CHAPTER 5

FREE ENERGY OF FORMATION OF MICROEMULSION

Formation of microemulsion depends on various factors like temperature, pressure, and composition of each components. A pseudoternary phase diagram shows the effect of each component at a particular temperature. The one phase microemulsion forms over particular oil/water/surfactant ratios. The different phases in the triangular map shows that there is a range in the concentration ratios over which the 1ϕ microemulsion remains present. At other ratios, the microemulsion is in equilibrium with other phases like oil or water.

Looking at the pseudoternary phase diagram, it is clear that one of the components i.e. either oil or water gets dissolved completely in the other at the lower boundary curve of the region to form a one phase microemulsion.

At the turbidity or phase separation point, the dispersed phase in mole fraction is at the state of its maximum solubility considering the dispersed phase water or oil as the solute, from the well known thermodynamic relation,[303] the free energy of dissolution of solute (ΔG_{sol}) can be calculated by

$$\Delta G_{sol} = RT\ln a \qquad \text{...............(1)}$$

where a is the activity of the solute. Since, we are considering a very dilute solution, the amount of solute dissolved is very low and the activity coefficient can be considered to be unity and hence 'a' can be replaced with mole fraction of the solute. So the free energy of dissolution ΔG_{sol} to reach the turbid or phase separation point is given by the relation.

$$\Delta G_{sol} = RT\ln x \qquad \text{...............(2)}$$

where x is mole fraction of the solute.

We have selected some composition of SDS and TX100 system along the 1ϕ - 2ϕ transition line where oil or water concentration was very low. This line

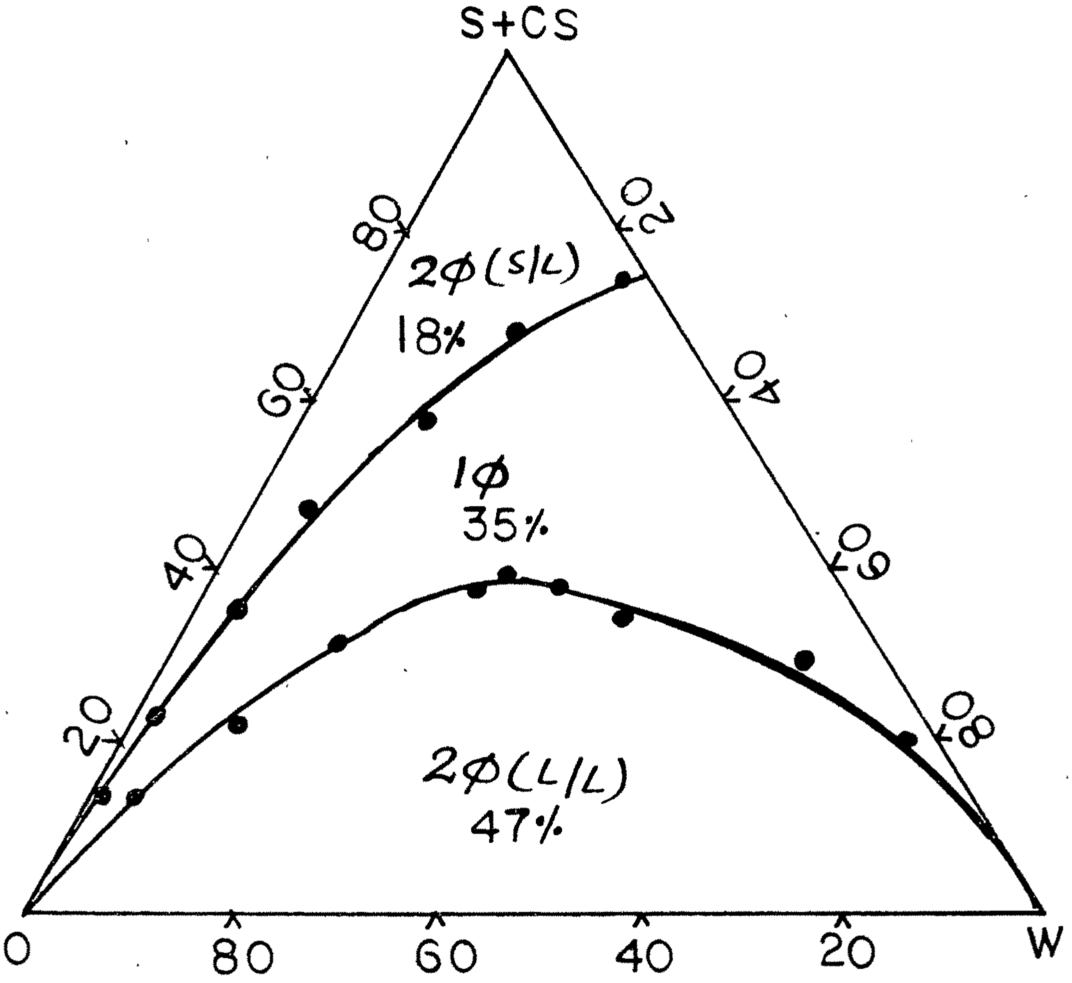

Fig.5.1 Pseudoternary phase diagram of cyclohexane/SDS +n-propanol (1:5)/water at 40°C.

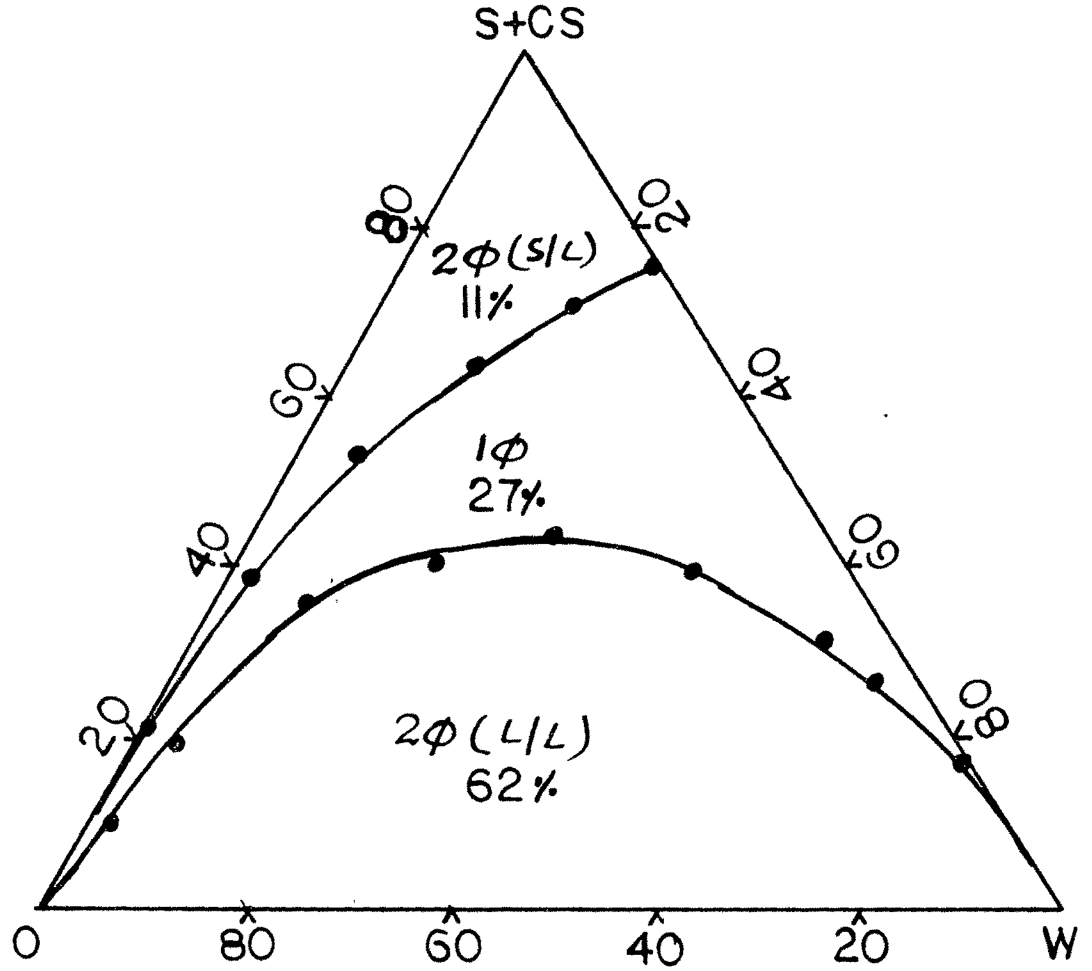

Fig.5.2 Pseudoternary phase diagram of cyclohexane/SDS+n-propanol (1:9)/water at 40°C.

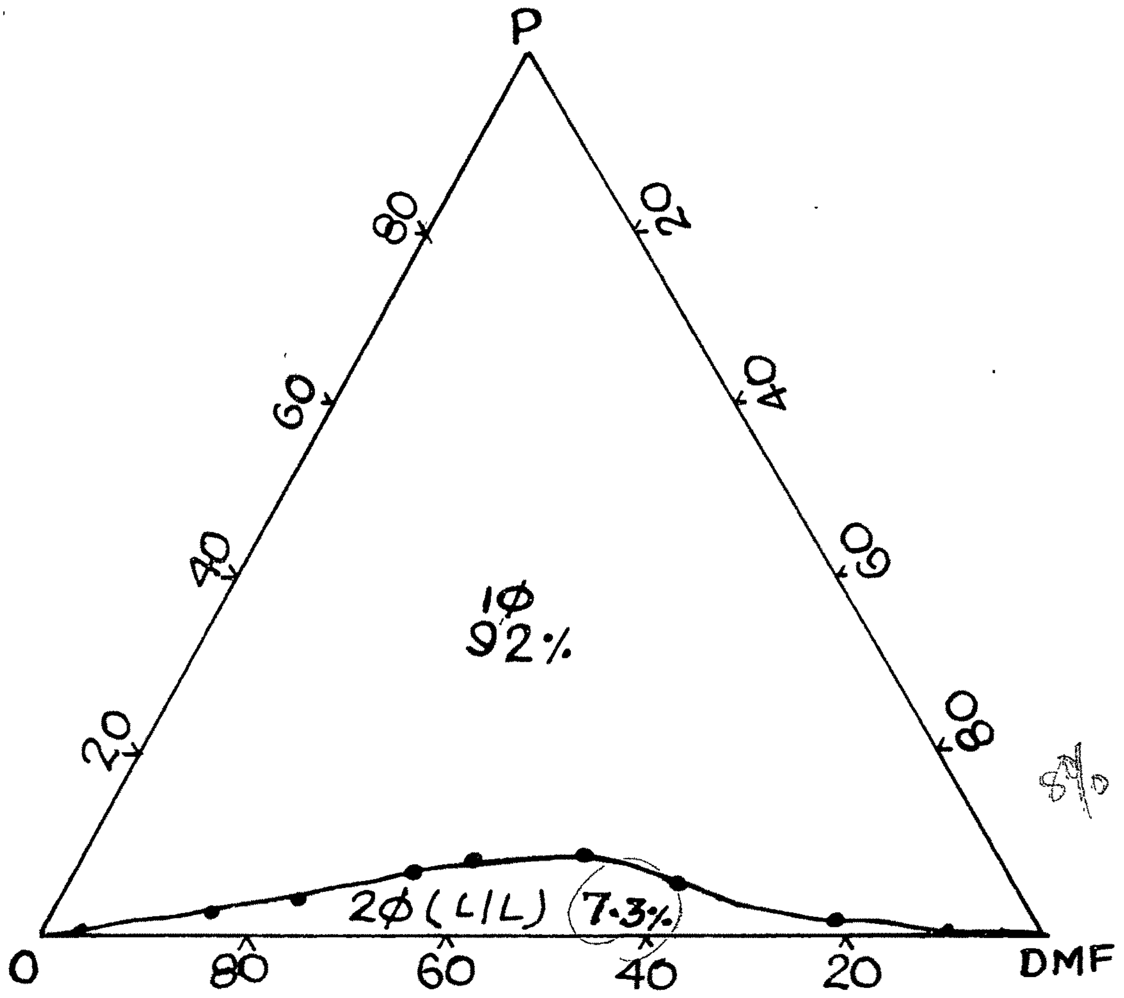

Fig.5.3 Ternary phase diagram of cyclohexane/n-propanol/Dimethyl formamide at 40°C.

Table 5.1 ΔG_{sol} values in kJ mol^{-1} for SDS microemulsion

S	Cyclohexane/SDS+Propanol (1:5)/water		Cyclohexane/SDS+Propanol (1:9) / Water	
	O/W	W/O	O/W	W/O
10	-	-5.43	-	-5.80
15	-14.97	-3.89	-	-5.00
20	-12.65	-3.08	-15.08	-4.85
25	-11.15	-2.48	-12.55	-4.38
30	-9.90	-2.17	-11.04	-3.93

Table 5.2 ΔG_{sol} values in kJ mol^{-1} for aqueous TX100 microemulsion

S	Cyclohexane/Propanol/water		Cyclohexane/TX100+Propanol (1:2) water	
	O/W	W/O	O/W	W/O
10	-	-	-13.34	-8.06
15	-	-8.21	-10.78	-6.34
20	-17.40	-6.52	-9.69	-5.80
25	-15.46	-6.04	-9.64	-4.21
30	-14.10	-5.29	-9.84	-3.49

Table 5.3 ΔG_{sol} values in kJ mol^{-1} for nonaqueous TX100 microemulsion

S	Cyclohexane/ Propanol/DMF		Cyclohexane/TX100 DMF		Cyclohexane/TX100 propanol (1:2) DMF	
	O/D	D/O	O/D		O/D	D/O
2.5	-3.80	-4.65	-3.33		-3.27	-6.40
5.0	-3.02	-3.30	-3.24	-	-2.96	-4.23
7.5	-2.83	-2.54	-3.21		-2.76	-3.09
10.0	-	-	-3.14		-	-

indicating the transition from a Winsor IV to Winsor I or Winsor II where either excess oil or water was in equilibrium with microemulsion. Number of moles of each component was calculated from the composition and the mole fraction of solute i.e., either oil or water was determined. By substituting these values in equation 2, ΔG_{sol} was obtained for SDS system for 1:5 & 1:9 S to CS weight ratio (Fig. 5.1, 5.2 & 5.3) and for TX100 systems see Chapter 3. The ΔG_{sol} values are reported in Table 5.1,5.2,5.3 respectively for SDS and TX100 systems.

For all the systems we are getting a negative $\Delta G_{sol.}$ Negative ΔG_{sol} suggests that the microemulsion formation is spontaneous and thermodynamically stable. The higher negative values of O/W systems indicate that the formation of O/W droplet was more spontaneous than W/O droplets.

It has been reported that the eqn (2) can be used to calculate the thermodynamic parameters for the solubilization of oil in water or vice versa as microdroplets forming the microemulsion phase; but this relation is true only if the amount of solubilized substance is very low.[110,142,304]