Adsorption Properties of Mixed Surfactant for Nonyl phenol Ethoxylate and Dehyquarte E-CA in Aqueous System at Liquid – Air Interface

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Abstract

The micellization for an aqueous binary mixed system of Nonyl Phenol Ethoxylate (NPE) and Dehyquarte E-CA (DE-CA) were studied by means of surface tension measurement. The surface tension was measured for the solutions of the single and five mixed systems at 25°C in order to determine critical micellization concentrations (CMC), surface excesses (Γ), and the surface area occupied by a molecule (A_m) as a function of mole fraction of (NPE). The CMC's values obtained decrease with increasing mole fraction of NPE in the mixture, and the synergism was observed at 0.9 mole fraction. Based on the regular solution theory, the compositions of the micellar phase (X_1^m) and the interaction parameter in micelles (β^m) were calculated, and the result obtained at a low mole fraction indicates a mutual electrostatic repulsion between the surfactant molecules in the micelles, but at high mole fraction an attraction have been observed. The synergism in surface tension reduction was examined by minimum surface free energy (G_{min}^{s}). The CMC-X_2 curve showed a negative deviation from ideal mixing.

Keywords: micellization, mixed surfactants, synergism in surface tension reduction, surface excess, minimum molecular area.

الصفات الامتزازية لمزيج المحلول المائي للمواد الفعالة سطحيا Nonyl Phenol Ethoxylate و Dehyquarte E−CA على السطح البيني سائل – هواء

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الخلاصة

تم في هذا البحث دراسة عملية تكوين الميسل للمحلول المائي لمزيج ثنائي للمادتين الفعالتين سطحيا Nonyl Phenol Ethoxylate و Dehyquarte E−CA باستخدام قياسات الشد السطحي. قيست بدقة قيم الشد السطحي لمحاليل المواد الفعالة قيد الدرس منفردة ولخمسة مزيجات عند درجة حرارة 25°C ، لغرض ايجاد التركيز الحرج لتكوين الميسل (CMC) وتركيز المادة الفعالة على السطح (Γ) ومعدل المساحة السطحية التي تشغلها الجزيئة (A_m) كدالة للكسر المولي للمادة الفعالة سطحيا NPE . وكانت قيم CMC التي تم الحصول عليها تقل مع زيادة الكسر المولي للمادة الفعالة سطحيا NPE وتم الحصول على التآثر التازري (synergism) عند الكسر المولي 0.9. تم حساب قيم الكسر المولي داخل الميسل (X_1^m) وقيم التآثر داخل الميسل (β^m) اعتمادا على نظرية Regular solution . ودلت النتائج التي حصلنا عليها عند الكسور المولية القليلة على وجود تنافر الكتروستاتيكي متبادل بين جزيئات المواد الفعالة سطحيا في داخل الميسل، ولكن لوحظ ان التآثر اصبح تنافرا عند الكسور المولية العالية. كما تم تقييم التآثر التازري لاختزال الشد

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السطحي من خلال حساب الطاقة الحرة الدنيا على السطح (G^{s}_{min}). ومن رسم منحي الطور بين CMC ضد X_2 نرى بوضوح الانحراف السالب عن قيم المزيج المثالي.

1- Introduction

In practical applications, surfactants are used in mixed systems to obtain some desired performance. So, mixed systems of different combinations have been studied extensively to develop better functions or to make clear the nature of synergistic effects [1, 2].

Surface tension study on binary mixed systems of anionic/nonionic surfactants was performed by using precise tensiometer. In this study, the synergistically in the surface activity and the relationship among compositions of monomers in bulk, micelles, and adsorbed film at air/water interface were discussed in detail [3].Micelle formation of a combination of hydrocarbon/fluorocarbon anionic surfactants, sodium n-tetradecylsulfate and sodium perfluorononate in water, was studied paying an attention to the interaction between the two surfactants and the aggregation number, as a function of composition in the mixture. The micellar composition and interaction parameter were estimated on the basis of Rubingh"s equations [4].

Jeong-Soo K. et al. [5] used three combinations of a typical anionic surfactant, sodium dodecylsulfate with n-alkyl (octyl, nonyl and decyl)-N-methylglucamides and they marked synergistic phenomena in surface activity as well as in micellization, suggesting that these combination have a strong intermolecular interaction particularly between head groups. Katarzyna S. and Bronislaw J. [6] studied the interaction of ternary surfactant system (cetyltrimethylammonium bromide [CTAB] + Triton X-100 + Triton X-165) at the water – air interface. They found that the best synergetic effect in the surface tension reduction was determined on the basis of the values of the molecular interaction parameter for aqueous solutions of ternary mixtures of CTAB + Triton X-165. Soheila J. et al. [7] used the conductometry and surface tension techniques to investigate adsorption behavior and micellar properties of the mixed binary ionic/nonionic surfactants CTAB and Triton X-100 in aqueous mixture of ethylene glycol. It was suggests that the surface activity of CTAB or Triton X-100 and their mixtures decreases with the increase in the amount of ethylene glycol in aqueous media. Lu et al. [8] studied the micellar evolution in mixed nonionic/anionic surfactant systems using a range of techniques such as surface tensiometry. Katarzyna S. et al. [9] studied the influence of CTAB and Triton X-100 on their adsorption at the water-air interface. The area of particular surfactants in the mixed saturated monolayer changes as a function of Triton X-100 and CTAB mixture concentrations close to critical micellization concentrations (CMC) or higher the area occupied by both surfactants is the same.

The aim of this paper is to elucidate aqueous and surface properties of mixtures of Nonyl Phenol Ethoxylate (NPE) and Dehyquarte E-CA (DE-CA) using surface tension measurements in order to determine synergism in micellization and surface tension reduction at the air/water interface.

2-Experimental

Chemicals:

Nonyl Phenol Ethoxylate (NPE) as nonionic surfactant and Dehyquarte E-CA (DE-CA) as cationic surfactant were supplied by the state company of plant oils – ministry of industry and minerals – Iraq, and used as received. NPE has an empirical formula $C_{35}H_{64}O_{11}$ and molecular mass 660gmol^{-1}. DE-CA has IUPAC name (2-hydroxyethyl-(2-hydroxyhexadecyl) dimethylazanium chlorides, empirical formula $C_{20}H_{44}NO_2Cl$, and molecular mass 365gmol^{-1}. The structures of these surfactants are shown in figure -1.

(a) **(b)**

Figure 1- The structure of (a) DE-CA and (b) NPE surfactants.

Measurements:

The surface tension of the aqueous solutions of each surfactant and mixed surfactants solution were made by Du Noey technique tensiometer, model DST 30 M, Surface and Electro Optics (SEO) Company- Korea, with platinum ring. Measurements were taken until constant surface tension values indicated that equilibrium had been reached.

3-Results and discussion

The CMC was determined as the concentration at the intersection of the lines from the plots of surface tension–logarithm molar concentration. Figure -2 shows the curves of surface tension (γ) against logarithm concentration for the single systems of NPE and DE-CA at 25 °C, and those for three mixed systems at different mole fractions of NPE(X_2) in the surfactant mixture. (Curves for other mixtures at mole fractions of 0.5 and 0.7 are not shown in order to avoid overcrowding).

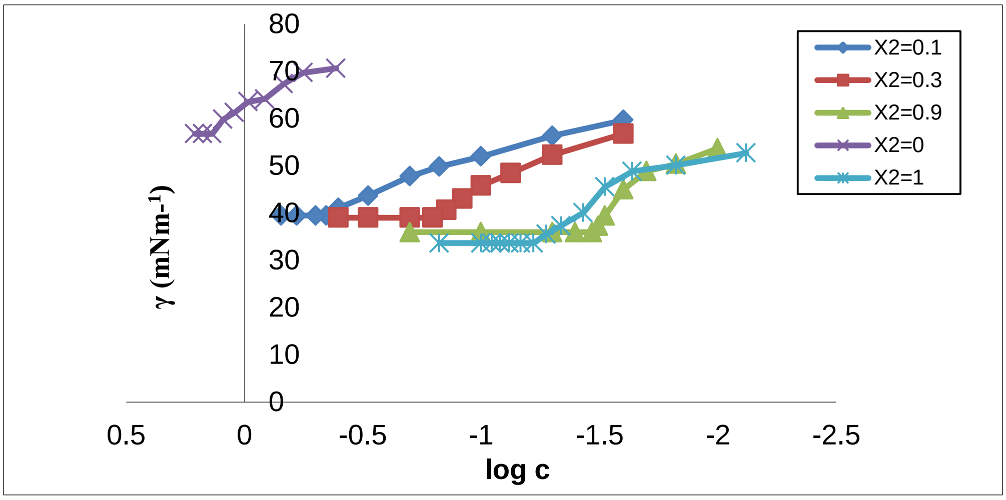

Figure 2- Plots of surface tension vs logarithm molar concentration for NPE, DE-CA and their mixtures at 25 °C.

The figure demonstrates that DE-CA has a higher CMC and a higher surface tension minimum (γ_{cmc}) while NPE has a lower CMC and a lower γ_{cmc}. Further, as shown in the figure, all curves for mixed systems fit between those of the two single systems except the curve for mole fraction of 0.9, and both CMC and the γ_{cmc} were changed in the order of mole fraction change. The CMC values together with the γ_{cmc} values are listed in table -1.

The total surface excess $\Gamma_t = \Gamma_1 + \Gamma_2$ for mixed system of a 1-1 electrolyte type ionic surfactant 1 and a nonionic surfactant 2 can be calculated from the following equation [10, 11]:

$$\Gamma_t = -\frac{1}{(2-X_2)RT}\left(\frac{d\gamma}{dlnc}\right) \text{ ...... (1)}$$

Where, X_2 denotes mole fraction of the surfactant 2 (nonionic) in bulk solution. dγ/dlnc was evaluated using the slopes of the straight line just below the CMC of γ-lnc curves figure- 2.
The value of mean molecular area A_m was calculated from the equation:

$$A_m = \frac{1}{N.\Gamma_t} \text{ .... (2)}$$

Where, N is Avogadro constant. Also, we have used a thermodynamic quantity, minimum surface free energy G^s_{min}, for the evaluation of synergism upon mixing which is defined as follows [10,11]:

$$G^s_{min} = A_m . \gamma_{cmc} . N \text{ .... (3)}$$

The Γ_t, A_m and G^s_{min} values are listed in table -1.

Table 1- Micellization parameters of NPE and DE-CA surfactants and their mixed system at 25°C.

X_2	CMC/ mmolL^{-1}	γ_{cmc} / mNm^{-1}	Γ_t * 10^3/ mmol m^{-2}	A_m / Å^2 molecule^{-1}	G^s_{min}/ kJmol^{-1}
0.0	1.37	56.78	1.30	127.7	43.7
0.1	0.43	39.48	1.36	122.1	29.0
0.3	0.16	39.04	1.38	120.3	28.3
0.5	0.13	38.33	1.40	118.6	27.4
0.7	0.06	36.43	1.98	83.9	18.4
0.9	0.03	35.97	2.41	68.9	14.9
1.0	0.06	33.66	3.99	41.59	8.4

G^s_{min} is the work needed to make an interface per mole or the free energy change accompanied by the transition from the bulk phase to the surface phase of the solution components. So, the lower the value of the free energy, the more thermodynamically stable a surface is formed, or the greater surface activity is attained [5]. The result obtained for G^s_{min} indicates that the mixture of 0.9 mole fraction of NPE was the greater surface activity. Also, the results of table -1 indicates that no synergism was observed in the mixed system for the surface tension reduction because the values of γ for the total mixed surfactant concentration are not lower than that required of either surfactant singularly. It is reported [1] that the synergism is presented when a given γ of the mixed surfactant lower than of the surfactant singularly. Synergism in the CMC is presented in an aqueous system containing two surfactants when a given CMC for mixed surfactant lower than either surfactant singularly [12]. So, the result of CMC at 0.9 mole fraction indicates the synergism was presented in the aqueous mixture of NPE and DE-CA surfactants.
Interactions between surfactants are measured by β^m parameter for interaction in the mixed micelle in aqueous media. β^m values can be easily determined from surface tension – concentration curves of the individual surfactants and at least one mixture of them at a fixed molar ratio of the two surfactants, by using the nonideal solution treatment (often called the regular solution treatment) and the following equations[8,13,14]:

$$\frac{(X_1^m)^2 \ln\left(\frac{X_2\, C_{12}^m}{X_1^m\, C_2^m}\right)}{(1-X_1^m)^2 \ln[\frac{(1-X_2)C_{12}^m}{(1-X_1^m)\, C_2^m}]} = 1 \ldots\ldots(4)$$

$$\beta^m = \frac{\ln\left(\frac{X_2 C_{12}^m}{X_1^m C_1^m}\right)}{(1-X_1^m)^2} \ldots\ldots\ldots\ldots (5)$$

Where X_1^m is the mole fraction of surfactant NPE in mixed micelles, C_1^m, C_2^m, and C_{12}^m are CMCs for surfactants NPE, DE-CA, and their mixtures respectively. C_{12}^m, X_1^m, and β^m parameters obtained for all mole fractions are given in table -2. The values of CMCs (theoretical) were calculated using the following equation assuming to non ideal mixing [1]:

$$\frac{1}{CMC_{12}} = \frac{X_1}{CMC_1} + \frac{X_2}{CMC_2} \ldots\ldots\ldots\ldots (6)$$

Where X_1 and X_2 are the mole fractions of NPE and DE-CA surfactants respectively, while CMC_1, CMC_2, and CMC_{12} are the critical micelle concentration of NPE and DE-CA surfactants and their mixture respectively.

Table 2- parameters of NPE and DE-CA surfactants system obtained from surface tension data analysis in mixed micelle.

NPE/DE-CA	0:10	1:9	3:7	5:5	7:3	9:1	10:0
X_2	0	0.1	0.3	0.5	0.7	0.9	1.0
C_{12}^m(mmol/l)	1.37	0.425	0.16	0.13	0.06	0.034	0.061
CMC (mmol/l) (theoretical)	-	0.43	0.18	0.11	0.084	0.066	-
X_1^m	-	0.624	0.722	0.880	0.746	0.730	-
β^m	-	0.821	1.191	10.950	-1.149	-5.060	-

The CMC values obtained are plotted as a function of mole fraction of NPE in surfactants mixture (X_2) as shown in figure -3.

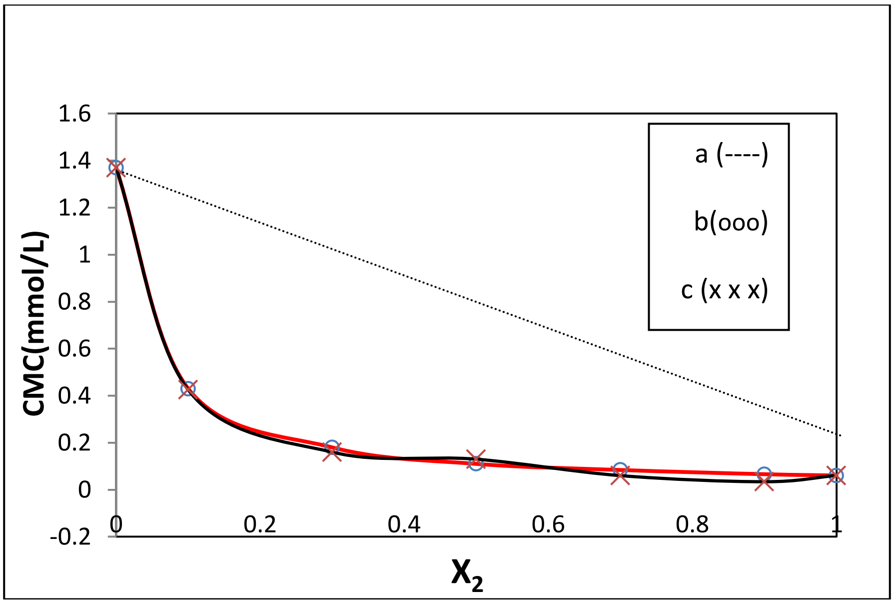

Figure 3- Phase diagram of NPE/DE-CA mixed system at 25 °C, a; ideal mixing, b; theoretically, c; experimentally.

The relation of CMC with X_2 should be a straight line (line a) when the two surfactants can form a micelle of ideal mixing. It is clearly from figure-3 that the CMC- X_2 (line b,c) curves negatively deviate from the relation of ideal mixing (where CMC in line b obtained theoretically and CMC in line c obtained from experimental). A positive β^m means that there is a net repulsion between the surfactant molecules in the micelle, whereas a negative β^m means a net attraction [13]. From 0.1 to 0.5 mole fraction the positively of β^m is increased with increasing NPE related to DA-CE reflecting the mutual electrostatic repulsion between the surfactant molecules, but at X_2 of 0.7 and 0.9 the β^m were negative and the negatively is increased with increasing mole fraction from 0.7 to 0.9 reflecting the mutual electrostatic attraction between the surfactant molecules.

Conclusions:

Adsorption properties of mixed surfactant for NPE and DE-CA were studied by means of surface tension. Data analysis of the mixed system provided the results that the CMC and γ_{cmc} values were changed in the order of mole fraction of NPE in the mixture change. G^s_{min} values indicates that the mixture of 0.9 mole fraction of NPE was the greater surface tension reduction, while the results of CMC's indicate the synergism was present at 0.9 mole fraction because the value of CMC is lower than of surfactant singularly. The CMC-X_2 curves indicate that the relation of CMC with X_2 was negatively deviate from the relation of ideal mixing. The β^m values obtained were positive at 0.1, 0.3, and 0.5 mole fractions of NPE and increased with increasing mole fraction, but at mole fraction 0.7 and 0.9 the β^m values were negative and the negatively is increased with mole fraction.

Reference

1- Rosen, M. J. **2004**. *Surfactants and Interfacial Phenomena*. Third Edition. John Wiley, New York.

2- Ogino, K. and Abe, M. **1993.** *Mixed Surfactant Systems*. Surfactant Science Series 46. Marcel Dekker, New York.

3- Okano, T., Abe Y., Hotta D., Nakano T., Sugihara G. and OH, S. G. **1998**. Binary Mixed Systems of Anionic/Nonionic Surfactants: Synergistically Enhanced Surface Activity and Relationship among Compositions of Monomers in Bulk, Micelles and Adsorbed Film at Air/Water Interface. *J. Japan Oil Chemical Society*, 49, pp:915-928.

4- Nakano, T. Y., Sugihara, G., Nakashima, T. and Yu, S. C. **2002.** Thermodynamic study of mixed hydrocarbon/fluorocarbon surfactant system by conductometric and fluorimetric techniques. *Langmuir*, 18, (23), pp:8777-8785.

5- Jeong, K., Woung O., Yu-Seung K., Noriko N., Shigemi N. and Gohsuke, S. **2004**. Adsorption and Micelle Formation of Mixed Surfactant Systems in Water. IV. Three Combinations of SDS with MEGA-8, -9 and -10. *J. Oleo Science*, 53 (3), pp:109-126.

6- Katarzyna, S. and Bronislaw, J. **2010**. A Study of the Interactions of Ternary Surfactant Systems at the Water – Air Interface. *Langmuir*, 26(4), pp:2491 – 2496.

7- Soheila, J., Hussein G. and Hajar, T. F. **2010**. Adsorption and Micellar properties of Binary Ionic/Nonionic Surfactant Mixtures in Ethylene Glycol – Water. *J. Chemical Engineering Data*, 55(3), pp:1122 – 1130.

8- Shaohua Lu, Jun Wu, and Ponisseril S. **2012**. Micellar Evolution in Mixed Nonionic/Anionic Surfactant Systems. *J. Colloid and Interface Science*, 367, pp:272 – 279.

9- Katarzyna, S., Anna Z., Joanna K. and Bronislaw, J. **2013**. Mutual Influence of Cetyltrimethylammonium Bromide and Triton X-100 on Their Adsorption at the Water – Air Interface. *J. Thermodynamics*, 59, pp:35 – 42.

10- Sugihara, G., Miyazono A., Nagadome S., Oida T., Hayashi Y. and Ko, J.S. **2003**. Adsorption and Micelle Formation of Mixed Surfactant Systems in Water. II: A Combination of Cationic Gemini-type Surfactant with MEGA-10. *J. Oleo Sci*ence, 52, pp:449-461.

11- Oida ,T., Nakashima, N., Nagadome S., Ko, J.S., Oh, S. and Sugihara, G. **2003**. Adsorption and Micelle Formation of Mixed Surfactant Systems in Water. II: A Comparison between Cationic Gemini/Cationic and Cationic Gemini/Nonionic Combinations. *J. Oleo Science*, 52, pp:509-522.

12- Rosen, M. J. **1994**. Predicting Synergism in Binary Mixtures of Surfactants. *Progress in Colloid and Polymer Sci*ence, 95, pp:39-47.
13-Hoffimann, H. and Possnecker, G.**1994**. The Mixing Behavior of Surfactants. *Langmuir*, 10, pp:381-389.
14- Rubingh, D. N. **1979**. *In Solution Chemistry of Surfactants*. K. L. Mittal Ed., 1, Plenum, New York, pp:337-354.