CHAPTER 6

THERMODYNAMICS OF DROPLET FORMATION

6.1 THERMODYNAMICS OF DROPLET FORMATION

Microemulsions are formed only at some fixed range of compositions of its components,i.e. oil, water and surfactant. These compositions can be readily obtained from the carefully constructed phase diagrams. Water and oil have very high interfacial tension between them and hence they are immiscible. But the presence of surface active agents lowers the interfacial tension and solubilizes (as micro droplets) one liquid into the other. This resulted in the formation of monophasic microemulsion (Winsor IV) system.

From the previous chapters (Chapter 3 - 5), it could be noted that alkane/Brij 35 + propanol/water system forms this phase at high surfactant concentration. At lower surfactant concentration, this sytem separates into a 20 or 30 liquid system depending upon the conditions. When surfactant used was the mixture of SDS and Brij 35, a solid/liquid 2 phase system exists prior to the 10 microemulsion region.

The free energy of dissolution of a solute in the solvent can be calculated using the well known thermodynamic relation [250].

$$\Delta G = RT \ln a$$

where ΔG is the free energy change and 'a' is the activity of the solute. When the solute concentration is very low, i.e. at infinite dilution, activity coefficient can be taken as unity and activity can be replaced with mole fraction (X) of the solute. Thus the relation becomes

$$\Delta G = RT \ln X \quad \ldots\ldots\ldots (1)$$

It has been reported that this relation can be used to calculate the thermodymanic parameters for the solubilization of oil in water or vice versa as microdroplets, forming the microemuslion phase [251]. However, as stated earlier, this relation is true only if the amount of solubilized substance is low.

We have selected some microemulsion compositions along the 10 - 20 transition line from all the studied phase diagrams. This line indicating the transformation from a Winsor IV to Winsor I where excess oil is in equilibrium with microemulsion. In general oil mole fraction was kept below 0.03. Number of moles of each component was calculated from the composition and the molefraction of alkane was determined. By substituting these values in equation (1), ΔG was obtained for all systems studied. Free energy values tend to be relatively more positive at higher surfactant concentration indicating higher alkane solubility (Table 6.I)

Variation of ΔG against temperature is approximately linear for almost all systems (Fig.6.1-6.3). The entropy change for the processes were calculated from the slope of these lines. Then enthalpy change was computed using the well known relation,

$$\Delta H = \Delta G + T\Delta S \quad .... \quad (2)$$

All these values at 60°C are presented in Table 6.I. The positive values of the entropy change reveal the randomness associated with these solubilizing processes. Though the enthalpy changes for these processes were not large, the negative values indicate the exothermic nature of the solubilization process. But earlier studies show it as an endothermic process [251]. Various phenomena like droplet formation, dispersion, surfactant adsorption etc. have different energy requirements. The above mentioned values are the result of overall effect. Hence a prediction about the nature of ΔH values are not always possible.

The enthalpy and entropy of oil solubilization was found to fairly compensate each other for the system alkane/Brij 35 + propanol/water. In Fig.6.4 all these values are plotted. A good straight line graph was obtained.

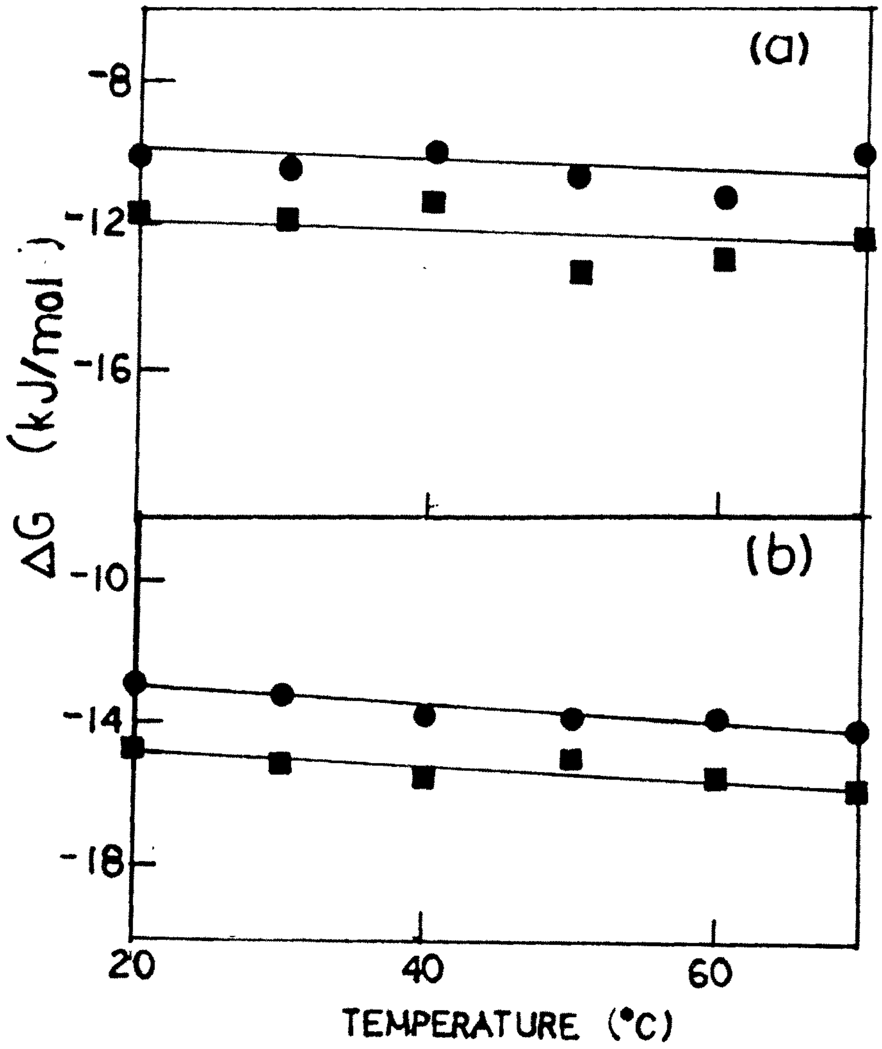
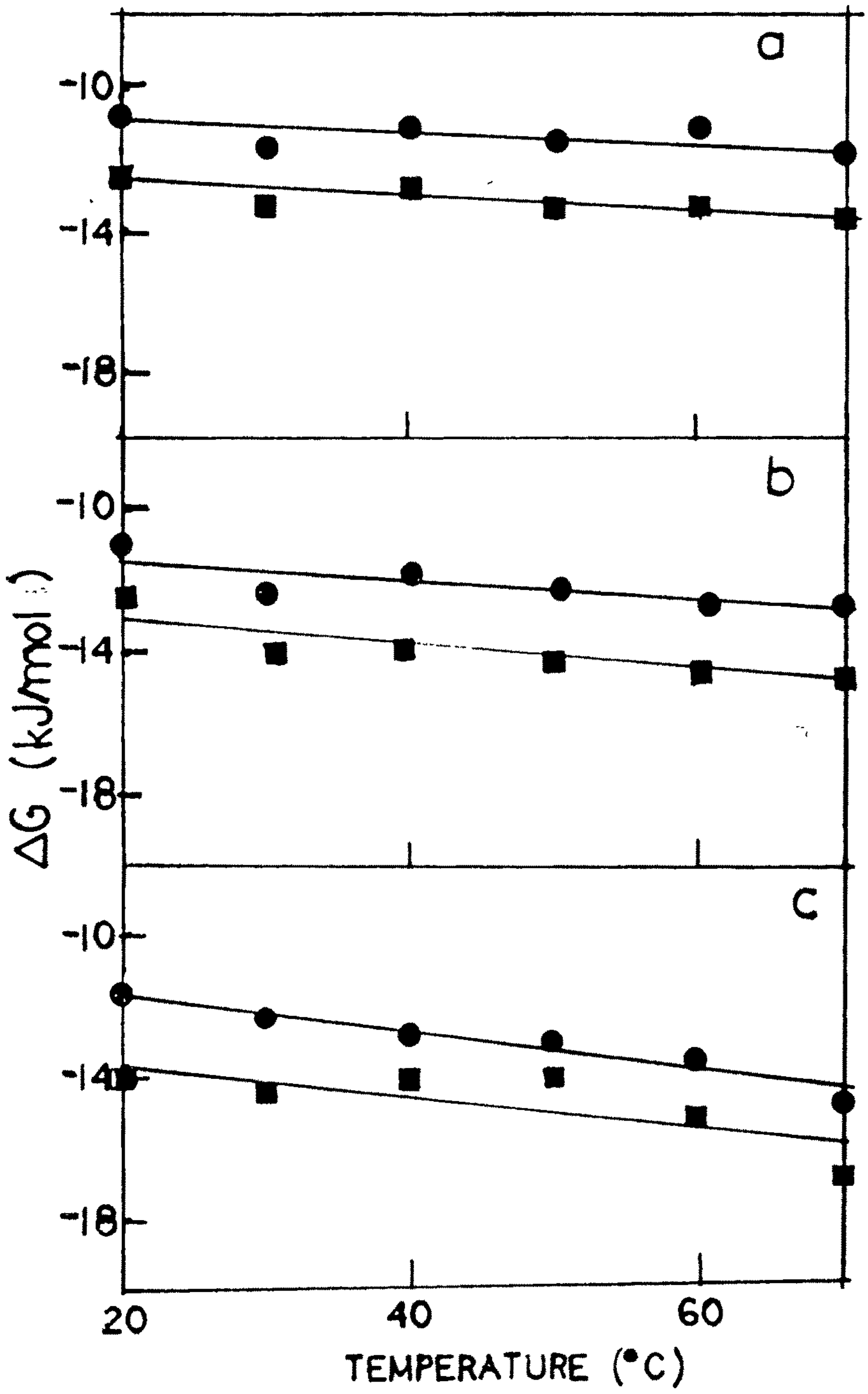


Fig. 6.1 Plot of ΔG against temperature for the system Alkane/Brij 35 + propanol/water. Alkanes are (a) Heptane and (b) Nonane.
■ 50% (w/w) surfactant
● 60% (w/w) Surfactant



Fi.g 6.2 ΔG - T plot for Alkane/Birj 35 + propanol/water system. Heptane-Nonane mixed alkane were used in (a) 3:1 (b) 1:1 (c) 1:3 mole ratios.
■ 50% (w/w) Surfactant
● 60% (w/w) surfactant.

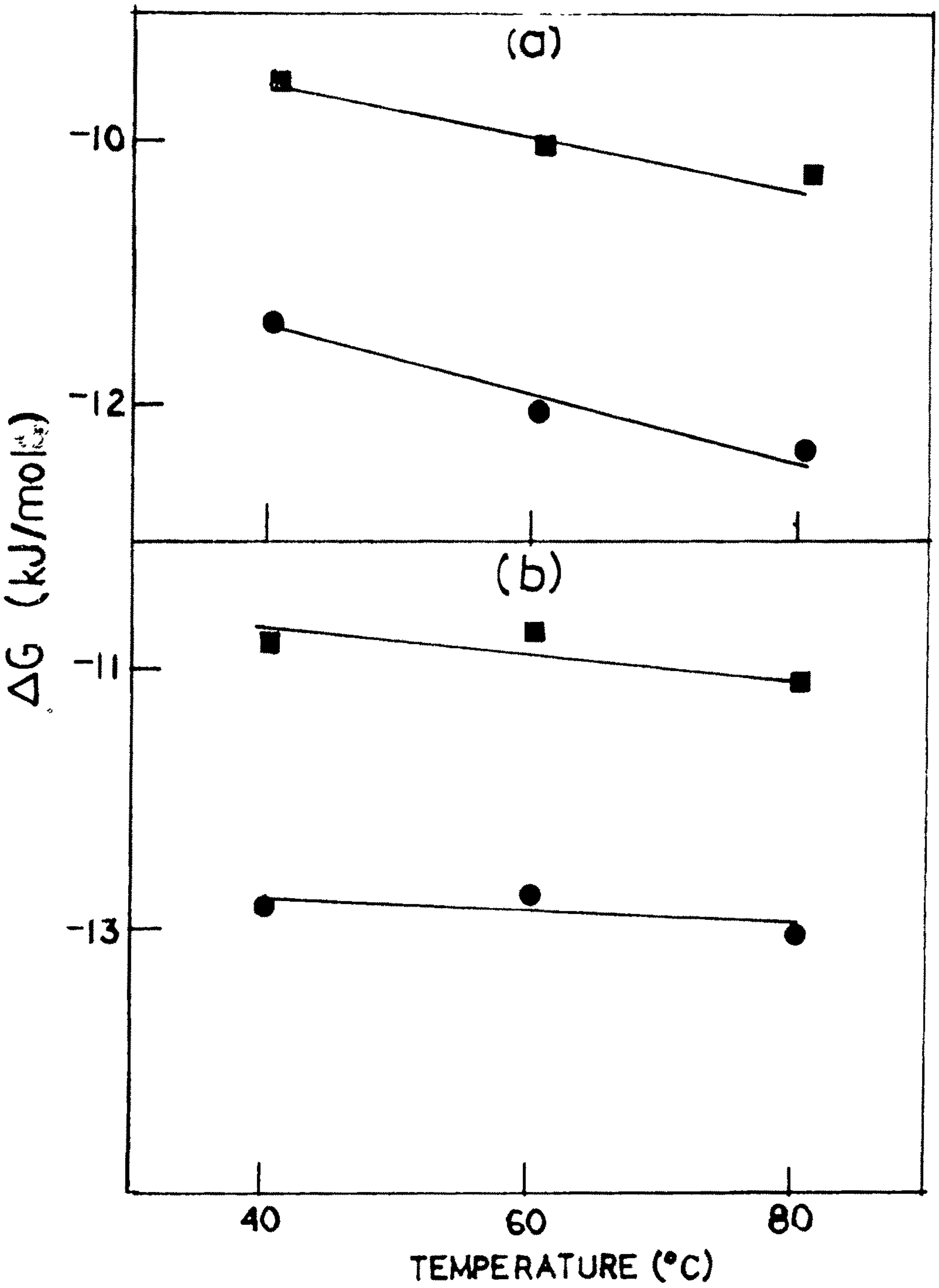


Fig.6.3 ΔG - T plot for alkane/Brij 35 + propanol/1M NaCl system. Alkanes are (a) heptane and (b) nonane
● 2.5 % (w/w) alkane
■ 5.0 % (w/w) alkane

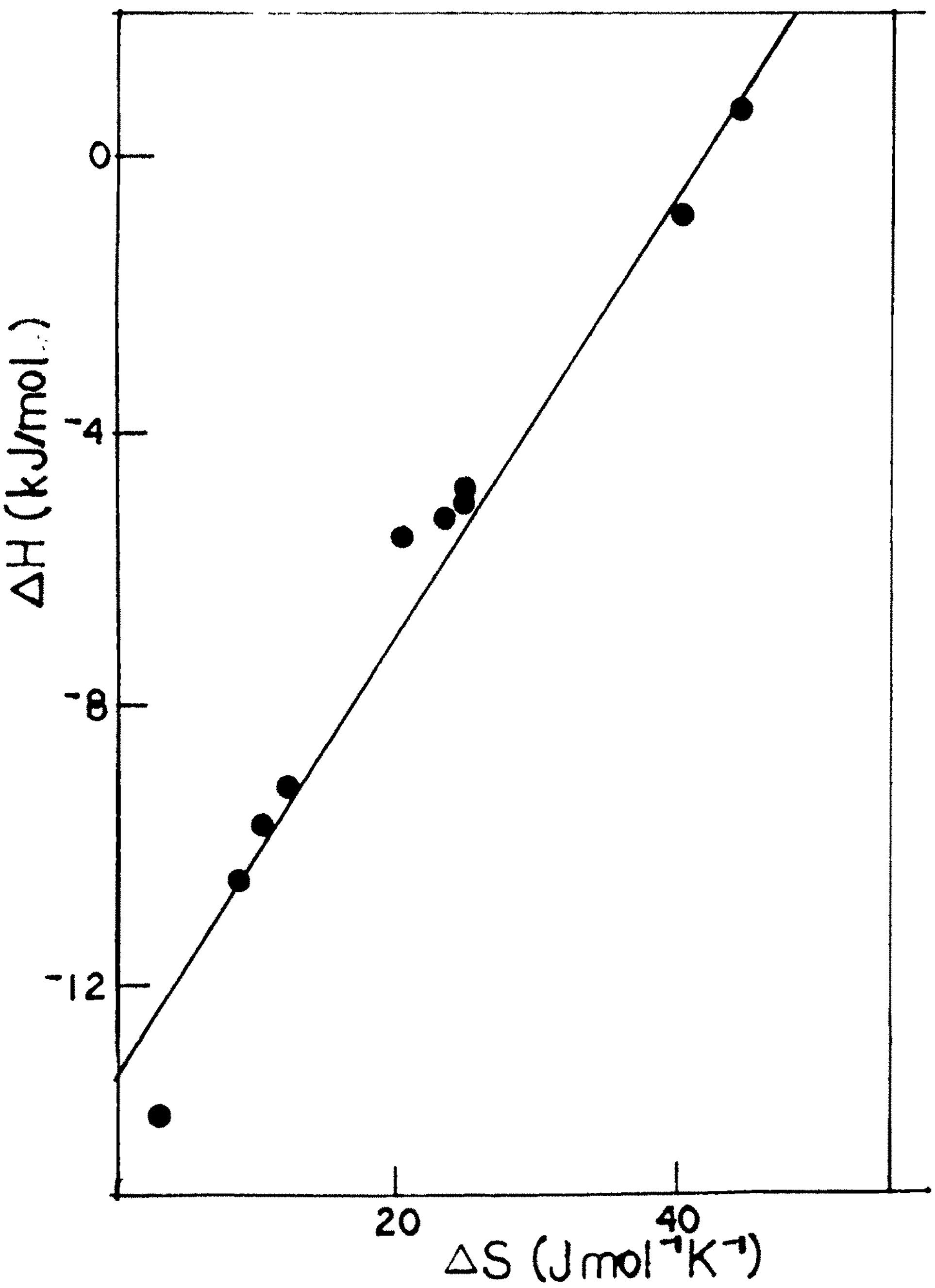


Fig.6.4 Plot showing enthalpy-entropy compensation for all the alkane/Brij 35+propanol/water system taken together (Cf.Table 6.I to 6.III)

TABLE 6.I

Thermodynamic parameters of Alkane/Brij 35 + propanol/Water

Surfactant concentration % (Wt.)	Alkanes														
	Heptane (H)			H+N (3:1)			H+N (1:1)			H+N (1:3)			Nonane (N)		
	ΔG^* (kJ/mol)	ΔH	ΔS J/mol/k	ΔG^* (kJ/mol)	ΔH	ΔS J/mol/k	ΔG^* (kJ/mol)	ΔH	ΔS J/mol/k	ΔG^* (kJ/mol)	ΔH	ΔS J/mol/k	ΔG^* (kJ/mol)	ΔH	ΔS J/mol/k
50	-13.2	-9.2	12	-12.9	-4.9	24	-14.3	-1.0	40	11.1	0.5	44	-15.0	-14.0	3
60	-13.0	-9.7	10	-12.1	-5.5	20	-13.1	-5.1	24	-13.5	4.0	52	-13.7	- 5.3	25

* The free energy was calculated at 60°C

Alkane/Brij 35 + propanol/1 M NaCl

Alkane	Alkane % (w/w)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol /k)
Heptane	2.5	-12.0	-3.4	26
	5.0	-10.0	-3.4	20
Nonane	2.5	-12.8	-11.4	4
	5.0	-10.7	- 7.0	11

TABLE 6.II

ΔG values for the system Heptane/Mixed surfactant + propanol/Water at different surfactant mixing ratio at 40°C.

Surfactant Mixture	Surfactant concentration S+CS (wt.%)	ΔG (kJ/mol) at different mixing molar ratio of surfactant				
		SDS : Brij 35				
		1:0	2:1	1:1	1:2	0:1
	40	-	-11.11	-12.99	-12.32	-12.77
SDS + Brij 35	50	-	- 8.80	- 9.40	-10.76	-11.30
	60	-	- 8.72	- 9.50	- 8.58	- 9.93
		Tween 20 : Brij 35				
	40	-12.78	-	-12.32	-	-12.77
Tween 20 + Brij 35	50	- 9.60	-	-10.59	-	-11.30
	60	- 7.38	-	- 9.0	-	- 9.93

The equation for this straight line can be written as

$$\Delta H = k_1 + k_2 \, \Delta S \quad \ldots\ldots\ldots \quad (3)$$

but,

$$\Delta G = \Delta H - T \, \Delta S \quad \ldots\ldots\ldots \quad (4)$$

Therefore,

$$\Delta G = k_1 + (k_2 - T) \, \Delta S \ldots\ldots \quad (5)$$

From equation (5), it can be seen that, when $T = k_2$, the free energy becomes independent of the entropic effect. This temperature is known as compensation temperature. For the above mentioned system, this temperature was found to be 58°C. Above 58°C, the solubilizing process of this system is enthalpy driven.

ΔG values of mixed surfactant (Brij 35 + SDS and Brij 35 + Tween 20) systems were also calculated at 40°C. The values are given in Table 6.II. The ΔH values did not vary much with the change of the surfactant mixing ratio.

ΔG values for water solubilization was also calculated for comparison. The ΔG values calculated for alkane/Brij 35 + propanol / 1 M NaCl system was given in Table 6.III. Here also, ΔG values become less negative at higher surfactant concentration. The values are comparatively smaller than that of oil solubilization process. As the ΔG-T plots were not linear, we did not

TABLE 6.III

ΔG values for water solubilization of the system Alkane/Brij 35 + propanol/1 M NaCl

Alkane	Surfactant concentration S+CS (wt.%)	ΔG kJ/mol		
		40°C	60°c	80°C
Heptane	50	-6.79	-6.79	-4.70
	60	-4.66	-5.30	-4.64
Nonane	50	-13.57	-12.54	-7.38
	60	- 9.04	- 6.76	-6.27

calculate the ΔH and ΔS values. This could have been done if ΔG values at some other temperatures were known which unfortunately we do not have.

Overall it could be said that the thermodynamics of droplet formation helps in understanding the spontaneity of the microemulsion formation at low OWR or WOR for oil or water respectively.