure 1.

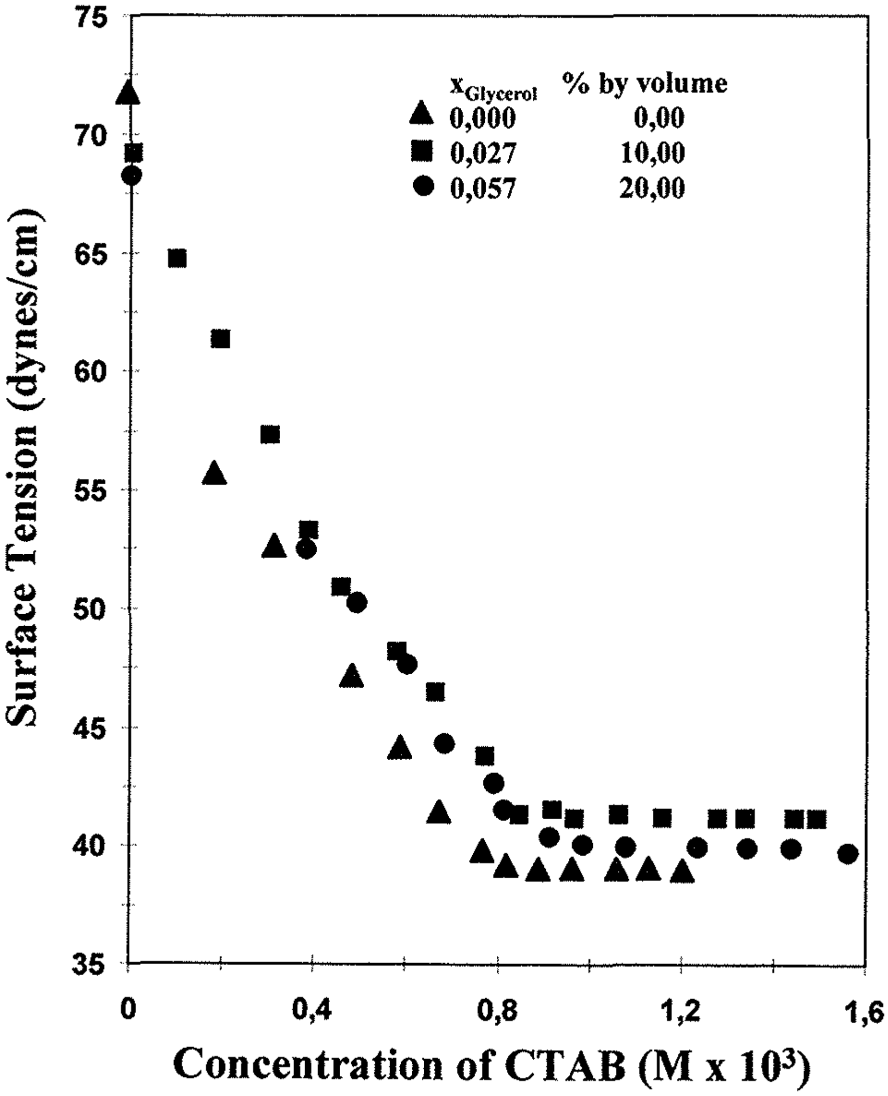

Figure 1. Plot of Surface Tension versus Concentration of Cetyltrymethylammonium Bromide (CTAB) for the Water-CTAB-Glycerol System at 25 °C.

All plots of surface tension versus the concentration of CTAB exhibited initial marked drops and subsequent leveled off. The inflection point in the given curve was taken as the CMC. At times, plots of surface tension versus the logarithm of the concentration of surfactant gave a better determination for the CMC. Results similar to those of Figure 1 were obtained for the entire range of water-glycerol solutions at 25 °C, 32 °C and 40 °C. A summary of the CMC's determined is given in Table I.

Table I. Critical Micellar Concentration (CMC) of Cetyltrimethylammonium Bromide (CTAB) in Aqueous Solutions of Glycerol

Percent of Glycerol by Volume (% vol.)	Mole Fraction of Glycerol (x_G)	CMC at 25 °C ($M \times 10^3$)	CMC at 40 °C ($M \times 10^3$)
0.00	0.000	0,92	1.00
10.0	0.027	0,98	1.15
20.0	0.057	1.10	1.25
30.0	0.095	1.23	1.45
40.0	0.142	1.50	1.90
50.0	0.197	1.90	2.50
60.0	0.270	2.50	3.70
70.0	0.366	3.50	5.20
80.0	0.498	6.00	8.50
90.0	0.687	8.50	11.50
100.0	1.000	*	18.00

* Surfactant precipitates.

The dependence of the critical micellar concentration of CTAB on the percent by volume and the mole fraction of glycerol at two temperatures is given in Figures 2 and 3, respectively.

The experimental values obtained for the thermodynamic functions, i.e., the standard free energy of micellization, ΔG^{o}_{mic}, the enthalpy, ΔH^{o}_{mic} and the standard entropy of micellization, ΔS^{o}_{mic}, at 25 °C and 40 °C are given in Tables II and III. The results obtained at 25 °C are also illustrated in Figure 4.

The experimental results shown in Table I and Figure 2 indicate that the critical micellar concentration (CMC) increases with the rise in temperature. However, a strict thermodynamic analysis (Tables II and III) shows that the free energy of micellization is more negative at 40 °C, indicating that micelle formation is somewhat more favored by the slight increase in temperature. The critical micellar concentration is known to frequently depend on temperature, but in many cases the dependence is highly irregular. The nature of this effect is hard to predict because it depends on a series of factors related to the restructuring of water and the interactions between water and the surfactant. For example, in the case of N-alkylbetaines in water (C_{10} and C_{11}) the CMC decreases, reaches a minimum and then increases as a function of temperatures and for N-alkylbetaines (C_{12}) the CMC increases as a function of temperature[28,29]. For the case

Water-CTAB-Glycerol system interactions between water and glycerol and the surfactant must also be taken in consideration.

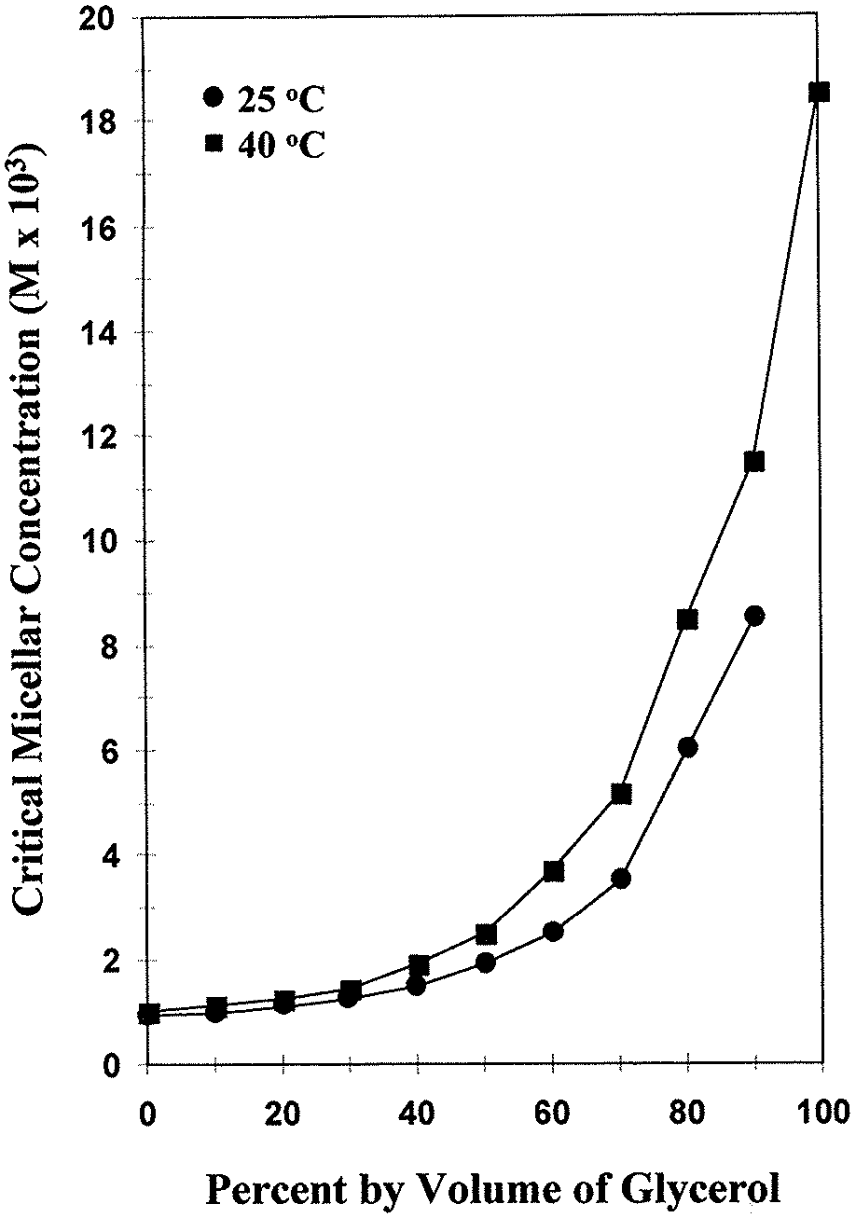

Figure 2. Dependence of the Critical Micellar Concentration of Cetyltrymethylammonium Bromide (CTAB) on the Percent by Volume of Glycerol for the Water-CTAB-Glycerol System.

The thermodynamic parameters shown in Tables II and III do not sort out the different types of interactions (water-surfactant, water-glycerol and glycerol-surfactant) as they were determined using equations derived for the micellization process in water[11]. In a wider sense, without starting out water-cosolvent and surfactant-cosolvent interactions, the micellization process can be explained in terms of hydrophobic interactions and the break up of the water structure. Higher temperatures, on one hand, help disrupt the water structure, and on the other hand diminish hydrophobic interactions. At lower temperatures the effect is exactly the contrary. The net result is the balancing of two effects in the temperature range used.

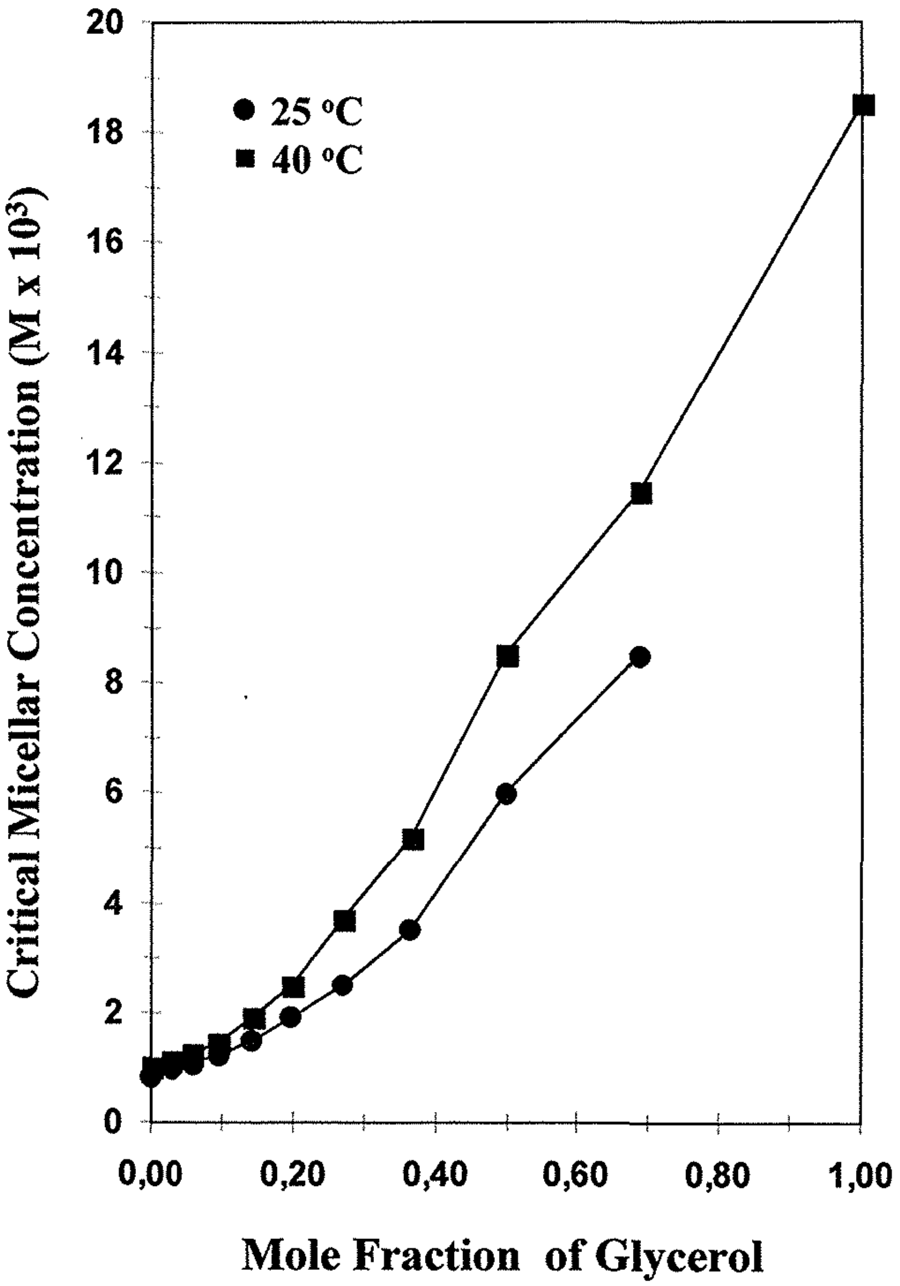

Figure 3. Dependence of the Critical Micellar Concentration of Cetyltrymethylammonium Bromide (CTAB) on the Mole Fraction of Glycerol for the Water-CTAB-Glycerol System.

Table II. Some Thermodynamic Properties for the Formation of Micelles of Cetyltrimethylammonium Bromide in Water-Glycerol Solutions at 25 °C.

Mole Fraction of Glycerol (x_G)	Free Energy of Micellization at 25 °C ΔG^o_{mic} (kcal/mole)	Enthalpy of Micellization ΔH^o_{mic} (kcal/mole)	Entropy of Micellization at 25 °C ΔS^o_{mic} (e.u.)
0.000	-4.14	-1.03	+10.43
0.027	-4.10	-1.97	+ 7.14
0.057	-4.04	-1.58	+ 8.25
0.095	-3.97	-2.03	+ 6.51
0.142	-3.85	-2.92	+ 3.12
0.197	-3.71	-3.39	+ 1.07
0.270	-3.55	-4.84	- 4.33
0.366	-3.35	-4.89	- 5.17
0.498	-3.03	-4.30	- 4.26
0.687	-2.82	-3.73	- 3.10
1.000	*	*	*

* Surfactant precipitates.

Table III. Some Thermodynamic Properties for the Formation of Micelles of Cetyltrimethylammonium Bromide in Water-Glycerol Solutions at 40 °C.

Mole Fraction of Glycerol (x_G)	Free Energy of Micellization at 40 °C ΔG^o_{mic} (kcal/mole)	Enthalpy of Micellization ΔH^o_{mic} (kcal/mole)	Entropy of Micellization at 40 °C ΔS^o_{mic} (e.u.)
0.000	-4.30	-1.03	+10.40
0.027	-4.21	-1.97	+ 7.15
0.057	-4.16	-1.58	+ 8.24
0.095	-4.07	-2.03	+ 6.51
0.142	-3.90	-2.92	+ 3.13
0.197	-3.73	-3.39	+ 1.09
0.270	-3.48	-4.84	- 4.34
0.366	-3.27	-4.89	- 5.17
0.498	-2.97	-4.30	- 4.25
0.687	-2.78	-3.73	- 3.03
1.000	-2.50	-	-

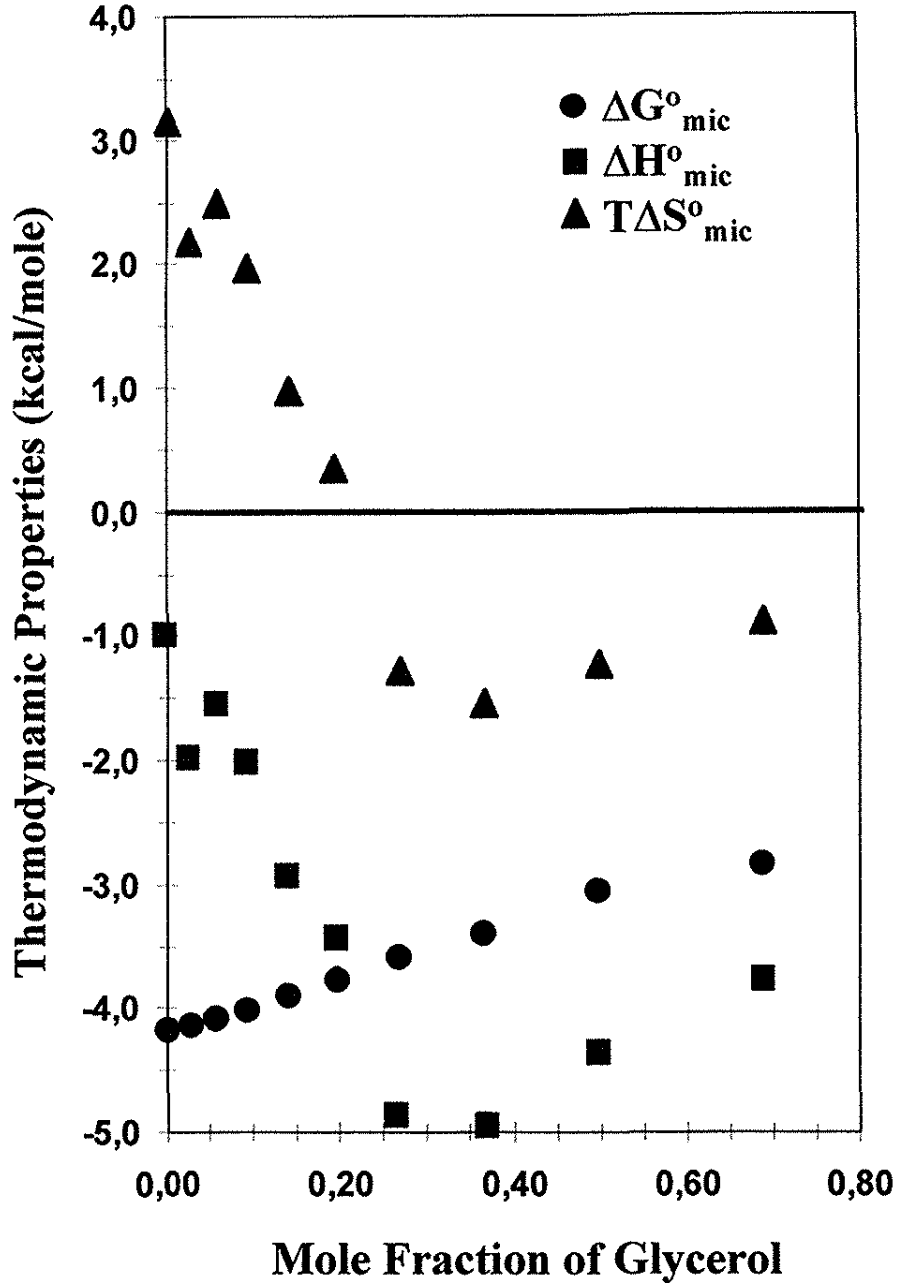

Figure 4. Plot of the Thermodynamic Properties as a Function of the Mole Fraction of Glycerol for the Water-CTAB-Glycerol Ternary System at 25 °C.

A careful analysis of the experimental results shows that at 40 °C the surfactant cetyltrimethylammonium bromide forms micelles in pure water, pure glycerol and the entire range of water-glycerol solutions. The free energy of micellization increases linearly from -4.30 kcal/mole (pure water) to -2.50 kcal/mole (pure glycerol), as can be seen in Table III. Attempts to determine CMC for CTAB in pure glycerol at 25 °C were not successful as the surfactant precipitates at a concentration higher than 14 x 10^{-3} M at this temperature. However, CTAB forms micelles in water-glycerol solutions at this temperature up to the case of solutions containing 90% by volume of glycerol.

As can be clearly noted in Figure 4 and in Tables II and III, the addition of glycerol to water solutions containing CTAB has an inhibitory effect on micelle formation. This inhibitory effect can be explained by interactions between water and glycerol due to hydrogen bonding that eventually decrease the "hydrophobic" or "solvophobic" forces of the medium. As previously mentioned, it is well known that both glycerol and ethylene glycol form hydrogen bonds with water and disrupt the water structure[21-23].

Study of glycerol-water solutions by surface tensiometric measurements also showed the presence of interactions between the two solvents. This interaction reaches a maximum at mole fraction of glycerol of 0.18 and results in an excess surface free energy of 7dynes/cm somewhat higher than the values measured for ethylene glycol and formamide, that are similar polar solvents[30-31].

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