Thermodynamics of clustering of droplets in water/AOT/heptane microemulsion

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Abstract   After a threshold volume fraction of the dispersed phase, the microdroplets in W/O microemulsion cluster to form open structure. The thermodynamics of droplet clustering in Water/AOT/Heptane system has been studied conductometrically and calorimetrically. The process has been found to be endothermic associated with positive change of entropy. The thermodynamic parameters have been found to depend on the H_2O/AOT mole ratio.

INTRODUCTION

Microemulsion(ref. 1) is an isotropic, stable and usually low viscous mixed solution of oil, water and amphiphile in which the dispersed droplets (either of water or of oil) are on the average 10 - 50 nm in size. Water-in-oil type microemulsions may exhibit significant rise in conductance (100 - 1000 fold or more) after a threshold volume fraction of the dispersed phase which is called percolation (ref. 2). Percolation can be also initiated by temperature for a fixed composition, generally at a moderate water/amphiphile mole ratio. It is considered that during percolation, the dispersed water particles cluster and the conductance is enhanced by either the 'hopping of the amphiphile ions' from droplet to droplet or by 'transient fusion and mass(ion) exchange' mechanism (ref. 3). At the percolation stage, viscosity may also rise significantly. Although the phenomenon of percolation has been adequately studied, the thermodynamics of clustering of the microdroplets (the essential basis of percolation) has not been so far studied. The thermodynamics of microemulsion formation has been insignificantly investigated(refs. 4-6). Such studies are, therefore, important.

In this presentation, attempt has been made to estimate the energetics of clustering of microdroplets in Water/AOT/Heptane system by conductometry as well as by calorimetry. The former method is based on the determination of the percolation threshold at different temperatures and analysis of data according to Gibbs - Helmholtz equation.

The calorimetric method, on the other hand, determines the enthalpy directly. We shall see that the results of both the methods compare well in absence of additives. In presence of salts, the calorimetric method yields higher values.

EXPERIMENTAL

The materials heptane, Aerosol OT(AOT), sodium chloride, sodium cholate (NaC) and water were the same as reported earlier(ref. 7).

The method of preparation of microemulsion and the measurement of conductance were described elsewhere (ref. 3). The threshold volume fractions (ϕ_t) of the dispered phase (here water + AOT) were determined at four different temperatures and the enthalpy of clustering was found out from the slopes of the plots of $\ln \phi_t$ vs T^{-1} .

In the calorimetric method, the apparatus and the procedure of measurement of heat were the same as described earlier(ref. 6). The heat of dilution of the clustered dispersion ($\phi >> \phi_t$) in heptane was found to be very low. The heat of dilution of declustered microemulsion ($\phi < \phi_t$) in heptane was also found to be small. The heat of cluster $\longrightarrow$ decluster transition was found to be appreciable. It was determined by diluting the clustered microemulsions in heptane and bringing the final concentration always below the clustering threshold (ϕ_t), determined conductometrically. Each run was duplicated and the mean value was considered. The reverse heat was considered as the heat of clustering.

RESULTS AND DISCUSSION

In Fig.1, the dispersed phase concentration induced percolation of conductance of the Water/AOT/Heptane microemulsion system at different temperatures are presented. Transitions after a threshold volume fraction (ϕ_t) are evidenced which decrease with increased temperature.
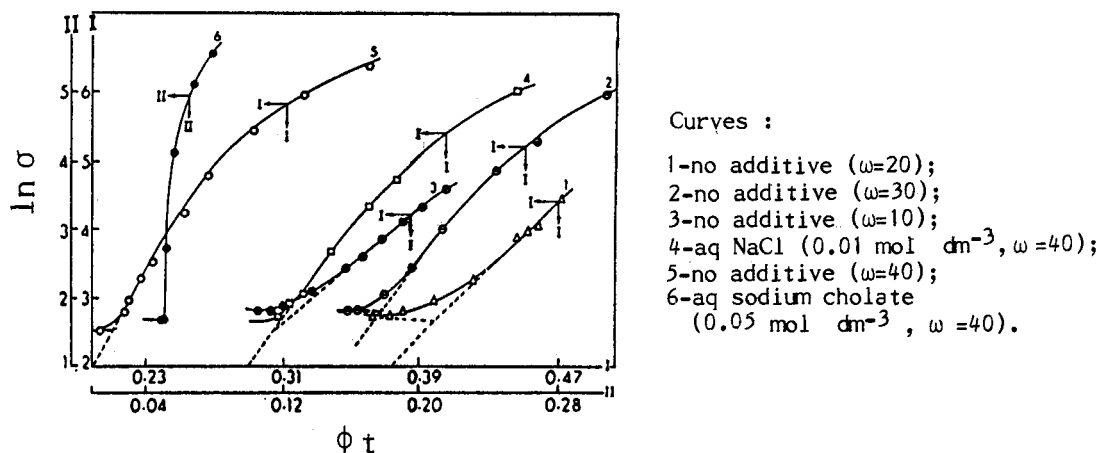

Curves :

1-no additive (ω=20);
2-no additive (ω=30);
3-no additive (ω=10);
4-aq NaCl (0.01 mol dm^{-3}, ω =40);
5-no additive (ω=40);
6-aq sodium cholate
 (0.05 mol dm^{-3} , ω =40).

Fig.1. $\ln \sigma$ vs ϕ_t profiles at constant ω at 303K of H_2O/AOT/Heptane microemulsion in different additive environment.

The process of clustering appears to be endothermic. In a microemulsion, the dispersed particles are separated by solvent barrier. Thermal energy removes this inter-particle barrier for easy accumulation via increased proximation and easier transportation. At a constant temperature, increased population of microdroplets results easier accumulation to initiate percolation. Since increase of temperature enhances the process of clustering, it is expected to be endothermic. The standard enthalpies of clustering (ΔH^o_{cl}) are realised by treating the data according to the equation $\Delta H^o_{cl} = R(d\ln \phi_t / dT^{-1})$. The results are given in Table 1. The values are all positive.

TABLE 1. The energetics of clustering of microdroplets as a function of [water]/ [AOT] (ω) at different temperatures

[water]/[AOT]	T^oK	$\Delta G^o_{cl}/kJmol^{-1}$	$\Delta H^o_{cl}/kJmol^{-1}$	$\Delta S^o_{cl}/Jmol^{-1}K^{-1}$
40	298	-19.3		
	303	-20.6		
	308	-23.1	97.3 (117.4)	391
	313	-25.0		
30	303	-17.8		
	308	-19.6	77.9 (71.4)	316
	313	-21.0		
20	303	-16.0		
	308	-17.0	42.0 (47.0)	191
	313	-18.0		
10	303	-13.6		
	308	-14.0	16.3 (5.4)	98
	313	-14.6		
40[a]	308	-27.1	63.6 (125.3)	294
	313	-29.1		
40[b]	308	-21.8	81.8 (155.2)	336
	313	-23.8		

[a] at 0.05 mol dm^{-3} NaC ; [b] at 0.01 mol dm^{-3} NaCl

Thermograms of the cluster $\longrightarrow$ decluster transition are presented in Fig. 2. The corresponding endothermic enthalpies (ΔH^o_{cl}) are included within bracket in column 4 of Table 1. The two modes of evaluation of enthalpy are in satisfactory agreement. An exact agreement is not expected. The enthalpy derived by the conductance method using Gibbs-Helmholtz equation is associated with more error and a near agreement with the direct calorimetric method is good enough.

A complete thermodynamic analysis has been made by evaluating the free energy of clustering (ΔG^o_{cl}) by the relation, $\Delta G^o_{cl} = RT \ln \phi_t$ and using this in the Gibbs equation in the form $(\Delta G^o_{cl} = \Delta H^o_{cl} - T \Delta S^o_{cl})$.
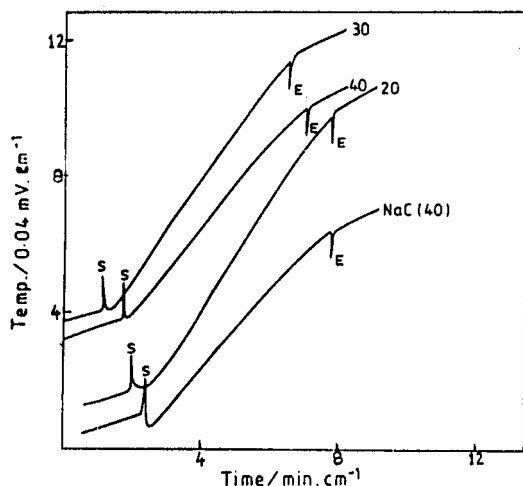
Fig.2.

Thermograms for the declustering of microemulsions at 303K. S and E denote start and end of a run. The numbers against the curves indicate ω values.

The free energy equation is comparable with the free energy relation for micelle formation (ΔG^{o}_{mic} = RT ln CMC, where CMC represents the critical micellisation concentration (ref. 8) :ϕ_t for clustering is comparable with CMC). According to the pseudophase micellar model, the surfactant monomers assemble to form micelle which is considered to be in a separate phase. The microdroplets in microemulsion cluster at ϕ_t and the clustered body is considered to be in a separate phase. The thermodynamic analysis is, therefore, essentially the same as adopted for micelle formation. The thermodynamic results are presented in Table 1.

    It is seen that both ΔH^{o}_{Cl} and ΔS^{o}_{Cl} are positive. An endothermic process is usually associated with increase in entropy. (Solubilisation of nonpolar compounds in water may, however, be both endo- and exothermic with negative entropy change. The clustering phenomenon is essentially composed of two processes ; 1) removal of oil barrier surrounding the dispersed droplets in heptane and 2) association of detached droplets to form clusters. The first process should absorb heat and, therefore, endothermic, whereas the second process should release heat and, therefore, exothermic. Their individual magnitudes should guide the enthalpy of the overall process. The resultant enthalpy for clustering process has been found to be positive ; the first process, therefore, outweighs the second. The disruption of the solvent microenvironment of the dispersed droplets in the first process more than compensates for their organisation (association) in the cluster to manifest a positive entropy for the whole process. The phenomenon has similarity with the energetics of micelle formation (normally an endothermic process) where the entropy change is usually positive (ref. 9). Like many kinetic and equilibrium processes, a nice compensation between the enthalpy and entropy of clustering has been observed (refs. 10,11). This signifies that the major fraction of the heat is utilised for the underlying order-disorder events in the clustering process. The compensation phenomenon is exemplified in Fig.3.
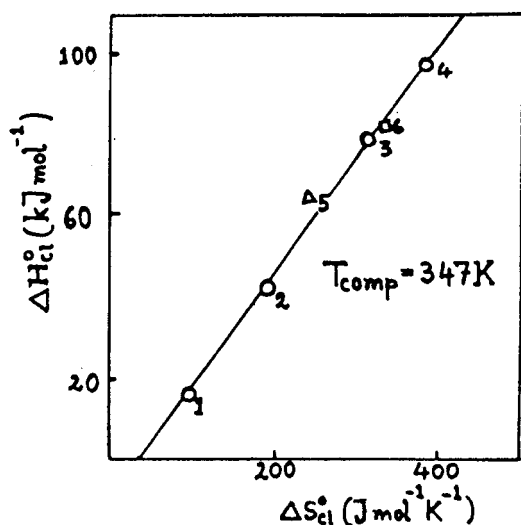
Fig.3.

ΔH^o_{Cl} vs. ΔS^o_{Cl} compensation plots. Points 1,2,3 and 4 refer to ω values 10,20,30 and 40 ; Points 5 and 6 refer to 0.05 mol dm^{-3} NaC and 0.01 mol dm^{-3} NaCl (Both at ω = 40).

At constant temperature, the clustering process is more spontaneous with increased ω i.e. with increased particle size. Both the enthalpy and entropy have also increased with ω . A four fold rise in ω (equivalent to four fold rise in particle size) has manifested six fold rise in enthalpy and thirtytwo fold rise in entropy. NaCl (0.01 mol dm^{-3}) and NaC (0.05 mol dm^{-3}) in the dispersed aqueous phase have made the clustering process more spontaneous with increased enthalpy and decreased entropy. The former is more effective than the latter in this respect.

Acknowledgement

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