
CHAPTER 6

THERMODYNAMICS OF DROPLET FORMATION

6.a. Preview

The microemulsion formation occurs at a particular oil/water/surfactant ratio. The area in the triangular phase diagram indicates that there is a range in the concentration ratios over which the microemulsion remains present. At other ratios of the phase diagram the microemulsion will not be present.

Considering the one phase microemulsion (Winsor IV), it can be clearly seen that one of the components, oil or water get dissolved completely in the other at the lower boundary curve of the region. At very high surfactant concentration a solid-liquid two phase system exists. It is well known, from thermodynamics, that the free energy of dissolution of a solute in a solvent is given by [204]

$$\Delta G_{sol} = RT \ln X \quad (1)$$

where ΔG_{sol} is the free energy change and X is the mole fraction of the solute when the concentration of the solute is very low i.e. at infinite dilution. Under this condition the activity coefficient can be taken as unity and the activity of the solute can be taken to be the mole fraction of the solute.

6.b. Results and Discussion

We have considered the system where oil concentration was very low. The free energy of microemulsion formation i.e. the droplet formation of oil in water was calculated by calculating the mole fraction of the oil in water at a particular surfactant concentration. Number of moles of cyclohexane, SDS, propanol and water were determined and mole fraction of cyclohexane was computed. In Table 6.1 such data are given for system even where aqueous polyacrylamide solutions or NaCl solutions were used as aqueous phase. In Figs.6.1 - 6.5 we have plotted the variation of ΔG_{sol} with temperature ($^{\circ}K$). It is interesting to note that for all systems, at low surfactant concentration the $\Delta G_{sol} - T$ plots were linear, but at higher surfactant concentration a maximum was observed. The maxima for different systems were not at the same temperature value. The maximum indicates that one particular composition of oil/water/surfactant is preferred at a particular temperature. Higher or lower temperature does not satisfy the requirement of more solubility. The structure hence seems to be very important.

As far as this study is concerned, most of the systems did show a clear linear variation with

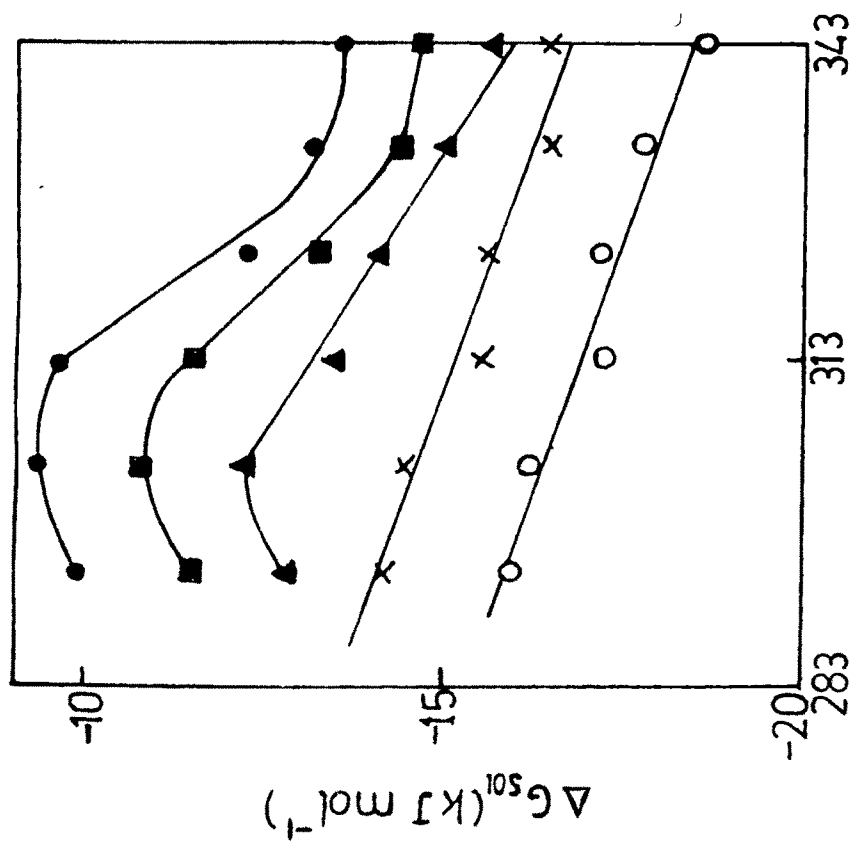


Fig.6.2 Temperature plots for the system cyclohexane-SDS+propanol-0.003% (w/v) aqueous PAA at surfactant weight percentage 10 O ; 15 X ; 20 ▲ ; 25 ■ ; 30 ● .

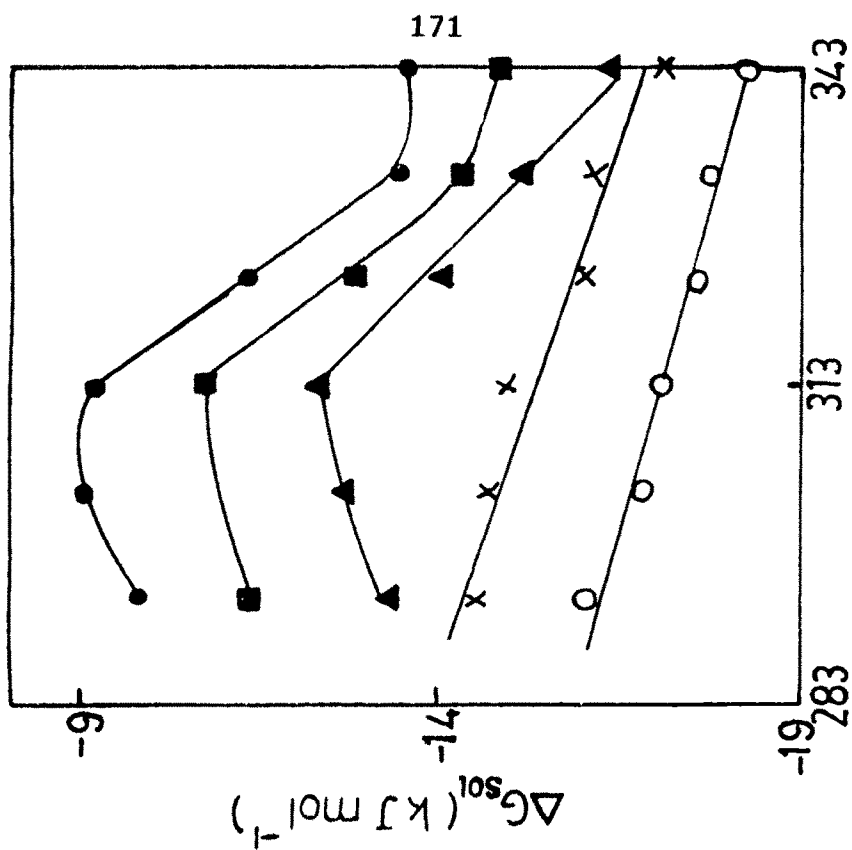


Fig.6.1 Plots of ΔG_{sol} against temperature for the system cyclohexane-SDS+propanol-water at different surfactant weight percentage: 10 O ; 15 X ; 20 ▲ ; 25 ■ ; 30 ● .

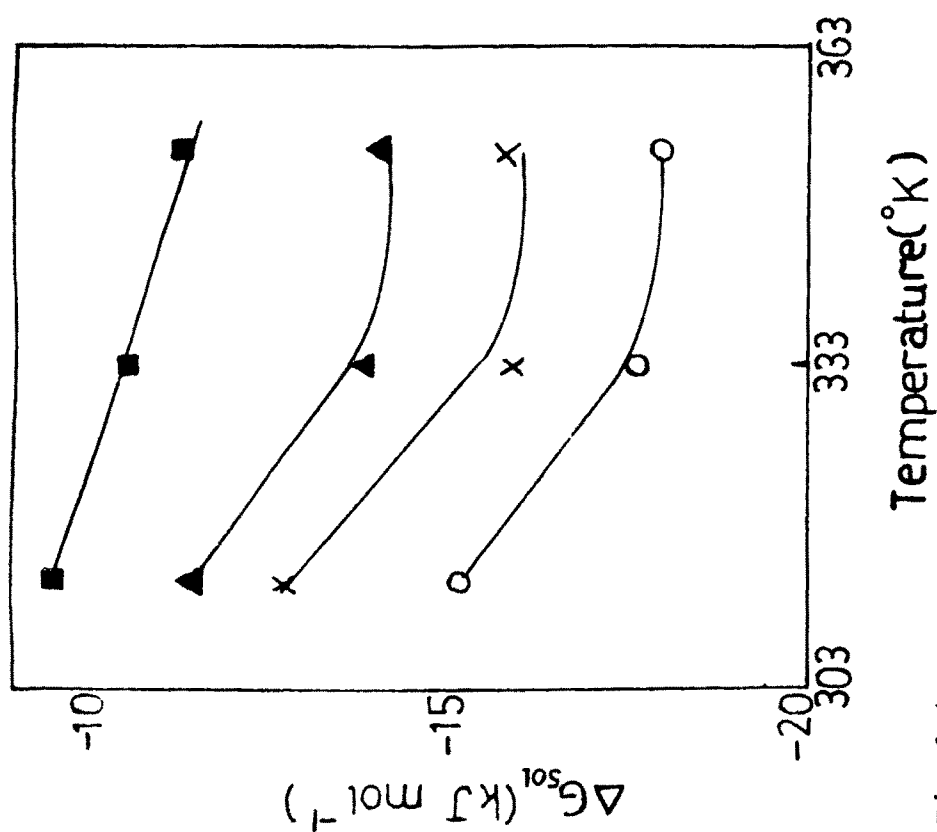


Fig.6.4

ΔG_{sol} - Temperature plots for the system cyclohexane-SDS+propanol-0.5 mol dm^{-3} aqueous NaCl at surfactant weight percentage 10 O; 15 X; 20 Δ; 25 ■.

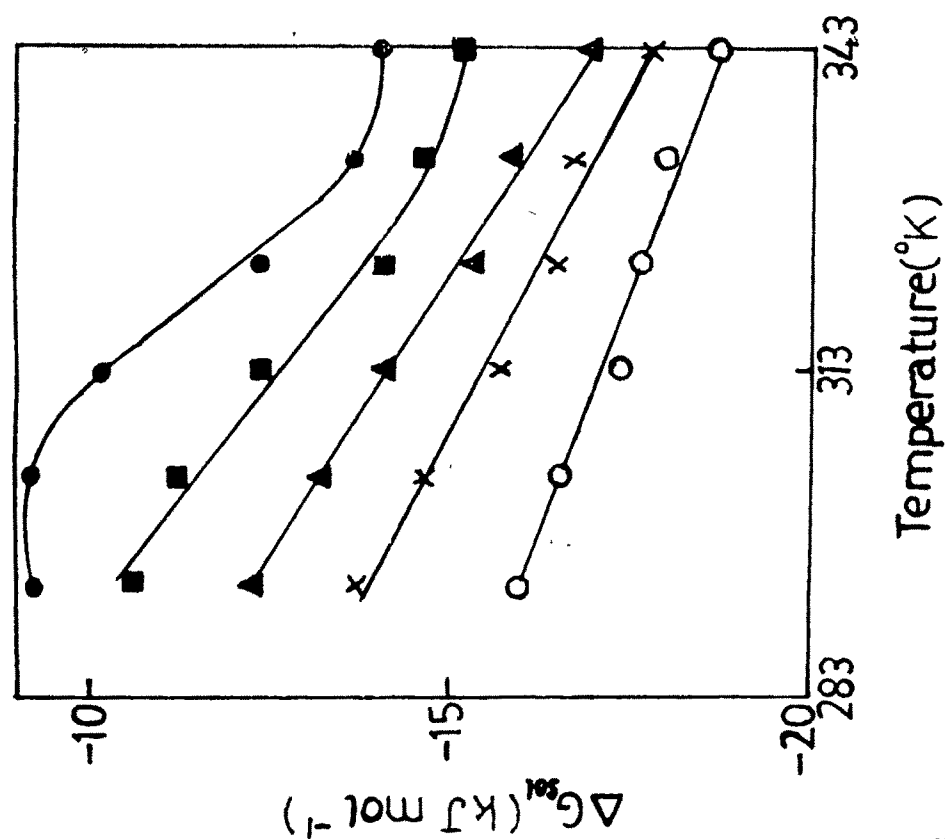


Fig.6.3

ΔG_{sol} - Temperature plots for the system cyclohexane-SDS+propanol-0.005% (w/v) aqueous PAA at surfactant weight percentage 10 O; 15 X; 20 Δ; 25 ■; 30 ●.

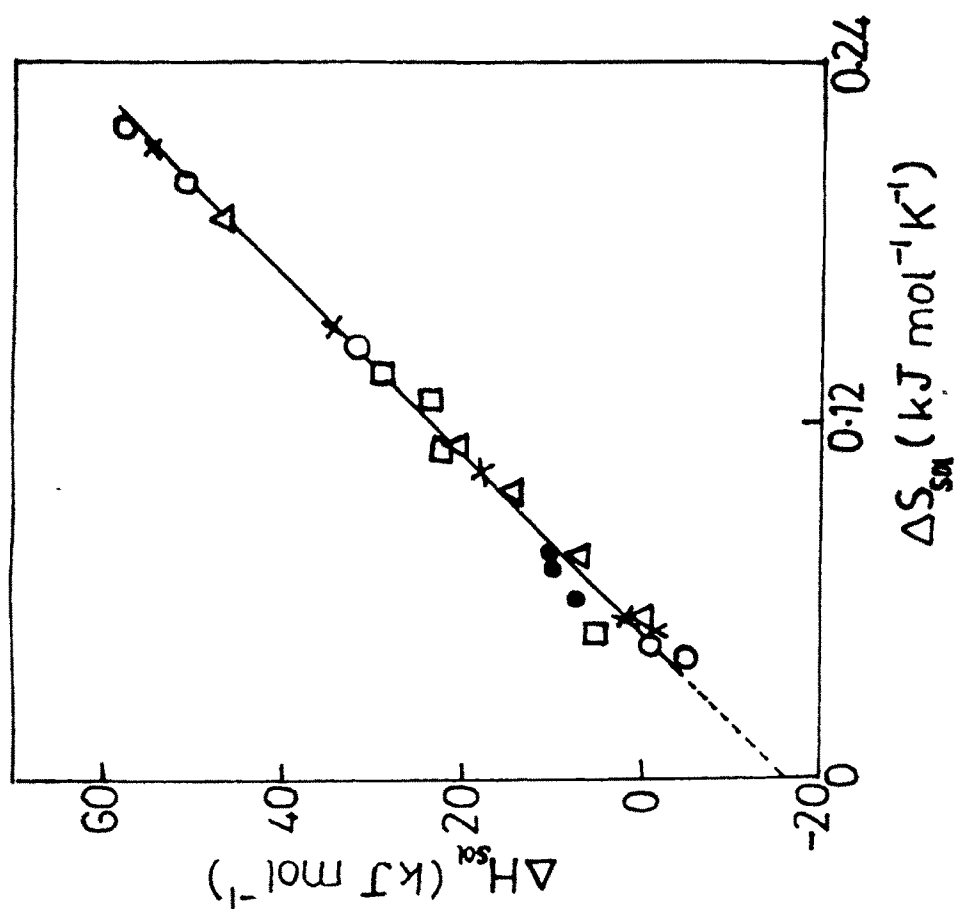


Fig.6.6

The plot showing the compensation effect of ΔH_{sol} against ΔS_{sol} for all the systems together. Water O ; 0.003 % PAA X ; 0.005 % PAA Δ ; 0.5 mol dm^{-3} NaCl \square ; 1 mol dm^{-3} NaCl \bullet .

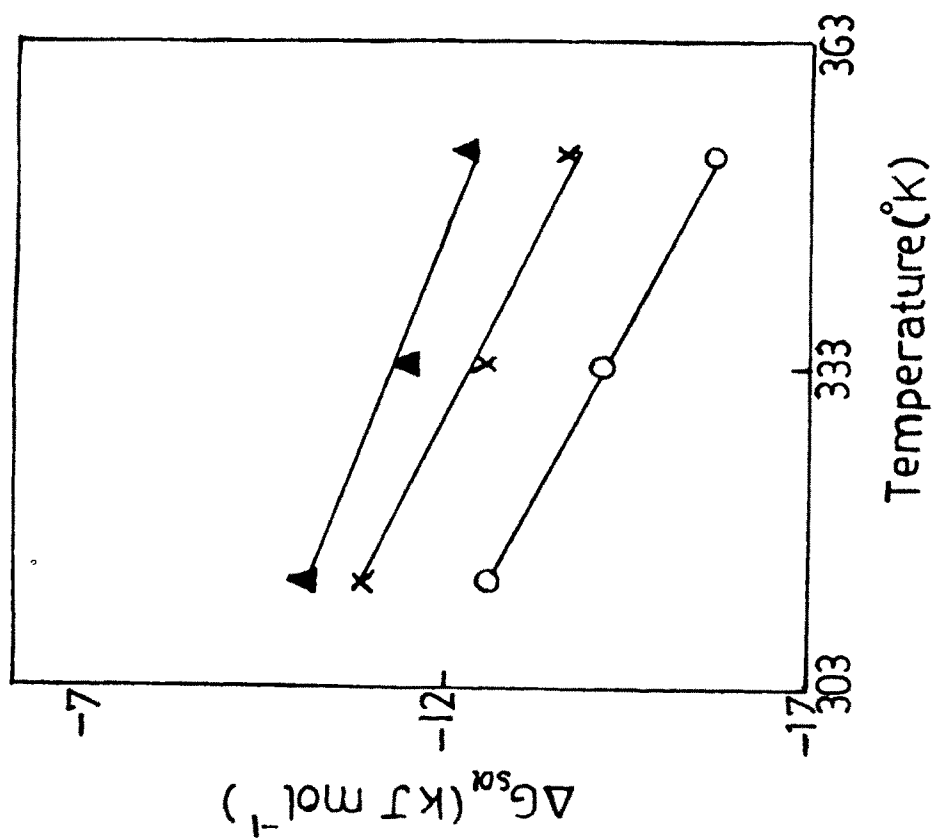


Fig.6.5

ΔG_{sol} -Temperature plots for the system cyclohexane-SDS+propanol-1 mol dm^{-3} aqueous NaCl at surfactant weight percentage 10 O ; 15 X ; 20 \blacktriangle .

temperature. The slope of this line was taken to be equal to the entropy change of the system. Where there are variations from linearity, a smooth curve was drawn and slope of the curve at 50°C was determined. This was taken as the entropy change for the dissolution of oil droplets into water. Hence the enthalpy change for such dissolution process was calculated from the relation

$$\Delta H_{\text{sol}} = \Delta G_{\text{sol}} + T \Delta S_{\text{sol}} \quad (2)$$

All these values at 50°C are given in Table 6.1. It is important to note that these values compare well with other systems found in the literature [180]. The thermodynamic parameters were computed on the basis of dilute ideal solution which can be taken to be their standard states.

From Table 6.1 some interesting features were observed. As the concentration of the surfactant increases, the free energy values tend towards relatively more positive one indicating higher oil solubility. The enthalpy changes are positive indicating endothermic process which compare well with Moulik's data [180]. Only a few systems show low exothermicity at very low oil concentration. This negative heat change though, is a bit unusual. It should be pointed out that in general, from the fundamentals of solubility, an exothermicity would have been more straightforward though in most cases

TABLE 6.1

Thermodynamic quantities of o/w microemulsion formation, at 50°C

Surfactant weight percentage	Water			0.003% (w/v) PAA			0.005% (w/v) PAA			0.5 M NaCl			1 M NaCl		
	ΔG_{sol} (kJ/ mol)	ΔH_{sol} (kJ/ mol)	ΔS_{sol} (J/mol/ K)	ΔG_{sol} (kJ/ mol)	ΔH_{sol} (kJ/ mol)	ΔS_{sol} (J/mol/ K)	ΔG_{sol} (kJ/ mol)	ΔH_{sol} (kJ/ mol)	ΔS_{sol} (J/mol/ K)	ΔG_{sol} (kJ/ mol)	ΔH_{sol} (kJ/ mol)	ΔS_{sol} (J/mol/ K)	ΔG_{sol} (kJ/ mol)	ΔH_{sol} (kJ/ mol)	ΔS_{sol} (J/mol/ K)
10	-17.7	-4.7	40	-17.2	-1.1	50	-17.7	0.1	55	-16.3	24.1	125	-13.4	10.8	75
15	-16.2	-1.6	45	-15.7	2.2	55	-16.8	7.5	75	-14.2	29.4	135	-11.6	11.0	70
20	-14.3	32.5	145	-14.1	18.2	100	-15.5	15.2	95	-12.6	22.9	110	-10.6	8.8	60
25	-12.9	51.7	200	-13.4	35.1	150	-14.3	21.2	110	-10.0	6.2	50	-	-	-
30	-11.3	58.2	215	-12.4	55.4	210	-12.5	47.3	185	-	-	-	-	-	-

endothermicity was observed. Various phenomenon like droplet formation, dispersion, surfactant adsorption etc. have different energy requirement and our observation is the overall effect only. Only at very low surfactant concentration, exothermicity was observed. As the concentration of the surfactant increased the exothermicity gave away to endothermicity. This probably indicate structural changes with the high surfactant concentration. The entropy change values are reasonably high and it increases with higher surfactant concentration. We feel that this happens because, as the oil gets soluble in water with a large amount of surfactant and cosurfactant present (in some cases polyacrylamide) the whole system gets totally randomized and loses its droplet structure. Under this condition the entropy value should increase.

In presence of NaCl, the entropy value decreases with higher surfactant concentration. In this case the systems are relatively less endothermic with higher surfactant. The presence of NaCl brings in some structuration in the systems as discussed in earlier chapters and thereby the entropy value decreases.

The enthalpy and entropy of droplet formation were found to compensate each other. In Fig 6.6 the ΔH_{sol} was

plotted against ΔS_{sol} for all the systems, and one recognises an almost perfect linearity. The equation of the line hence can be written as

$$\Delta H_{sol} = k_1 + k_2 \Delta S_{sol} \quad (3)$$

Now

$$\Delta G_{sol} = \Delta H_{sol} - T \Delta S_{sol} \quad (4)$$

Putting equation (3) in equation (4) we can write

$$\Delta G_{sol} = k_1 + (k_2 - T) \Delta S_{sol}.$$

Hence at temperature where $k_2 = T$, the free energy becomes independent of entropy effect. This temperature is termed as compensation temperature and for all systems together (Fig.6.6) the value is 66°C. Above 66°C the microemulsion formation process is enthalpy driven. This is because the intercept k_1 is -15.8 kJ/mole. This also indicates that the oil droplet formation will not be possible at a temperature over $\sim 80^\circ\text{C}$ for the system where weight fraction of surfactant is more than 0.3.

The enthalpy-entropy compensation effect is quite convincing and is similar to the values obtained in the micellization process [205] and the values obtained by Moulik et al [180]. They obtained a compensation temperature of 74°C. In both cases water was considered as the solvent.