CHAPTER - 4

PERFORMANCE PROPERTIES OF SURFACTANTS

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4.1 PREVIEW :

Surfactants are ubiquitous and major effects are devoted to synthesizing and producing new surfactants for diverse purposes. Surfactants as mentioned earlier are the active ingredients in detergents, emulsions, cosmetics, foods, drugs etc. where they provide the capability to solubilize water- and oil-like substances into homogenous systems. In the formulation of surfactant systems for practical applications like detergency, paints, enhanced oil recovery, the properties like foaming, wetting, viscosity, solubilization etc. are very significant. All these properties are highly sensitive to different environmental conditions like pH, temperature and presence of additives. Moreover, the solution properties of surfactant mixtures are often superior in applications to the properties of individual surfactants. Surfactants used in practical and commercial applications are almost always consist of mixtures. Hence, such systems offer a convenient way to optimize their performance properties. For example, anionic surfactants are high foaming and nonionic surfactants are poor foamers. In preference to an optimum condition such ionic / nonionic mixtures would be very important to tune to the user's requirement.

In this chapter, we discuss the various performance properties such as viscosity, wetting, foaming, detergency of Myrj 45, $C_{12}E_{10}$, SDBS and SDBS / $C_{12}E_{10}$ mixtures in presence and absence of PEG 400, sucrose and urea.

4.2 RESULTS AND DISCUSSION :

4.2.a. Viscosity : .

The viscosity of 5% (w/v) solution of $C_{12}E_{10}$ was determined at different temperatures of 35, 40, 45 and 50°C in presence and absence of PEG 400, sucrose and urea. The intrinsic viscosity, which indicates the solute solvent interaction and also the size and shape of the particle can be calculated from the relative viscosity by the relation[331].

$$[\eta] = \lim_{C \to O} (\eta_r - 1)/C$$

where zero concentration limit indicates the absence of interparticle interactions. Some researchers have taken $[\eta]$ to be equal to $(\eta_r\text{-}1)/C$ without the condition for limiting concentration. It has been defined to be the shape factor[332] and is expected to have a value of 2.5 - 4.0 $cm^3\ g^{-1}$ for globular particles. If the limit of concentration is taken to zero then the effect of concentration on the geometry of the particle is lost and hence we computed the shape factor without taking limit to zero as was done earlier by other researchers[232, 333]. The $[\eta]$ values for $C_{12}E_{10}$ obtained are reported in Table 68-70. The intrinsic viscosity $[\eta]$ values decreased as temperature was increased. This was anticipated as micelles become compact with increase in temperature due to the dehydration of polyoxyethylene chains[334]. However, in presence of additives a different behavior with respect to temperature is observed. Decreased hydration of ethylene oxide chains of the micelle in presence of sucrose probably leads to a lower $[\eta]$ value while cosolubilization and probable formation of mixed micelles with PEG 400 and urea may be the reason for increasing $[\eta]$ values.

It is reported that the $C_{12}E_n$ micelles used in present study (i.e. $C_{12}E_{10}$) are all spherical[335] and the dependence of micellar molecular weight (M_m) on the oxyethylene chain length (m) for a series of $C_{12}E_n$ is given by the relation[336].

Table 68 : Intrinsic viscosity [η], micellar volume (V_h) and volume of the oxyethylene chain (V_{OE}) of polyoxyethylene (10) lauryl ether (5% w/v) in presence of PEG 400 :

Conc. of PEG 400 % (w/v)	**35°C**			**40°C**			**45°C**		
	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})
0.0	7.09	28.7	25.3	6.93	28.0	24.6	6.81	27.6	24.2
0.1	7.10	28.8	25.3	6.94	28.1	24.7	6.83	27.7	24.2
0.5	7.31	29.6	26.2	7.14	28.9	25.5	7.01	28.4	24.9
1.0	7.91	32.0	28.6	7.71	31.2	27.8	7.58	30.7	27.3

Table 69 : Intrinsic viscosity [η], micellar volume (V_h) and volume of the oxyethylene chain (V_{OE}) of polyoxyethylene (10) lauryl ether (5% w/v) in presence of sucrose at different temperatures :

Conc. of PEG 400 % (w/v)	**35°C**			**40°C**			**45°C**		
	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})
0.0	7.09	28.7	25.3	6.93	28.1	24.6	6.81	27.6	24.2
0.1	7.11	28.8	25.4	6.94	28.1	24.7	6.83	27.7	24.2
0.5	6.83	27.7	24.2	6.66	26.9	23.5	6.53	26.4	23.0
1.0	6.76	27.4	23.9	6.59	26.7	23.3	6.46	26.2	22.7

Table 70 : Intrinsic viscosity [η], micellar volume (V_h) and volume of the oxyethylene chain (V_{OE}) of polyoxyethylene (10) lauryl ether (5% w/v) in presence of urea :

Conc. of PEG 400 % (w/v)	**35°C**			**40°C**			**45°C**		
	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})	[η] (cm^3/g)	V_h (x10^4 A^{o3})	V_{OE} (x10^4 A^{o3})
0.0	7.09	28.7	25.3	6.93	28.0	24.6	6.81	27.6	24.2
0.1	7.10	28.8	25.3	6.98	28.3	24.9	6.88	27.9	24.5
0.5	7.23	29.3	25.9	7.17	29.0	25.6	7.04	28.5	25.1
1.0	7.69	31.1	27.7	7.83	31.7	28.3	7.68	31.1	27.7

$$M_m = A_n M = (1025 / m - 5.1) M$$

where A_n is the aggregation number and M is the molecular weight of $C_{12}E_n$. Also, the micellar volume, including hydration (V_h) can be calculated from the intrinsic viscosity, $[\eta]$[337],

$$V_h = [\eta] M_m / 2.5 N$$

where N is the Avrogadro number. In addition, the volume of the hydrocarbon core (V_c) and the volume of the palisade layer of oxyethylene units (V_{OE}), that is, the hydrophilic region in $C_{12}E_n$ micelles, were estimated from the following equations[338-340].

$$V_c = A_n V = 1024 A_n M_c / d.N$$

$$V_{OE} = V_h - V_c$$

where V is the volume of alkyl chain in a single $C_{12}E_n$ molecule, M_c is the molecular weight and d is the density (0.802 g cm^{-3}) of the corresponding liquid n-alkane at 25°C.

Both the hydrated micelle volume (V_h) and the volume of the palisade layer of ethylene oxide (V_{OE}) units decrease as both temperature and concentration of sucrose increase. This is because water and the aquo-sucrose medium became poorer solvents at higher temperature. The replacement of water molecules by urea molecules in the solvation layer of the micelle may also be a reason for increase in V_{OE}. However, the increase in V_h and V_{OE} in presence of PEG 400 may probably be because the OCH_2 CH_2 group of PEG which are identical to the hydrophilic part of the nonionic surfactant assume themselves to be part of it[341], leading to an increase in the volume of oxyethylene chain. Such behavior is not seen when sucrose and urea are used as additives.

The viscosity of 5% (w/v) sodium dodecyl benzene sulfonate (SDBS) was also determined in presence and absence of PEG 400, sucrose and urea. The intrinsic viscosity [η], thus calculated was found to decrease for SDBS in absence of any additive. The value of [η] was 5 cm^3/g which indicates that the SDBS micelles at 5% (w/v) concentration are not exactly spherical in nature. Also, in presence of different concentrations of additives [η] values were around 5-7 cm^3/g implying that all three additives i.e. PEG 400, sucrose and urea do not change the shape of the micelle to a large extent as shown by the maximum value of 7 cm^3/g.

The Fig. 34 shows the viscosity of 5% and 10% (w/v) of SDBS / $C_{12}E_{10}$ mixed surfactant solution as a function of SDBS mole fraction at different temperatures. A maximum is observed for both the total surfactant concentrations of 5% as well as 10% (w/v) i.e. at $N_{SDBS} = 0.2$ for 5% (w/v) and $N_{SDBS} = 0.92$ for 10% (w/v). It should be noted here that at all temperatures, the relative viscosity shows positive deviation from linearity indicating mixed micelle formation. The maximum in viscosity arises because of the formation of mixed micelle as well as due to electroviscous property[342]. The electroviscous effect of mixed micelle is larger than that of single solution. This result also indicates that the geometry of the particles change with the increases in total surfactant concentration.

The intrinsic viscosity [η], for the SDBS / $C_{12}E_{10}$ mixed system at $N_{SDBS} = 0.2$ for 5% (w/v) total concentration of the surfactant solution is 6.5 cm^3/g. As mentioned earlier [η] = 2.5 - 4 cm^3/g indicates globular particles[333]. Hence, it is surmised that the micellar particles are not spherical in nature at all N_{SDBS} mole fractions. The [η] values obtained for 5% (w/v) and 10% (w/v) indicate that as the surfactant concentration is increased the micellar structure becomes elongated and nonspherical. The interparticle interaction hence changes. That is why the maximum is observed at different values of N_{SDBS} as the total concentration of the surfactant changes.

The thermodynamic activation parameters for the viscous flow were evaluated using the Frenkel-Eyring equation[343].

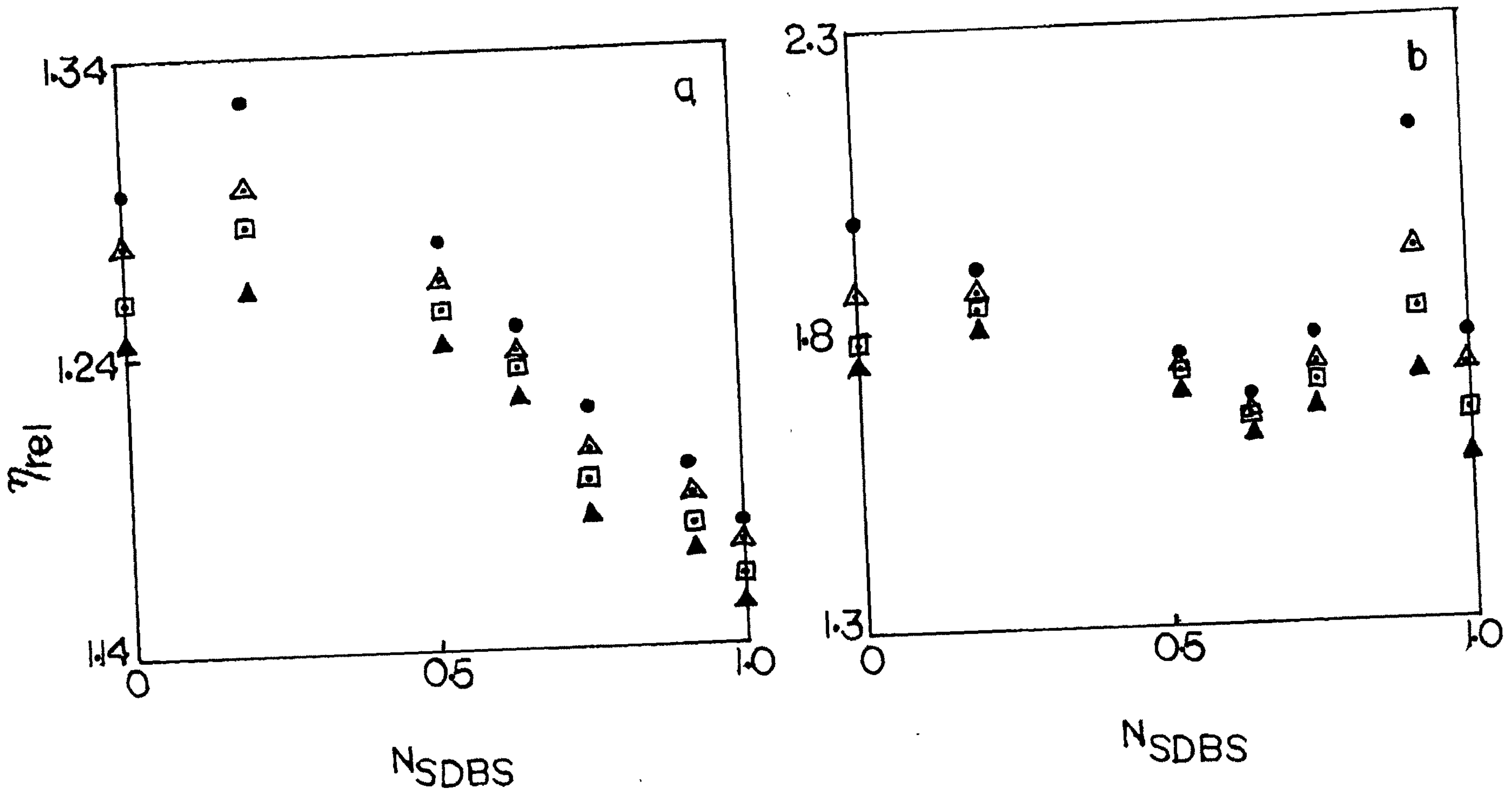


Fig. 34 : Plot of relative viscosity (η_{rel}) Vs mole fraction of SDBS for SDBS / $C_{12}E_{10}$ mixed system at different temperatures at total surfactant concentration (a) = 5% (w/v), (b) 10% (w/v) ● 35°C; △ 40°C; □ 45°C; ▲ 50°C.

$$\ln(\eta V / Nh) = \frac{\Delta H_{vis}^{\neq}}{RT} - \frac{\Delta S_{vis}^{\neq}}{R}$$

where V, N, h and R are the molar volumes, Avogadro number, Planck's constant and the universal gas constant respectively. $\Delta H_{vis}^{\neq}$ and $\Delta S_{vis}^{\neq}$ are the viscosity activation enthalpy and entropy respectively obtained from the intercept and slope of ln (ηV/Nh) against I/T plots. The ηV/Nh is an unitless quantity (If η is in centipoise, V is in cm^3/mole, N is molecule / mole and h is in J molecule^{-1}.

$$\frac{\eta V}{Nh} = \frac{10^{-1} \text{ x } 10^{-4} \text{ Kg m}^{-1} \cancel{\text{s}^{-1}} \text{ x } 10^{-6} \text{ m}^3 \cancel{\text{mol}^{-1}}}{\cancel{\text{molecule}} \text{ x mol}^{-1} \text{ x } 10^{-2} \cancel{\text{Kg}} \text{ m}^2 \text{ s}^{-1} \text{ x } \cancel{\text{molecule}^{-1}}}$$

an unitless quantity).

The thermodynamic activation parameters for SDBS and $C_{12}E_{10}$ systems are shown in Table 71, 72. The $\Delta G_{vis}^{\neq}$ values are positive indicating a non-spontaneous flow. The constancy in $\Delta G_{vis}^{\neq}$ indicates no effect of additives in the viscous flow at the concentration level studied. $\Delta H_{vis}^{\neq}$ values indicate that the viscous flow is endothermic. A negative $\Delta S_{vis}^{\neq}$ indicates a more ordered environment both in presence and absence of additives.

However, the free energy of activation, $\Delta G_{vis}^{\neq}$ for SDBS / $C_{12}E_{10}$ mixed system was computed from Eyring equation[344].

$$\ln(\eta / \eta_o) = \Delta G_{vis}^{\neq} / RT$$

η and η_o are the viscosities of solution and solvent respectively and other symbols have their usual meanings. The $\Delta G_{vis}^{\neq}$ is the quantity that measures the non-mechanical amount of energy to be spent for the flow process of occur. The $\Delta G_{vis}^{\neq}$ shows a maximum with N_{SDBS} mole fraction as in Fig. 35, 36.

Table 71 : Thermodynamic activation parameters for viscous flow of polyoxyethylene(10) lauryl ether (5% w/v) in the presence and absence of PEG 400, sucrose and urea :

Conc. of Additives % (w/v)	**$\Delta G_{vis}^{\neq}$ (kJ mol^{-1})**	**$\Delta H_{vis}^{\neq}$ (kJ mol^{-1})**	**$\Delta S_{vis}^{\neq}$ (J mol^{-1} K^{-1})**
PEG 400			
0.0	63.9	0.52	-0.2
0.1	63.9	0.53	-0.2
0.5	63.9	0.61	-0.2
1.0	64.0	0.67	-0.2
Sucrose			
0.1	63.9	0.55	-0.2
0.5	63.9	0.61	-0.2
1.0	63.9	0.60	-0.2
Urea			
0.1	63.9	0.56	-0.2
0.5	63.9	0.64	-0.2
0.7	63.9	0.68	-0.2

Table 72 : Thermodynamic activation parameter for viscous flow of sodium dodecyl benzene sulfonate (SDBS) in presence and absence of additives :

Conc. of Additives % (w/v)	**$\Delta G_{vis}^{\neq}$ (kJ mol^{-1})**	**$\Delta H_{vis}^{\neq}$ (kJ mol^{-1})**	**$\Delta S_{vis}^{\neq}$ (J mol^{-1} K^{-1})**
PEG 400			
0.0	0.54	2.20	5.4
0.1	0.55	2.21	5.4
0.5	0.55	2.20	5.3
1.0	0.54	2.23	5.4
Sucrose			
0.1	0.54	2.22	5.4
0.5	0.55	2.21	5.4
1.0	0.55	2.22	5.4
Urea			
0.1	0.55	2.23	5.4
0.5	0.56	2.22	5.4
0.7	0.55	2.24	5.5

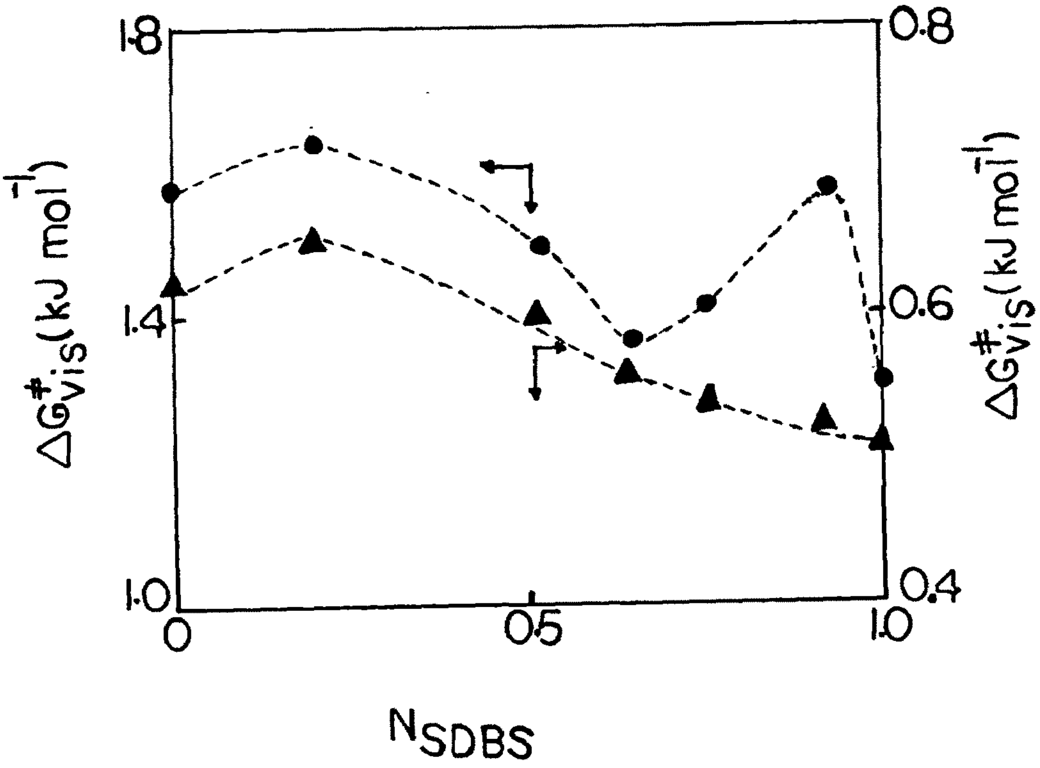


Fig. 35 : Free energy of activation for the viscous flow ($\Delta G_{vis}^{\neq}$) - SDBS mole fraction ▲ 5% (w/v); ● 10% (w/v).

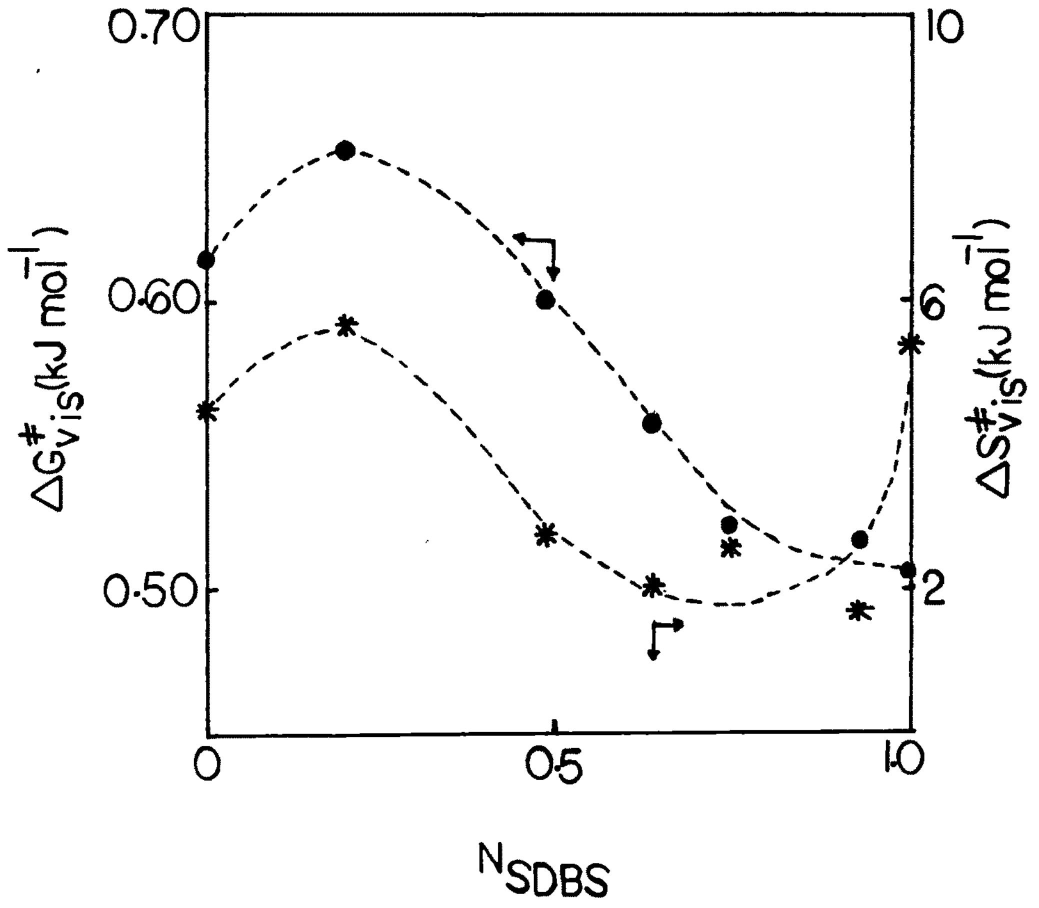


Fig. 36 : Plot of ΔG_{vis}^{*} and ΔS_{vis}^{*} Vs SDBS mole fraction.

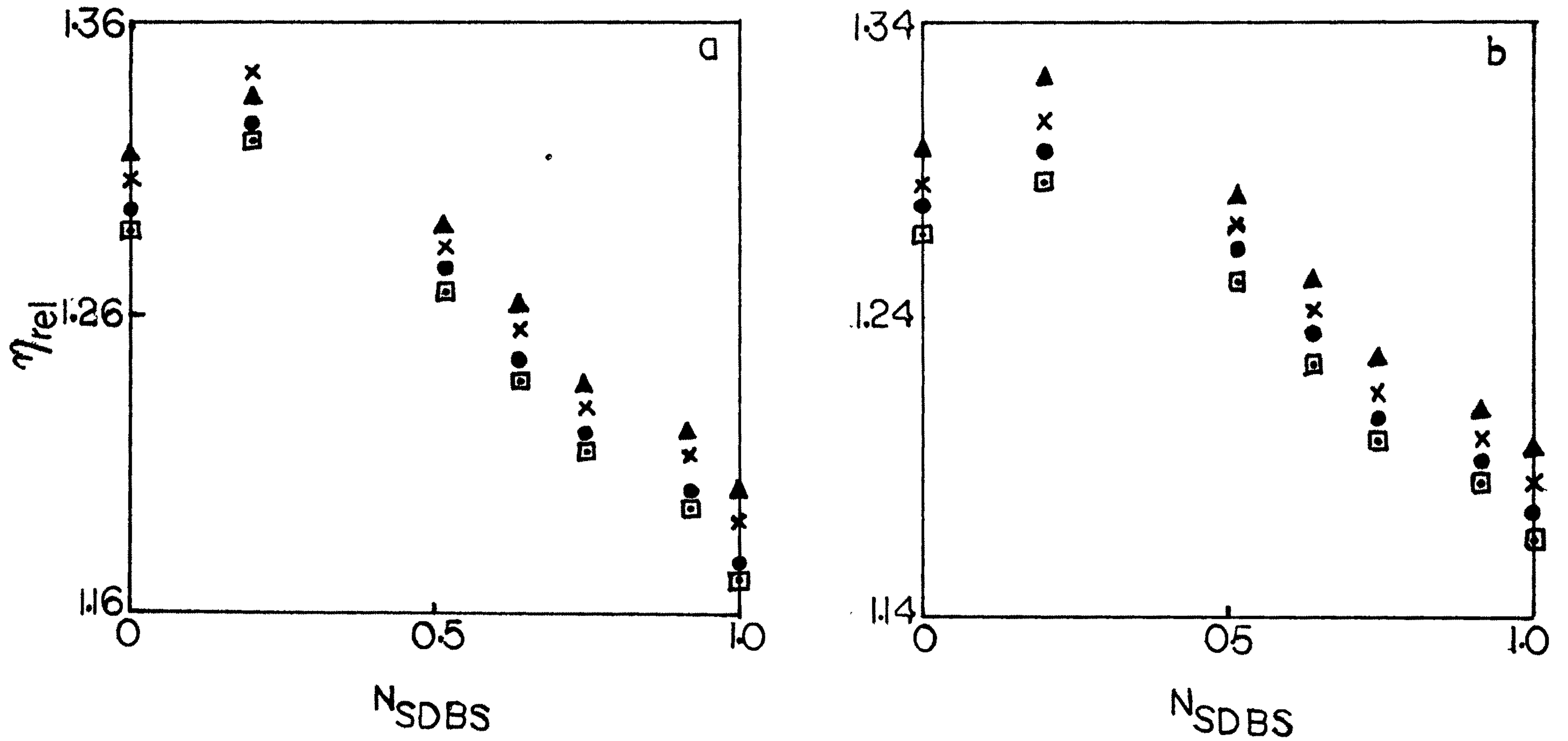


Fig. 37 : Plot of relative viscosity (η_{rel}) Vs SDBS mole fraction in presence of additives for SDBS / $C_{12}E_{10}$ mixed system (total surfactant concentration = 5% w/v). ● 0.0% Additive; ▲ 0.5% PEG 400; ✖ 0.5% Urea; ⊡ 0.5% Sucrose at (a) = 35°C; (b) = 40°C.

In presence of PEG 400, sucrose and urea a marked effect on the relative viscosity of SDBS / $C_{12}E_{10}$ mixed system was observed as shown in Fig. 37, 38. The intrinsic viscosity [η] values show a slight decrease in presence of sucrose and an increase in presence of PEG 400 and urea especially at lower SDBS mole fraction. However, in all these cases the [η] values are much higher than what is expected for a globular particle i.e. 2.5-4 cm^3/g. The presence of these additives at micelle-solvent interface increases the values of intrinsic viscosity [η]. It is to be noted that even in presence of these additives, although the magnitude of the viscosity varied, there was no shift in the maximum observed in the relative viscosity - N_{SDBS} plots for SDBS / $C_{12}E_{10}$ mixed system as shown in Fig. 37, 38.

The free energy of activation $\Delta G_{VIS}^{\neq}$, for the viscous flow as shown in Fig. 39, showed maximum for 5% (w/v) SDBS / $C_{12}E_{10}$ mixture at SDBS mole fraction i.e. $N_{SDBS} = 0.2$. However, with increase in the additive concentration $\Delta G_{VIS}^{\neq}$ values did not change much, rather remained almost constant as in their absence. In other words, the nature of the solution becomes independent of the additives at the concentration range studied.

4.2.b Foaming :

Foaming is a property inherent to surfactant solutions. It is well known that nonionic surfactants containing the polyoxyethylene groups produce both less foam and also less stable foam than ionic surfactants. However, the foaming efficiency of these surfactants can be altered by the addition of certain additives[29, 239]. In the present study the initial foam height of Myrj 45, $C_{12}E_{10}$, SDBS and SDBS / $C_{12}E_{10}$ mixed systems were measured in presence and absence of PEG 400, sucrose and urea at different temperatures. Foam height was measured using Ross Miles method (experimental procedure is described in Chapter 2). The initial foam height for Myrj 45, a nonionic surfactant was too low to be measured. In Fig. 40 the initial ~~form~~ foam heights of 0.01% (w/v) of polyoxyethylene (10) lauryl ether i.e. $C_{12}E_{10}$ at 40°C and

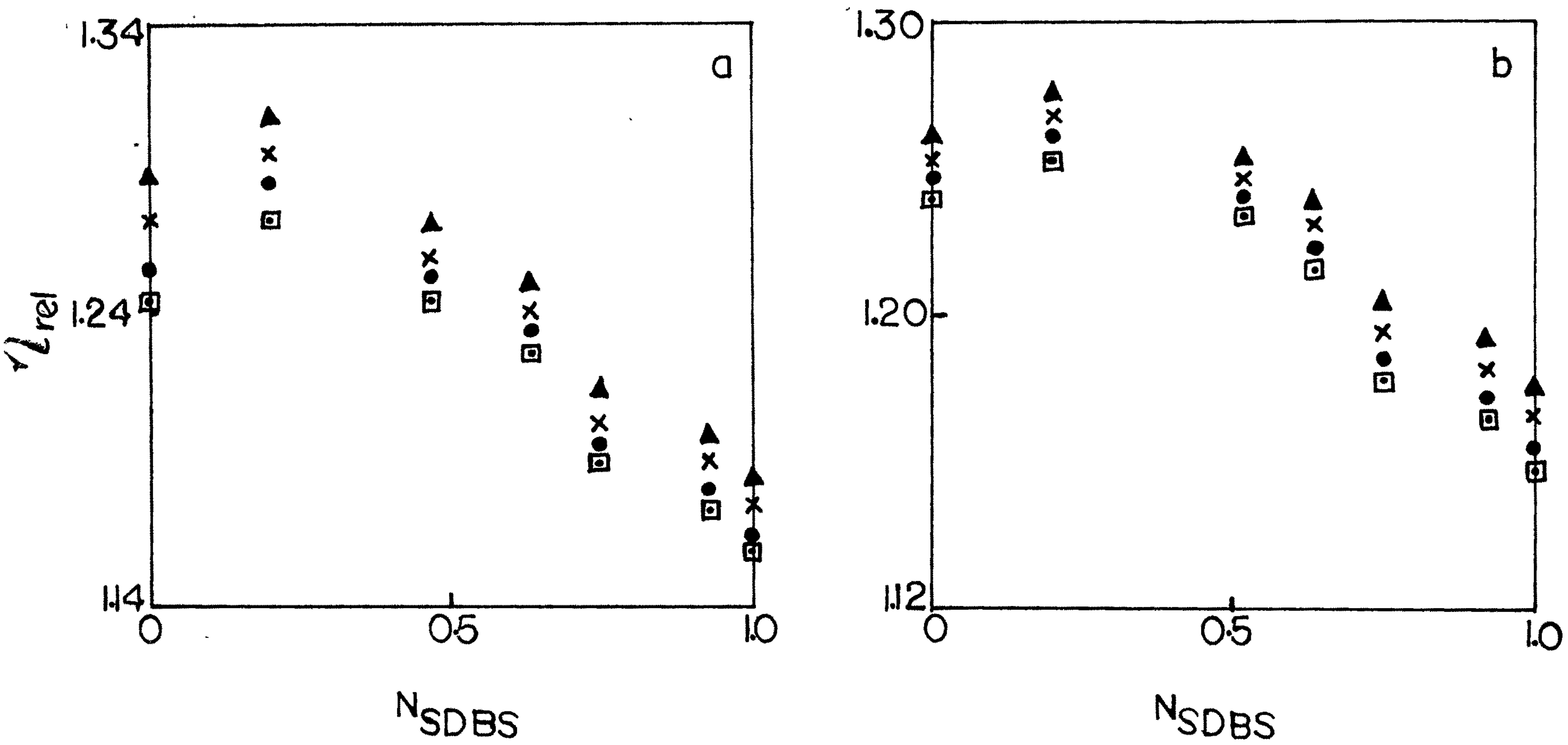


Fig. 38 : Plot of relative viscosity (η_{rel}) Vs SDBS mole fraction in presence of additives for SDBS / $C_{12}E_{10}$ mixed system (total surfactant concentration = 5% (w/v). ● 0.0% Additive; ▲ 0.5% PEG 400; ✖ 0.5% Urea; ⊡ 0.5% Sucrose at different temperatures (a) = 45°C; (b) = 50°C.

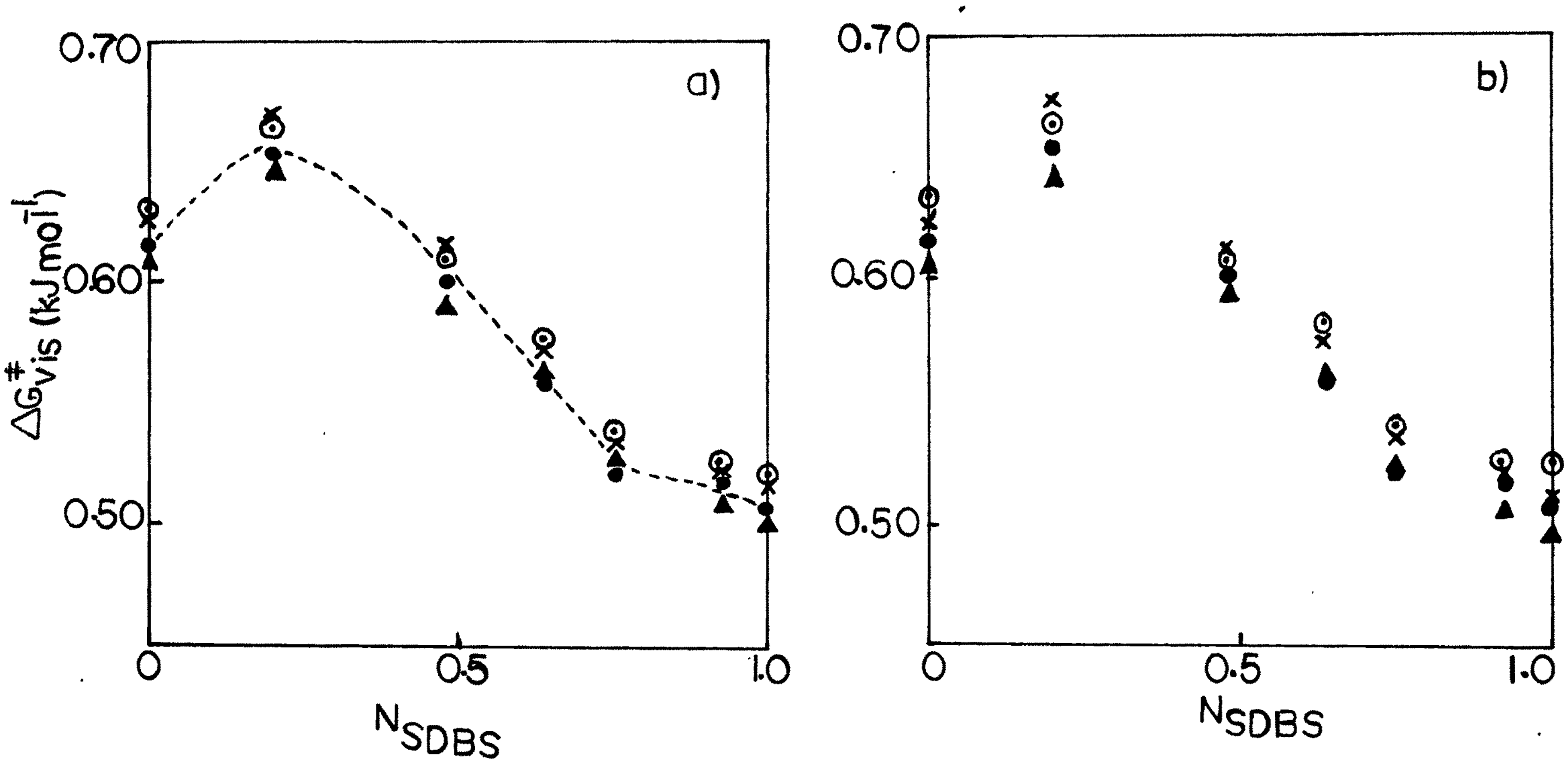


Fig. 39 : The free energy of activation (ΔG_{vis}^{*}) for the viscous flow Vs SDBS mole fraction in presence and absence of additives for SDBS / $C_{12}E_{10}$ mixed system (a) 0.5% (w/v) additives; (b) 0.7% (w/v) additive. ● no additive; ⊙ PEG 400; ✖ Sucrose; ▲ Urea.

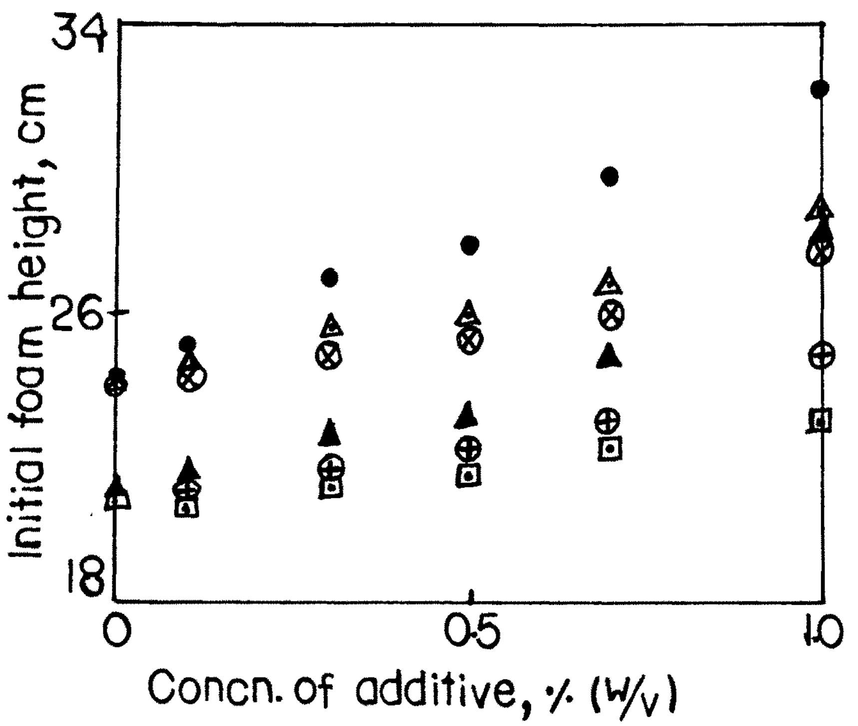


Fig. 40 : Initial foam height Vs concentration of additive for $C_{12}E_{10}$ (= 0.01% w/v) system. ● PEG 400 at 40°C; ⊗ Sucrose at 40°C; ◬ Urea at 40°C; ▲ PEG 400 at 50°C; ⊡ Sucrose at 50°C; ⊕ Urea at 50°C.

50°C in presence of different additive concentrations are shown. The increase in the initial foam height especially in PEG 400 can be attributed to enhanced viscosity, which retards the draining of liquid from the bubbles, leading to enhanced foam stability.

Both PEG 400 and sucrose decrease the CMC of $C_{12}E_{10}$ surfactant. It has been reported[243] that the additives which decrease the CMC of the surfactant solution lower the activity of the monomeric surfactant in solution, therefore decrease the rate of migration of the surfactant to the surface and the rate of attainment of surface tension equilibrium, leading to an increase in the foam height. Further, the formation of structure occurs because of the hydrogen bond between the free water molecules and these additives. The multiple hydrogen bonds with water prevent these polar additives from being forced out from between the surfactant molecules and into the interior of the micelles in the bulk phase, i.e. these bonds hold the additives in the palisade layer of micelles giving rise to greater stabilization of the foam. Another reason for the foam stabilization other than the solubilization of additives in the palisade layers of micelles is based on the similar phenomena occuring in the surface layers at the solution - air interface of foams. Additives that are solubilized into the micelle interior are not available for surface films, whereas those that are solubilized into the palisade layers of micelles are present in the surface films of the foam lamellae. Hence, in this case, tighter packing, lower surface tension and higher surface viscosity serve to enhance the foam stability[242].

foam

In case of sodium dodecyl benzene sulfonate (SDBS), which is an anionic surfactant the foaming efficiency is much higher than the nonionic surfactants. Once, the additives were present the initial form height of the surfactant showed very little change. This is shown in Fig. 41. It is to be noted that the initial foam height was a function of temperature. As the temperature increases the foam height decreases in nonionics and increases in case of ionics. This is quite understandable as nonionic surfactants above a critical temperature i.e. the cloud point separates into two phases :

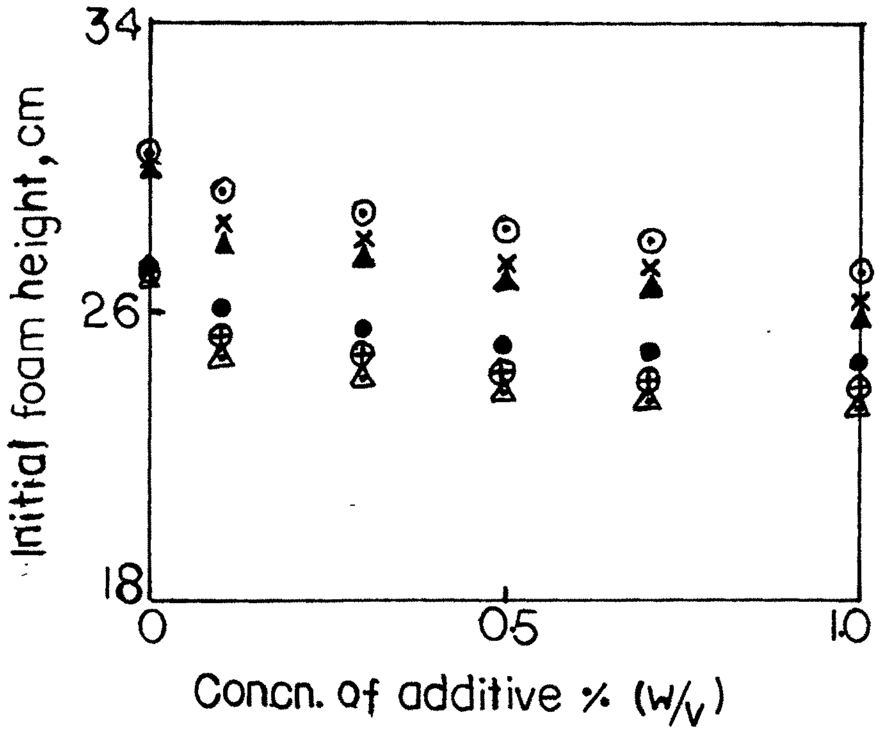


Fig. 41 : Initial foam height Vs concentration of additive for SDBS (= 0.15 mM). ● PEG 400 at 40°C; ⊕ Sucrose at 40°C; △ Urea at 40°C; ⊙ PEG 400 at 50°C; ✖ Sucrose at 50°C; ▲ Urea at 50°C.

role

a micelle rich phase and a very dilute one. This phase separation is accompanied by reduction in foamability[243]. In other words, the drops of the micelle-rich phase separate out of the dilute solution and play the rate of antifoam agent by emerging into both air / water interfaces of the foam films and rupturing the film by dewetting. However, in case of ionic surfactants the increasing solubility with increase in temperature leads to an increase in foam height.

In Fig. 42, the foaming efficiency of SDBS / $C_{12}E_{10}$ mixture at various SDBS mole fraction is shown. A mixture of these two types of surfactants show somewhat synergistic foaming property. Foam height for mixed systems is in general a function of total concentration of surfactant, the ratio of the concentration of the two surfactants and temperature[285, 345]. It is well known that the foams are very complex and it seems that a clear relation between the foam height and the variables does not exist. Moreover, drainage, evaporation, interaction between environments and foams etc. also determine the foam stability[346]. The foam happens to occur because of low interfacial tension. Also, more importantly the foams are stable, if there is stability of the films at the air / water interface and also where surface tension varies rapidly with concentration[347]. We postulate that in the mixed systems, the possibility of rapid variation of concentration at the interface is higher than in pure system. Initial foam heights are reasonably stable just below CMC (i.e. maximum foam stability). The foaming studies were done well below CMC[250]. The higher foam heights in case of mixed system indicates higher interfacial activity i.e. a synergistic behavior.

Similarly, the initial foam heights were determined for SDBS / $C_{12}E_{10}$ at various mole fractions of SDBS in presence of PEG 400, sucrose and urea. This is shown in Fig. 43. It is to be noted that although a synergistic behavior in foaming property was observed even in presence of additives for SDBS / $C_{12}E_{10}$ mixtures, much variation in the foam height was observed only at lower mole fractions of SDBS. For PEG 400 at lower N_{SDBS}, the foam height increased whereas with increase of sucrose and urea, a small decrease in foam height was observed.

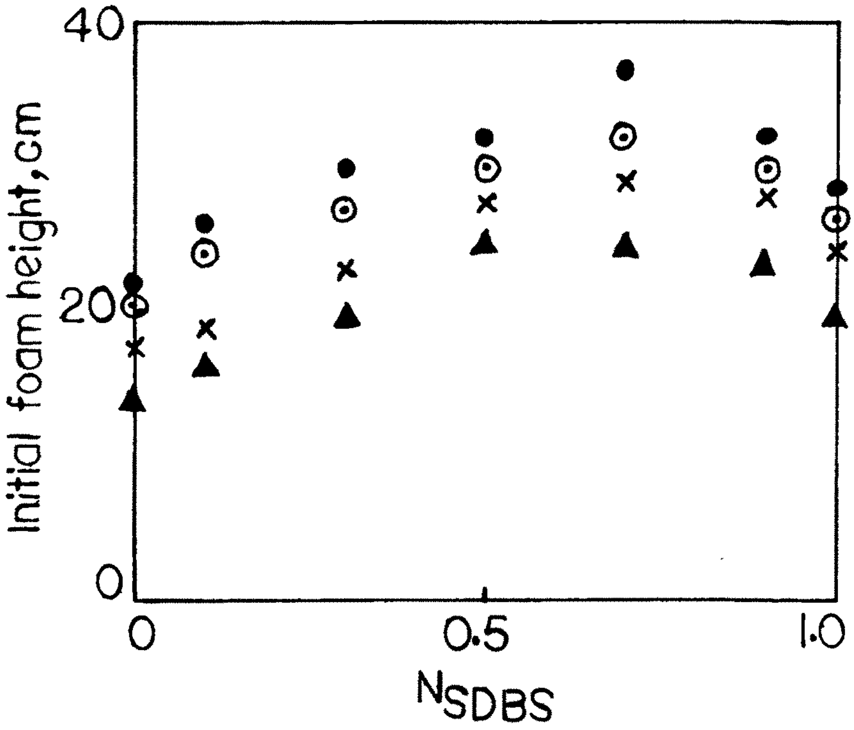


Fig. 42 : Initial foam height Vs SDBS mole fraction for SDBS / $C_{12}E_{10}$ mixed system at total surfactant concentration. ● 0.05 mM at 40°C; ⊙ 0.05 mM at 50°C; ✖ 0.01 mM at 40°C; ▲ 0.01 mM at 50°C.

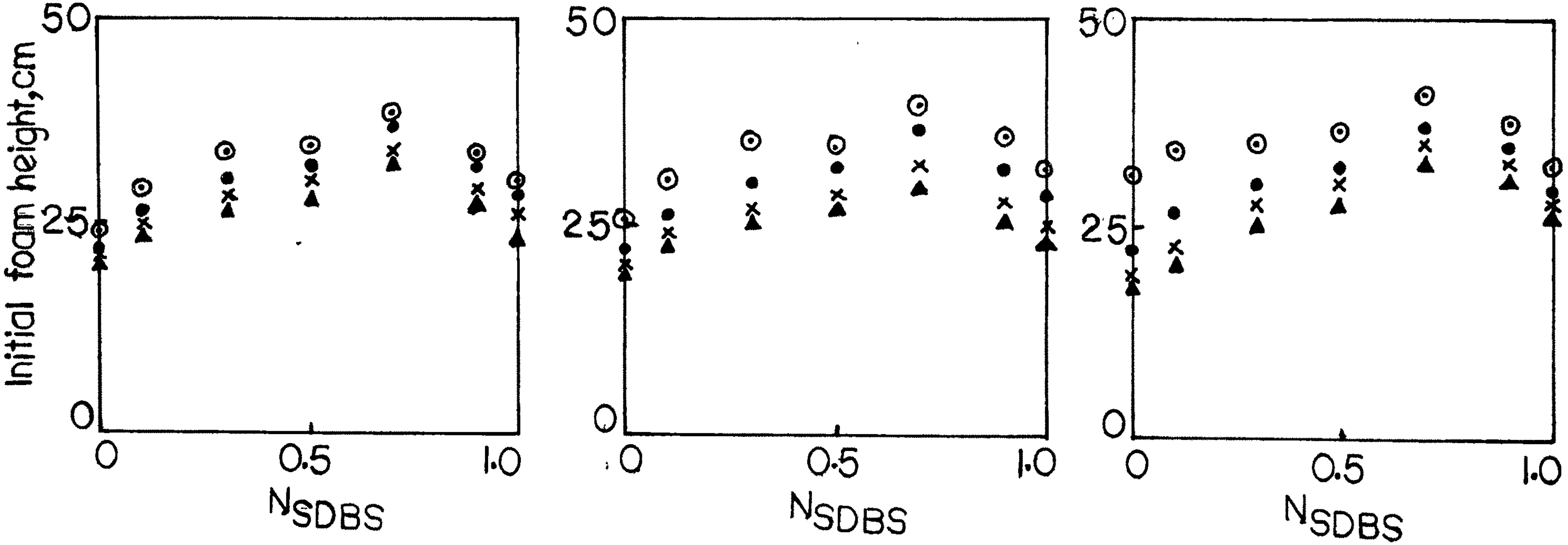


Fig. 43 : Initial foam height Vs SDBS mole fraction for SDBS / $C_{12}E_{10}$ mixed system in presence of additives at 40°C of concentrations. (a) 0.3% w/v; (b) 0.5% w/v. (c) 0.7% (w/v). ● no additive; ⊙ PEG 400; ✖ Sucrose; ▲ Urea.

4.2.c Detergency :

Detergency is where by far the largest single use of surfactants is seen. It may be defined, in practise as the removal of foreign materials from solid surfaces by surface chemical means. This includes extensively the soil removal from fabrics, metal surfaces etc. The mechanism of detergent action can be explained as follows[1, 126] -

For an oily soil particle adhering by surface tensional forces, the surface free energy for the detachment of the soil is just -

$$\Delta G = \gamma_{w/o} + \gamma_{s/w} - \gamma_{s/o}$$

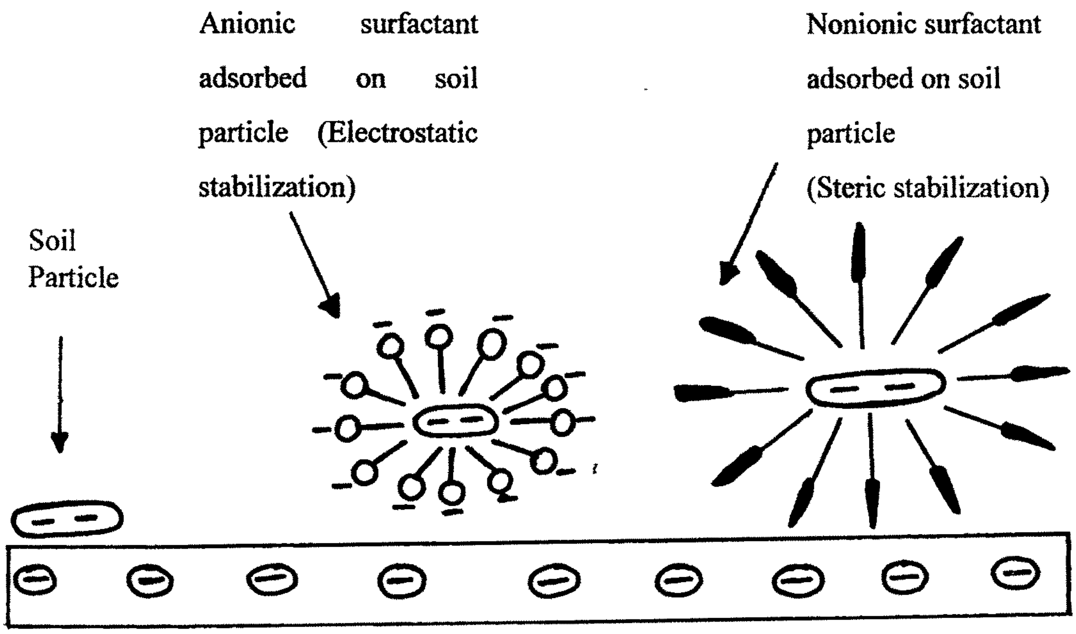
Define symbols

Therefore, for a spontaneous detachment of the oily soil particle from the solid surface-

$$\Delta G \leq 0 \quad \text{or} \quad \gamma_{s/o} \geq \gamma_{w/o} + \gamma_{s/w}$$

In order to make the adhesion of the oily soil to the solid, zero or negative, $\gamma_{w/o}$ and $\gamma_{s/w}$ should be substantially decreased as much as possible with minimum change in $\gamma_{s/o}$. A surfactant that adsorbs both at the solid / water and at oil / water interface is thus effective. If the dirt is a fluid, its removal can be considered a contact angle phenomenon. The addition of detergent lowers the contact angle at the triple solid-oil-water interface as a result of which the oil "rolls up" and then gets easily detached. Hence, "detergency" is accomplished by a combination of effects involving adsorption at interfaces, alteration of interfacial tensions, solubilization, emulsification and the formation and dissipation of surface charges.

It is to be noted that although detergency involves lowering of the work of adhesion of soil to a surface which is a function of soil-water-substrate interfacial tensions, adsorption of surfactant affect other properties of surface[348]. For example, they change the surface charge or form a steric barrier at the surface of the soil particle as illustrated in following Figure (Ref. 23).



In detergency, solubilization of soil from fabric into the detergent solution is one of the most important events that involves the removal of oily soil. Solubilization is defined as the spontaneous formation of a thermodynamically stable isotropic solution of a substrate (i.e. solubilizate) normally insoluble or soluble only slightly in a given solvent by the addition of surfactant[255]. The location in the micelle where solubilization occurs varies with the nature of solubilized material and is important in that it reflects the type of interaction that occurs between the surfactant and the solubilizate. The solubilization capacity of micellar solution depends on conditions such as structure of surfactant, the solubilizate temperature and the presence of additives. Chan et al.[349] proposed a theory of solubilization kinetics in micellar solution based on an analysis of five steps; (1) surfactant molecules diffuse to the surface as micellar species; (2) these molecules adsorbs on the surface of the solubilizate; (3) the surfactant and solubilizate form mixed micelle; (4) the mixed micelles are desorbed and (5) diffuses away into the bulk solution.

In the present study, the solubilization of oil soluble Blue 2089 [9, 10 anthracene dione 1,4 bis (methylamine)] in surfactant solution of Myrj 45, $C_{12}E_{10}$, SDBS and SDBS / $C_{12}E_{10}$ mixed system in presence and absence of PEG 400, sucrose and urea at room temperature was investigated. Solubilization of the dye represents the ability to clean a fabric of adsorbed hydrophobic material. In this experiment, the fabric was treated with benzene solution of dye and the solvent was allowed to evaporate. The fabric was then placed into an agitated solution of surfactant. The dye removal efficiency of nonionic surfactants was much higher than for ionic SDBS. This is well expected as nonionic surfactants, because of their low critical micelle concentration (CMC), are better solubilizing agents than ionics in dilute solution[240].

In the nonionic surfactants the nature of the polar head groups especially the polyoxyethylenes are such that relatively larger fraction of micelle volume is in the palisade layer. Due to the nature of polyoxyethylene chains and their attendant solvent molecules, it has been suggested that the hydrophilic chain is arranged in spiral form from the micelle core outward in solution[350]. As a result of this, the areas of the palisade region near the core is sterically crowded with polyoxyethylene chains with very little room left for the waters of hydration. As the distance from the core exceeds the palisade layer becomes more hydrophilic, acquiring the characteristic of aqueous solution. The net effect of such situation is that ~~the~~ deep in the palisade layer, the chemical environment will closely approximate that of a polyether, so that the substances which are soluble in such solvents preferentially get located in that region[350]. However, in case of ionic SDBS, the cleaning efficiency relatively decreased. This lowering of solubilization can be ascribed to looser packing of the micelles due to coloumbic repulsions between them.

The effect of different concentrations of additives on the dye removal efficiency of Myrj 45, SDBS and $C_{12}E_{10}$ are shown in Figs. 44-46. All these additives in solution decrease the solubilization capacity of surfactants although not to a great extent. All these additives are non-penetrating ones and they are expected to locate themselves at the micelle solvent interface. This prevents the micelles getting close to one another and thereby increases the intermicellar distance. In order words the micelles are no more packed closer to one another.

For SDBS / $C_{12}E_{10}$ mixed system the dye removal efficiency of the mixtures is favoured as shown in Fig. 47. The cleaning efficiency of SDBS for dye removal increased on the addition of $C_{12}E_{10}$. In case of anionic / nonionic mixed systems it is reported that increased solubilization of the dye occurs when there is interaction between the polyoxyethylene chains and benzene sulfonate groups[29]. Such interactions have been reported for anionic / nonionic mixtures from the observed interaction parameter, β values. In other words, a synergistic behavior in the detergence property is observed for the SDBS / $C_{12}E_{10}$ mixtures.

Similarly, the effect of additives on the detergency was investigated for the SDBS / $C_{12}E_{10}$ mixed system. Fig~~s~~. 48 show the dye removal efficiency in presence of additives. Although, very small change in the solubilization capacity at all SDBS mole fraction was observed, it was lowered in presence of PEG 400, sucrose and urea.

4.2.d **Wetting** :

Besides, the bulk properties, the surface properties of surface active agents are also necessary to understand the adsorption process. The wetting is a term generally applied to the displacement of air from a liquid or a solid surface by water or an aqueous solution. The wetting property of the surfactant solutions were studied by determining the contact angle θ of the solution with a clean teflon surface. When a drop of liquid is placed on a flat solid surface, it may spread completely over the surface or it may remain as a drop having a definite angle of contact with the solid

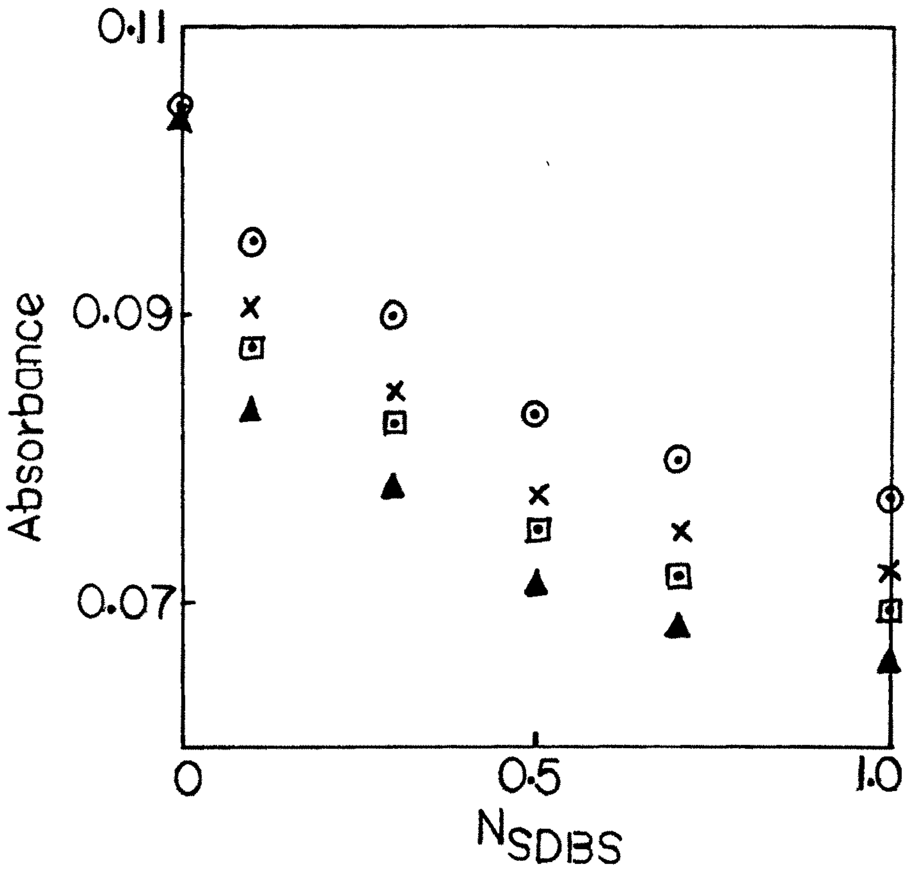


Fig. 44 : Absorbance Vs additive concentration for $C_{12}E_{10}$ (total conc. = 10 mM) after 10 minutes. ● PEG 400; ⊗ Sucrose; ▲ Urea.

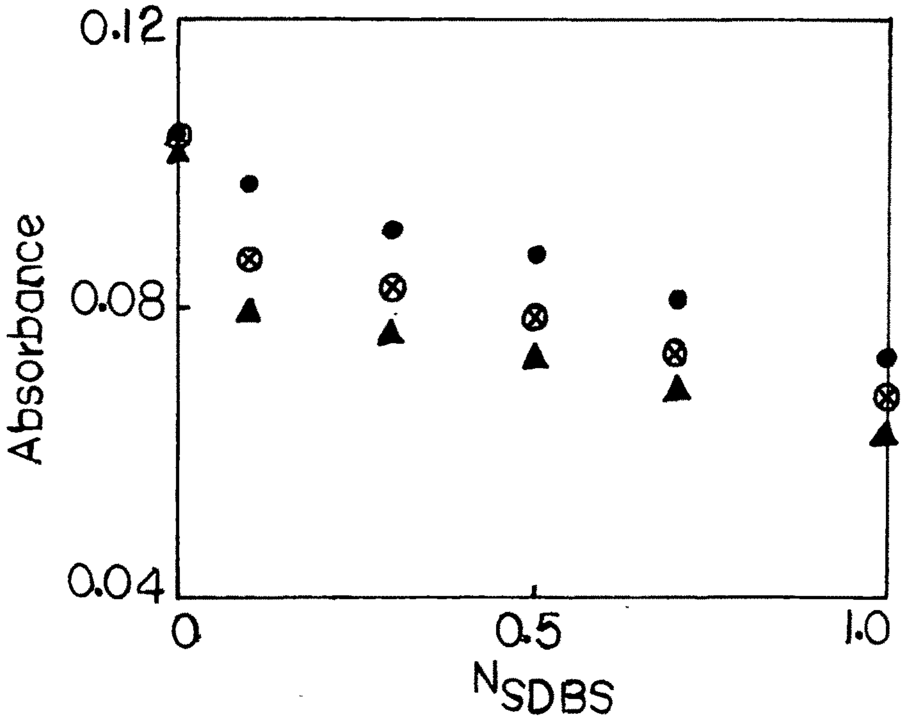


Fig. 45 : Absorbance Vs additive concentration for $C_{12}E_{10}$ (total conc. = 10 mM) after 10 minutes. ● PEG 400; ⊗ Sucrose; ▲ Urea.

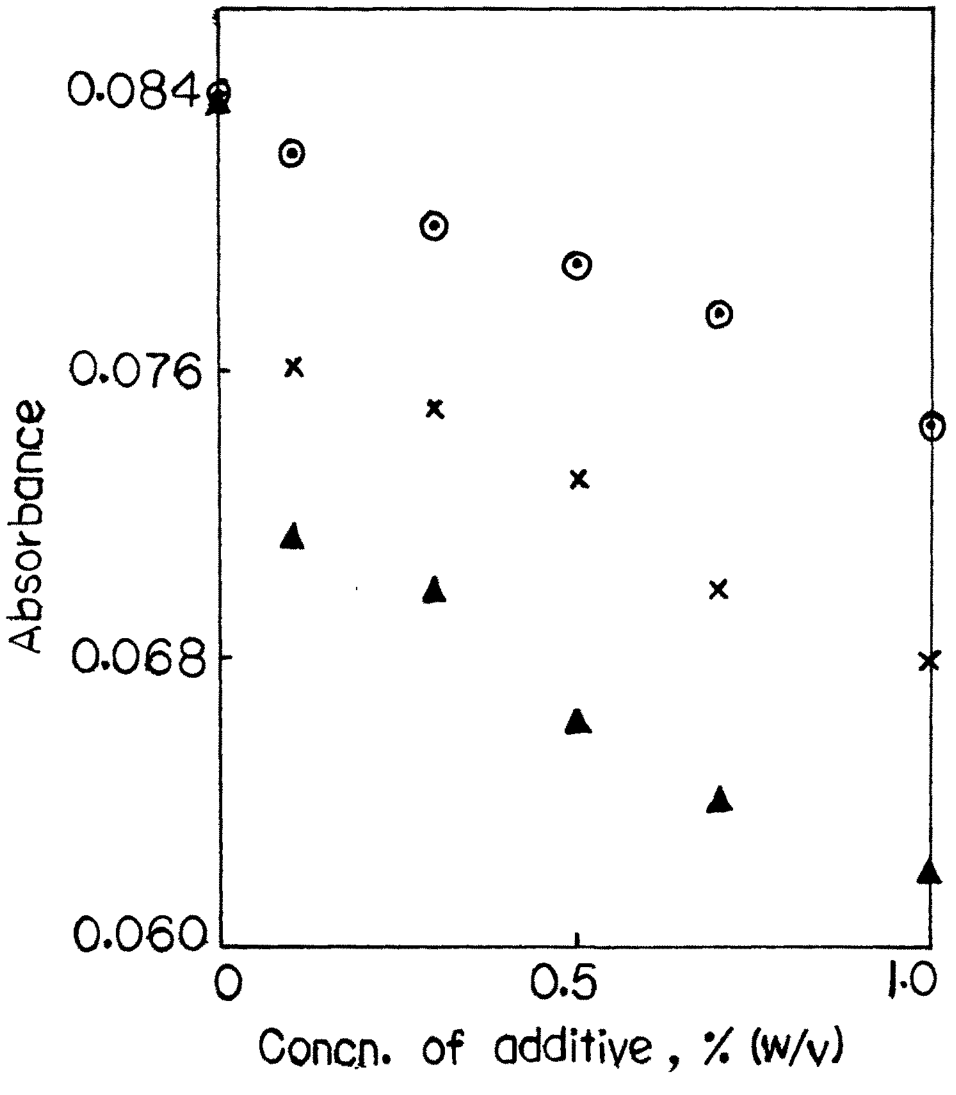


Fig. 46 : Absorbance Vs additive concentration for SDBS (total conc. = 10 mM) after 10 minutes. ⊙ PEG 400; ⊗ Sucrose; ▲ Urea.

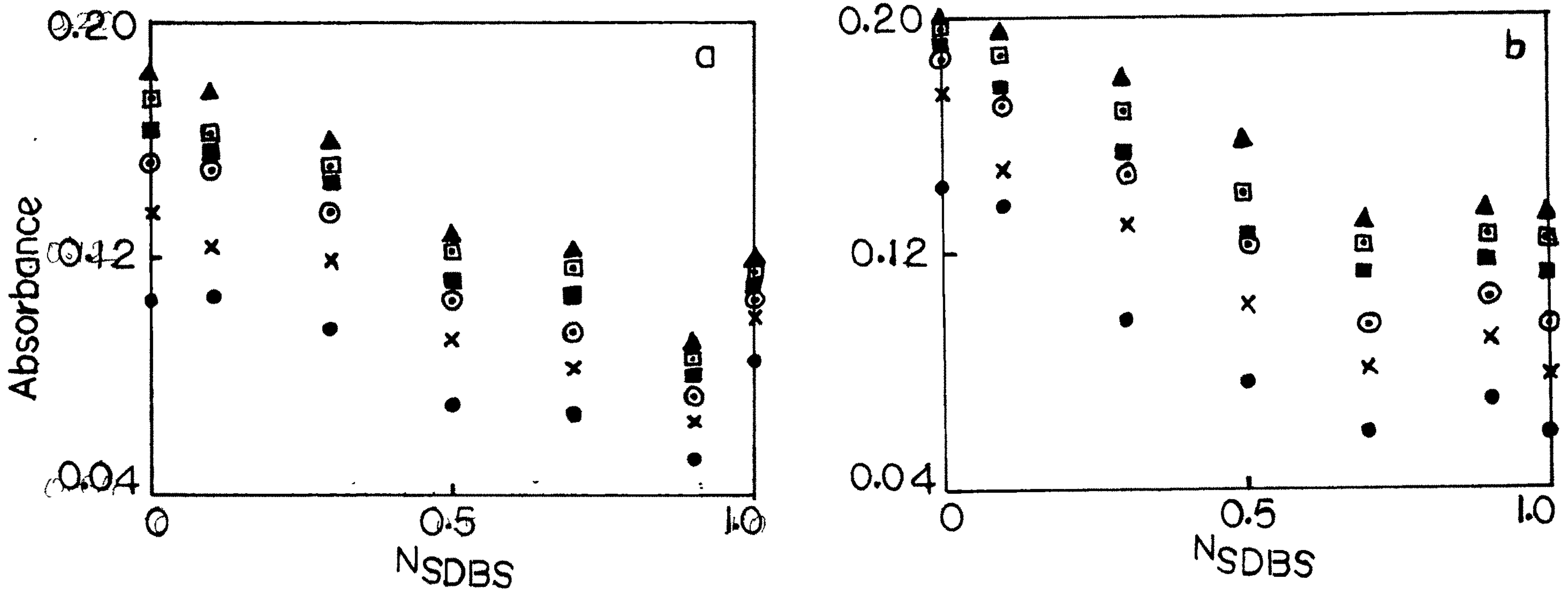


Fig. 47 : Absorbance Vs N_{SDBS} for SDBS / $C_{12}E_{10}$ mixed system at different time intervals at total surfactant concentration. (a) = 10 mM; (b) = 40 mM.
● 10 mts; ✖ 20 mts; ⊙ 30 mts; ■ 40 mts; ⊡ 50 mts; ▲ 60 mts.

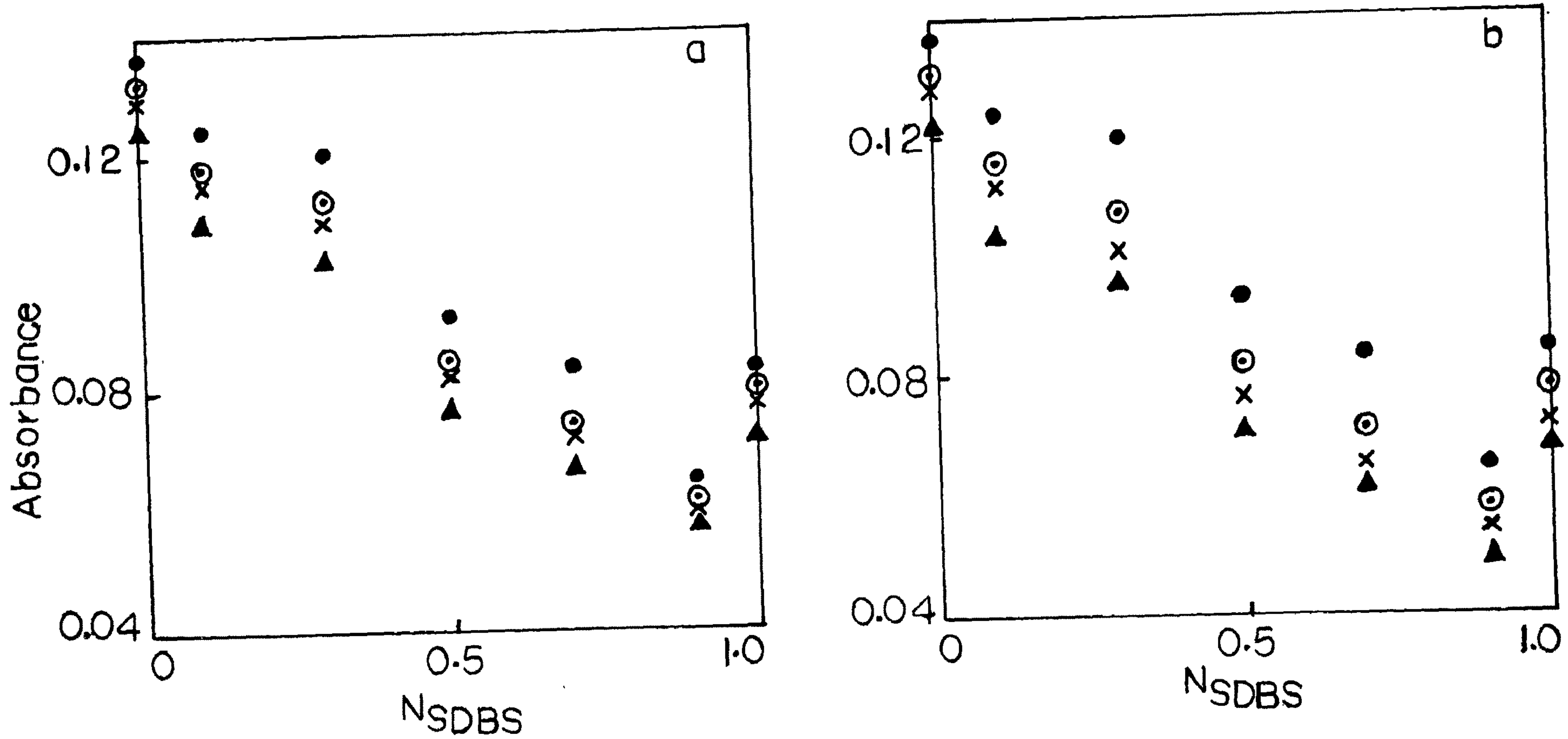


Fig. 48 : Absorbance Vs N_{SDBS} for SDBS / $C_{12}E_{10}$ mixed system at different additive concentrations. (a) = 0.3% (w/v); (b) = 0.7% (w/v) after 20 minutes (total surfactant concentration = 10 mM). ● no additive; ⊙ PEG 400; ✖ Sucrose; ▲ Urea.

surface. This angle is known as the contact angle. The zero contact angle results when the forces of attraction between the liquid and the solid (i.e. forces of adhesion) are equal to or greater than those between the liquid and liquid (forces of cohesion) and a finite contact angle results when the liquid adheres to the solid less than it coheres to itself. The solid is completely wetted by the liquid if the contact angle is zero and only partially wetted if the contact angle is finite. Complete non-wetting implies a contact angle of 180°.

The contact angle 'θ' was measured using a contact 'θ' meter. Figs. 49-51 shows the effect of additives on the wetting efficiency of nonionic Myrj 45, $C_{12}E_{10}$ and anionic SDBS. The contact angle 'θ' in all these cases is found to decrease with increasing additive concentration. This reduction in the contact angle indicates the lowering of interfacial energy of the solid / liquid interface, by the surfactant in presence of additives.

The wetting property of the SDBS / $C_{12}E_{10}$ mixed surfactant system was also investigated both in presence and in absence of PEG 400, sucrose and urea at room temperature. It was observed that the wetting property of the mixed system is actually lower than that of the pure components. This was true at all mole fractions of SDBS. The total concentration of surfactant was 5, 10, 25 mM, respectively. In presence of PEG 400, sucrose and urea of different concentrations decrease in contact angle 'θ' was observed (Fig. 52, 53). Hence, one can postulate that the wetting characteristic of the solution depends on the amount of each of the component as well as the presence of additives. This is because the surface activity of pure components are not same and hence the change in the ratio of components and additives change the surface activity, which regulates the contact angle.

CONCLUSIONS :

The various performance properties of nonionic surfactant Myrj 45 and $C_{12}E_{10}$, anionic surfactant SDBS and SDBS / $C_{12}E_{10}$ mixed systems were investigated. This

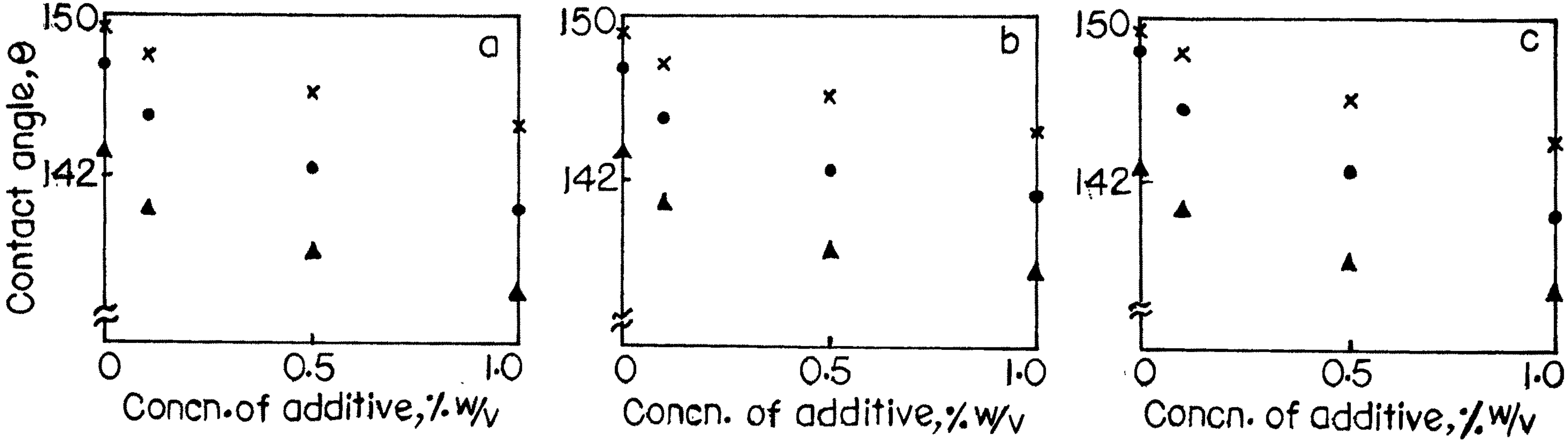


Fig. 49 : Plot of contact angle (θ) Vs additive concentration for Myrj 45 in presence of (a) PEG 400; (b) Sucrose; (c) Urea at total surfactant concentration.

✖ 1 mM; ● 3 mM; ▲ 5 mM.

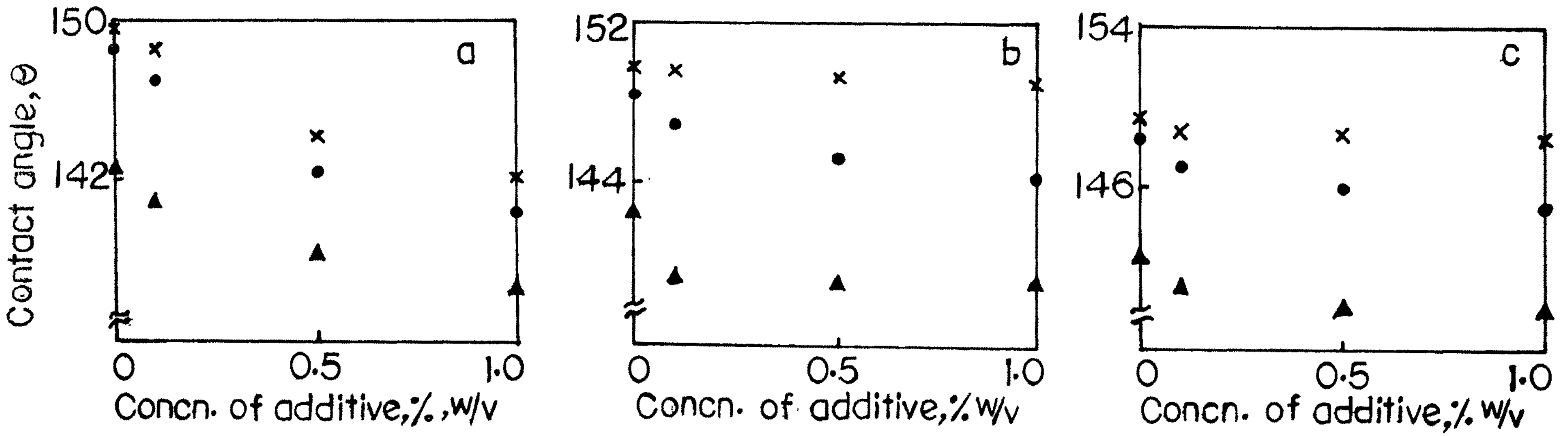


Fig. 50 : Plot of contact angle (θ) Vs additive concentration for $C_{12}E_{10}$ in presence of (a) PEG 400; (b) Sucrose; (c) Urea at total surfactant concentration.

✖ 0.25%; ● 0.5%; ▲ 1.0% (w/v).

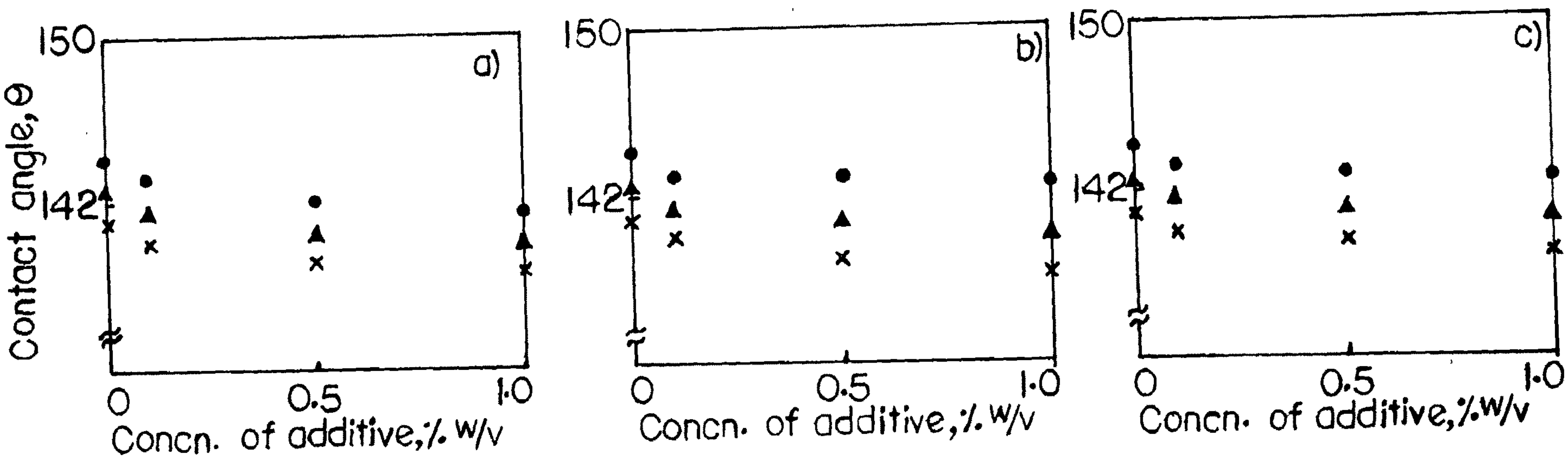


Fig. 51 : Plot of contact angle (θ) additive concentration for SDBS in presence of (a) PEG 400; (b) Sucrose; (c) Urea at total surfactant concentration. ● 5 mM; ▲ 10 mM; ✖ 20 mM.

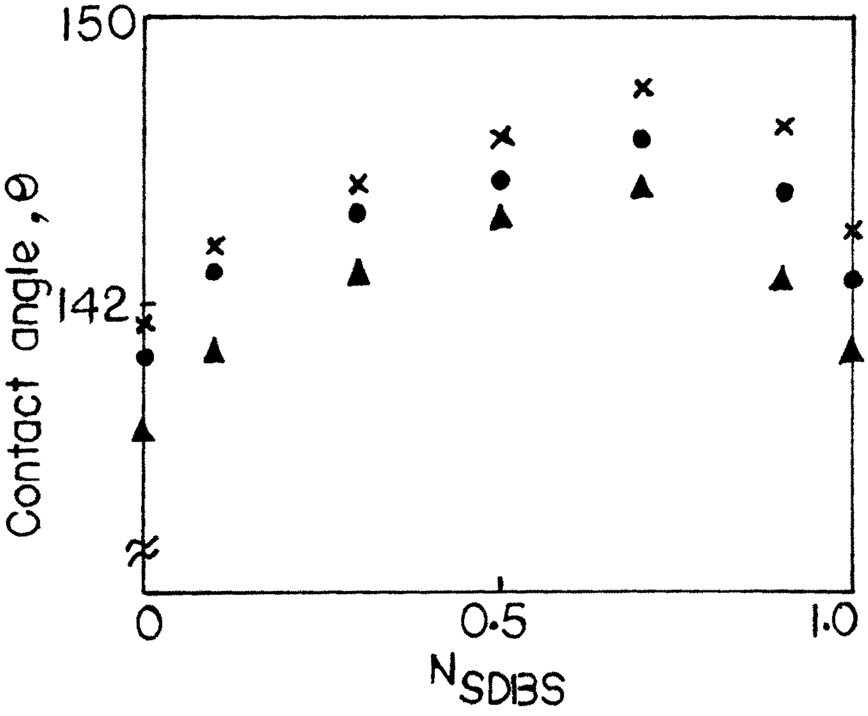


Fig. 52 : Plot of contact angle (θ) Vs mole fraction of SDBS of SDBS / $C_{12}E_{10}$ mixed system. ▲ 5 mM; ● 10 mM; ✖ 25 mM.

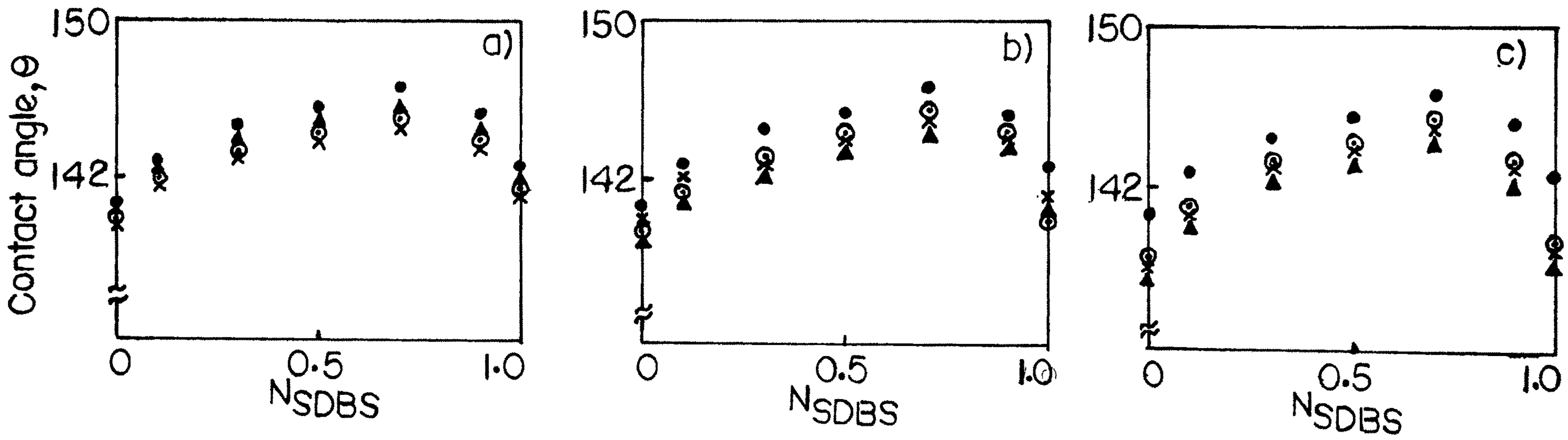


Fig. 53 : Plot of contact angle (θ) Vs mole fraction of SDBS for SDBS / $C_{12}E_{10}$ mixed system in presence of additives (total surfactant concentration = 25 mM). ● no additive; ⊙ PEG 400; ✖ Sucrose; ▲ Urea.

includes the viscosity, foaming, detergency and wetting studies of these surfactants in presence and absence of different concentrations of PEG 400, sucrose and urea. The intrinsic viscosity values obtained for all these systems in presence and absence of additives indicate a non-globular particle. The volume of the micelle including the hydration (V_h) and the volume of oxyethylene chain (V_{OE}) for $C_{12}E_{10}$ was computed both in presence and absence of additives. Both PEG 400 and urea increase while sucrose decreases, the V_h and V_{OE} values. The relative viscosity - SDBS mole fraction plot for SDBS / $C_{12}E_{10}$ system shows a maximum indicating a mixed micelle formation and/or higher electroviscous effect. The plots also show a positive deviation from ideality. In presence of various additive concentrations also although the maximum in η_r - N_{SDBS} plot is present small variations in the $[\eta]$ values were observed in presence of additives.

The foam height was measured for these surfactant systems in presence of additives. The initial foam height increases slightly in presence of sucrose and urea. Nonionics $C_{12}E_{10}$ has been found to have a lower foaming efficiency than anionic SDBS. The SDBS / $C_{12}E_{10}$ mixtures show somewhat synergistic behavior in the foaming property. Although the synergism was observed in presence of additives the foaming efficiency decreased.

The detergency studies were carried out by the dye (an oil soluble dye used as a model compound) removal efficiency of the surfactants. Nonionic surfactants Myrj 45 and $C_{12}E_{10}$ were found to have higher dye removal efficiency compared to ionic SDBS. In case of mixed surfactant system, SDBS / $C_{12}E_{10}$, it was observed that the cleaning efficiency of ionic SDBS was improved on the addition of nonionic $C_{12}E_{10}$. The additives, PEG 400, sucrose and urea decreased the overall dye removal efficiency of the surfactants due to their presence at the micelle solvent interface.

In the wetting studies it was found that additives decrease the contact angle of the surfactant. A synergistic behavior was observed in the wetting efficiency of SDBS /

$C_{12}E_{10}$ mixed systems. Additives decreased the contact angle 'θ' not only for the pure components but also for mixtures. This has been ascribed to the variation of surface activity of the surfactants in presence of additives. The overall studies indicates that additives show pronounced effect on various performance properties.