

Formulation characteristics, phase and physicochemical behaviours of *n*-heptane/AOT/water microemulsion in the presence of water soluble polymers

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The formation characteristics (phase behaviours) and physicochemical properties (conductance and viscosity) of *n*-heptane/AOT/water microemulsion have been studied in the presence of a number of additives (water soluble polymers) viz. carboxymethylcellulose, starch, polyethylene glycol, gelatine and polyacrylamide. It has been found that a significant monophasic microemulsion (Winsor type IV) can be realised in the presence of all the polymers except for carboxymethylcellulose. The microdispersions are stable, conducting and viscous. The normal mode of percolation of conductance with a threshold temperature of 40°C has been observed in all the cases except for 10% polyethylene glycol 6000 showing a lowering of the percolation threshold. The dispersions are essentially non-Newtonian in their flow behaviours. The shear viscosities have been found to depend on the type of polymer. The preparations have exhibited shear rate dependent thinning and thickening properties.

Microemulsions are single-phase isotropic thermodynamically stable, low viscous dispersions of oil/water or water/oil stabilised by a suitable surfactant or surfactant-cosurfactant mixture^{1,2}. As these liquid phases occur over a specific part of the ternary phase diagram, such phase diagrams are a pre-requisite for the study of microemulsions³⁻⁵. Moreover, the properties of such fluid mixtures depend on many factors⁶, such as temperature, pressure and the nature of the components including additives. Though the effect of pressure has been found to be weak⁶, temperature has a significant say⁷⁻⁹ on the phase and other physico-chemical behaviours. Besides, the presence of additives may impart special characteristics to this kind of compartmentalised liquids^{8,10-12}. Such studies are, therefore, of considerable importance. The study of microemulsion formation and its properties in the presence of polymers are important at least for the purpose of enhanced oil recovery to impart adequate viscosity for convenient flow of the displaced oil in the underground porous rocks. Moreover, polymercontained microemulsions have uses in pharmaceutical preparation and industrial processes.

In this paper we have presented the results of the investigation on the formation and physical properties (phase behaviour, conductance and viscosity) of ternary system of *n*-heptane/AOT/water in the presence of a number of water soluble polymers, viz. polyethylene glycol (PEG), carboxymethylcellulose

(CMC), gelatine, starch and polyacrylamide (PAA). Attempt has been made to rationalise the results in terms of existing physico-chemical concepts.

Materials and Methods

Aerosol-OT (sodium diethylhexylsulfosuccinate or AOT) was a 99% pure product of Sigma (USA) of physical characteristics reported earlier¹⁰. *n*-Heptane was purchased from E. Merck, Germany. Starch (amyllose) and carboxymethylcellulose (Na salt, mol. wt. 2.08×10^5 ; CMC) was products of BDH (England). Gelatine (mol. wt. 45000) used was obtained from E. Merck (Germany). Polyethylene glycols (mol. wt. 1000 and 6000), PEG 1000 and PEG 6000 were purchased from S.D. Fine Chemicals (India). The polyacrylamide (mol. wt. 4100000; PAA) was a gift sample by courtesy of Dr B.M. Mandal of IACS, Calcutta.

Doubly distilled conductivity water of specific conductance $2-4 \mu\text{Scm}^{-1}$ at 30°C was used for all preparations.

Sample preparation and determination of phase boundary

The boundaries of the single phase microemulsion regions were determined by the titration technique. Known amounts of *n*-heptane or water was taken with AOT in stoppered test tubes and kept in a thermostated water bath at required temperature ($\pm 0.1^\circ\text{C}$). The mixtures were then titrated with either water or oil from a microburette under the condition

of constant agitation upto the point of turbidity. For the preparations with polymer, aqueous polymer solutions of known strengths were used and the titration procedure followed as usual. The wt. per cent concentrations of the different polymers used were starch (1%), PEG 1000 (10%), PEG 6000 (5%), CMC (1%), gelatine (2%) and PAA (1%).

Measurement of conductance

The measurement of conductance of microemulsion, samples in the monophasic region was performed with a Jenway (England) conductometer in a cell of cell constant 0.2 cm^{-1} in the temperature range of $25\text{--}60^\circ\text{C}$ at a maximum of 5°C intervals with an equilibration time of 20 min at each stage. The weight percents of AOT, *n*-heptane and water (or polymer solutions) were 23.5, 53 and 23.5 respectively that corresponded to ϕ_d (droplet fraction) = 0.36 and water/AOT mole ratio (ω) = 24. The measured conductance were accurate within $\pm 2\%$.

Measurement of viscosity

The microemulsion systems obtained were fairly viscous and Newtonian flow was not observed. The viscosity was, therefore, measured with a ROTO viscometer of Haake, Germany (Model RV-20) at different shear rates. The studied weight per cent composi-

tions of *n*-HP/AOT/aqueous solution were as follows: set-1 (30/40/30), set-2 (70/20/10), set-3 (60/20/20) and set-4 (50/50/30). The measured viscosity was 1% uncertain to the maximum.

Results and Discussion

Phase diagrams

The ternary phase diagrams are presented in Fig. 1. Distinct large one phase (1 ϕ) microemulsion (μE) zones are observed for all the cases except 1% w/w CMC compared to pure aqueous systems, 5 and 10% aqueous PEG have yielded lower two phase (2 ϕ) zones. Aqueous 2% gelatine, 1% starch and 1% PAA have given area wise comparable 1 ϕ and 2 ϕ zones although critically their overall shapes differ. The percent 1 ϕ zones relative to the total area are presented in Table 1.

The results indicate that PEG helps to form greater proportions of 1 ϕ zone, whereas 1% CMC drastically reduces the homogenisation of water/*n*-Hp/AOT to form a single phase. A general comparison of the effects of the polymers may not be meaningful for their varied mol. wt., type and extent of addition. At 1% addition level, the CMC is strikingly different than starch and PAA although their molecular weights were all on the higher side. The droplet radius estima-

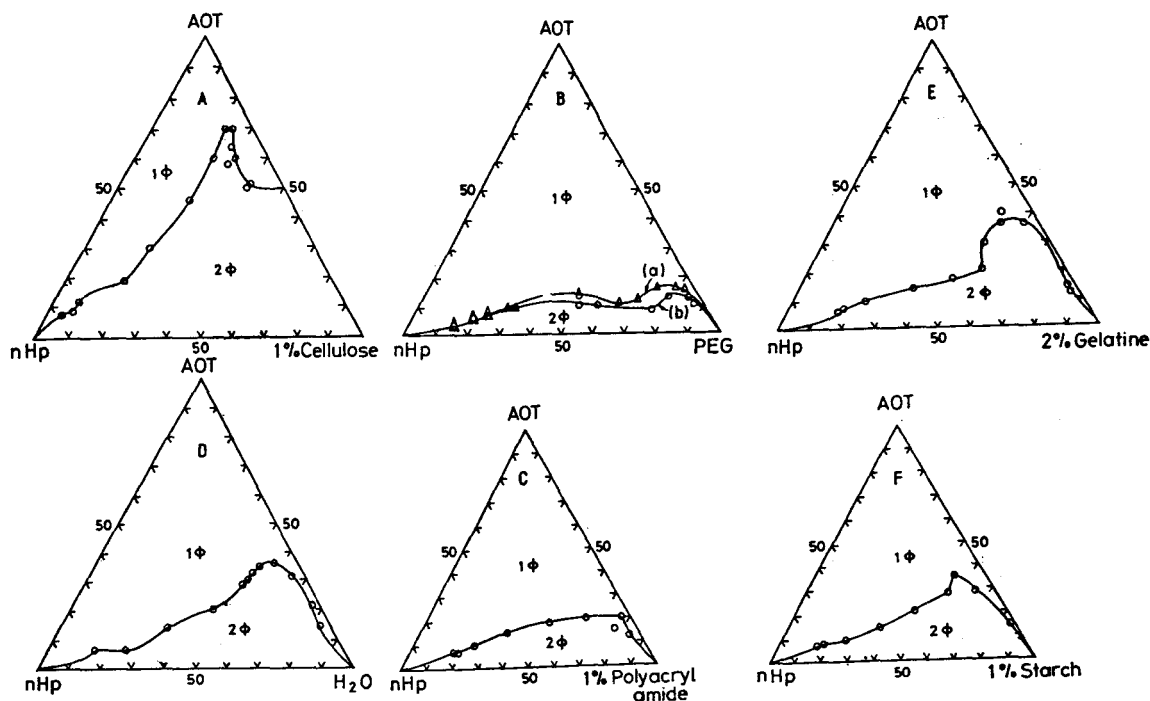


Fig. 1—Triangular phase diagrams of *n*-Hp/AOT/water (or aq. polymer) systems at 308 K. [A, 1% CMC (w/v); B, PEG (a, 5% PEG 6000 w/v; b, 10% PEG 1000 w/v); C, 1% polyacrylamide (w/v); D, without polymer; E, 2% gelatine (w/v); F, 1% starch (w/v). 1 ϕ , monophasic; 2 ϕ , biphasic].

Table I—Percent areas of I ϕ μ E zones of the studied systems relative to the total triangular area and the droplet dimensions at the minimum and maximum addition of oil at 308 K

System	% Area	Droplet radius nm	
		O/W	W/O
H ₂ O	70	21.3	9.2
1% CMC	39	22.5	13.0
1% Starch	70	28.7	12.3
10% PEG 1000	82	15.9	11.3
5% PEG 6000	81	24.3	11.8
2 % Gelatine	69	23.5	10.5
1% PAA	75	21.6	9.2

ted at minimum and maximum addition of oil in all the systems studied on the basis of the procedure adopted by Roy, Bisal and Moulik¹³ are also presented in Table I. The oil microdroplets are always nearly twice as high as the water microdroplets. It has been observed that with AOT > 70% and the polymers < 10% the microemulsions (μ ES) form gel: at AOT > 80% and polymer < 5% the preparations are thick gel with the formation of foam. Further, 5 and 10% PEG give almost identical phase diagrams. Aqueous PEG solutions thus show comparable (in true sense to some extent better) phase forming behaviour with aqueous medium with *n*-Hp as oil and AOT as surfactant.

Conductance behaviour

Single phase μ ES with ionic amphiphiles normally exhibit conductance that depends on the water/AOT mole ratio (ω). Generally, at $\omega \approx 20$ -30, the conductance of water-in-oil type μ E may rapidly increase either with increase in water content or increase in temperature at fixed ω , known as percolation of conductance^{10,14-17}. In the percolation state, the dispersed micro water particles form infinite cluster and enhanced conductance is effected by way of either the hopping¹⁸⁻²¹ of surfactant ion from droplet to droplet or the transient fusion^{10,14,22,23} of droplets and mass exchange. In Fig. 2, conductance temperature profiles are exemplified for water (or aquo-polymer)/AOT/*n*-Hp composition 23.5/23.5/53 i.e. at [water]/[amphiphile] mole ratio, $\omega = 24$. All the compositions have practically the same conductance behaviour with a threshold percolation temperature of 40°C. The polymers have not affected the percolation behaviour. But the nature of the conductance temperature profile in the presence of 10% PEG 6000 is different in the range of lower temperature. The threshold temperature appears to be lowered.

In this comparison, the aqueous solution of 1% CMC is different since it gives a smaller I ϕ area in the phase diagram and preparation of μ E at $\omega = 24$ is not possible. Conductometric percolation has been studied in the presence and absence of additives at various

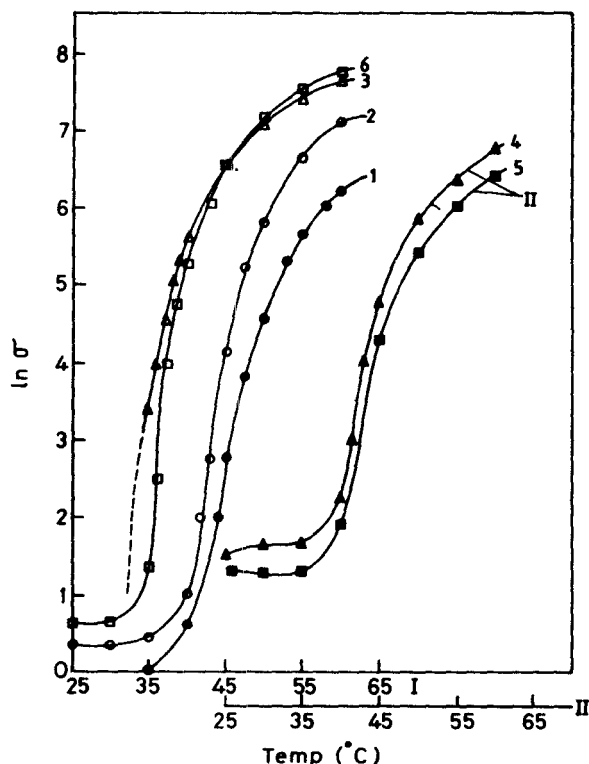


Fig. 2—Temperature induced percolation behaviour of the *n*-Hp/AOT/Water (aq. polymer) microemulsions [composition. *n*-Hp/AOT/water as 53/23.5/23.5 % w/w. 1-6, water; 5% PEG 6000 (w/v); 10% PEG 6000 (w/v); 1% starch (w/v)—Scale I; 1% polyacrylamide (w/v)—Scale II; 10% PEG 1000 (w/v) respectively].

droplet fraction and temperature variation at fixed mole ratio of [water]/[AOT] (ref. 13).

Viscosity behaviour

A fairly large region of the ternary phase diagram towards the higher amphiphile region has been found to be considerably viscous and obviously non-Newtonian in behaviour. Four compositions of each system at aq. polymer/HP/AOT weight ratios, 1 (30/30/40); 2, (10/70/20); 3, (20/60/20); and 4, (30/50/20) have been considered and their shear viscosities are presented in Figs 3 and 4, where $\ln \eta$ (η expressed in Pascal.s⁻¹) has been plotted against the shear rate D (expressed in s⁻¹). For all the systems, the viscosity has decreased with increased rate of shear and has shown a minimum. The position of the minimum depends on the type of the system. For aqueous, 5% PEG, 1% PAA and 2% gelatine, the minimum are all at $D = 1000$. In the case of 1% starch for the composition 4 it is at $D = 1000$ and for the compositions 2 and 3, the viscosities are almost equal and the minimum are at $D = 1800$. It has been observed that for PEG and starch contained systems, there is a mild tendency of increase in viscosity after the minimum. The viscosities of the systems studied have followed an order in respect of their compositions. At all shear rates the

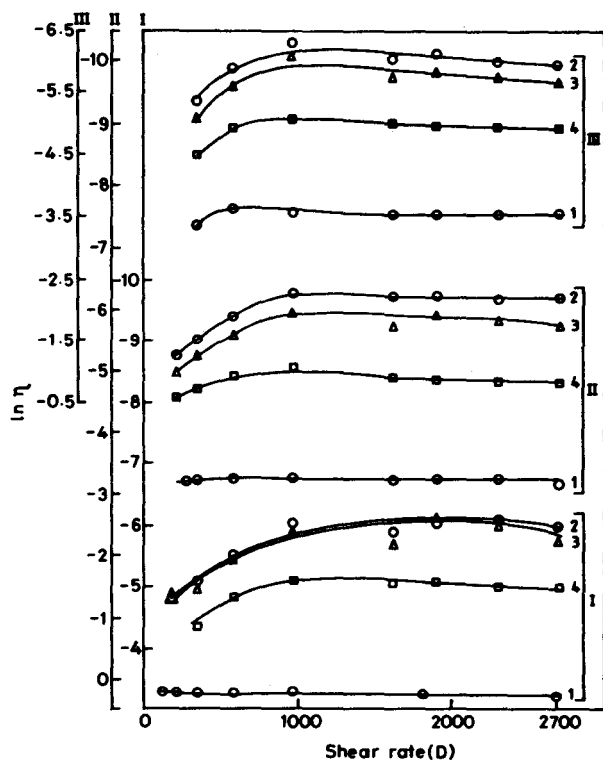


Fig. 3—Viscosity-shear rate profiles of *n*-Hp/AOT/water (or aq. polymer) microemulsion systems at 308 K. [Compositions, 1-4, *n*-Hp/AOT/water (aq. polymer) as 30/40/30, 70/20/10, 60/20/20 and 50/20/30 respectively. Ordinate scale, I, 1% starch (w/v); II, water; III, 5% PEG 6000 (w/v)].

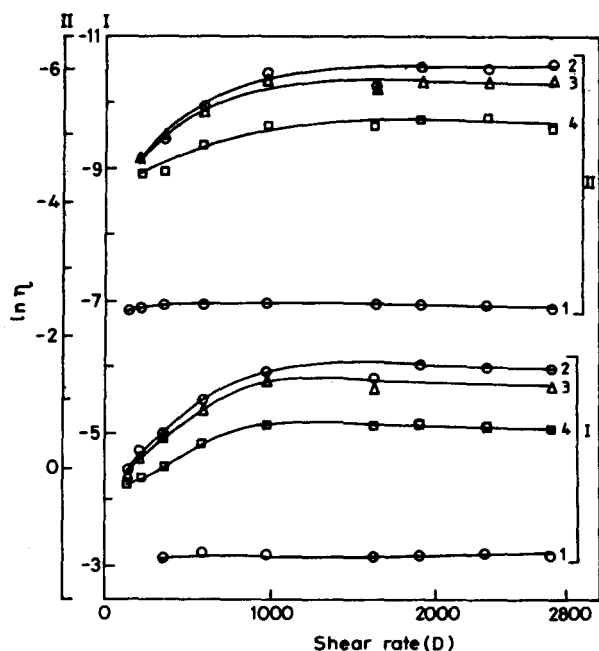


Fig. 4—Viscosity-shear rate profiles of *n*-Hp/AOT/water (or aq. polymer) systems at 308 K. [Compositions, 1-4 same as in Fig. 3. Ordinate scale, I, 2% gelatine (w/v); II, 1% polyacrylamide (w/v)].

viscosity decreased in the order comp. 1 < comp. 4 < comp. 3 < comp. 2. The composition-2 has shown minimum viscosity. This sequence is in accordance with the percent composition of the oil but not with the trend of [water]/[AOT] ratio (ω). Further, for all the types, the viscosity of comp. 1 has been very little affected by shear rate. The order of the shear rate influenced decrease in viscosity is comp. 2 > comp. 3 > comp. 4 > comp. 1.

Application of shear can cause both thinning and thickening of a non-Newtonian liquid. In the former case, the viscosity decreases with the shear rate. In viscous dispersion, the dispersed particles remain associated with the solvent. Application of shear may desolvate them, the solvent gets detached and this causes thinning. Break down of chain type structure or orientation of match stick like particles in the direction of shear may also cause viscosity decrease with shear. Such systems are called pseudoplastic²⁴. The system herein studied are to a certain extent pseudoplastic, wherever there has been increase of viscosity after the minimum the system has acquired the property of dilatancy²⁴. At higher shear rates the particles either have aggregated or formed network structure to yield increased viscosity.

The investigation leads to the following conclusions: Significant microemulsification of water and *n*-heptane with AOT forming Winsor type IV stable dispersions can be obtained in the presence of various water soluble polymers; the dispersions of w/o type μ Es show normal conductance behaviours including percolation; and the oil rich preparations are non-Newtonian in viscous behaviour, the viscosity depends significantly on the rate of shear.

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