Conductometric study of ionic – nonionic surfactant mixed micelles in aqueous solution

***Ass. Lec. Duha Mohammed Murtadah , * Ass. Prof. May Essa Mahmood**
Faculty of Pharmacy, University of Kufa

الخلاصة :

في هذا البحث عين التركيز الحرج لتكوين المايسل لمزيج من سلفات دودوسيل الصوديوم مع تريتون ١٠٠ وكذلك بروميد سيتيل ثلاثي امونيوم مع تريتون ١٠٠ لقيم مختلفة من الكسر المولي للمواد ذات السطوح النشطة الايونية بواسطة القياسات التوصيلية الكهربائية ، وجدت ان القيم المثلى لهذين المزيجين عند α = ٠.٢ و α = ٠.٦ على التوالي . كما حسبت الدالات المهمة في تكوين مزيج المواد ذات السطوح النشطة من الكسر المولي لمادة ذات السطح النشط ، ومعاملات الفعالية وعامل التداخل الجزيئي لقيم الكسر المولي المختلفة . كما عينت مقادير الطاقة الحرة لعملية تكوين مزيج المايسل بثلاث معادلات رياضية مختلفة للمزيجين اعلاه ، وكانت قيم الطاقات الحرة عند القيم المثلى للتركيز الحرج ٢٠.١- و ٣١.٢ - كيلو كلوري / مول على التوالي .

Abstract:

This study is concerned with the determination of critical micelle concentration (cmc) of mixed micelle of sodium dodecyl sulfate (SDS) and cetyltriammnum bromid(CTAB) as an ionic surfactants (as anionic and cationic respectively) with Triton x-100 as nonionic surfactant from conductance measurements , the optimal cmc for mixed micelle (SDS/Tritonx-100) and (CTAB/Tritonx-100) at different mole fraction (α) are determined that are 0.2 and 0.6 respectively .the values of the mole fraction of ionic surfactant in mixed micelle (X_1^M) , the activity coefficients of the surfactants 1 and 2 in the micelle (f_1^M and f_2^M) and the molecular interaction parameter (β^M) in mixed micelle are determined for two mixed solution in different mole fraction . the standard free energy of micellization for mixing surfactants (ΔG^omic)is calculated by three equation , the values of free energy at the optimal α are (-20.1 and -31.2) Kcal/mole for mixing (SDS/Tritonx-100) and (CTAB/Tritonx-100) are respectively .

Keywords : conductometric measurement , ionic &,nonionic surfactant ,mixed surfactant, critical micelle concentration .

Introduction

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads) (1,2) .

One outstanding property of surfactants , in the bulk aqueous phase , they arrange themselves into organized molecular aggregates known as micelles. This phenomenon is driven by hydrophobic effect and opposed by electrostatic repulsions between the ionic head groups (3). The concentration at which micelle formation occurs is known as the critical micelle concentration (cmc) (4-6) .

The synergistic interactions between the surfactants in binary mixed surfactant systems resulted in the successful practical applications.The synergism of these interactions can be forecasted by some theories.There are two common models used to describe the interactions and they are classified as the ideal and non-ideal models.In the case of ideal mixing of the surfactants, the phase separation model can be used to calculate the critical micelle concentration (cmc) of the mixture, CMC_{mix}, from the individual cmc, CMC_1, and CMC_2, and the respective mole fractions of surfactants (α).Based on the theoretical work by Clint,(7-9) CMC_{mix} can be calculated using a fundamental equation:

$$\frac{1}{CMC_{mix}} = \frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2} \qquad (1)$$

where CMC_1 and CMC_2 are the CMC of the pure surfactant 1 and 2.

In the non-ideal model, a very useful formula to calculate the extent of synergistic interaction is provided by Rubingh(10-20) . A non-ideality parameter (β) is required in the regular solution theory (RST) description of a binary system.This interaction parameter is related to the activity coefficients of the surfactants.

The focus of this paper is on the conductometric method. This method is frequently used for the determination of the cmc of ionic and mixed surfactants because it is simple and accurate.

We have measured the conductivities of SDS and CTAB and mixture these ionic surfactants with nonionic surfactant (Triton-X100)at definite temperatures.

Material and Method :

Sodium dodecyl sulphate (99%) was purchased from Panreac , Spain , CTAB (97%) from SRC ,China while Triton x-100 from Hi Media , India. The surfactants were used without further purification. Their purity was checked by determining the cmcs of the pure surfactants, and these were in agreement with literature values. The molecular architecture of these surfactants are shown in the Table (1).

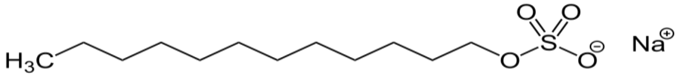
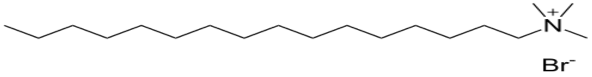
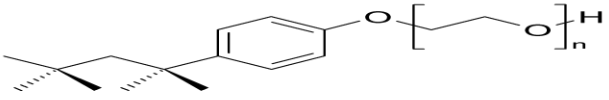
Preparations of the binary mixtures :

Stock solutions of surfactants: 20mM SDS, 5mM CTAB , and 4mM Triton X-100[the cmc is determined from literature (0.27 mM)] were prepared by dissolving in water with gentle stirring. All solutions were prepared in deionized water water having a specific conductance 3–5.5 µS cm^{-1} at 22 °C. Binary mixtures of nonionic surfactants and ionic surfactant were prepared by mixing the required volumes of stock solutions in different ratio (α) . Before further use, the mixtures were left for 24 h at room temperature (21-24) .

Conductometry :

Conductivity measurements were realized at 22 °C, in water bath H.JRGENS & CO. D2800 bremen by adding 0.2 cm^3 portions of titrant to 50 cm^3 of analyte. After the addition of each portion, the solution was stirred until a steady conductance value was achieved. Specific conductance was measured using conductivity meter 7110 , WTW 92382 WELHEIM , Germany and conductivity cell with the cell constant of 1.00 cm^{-1} .The conductivity meter was calibrated with 10 mM KCl solution prior to the experiment. The uncertainty in conductivity measurements was estimated to be ± 0.5 µS cm^{-1} (25-29) .

Table (1): Molecular structure for surfactants

Surfactant	Molecular structure
Sodium dodecyl sulphate (SDS) Mwt =288.37 g/mole	
Cetyl triammonium bromide(CTAB) Mwt= 364.45g/mol	
t-octylphenoxypoly- ethoxyethanol,Octoxynol-9 (Triton x- 100) Mwt= 647 g/mol	

Results and Discussion :

1. the conductivity-concentration curve for individual surfactant :

Because cmc is a 'phase transition' between two different regimes of a surfactant solution, The cmc can be determined by the conductivity method of the SDS solution (Na^{+} and $^{-}OSO^{-3}C_{12}H_{25}$ ions) and CTAB solution (Br^{-} and $C_{19}H_{42}N^{+}$ ions) are known as charge carriers which will increase the conductivity of the solution when ionization takes place. the plot of conductivity versus concentration shows a linear behaviour with two different slopes. Usually, the intersection of the two straight lines below and above the cmc gives the cmc of the surfactant. Figures (1 and 2)show a plot of conductivity as a function of SDS and CTAB concentrations , the cmc values of SDS and CTAB are 7.95 mM and 0.909 mM that consistent with those reported (23, 30-31) , the cmc of SDS is higher than that of CTAB . These observations are due to the tendency of the hydrocarbon chains to remove themselves from water. There are two competing processes in the formation of micelles of ionic surfactants in aqueous systems as mentioned earlier on. The binding affinity of the counterion to the micelles, which depends on the magnitude of its charge and size (3,32). Nevertheless, the behaviour of the hydrocarbon tails account for the observed difference in the cmc of these surfactants.

2. The cmc of mixed surfactant :

The critical micelle concentrations of the binary surfactant solutions were studied through conductivity measurements at different mole fractions of the ionic surfactants (α). Prepared mixtures consisted of 0.2, 0.4, 0.6 or 0.8 mole fractions of ionic surfactant (α), as seen in Tables (2) . A break in the conductivity against concentration plots, characteristic of micelle formation, was observed (Figures 3 and 4) For SDS–Triton x-100 and CTAB –Triton x-100 mixtures respectively. The optimal micellar values for two mixed surfactants are at α =0.2 and α =0.6 respectively , the minimum of cmc appears where the molecular mole fraction of ionic surfactant (SDS and CTAB) is lower in the mixed micelle than in the bulk phase. And the molecular interaction parameter in the mixed micelle, β^M, calculated from Eq. (2) (Table 2) has also the lowest value(23) .

3. The interaction parameter for mixed micellization :

Table (2) illustrate the interaction parameters for binary system that have negative values indicating synergism in the micellar systems. The Phenoxy part of Triton X-100 is shorter and less hydrophobic than hydrocarbon tails of examined for another nonionic surfactants, creating the weakest synergistic effect(33) . However, taking into account the lowest value of β^M the best synergism exists on the basis of the data presented above it is difficult to explain exactly why the minimum of cmc calculated theoretically appears at a different composition of the mixed micelle that obtained from measurements of the conductivity of mixtures surfactant(34) .

the molecular-thermodynamic theory of mixed surfactant solutions (23,35) . This theory allows us to predict the molecular interaction parameter in the mixed micelle, β^M, that calculated from the relation of Rubingh and Rosen (23, 36):

$$\beta^M = \frac{ln(\alpha C^M_{12}/X^M_1 C^M_1)}{(1-X^M_1)^2} \qquad (2)$$

where $C^M{}_1$, $C_{12}{}^M$ are the critical micelle concentrations (cmc) of the individual surfactant 1, and mixture of surfactants 1 and 2, respectively, and X_1^M 1 is the mole fraction of surfactant 1 in the mixed micelle. The X_1^M can be evaluated from the equation:

$$\frac{(X_1^M)^2 \ln(\alpha C_{12}^M / X_1 C_1^M)}{(1 - X_1^M)^2 \ln[(1 - \alpha) C_{12}^M / (1 - X_1^M) C_2^M]} = 1 \qquad (3)$$

where C_2^M is the cmc of the individual surfactant 2.

Knowing the interaction parameters for the mixed monolayer and micelles it is possible to determine the activity coefficient

of the surfactants in the mixtures. From the nonideal solution theory it results that the activity coefficients of the surfactants 1

and 2 in the micelle (f_1^M and f_2^M) are calculated from these equations, respectively:

$$\ln f_1^M = \beta^M (1 - X_1^M)^2 \qquad (4)$$

$$\ln f_2^M = \beta^M (X_1^M)^2 \qquad (5)$$

4. The standard free energy of mixed micellization :

The tendency of surfactants to form micelles can be established on the basis of standard free energy of micellization (ΔG°_{mic}). In the literature there are many different ways for determination of this energy (23) . The figures (7 and 8) illustrate three ways to determine the free energy of mixed micellization ,one of these ways has introduced from the following equation :

$$\Delta G^o_{mic} = RT \ln cmc \qquad (6)$$

The values determined in this way are higher than those obtained from Equation :

$$\Delta G_{mic} = X_1^M \Delta G_{mic1} + X_2^M \Delta G_{mic2} \qquad (7)$$

the term of the free energy of micellization resulting from the mixing process of the surfactants in the micelles. This term should fulfil the quation:

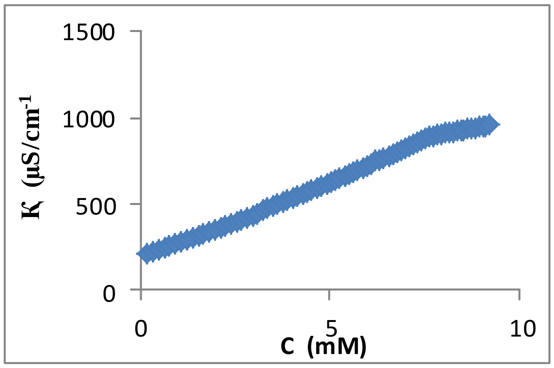
$$G^M = RT\ (X_1^M \ln f_1^M + X_2^M \ln f_2^M) \qquad (8)$$

The third equation to determine the free energy of mixed micellization by adding the equations (7) to (8) :

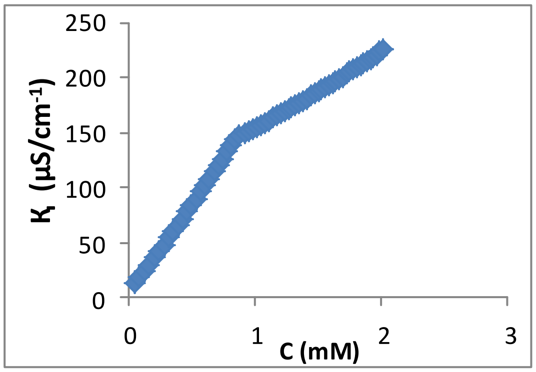
$$\Delta G_{mic} = X_1^M \Delta G_{mic1} + X_2^M \Delta G_{mic2} + G^M \qquad (9)$$

from Eq. (9) are presented in Figures (7 and 8) , it appears that the values of the standard free energy of mixed micellization are approximately identical as those determined from Equation (7) , but there are minimum values of _ΔG_{mic} at α equal 0.2 for the mixture (SDS –Triton x-100) and equal 0.6 for the mixture

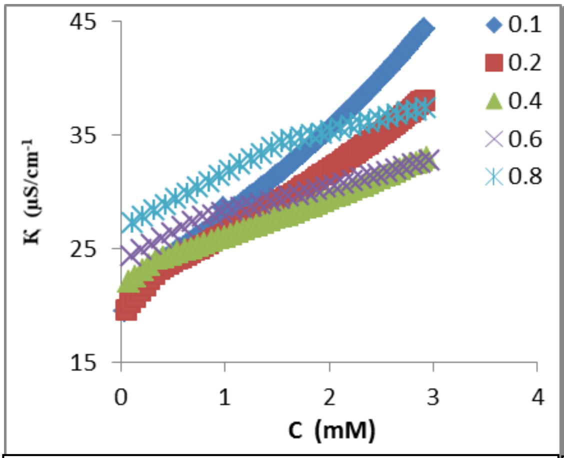
(CTAB –Triton x-100) . These calculations indicate that using Eq. (8) it is possible in a accurate way to obtain the values of the standard free energy of micellization for mixtures of two surfactants (23) .



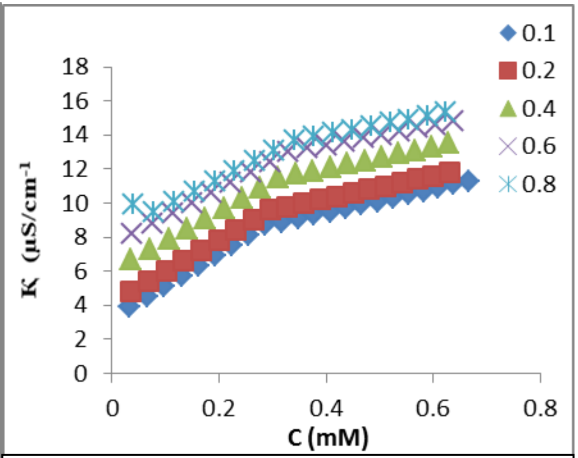
figure(1):Experimental data of conductivity versus concentration of surfactant(SDS)



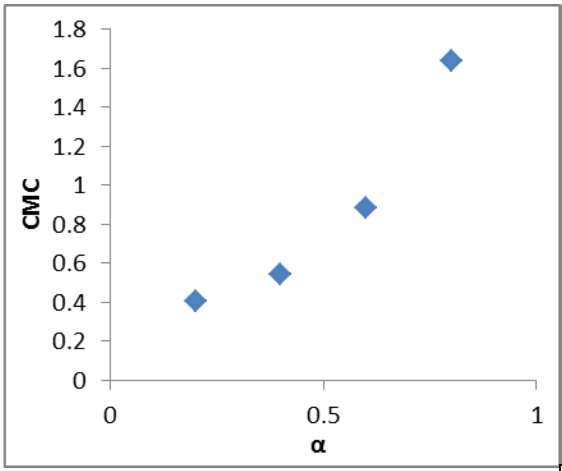
figure(2):Experimental data of conductivity versus concentration of **surfactant (CTAB)**



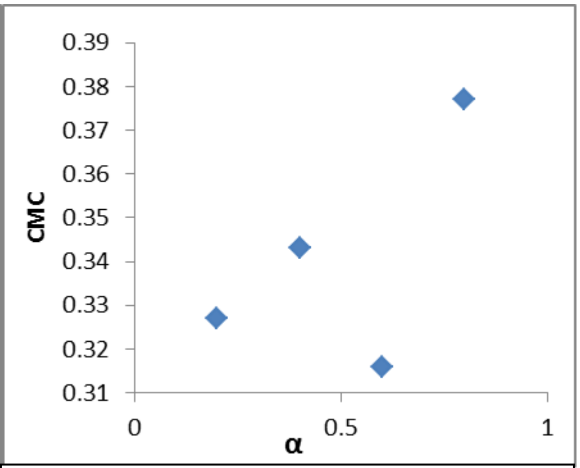
figure(3):Experimental data of conductivity versus concentration of mixed surfactant (SDS & TritonX-100)



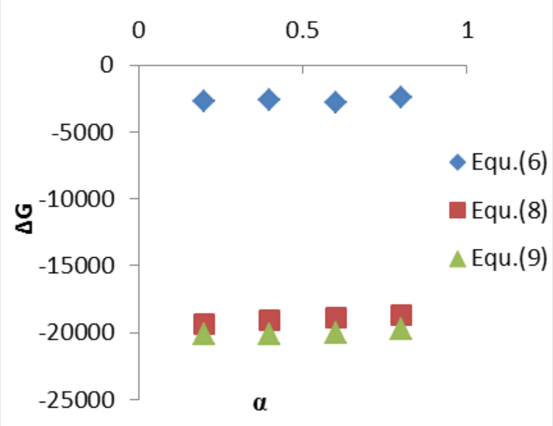
figure(4):Experimental data of conductivity versus concentration of mixed surfactant (CTAB & Triton X-100)



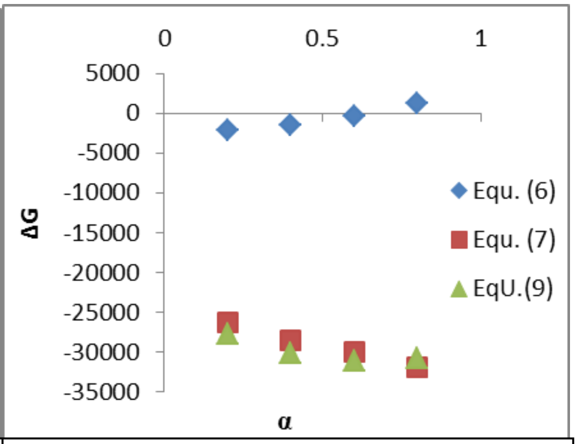
figure(5):Relationship between cmc & the mole fraction (α)of mixed surfactant (SDS +Triton X-100)



figure(6):Relationship between cmc & the mole fraction (α)of mixed surfactant (CTAB +Triton X-100)



figure(7):Relationship between ΔG & the mole fraction (α)of mixed surfactant (SDS +Triton X-100) by different equation



figure(8):Relationship between ΔG & the mole fraction (α)of mixed surfactant (CTAB +Triton X-100) by different equation

Table (2):values of the cmc ,the mole fraction of surfactant(X_1^M),molecular interaction parameter (β^M), activity coefficient of the surfactants 1 and 2 (F_1^M and F_2^M) in mixed micelle.

Surf.mix.	**α**	**cmc (mM)**	**X_1^M**	**β^M**	**F_1^M**	**F_2^M**
SDS+Tritonx-100	0.2	0.4093	0.422	-2.51879	0.431069	0.63855
	0.4	0.5457	0.573	-2.4315	0.618908	0.421474
	0.6	0.883	0.664	-2.2134	0.778891	0.376861
	0.8	1.642	0.793	-1.9888	0.918312	0.286317
CTAB+Triton x-100	0.2	0.327	0.2015	-1.6152	0.357058	0.936523
	0.4	0.343	0.3392	-1.85441	0.444974	0.807864
	0.6	0.316	0.4123	-1.97291	0.505896	0.715069
	0.8	0.377	0.5111	-1.80758	0.649175	0.62364

Conclusion :

The results of the measurements of the conductivity and the calculations of the cmc of mixed micellization of aqueous solution of SDS- Triton x-100 and CTAB –Triton x100 suggest that:

1. the conductivity depends on the concentration and composition of aqueous solution of SDS- Triton x-100 and CTAB –Triton x100 mixture

2.the optimal values of the cmc for all α values for SDS- Triton x-100 and CTAB – Triton x100 are 0.2 and 0.6 respectively .

3. for all α values the parameter of intermolecular interaction in mixed micelle β^M has a negative value and increases with α in mixed micelle SDS –Triton x-100 while it has minimum value at α = 0.6 in mixed micelle CTAB –Triton x-100 .

4. knowing the composition of the mixed micelle it is possible to determine in a simple way the standard free energy of micellization process of SDS –Triton x-100 and CTAB –Triton x - 100 surfactant mixtures

References :

1. Jeea Louis Salager , Surfactants types and uses , 2002

2. Manisha Mishra , P.Muthuprasanna and K.Surya prabha , Basics and potential application of surfactants –A review , vol. 1 , no. 4 , pp1354-1365, 2009 .

3. Jiang N, Li P, Wang Y, Wang J, Yan H and Thomas RK, Journal of Colloid and Interface Science, 286: 755-760 , 2005.

4. Farn RJ, Chemistry and Technology of Surfactants , 2006.

5. Domínguez A, Fernández A, González N, Iglesias E, and Montenegro L, Journal of Chemical Education, 74 , 1227-1231 ,1997.

6. Nasiru T, Avila L, and Levine M, Journal of High School Research , 2 , 1-5 , 2011 .

7. Clint j. , J. Chem. Soc. Faraday Trans. 71 , 1327 ,1975 .

8. Lange H. , and Beck K. H. , Polymere , 251, 424 ,1983 .

9. Nishikido N. , Morio Y. , and Matuura R. Bull , Chem. Soc. Japan, 48, 1387 , 1975 .

10. N.D.Denkor and S.Tcholakova , Surfactants classification , features and application , 2010 .

11. De Lisi , R. Inglese , A. Milioto , and S. Pellerito, Langmuir,
13, 192 , 1997 .

12. Paul M. Holland1 and Donn N. Rubingh Mixed Surfactant Systems , An Overview Chapter 1 , PP1-30 ,1992

13. Rosen, M. J. Surfactants and Interfacial Phenomena, 2nd Ed.; John Wiley & Sons: New York , Chapter 11, pp. 393-419 , 1989.

14. Rosen, M. J. Langmuir, 7, 885 , 1991 .

15. Jost F. , Leiter H. , and Schwuger M. J. Colloid Polym. Sci., 266, 554 , 1989 .

16. Kamrath R. F. , and Franses E. I., Ind. Eng. Chem. Fundam., 22, 230 , 1993 .

17. Rubingh D. N. , Plenum Press , New York , 3 , pp 337-354 , 1979 .
18. Muller, A. Colloids Surf., 57, 239 , 1991 .

19. Stecker M. M. , and Benedek G. B. , J. Phys. Chem., 88, 6519 , 1984 .

20. Holland P. , Adv. Colloid Interface Sci. 26, 111 , 1986 .

21. AT Tyowua1 , SG Yiase1, RA Wuanna , Chemical Sciences Journal , Vol. 79 , PP1-9 ,2012 .

22. P. Carpena, J. Aguiar, P. Bernaola-Galvan, and C. Carnero Ruiz , Simulations and Experiments Langmuir, 18, 6054-6058 , 2002 .
23. Katarzyna Szymczyk, and Bronisław Ja´nczuk , Physicochem. Eng. Aspects , 293 , 39–50 , 2007 .

24. Dejan M. Ćirin, Mihalj M. Poša, Veljko S. Krstonošić, and Maja Lj. Milanović , Hem. Ind. 66 , 21–28 , 2012 .
25. Tharwat F. Tadros , Applied Surfactants: Principles and Applications , 2005 .
26.Y.Zhang and Y.M.Lam , journal of Nanoscience and Nanotechnology , 6, 1-5 , 2006 .

27. Rashmi Mandavi, Santosh. K. Sar and Nutan Rathore , Oriental Journal of Chemistry , 24 , 559-564 , 2008 .
28. Krassimir D. Danov , Peter A. Kralchevsky , and Kavssery P. Ananthapadmanabhan , Advances in Colloid and Interface Science, 206 , 17–45 , 2014 .

29. Lidija B. Petrović , Verica J. Sovilj , Jadranka L. Milanović
and Jaroslav M. Katona , J. Serb. Chem. Soc. , 79 , 1421–1432 ,2014 .

30. Carpena P. , Aguiar J. , Bernaola-Galván P., and Carnero Ruiz C., Langmuir , 18 , 6054-6058 , 2002 .

31 . Jover A. , Meijide F. , Mosquera V. , and Tato JV, 60 , 530-532 ,1990.

32. Benrraou M. , Bales B. , Zana R. , Journal of Colloid Interface Science, 267 , 519-523 , 2003. .

33.M.Munoz , A.Rodriguez , M.Graciani , and M.L.Moya , Langmuir , 20 , 10858–10867 , 2004 .

34. F.Ysambertt , F.Vejar , J.Paredes , and J.L.Salager , Coll. Surf. A , 137 , 189–196 , 1998 .

35. A. Shiloach, and D. Blankschtein, Langmuir ,14 , 7166–7182 , 1998 .

36. D.N. Rubingh, Langmuir , 12 , 337 -351 , 1989 .