



ORIGINAL ARTICLE

Surface Properties of Chitosan Aqueous Solution in the Presence of Gemini Anionic Surfactant

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ABSTRACT

The present research examined the role of chitosan as a cationic polysaccharide adjacent to dioctyl sulfosuccinate as a Gemini anionic surfactant (insoluble in water) and measured the impact of chitosan on a surfactant-water-toluene system using conductometry, colorimetry, and viscometry. Surface tension, CMC, and thermodynamic parameters, including ΔG° , ΔS° , ΔH° , were determined. The effect of chitosan on the stability of the emulsion system was measured using the half-decay time. The growth and homogeneity of micelles in the aqueous and organic phases were investigated using scanning electron microscopy. The results indicate that, as chitosan is added to the system, the surface tension, CMC in the presence of anionic surfactant, and the chitosan solution in the insoluble phases of water-toluene decreased as the stability of the emulsion system increased. It was found that chitosan may be used as an effective co-surfactant for insoluble phases of a water-toluene-anionic surfactant.

Keywords: chitosan; dioctyl sulfosuccinate; critical micelle concentration; scanning electron microscopy;

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INTRODUCTION

The use of emulsifiers in the formation of micelles is especially important to decrease surface tension and increase the stability and emulsification properties in soluble systems. Some chitosans can decrease the critical micelle concentration (CMC) as co-surfactants. These chitosans, which may increase electrical conductivity in emulsions, can affect the CMC and be used in industry.

Gemini surfactants are more advantageous than current chitosan surfactants in many cases. These substances have more surface activity and their CMC rate is 10-100 times smaller than the CMC of current materials.[1-4] They are more useful in decreasing surface tension in common levels of oil-water. Micelles of active surfactants may take on geometric configurations under concentrations used to produce nanoparticles. For example, Gemini active surfactants are used to produce cubic nano-particles usually displaying further moisture properties and antibacterial activity.

Polysaccharides are natural polymeric coagulants widely used in industry. Foremost polysaccharides, such as chitosan and starch, have cationic properties. They are highly efficient and, in many cases, they have been used as substitutes for natural polymers. Cationic polyelectrolytes link directly with particles existing in suspension by electrostatic attraction, making them more effective than other types.[5-8] Payet et al was studied the emulsifying mechanism and its stability in a water-oil (paraffin) system in the presence of chitosan without adding a surfactant.[9] Sadosky et al studied the interaction with a polymer-surfactant and its effect on spherical concentration and reported on the absorption of polymers and surfactants onto solid surfaces on the stability of the polymer-surfactant and polymer-solid surface[10]

Ogawa examined properties of water-paraffin emulsions and stability of drops formed by multilayer lecithin-chitosan-pectin.[11] Bajaj reviewed the dispersion of castor oil in the aqueous phase and the stability of the emulsion system in the presence of chitosan.[12] Ariyaprakai reported on the impact of surfactant structure on micelle formation of petroleum emulsions in water at different weight percentages (1%, 2%) using light diffraction in water [13]. Kishk studied the inhibition of free radicals and antioxidant activity in polysaccharides. This study showed that *rhizobium meliloti* and *cordilin* might be useful as surfactants of an emulsion system and inhibitors of free radicals for petroleum [14].

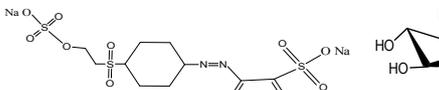
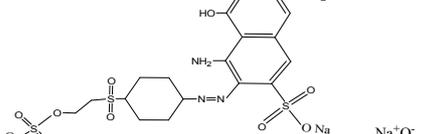
The reaction of chitosan and bovine lipid extract surfactant decreases surface tension and inhibits anesthesia in the lungs [15]. Catterjee et al. studied the absorption of Congo red color from aqueous solutions by chitosan hydrogel seeds stained with bromide tri-methyl. A review of absorbent isotherms reported that a decrease in pH increased absorption [16]. Sarkar indicated that an improvement in chitosan structure from the anionic surfactant sulfate-dodecyl sodium increased the efficiency of absorption of Zn (II), Ni(II), and Cu(II) ions in aqueous solution for absorbent Langmuir, Freundlich, and Temkins isotherms [17].

Aoki et al. studied the impact of environmental stress on the stability of an oil-water emulsion system including stabilized drops by multilayer membrane using an electro-motive force. The effect of sulfate-dodecyl sodium, chitosan, and chitosan-pectin was evaluated in an emulsion system [18]. Hiorth et al. measured the structural and dynamic properties of pectin and chitosan aqueous mixtures using turbidometric techniques, light diffraction, and small-angle neutron scattering [19].

Pei et al. studied the hydrophobic effects, electrostatic attraction, and hydrogen bonds on the formation of micelles in cationic and anionic Gemini surfactant mixtures in aqueous solutions [20]. Tiyaboonchai et al. investigated the easy and simple production of chitosan nano-particles as an appropriate drug-delivery system and indicated that the presence of chitosan nano-particles might increase the time of contact between the substrate and cellular membrane [21].

The application of chitosan amphiphilic derivatives and the lack of toxicity of these compounds were examined and reported by Aranaz [22]. Auzely studied the acetalization of chitosan and chitin, viscosity, CMC, surface properties, and surface tension in the presence of a surfactant using fluorescence spectrometry and light diffraction [23]. Zhao et al. studied the preparation, determination of structure, and crystallization of chitosan nano-fibers by separation of the solid-liquid phase [24]. Calero et al. reported on the viscoelastic behavior of chitosan aqueous solutions by measuring small amplitude oscillatory shear and tensile behavior, linear viscosity, and evaluated the surface properties of these solutions [25].

Table 1: Chemical structure and properties of the materials used in this study

Name and color index(C.I)	Structure	Molecular Weight
Chitosan		480000Da
R – BLACK – B		991.82g
DSS		444.56g

Mechanical mixtures in chitosan aqueous solutions were examined using dioctyl sulfosuccinate (DSS) anionic surfactant by Chovwatat et al. to investigate variations in chitosan using x-ray diffraction, thermogravimetric analysis, and Fourier transform infrared spectrometry [26].

The present study explored the surface properties of chitosan aqueous solutions and their interaction with Gemini anionic surfactant insoluble in water. DSS was explored in reverse micro-emulsions (water-toluene). The parameters of CMC surfactant, surface tension and behavior of a micro-emulsion system in before and after micelle formation, and thermodynamic parameters including enthalpy and surface entropy in the presence and absence of chitosan were investigated.

MATERIALS AND METHODS

Chitosan (99% purity) was purchased from Merck and was used after purification. Other chemical compounds were prepared according to Table 1. DSS was obtained from Sigma Inc. and anionic color R-Black-B from the Institute for Color and Technology (ICST) (Iran). A conductometer (Crison GLP 32) was utilized to measure electrical conductivity and to determine the point of CMC. The behavior of the

chitosan in aqueous solution at different concentrations was studied by UV-Vis spectrometry (CW009 Digital) to measure the wavelength at maximum absorption ($\lambda_{\max} = 597 \text{ nm}$). Scanning electron microscopy (SEM; KYKY Technology; EM 3200) was used to investigate the morphology and homogeneity of micelle size.

Distribution of chitosans between water-toluene phases

Half-decay time was used to determine the stability of the emulsion. The longer it takes for separation of the two phases, the more stable is the resulting emulsion in this system; therefore, the water-toluene system was utilized. First, Sol 1 to 3 were prepared and mixed thoroughly. Then the period of separation was measured using a chronometer.

- Sol 1: 2 ml DSS 2% + 1 ml distilled water + 2 ml toluene
- Sol 2: 2 ml DSS 1% + 1 ml distilled water + 2 ml toluene
- Sol 3: 2 ml DSS 0.5% + 1 ml distilled water + 2 ml toluene

Next, to examine the impact of the chitosan at the time of separation of the phases, 1 ml chitosan (4% vol) was added the solutions and the period of the phases were measured by chronometer.

Impact of chitosan on stability of emulsion system and CMC

Initially, solutions were prepared using several surfactant concentrations with volumes of 15 ml and their electrical conductivity was measured in the absence of chitosan. Different concentrations of chitosan solution (4%) (0.25 ml, 0.5 mL, 0.75 ml, 1 ml, and 2 ml) were added to the prepared solutions and their electric conductivity was measured and thermodynamic parameters were determined [27].

Determination of thermodynamic parameters by conductometry

The Gibbs free energy, enthalpy, and surface entropy were measured by conductometry and the CMC point was determined. The Gibbs free energy for standard micelle formation ($\Delta G^{\circ}_{\text{mic}}$) was computed as:

$$\Delta G^{\circ}_{\text{mic}} = -2.303RT(\log \text{CMC} - \log W) \quad (1)$$

where W is the molar concentration of water, that is 55.3 at 298K.

Variations in the standard entropy of micelle formation ($\Delta S^{\circ}_{\text{mic}}$) were calculated as:

$$\Delta S^{\circ} = -d(\Delta G^{\circ})/dT \quad (2)$$

The variation in the standard enthalpy of micelle formation was computed as:

$$\Delta G^{\circ}_{\text{mic}} = \Delta H^{\circ}_{\text{mic}} - T\Delta S^{\circ}_{\text{mic}} \quad (3)$$

Effect of chitosan on stability of water-toluene-chitosan system

Measurements of molar conductivity in the absence and presence of a chitosan was studied to review variations in CMC for a water-toluene system at ratios of (1:1) and (1:2). In this step, the surfactant concentration was 0.1 M and variations in the electrical conductivity of the solution over time were recorded. All measurements were done at a fixed temperature of 298K [27].

Determination of thermodynamic parameters (surface properties) using drip technique

To characterize thermodynamic parameters of surface tension, surface enthalpy, and surface entropy, the drip method was adapted for temperatures of 298, 303, and 323 K. The weight of 20 drops of distilled water was measured at these temperatures. The weight of 20 drops of an unknown sample was used for a control for water surface tension and:

$$\frac{m_1}{V_1} = \frac{m_2}{V_2} = \frac{W_1}{W_2} \quad (4)$$

where γ_1 is water surface tension; γ_2 is unknown surface tension; $m_1 \text{ g}$ is the weight of distilled water; $m_2 \text{ g}$ is the weight of the unknown sample. Surface enthalpy and surface entropy were calculated as [28-31]:

$$\gamma = G^s = H^s - TS^s \quad (5)$$

Determination of CMC by absorption technique

In this technique, distilled water was initially added to 0.0148 g of cationic color R-Black-B to reach a volume of 100 ml. As shown in Tables 2 and 3, 10 drops of this solution were added to the prepared solutions and the variation in absorption in surfactant at different concentrations without chitosan and in the presence of 0.75 ml, 0.5 ml, and 0.25 ml chitosan were measured. Color absorption was measured using UV-Vis spectrometry at the color absorption wavelength ($\lambda_{\max} = 597 \text{ nm}$) at 298K [32]. Micelle size morphology by SEM

Sol 2 was prepared in two cuvettes as described in Section 2.2 and then, 0.25 ml of chitosan was added to one cuvette; the solutions were stirred well and allowed to separate. SEM was used to records images of the isolated organic and aqueous phases and the condition of the micelles was examined.

Table 2: Half-decay time for DSS in the absence of chitosan (T = 298K)

(water.DSS) (g.mL)	% 0.5	%1	%2
T (min)	3:30	5:37	7:50

Table 3: Half-decay time for DSS in the presence of 1 ml chitosan (4%; T = 298K)

(water.DSS) (g.mL)	% 0.5	%1	%2
τ (min)	8:10	9:53	12:15

CMC measurement by viscometry

DSS surfactant is soluble in ethanol, so 10 ml ethanol solvent was poured into the viscometer and the period of flow was measured using a chronometer.

Next, the viscometer was washed and dried and the period of flow was measured for the solutions prepared according to Tables 2 and 3 in the absence of a chitosan. Chitosan was then added to the prepared solutions in concentrations of 0.25 ml, 0.5 ml, and 0.75 ml and the flow rate for each was measured. The relative viscosity (η_r) was calculated and a diagram of relative viscosity was created using:

$$\eta_r = \eta / \eta^0 = t \cdot \rho / t^0 \rho^0 \quad (6)$$

where η^0 denotes solvent viscosity; η is the viscosity of a given solution; t is flow time of the solution; t^0 is the flow time of the solvent; ρ is the density of the solution, and ρ^0 is the density of the solvent[33].

RESULTS AND DISCUSSION**Chitosan distribution for two-phase water-toluene separation**

To determine the stability of the emulsion, measurement of the half-decay time was adapted for a longer period of separation where the emulsion is more stable. The results of half-decay time in the absence and presence of a chitosan-DSS surfactant at 298K W were shown in Table2, 3.

The results show that:

$\tau_{\frac{1}{2}} \text{ min (DSS 2\% + 1 ml chitosan (4\%))} > \tau_{\frac{1}{2}} \text{ (DSS 1\% + 1 ml chitosan (4\%))} > \tau_{\frac{1}{2}} \text{ (DSS 0.5\% + 1 ml chitosan (4\%))} > \tau_{\frac{1}{2}} \text{ (DSS 2\%)} > \tau_{\frac{1}{2}} \text{ (DSS 1\%)} > \tau_{\frac{1}{2}} \text{ (DSS 0.5\%)}.$

These results indicate that chitosan plays an appropriate and intensifying emulsification role in the presence of Gemini anionic surfactant.

Effect of chitosan on stability of emulsion system and CMC

The results show that, as the chitosan increased from 0.25 ml to 2 ml, electrical conductivity increased from 345 μS to 440 μS and CMC decreased from 0.002 M to 0.0015 M. This was caused by the increased micelle accumulation at the CMC point and decreased surface tension as shown in (Fig. 1).

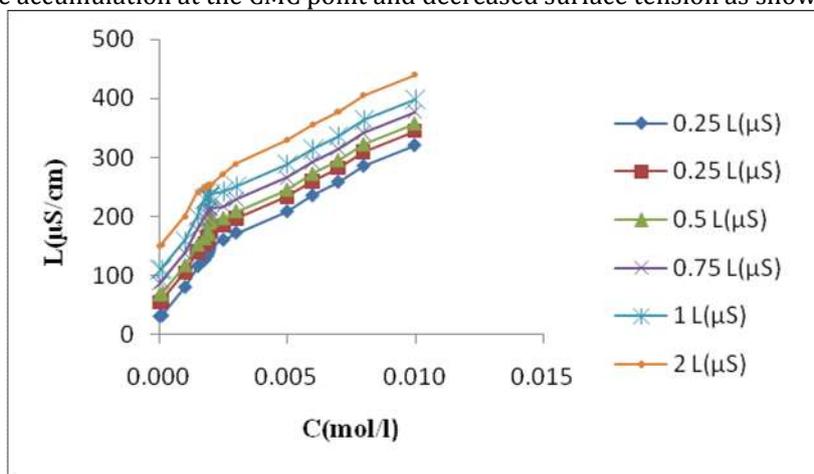


Fig 1: Total variations curve for DSS electrical conductivity in water- chitosan system in the presence of 0.25 ml to 2 ml, chitosan 4% and 0.1 M DSS (T = 298K).

Effect of chitosan on stability of the water-toluene-chitosan system

To investigate the effect of the chitosan in organic solvent and on CMC, electrical conductivity was measured in the presence and absence of the chitosan (water-toluene: 1:2; water-toluene: 1:1). Solutions of water-toluene-surfactant were prepared and their electrical conductivity was measured. The surfactant concentration was 0.1 M and the chitosan concentration was 4% for all phases. Chitosan solution was then added at volumes of 1 ml, 2 ml, 0.25 ml, 0.5 ml, and 0.75 ml and the electrical conductivity was measured. A curve of the variations was drawn based on concentration density. (Fig. 2) indicate that electrical conductivity decreased in the presence of toluene organic solvent and CMC increased from 0.002 M in the absence of organic solvent to 0.003 M in the presence of toluene. An increasing trend for CMC was observed in the presence of chitosan. Because chitosan is insoluble in

toluene, the repulsion force increased between the charged groups on surface of the micelles that demonstrated the destructive role of toluene as an insoluble solvent.

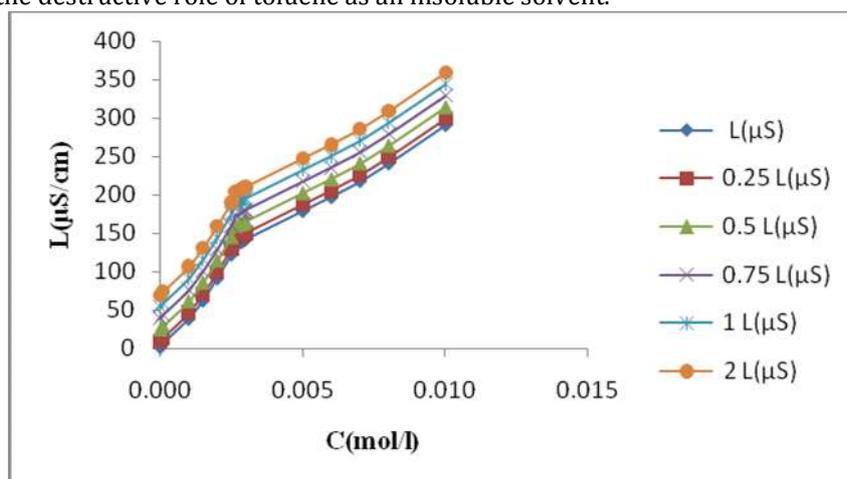


Fig 2: Total variations curve for DSS electrical conductivity in water-toluene: 1:2 system in the presence of 0.25 ml to 2 ml, chitosan 4% and 0.1 M DSS (T = 298K).

Thermodynamic parameters for water-chitosan system

Table 4 results indicate that, in all cases, ΔG°_{mic} was negative and increased in negativity as the chitosan increased. This may represent better accumulation and optimal micelle formation. ΔS°_{mic} increased and positivity increased as the chitosan increased, also as a result of increased micelle accumulation. Table 5 shows the thermodynamic parameters for DSS in the absence and presence of 4% chitosan (T = 298K). A comparison of the results in Tables 4 and 5 show that ΔG°_{mic} increased in the water-chitosan-toluene system from the accumulation and formation of micelles.

Table 4: Thermodynamic parameters for DSS in the absence and presence of 4% chitosan at T = 298K in a water-toluene-chitosan system.

	V_{crs} (mL)	CMC (mol dm ⁻³)	$-\Delta G^{\circ}_{mic}$ (J mol ⁻¹)	ΔS°_{mic} (JK ⁻¹ mol ⁻¹)	ΔH°_{mic} (J mol ⁻¹)
1	0	0.00200	25356	85.05	1.66
2	0.25	0.00197	25397	85.18	-0.58
3	0.5	0.00194	25437	85.32	1.16
4	0.75	0.00190	25477	85.45	-0.08
5	1	0.00176	25666	86.09	1.73
6	2	0.00150	26070	87.44	0.24

No	V_{crs} (mL)	CMC (mol dm ⁻³)	$-\Delta G^{\circ}_{mic}$ (J mol ⁻¹)	ΔS°_{mic} (JK ⁻¹ mol ⁻¹)	ΔH°_{mic} (J mol ⁻¹)
1	0	0.00300	24351	81.67	-1.0895
2	0.25	0.00295	24392	81.81	-0.3485
3	0.5	0.00290	24432	81.95	1.3925
4	0.75	0.00286	24472	82.08	0.152
5	1	0.00281	24511	82.21	-0.0885
6	2	0.00265	24661	82.71	-1.0135

Table 5: Thermodynamic parameters for DSS in the absence and presence of 4% chitosan (T = 298K).

Thermodynamic surface properties from drip method

Surface properties were measured for the emulsifier at DSS = 1%; chitosan = 4%; T = 298, 303, and 323 K. The Gibbs surface free energy (unknown surface tension) was derived for the aqueous and organic phases at 298.15 K, 303.15 K, and 323.15 K using Eqs. (3) and (4). The results indicate that, as temperature increased from 298.15 K to 323.15 K, surface tension decreased in the absence and presence of the chitosan in both phases, since entropy increased as the temperature of the interaction between the two materials increased, which further decreased surface tension.

After determination of surface tension, surface thermodynamic functions (surface enthalpy and surface entropy) are identified with using Eqs. (3) and (4). Variations in surface tension by temperature and determination of the quadratic line function were diagrammed using Eqs. (3) to (5).

Table 6 shows that an increase in temperature in the organic and aqueous phases in the presence of DSS surfactant decreased surface tension. An increase in temperature may increase the interaction between surfactants; increasing the temperature may intensify this effect because the surfactant decreases surface tension between the two insoluble phases. (Fig 3)

	DSS									
	$\gamma(298.15\text{ K})$ (J.mol)	$\gamma(298.15\text{ K})+$ In the presence of chitisan (J.mol)	$\gamma(303.15\text{ K})$ (J.mol)	$\gamma(303.15\text{ K})+$ In the presence of chitisan (J.mol)	$\gamma(323.15\text{ K})$ (J.mol)	$\gamma(323.15\text{ K})+$ In the presence of chitisan (J.mol)	$H^s(\text{J})$	H^s	$S^s(\text{J.K})$	S^s
Organic phases	28.04	27.43	27.38	26.71	25.78	24.59	53.90	60.60	0.087	0.111
Water phases	26.82	25.66	26.71	25.33	26.38	24.65	38.21	91.12	0.0177	0.038

Table 6: DSS surface parameters for organic and aqueous phases in the presence and absence of 4% chitosan measured by drip (T= 298, 303, 323 K).

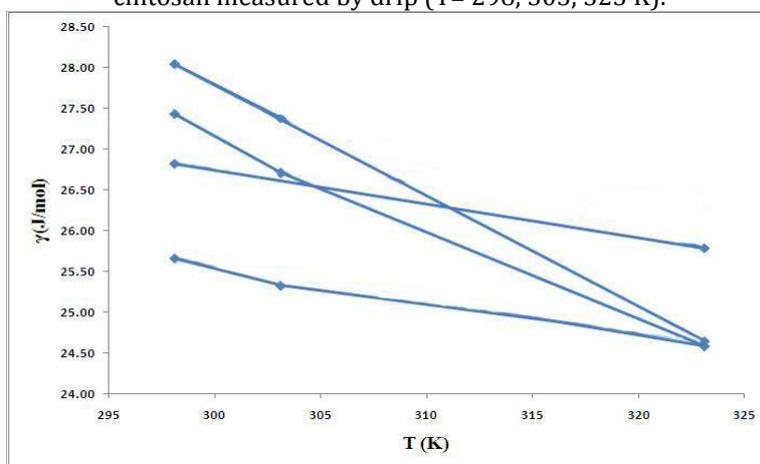


Fig. 3: Total variations curve for Surface tension in the water-toluene: 1:2 systems in the presence of chitosan 4% in water-toluene.

CMC by UV spectrometry

The results show that, absorption increased and reached a maximum, and then decreased slightly and finally increased. It was follow by a concentration of color and surfactant molecules in the pre-micellar region. After CMC, absorption value decreased as the resultant of dissolving of color molecules into the micelles. (Fig 4)

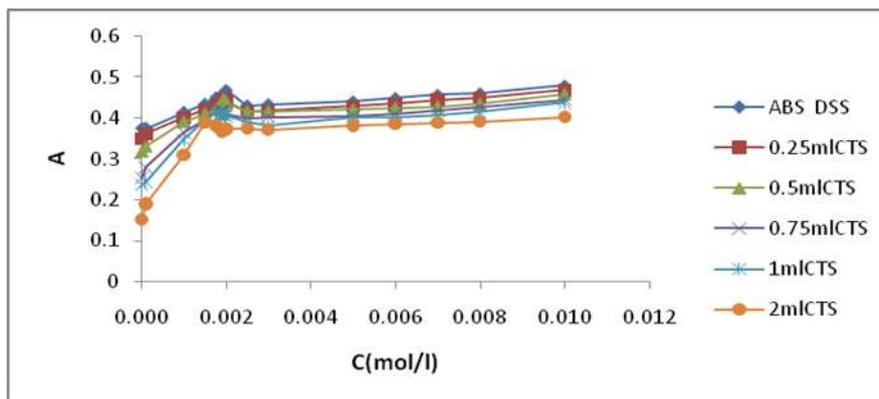


Fig 4: Total variations in absorption curve in water-toluene: 1:2 system in the presence of 0.25 ml to 2 ml, chitosan 4% and 0.1 M DSS ($T = 298\text{K}$).

Size and morphology of micelles using SEM

The stability and homogeneity of the emulsion systems in the absence and presence of a chitosan were investigated using SEM. Figs. 5 and 6 show the images of the organic and aqueous phases and micelle variations.

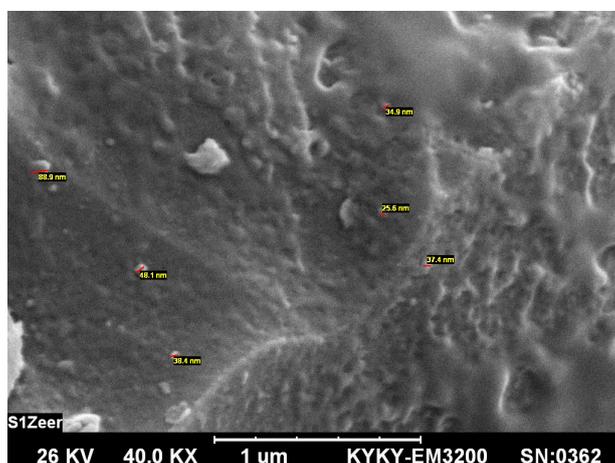


Fig 5: SEM image of aqueous water-toluene system in the absence of chitosan (40 kx).

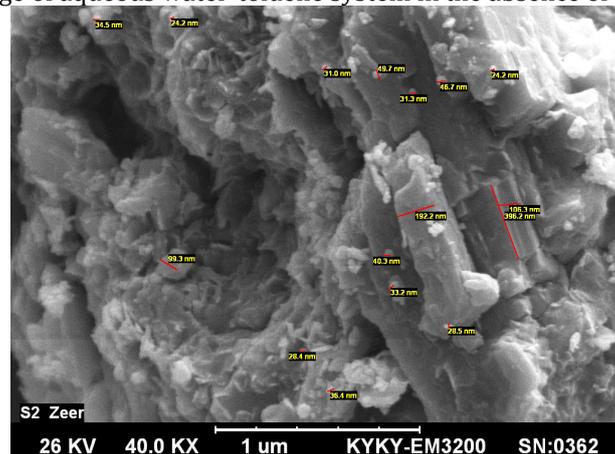


Fig 6: SEM image of aqueous water-toluene system in the presence of 4% chitosan (40 kx).

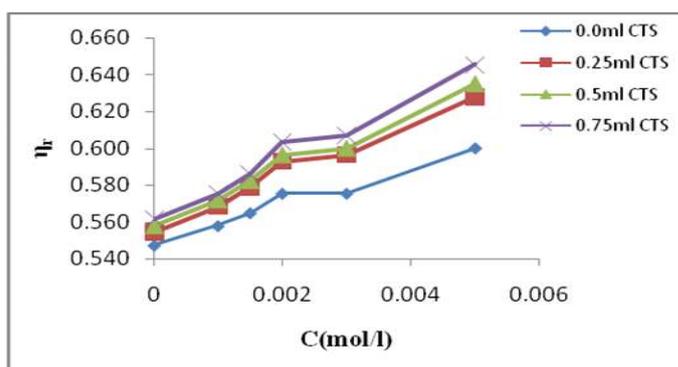
The results indicate that the size of the micelles increased in the presence of chitosan because of polymer-surfactant interaction in the aqueous phase that increased the rate of formation of the micelles. This verifies the effect of chitosan on increasing the stability and homogeneity of the system in the aqueous phase; the size and diameter of the particles increased. This was not observed for the organic phase.

Relative viscosity measured by viscometry

Variations in viscosity in the presence and absence of a chitosan were measured by viscometry as described in Section 2.9 (Table 7). (Fig. 7) show the relative viscosity (η_r) based on concentration.

Table 7: Variations in relative viscosity in the absence and presence of chitosan in the water-chitosan system at T = 298K (DSS = 0.1 M).

No	C(mol.L) [CTS]	(η_r)	(η_r)	(η_r)	(η_r)
		0.0mL	0.25mL	0.5mL	0.75mL
1	0.00001	0.547	0.554	0.558	0.561
2	0.001	0.558	0.568	0.572	0.575
3	0.0015	0.565	0.579	0.582	0.586
4	0.002	0.575	0.593	0.596	0.604
5	0.003	0.575	0.596	0.600	0.607
6	0.005	0.600	0.628	0.635	0.646

**Fig 7:** Total variations curve for relative viscosity in water- chitosan system in the presence of 0.25 ml to 0.75 ml, chitosan 4% and 0.1 M DSS (T = 298K).

The results in Table 7 and Fig. 7 show that, as chitosan increased from 0.25 ml to 0.75 ml, relative viscosity at the CMC point increased from 0.593 to 0.604. This created a latticework and formation of a polymer-surfactant complex, increasing viscosity. The maximum value occurred at the CMC point. The formation of stable drops at the CMC first fixed viscosity and then increased viscosity at higher concentrations, as indicated by the SEM images.

CONCLUSION

In this study, chitosan was used as a cationic polysaccharide in the presence of DSS Gemini anionic surfactants. The investigation showed that the surfactant and chitosan in a water-toluene environment are appropriately stable while the CMC decreased from 0.002 M to 0.0015 M in the presence of 2 ml 4% chitosan solution.

The half-decay time (isolation of organic-aqueous phases) increased approximately 2.5 times in the presence of chitosan solution. The improvement in thermodynamic parameters represents an optimal interaction between Gemini anionic surfactant and chitosan, followed by increasing entropy.

Application of color R-Black-B to CMC measurement using UV spectrometry showed appropriate results and was a suitable and safe method. The colors having a diazo structure could be used to determine the CMC in emulsion systems.

Viscometry can be utilized with selection of an appropriate fluidity time (Ostwald and Ubbelohd viscometer) as a simple method to determine CMC. The findings in this study verify appropriate interaction between chitosan and anionic surfactant in the insoluble aqueous and organic environments and of the co-surfactant role of chitosan. This confirms that chitosan can be used as a co-surfactant in textiles, color manufacturing, and pharmaceutical industries.

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