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The effects of various foreign substances on the cloud point of Triton X 100 and Triton X 114

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Abstract The nonionic surfactants Triton X 100 and Triton X 114 form isotropic micellar solutions around 25 °C. One of the characteristic features of these solutions is the fact that at higher temperatures they undergo clouding and liquid–liquid phase separation. Addition of various additives to the surfactant solutions does change the temperature at which the clouding phenomenon occurs. In this paper such effect of additives on

the clouding phenomenon of Triton X 100 and Triton X 114 are discussed.

Key words Triton X 100 – Triton X 114 – cloud point – additives

In continuation of our interest in the properties of nonionic surfactants [1–4], we studied the effect of various additives on one of the most characteristic features of a nonionic surfactant – the cloud point. The nonionic surfactants are very useful in the formation of emulsions [5]. The commercial products are in general polydisperse [6]. The aqueous solutions of these surfactants show a complex phase behaviour including liquid–liquid phase separation at high temperature [7]. This temperature at which the isotropic micellar solution breaks up into two phases is known as the cloud point (CP). Almost all nonionic surfactants show this characteristic behaviour though most ionic surfactants do not have this property [8]. However most ionic surfactants in presence of large amount of NaCl show cloud point [9].

There are many theories to explain the presence of cloud point. However it is still not completely resolved [10, 11]. In one case it is generally assumed that the nonionic micelles grow, on heating the solution, upto the cloud point and hence phase separation occurs [12]. The suggestion by Conti and Degiorgio [13] is that the cloud point is the lower consolute temperature of a binary mixture. This indicates that the micelles come together as

the temperature is approached and at the CP they separate out as the second phase. This inter-micellar interaction has been studied by Kjellander et al. [14] and they suggested that this increased interaction is the result of strong entropy dominance. The ethylene oxide groups are highly hydrated and well structured (i.e., less entropy). When two micelles approach each other, there is always overlap of the hydration spheres and some water molecules are freed hence the increase in entropy. At the cloud point this increase in entropy is more and the corresponding ΔG is much more negative than that which arises for the repulsive forces. Thereby the total free energy is negative and cloud point appears.

Triton X-100 (T X100) and Triton X-114 (T X114) are $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$ where $x = 9.5$ for T X 100 and 8 for T X 114. T X 100 is widely used as detergent in molecular biology [15]. T X 114 has been used for preconcentration in analytical chemistry [16]. It was shown earlier by Valaulikar and Manohar [17] that at very small concentration of NaCl the CP of T X 100 is not affected by the additives. They have also shown that small amounts ($\sim 10^{-5}$ M) of ionic surfactant increase the CP. The concentration of T X 100 was kept at

10% (w/v) or higher. In the present case we have varied the concentration of the surfactant from about 1% (w/v) to 10% (w/v). We have used various additives e.g. polyethylene glycol (PEG) of molecular weights 200, 300 and 400. Ionic surfactants e.g. cetyltrimethyl ammonium bromide (CTAB) and cetylpyridinium bromide (CPB). Substances like sucrose, tetraethylammonium bromide (TEAB) acetamide and electrolytes like LiCl, NaCl, NaBr, NaI, KCl, MnCl_2 and CrCl_3 at various concentrations to get a wider idea about the behaviour of CP. However, the concentrations of the additives in this study are generally in the higher region.

Materials and methods

T X 100 (KOCH Light Laboratories Ltd., England), T X 114 (Sigma Chemical Company, USA) and Cetylpyridinium bromide (CPB) (Fluka, Switzerland) were used without further purification. PEG 200, 300 and 400 (Merck, India) were used as received. The electrolytes used in all experiments were of analytical grade. Cetyltrimethyl ammonium bromide (CTAB) and Tetraethylammonium bromide (TEAB) (National Chemical, Baroda, India) were recrystallized from acetone and acetone/methanol (75/25) ratio and dried before use. Sucrose and acetamide were from Qualigens, India. Acetamide was recrystallized from benzene and dried before use. Triply distilled water was used to prepare sample solutions.

Cloud points of surfactant solutions were determined visually by noting the temperature at which turbidity was observed. We also noted the temperature at which turbidity disappeared on cooling. The average of the two was taken as the cloud point of the system. Heating and cooling were regulated to $0.5^\circ\text{C}/\text{min}$ around the cloud point. The maximum error in cloud point value is 0.5% calculated from at least three determinations. The maximum difference in cloud point was found to be 0.4°C .

Results and discussion

In Fig. 1 the variations of cloud point as a function of surfactant concentrations are shown. Best possible curves were drawn. It is to be noted that for Triton X 100, the CP is 66.9°C at 10% solution which compares well with the literature value of 67°C [17]. However the CP of T X 114 is somewhat different from the literature value of 22°C [18]. However it is obvious that the CP-concentration curve shows a minimum for T X 100 system (cf. ref. [13]) whereas for T X 114 the CP increases from around 3% solution. At the lower concentration range CP remains more or less constant (within 1 to 10% w/v concentration

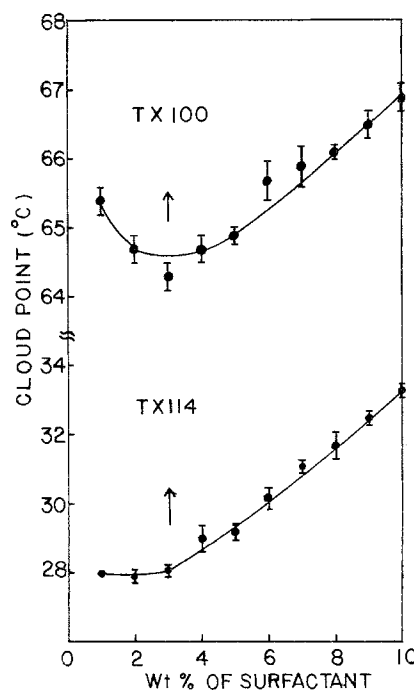


Fig. 1 Variation of cloud point of T X 100 and T X 114 with weight percent of surfactant in solution

range of surfactant studied). Similar results were obtained earlier by Heusch [19]. The decrease in cloud point with increase in T X 100 concentration is due to the increase in micelle concentration. The phase separation results from micelle-micelle interaction. However at higher concentration the CP continues to increase. This is because at high surfactant concentration a structured water-surfactant system is present [19]. With rise in temperature this structure breaks though the molecules do not become free of the surfactant effect. In other words, some of the water molecules are attached to no micelle in particular but to the micelle system in general, forming buffers between micelles. However the micelles are still separated because of the presence of these water molecules. It has been suggested earlier that in polyglycol ether surfactant systems the water molecules is available for total tenside molecules [20]. Therefore higher temperature is required to remove these "floating" water molecules which are barriers for micellar interaction. Once they move out at higher temperature the micelle-micelle interaction becomes easier. That is why the cloud point is seen at higher temperature.

In Fig. 2 we show the change in the CP as a function of the mole percent of PEG of different molecular weights. The salient feature of Fig. 2 is the fact that the effect of PEG 400 is most and that of PEG 200 is least in both cases. However the effects on cloud points of PEGs are

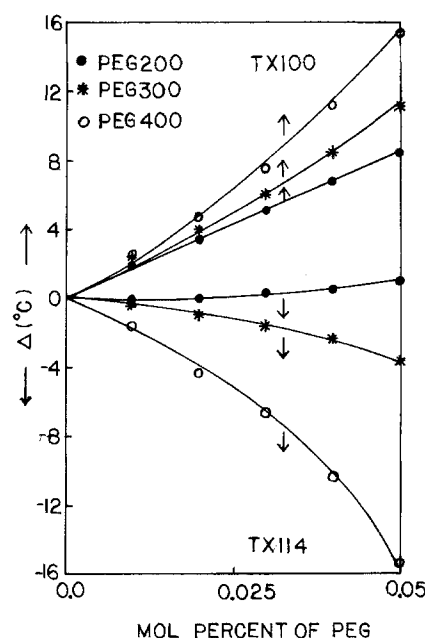


Fig. 2 Plot of change in cloud point ($\Delta^\circ\text{C}$) of T X 100 and T X 114 (1% w/v) with mole percent of PEG

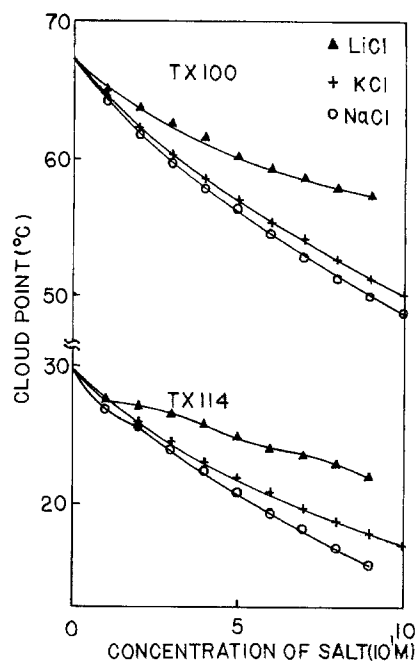


Fig. 3 Variation of cloud point of T X 100 and T X 114 (1% w/v) with concentration of alkali metal chlorides

positive for T X 100 and negative for T X 114. This observation was a most unexpected one; we expected similar behaviour in both cases. However it is known [21] that the solutes which get solubilized in the POE mantle of the micelle decrease the cloud point. Hence, it is suggested that the PEG 200, PEG 300 and PEG 400 get solubilized only in the POE mantle. They do not undergo deep penetration to the core of the micelle, that is, CP increases. It can be noted from Fig. 2 that in T X 100 system the CP increases; CP generally is higher if higher number of oxyethylene groups are present. It was suggested earlier [22–23] that oxyethylene groups of PEG “feel” themselves as a part of T X 100 oxyethylene group. That is the system feels that there is an increase in the number of oxyethylene group in T X 100. Therefore the effect will be PEG 400 > PEG 300 > PEG 200. Hence the CP should show PEG 400 > PEG 300 > PEG 200 for T X 100 system. That was experimentally observed. However it is not clear as to why in T X 114 micellar system such behaviour is not seen. We feel that both in T X 100 and T X 114 micellar systems, both the properties are present. That is solubilization decreases the CP and the sensing of the increase in the length of POE chain increases CP. The experimental value is the resultant of these two contradictory reasons. We are not yet in a position to compute the contribution of each factor.

The effect of the electrolytes on the CP of T X 100 and T X 114 were also studied. The experimental results are

also shown in Fig. 3. Earlier Marszall [24–25] as well as Valaulikar and Manohar [17] studied the effect of NaCl on the CP of T X 100. We have here studied the effect of the concentration of NaCl which was more than several orders of magnitude larger than earlier studies. We have not been able to find any such earlier study on CP of T X 114. From Fig. 3 it is quite clear that LiCl, NaCl and KCl decrease the cloud point of both T X 100 and T X 114. Such decrease in cloud point of T X 100 by NaCl was observed earlier by Heusch [19]. The effect seems to be more with NaCl than with LiCl and KCl. It was shown by Marszall [24] that LiCl, NaCl and KCl have the same effect on CP lowering of T X 100 in presence of SDS at low electrolyte concentration. At very low (10^{-5} M) NaCl concentration, the CP of T X 100 is not affected at all [17]. However we found that it was not so at higher concentrations of electrolytes. It was observed earlier that most of the electrolytes decrease the cloud point and follows the lyotropic series in their effect [26]. The higher the lyotropic number of the cation the greater is the effect. In other words Na^+ is expected to have more effects than Li^+ . We expected K^+ to have more effect than Na^+ which was not observed. The same behaviour was observed earlier also [27] for T X 100 systems. The decrease in CP by electrolytes is because of dehydration of the EO group of T X 100 and T X 114 surfactants because of the competition for water between EO groups and alkali metal ions. However it was suggested [28] earlier that Li^+ probably

forms complexes with the surfactant and increase the CP as it cannot compete with ether groups for water of hydration. On the other hand, Na^+ and K^+ cannot form complexes and compete for water of hydration.

From the lyotropic series it is expected that the effect of $\text{Cl}^- > \text{Br}^- > \text{I}^-$ on the decrease in CP. It was observed earlier that NaI actually increases the CP. We also observe the same. NaI increases the CP for both surfactants. The salts which break the water structure seem to increase the CP [29]. NaCl and NaBr decrease the CP (Fig. 4). The positive change influenced by NaI is much more for T X 114. For example, for 1 M NaI the increase in CP for T X 114 was 17°C whereas for T X 100 it was only $\sim 10^\circ\text{C}$. The decrease in CP by 1 M NaCl is $\sim 14^\circ\text{C}$ for T X 114 and $\sim 19^\circ\text{C}$ for T X 100. NaBr does not have much of an effect on the CP of T X 114 whereas for T X 100 the effect is measurable though negative. These results (Figs. 3 and 4) indicate that the effect depends upon the number of the EO group present in the surfactant as well as the charge density on the anion and the capacity to break water structure. The higher the negative charge density the more the decrease in CP.

We also determined the effect of the cationic charges on the cloud point. In Fig. 5 the effect of the NaCl, MnCl_2 and CrCl_3 are shown. CPs are plotted against ionic strength. In both systems the CP decreases and higher valency ions have the least effect. That is, the effect is $\text{Na}^+ > \text{Mn}^{2+} > \text{Cr}^{3+}$ at the same ionic strength of the salt solution. Once again the decrease in CP is higher for T X 100 than in the case of T X 114. In other words, it is noted that where there is decrease in CP, T X 100 system is more affected, whereas wherever there is increase in CP, the T X 114 system is more affected. It should be noted here that CP decreases more sharply when Na_2SO_4 or Na_2CO_3 is used instead of NaCl [30]. It seems that the nature of the charge (positive or negative) determines the total amount of effect.

The effect of the two cationic surfactants cetyltrimethyl ammonium bromide (CTAB) and cetylpyridinium bromide (CPB) were also studied. The experimental concentrations of these additives were kept constant whereas the concentrations of T X 100 and T X 114 were varied. In both cases, at all concentrations of additives or of surfactants the CP shows increments. Interestingly, at a particular additive concentration the CP increase is higher at lower surfactant concentration. The additives do form mixed micelles. The micelles being charged, the cloud point increases. Both Marszall [24] and Valaulikar et al. [17] have observed similar behaviour. The lower the concentration of the surfactant at a particular additive concentration, the higher will be charge density of the mixed micelle; the repulsive forces, hence, become more prominent and therefore the CP was at higher temperature

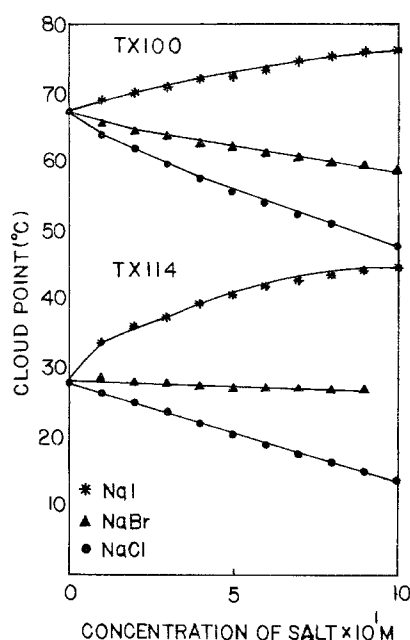


Fig. 4 Variation of cloud points of T X 100 and T X 114 (1% w/v) with concentrations of various sodium halides

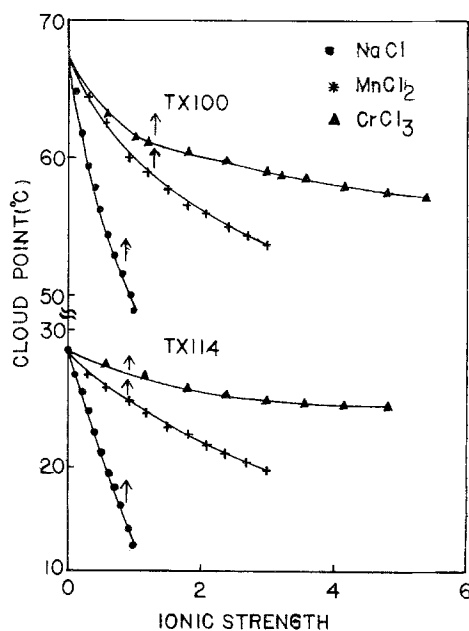


Fig. 5 Variation of cloud point of T X 100 and T X 114 (1% w/v) with ionic strength of halide solutions

(Table 1, Fig. 6). It can also be noted that for the same surfactant concentration when additive concentrations are increased then in general the CP increases, indicating the increase in the micellar charge density. Hence, it is suggested that the charge density on mixed micelle will determine

Table 1 Cloud points (CP) of various solutions of T X 100 and T X 114 and the effect of CTAB and CPB on the cloud points

Additive concentration	T X 100						T X 114					
	1%	3%	5%	7%	9%	10%	1%	3%	5%	7%	9%	10%
CTAB	cp						cp					
0%	65.4	64.3	64.9	65.9	66.5	66.9	28.0	28.0	29.2	31.1	32.5	33.3
	Δ in cp						Δ in cp					
0.005%	15.4	5.0	0.8	0.9	0.1	2.5	24.7	1.0		0.5	0.5	0.4
0.01%	22.4	21.5	2.6	1.2	0.8	0.4	38.7	5.6	1.2	0.9	0.9	0.9
0.02%	*	23.6	7.5	3.8	1.7	1.0	66.6	15.7	2.6	1.5	1.6	1.5
0.1%	*	*	30.9	24.8	22.4	20.6	*	39.6	31.5	18.8	15.7	10.4
CPB												
0.005%	22.6	3.5	1.0	0.8	—	0.4	25.8	1.4	1.1	0.4	0	0
0.01%	*	6.2	2.2	1.2	1.3	1.0	30.4	13.1	2.5	1.2	0.8	0
0.02%	*	16.2	3.0	1.7	1.3	1.0	68.7	28.1	6.9	3.6	2.5	1.4
0.1%	*	16.2	4.3	2.6	1.6	—	*	39.3	32.1	31.5	15.4	12.0

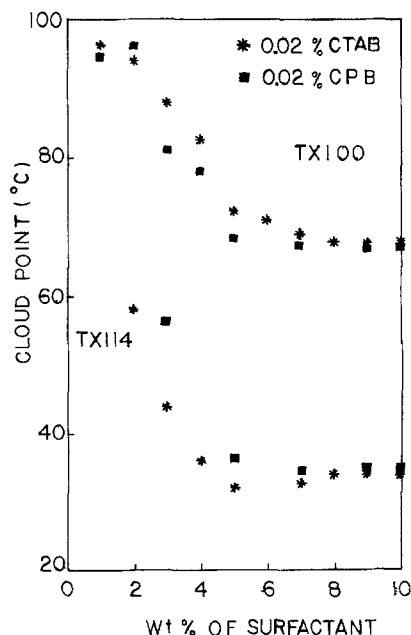
— Not done.

* Could not be obtained, CP is over 100 °C.

Table 2 Effect of Acetamide, TEAB and Sucrose on cloud point shift values of T X 100 and T X 114

Conc. of Surfactant		Acetamide Δ (°C)					TEAB Δ (°C)					Sucrose Δ (°C)				
		1%	5%	10%	15%	20%	1%	5%	10%	15%	20%	1%	5%	10%	15%	20%
T X 100	1%	1.8	7.9	14.6	21.2	—	0.0	1.5	2.5	3.1	3.4	0	—1.3	—3.3	—5.3	—
	5%	1.3	8.5	15.4	22.8	—	0.0	1.3	3.3	4.2	5.2	—0.2	—2.0	—3.8	—6.4	—
	10%	1.3	8.2	15.2	22.6	—	0.0	0.2	2.9	3.2	4.1	—0.7	—3.3	—6.5	—7.2	—
T X 114	1%	1.3	7.2	13.9	19.9	27.7	—	2.1	2.9	3.3	2.8	—0.6	—2.5	—4.9	—7.7	—10.1
	5%	0.5	9.3	14.2	21.2	28.5	0.6	1.5	3.1	2.7	2.7	—1.8	—2.3	—4.7	—7.5	—10.7
	10%	1.6	7.6	14.9	21.2	27.6	0.8	2.4	3.5	2.6	1.8	—0.4	—2.6	—5.6	—8.7	—11.7

— Not done.

**Fig. 6** Variation of cloud point of T X 100 and T X 114 in presence of CPB and CTAB

the cloud point. The higher the charge density, the higher the cloud point. The increase in the concentration of the additives need not always increase the charge density because the charge density will be dependent on micelle size. The micelle size might change, due to the addition of the additives. From Table 1 it can also be noted that the effect of CTAB and CPB on the cloud points of T X 100 and T X 114 is dependent on various factors and it seems (though it is not very clear) the effects are similar, i.e., they are dependent only on the charges of the micelle.

In Table 2 and Figs. 7a and b, we present the effect of acetamide, Tetraethylammonium bromide (TEAB) and sucrose on the cloud points of T X 100 and T X 114. Here again the studies were done by changing the concentration of the surfactant as well as the additives. It is to be noted that the CP increases when the additives are acetamide, and TEAB. However CP decreases in presence of sucrose for both surfactants. The solubilization of TEA⁺ in the micelle makes the micelle charged and thereby, as discussed above, the CP increases. Acetamide is also polar and hence the CP increases. However in both cases the CP increase is not very high in comparison to the effect of CTAB and CPB as in later cases mixed micelles are

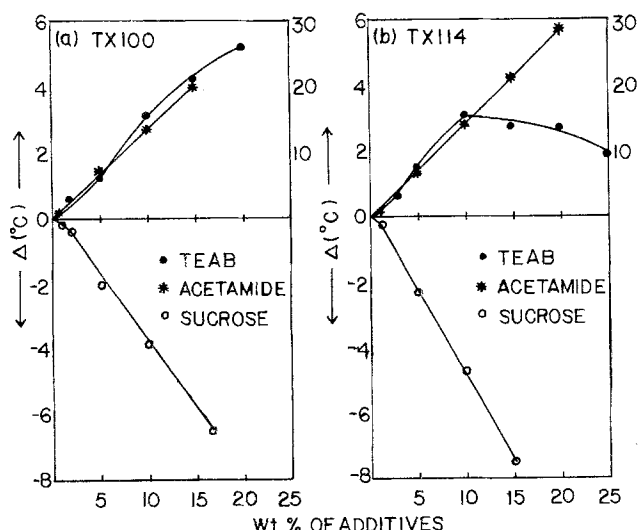


Fig. 7 Change of cloud point ($\Delta^\circ\text{C}$) of a) T X 100 and b) T X 114 (5% w/v) with concentration of additives

formed. In contrast to TEAB and acetamide, the sucrose shows decrease in CP. Here the decrease is much sharper, though again the effect is not as high as CTAB and CPB, but is somewhat similar to PEG 300 effect on T X 114 (cf. Fig. 2). The neutral hydrophilic sucrose molecule competes with the water associated with EO groups of Tritons

and removes some of these associated water molecules to itself and hence the decrease in cloud point.

Conclusion

The effects of various additives on the cloud points of T X 100 and T X 114 were studied. The effects of various polyethylene glycols were different in T X 100 and T X 114. This was probably because of simultaneous presence of two competitive phenomena in the system. These are the removal of water from the EO group, thereby decreasing the CP, as well as the fact that the EO groups of PEG feel themselves attached to the tritons, thereby increasing the CP. The dominance of the particular phenomena determines the final result. The CP also was found to show a minimum in the variation with concentration. The various electrolytes, sucrose, TEAB, and acetamide do change the CP to a large extent. The effect of the Li^+ is somewhat different from that of Na^+ or K^+ because of its complexing property. Similarly, water structure breaking property of NaI makes its effect different from that of NaCl or NaBr.

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References

- Sharma BG, Rakshit AK (1989) *J Colloid Interface Sci* 129:139
- Sharma BG, Rakshit AK (1989) In: Mittal KL (ed) *Surfactants in Solution*. Plenum, NY 7:319
- Koshy L, Rakshit AK (1991) *Bull Chem Soc Jpn* 64:2610
- Ajith S, Rakshit AK (1995) *Langmuir* 11:1122
- Becher P, Schick MJ (1987) In: Schick MJ (ed) *Nonionic Surfactants physical chemistry*, Vol 23, p 437, Marcel Dekker, NY
- Sadagania AS, Khan A (1991) *J Colloid Interface Sci* 144:191
- Triolo R, Magid LJ, Johnson JS, Jr Child HR (1982) *J Phys Chem* 86:3689
- Warr GG, Zemb TN, Driford M (1990) *J Phys Chem* 94:3086
- Porte G, Appell J (1983) *J Phys Lett* 44:L-689
- Zana R, Weill C (1985) *J Phys Lett* 46: L-953
- Strey R, Pakusch A (1987) In: Mittal KL, Brothorel P (ed) *Surfactants in Solution*, Vol 4, P 465, Plenum, NY
- Mackay RA (1987) in Ref 5, p 321
- Corti M, Minero C, Degiorgio V (1984) *J Phys Chem* 88:309
- Kjellander R, Floriu E (1981) *J Chem Soc Faraday Trans* 77:2053
- Loizaga B, Gurtubay IG, Marcella JM, Gani FM, Gomez JC (1979) *Priochem Soc Trans* 7:648
- Pinto CG, Perez Pavon JL, Cordero BM (1992) *Anal Chem* 64:2334
- Valauliker BS, Manohar C (1985) *J Colloid Interface Sci* 108:403
- Hillar GK, Von Wandruszka R (1995) *J Phys Chem* 99:1436
- Heusch R (1986) *BTF-Biotech Forum* 3:1
- Heusch R (1992) *Naturwissenschaften* 79:430
- Mackey RA (1987) in Ref 5, p 321
- Lin IJ, Metz JA (1971) *J Phys Chem* 75:3000
- Hato M, Shinoda K, Miyagawa T (1970) *Bull Chem Soc Jpn* 49:1257
- Marszall L (1988) *Langmuir* 4:90
- Marszall L, Valkenburg J (1981) *Ind Eng Chem Prod Res Dev* 20:708
- MeBain JW (1950) *"Colloid Science"*, DC Health, Boston, Ch 9
- Mackay RW (1987) in Ref 5, Table 4, p 310
- Schott H, Royce AE, Han SK (1984) *J Colloid Interface Sci* 98:196
- Schott H, Han SK (1976) *J Pharm Sci* 65:975
- Shinoda K, Takeda H (1970) *J Colloid Interface Sci* 32:642