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Original Research

Determination of the critical micelle concentration of 12-4-12 gemini cationic surfactant in the presence of methacrylamide by different methods

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ABSTRACT:

In this study, after synthesizing gemini cationic surfactant 12-4-12, it's interaction with methacrylamide by conductometry, viscommetry and UV-Vis spectroscopy were investigated. The results showed that, in the presence of methacrylamide, the Critical Micelle Concentration (CMC) was decreased. Thermodynamic parameters such as enthalpy, entropy and surface free gibbs energy at 298 K was calculated. The results of viscommetry and colorimetry confirmed that these techniques can be used as drastic and simple methods for CMC determination.

Keywords:

Surfactant , critical micelle concentration, thermodynamic parameters,

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Several applications like detergents (Cutler and Kissa, 1987), paint (Stoye, 1993), cosmetics (Reiger, 1985), pesticides (Becker, 1985), fibers (Jakobi and Loehr, 1987) and food (Friberg, 1976) were utilized as surfactants. It is more economically beneficial to use mixed surfactant systems. The mixture of ionic-nonionic surfactants may indicate reasonable synergism (Rosen and Hua, 1982). The cationic-anionic surfactants may also cause more synergistic effects like reductions in CMC and surface tension (Lucassen-Reynders *et al.,* 1981). The effects of systems which form surface complexes of polymer-surfactant monomers type are the same as mixtures interacting effects (Penfold *et al.,* 2006) In this research, synergistic effect of methacrylamide / 12-4-12 gemini cationic surfactant was studied using different methods at 298^0C.

MATERIALS AND METHODS

Methacrylamide as a monomer was obtained from Merck, Germany and it was purified with chloroform for further uses. Dimethyl dodecyl amine, ethyl acetate, 1,4 –dibromo butane and ethanol from Sigma Aldrich and Fluka were used. R-Black-B for the tests was prepared from the Institute for Color and Technology (ICST) (Iran). CMC determination was performed using Crison GLP-32 conductometer, CW 009 UV-Vis

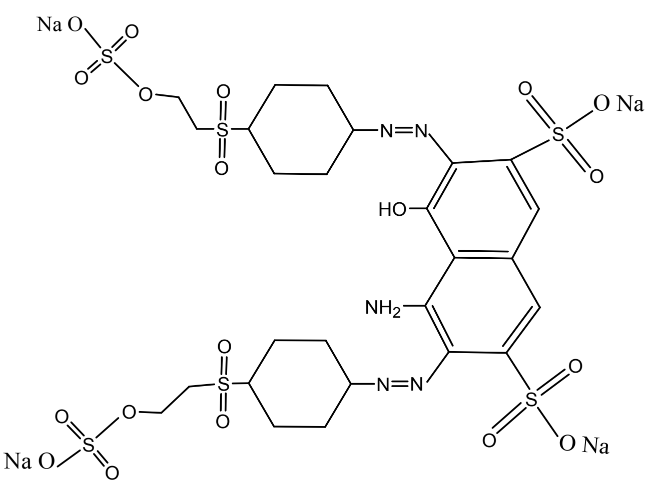

Figure 1. Structure of dye (R-Black-B)

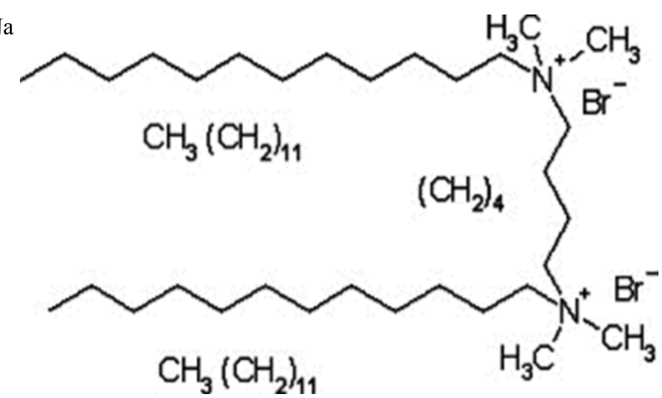

Figure 2. Structure of 12-4-12 gemini cationic surfactant

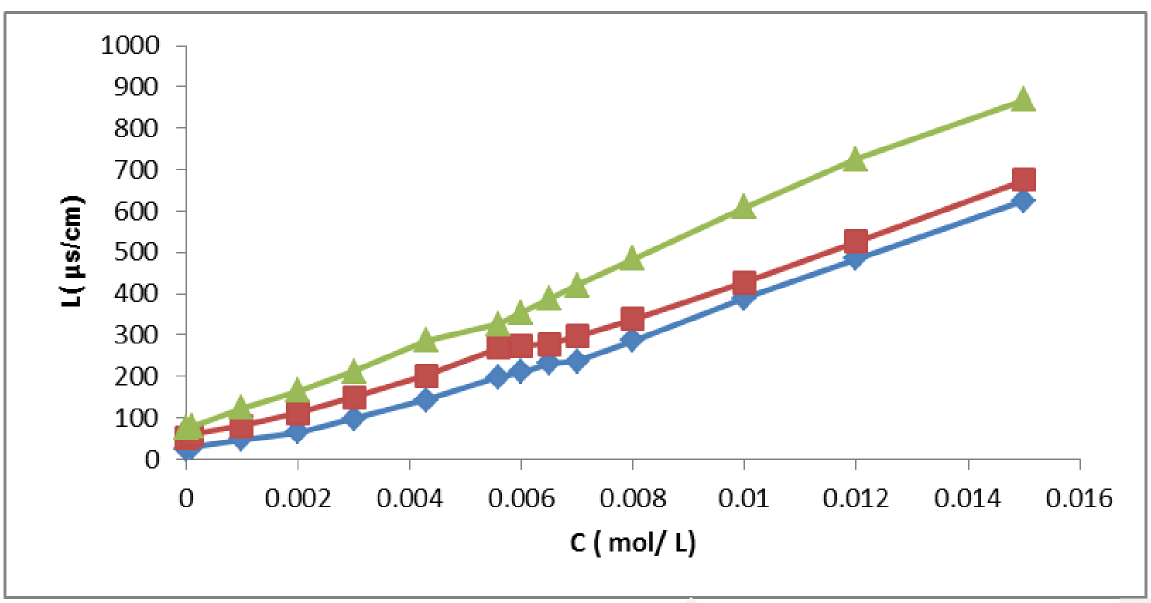

Figure 4. Variation of the absorption of R-black B_ surfactant in the absence and the presence of 0.5 g and 1.0 g monomer

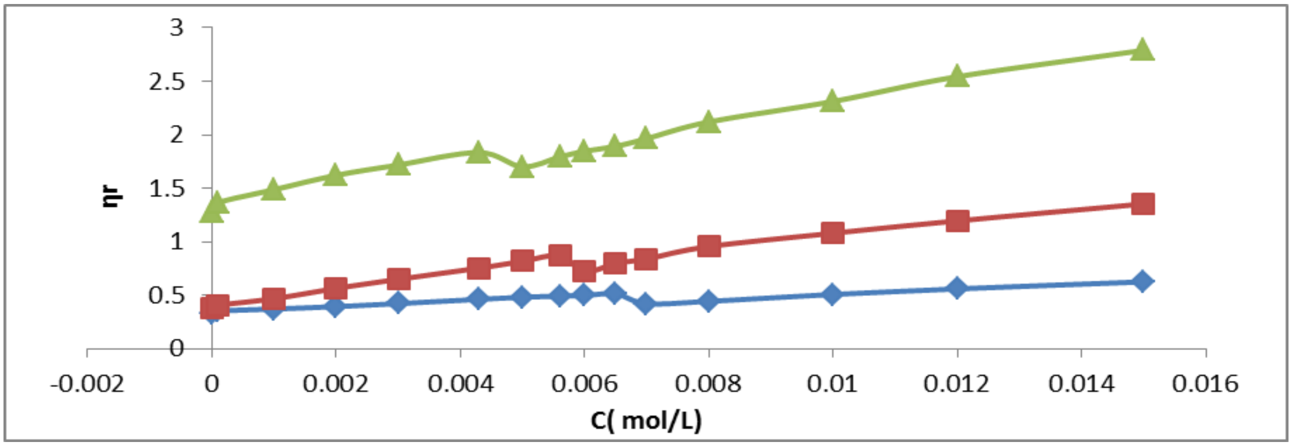

Figure 4. Variation of the absorption of R-black B_ surfactant in the absence and the presence of 0.5 g and 1.0 g monomer

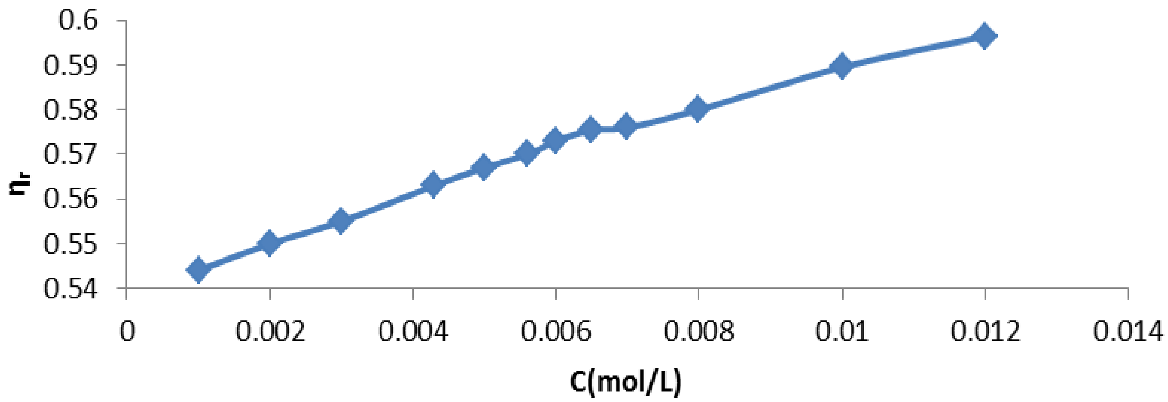

Figure 5. Variation of the relative viscosity vs concentration in the absence of monomer

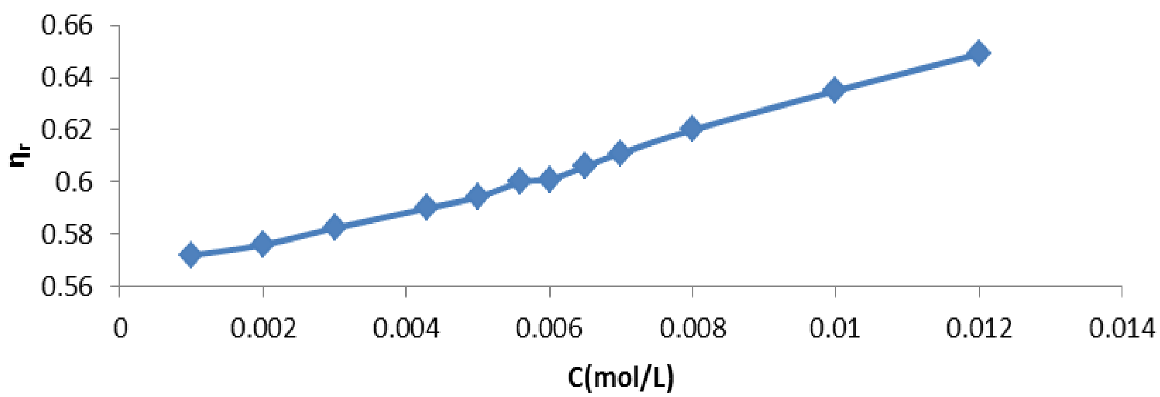

Figure 6. Variation of the relative viscosity vs concentration in the presence of 0.5 g monomer

spectrophotometer and Ostwald viscometer.

Synthesis of gemini cationic surfactant

At the first step, 44 mmol dimethyl dodecyl amine dissolved in 30 ml ethanol, 20 mmol 1,4 dibromo butane dissolved in 20 ml ethanol were added to the containers, carefully. Distillation of all containers took 24 hours. After removing ethanol by distillation at the reduced pressure, the oily substance was recrystallized in the mixture of ethanol/ethyl acetate.

Determination of CMC by conductometry

The changes of electrical conductivity vs surfactant concentration was measured and plotted. The

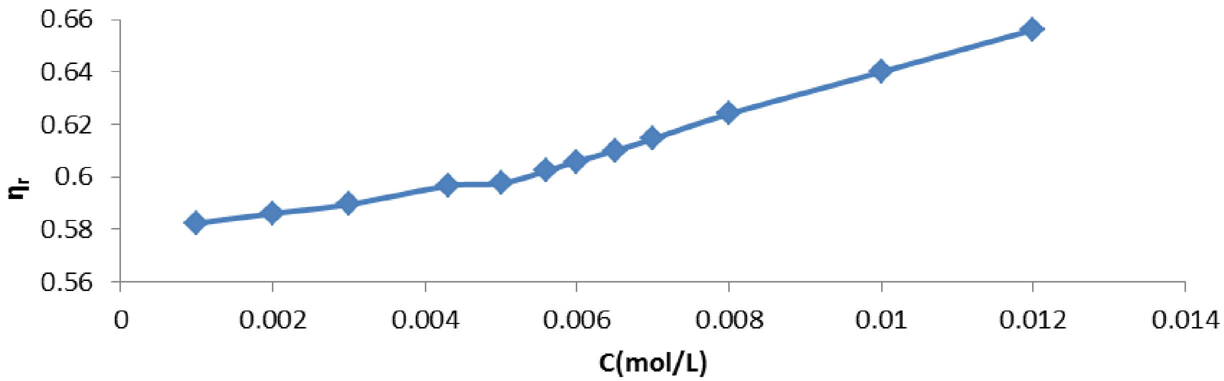

Figure 7. Variation of the relative viscosity vs concentration in the presence of 1.0 g monomer

Table 1. Thermodynamic parameters for surfactant in the absence and presence of methacrylamide at 298K

Surfactant	Monomer(g)	CMC(mol/L)	$-\Delta G_{mic}$(kJ/mol)	ΔS_{mic}(kJ/K.mol)	ΔH_{mic}(kJ/mol)
	0	0.0065	22.42	0.0750	-0.059
	0.50	0.0056	22.80	0.0765	-0.008
	0.75	0.0050	23.07	0.0770	-0.113
	1.00	0.0043	23.44	0.0780	-0.185

Determination of CMC by colorimetry

Distilled water was added to 0.0148 g of dye (R-Black-B) to reach a volume of 100 ml. 10 drops of this solution was added to the solutions which contains surfactants. The color absorption was evaluated at different concentration of surfactants in the color absorption wavelength (597 nm) at 298 K (Rosen, 2004).

Determination of CMC by viscometry

Different surfactant concentration was prepared and the flow time was determined by an Ostwald viscometer in the absence and presence of 0.5 g and 1.0 g methacrylamide (Wang *et al.*, 2204).

$$\eta_r=\eta/\eta^0=t\ .\rho\ /t^0\ \rho^\circ \quad (1)$$

In the above equation 'η°' denotes solvent viscosity; 'η' is the viscosity of a given solution; '*t*' is the flow time of the solution; '*t*°' is the flow time of the solvent; 'ρ' is the density of the solution, and 'ρ°' is the density of the solvent.

Determination of thermodynamic parameters

Thermodynamic parameters like gibbs free energy, enthalpy and entropy were estimated using the equations below: (Rosen, 2004).

$$\Delta G^\circ_{mic} = -2.303RT(\log CMC - \log W) \quad (2)$$

$$\Delta S^0 = -\, d\,(\Delta G^0)/\,dT \quad (3)$$

$$\Delta G^\circ_{mic} = \Delta H^\circ_{mic} - T\Delta S^\circ_{mic} \quad (4)$$

where, *W* is the molar concentration of water, that is 55.4 mol/L at 298 K.

RESULTS AND DISCUSSION

As indicated in the Figs 3-7, it can be seen that, with an increase of monomer concentration from 0.0 to 1.0 g, the CMC values decreased. CMC point in the absence of monomer was recorded 0.0065mol/L and in the presence of 0.5 g and 1.0 g were determined 0.0056 and 0.0043 mol/L . In addition, the results of this research revealed that viscometry and colorimetry can be used as simple and drastic methods for CMC determination. It seems that, at the CMC point, the complexation of surfactant – monomer occurred and then at the higher concentration due to dissolving of dye molecules into the micelles a decrease was observed . Our finding showed that by choosing the suitable viscometer, the CMC values can be determined simply. On the other hand, the thermodynamic parameters were improved in the presence of monomer (Table 1). Consequently, this monomer can be used as a suit co-surfactant in aqueous solutions which contain gemini cationic surfactant. According to increase of ΔS, the interaction between surfactant and monomer has also increased and this reaction is exothermic.

CONCLUSION

In this research, methacrylamide as monomer was used as an anionic co-surfactant in the presence of 12-4-12 gemini cationic surfactant. The CMC values decreased from 0.0065 to 0.0043 mol/L in the absence and presence of 1.0 g methacrylamide. The thermodynamic parameters were improved and indicated that the interaction of methacrylamide- surfactant was noticeable.

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