

## Solvent effects on reverse micellisation of Tween 80 and Span 80 in pure and mixed organic solvents

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**Abstract.** Reverse micellisations of nonionic surfactants (Tween 80 and Span 80) in various pure nonaqueous solvents like carbontetrachloride, benzene, toluene, chloroform, cyclohexane and xylene, and in mixed solvent systems like  $\text{CCl}_4$ -DMF and  $\text{CCl}_4$ -DMSO covering the low dielectric range, are studied by UV electronic spectroscopy at 25°C. Micellar aggregation number ( $n_s$ ) in various solvents is evaluated using the hydrophobic dye, Oil Red. 0. The critical micellar concentration ( $cmc$ ) and  $n_s$  dependencies on the solvent dielectric, solvent ionization potential, solvent-surfactant interaction potentials, mole fractions of solvents in mixtures and internal pressures are studied. The  $\text{CCl}_4$ -DMSO system shows a  $cmc$  increase effect, while the  $\text{CCl}_4$ -DMF system shows a  $cmc$  decrease effect and the excess functions of  $\text{CCl}_4$ -DMSO and  $\text{CCl}_4$ -DMF show increase and decrease effects respectively. Rationalisations of the results and the role of the solvent cage effect have been discussed.

**Keywords.** Solvent cage effect; reverse micellisation; Tween 80; Span 80; nonionic surfactants.

### 1. Introduction

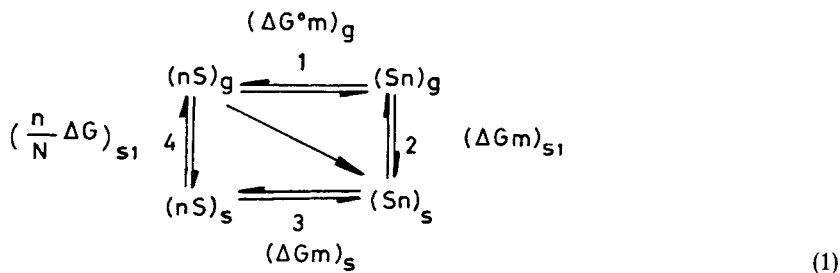
Micellisation of surfactants in solvents of low dielectric constant differs from those in aqueous media due to the differences in the solute-solute, solute-solvent and solvent-solvent interactions (Fendler and Fendler 1975; Clint 1992). Surfactants in nonaqueous and nonpolar solutions form reverse micelles with hydrophilic core (Mittal 1979; Parameshwari 1992). Reverse micelle parameters like the  $cmc$  and  $n_s$  are generally found to be lower than those of the normal micelles since weak dipole-dipole interactions predominate compared to the stronger counterparts like the ion-ion and ion-dipole interactions in the aqueous solutions of ionic surfactants (Kon-No *et al* 1974). In our laboratory, Tween 80 (polyoxy ethylene (20) sorbitan mono oleate) and Span 80 (polyoxy ethylene (20) sorbitan mono stearate) belonging to the class of nonionic surfactants are found to form reverse micelles in low dielectric solvents like  $\text{CCl}_4$ , benzene, toluene etc. Also, Tween 80 and Span 80 show variation in  $cmc$  values in different organic solvents. This indicates that the dielectric constant of the medium may not be the exclusive factor in the solvent effect of reverse micellisation process. Literature on the effect of solvents, with low dielectric values, on the reverse micellisation of Tween 80 and Span 80 in some of nonaqueous solvents of similar dielectric

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constant values are only a few (Fowkes 1967; El Seoud and Fendler 1975). We report here studies on the reverse micellisation of Tween 80 and Span 80 in some nonaqueous solvents of similar dielectric constant values. Also, when high dielectric constant (aprotic) solvents like DMF and DMSO are involved, a shift in the *cmc* value is seen. Variations in the micellar properties in various mole fractions of the mixed solvents form interesting cases of study (Fowkes 1967; Ritchie 1969). Using CCl<sub>4</sub>–(nonpolar) and DMSO and DMF (aprotic, polar) solvents, CCl<sub>4</sub>–DMF and CCl<sub>4</sub>–DMSO solvent mixtures with continuously varying compositions may be achieved when varying proportions of each solvent are mixed. An attempt is made to correlate the micellar properties with the mole fractions of the solvent mixtures, their dielectric constants, internal pressures and excess volumes. The *cmc* and *n<sub>s</sub>* results are rationalized in the light of solvation forces involving dipole–dipole interactions, solvent ionization potentials, surfactant solvent interaction potentials, solvent mole fractions in mixtures, internal pressures and excess volumes. The *cmc* and *n<sub>s</sub>* are determined adopting UV absorption and dye visible spectrometry.

## 2. Theory

The solvent effects may be viewed on the basis of the following solvation cycle including the transition from the ideal gas to the ideal solution states (Ritchie 1969; Ratajczak and Orville 1982),



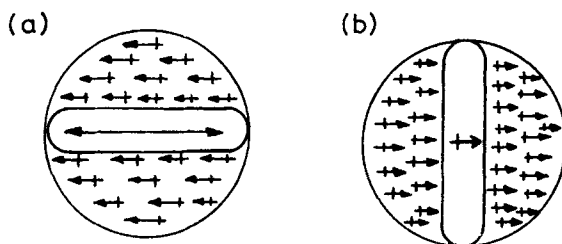
where, *S*, *S<sub>n</sub>*, *n*, *N*,  $\Delta G$ , *m*, *s1* and *g* denote the free surfactant, aggregate, aggregation number, Avagadro number, change in the free energy, micellisation, solution and gaseous state respectively. Equilibria 1 to 4 signify processes like surfactant micellisation in gas phase (ideal condition), solvation of micelles by the solvent dielectric, solvation of free surfactant molecules by the solvent dielectric and micellisation of the solvated surfactant molecules respectively. The  $\Delta G$  of  $(Sn)_s$  may be obtained by combining equilibria 1 and 2 or 3 and 4,

$$\text{i.e. } (\Delta G^{\circ}m)_g + (\Delta Gm)_{s1} = ((n/N)/\Delta G)_{s1} + (\Delta Gm)_s \quad (2)$$

Solvation of nonionic (dipolar) surfactant molecules by nonpolar low dielectric solvents is predominantly disperse in nature, so that the difference in the interaction energies of solvation of free molecules and micelles stands negligible. For a large value of free energy change of micellisation, micellisation in the gaseous phase approximates those in the solution phase  $(\Delta Gm)_g = (\Delta Gm)_s$ . This makes the micellisation of nonionic surfactant occur favourably against dipole–dipole solvation interactions.

Considering long chain amphiphilic molecules as dipolar ellipsoidal molecules, each being enclosed in solvent dipole cages, solvation forces between overall solute

orientations differ. For parallel orientations of the solute molecular dipole on the molecular axis, the solvent dipoles in the solvent cage may interact in a manner reducing the effective dipole moment of the solute. In the perpendicular orientation of the molecular dipole on the molecular axis, the solvent interactions increase the effective dipole moment. The processes schematically shown below may be referred to as negative (a) and positive (b) solvent effects respectively and may be exhibited by solvents of similar dielectric constant values (Hill *et al* 1969).



The phenomenon of negative solvent effect reduces the solute-solvent interactions, thereby increasing the solute-solute interactions. This favours the aggregation process. Hence in such solvents a decrease in *cmc* values would result. Likewise, a positive solvent phenomenon which increases the effective molecular dipole moment increases the solute-solvent interactions resulting in a *cmc* increase effect. Such effects are nil for spheroidal aggregate systems. The dipole-dipole interaction energies averaged over all orientations may be approximated to the function  $\mu^2/r^3$ , where  $\mu$  is the effective molecular dipole moment in solution and  $r$  is the closest distance of approach, for lateral associations between pairs of surfactant molecules (Amis 1973).  $r = r_s$  and  $r_m$  if the molecule is in the free and in the micellised states respectively. During micelle formation  $n_s/2$  such pairs interact where  $n_s$  is the aggregation number. Based on the Kirkwood expression for Gibb's energy of charging a sphere by dipolar solvation forces (Laidler and Muirhead-Gould 1966; Mittal 1979) the free energy change of micellisation  $(\Delta Gm)_{s1}$  between the free and the associated states in the solvent/solution dielectric constant  $\xi_s$  ( $\xi_0 =$  dielectric constant of vacuum) with aggregation number ' $n_s$ ' is taken as

$$(\Delta Gm)_{s1} = \frac{3n_s}{32\pi\xi_0\xi_s} \left( \frac{\mu_m^2}{r_m^3} - \frac{\mu_s^2}{r_s^3} \right). \quad (3)$$

In the cross-section of a micelle the surfactant molecules possess different orientations so that the resultant micellar dipole moment ( $\mu_m$ ) is lower in value than that of the free molecule ( $\mu_s$ ),

$$\text{i.e. } (\mu_m \ll \mu_s, r_m \gg r_s)$$

Hence (3) may be approximated to

$$(\Delta Gm)_{s1} = -3\mu_s^2/32\pi\xi_0\xi_sr_s^3. \quad (4)$$

For the surfactant micellisation equilibria  $(\Delta Gm)_{s1} = RT \ln cmc$ . Thus (4) may be expressed in terms of *cmc* as,

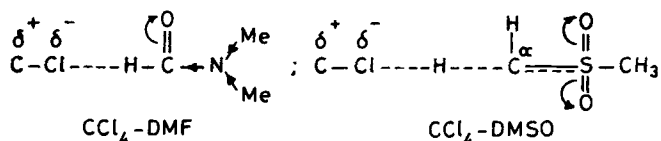
$$\log cmc_s = -3\mu_s^2/(2.303 RT 32\pi\xi_0\xi_sr_s^3), \quad (5)$$

$$\log \left( \frac{(cmc)_{s1}}{(cmc)_{s2}} \right) = \frac{-3n_s\mu_s^2}{2.303 RT 32\pi\xi_0r_m^3} \left( \frac{1}{\xi_{s1}} - \frac{1}{\xi_{s2}} \right), \quad (6)$$

where  $s_1$  and  $s_2$  represent different solvent media 1 and 2,  $\mu_s$  is the surfactant dipole moment in solution,  $n_s$  is the aggregation number and  $r$  is the micellar radius.

Equations (5) and (6) depict a linear dependence of  $\log cmc$  on  $\xi_s^{-1}$ , provided  $n$  and  $r$  are constants. For spherical micellar systems there is no resultant dipole moment of the micelle and the nonlinear variation of  $cmc$  with  $\xi_s$  may be viewed as due to the differences in the solute-solute and solute-solvent interactions.

When  $CCl_4$  is mixed separately with DMF and DMSO the intermolecular interactions such as weak hydrogen bonding which is facilitated by the two methyl groups of DMF in the  $CCl_4$ -DMF mixture and bond facilitated by a hyper conjugative hydrogen of the methyl group of DMSO in  $CCl_4$ -DMSO mixture may be envisaged.



The extent of such intermolecular interactions differ when different mole fractions of the two are mixed and are reflected in mixture properties like the excess volume, density and surface tension of the mixtures. Also the intermolecular forces bear a collective correlation to the dielectric constant, refractive index, molecular ionization potential and also to the internal pressure or cohesive energy through factors like surface tension and specific molar volume (Hildebrand and Scott 1950; Rowlinson 1969). The internal pressure in dynes/cm is given as  $\gamma\xi/v$  where  $\gamma$  is the surface tension,  $\xi$  is the surface area/mol ( $N_{AV} \sigma$ ) and  $\sigma = (v/N_{AV})^{2/3}$  where 'v' is the specific molar volume of the binary mixture.  $v = [(x_1 m_1 + x_2 m_2)/d_{12}]$  where  $x$ ,  $m$ ,  $d$  are the mole fractions, molecular weight and density of the pure components, and the solution given by 1, 2, 12 respectively.

In fact, the correlation of  $cmc$  I with internal pressure may be utilised in micellar radii determinations by adopting the solvent hole theory, where the free energy of micellisation ( $\Delta G_m$ ) supplements the pressure exerted by the solvent molecular collisions on the micellar interfacial area (Laidler 1987). The collisional force per unit interface area equalises the  $\Delta G_m$  value. Such derivation is beyond the scope of this work.

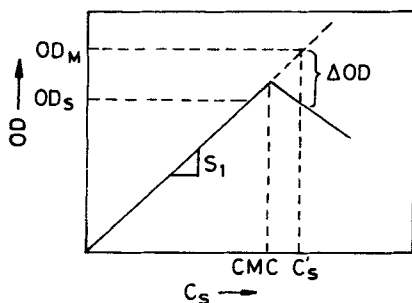
### 3. Experiment

Tween 80 and Span 80 belonging to the Analar grade of Fluka, Switzerland, AG samples are used without further purification. Solvents like benzene, toluene, xylene, chloroform, carbontetrachloride, chlorobenzene are freshly distilled over anhydrous calcium chloride before use.

Critical micelle concentration ( $cmc$ ) values are detected from the break point in the optical density versus surfactant concentration plots at 25°C. Optical density values are obtained from Carl-Zeiss Specord Electronic Spectrometer.

Aggregation number values are determined using an oil soluble dye Oil Red.O in the surfactant solutions. The OD of the dye drastically changes at the onset of the  $cmc$  of the surfactants as shown in the diagram below. When the surfactant concentration  $C_s > cmc$  the  $\Delta OD = OD_m - OD_s$  is related to the micelle concentration as  $[\text{mic}] = \Delta OD_m / S_1$ ;  $= (C_s - cmc) / n_s$ .

Therefore the linear plot of  $\log (C_s - cmc)$  versus  $\log [\text{mic}]$  will furnish the aggregation number  $n_s$  as the antilog [intercept]. The  $n_s$  values are only approximate and hold



good only for the 1:1 dye surfactant interactions before micellisation. This is ensured from the Hildebrand–Scott plot slope for the dye–surfactant system (Konno and Kithara 1971; Anandhi 1995).

Binary solvent mixtures were prepared by adding weighed amounts corresponding to the mole fractions. Surface tension and density of the thermostated mixtures at 303 K were determined adopting the capillary rise technique with a capillary of ID = 0.025 cm and a pycnometer of 10 ml capacity respectively.

#### 4. Results and discussion

Typical *cmc* detection plots for Tween 80 and Span 80 in benzene are given in figure 1. Table 1 summarizes the *cmc* values of the surfactant in various non-polar solvents. Figure 2 depicts the solvent dielectric constant effect on the surfactant micellisations while figure 3 represents correlation between the *cmc* and solvent ionization potentials.

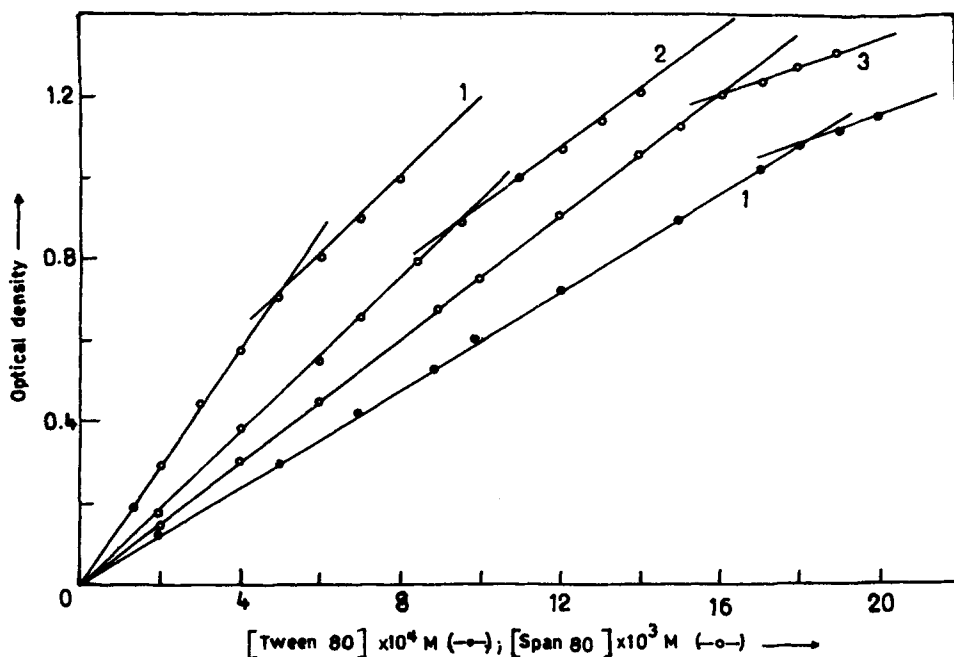
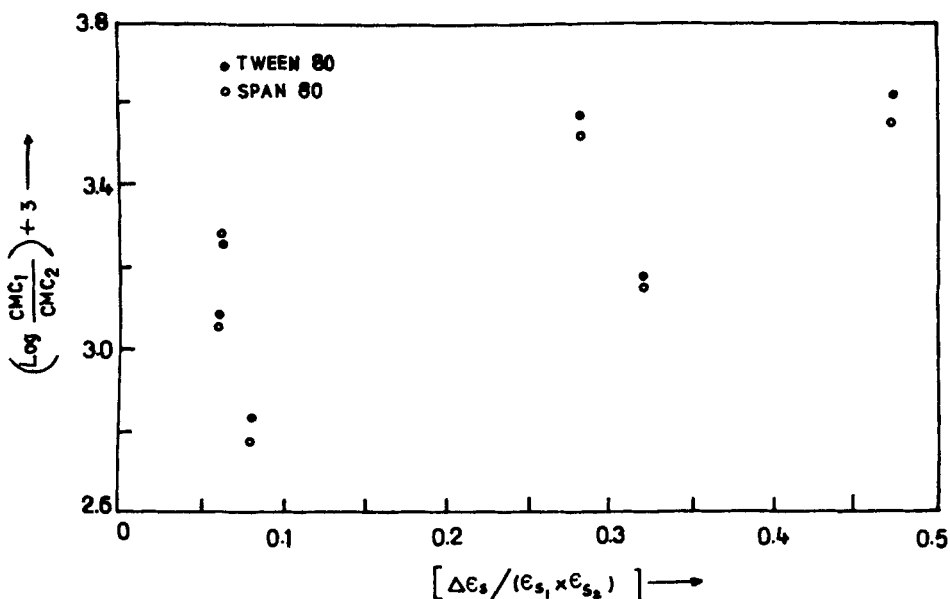


Figure 1. *cmc* detection plots of Tween 80 (●) and Span 80 (○) in nonaqueous solvents (1)  $\text{CCl}_4$ ; (2) benzene; (3) toluene.

**Table 1.** *cmc* data in various nonaqueous solvents at 25°C, of Tween (Tw) 80 and Span (Sp) 80  $\xi_s$  = solvent permittivity;  $I_p$  = ionization potential;  $U$  = interaction potential.

Solvents	$\xi_s$	$I_p$ (ev)	<i>cmc</i> ( $\times 10^2$ )M		- $U$ (mev)	
			Tw 80	Sp 80	Tw 80	Sp 80
Xylene	2.404	8.55	1.05	3.12	8.8	7.4
Cyclohexane	2.023	8.72	0.73	1.80	9.3	8.1
Toluene	2.284	8.81	0.60	1.60	9.5	8.3
Cholorobenzene	5.800	9.07	0.48	1.21	9.8	8.6
Benzene	2.348	9.24	0.40	0.95	10.10	8.9
Chloroform	4.740	11.42	0.19	0.53	11.0	9.6
Carbontetra chloride	2.238	11.47	0.18	0.51	11.1	9.7



**Figure 2.** *cmc* dependence on the solvent permittivities of Tween 80 and Span 80 in nonaqueous solvents at 25°C.

In table 2 the  $n_s$  and  $[mic]$  values obtained at various surfactant concentration for Tween 80 and Span 80 in benzene are represented. The forces and charges involved in surfactant aggregation in non-aqueous solvents differ considerably from those of water-based systems. The so-called "hydrophilic effect" lowers the unfavourable interactions between the hydrophilic part of the surfactants and the non-polar solvent molecules and concomitantly increases the interactions between the hydrophilic groups. This is the primary driving force for the formation of micelles in non-polar solvents. In the hydrophilic effect due to the grouping of hydrophilic groups, the proportion of the solvent molecules interacting unfavourably with the monomeric hydrophilic part of the surfactants is greatly decreased. In certain instances, the

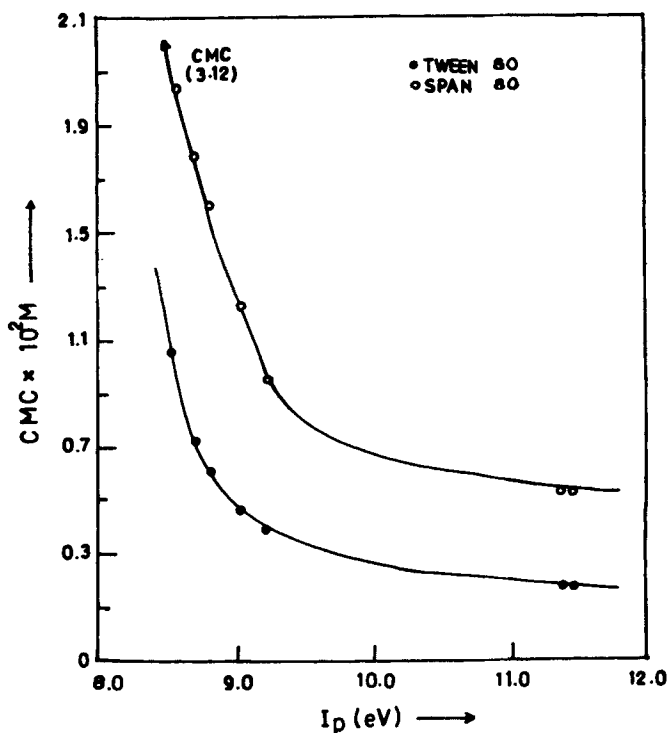


Figure 3. *cmc* dependence on the solvent ionization potentials (25 °C).

Table 2. The aggregation number ( $n_s$ ) and the micelle concentration [mic] values obtained from Oil red. O-Tw 80, Sp 80 interaction studies in benzene at 25 °C.

Tw 80		Sp 80	
[mic] ( $\times 10^5 M$ )	$n_s$	[mic] ( $\times 10^5 M$ )	$n_s$
3.2	48.0	2.4	47.1
4.4	48.1	3.4	48.0
6.4	50.0	4.4	48.5
8.8	50.5	6.4	49.0
9.2	53.0	8.4	49.8

presence of trace amounts of polar substances like water is essential to induce the hydrophilic effect (Nelson and Pink 1952; Zhu *et al* 1992). Presently for the Tween 80 and Span 80 systems due to their longer hydrophobic tails, the micellisation occurs without such requirements.

The *cmc* I and II values obtained from the optical density measurements for Tween 80 correspond to  $1.8 \times 10^{-3} M$  and  $5.1 \times 10^{-3} M$  in carbontetrachloride at 25 °C. Such low values are in accordance with the reverse micellisation process. When (6) is utilized to study the pure solvent dielectric constant effect (figure 2), a nonlinear dependence is observed. Assuming the micellar parameters ( $n_s$ ) to remain unaltered the nonlinear

variation may be considered to arise from the nonlinear dependence of the solute-solute interaction potentials on  $\xi_s$ . The consistency of  $n_s$  over a range of low  $\xi_s$  values show that the micellar properties may remain constant due to the similar solvent-solute interaction energies. Alternatively, the possibility of the nonlinear variation of the surfactant molecular dipole moment with the solvent dielectric would also result in a similar phenomenon. Changes in the aggregation number ( $n_s$ ) of the reverse micelles involve drastic changes in the hydrophilic effect, since grouping of hydrophilic groups are involved in the micellisation process. Changes in energetics due to the small changes in the  $n_s$  may be attributed to the changes in the *cmc* values in different solvents. Since micellisation is the result of strong solute-solute interactions, the lowered interaction potentials ( $U$ ) between surfactant molecules during micellisation is known from the free energy change expressed in milli electron volts (*mev*) (table 1). These values are the result of solvent-solvent, surfactant-solvent and surfactant-surfactant interaction potentials. Nevertheless when the solvent ionization potentials are considered (Franklin *et al* 1966) a regular variation seems to exist in the *cmc* values. Solvents with larger  $I_p$  values prove to be poorer in solvations while being favourable to micellisation effects. This may be seen in figure 3. At the microscopic level, inside a solvent cage at each interacting site, electromeric shifts from the solvent to solute molecules decide the firmness of solvation. Under such conditions for nonionic surfactants, which are more sensitive to the difference in solvation forces, solvents with low dielectric but high ionization potentials may prove fruitful for the reverse micellisation process.

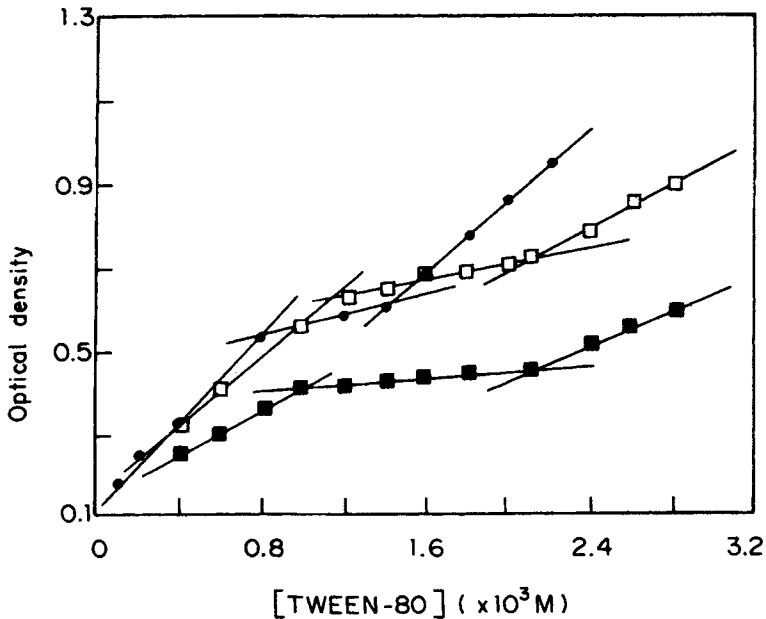
## 5. Studies in solvent mixtures

Table 3 summarizes the mixture properties of  $\text{CCl}_4$ -DMF and  $\text{CCl}_4$ -DMSO solvent mixtures at various mole fractions of the pure components. Figure 4 furnishes typical *cmc* detection plots in mixed solvents and in pure DMSO. In pure DMF no micellisation of Tween 80 occurs. In table 4, micellar parameters such as *cmc* I, *cmc* II and aggregation number ( $n_s$ ) in mixed solvents are given. In figure 5, mixtures excess properties such as internal pressure and *cmc* I variations with mole fractions of  $\text{CCl}_4$  are depicted. Log *cmc* dependence on internal pressure of the solvent mixtures is shown in figure 6. Optical density variations with the surfactant concentrations for Tween 80 in pure  $\text{CCl}_4$  and DMSO and in solvent mixtures show good deflection points corresponding to *cmc* I and *cmc* II respectively. The variation of *cmc* values with dielectric constant of solvent mixtures proves to be nonlinear and sometimes of

**Table 3.** Surface tension ( $\gamma$ , dyne  $\text{cm}^{-1}$ ), molar volumes ( $v$ ,  $\text{cc}^{-1}$ ) and internal pressure ( $I_p$ , dyne  $\text{cm}^{-2}$ ) values of pure and mixed  $\text{CCl}_4$ (1)-DMF (2)  $\text{CCl}_4$ (1)-DMSO (3) binary solvents at 303 K. Mole fraction  $x_2 = x_3 = 1 - x_1$

$x_1$	$\gamma$		$v$		$I_p (\times 10^{-10} \text{ ev})$		$\xi$	
	(1,2)	(1,3)	(1,2)	(1,3)	(1,2)	(1,3)	(1,2)	(1,3)
1.0	26.95	26.95	97.88	97.88	4.91	4.91	2.23	2.23
0.8	24.63	35.47	96.12	86.21	4.45	6.19	9.10	11.10
0.6	28.75	37.51	95.94	85.40	5.10	6.30	16.00	20.00
0.4	31.42	39.56	89.86	79.53	5.30	6.39	22.90	28.90
0.2	35.80	43.00	84.38	72.49	5.73	6.60	29.80	37.80
0	43.63	52.85	84.18	71.79	6.87	6.46	36.70	46.68





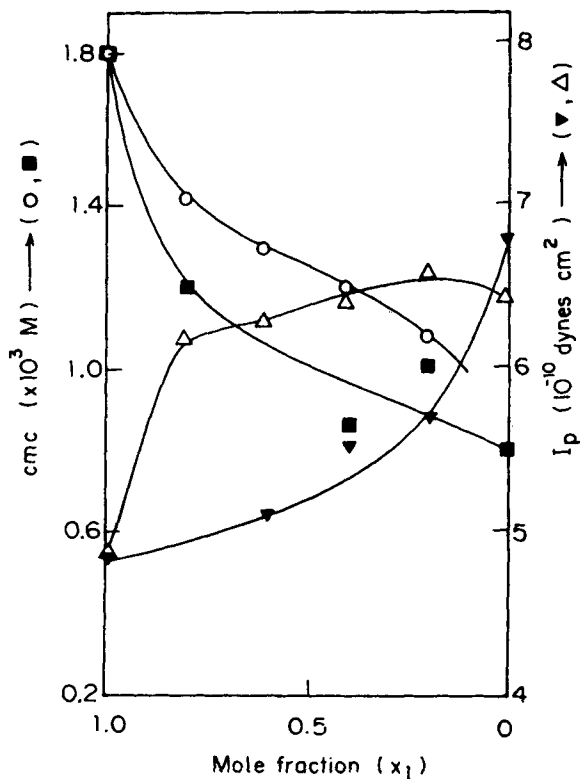
**Figure 4.** *cmc* detection plots of Tween 80 in pure DMSO (●-), CCl<sub>4</sub>-DMF mixture (□-) at CCl<sub>4</sub> mole fraction = 0.2 and CCl<sub>4</sub>-DMSO mixture (■-) at CCl<sub>4</sub> mole fraction = 0.2.

**Table 4.** *cmc*,  $n_s$  and interaction energy ( $U$ ) values of Tween 80 in pure (1, 2, 3) and mixed CCl<sub>4</sub> (1)-DMF (2); and CCl<sub>4</sub> (1)-DMSO (3) solvents at various CCl<sub>4</sub> mole fractions ( $x_1$ ) at 303 K.

$x_1$	I <i>cmc</i> (x10 <sup>3</sup> M)		$n_s$		II <i>cmc</i> (x10 <sup>3</sup> M)		- $U$ (mev)	
	(1,2)	(1,3)	(1,2)	(1,3)	(1,2)	(1,3)	(1,2)	(1,3)
1.0	1.78	1.78	55	55	2.74	2.74	8.1	8.1
0.8	1.42	1.20	145	200	1.40	1.20	8.4	8.6
0.6	1.30	1.30	175	175	2.06	2.45	8.5	8.5
0.4	1.20	0.86	200	285	2.58	2.85	8.6	9.0
0.2	1.08	1.00	230	250	2.12	2.10	8.76	8.9
0	—	0.80	—	300	—	—	—	9.2

a zig-zag type. Hence, physical properties like internal pressure derived from the surface tension and molar volumes may be utilized in lieu of the dielectric continuum to correlate the *cmc* dependence on mole fraction.

Internal pressure variations with continuously varying  $x_1$  lie above the line joining the  $I_p$  values of pure solvents in the CCl<sub>4</sub>-DMSO system (figure 4). This behaviour indicates a positive excess function type, particularly so when stronger interactions like hyperconjugation and hydrogen bonding are involved between the CCl<sub>4</sub> and DMSO molecules. The CCl<sub>4</sub>-DMF binary system depicts a negative mixture property as seen from the points that lie below the line of ideal behaviour that joins internal pressures of CCl<sub>4</sub> and DMF. This mixture property increases the surfactant solvent solubilisation

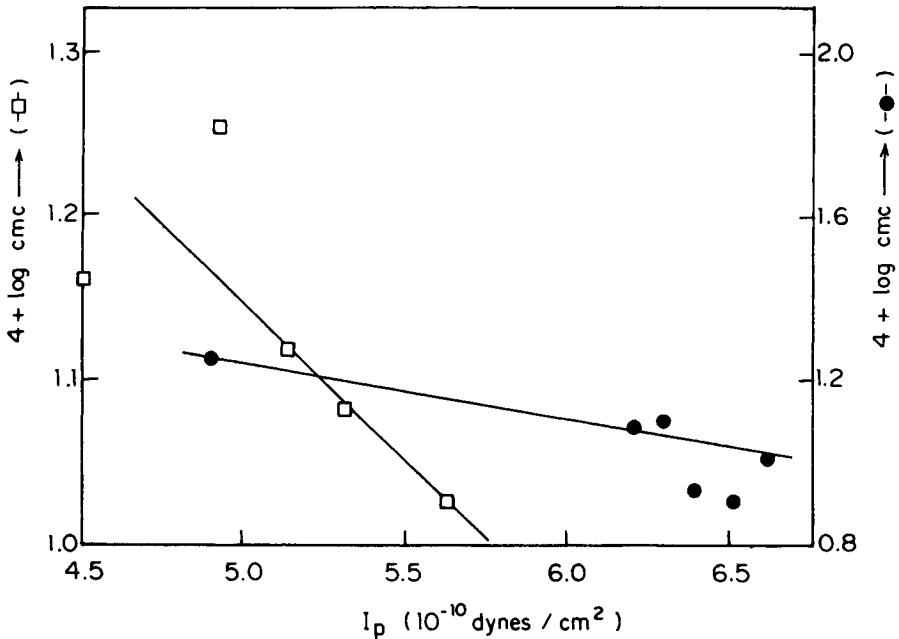


**Figure 5.** *cmc* (○, ■) and internal pressure (▼, △) variations on the  $\text{CCl}_4$  mole fraction ( $x_1$ ) in  $\text{CCl}_4$ -DMF and  $\text{CCl}_4$ -DMSO (■, △) mixtures at 303 K.

property such that the *cmc* values are higher than in the  $\text{CCl}_4$ -DMSO system showing a *cmc* increase effect. Interactions of the hydrophilic-hydrophilic bond formation in case of Tween 80 induce the onset of micellisation at lower concentrations, thereby exhibiting a *cmc* decrease effect with  $x_1$ , as seen in figure 6. Also, Tween 80 being more soluble in DMF, the reverse micellisation could not be detected in the pure solvent. Since there exists a definite solvent effect on the reverse micellisation of Tween 80, when the internal pressures of the solvent mixtures are related to the *cmc* values instead of the dielectric constant values, a better correlation seems to exist.

Alternatively the  $\text{CCl}_4$ -DMSO and  $\text{CCl}_4$ -DMF solvent mixtures seem to favour the reverse micellisation process of Tween 80. Higher aggregation numbers occur in the micelles and balance the higher extents of internal pressures of the solvents. Since hydrophobic groups are extended into the solvent medium through solvation, greater internal pressures dictate greater numbers of reverse micelles in the solvent medium. These factors linearise the correlation between the *cmc* and internal pressure values.

From the free energy change of micellisation ( $\Delta G_m$ ) which is expressed as  $RT \ln \text{cmc}$ , the resultant solute-solute interaction potentials in milli electron volts may be derived in the respective solvent media. There seems a slight increase in the interaction potential values in case of  $\text{CCl}_4$ -DMSO than in the  $\text{CCl}_4$ -DMF system. This once



**Figure 6.**  $\log cmc$  and internal pressure dependence plots for Tween 80 reverse micellisation in  $CCl_4$ -DMF (-□-) and  $CCl_4$ -DMSO (-●-) mixed solvents at 303 K.

again emphasises that the interaction between  $CCl_4$  and DMSO is dominant and thereby increases the surfactant-surfactant interactions which result in reverse micellisation.

## 6. Conclusions

Reverse micellisations of Tween 80 and Span 80 are favoured in pure solvents like benzene, toluene, xylene and  $CCl_4$ , DMSO and in mixtures like  $CCl_4$ -DMSO and  $CCl_4$ -DMF media similar to those noted in the pure organic solvent systems. The  $cmc$  and  $n_s$  values continuously vary from the pure  $CCl_4$  towards the pure DMF/DMSO solvent media in the micellar properties-mole fraction dependence plots. Solvent mixtures with positive excess functions seem to bring in a  $cmc$  decrease effect and the negative excess functions bring in a  $cmc$  increase effect. Also,  $n_s$  values in mixed solvent systems are higher than those in pure solvent which may be attributed to the resultant polarity of the media. Instead of the dielectric constant, internal pressure seems to bear a linear correlation with  $\log cmc$  values. A similar effect has been noted in pure organic solvents as well. Among the two pairs of solvent mixtures  $CCl_4$ -DMSO system favours reverse micellisation to a considerable extent rather than the  $CCl_4$ -DMF.

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