CMC Determination and Thermodynamic Micellisation Of NPE Surfactant In Aqueous And $CH_3OH – H_2O$ Solvents

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Abstract:

The critical micelle concentration (CMC) of nonylphenolethoxylate (NPE) surfactant has been determined by measuring the surface tension as a function of the molar concentration of the surfactant in aqueous and binary mixture of water + methanol solutions at a temperature range from 20˚C to 35˚C. The interfacial parameters Γmax, A_{min}, Π_{cmc} and ΔG°_{ads} were calculated. The results indicate that the CMC increases as the temperature increases and that the addition of methanol the CMC decreases. The thermodynamic parameters such as standard Gibbs free energy (ΔG˚), enthalpy (ΔH˚), and entropy (ΔS˚) of micellization were estimated using the change of CMC with temperature. The enthalpy – entropy compensation behavior of the surfactant was evaluated and a good linearity in the compensation plot has been observed.

Key words: Thermodynamic Micellisation, $CH_3OH – H_2O$ Solvents

Introduction:

Critical micelle concentration (CMC) of a surfactant is defined as the optimum aqueous concentration of the surfactant at which micelles begin to form under a specific reaction condition. CMC of a surfactant is an extremely important parameter in view of its importance in determination and optimization of various characteristic properties of micelles such as micellar stability and binding affinity, binding constant of a solubilizate as well as surfactant use in facial cleansers, shampoo, and baby-care products [1].

Thermodynamic parameters that describe the hydrophobic interaction of different surfactant (ionic and nonionic) with water have been the subject of numerous studies. The CMC and thermodynamic functions ΔG°_m, ΔH°_m and ΔS°_m for the micellization process of two pyridinium cationic surfactants in aqueous solution were studied by a potentiometric method using surfactant cation sensitive membrane electrodes [2]. Micellization, surface activity and structures of the aggregates of nonionic surfactant n-octyl-ß-D-thioglucopyranoside in aqueous solutions through a temperature range have been investigated by using surface tension measurements [3]. The mixed micellization of 1, 2-bis (dodecyl dimethyl ammonium) ethane di-bromide and sodium lauryl ether sulfate has been investigated using a surface and electrical conductometry apparatus [4]. The effect of some organic additives such as glucose, phenol, caffine, urea and formamide on the CMC of an anionic surfactant sodium dodecyl sulfate has been studied by conductance measurements [5]. The CMC for aqueous solution of C_{10},C_{12},C_{14} and C_{16}triphenylphosphonium bromide and thermodynamic

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parameters ΔG°_{m} , ΔH°_{m} , ΔS°_{m} were estimated using conductivity data[6].

In the present work, we have investigated the CMC and thermodynamics of micellization of nonylphenolethoxylate (NPE) surfactant by surface tension method in aqueous binary mixture water + methanol solution and at temperature range between (20-35) ˚C.

Materials and methods:

The nonylphenolethoxlate (NPE) surfactant of the highest purity commercially available were obtained from the state company of vegetables oil and used as received. It's a chemical formula $\mathbf{C_{35}H_{46}O_{11}}$ and molecular mass 660 g mol$^{-1.}$

Anhydrous methyl alcohol was analytical purity. The mother surfactant solutions were prepared by weight and stored at room temperature until use. The CMC were determined by surface tension. They were performed using Du-Nony type tensiometer with Pt ring. It was derived from the break points in the plots of surface tension versus molar concentrating.

Results and Discussion:

The surface tension of NPE solution was measured as a function of surfactant concentration at various temperatures. The plots of surface tension versus the concentration of surfactant at different temperatures were presented in Figure (1).

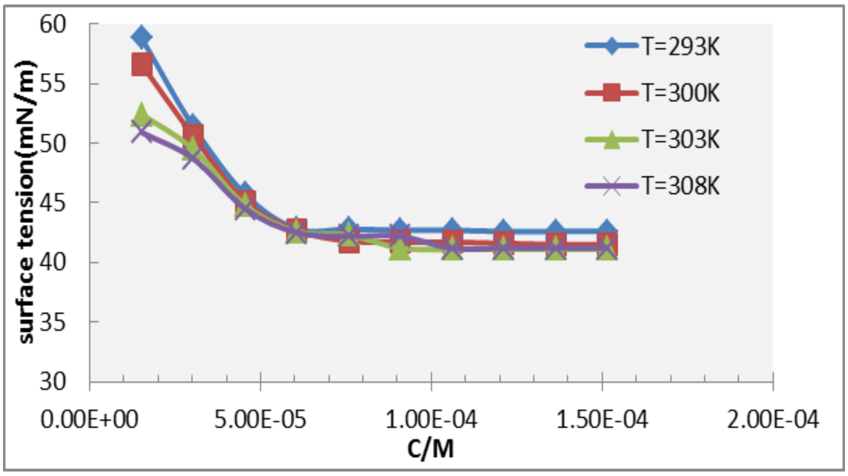

Fig (1):The variation of surface tension versus molar Concentration.

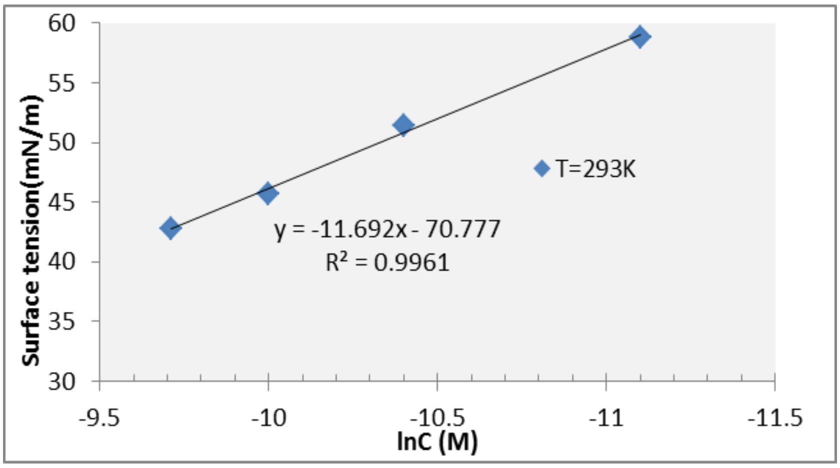

Fig (2):Typical plot of surface tension versus lnC at 293K.

The sharp breakpoint shown in the plots of Figure (1) which corresponded to the CMC value at each temperature are listed in Table (1) along with their respective maximum surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}), surface pressure at the CMC (Π_{cmc}) and standard free energy of adsorption ($\Delta G°_{ads}$) values.

The maximum surface excess concentration and the minimum area per molecule were computed from the surface tension plots using the following relations:

$$\Gamma\,\max = -\frac{(\partial\gamma/\ln C)CMC}{RT} \text{-------}(1)$$

$$Amin = \frac{1}{NA\,\Gamma max} \text{-------}\ (2)$$

Where N_A is Avogadro number and ($\partial\gamma / \partial \ln c$) is determined from the slope of the plot of γ versus lnC which are illustrated in Figure (2) as a typical form .The surface pressure at the CMC, Π_{cmc} ,was obtained from the relationship:

$$\Pi_{cmc} = \gamma - \gamma_{cmc} \text{ -----}\ (3)$$

Where γ and γ_{CMC} are surface tensions of the solvent and of the micellar solution at the CMC respectively .The standard free energy of adsorption, ΔG°_{ads}, was determined using the equation:

$$\Delta G_{ads.} = \Delta\mathring{G}m - \frac{\pi CMC}{\Gamma max} \text{ -------}\ (4)$$

Where $\Delta\mathring{G}_m$ is standard free energy of micelle formation

Table (1): surface Excess concentration (Γ_{max}), minimum area per molecule (Amin), surface pressure at the CMC (Π_{cmc}), and Gibbs Energy of adsorption (ΔG°_{ads}) for NPE at different temperatures.

T (K)	CMC (M)	Π_{cmc} (mN/m)	Γ_{Max} *10^3 (mmol/m^2)	A_{min} (A^2/molecule)	-G$^{\circ}_{ads}$Δ (KJ/mol)
293	6.06×10^{-5}	42.94	3.99	41.59	22.68
298	7.58×10^{-5}	42.01	3.812	43.56	22.42
303	9.09×10^{-5}	41.73	3.39	48.98	21.19
308	10.60×10^{-5}	40.88	2.85	58.26	19.36

The data in Table (1) indicate that in the temperature range studied the CMC of surfactant increases as the temperature increased. This may be due to the fact that the surfactants molecules dissolved in water; the hydrophobic group distorts the water structure. The increase in temperature also causes the increase in breakdown of the structured water surrounding the hydrophobic group, which disfavors micellization [7]. Also, it can be seen from Table (1) that ΔG°_{ads} values are negative and became less negative as temperature increases which indicate that the adsorption of the surfactant in the air-liquid interface occurs spontaneously and becomes less spontaneous at higher temperatures.

The temperature dependence of the CMC of the surfactact has been used to obtain the thermodynamic parameters of micellization. The standard free energy of micelle formation ΔG°_m in the case of nonionic surfactant was calculated by the equation :

$$\Delta G^{\circ}_m = RT \ln X_{CMC} \text{ -------}\ (5)$$

Where X_{CMC} is the mole fraction of surfactant at the CMC. The enthalpy of micellization ΔH°_m was obtained by applying the Gibbs-Helmholtz equation to the equation above :-

$$\Delta H^{\circ}_m = - RT^2\ (\partial \ln X_{CMC} / \partial T) \text{ ----}(6)$$

ΔH°_m was evaluated from the slope of the plot of lnXcmc versus temperature, Figure (4). The entropy of micellization process ΔS°_{m} was estimated from the equation:-

$\Delta G^{\circ}_{m} = \Delta H^{\circ}_{m} - T\Delta S^{\circ}_{m}$ -----(7)

ΔG°_{m}, ΔH°_{m} and ΔS°_{m} that have been obtained by applying the above equations for the NPE surfactant are reported in Table (2).

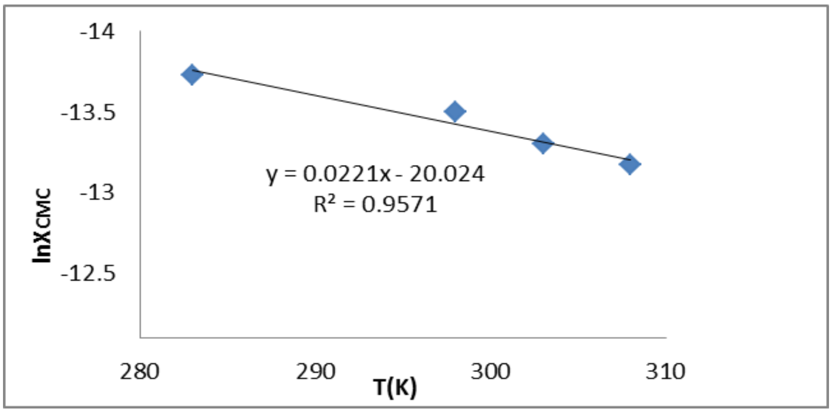

Fig (3): The plot of lnX$_{CMC}$ versus temperature

Table (2): Thermodynamic parameter of micellization for NPE at different temperatures .

T (K)	- ΔG°_{m} (KJ/mol)	-ΔH°_{m} (KJ/mol)	ΔS°_{m} ($JK^{-1}mol^{-1}$)
293	33.44	15.77	17.68
298	33.44	16.32	17.13
303	33.50	16.87	16.63
308	33.72	17.43	16.29

From the results presented in Table (2), it can be generalized that the free energy ΔG°_{m} is negative in the whole temperature range studied which indicates that the micellization process is spontaneous. ΔH°_{m} is negative and increased as temperature increased which indicates that the micellization is exothermic. The entropy of micellization ΔS°_{m} is positive in all temperature range and decreases with increase in temperature. This is due to the fact that the head group is more hydrated than the hydrophobic tail with increasing temperature which leads to an overall ordering of the system hence, the lowering of the entropy with increase in temperature [6].

Several chemical processes exhibit a linear relation between ΔH°_{m} and ΔS°_{m}, and shown for the present surfactant in Figure (4).

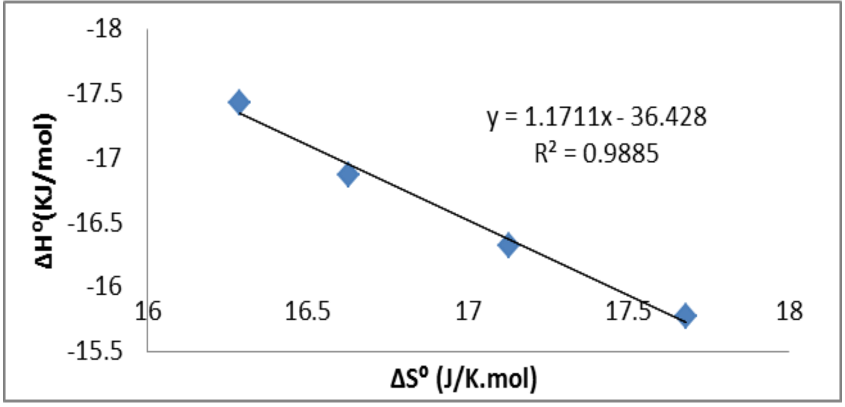

Fig (4).The enthalpy – entropy compensation

This phenomenon is known as enthalpy-entropy compensation [8], and a good linearity ($R^2 = 0.9885$) in the compensation plot has been observed.

Water- methanol mixed media

Figure (5) shows a representative plot of the surface tension of the NPE solution of 15% methanol against the ln [NPE] at 293 and 303 K.The CMC of the surfactant solution was estimated from the break point in the surface tension plots and recorded in Table (1).

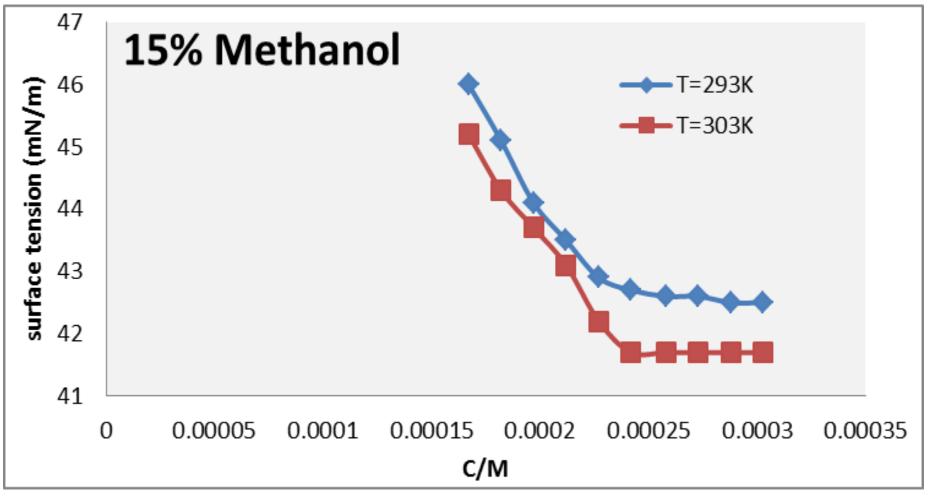

Fig (5). The variation of surface tension with concentration in binary mixture

It was observed that the CMC of the surfactant in the mixed solvent (15% methanol) increased as compared with aqueous solvent. This indicates that the addition of methanol, which act as water structure breakers, decrease the hydrophobic effect resulting into an increase in the CMC of the surfactant [9]. Breaking of water structure by organic solvents would facilitate interactions between the hydrophobic tail of the surfactant molecules and the hydrophobic part of organic solvent molecules by hydrophobic part of organic solvent that would lead to delaying the aggregation of the surfactant monomers form micelles and hence the increase in the CMC of the surfactant. The estimated values of Γ_{max}, A_{min}, Π_{max} and ΔG°_{ads} for the NPE solution for the mixed media are recorded in Table (3).

Table (3): surface Excess concentration (Γ_{max}), minimum area per molecule (Amin), surface pressure at the CMC (Π_{max}), and Gibbs Energy of adsorption (ΔG°_{ads}) for NPE in 15% methanol .

T/K	Π_{max} (mN/m)	Γ_{Max} $*10^3$ (mmol/m^2)	A_{min} (A^2/molecule)	$-\Delta G^{\circ}_{ads}$ (KJ/mol)
293	0.322	2.4	6.92	43.63
303	0.295	2.5	6.64	42.79

The thermodynamic parameters of micellization that we have obtained by applying the same procedure as aqueous solution are reported in Table (4).

Table (4):The thermodynamic parameters of micellization for NPE in 15% methanol.

T/K	CMC(M)	$-\Delta G^{\circ}_{mic}$ (KJ/mol)	ΔG°_{trans}
293	0.000227	30.21	3.236
303	0.000242	30.99	2.51

It is possible to evaluate the effect of the co-solvent on the micelle aggregation process by means of free energy of transfer, $\Delta G^{\circ}_{trans,}$ which is defined by [10]:

$$\mathbf{\Delta G^{\circ}_{trans} = (\Delta G^{\circ}_{m})_{CH3OH-H2O} - (\Delta G^{\circ}_{m})_{H2O}} \text{ -------- } \mathbf{(8)}$$

ΔG°_{trans} estimated are listed in Table (4). The positive values of ΔG°_{trans} can be understood on the basis of a reduction in the solvophobic interaction caused by the improved solvation, which leads to an increase in the solubility of the hydrocarbon tails in the presence of organic solvent and consequently in an increase in the CMC[11].

Conclusions:

It can be concluded the followings:

1-From the surface tension measurements, we have obtained the CMC of NPE solution and surface properties of the surfactant between 20 and 35 °C.

2-The adsorption data in the air-liquid interface showed that the adsorption of the surfactant occurs spontaneously and becomes more spontaneous at higher temperatures.

3-In the investigated systems we found that the enthalpy–entropy compensation operates and a good linearity has been observed.

4-The thermodynamic parameters of micellization, ΔG^{o}_{m}, ΔH^{o}_{m}, and ΔS^{o}_{m} were calculated and indicate that the micellization process is spontaneous and exothermic in nature.

4- The study of the effect of CH_3OH content on the CMC shows that the micellization process is less favorable in the methanol - water mixture. This effect has been ascribed to the structure-breaking ability of CH_3OH.

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ايجاد تركيز المسيل الحرج وثرموداينمك عملية تكوين المسيل للمادة الفعالة سطحيا Nonyl Phenol Ethoxylate في المذيب المائي ومزيج ماء وميثانول.

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الخلاصة:

تم ايجاد تركيز المسيل الحرج (CMC) للمادة الفعالة سطحيا NonylphenolEthoxylate من خلال قياس الشد السطحي كدالة للتركيز المولاري في محيط مائي وفي مزيج ثنائي من الماء والميثانول في مدى من درجات الحرارة تراوحت بين 20 و35°م. كما تم حساب بعض الدوال السطحية مثل Γ_{max} و A_{min} $\prod_{cmc}$ وΔG°_{ads} لهذا النظام. ودلت النتائج التي تم الحصول عليها بأن CMC تزداد بزيادة درجة الحرارة بينما تقل عند أضافة كمية محدودة من الميثانول الى المحيط المائي . وتم استخدام تغير CMC مع درجة الحرارة في حساب الدوال الثرموديناميكية ΔG°_m ΔH°_m وΔS°_m لعملية تكوين المسيل ،ولوحظ كذلك أن تاثير التعويض بين ΔH° و ΔS° سارياً.