CONDUCTOMETRIC INVESTIGATION OF THE INTERACTION OF CHITOSAN-DIODYL SULFO-SUCCINATE SURFACTANT IN WATER-TOLUENE SOLUTION

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ABSTRACT
The wide application of emulsifiers in formation of micelle is important for reducing surface tension and they improve stability and emulsification property in solution system. Some of monomers may provide reduction of Critical Micelle Concentration (CMC) as co-surfactants. Those monomers, which can typically increase electric conductivity of emulsifier solutions, may effect on critical micelle concentration and they may be consumed in industry after achieving optimal experimental results. In the present research, role of chitosan, as a cationic polysaccharide adjacent to DioctylSulfoSuccinate (DSS) as Gemini anionic surfactant (Insoluble in water), was studied and the impact of chitosan was examined in the system (surfactant-water-toluene) by conductometry technique. Keywords: Chitosan- DioctylSulfoSuccinate (DSS) - Critical Micelle Concentration (CMC) - Electric Conductivity

Received 19/11/2013 Accepted 30/12/2013 ©2014 AELS, INDIA

INTRODUCTION
The wide use of emulsifiers in formation of micelle is especially important to reduce surface tension and they increase stability and emulsification property in soluble systems. Compared to current monomer surfactants, Gemini surfactants are more advantageous in many cases. These substances have more surface activity and their CMC value is 10-100 times smaller than CMC of the current related materials. Similarly, they are more helpful in reduction of surface tension in common level of oil-water. Polysaccharides are one of natural polymeric coagulants that widely used in industry. One could refer to some foremost members of this group as chitosan and starch, which have cationic property, and due to their high efficiency, in many cases they have been substituted with natural polymers. Cationic polyelectrolytes are linked directly to the existing particles in suspension and through electrostatic attraction. Thus, they are more effective than other types. Chitosan is a derivative from glucan with iterative units of chitin that was introduced by Roget with a known agent in 1859. Emulsifying mechanism and its stability in water-oil (paraffin) system in the presence of chitosan was studied without adding surfactant by Payet [1]. Sadowsky et al studied on interaction of polymer-surfactant and its effect on spherical concentration and reported absorption of polymers and surfactants on solid surfaces in stability of polymer-surfactant and polymer-solid surface [2]. Ogawa examined properties of water-paraffin emulsions and stability of drops formed by multilayer lecithin-chitosan-pectin [3]. Bajaj reviewed on dispersion of castor oil in aqueous phase in the presence of chitosan and stability of emulsion system was reported in the presence of chitosan [4]. In another survey that was conducted by Ariyaparakai, the impact of surfactant structure in micelle formation of petroleum emulsions in water with several weight percentages (2%, 1%) was reported from light diffraction in water [5]. In other investigation that was carried out by Kishk, inhibiting free radicals and antioxidant activity in some polysaccharides were explored. This study showed that rhizobium melliloti and cordilin might be used as surfactants of emulsion system and inhibitors of free radicals for petroleum [6]. The reaction among chitosan and Bovine Lung Extract Surfactant (BLES) will be followed by reduced surface tension and inhibits from anesthesia of lungs [7]. Caterjee et al studied on absorption of Congo Red Color from aqueous solutions by chitosan hydrogel seeds stained by bromide tri-methyl. The review on adsorbent
isotherms characterized that with reduction pH, the rate of absorption would be increased [8]. In this article, CMC variations of Gemini anionic surfactant in the presence of chitosan and its distribution in water-toluene system were investigated.

MATERIALS AND METHODS
Chitosan (medium molecular weight) and toluene with high purity grade were purchased from Merck Company. DioctylSulfoSuccinate (DSS) was provided by SIGMA Inc, and doubly distilled water was used in all experiments. CRISON GLP 32 conductometer was utilized to measure electric conductivity and for determination of point of critical micelle concentration.

The impact of monomer on stability of emulsion system and critical micelle concentration
Initially, some solutions were prepared by several surfactant concentrations with volume of 15mL and electric conductivity of them was measured in the absence of chitosan. Then, some concentrations of chitosan solution (4%) (0.25ml, 0.5mL, 0.75mL, 1mL, and 2mL, respectively) were added to the prepared solutions and their electric conductivity was determined.

Determination of thermodynamic parameters by means of conductometry technique
Gibbs free energy, enthalpy, and surface entropy were derived by means of conductometry method and determination of CMC point and the following formulas. Gibbs free energy of standard micelle formation ($\Delta G_{mic}^\circ$) has been computed by means of Eq. 1.

$$\Delta G_{mic}^\circ = -2.303RT (\log_{cmc} - \log W)$$

In this formula, $W$ denotes water concentration is based and molar and 55.3 at 298K. The variations in standard entropy of micelle formation ($\Delta S_{mic}^\circ$) were also calculated with the Eq. 2.

$$\Delta S_{mic}^\circ = -\frac{d \Delta G_{mic}^\circ}{dT}$$

And variation in standard enthalpy of micelle formation has been also computed from the Eq. 3.

$$\Delta G_{mic}^\circ = \Delta H_{mic}^\circ - T \Delta S_{mic}^\circ$$

The effect of chitosan on stability of (water- toluene- chitosan) system
The measurements of conductivity in the absence and presence of chitosan was also studied to review on variations in critical micelle concentration for water- toluene system with ratios of (1:1) and (1:2). At this step, surfactant concentration is the same as 0.1M and variations in electric conductivity of solution in respect of time was recorded. All measurements were done at fixed temperature 298K.

RESULTS AND DISCUSSION
The results of chitosan effect on stability of emulsion system and critical micelle concentration
The given results reflect that as chitosan is increased from 0.25mL to 2mL, the electric conductivity is improved from 345 μs to 440 μs and critical micelle concentration has been reduced from 0.002M to 0.0015M and this is due to rising of micelles accumulation in critical micelle concentration point and reduction of surface tension, which has been presented in Figs 1-6.

Fig 1: DSS electric conductivity in the absence of chitosan (CMC 0.002M) (T = 298K)

Fig 2: DSS electric conductivity in the presence of 0.25mL chitosan (CMC 0.00197M) (T = 298K)
Fig 3: DSS electric conductivity in the presence of 0.5mL chitosan (CMC 0.00194M) (T = 298K)

Fig 4: DSS electric conductivity in the presence of 0.75mL chitosan (CMC 0.00190M) (T = 298K)

Fig 5: DSS electric conductivity in the presence of 1mL chitosan (CMC 0.00176M) (T = 298K)

Fig 6: DSS electric conductivity in the presence of 2mL chitosan (CMC 0.0015M) (T = 298K)

Fig 7: DSS electric conductivity in the absence of chitosan in (water- toluene- 1:1) system (CMC 0.003M) (T = 298K)
Fig 8: DSS electric conductivity in the presence of 0.25mL chitosan 4% in (water- toluene- 1:1) system (CMC 0.0295M) (T = 298K)

Fig 9: DSS electric conductivity in the presence of 0.5mL chitosan 4% in (water- toluene- 1:1) system (CMC 0.0290M) (T = 298K)

Fig 10: DSS electric conductivity in the presence of 0.75mL chitosan 4% in (water- toluene- 1:1) system (CMC 0.0286M) (T = 298K)

Fig 11: DSS electric conductivity in the presence of 1mL chitosan 4% in (water- toluene- 1:1) system (CMC 0.0281M) (T = 298K)
Table 1: The results of thermodynamic parameters for DioctylSulfoSuccinate (DSS) in the absence and presence of chitosan 4% at temperature (T= 298K)

<table>
<thead>
<tr>
<th>No</th>
<th>VCTS (mL)</th>
<th>CMC (mol dm(^{-3}))</th>
<th>$\Delta G^\circ_{\text{mic}}$ (J mol(^{-1}))</th>
<th>$\Delta S^\circ_{\text{mic}}$ (JK(^{-1})mol(^{-1}))</th>
<th>$\Delta H^\circ_{\text{mic}}$ (J mol(^{-1}))</th>
</tr>
</thead>
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<tr>
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<td>1.16</td>
</tr>
<tr>
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<td>0.00190</td>
<td>25477</td>
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<tr>
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<td>1.73</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0.00150</td>
<td>26070</td>
<td>87.44</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 2: The results of thermodynamic parameters for DioctylSulfoSuccinate (DSS) in the absence and presence of chitosan 4% at temperature (T= 298K) in the (water- toluene-chitosan) system

<table>
<thead>
<tr>
<th>No</th>
<th>VCTS (mL)</th>
<th>CMC (mol dm(^{-3}))</th>
<th>$\Delta G^\circ_{\text{mic}}$ (J mol(^{-1}))</th>
<th>$\Delta S^\circ_{\text{mic}}$ (JK(^{-1})mol(^{-1}))</th>
<th>$\Delta H^\circ_{\text{mic}}$ (J mol(^{-1}))</th>
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</table>

Fig 12: DSS electric conductivity in the presence of 2mL chitosan 4% in (water- toluene- 1:1) system (CMC 0.0265M) (T = 298K)

The results of chitosan effect on stability of (water- toluene- chitosan) system

To investigate into chitosan effect in organic solvent and its impact on variations of critical micelle concentration (CMC), electric conductivity was measured in the presence and absence of chitosan in systems (water- toluene- 1:2) and (water- toluene- 1:1). For this aim, solutions with content of water-toluene- surfactant were prepared and electric conductivity of solutions was measured. Surfactant concentration is 0.1M and concentration of the used chitosan is 4% at all phases. Then, the prepared chitosan solution was added respectively with volumes (1mL, 2mL, 0.25mL, 0.5mL, and 0.75mL) and their electric conductivity was measured and with respect to electric conductivity of solutions, variations curve was drawn for electric conductivity based on concentration. Figs 7-12 indicate that electric conductivity is reduced in the presence of toluene organic solvent and CMC has been increased from 0.002M in the absence of organic solvent to 0.003M in the presence of toluene. A rising trend of CMC was also observed in the presence of chitosan and whereas chitosan is insoluble in toluene thus repulsion force is increased between charged groups on surface of micelle that was followed by observation and demonstration of destructive role of toluene as an insoluble solvent.[9-11]

The results of survey on thermodynamic parameters by conductometry technique

The results of this study have been given in Tables 1, 2 and they indicate that in all cases ($\Delta G^\circ_{\text{mic}}$) was negative and this value becomes more negative with increase of monomer so this may represent better
accumulation and micelle optimal formation and \((\Delta S_{mic}^{\circ})\) has been increased and become more positive with adding chitosan to this mixture also because of rising micelles accumulation. The acquired results from comparison between Tables 1 and 2 may show that \((\Delta G_{mic}^{\circ})\) value has been increased in (water-chitosan- toluene) system and this due to accumulation and formation of micelle.

**CONCLUSION**

In this study, chitosan was used as a cationic polysaccharide in the presence of DSS Gemini anionic surfactant. The conducted investigations showed that adaptability of surfactant and chitosan in (water-toluene) environment might be appropriately stable while CMC value was reduced from 0.002M to 0.0015M in the presence of 2mL of chitosan solution (4%). Improvement in thermodynamic parameters represents the optimal interaction among Gemini anionic surfactant and chitosan and it was followed by rising entropy. The results of findings in this research verify appropriate interaction among chitosan and anionic surfactant in both insoluble aqueous and organic environments and cosurfactant role of chitosan.

**REFERENCES**


**How to cite this article:** Fariborz A., Maryam T. A. Conductometric Investigation of the Interaction of Chitosan- Dioctyl Sulfosuccinate Surfactant in Water-Toluene Solution. Bull. Env. Pharmacol. Life Sci. 3 (2) 2014: 39-44