



ORIGINAL ARTICLE

Interaction of poly methyl methacrylate with cationic and anionic emulsifiers in emulsion system

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ABSTRACT

The application areas of micelle-forming emulsifiers depend on surface properties of their aqueous solutions, and emulsifying and stabilizing abilities. In the present study, the effect of poly methyl methacrylate (PMMA) on the stability of emulsion system (water-toluene) in the presence of sodium dodecyl sulphate (SDS) and dodecyl trimethyl ammonium bromide (DTAB) was studied. Also, the homogeneity of micelles in aqueous and organic phases was investigated by scanning electron microscopy (SEM). Results showed that, as PMMA was added to the water-toluene-SDS system, the critical micelle concentration and surface tension was decreased. But in the presence of DTAB any changing did not observed. The experimental data indicate that, micellisation is more favourable at the higher polymer and SDS quantity.

Keywords: *Methyl methacrylate, critical micelle concentration, emulsion*

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INTRODUCTION

Polymers and surfactants are extensively used in various industries such as, paints, detergents, pharmacology, cosmetics and etc. Usually, polymers cause improving the interfacial properties of solution compared to the individual surfactants. Many researchers believe that, in aqueous solution, the surfactant adsorbed on the polymer and formed a complex of polyelectrotype character. Generally, the solubilisation of this complex is better than individual surfactant. [1] It has been reported that the interaction between uncharged water soluble polymer is so easier with many facile anionic surfactants. [2-6] In comparison to anionic surfactants, these polymers have been associated weakly with cationic surfactants.[7,8] Interaction of water insoluble PMMA with anionic and cationic surfactants in emulsion (water-toluene) system have not been reported. For this aim, surface properties of PMMA in aqueous solutions and its interaction with SDS and DTAB in water – toluene system has been studied. Likewise, some parameters like CMC, surface tension, thermodynamic parameters (surface enthalpy, surface entropy, surface Gibbs energy) have been determined by conductometry.

MATERIALS AND METHODS

MMA (Merck-Germany) as monomer has been used after distillation under reduced pressure in inert atmosphere (29.3mmHg,370K).SDS and toluene were purchased from Merck.co(Germany) and DTAB were provided from Aldrich.co (England). They were high purity grade and used without further purification. Anionic color (R-Black-B) was purchased Institute for Color and Technology (ICST) (Iran). Determination of the CMC was fulfilled by Crison-GLP 32 conductometer. For this aim, the variation of the specific conductivity versus surfactant concentration was plotted. The CMC of the solution was the break point of the curve. UV-Vis spectrometry was used for determination of CMC. For this aim, the measurements were accomplished in the presence of 10 drops of dye solution (0.003M) and 0.75mL MMA at the color absorption wavelength ($\lambda_{max} = 597 \text{ nm}$) at 298K.[15,16] The relative viscosity (η_r) of solutions were determined by Ostwald viscometer at 298K. For this purpose, 10 mL doubly distilled water and solutions were poured in viscometer, and the period of flowing was measured, respectively. Mean value of 4 measurement was recorded as time of flowing. According to the following equation the relative viscosity was determined:

$$\eta_r = \eta / \eta^0 = t \cdot \rho / t^0 \rho^0$$

Where, η° and η are the solvent and the solution viscosity, respectively. t is 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. [9] The stability and homogeneity of the emulsion systems in the absence and presence of MMA were investigated using SEM (KYKY-EM 3200). Thermodynamic parameters like surface tension, surface enthalpy and surface entropy were determined by the use of dripping method. For this aim, the weight of the 20 drops of distilled water was measured. Then the weight of 20 drops of unknown solution was determined. These experiments for both steps were fulfilled at 298, 303 and 328K. By the help of the following equation the surface tension of unknown sample was calculated:

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1 g}{m_2 g} = \frac{W_1}{W_2}$$

$$\gamma = G^S = H^S - TS^S$$

Where, γ_1 is water surface tension; γ_2 is unknown surface tension; $m_1 g$ is the weight of distilled water; $m_2 g$ is the weight of the unknown sample. Surface enthalpy and surface entropy were calculated as. [10-14] By means of the following equations the thermodynamic parameters were determined:

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

$$\Delta S^\circ = -d(\Delta G^\circ) / dT$$

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

Where, w is the water concentration at 298K (55.3M).

RESULTS AND DISCUSSION

As shown in Figs1-12. The CMC values in the presence of 0.75 mL monomer and SDS showed a decreasing from 0.0086M to 0.0046M. But, in the presence of DTAB any changing did not observe. This is related to the formation of the polymer-SDS complex. The presence of MMA in the mixture of water-toluene-SDS showed more decreasing in the CMC point. This is attributed to the solubility of PMMA in toluene. Therefore, the presence of PMMA in this solution is optimum. The results of UV-Vis spectroscopy showed that, in the presence of 0.75 mL MMA and 10 drops of dye solution (0.003M), the absorption was increased and then it was reached to the maximum value and then a little reduction was observed Figs 14-16.

The results of CMC that derived by means of absorption technique, had good agreement with the given results from CMC in water-toluene-SDS system derived by conductometry method. As shown in Figs17-20 the plot of η_r versus concentration was drawn. At the CMC point, η_r showed a minimum value. This is related to the formation of stable drops and complexation. The micrographs taken from SEM confirm this issue. The SEM micrographs of both phases(water and toluene) in the absence and presence of 1 mL MMA showed that the stability, homogeneity and sizes of stable drops, especially in the organic phase was improved. This fact, identify that the role of MMA in the water-toluene-SDS as an optimum co-surfactant. With an increase at temperature from 298K to 323K, surface tensions in both phases have been decreased. Results are presented in Figs25-32.

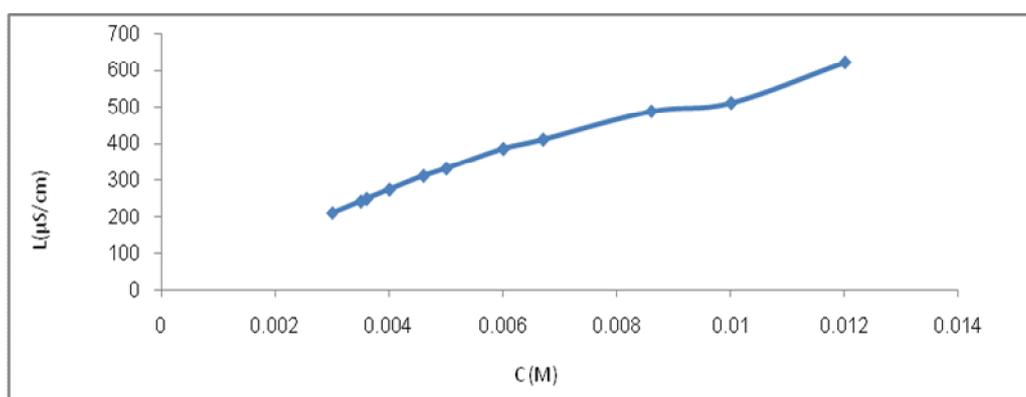


Fig1.SDS electrical conductivity in the absence of MMA (CMC=0.0086M, T=298K)

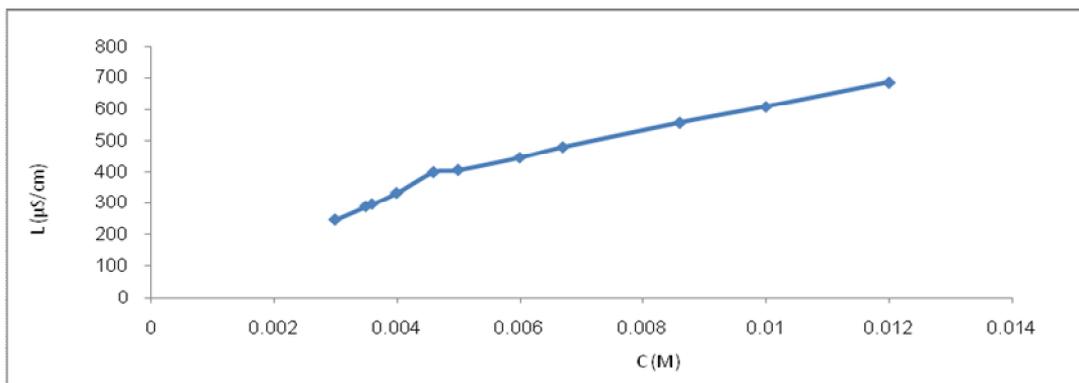


Fig2.SDS electrical conductivity in the presence of 0.75mL MMA (CMC=0.0046M, T=298K)

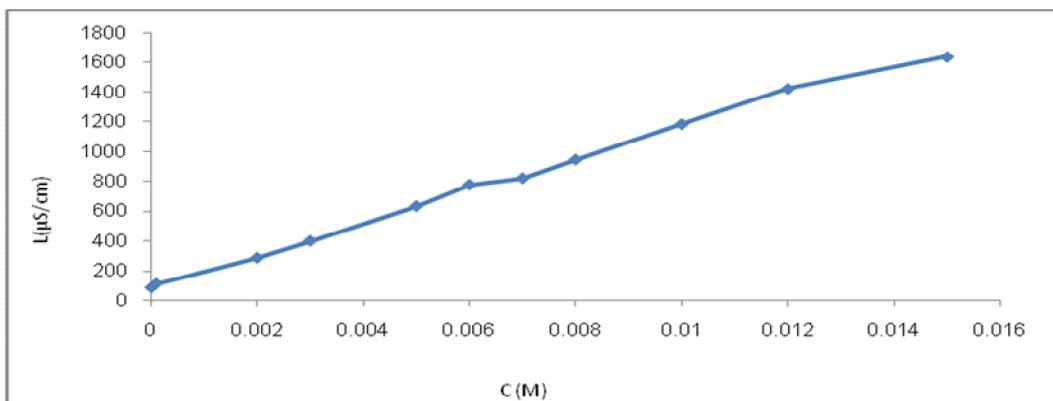


Fig3. DTAB electrical conductivity in the absence of MMA (CMC=0.0006M, T=298K)

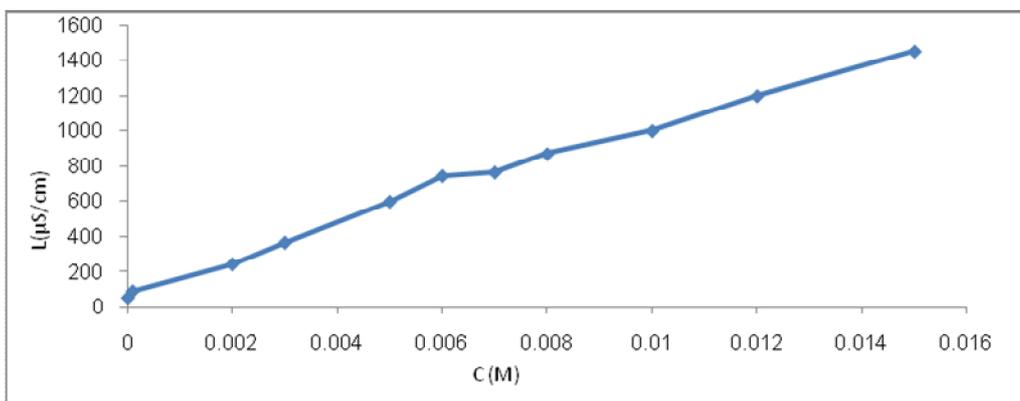


Fig4. DTAB electrical conductivity in the presence of 0.75 mL MMA (CMC=0.006 M, T=298K)

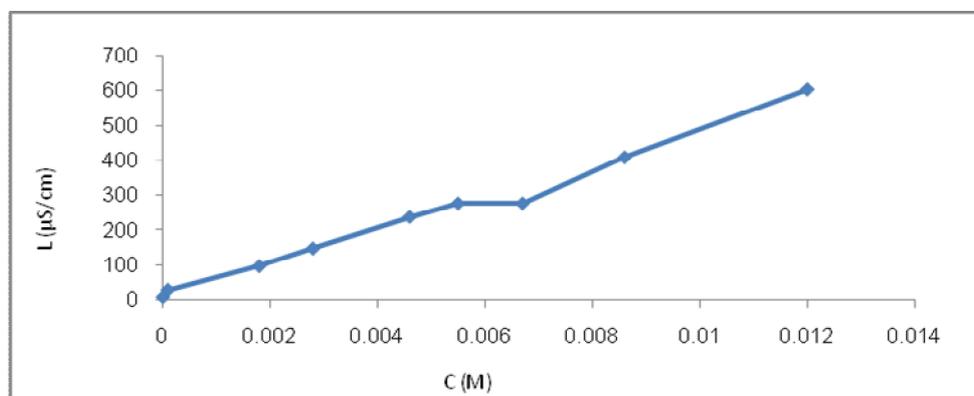


Fig5. SDS electrical conductivity in the absence of MMA (T/W=2/1 ,CMC=0.0055M,T=298K)

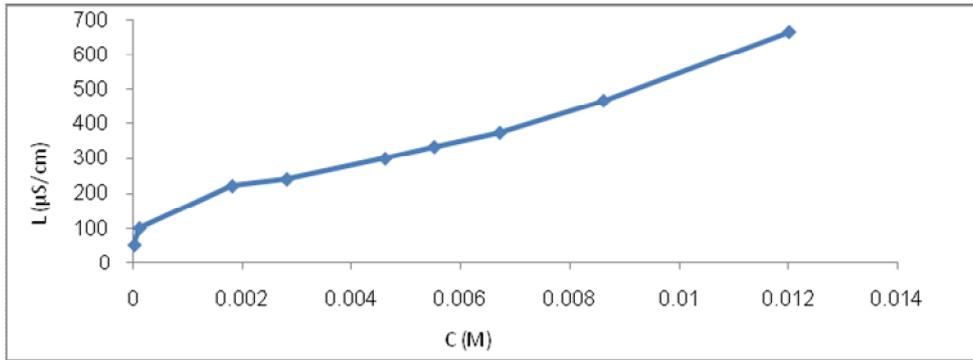
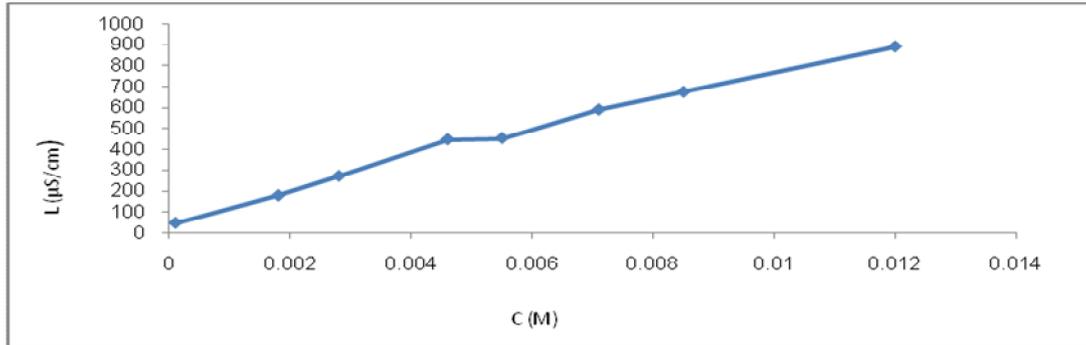


Fig 6. SDS electrical conductivity in the presence of 0.75ml MMA(T/W=2/1,CMC=0.0018M



Conductivity in the absence of MMA(T/W=2/1,CMC=0.0046M,T=298K) Fig7.DTAB electrical

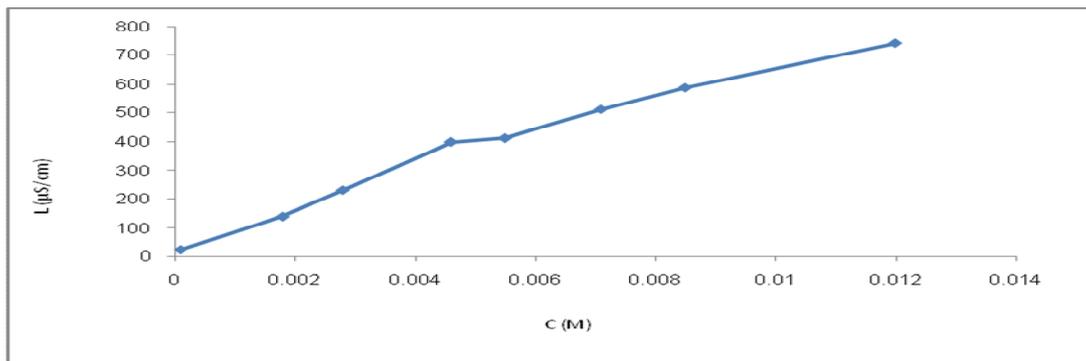


Fig8.DTAB electrical conductivity in the presence of 0.75ml MMA (T/W=2/1,CMC=0.0046M,T=298K)

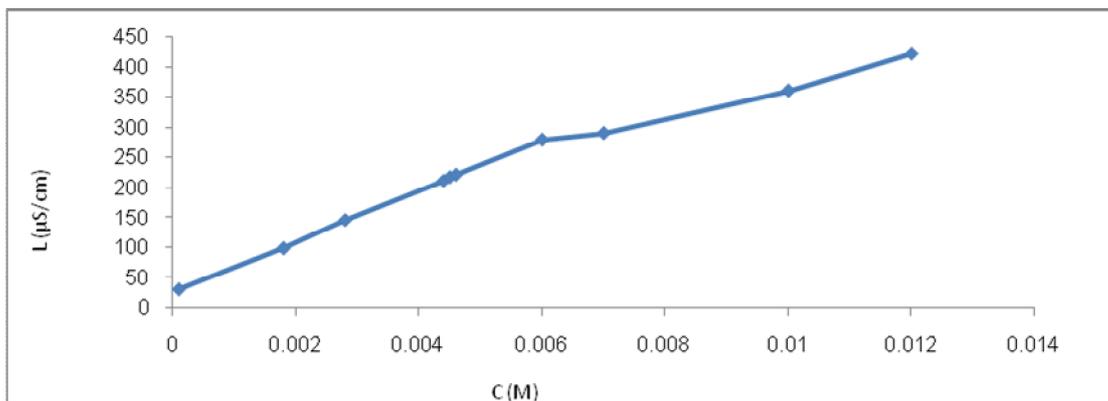


Fig9. SDS electrical conductivity in the absence of MMA (T/W=1/1, CMC =0.006 M, T=298K)

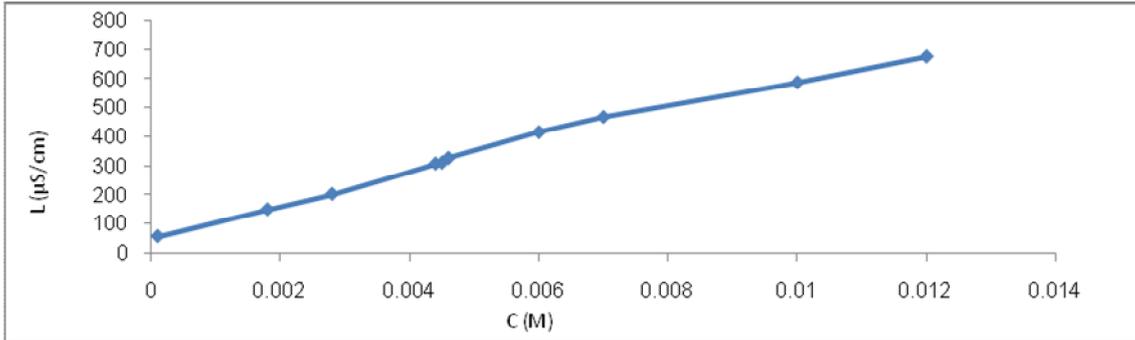


Fig10. SDS electrical conductivity in the presence of 0.75ml MMA (T/W=1/1, CMC=0.0044 M, T=298K)

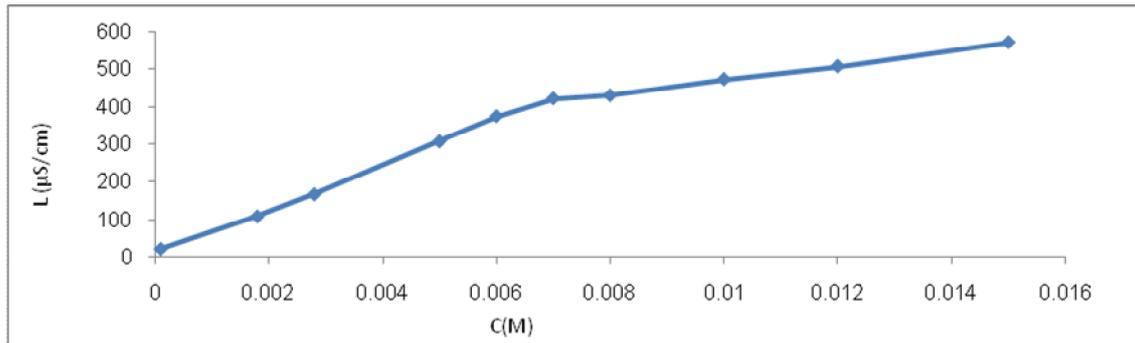


Fig11. DTAB electrical conductivity in the absence of MMA (T/W=1/1, CMC=0.007 M)

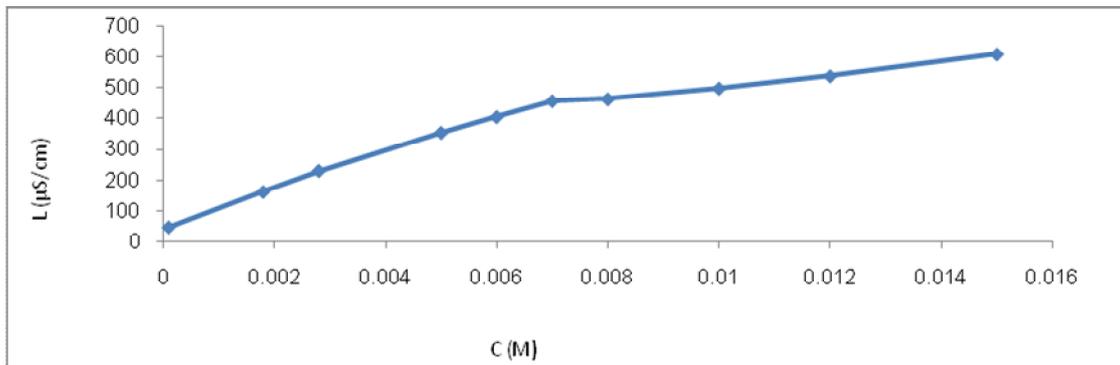


Fig12. DTAB electrical conductivity in the presence of 0.75ml MMA (T/W=1/1, CMC =0.007 M)

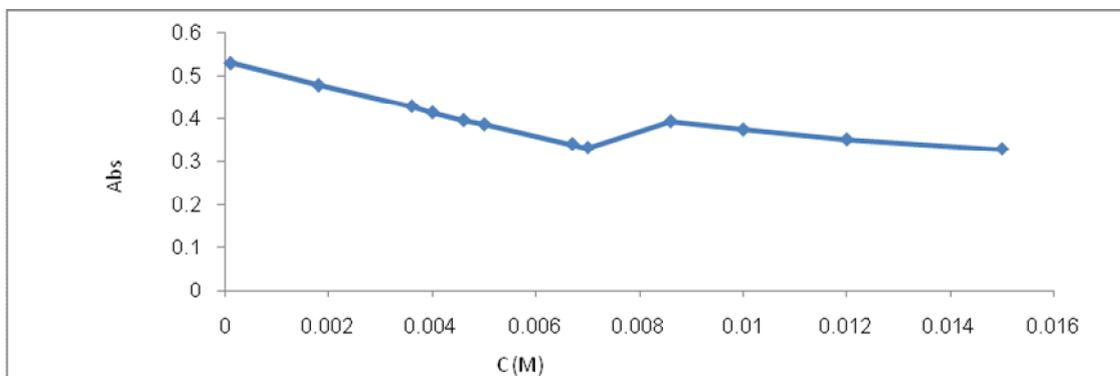


Fig13. Variation in absorption curve of SDS in the absence of MMA (CMC = 0.0086 M, T = 298 K)

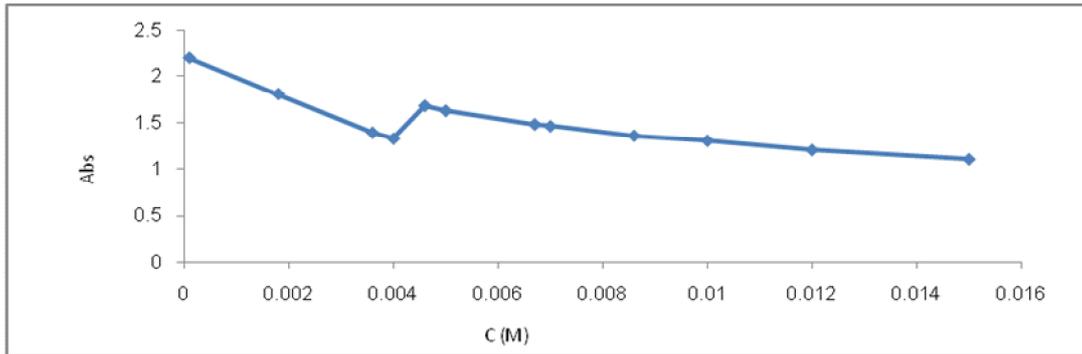


Fig14. Variation in absorption curve of SDS in the presence of 0.75 ml MMA (CMC=0.0046 M,T=298K)

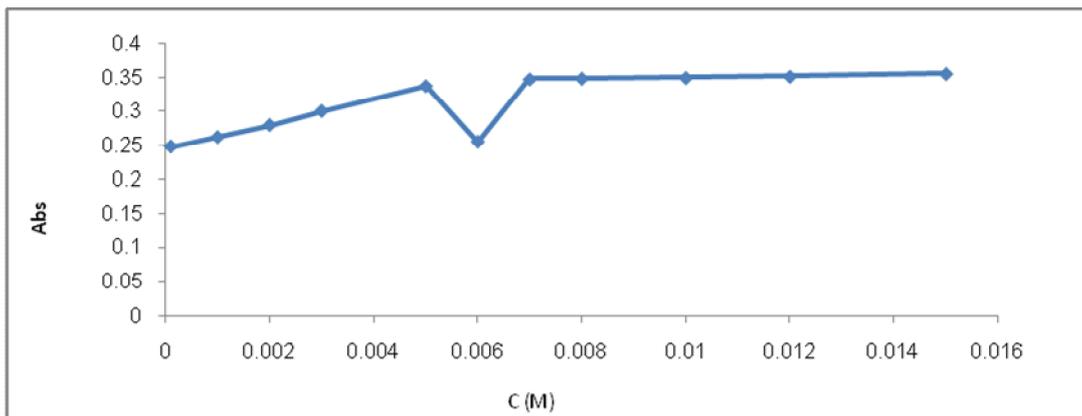


Fig15. Variation in absorption curve of DTAB in the absence of MMA (CMC=0.006 M, T=298 K)

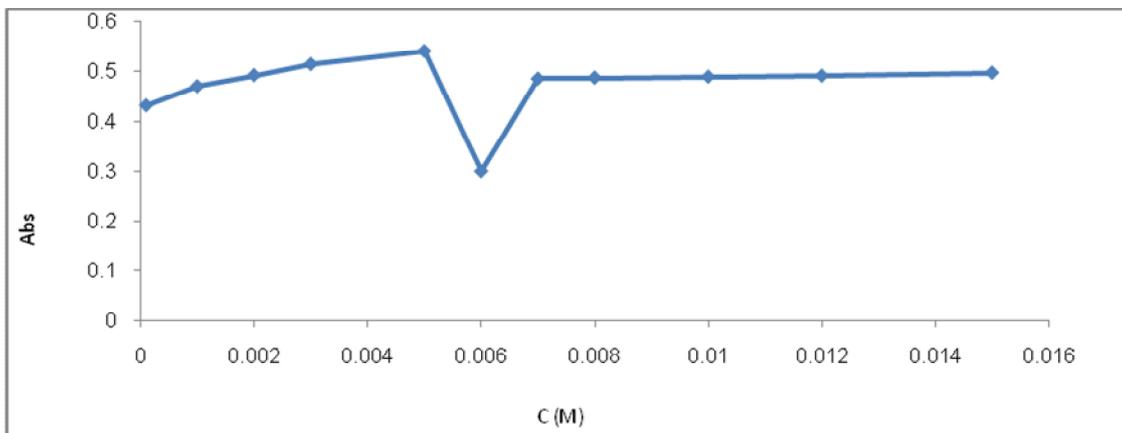


Fig16. Variation in absorption curve of DTAB in the presence of 0.75ml MMA (CMC=0.006 M,T=298K)

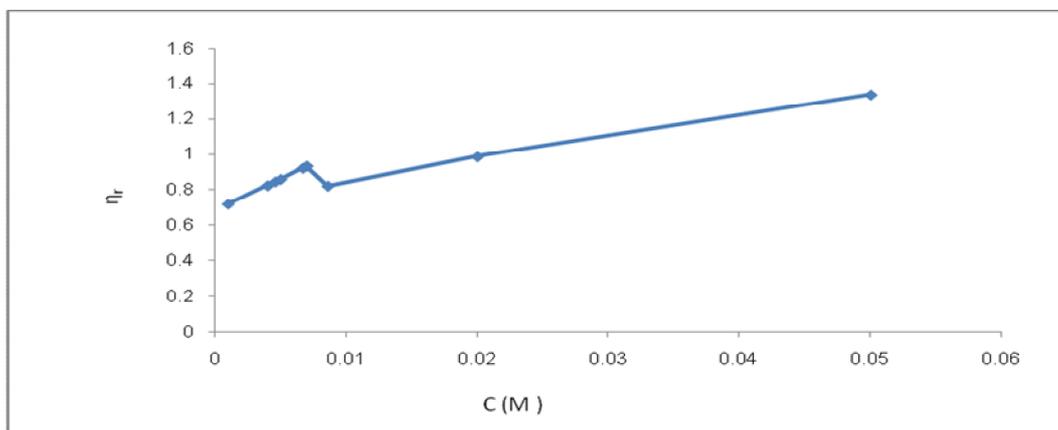


Fig17. Relative viscosity curve of SDS in the absence of MMA (CMC = 0.0086M,T=298K)

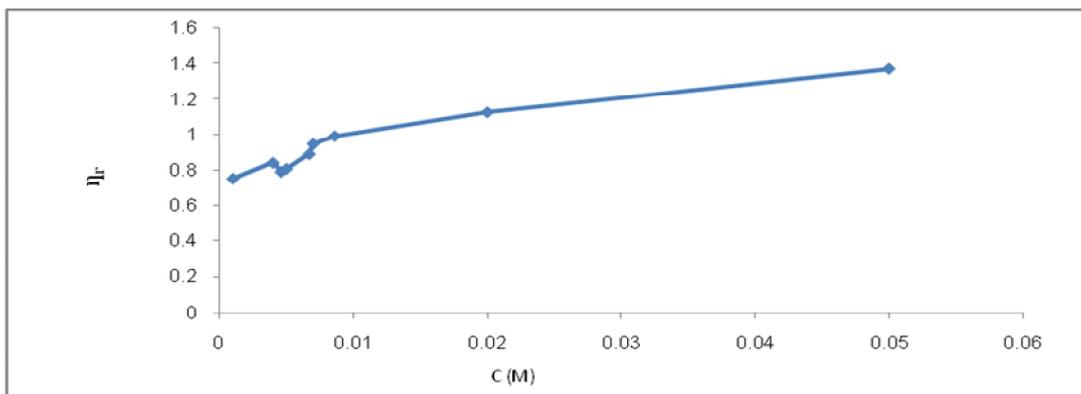


Fig18. Relative viscosity curve of SDS in the presence of 0.75ml MMA(CMC= 0.0046M,T=298K)

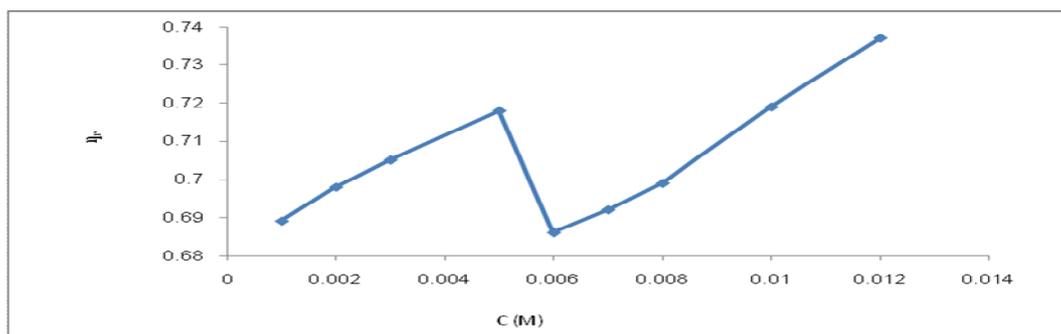


Fig19. Relative viscosity curve of DTAB in the absence of MMA (CMC=0.006M,T=298K)

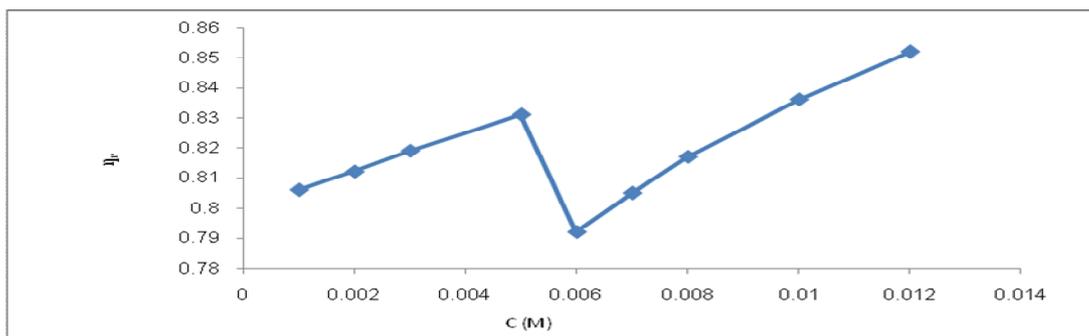


Fig20. Relative viscosity curve of DTAB in the presence of 0.75ml MMA (CMC=0.006M,T=298K)

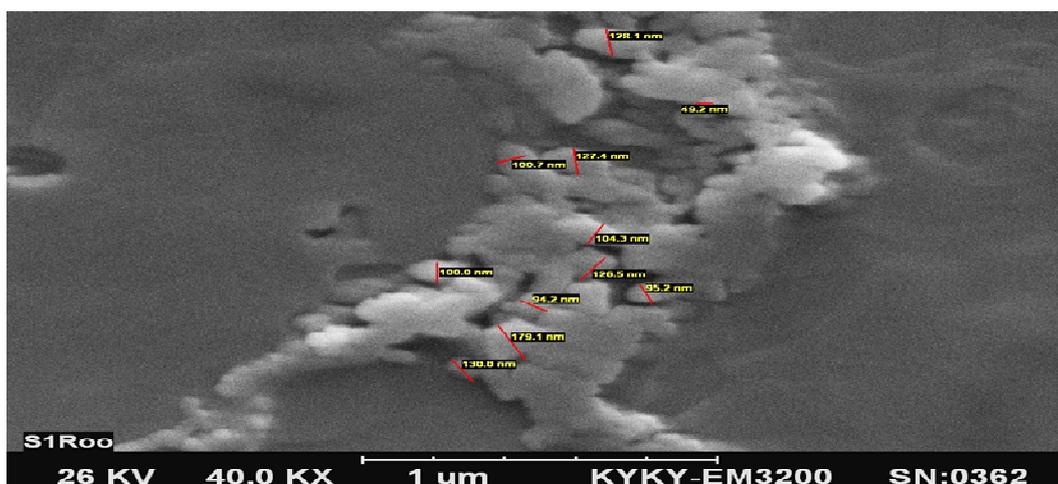


Fig 21. SEM micrograph of SDS in organic phase in the absence of MMA

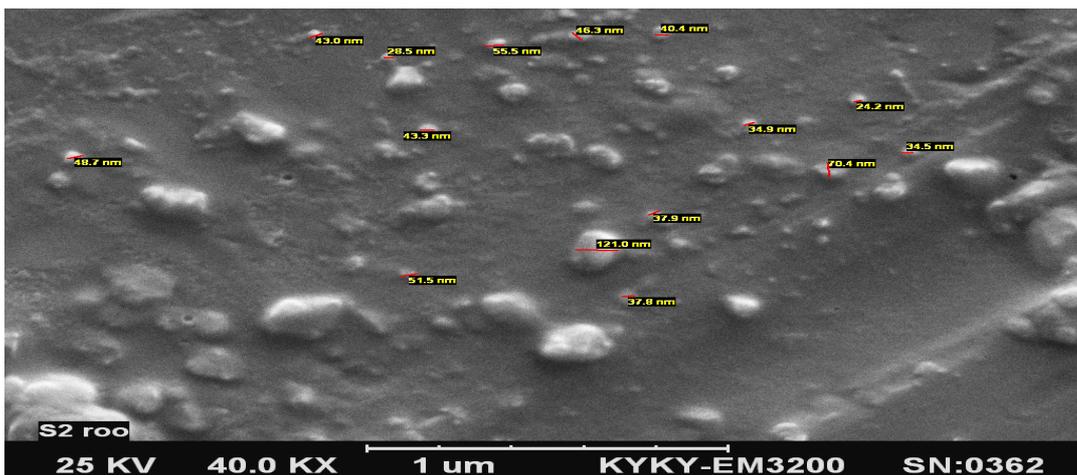


Fig 22. SEM micrograph of SDS in organic phase in the presence of 1ml MMA

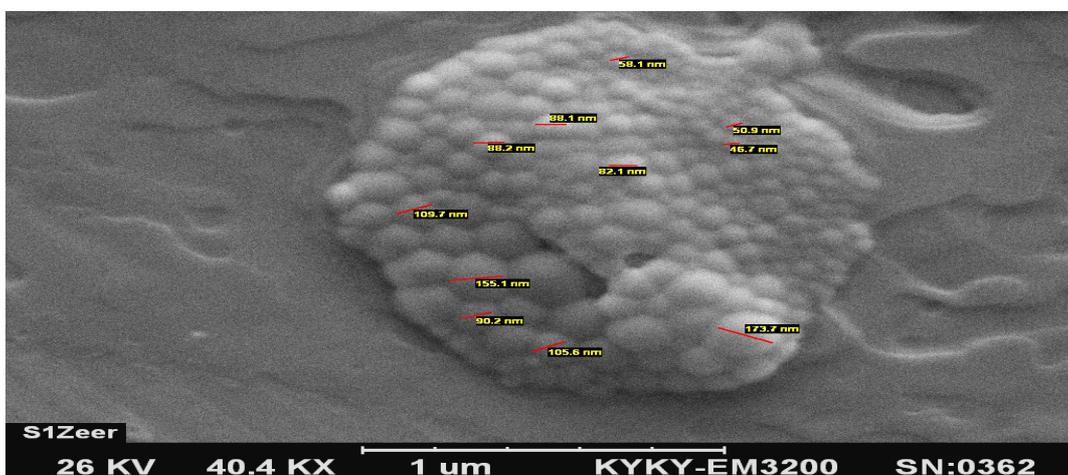


Fig 23. SEM micrograph of SDS in aqueous phase in the absence of MMA

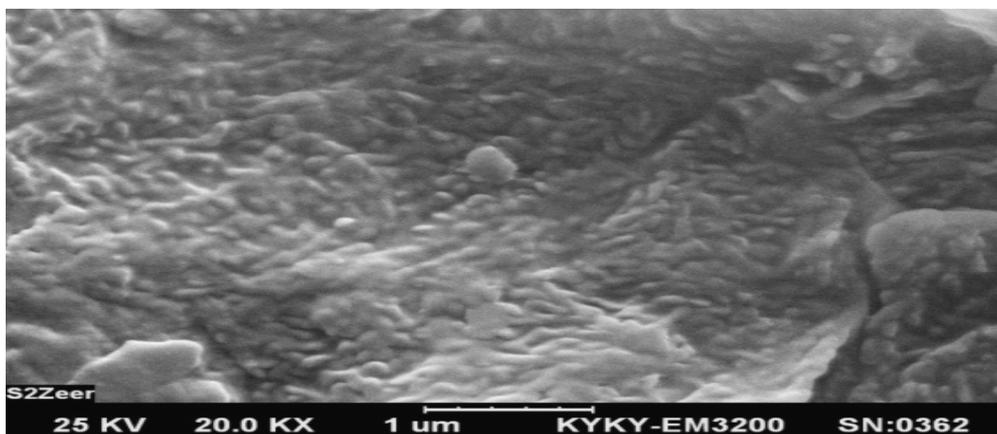


Fig 24. SEM micrograph of SDS in aqueous phase in the presence of 1ml MMA

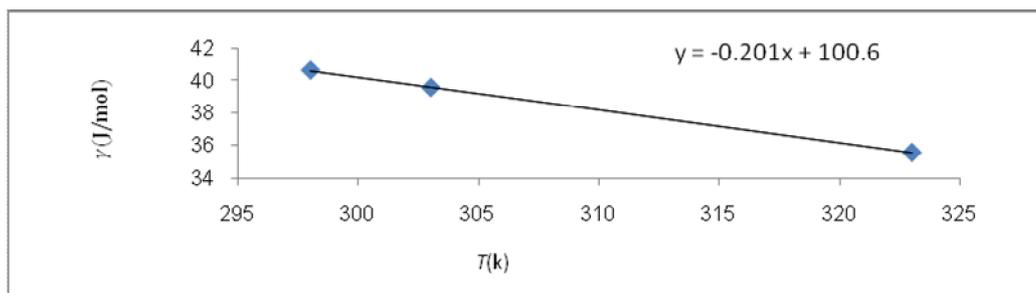


Fig25. Surface tension of SDS in organic phase in the absence of MMA (T=298 , 303 , 323K)

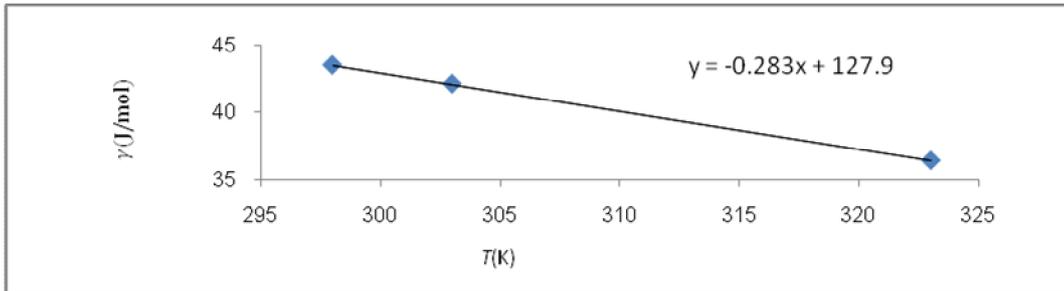


Fig26. Surface tension of SDS in aqueous phase in the absence of MMA (T=298 , 303 , 323K)

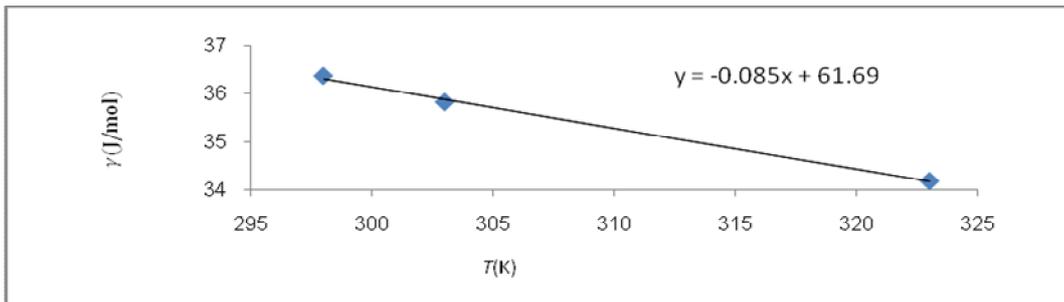


Fig27. Surface tension of SDS in organic phase in the presence of 1 ml MMA (T=298,303,328K)

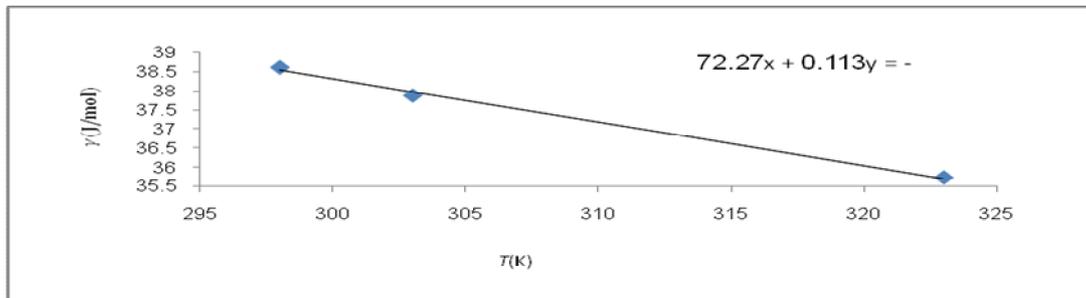


Fig 28. Surface tension of SDS in aqueous phase in the presence of 1 ml MMA (T=298,303,323K)

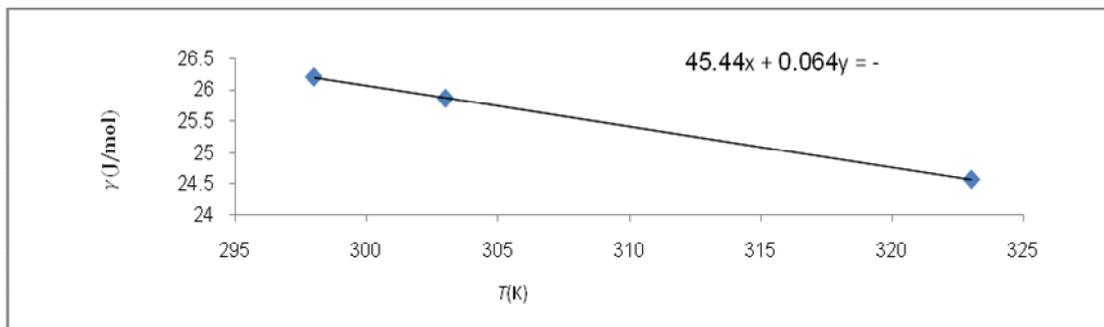


Fig 29. Surface tension of DTAB in organic phase in the absence of MMA (T=298,303,323K)

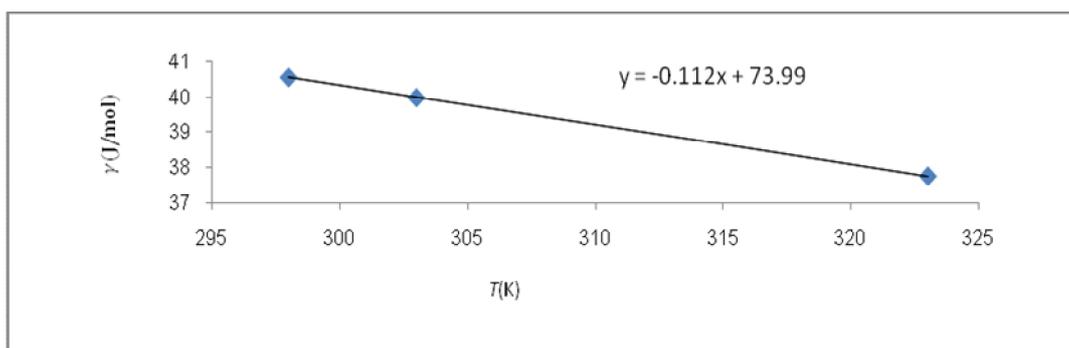


Fig 30. Surface tension of DTAB in aqueous phase in the absence of MMA (T=298,303,323K)

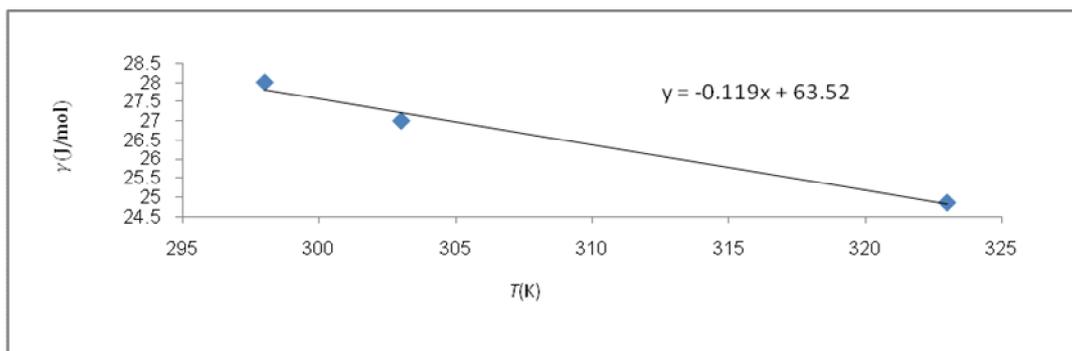


Fig31. Surface tension of DTAB in organic phase in the presence of 1ml MMA (T=298,303,323K)

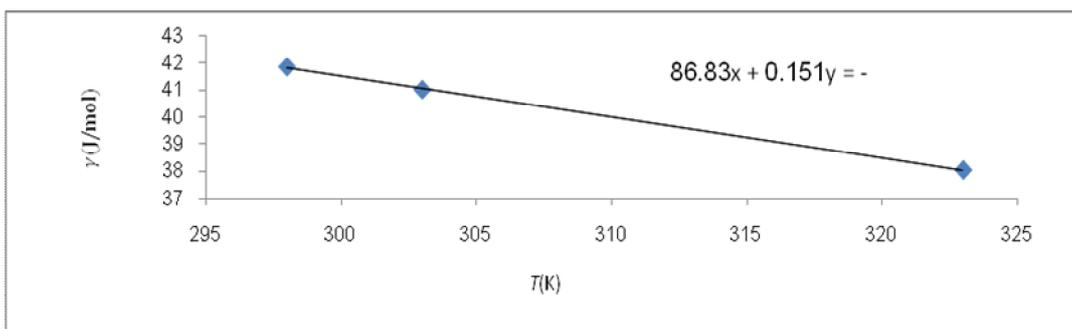


Fig32. Surface tension of DTAB in aqueous phase in the presence of 1ml MMA (T=298,303,323K)

Table1. Thermodynamic parameters for SDS

SDS+V _{mL} MMA	CMC (mol/L)	$-\Delta G_{mic}^{\circ}$ (kJ/mol)	ΔS_{mic}° (kJ/K.mol)	ΔH_{mic}° (J/mol)
0 mL MMA	0/0086	21/731	0/0729	-6/8
0/75 mL MMA	0/0046	23/125	0/0776	-0/2

Table 2. Thermodynamic parameters for DTAB

DTAB+V _{mL} MMA	CMC (mol/L)	$-\Delta G_{mic}^{\circ}$ (kJ/mol)	ΔS_{mic}° (kJ/K.mol)	ΔH_{mic}° (J/mol)
0 mL MMA	0/006	22/623	0/0759	-4/8
0/75 mL MMA	0/006	22/623	0/0759	-4/8

CONCLUSION

A comparison of the effect of PMMA in the presence of anionic(SDS) and cationic(DTAB) surfactants showed that, the interaction of the polymer in water-toluene-SDS is better than water-toluene-DTAB. On the other hand, the thermodynamic parameters such as CMC and surface tension in water-toluene-SDS-PMMA have been improved. The results of the findings in this research, emphasize, PMMA can be used as a drastic co-surfactant in water-toluene-anionic surfactant system.

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