

# THE VISCOSITY BEHAVIOURS OF MICROEMULSIONS : AN OVERVIEW

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Detailed viscometric investigations on microemulsions composed of different kinds of oil (aliphatic, aromatic, alicyclic and vegetable) and amphiphile (cationic, anionic and nonionic) are presented in relation to their flow behaviours (Newtonian and non-Newtonian), percolation, structure and dynamics. The role of salt and polymer on the viscous behaviour has also been examined. The usefulness of the quantitative rationale such as the Walden rule and the different viscosity - concentration equations has been discussed.

**Key Words:** Microemulsion; Bulk and Microviscosity; Viscosity Equations; Percolation

## Introduction

The concept of microemulsion was introduced by Hoar and Schulman<sup>1</sup> during 1943. Since then there has been a prolific growth of literature on this microheterogeneous systems<sup>2-15</sup>. They are thermodynamically stable, optically isotropic dispersions (of water-in-oil or oil-in-water) usually stabilized by an interfacial film of amphiphiles (surfactant and cosurfactant molecules)<sup>6,16</sup>. The size of the dispersed droplets is usually ~10-100nm. Dispersions with particle size > 100 nm, are energetically unstable and separate into the two component phases, oil and water. They are called macroemulsions and are not transparent but milky in appearance.

The stability of a microemulsion is a consequence of the ultralow interfacial tension between the oil and the water phases. Co-surfactant and surfactant contribute in combination to the low tension; the co-surfactant molecules intercalate between the surfactant molecules at the oil-water interface, thus favouring the curvature of the droplet.<sup>2,3,6</sup> The molecular structure of the surfactant and co-surfactant, as well as their concentrations determine the microstructure; the structure of the oil, which can penetrate the interface, also contributes to this property<sup>17</sup>. A schematic representation of different thermodynamically stable single phase as well as multiphase regions for a system of water,

surfactant and oil, is presented in a triangular diagram (Fig. 1). These multiphase systems with the following distinct features were first experimentally demonstrated by Winsor<sup>18</sup>:

- (1) Two phases, the lower microemulsion phase in equilibrium with the upper excess oil phase (Winsor type I).
- (2) Two phases, the upper microemulsion phase in equilibrium with the lower excess water phase (Winsor type II).
- (3) Three phases, middle microemulsion phase in equilibrium with upper excess oil and lower excess water phases (Winsor type III).
- (4) Single phase, oil, water and surfactant are homogeneously mixed, and one dispersed in the other (Winsor type IV).

Other typical phases may also appear in the non-specified regions of Fig. 1 for some multicomponent phase-forming systems. In certain conditions, even four phases solution with two microemulsion phases in conjunction with oil and water may arise<sup>19,21</sup>. Depending on the nature of the components and environmental conditions, isotropic lamellar, liquid crystalline and viscous phases may also result<sup>22,23</sup>. Composition dependent internal structures (microstructures) of microemulsion systems are also illustrated in Fig. 1. In the water-rich corner, a single phase region of normal micelles (at low oil content; L<sub>1</sub>) or oil-in-water (o/w) microemulsions is formed. In the oil-rich domain reversed

micelles ( $L_2$ ) or water-in-oil (w/o) microemulsions is preferred. In reversed systems, the number of water molecules per surfactant molecule is often expressed as  $\omega = (\text{water})/(\text{surfactant})$ . Some authors prefer to talk about hydrated reversed micelles when  $\omega < 10$  and w/o microemulsions when  $\omega > 10^{23b}$ , others put the limit at  $\omega = 15^{23c}$ . At about equal mass fractions of all components in Fig. 1, a microemulsion with a bicontinuous structure may form, usually called a Winsor IV system. This type of a bicontinuous microemulsion is also found in the surfactant-rich microemulsion phase i.e., the middle phase in Winsor III system<sup>23d</sup>.

Some modern experimental techniques have been proven to be very useful in the characterisation (i.e., elucidation of the internal structure) of microemulsions. Small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), dynamic (or laser) light scattering (DLS), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR), time-resolved fluorescence quenching (TRFQ) methods are in growing use in the last two decades. Other methods viz., conductance, viscosity, ultrasonic interferometry, ultrasonic absorption, dielectric permittivity, thermal conductivity, transient electrical birefringence, infra-red spectroscopy, calorimetry, etc. are also in

frequent use for elucidation of the internal physico-chemical states of microemulsions. Of these techniques, viscosity finds a special status in literature.

The viscosity of a solution can give first hand information on its internal consistency; in case of macromolecular solutions and colloidal dispersions, an understanding of the overall geometry of the dispersed entities can as well be obtained. In the field of application, fluidity of a medium plays a major role; for localized application, high consistency (low fluidity) is wanted, whereas for solubilization, spreading and reaction study it is advantageous to have high fluidity. The knowledge of viscosity of colloidal dispersions (such as reverse micelles and microemulsions) thus have both fundamental and application importance. The results of our laboratory and from others have shown variable features, both rise and fall as well as maximum in viscosity have been witnessed with variation of dispersion concentration. These features, of course, depend on system composition and environmental conditions<sup>24,33</sup>.

In view of the above as well as the potential applications of microemulsions such as petroleum recovery to nanoparticle synthesis (of magnetic materials, superconductors etc.)<sup>12,13</sup>, liquid membrane,<sup>34,35</sup> reaction medium<sup>11,12</sup>, etc., an overview of

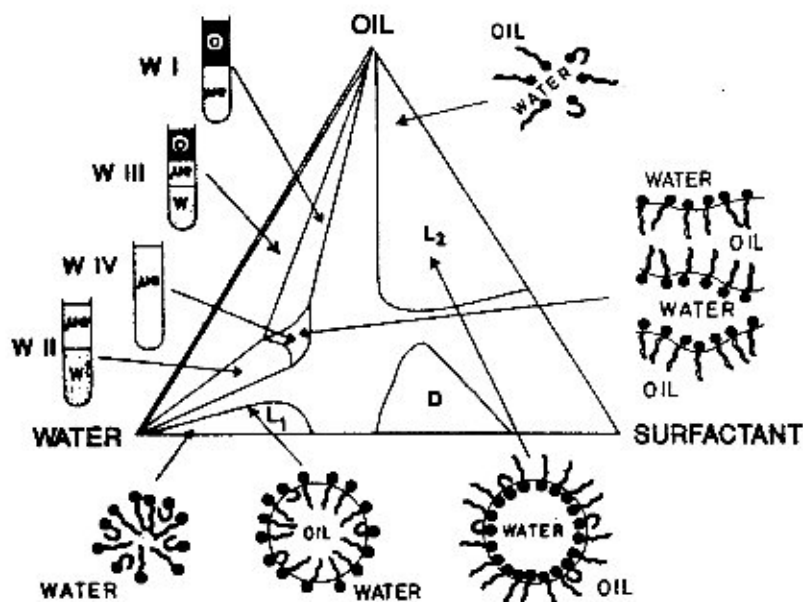


Fig. 1 Schematic ternary phase diagram of water-oil-surfactant mixtures representing Winsor classifications and probable internal structures.  $L_1$ , a single phase region of normal micelles or oil-in-water (o/w) microemulsions;  $L_2$ , reverse micelles or water-in-oil (w/o) microemulsions; D, anisotropic lamellar liquid crystalline phase. The microemulsion is marked by  $\mu$ , the oil by O and water by W<sup>153</sup>.

the studies of the viscous behaviours of microemulsions (versatile compartmentalized liquids) with reference to internal structure, data correlation, flow pattern, additive influence, etc. is wanted. Generalised reviews on microemulsions dealing with their different aspects can be found in literature<sup>7,9,12,14,15</sup>. In this article, we are concerned about the flow behaviours of microemulsions which are seldom treated in a comprehensive manner. A concise attempt on this has been made in what follows.

### Viscosity in Relation to Microemulsion Structure

In the past, a detailed investigation on binary (AOT/xylene) and ternary (water/AOT/xylene) systems using viscosity and other physical methods was reported by Ekwall *et al.*<sup>37</sup> The size and shape of micelles of reversed type were found to depend on the amount of solubilized water as evidenced from the measurements of intrinsic viscosity. Gradzielski and Hoffmann<sup>38</sup> studied the structure and properties of charged o/w microemulsions made up from a zwitterionic surfactant and hydrocarbon. The systems were characterized by the methods of light scattering, SANS, interfacial tension, conductivity and viscosity. The viscosity of microemulsions were measured as a function of concentration as against the volume fraction of the 'dry' microemulsion aggregates, and the results found corroboration from the light scattering technique. The microemulsions were shown to be composed of spherical aggregates consisting of anisotropic particles which was found to be in good agreement with the theoretical predictions made on dispersions of spherical particles<sup>39</sup>. They reported the values of the relative viscosity,  $\eta_{rel}$  of cationic and anionic systems, and explained it on the basis of higher effective volume fraction for anionic system which possesses a significantly larger effective hydration shell. The scattering properties of the anionic microemulsions were, therefore, different from that of cationic microemulsions. It was observed that for the AOT/decane microemulsion system, addition of NaCl decreased the relative viscosity of the solution inducing a spherical geometrical form to the dispersion<sup>40</sup>. The aggregation and shape of AOT reverse micelles in n-hydrocarbons, benzene, toluene, carbon tetrachloride, dibromoethylene, tert-amyl alcohol and methanol were studied by ultracentrifugation,

light - scattering and volumetric techniques<sup>41</sup>. The micelle formation was absent in methanol. The smallest micelle was obtained in tert - amyl alcohol (micellar wt. 2500). The AOT micelle essentially appeared to be monodisperse and slightly assymmetric in shape. Garcia-Rio *et al.*<sup>42</sup> reported the decrease in microemulsion viscosity and water solubilization capacity by the addition of salts, HCl, NaOH and guanidium chloride. This was attributed to the association of cations at the oil/water interface. This association increased the natural negative curvature of the surfactant and hindered the exchange of materials between droplets by way of increasing the interfacial rigidity and decreasing mutual droplet interaction energy. They further reported that the additives like urea, thiourea, formamide and ethylene glycol increased the viscosity of the microemulsion, but decreased the water solubilization capacity. It was suggested that the effect was related to the interfacial association of the additives with the AOT head groups; the binding of the additives at the interfacial layer reduced the droplet surface curvature and promoted attractive interdroplet attraction. In addition to several techniques, viscosimetry was used in support of complexation between sulfonated polystyrene monomers and AOT molecules in m-xylene<sup>43</sup>. It was reported that the ultimate composition of the complexes depended on the nature of the ionogenic groups and initial aggregation state of the AOT molecules.

The viscosity of water/SDS/pentanol/cyclohexane microemulsion system in presence of NaCl has been reported by Rakshit *et al.*<sup>44,45</sup> The increase in viscosity with the addition of water has been ascribed to the increasing diameter of water-filled conduits in the bicontinuous structure. The peak point in the viscosity - (water) profile denotes transition point of w/o system to o/w type. They have also reported that the viscosity of water/Brij 35/heptane or nonane microemulsion systems increases with increasing salinity. Heptane-derived microemulsion has witnessed larger increase in viscosity compared to nonane-derived microemulsion at all compositions, indicating that the hydrophobicity of the system controls the functioning of NaCl. Similar effect has been observed in the cloud point studies; same concentration of NaCl lowers the cloud point of nonane-based microemulsion to a much lesser extent than heptane system. The existence of

antagonistic effect of salinity and alkane chain length of the hydrocarbons has been envisaged. Similar conclusions were earlier arrived at by Shah *et al.*<sup>46</sup> The viscosity of mixed alkane (heptane+nonane) microemulsions has been reported by Ajith *et al.*<sup>47</sup> They have indicated that the systems retained their bicontinuous structure as in pure alkane systems. Recently, Joshi *et al.*<sup>48</sup> have reported that the viscosity of the PEG 400 containing microemulsion system (water/CTAB/1-propanol/cyclohexane) is higher than those without PEG and computed the activation enthalpy of the viscous flow using Frenkel-Eyring equation. Further reports on microemulsions exhibiting Newtonian viscosity behaviours and normal trends with the composition of components are due to Rakshit *et al.*<sup>49,50</sup> Lalanne *et al.*<sup>51</sup> have reported three transport properties (*viz.*, viscosity, mass diffusion and heat transfer) of the ternary system of AOT/water/ $\text{CCl}_4$  in the range of low volume fractions. A slow increase in viscosity with the volume fraction of the dispersed phase with an extrapolated slope near Einstein's value of 2.5 has been obtained implying an assembly of quite rigid spherical micelles with weak interaction. This has been largely confirmed by the results of Rayleigh scattering measurements. Viscosity measurements have also revealed altered water structure when it is dispersed in toluene, chlorobenzene and cyclohexane continuum in the form of w/o microemulsion<sup>52</sup>. Bennett *et al.*<sup>53</sup> have observed two peaks in viscosity with increasing salinity implying the existence of at least three microstructural regions; one before, after and in between the two peaks. The maxima are indicative of the transition from mono- to bicontinuous structure. If the microstructure is ordered, as in liquid crystals or relatively difficult to break as in gel, the viscosity is expected to increase with increasing bicontinuity. The structural consistency in microemulsions has also been observed by others<sup>54-56</sup> from viscosity measurements. The regular solution behaviour has been observed for some systems, and some have shown specific behaviour. A gradual increase of viscosity, conductivity and surface tension in the range of 0-20% (w/w) water content in water/TX100/n-alkanol/ $\text{CCl}_4$  microemulsion has been explained by Santhanalakshmi and Parameshwari<sup>57</sup> in terms of droplet dispersion. The clustering of water droplets (with TX100) has been envisaged by the mixed

monomolecular layer of surfactant - cosurfactant couple.

The different structures in the isotropic oil-surfactant-rich phase composed of aromatic oils/nonionic surfactants/water have been elucidated by Lundsten *et al.*<sup>58a</sup> from conductivity, viscosity and light scattering measurements at 298.2 K. The oils and surfactants used were benzene and 1,3,5-trimethylbenzene (mesitylene) and commercial nonyl phenyl polyoxyethylene type.  $\text{C}_9\text{Ph}(\text{EO})_m\text{OH}$  (*viz.*, Berol 02, Berol 268 and Berol 223) respectively. At low surfactant contents, aggregates solubilizing water were not formed in mixture of oils and nonionic surfactants, which have indicated that the water is sparingly soluble. On the other hand, at intermediate mass fractions of oil and surfactant, closed aggregates solubilizing water were formed at mass fractions of water around 0.1. At high surfactant contents, open structures were formed and the solubility depended on the surfactant used. In the mixture of benzene and Berol 02 ( $\text{C}_9\text{Ph}(\text{EO})_6$ ) indications of percolating structures were found. As nonionic surfactants were mixed with the anionic surfactant, AOT, closed aggregates solubilizing water were also formed at low surfactant contents, and the open structures were still present at high surfactant contents. All these interpretations were supported by viscosity, conductivity and light - scattering measurements. Lundsten<sup>58a</sup> further extended this investigation for 1,3,5-trimethylbenzene (mesitylene)/water/Berol 227 system using the same techniques with an objective to test this pseudo three component system as cocktails for liquid scintillation counting. The structure and nature of microemulsions were elucidated from viscosity and conductivity as was done in previous work<sup>58a</sup>. Phase equilibrium at different temperatures of the systems, hexanoic acid - hexylamine - water, heptanoic acid - heptylamine - water, octanoic acid - octylamine - water have been studied by Backlund *et al.*<sup>59,60</sup> and the structure in the solution phase has also been elucidated using macroscopic properties *viz.*, density, electrical conductivity and viscosity. The self-diffusion coefficients were also measured to distinguish whether a component is entirely or partly confined into closed aggregates.

Bagger - Jorgensen *et al.*<sup>61</sup> have investigated the impact on structure and rheology of pentaethylene glycol dodecyl ether ( $\text{C}_{12}\text{E}_5$ )/water/decane system



by the addition of small amounts of a hydrophobically modified poly- (sodium acrylate) (HMPA). The addition has induced a structural change in the microemulsion probed by using SANS and NMR self-diffusion measurements. Viscoelastic gels are formed in the droplet microemulsion - HMPA mixtures above a certain polyelectrolyte concentration. They have also reported that a viscous microemulsion can be transformed to a viscoelastic gel upon increasing the temperature. A dramatic change in surfactant aggregate structure is responsible for this spectacular effect. They have further reported<sup>62</sup> the effects of the addition of two polymers, poly (ethylene oxide) PEO and hydrophobically end-capped PEO (HM - PEO) on the phase behaviour, microstructure and rheology in the water part of the ternary systems as reported earlier. The polymers destabilize both the micellar and lamellar phases. The micellar phase containing HM - PEO has been investigated by NMR relaxation and self-diffusion measurements, SANS, shear viscosity and oscillatory frequency sweep measurements. Addition of HM-PEO ( $\leq 2$  wt%) led to a drastic decrease of the micellar self diffusion and to an increase in the low shear viscosity by several orders of magnitude. This has provided informations on the network structure formation in the system. Valliente *et al.*<sup>63</sup> have investigated the phase and rheological behaviours of the dodecyl tetraethylene glycol ( $C_{12}E_4$ )/benzyl alcohol/water microemulsion system at low surfactant and alcohol concentrations. With an increase in the alcohol concentration, the sequence of the phases is  $L_{ub}$ ,  $L_{\alpha}$ ,  $L_3/I_{\alpha}$ ,  $L_3$  and  $L_3/L$  (all bilayer structures). At low alcohol and surfactant concentrations, the anomalous lamellar phase  $L_{\alpha}^+$  is also formed. Upon comparing the phase sequence of  $C_{12}E_4$  ternary system with that of medium chain alkanols, they have concluded that benzyl alcohol stabilizes the lamellar phase. Rheological measurements were carried out at  $25^\circ \pm 0.1^\circ\text{C}$  by a Carri - Med CLS 100 controlled stress rheometer using a cone-plate configuration. The viscoelastic properties of the system were studied with oscillatory experiments. In all lamellar phase samples, the storage moduli ( $G'$ ) were greater than the loss moduli ( $G''$ ). The loss modulus became smaller with the alcohol concentration and it was neglected in the  $L_3$  phase. The samples with a more elastic response corresponded to  $L_{ub}$ , which was built up from vesicles. From all these results they have established a good correla-

tion between the proposed structures and the flow curves. The samples of  $L_{ub}$  subregion originated from vesicles (probably spherical) were closely packed with increasing shear rate. The samples of the  $L_{\alpha}$  subregion behaved as plastic fluid and represented the typical lamellar phase. At the intermediate region, both structures coexist and  $L_{ub}$  changed to  $L_{\alpha}$  under shear.

Eastoe *et al.*<sup>64</sup> investigated the effects of cation charge and size on the microscopic and macroscopic properties of systems containing various metal salts of the amphiphilic anion bis (2-ethylhexyl) sulfosuccinate (AOT). The counterions used were  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$ . At (AOT) = 0.75 mol  $\text{dm}^{-3}$  and  $\omega$  ((water)/(AOT)) values  $< 5.0$ , the systems are all far from phase boundaries so that interaggregate interactions get minimized. Under these conditions, both viscosity and SANS measurements indicated that for a hydrated metal counterion radius  $r_h < 3.0 \text{ \AA}$ , cylinder-shaped aggregates are favoured. These results have demonstrated the importance of the size of the hydrated counterion of ionic surfactants for the aggregate structure in w/o systems. The results obtained from the variation of  $\eta_r$  with  $c$  (concentration) for  $\omega = 5.0$  of  $\text{M}^{n+}$  (AOT)<sub>n</sub> aggregates in cyclohexane are classified into two distinct categories; (i) surfactants which form low viscous solutions with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{Ca}^{2+}$  as counterions, and (ii) high viscous solutions with  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . The intrinsic viscosity values obtained for surfactants of type (i) are all remarkably close to 2.5, suggesting the presence of spherical aggregates. For the more viscous solutions (ii), values of ( $\eta$ ) range from 10.0 to 21.0, characteristic of non-spherical structures. Systems consisting of rigid rod-shaped particles have been evidenced from SANS data. They have analysed the intrinsic viscosity in terms of the equation of Simha<sup>65</sup>,

$$(\eta) = 2.5 + 0.4075(J-1)^{1.508} \quad \dots (1)$$

to provide an estimate of the axial ratio  $J$  (ratio of the revolution of the major to the minor axis) of the aggregate. The values of  $J_{\text{visc}}$  for the  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  surfactants lie nearly between 8.0 and 11.0, suggesting a large distortion from the spherical shape found in the  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{Ca}^{2+}$  systems where  $J = 1.0$ .

In literature, reports on the structure and properties of cationic surfactant derived microemulsions

are scarce. Partial phase diagram, conductivity and viscosity behaviours of cationic microemulsions formed from didodecyldimethyl ammonium bromide (DDAB) in different hydrocarbons, viz., hexane, octane, decane, dodecane and tetradecane with water have been reported by Chen *et al.*<sup>66</sup> In the single phase region, the microemulsions weakly conduct at low water content and exhibit increased conductivity with increasing water concentration. A parallel viscosity behaviour has also been observed. The monophasic system becomes a rigid gel at very high water content. A high and systematic extent of oil specificity has been observed. Abillon *et al.*<sup>26</sup> have reported structural study of microemulsions formed with cationic surfactants, didodecyl ammonium bromide (DDAB) and cetyltrimethyl ammonium bromide (CTAB) and compared the results with their earlier investigations using anionic surfactants (sodium dodecyl sulphate, SDS and sodium hexadecyl benzene sulphonate, SHBS) derived microemulsions. They have explored the systems by way of composition analysis, structural analysis from viscometric measurements and quantitative structural characterization from SAXS measurements. It has been shown that the viscosity behaviours of the microemulsions can be correlated with their structure in terms of Krieger formula<sup>67</sup>, where a packing volume fraction has been taken into consideration. Inference on bicontinuous microemulsion structure can be achieved by this approach.

Structural studies of the didodecyldimethyl ammonium bromide (DDAB)  $L_2$ -phase at high (surfactant-water) volume fraction  $\phi \geq 0.20$ , using different techniques (viz., SAXS, electrical conductivity, viscosity etc.) have been reported<sup>68,71</sup>. Recently, Eastoe *et al.*<sup>72</sup> have expanded their preliminary SANS study<sup>73</sup> of DDAB/water/cyclohexane system by using viscometry and SANS. In dilute  $L_2$ -phase ( $0.008 < \phi < 0.16$ ), the structure of this system depends critically on the water concentration  $\omega$  ( $= (H_2O)/(DDAB)$ ). For  $2.0 < \omega < 8.0$ , cylindrical reverse micelles have been found. The SANS data were consistent with a constant cylinder of cross-section radius ca.  $15\text{\AA}$  and length in the range of  $250 - 90\text{\AA}$  depending on  $\omega$ . At  $\omega = 10.0$ , an abrupt structural change has been observed and for  $\omega > 10.0$  spherical aggregates are formed. The solubilization limit has been reached at  $\omega = 12.0$ , where spherical w/o microemulsion droplets co-exist with an excess water phase (Winsor II system). For the

spherical droplet, the mean water core radius of ca.  $19\text{\AA}$  and the overall radius including the DDAB monolayer of ca.  $30\text{\AA}$  have been obtained by neutron contrast variation method. According to them, the cylinder - to - sphere transition observed at  $\omega \approx 10.0$  and solubilization phase boundaries at  $\omega \approx 12.0$  are in good agreement with the predictions. Very recently, Shioi *et al.*<sup>74</sup> have investigated the structure and properties of the oil rich microemulsion ( $L_2$  - phase) containing anionic polyelectrolyte, poly (acrylic acid) (PAA-H,  $M_w = 450,000$ ) and its sodium salt PAA - Na ( $M_w = 30,000$ ) and didodecyldimethyl ammonium bromide, (DDAB) in cyclohexane using SAXS, DLS, electrical conductivity and viscosity measurements. Despite the strong electrostatic interaction, both polymers are dissolved in the water of DDAB aggregates without changing the original rodlike structure of DDAB microemulsions. PAA - Na is a strong electrolyte, but it behaves as an uncharged polymer in DDAB microemulsions by adsorption of the DDAB chain. PAA - Na got confined within the waterpool of DDAB aggregates because the length of the PAA - Na in the cylindrical waterpool is similar to the average length of the DDAB aggregates. Thus, the characteristic size obtained from the viscosity and other measurements were not affected by the presence of PAA - Na. The solubilization of PAA - H in the DDAB microemulsion has not caused a considerable structural change for the rodlike structure. The PAA - H chain connects the rodlike aggregates composed of DDAB, because the length of the PAA - H confined within the cylindrical water pool is much longer than the average length of the rodlike aggregates. Caboi *et al.*<sup>75</sup> have investigated the whole range of the  $L_2$  - region of Ca AOT/water/n-decane system by viscosity, conductivity, dynamic light scattering (DLS) and NMR self-diffusion measurements. They have followed different dilution criteria to map out the structural transitions and the variations of the interaction forces in relation to the phase diagrams. The occurrence of non-spherical particles at high volume fraction of the dispersed phase,  $\phi_d$  has been suggested from the analysis of viscosity data. The surfactant sodium bis (2-ethylhexyl) phosphate (NaDHEP) in benzene and n-heptane can form crystallites, which with addition of water transform into reverse micelles<sup>76</sup>. This behaviour has been corroborated from viscosity, dynamic light scattering (DLS) and other measurements.

The crystallite formation takes place at  $\omega < 3$ . The study has shown that for this surfactant NaDHEP, a certain amount of water is required for reverse micelle formation otherwise crystalline rods are formed.

The static microstructures for different kinds of microemulsion systems consisting of sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/n-hexane/water (NaCl) (I) and sodium bis (ethylhexyl) phosphate (SDEHP)/n-hexane/water (NaCl) (II) in the concentrated regions of the surfactants have been qualitatively elucidated through some typical macroscopic properties viz., viscosity, osmotic compressibility and electrical conductivity by Kurumada *et al.*<sup>77</sup>. The dependence of the specific viscosity,  $\eta_{sp}$  on  $\phi_{ns}$  (volume fraction of the aggregates in the microemulsion) for both microemulsions has been shown. The value of  $\eta_{sp}$  for AOT-based system has almost agreed with zero shear specific viscosity for the colloid system<sup>78</sup> composed of silica monodispersed spheres in the region  $\phi_{ns} \leq 0.6$ . The same results have been reported by Berg *et al.*<sup>33</sup> for the single phase microemulsion composed of AOT, n-decane and water in  $\phi_{ns} \leq 0.2$ . The results have indicated that the interaction between the aggregates coated by AOT (regarded as the hard-sphere systems) in the  $\phi_{ns} \leq 0.6$  condition are consistent with the results of osmotic compressibility. The  $\eta_{sp}$  for SDEHP-based systems has roughly agreed with that of the silica particle system in very dilute region, where the aggregates geometry is not far from a sphere. As  $\phi_{ns}$  has increased, the geometry has transformed to elongated aggregates, and in the same region, the value of  $\eta$  has deviated to larger values compared to the silica particle system. A steep increase in  $\eta_{sp}$  has been observed around the critical volume fraction,  $\phi_{ns} \approx 0.09$ .

In the SDEHP microemulsion, the scaling laws on the osmotic compressibilities and on the specific viscosities have been observed in the region  $\phi_{ns} < 0.2$  irrespective of salinity conditions, which has implied that a transient network structure has formed in the microemulsion. Subsequently, Kurumada *et al.*<sup>79,80</sup> have reported the microstructure of both the microemulsion systems in the concentrated surfactant region from DLS and rheological measurements. For the SDEHP system<sup>79</sup>, both type of measurements have indicated that the network structure forms in the

region of  $\phi_{ns} \geq 0.15 - 0.20$  and remain confined into a smaller size scale as  $\phi_{ns}$  increases. Rheological measurements have indicated that the relaxation time of elastic stress is shorter for more concentrated SDEHP-microemulsions, and it is interpreted in terms of the formation of more dense network structure for more concentrated systems. On the other hand, the characteristic time for recovery of the network structure from a broken state by a steady shear flow lengthens as  $\phi_{ns}$  is increased. The geometrical shape of the individual aggregates in the dilute region strongly influences the dynamical behaviour of the microemulsion in the concentrated region. In the rheological measurements, they have also examined<sup>80</sup> the response of the concentrated AOT microemulsions to an oscillatory shear flow and a steady shear flow. It has been shown that the retarded dynamical behaviours can be accounted for by the combination of the formation of the transient "clusters" in the dense microemulsion due to attractive interaction. This picture is consistent with that deduced from the DLS measurements.

The state of aggregation of metal salts,  $M^{n+}(\text{DEHP})_n$ , of the organophosphorus acid extractant bis (2-ethylhexyl) phosphoric acid (HDEHP) has been examined by Steytler *et al.*<sup>81</sup> from SANS and viscosity measurements in cyclohexane. A range of di- and trivalent counterions ( $\text{Ca}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Cr}^{3+}$ ) have been used as a function of their concentration and water content. Their study has clearly differentiated between systems comprising rod-shaped reversed micelles (aggregation number  $\gg 10$ ) from essentially spherical structures of limited aggregation number ( $< 5$ ). The length of the rod-shaped micelles is strongly dependent on the nature of the counter-ion. The shape and size of the reversed micelles has been reported to be independent of the surfactant concentration in the range of 0.04 - 0.08 g. cm<sup>-3</sup>. In the absence of water, the ammonium salt of the metal ion extractant bis (ethylhexyl) hydrogen phosphate ( $\text{NH}_4\text{DEHP}$ ) can form extended rod-shaped reversed micelles in oil media of length  $L > 300$  Å, giving rise to solutions of high viscosity<sup>82</sup>. With the addition of water, the micelles become progressively shorter in length until spherical droplets has formed at  $\omega \sim 4$ . With further addition of water, the droplets have grown in size with the increase in the core radius,  $R_c$  in proportion to the



water content,  $\omega$ . Various viscosity equations have been applied to these systems and will be discussed in a subsequent section.

Friberg *et al.*<sup>83</sup> have reported smooth increase in viscosity with the increase of glycerol in waterless microemulsion system of glycerol/SDS/hexanol/decanol. No anomalous viscosity behaviour, around the converging point of the lines in the viscosity-concentration profiles has been noticed.

The structure of a ternary system containing perfluoropolyether (PFPE) oil, PFPE surfactants, and water, near the oil-rich corner, has been investigated using viscosity, and static and dynamic light scattering by Sanguineti *et al.*<sup>84</sup> The existence of surfactant aggregates has been shown and the dependence of their size and interaction on  $\omega$ , molar mass of oil and ionic strength has been investigated. Aggregate size increases with either water content or oil molecular weight as found with hydrogenated microemulsions. Interactions among droplets become more and more attractive as  $\omega$  is decreased or oil molecular weight is increased.

### Flow Characteristics of Microemulsions

Microemulsions can have varied flow behaviours, lamellar (Newtonian) and nonlamellar (non-Newtonian). Low viscous microemulsions (usually Winsor I and II types) show Newtonian behaviour. The Winsor III and the bicontinuous types are usually non-Newtonian in nature, and they may show plasticity. Their rheology is complex in nature. Papaionnou and Davies have reported non-Newtonian viscosity features of quaternary microemulsion systems<sup>85,86</sup>. The flow of the ternary microemulsion (water/DDAB/dodecane) up to a high shear rate ( $\sim 3000\text{S}^{-1}$ ) has been reported to be Newtonian although some indirect evidence in favour of elasticity has been reported<sup>87</sup>. The densities and viscosities of  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ /AOT/heptane microemulsions have been studied by D'Aprano *et al.*<sup>88</sup> at different  $\omega$  and temperature, and the differences in apparent molar volumes and viscosities have been explained on the basis of the hydrogen bonding strengths of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , and the interdroplet interactions governed by the solvation of the head groups of AOT. The effects of droplet clustering on the shear viscosity of water/AOT/decanol microemulsion have been investigated by Ripple and Berg<sup>89</sup>. Very recently, the internal structure of microemulsions prepared

from vegetable oils, AOT, cinnamic alcohol and water has been studied by Mitra *et al.*<sup>90</sup>. The shear viscosity has been found to decrease with the rate of shear ( $D$ ), levelling off at  $D=1620\text{S}^{-1}$ , whereas it has increased for ricebran oil and levelled off also at  $D=1620\text{S}^{-1}$ . The deformation of the dispersed droplets under the rate of shear has been envisaged for the latter. Using alkanols (having carbon number 5 to 10) as oils and AOT as the amphiphile, Ray and Moulik<sup>91</sup> have prepared microemulsions and have elaborately studied their viscosity, conductance and thermodynamic behaviours. A fairly large region of the ternary phase diagram towards the higher amphiphile level has been found to be quite viscous and obviously non-Newtonian in behaviour. A more or less monotonic increase in viscosity has been observed with the rate of shear for w/o type (Winsor II) solutions; for the bicontinuous (Winsor III) preparations, the viscosity has increased to reach a plateau as shown in Fig. 2. The results have been rationalized in the light of structure break down, droplet deformation and interdroplet attractive interaction. The structure and dynamical properties of an isotropic  $L_3$ -phase of water/AOT/decanol microemulsion have been investigated by Kotlarchyk *et al.*<sup>92</sup> the  $L_3$ -phase (consisting of randomly lamellar sheets) has been witnessed to exhibit Newtonian behaviour up to  $D=790\text{S}^{-1}$ . Kar and Moulik<sup>93</sup> have prepared the quaternary microemulsion systems of water/polymers (polyethylene glycol, carboxymethyl cellulose, gelatin, starch and polyacrylamides)/AOT/heptane and have observed the preparations to be non-Newtonian with high amphiphile content. Both shear thinning and thickening behaviours have been observed; the systems have been found to be moderately pseudoplastic. The rheological properties of inverse microlattices (consisting of sterically solubilized particles of diameter  $< 130\text{nm}$ ) of polyacrylamide and polymethacrylate have been studied by Candau *et al.*<sup>94</sup> The data for high and low shear limiting viscosities have well fitted to Kreiger - Dougherty equation<sup>95</sup>. The rheology of the  $L$ -phase of the ternary system of water/SDS/poly (propylene glycol) has been reported by Sierra and Rodenas<sup>96</sup>. The samples have shown Newtonian behaviour at shear stress  $> 20\text{-}60\text{S}^{-1}$ . Under this condition the viscosity has increased with polymer concentration similar to  $\text{H}_2\text{O}/\text{CTAB}/\text{PPG}$  system<sup>97</sup>. The viscosity of the



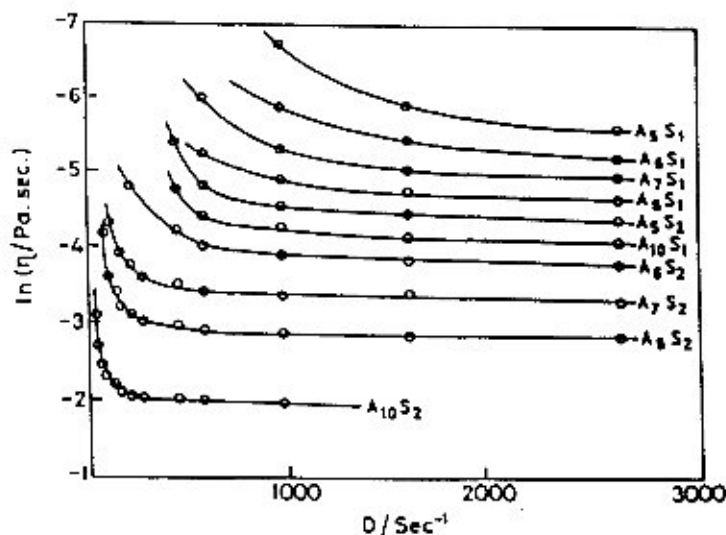


Fig. 2. Dependence of viscosity of microemulsions on the rate of shear at 303 K. Alkanol numbers are shown in the curve. Wt% compositions of water/AOT/alkanol; S<sub>1</sub>, 5/15/80; S<sub>2</sub>, 30/35/35<sup>91</sup>.

system relative to the polymer solution at constant (SDS) has shown a decreasing trend with increasing polymer content, which for the H<sub>2</sub>O/CTAB/PPG system has remained constant.

#### Viscosity in Relation to Percolation

The phenomenon of percolation in microemulsion is associated with droplet clustering and fusion, i.e., internal structure changes and hence it gets reflected on viscosity. A pronounced similarity in the behaviour of self-diffusion, specific conductivity and viscosity of water/AOT/isooctane microemulsions has been reported by Eicke *et al.*<sup>98</sup> The behaviours of percolating systems are illustrated in Fig. 3. Formation of a network structure in the percolation range (with discreteness of the droplet character) has been reported to be in agreement with viscous behaviours. The increase in viscosity with temperature has been attributed to the phenomenon of increased clustering of the droplets<sup>99</sup>. The structural inversion of w/o microemulsion to o/w type has also been studied from viscosity measurements along with conductivity and electro-optical Kerr effect<sup>100</sup>. With the increase in the oil content, the w/o microemulsion transforms into the bicontinuous form at roughly 20% (w/w) of oil (oil percolation threshold), the bicontinuous form transform into the o/w form.

The percolation in viscosity follows scaling type equations,<sup>101-103</sup>

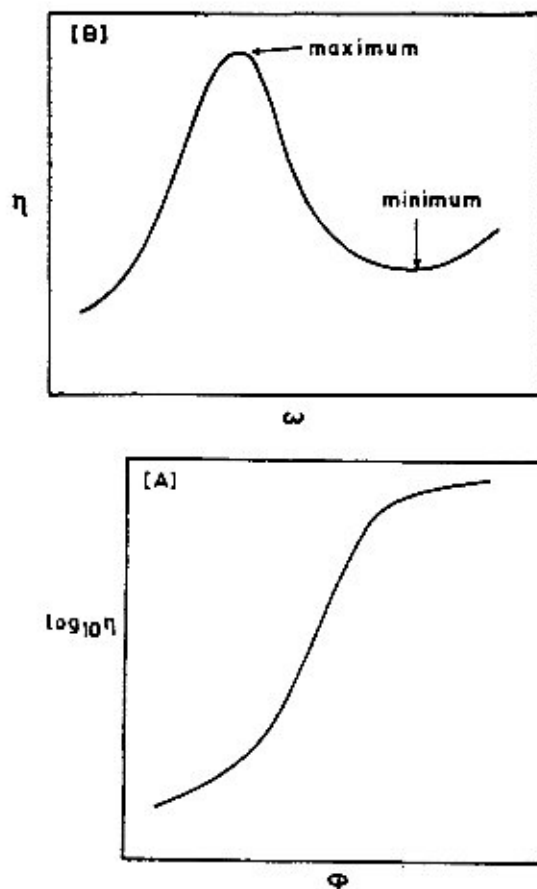


Fig. 3A Variation of viscosity ( $\eta$ ) with  $\phi$  at constant  $\omega$  and temperature of a percolating microemulsion system (arbitrary scale).

Fig. 3B Variation of viscosity ( $\eta$ ) with  $\omega$  at constant  $\phi$  and at constant temperature (arbitrary scale).

$$\eta = A (\varphi - \varphi_c)^{\mu'}, \text{ for } \varphi > \varphi_c + \delta'_1 \quad \dots (2)$$

$$\text{and } \eta = B (\varphi_c - \varphi)^{s'}, \text{ for } \varphi < \varphi_c - \delta'_2$$

where  $\varphi$  is the volume fraction of the dispersed matter (water and amphiphile),  $\varphi_c$  is the percolation threshold,  $A$  and  $B$  are prefactors, and  $\mu'$  and  $s'$  are scaling exponents. The  $\varphi_c + \delta'_1$  and  $\varphi_c - \delta'_2$  are the cross over regimes which also exist in case of pressure induced percolation<sup>104</sup>. The width of the cross over regime increases with decreasing  $\omega$ . The crossover regime  $\delta'_1 + \delta'_2$  may be obtained under simplified condition by stepwise eliminating the experimental point closest to  $\varphi_c$  until two straight lines in both regimes are obtained for the curve,

$$\log_{10} \eta = f(\log_{10} |\varphi - \varphi_c|) \quad \dots (3)$$

On the average, the values of  $\mu'$  and  $s'$  are 2.0 and 1.20 respectively which fairly agree with  $\mu$  and  $s$  values of 1.94 and 1.20 respectively obtained for conductance percolation<sup>105-107</sup>. But the  $s'$  values corresponding to the dynamic percolation is far off from the static percolation value of 0.7. In general, the scaling equations work much better in waterless microemulsions<sup>103</sup>. The percolation of conductivity is much clearly observed than that of viscosity, as the conductivity of water  $\gg$  conductivity of oil; since  $\eta_{\text{water}}$  is not greatly different from  $\eta_{\text{oil}}$ , parallel manifestation of percolation of viscosity like conductance does not occur. The systems produced by the dispersion of polar and viscous nonaqueous solvents like formamide, low molecular weight polyethylene glycols etc. have also manifested percolation<sup>108</sup>. According to Ray *et al.*<sup>108</sup> clustering induced viscosity increase occurs for systems, formamide/AOT/isooctane, ethylene glycol/AOT/isooctane and dimethyl formamide/AOT/isooctane at low  $\omega$ . In terms of conductance, the phenomenon of percolation occurs at higher threshold volume fraction ( $\varphi_d$ ); it cannot be induced by temperature. Although the low  $\varphi_d$  in the viscosity profile and high  $\varphi_d$  in the conductance profile are not corroborative, the results have suggested the possibility of structure formation in the waterless microemulsion. The results are exemplified in Fig. 4.

The viscosity of water/AOT/decane microemulsion has been studied as a function of temperature in presence of a good number of additives<sup>30</sup>. A maximum in viscosity has been

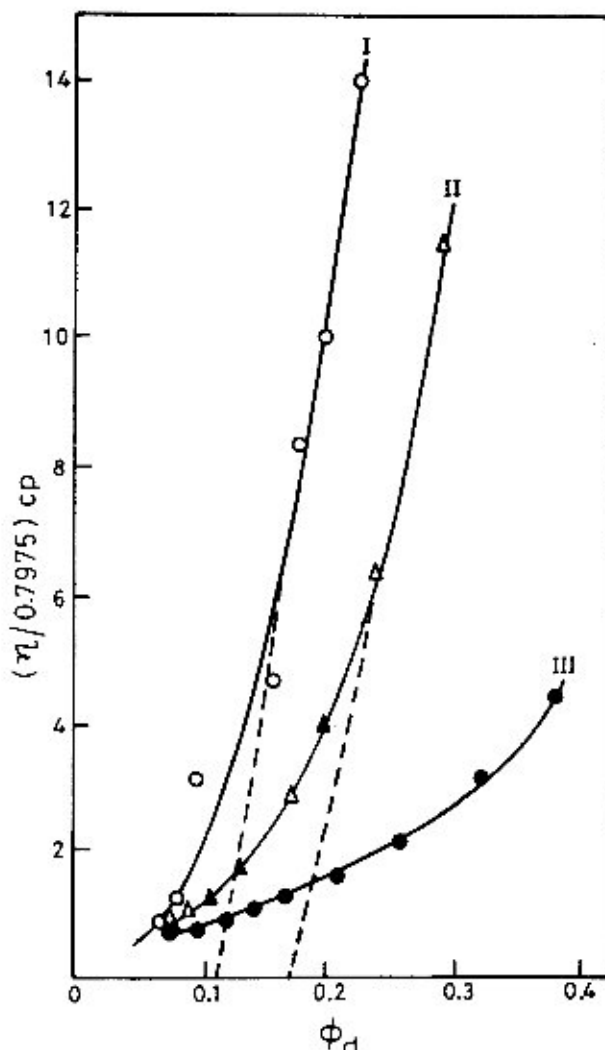


Fig. 4 The viscosity coefficient ( $\eta$ ) vs  $\varphi_d$  profiles for three microemulsion systems at 303 K; I, FA/AOT/i-Oc at  $\omega = 1.44$ ; II, EG/AOT/i-Oc at  $\omega = 1.85$ ; III DMP/AOT/i-Oc at  $\omega = 2.03$ <sup>108</sup>.

observed at 40°C in absence of additive which, has shifted toward higher temperature in presence of additives. Borkovec *et al.*<sup>100</sup> have reported similar viscosity behaviour. The initial rise in viscosity is also due to percolation, the decrease is caused by the overall change in the particle shape. The non-linear  $\log \eta$  vs.  $T^{-1}$  has suggested onward change in the activation energy for the viscous flow.

The observation of increase in viscosity of microemulsion with temperature for AOT-derived systems has been rationalized by the phenomenon of percolation<sup>109</sup>, but this needs further justification. Viscoelastic effects have been reported in dense AOT/n-decane inverted micelles<sup>110</sup> and dense water/AOT/n-decane w/o

microemulsions<sup>111</sup>. Such behaviour of both the systems has been interpreted on the basis of increased connectivity of the dispersed phase at high volume fraction ( $\phi$ ). But the correlation among the viscoelastic effect and anomalies of shear viscosity and electrical conductivity in percolation regime has not been fully analysed. Very recently, D' Aprano *et al.*<sup>112</sup> have reported that the process of momentum transfer (related to viscosity) and charge transfer (related to conductance) are different for water/AOT/n-heptane microemulsions as a function of the volume fraction of the dispersed phase ( $0 < \phi < 70$ ) and of the molar ratio  $\omega$  ( $0 < \omega < 40$ ) at 25°C. The densities and viscosities of AOT in heptane microemulsion system containing light and heavy water, as a function of molar ratio, ( $\omega = (\text{H}_2\text{O})/(\text{AOT})$  or  $(\text{D}_2\text{O})/(\text{H}_2\text{O})$ ) have been measured at four different temperatures (0, 5, 25, 40°C) by D' Aprano *et al.*<sup>113</sup> The viscosities of both  $\text{H}_2\text{O}/\text{AOT}/\text{n-heptane}$  and  $\text{D}_2\text{O}/\text{AOT}/\text{n-heptane}$  systems have been explained in terms of intermicellar interaction mainly governed by hydration of the head groups of AOT.

Boned *et al.*<sup>104</sup> have reported the effect of pressure on the percolation phenomenon in ternary microemulsions. They have measured the electrical conductivity,  $\sigma$  and dynamic viscosity,  $\eta$  of water-based water/AOT/undecane microemulsions and waterless glycerol/AOT/isooctane microemulsions as a function of volume fraction  $\phi$  of dispersed matter (water plus AOT or glycerol plus AOT) and pressure up to 1000 bar. The curves  $\eta(P)$  and  $\sigma(P)$  at constant  $\phi$  and temperature  $T$ , and the curves  $\eta(\phi)$  and  $\sigma(\phi)$  at constant  $P$  and  $T$  have been analysed within the framework of percolation theory. They have considered two ternary systems correspond to a dispersion of spheres in a continuum, the spheres being subjected to Brownian movement. The dynamic description of the phenomenon of percolation has been applied and the theoretical predictions have been verified. Whatever be the pressure, both the conductivity,  $\sigma$  and viscosity,  $\eta$  have increased with the content of the dispersed matter  $\phi$  (with  $(1/\sigma)(d\sigma/d\phi)$  and  $1/\eta(d\eta/d\phi)$  passing through a maximum as a function of  $\phi$ ). Quantitatively they have observed that when the conditions of application of the asymptotic laws of the theory are satisfied, the scaling components have been found to be the

same i.e.,  $\mu \approx 2$  above the threshold and  $s = 1.2$  below the threshold for all systems independent of the properties studied under various pressures. This indicates that the systems belong to the same class of universality.

Caboi *et al.*<sup>75</sup> have reported the percolation behaviour at a critical  $\phi_d^c = 0.142$ , along an oil dilution line at constant molar ratio of  $W/S = 26.4$  for  $\text{CaAOT}/\text{water}/\text{n-decane}$  system. The percolative threshold has not been found to be temperature dependent in the range of 15–30°C, suggesting the possibility of a static percolation. An interesting feature of apparent 'reverse percolation' on increasing  $\omega$  for cationic surfactant, didodecyldimethyl ammonium bromide (DDAB) in cyclohexane has been also reported<sup>66-71</sup>. The electrical conductivity of the  $\text{C}_6\text{H}_{12}$  - continuous system has decreased by about eight orders of magnitude with the increase of  $\omega$ ; the viscosity has similar trend. At low  $\omega$ , the system has been apparently bicontinuous that has transformed into a discrete droplet structure at higher  $\omega$ . The observed change is opposite to the behaviour found in microemulsions of nonionic surfactants and has suggested that water concentration is important for determining the structure and surfactant film curvature.

### Microviscosity of Waterpool in Microemulsion

There are several reports on the microviscosity estimation of reverse micelles specially with AOT as the amphiphile by steady state<sup>114-118</sup> and transient fluorescence depolarization<sup>119,120</sup> techniques. However, the microviscosity of water in AOT reverse micellar system cannot be easily estimated quantitatively because the rotational movements of both the dye solubilized in the waterpool and that of micelle itself are included in the depolarization. Very recently, Hasegawa *et al.*<sup>121-125</sup> have reported estimation of the microviscosity of the waterpool in the AOT reverse micelle as a function of  $\omega$  by using a viscosity sensitive fluorescence probe, AuO (Auramino O) with increasing  $\omega$ , microviscosity ( $\eta_w$ ) has rapidly decreased below  $\omega=10$  and then it has gradually decreased until the micellar solution gets turbid above  $\omega=50$ . But in the higher  $\omega$ -region, the microviscosity,  $\eta_w$  is considerably higher than the viscosity of ordinary (bulk) water. This has indicated that the solubilized water molecules are reasonably bound to the polar head groups of AOT.



These results corroborate well with the findings of fluorescence depolarization studies using a cationic dye, rhodamine B. The fluorescence depolarization of xanthene dyes with different ionic characters has suggested that the waterpool is heterogeneous with respect to the microviscosity. The effects of temperature, amphiphile concentration, solvent and counter ion on the waterpool microviscosity have also been examined in order to obtain detailed picture of the static structure of AOT reverse micelles. The dynamic fluctuation occurring near the vicinity of the phase separation in the process of cooling of microemulsion has been demonstrated by fluorescence depolarization measurements.

#### Microemulsion and the Walden Rule

The conductance of a well-defined and less complex system shows inverse dependence on viscosity. For electrolytic solutions media of variable viscosity, this has been found to be so and

the rule of Walden<sup>124</sup> (Walden product i.e.,  $\lambda\eta = \text{constant}$ , where  $\lambda$  is the equivalent conductance of the electrolyte solution) has been observed to be more or less valid.

This rule has been found to be very often violated in microemulsion medium, especially at the stage of percolation. Although conductance of microemulsion systems increases slowly or very rapidly either by increasing the volume fraction of the polar dispersed solvent (essentially water) at a constant temperature or by elevating the temperature of a constant composition, the corresponding viscosity may increase or decrease and it can pass through both maximum and minimum<sup>27-31,66,100,125</sup>. It has been reported that the maximum in viscosity with respect to the volume fraction of the dispersed phase may be independent of the type of alkanes used as oil and can depend on the temperature of measurement<sup>126</sup>. The mean radius of the dispersed droplets may have a reasonable say in this regard but it is difficult to

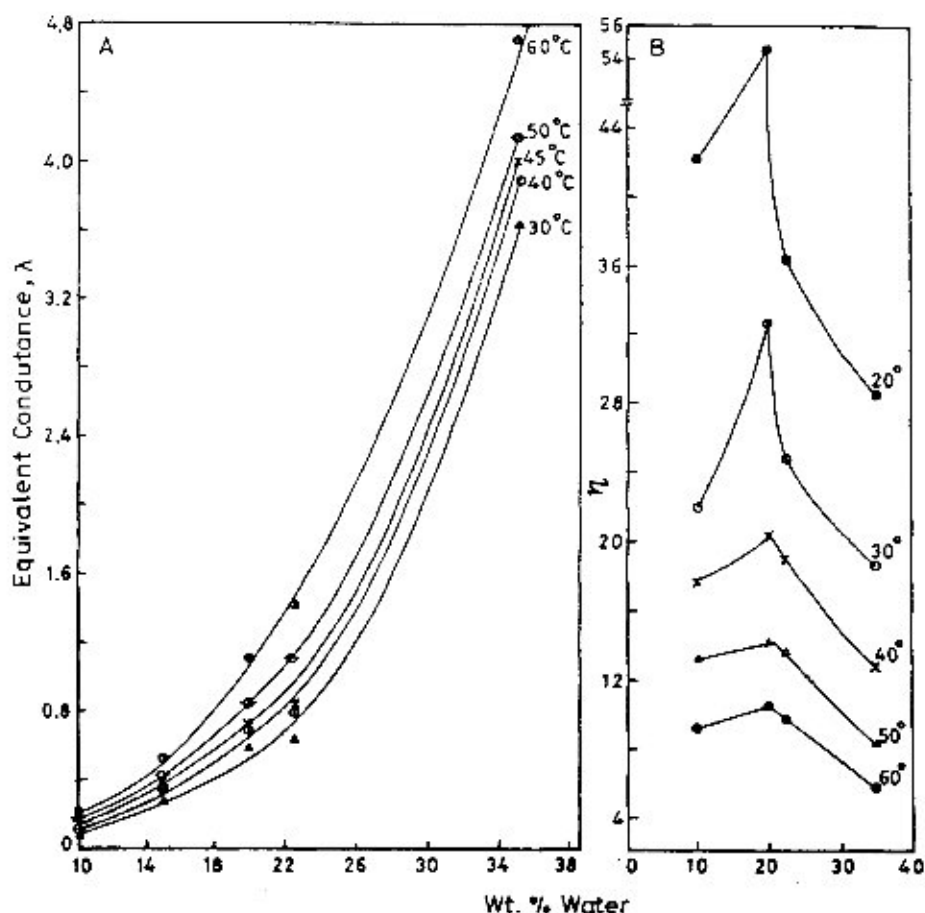


Fig. 5A & B Dependence of (A) equivalent conductance and (B) viscosity on wt% of water in microemulsion at different temperature<sup>31</sup>.

explain the appearance of a sharp peak in the viscosity-volume fraction curve.

The formation of aggregates or infinite clusters of dispersed droplets providing channels for enhanced ion conductance "by either "hopping" or "transient fusion and mass exchange" mechanism manifesting percolation should grossly end up with increased viscosity (i.e., viscosity percolation). Paul and Moulik<sup>31</sup> have elaborately studied viscosity and conductance of 'biological microemulsions' consisting of water/AOT/hexylamine/saffola oil and have shown serious invalidity of the Walden product mentioned above. In Fig. 5A, the equivalent conductance - wt.% water profile is exemplified and the corresponding viscosity - wt.% water dependence is depicted in Fig. 5B. A maximum in viscosity has been observed at 20% water, where the conductance appears to take a sharp turn. The maxima at a particular level of water addition have also been reported<sup>109</sup> in w/o microemulsions with cyclohexane, isooctane and undecane stabilized by AOT. The Walden product ( $\lambda\eta$ ) versus wt.% water is shown in Fig. 5C, where

a turn in the course is observed at 22.5% of water, particularly at temperatures below 60°C; at 60°C the course is linear. A close fluctuation is noticed at 20% at the two lower temperatures, 30°C and 40°C. The Walden product is never constant, the regular increasing trend is a consequence of sharp change in conductance, the viscosity decrease cannot compensate for it. This has supported a special internal structural organisation, which is reflected on conductance and not much on viscosity<sup>127</sup>. The variation of  $\lambda\eta$  with temperature is also revealing, the value decreases with temperature (Fig. 5D). However, at the lowest value of  $\omega$  ( $\omega=9$ ), the compensation is exact, it is shallow at  $\omega=20$ . For other values,  $\omega = 18$  and 39, the  $\lambda\eta$  sharply declines, which is much significant at  $\omega = 39$ . At higher  $\omega$ , water droplets of sufficient number collide<sup>10,128-130</sup> with greater frequency leading to large and sharp changes in conductance, which has little scope for response in viscosity. The reciprocal correlation is therefore, least quantitative. At  $\omega = 9$ , the collision probability among the droplets is low so that a significant

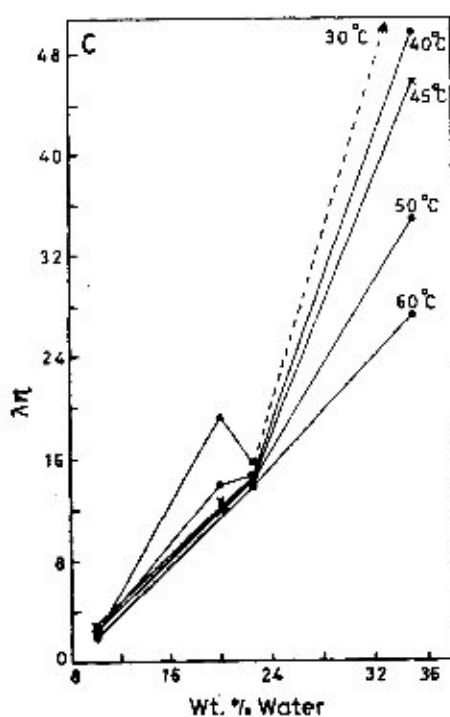


Fig. 5C Walden product ( $\lambda\eta$ ) of microemulsion as a function of wt.% of water at different temperature<sup>31</sup>.

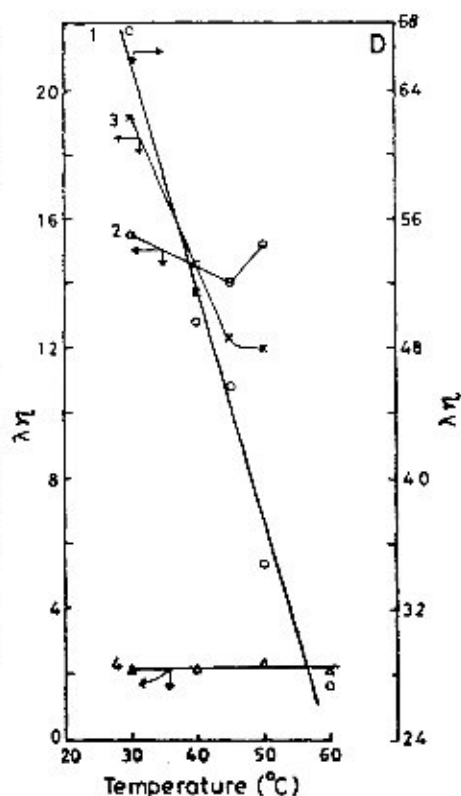


Fig. 5D Walden product ( $\lambda\eta$ ) of microemulsion at  $\omega = 34, 20, 18$  and 9 as a function of temperature<sup>31</sup>.

change in conductance is not possible, the viscosity and conductance, therefore, can compensate each other. These observations advocate complexity in the internal structural states of the studied w/o microemulsions. This finding may suggest weak dependence of membrane conductance on membrane viscosity; it is the channels that carry charges (ions) across it. A porous dispersed body can favourably allow transport of ions (matters) through its water-filled pores. The increased viscosity imparted in the solution by the presence of the porous body may thus have insignificant say on the ion conductance in the solution. A word of caution is relevant here regarding the thermodynamic validity of the Walden product. According to the Courie-Pregogine principle of irreversible thermodynamics<sup>131</sup>, forces and fluxes of different elements of symmetry should not couple. This seriously restricts the coupling of  $\lambda$  and  $\eta$ , the product is thus essentially extra thermodynamic.

#### Microemulsion in Relation to Viscosity Equations

There exists in literature a number of viscosity - concentration relations of quantitative and semi-quantitative nature valid in the lower and higher ranges of solute (dispersant) concentration. Attempts have been made to test the viscosity of microemulsion in the light of these equations. Mooney equation has been used in explaining the viscosity of microemulsion system of water/NaDBS/hexanol/xylene by Baker *et al.*<sup>132</sup> and Tadros<sup>133</sup>.

$$\eta_r = \exp \frac{a\phi}{1-k\phi} \quad \dots (4)$$

where  $\eta_r$  is the relative viscosity ( $\eta_{\text{sm}} / \eta_{\text{sol}}$ ),  $\phi$  is the volume fraction of water, and  $a$  and  $k$  are constants ( $a$ , is related to the intrinsic viscosity of the dispersion and  $k$  is the so-called "crowding coefficient" which accounts for interparticle interaction).

For the studied water/NaDBS/hexanol/xylene microemulsion,  $\eta_r$  has exponentially increased with  $\phi_{\text{H}_2\text{O}}$  and (NaDBS); the hydrodynamic radius has continuously increased with concomitant increase in the ratio of the surfactant layer to the droplet core radius with increasing (NaDBS).

The viscosity equation of Vand<sup>134</sup> is of similar form of Mooney,

$$\ln \eta_r = \frac{v\phi}{1-Q\phi} \quad \dots (5)$$

where  $v$  is the particle shape factor and  $Q$  is the inter-particle interaction parameter.

The viscosity of microemulsions prepared with CTAB, DTAB and SDS as surfactants, butanol as cosurfactant and dodecane as oil, when examined as a function of salinity, a broad maximum has been shown<sup>26</sup>. The Krieger viscosity formula<sup>67,95</sup> has been observed to fit the results,

$$\eta_i = (1 - \phi/\phi_p)^{-1/2} \quad \dots (6)$$

where  $\phi_p$  is the packing volume fraction and other terms have their usual significance. For compact cubic and random arrangements of spheres, the values of  $\phi_p$  are 0.75 and 0.65 respectively.

For the bicontinuous structure<sup>26</sup> the following relation holds,

$$\eta = \eta_{\text{aq}}\phi_{\text{aq}} + \eta_{\text{org}}\phi_{\text{org}} \quad \dots (7)$$

where  $\eta_{\text{aq}}$  and  $\eta_{\text{org}}$  are the viscosities of the excess phases, and  $\phi_{\text{aq}}$  and  $\phi_{\text{org}}$  are the corresponding volume fractions. The packing fraction,  $\phi_p$  has been revealed from viscosity measurements to pass through a maximum with wt% of NaCl (or salinity)<sup>26</sup>, the onset of droplet coalescence ( $\phi_p = 1$ ) has been observed. Due to nonaggregation of the droplets by poor attractive interaction among the droplets, peaks in viscosity are not observed for Winsor I and II. For Winsor III region, a good reason for coalescence i.e., attractive interaction (the vander Waals force) increases with droplet size<sup>135,136</sup>. The use of Frenkel-Eyring viscosity equation to calculate the activation enthalpy of viscous flow for mixed surfactant microemulsion systems, (Brij 35 + SDS)/1-propanol/heptane/water and (Brij 35 + Tween 20)/1-propanol/heptane/water have been reported by Ajith *et al.*<sup>50</sup> and the values are higher for more viscous o/w systems. The free energy of solubilization of oil in water has been found to be a function of surfactant composition and the enthalpy is more or less independent of composition.

Ray *et al.*<sup>137</sup> and Ray and Moulik<sup>108</sup> have made a detailed viscosity study of aqueous and waterless microemulsions prepared with AOT and a good



number of oils. The overall geometry and solvation of the droplets have been assessed. The Euler's voluminosity equation<sup>138</sup> as used by Ekwall *et al.*<sup>37</sup> for AOT/xylene reverse micellar system, has been considered by Ray<sup>137</sup> and Ray and Moulik<sup>108</sup> for analysis.

$$\eta_r = \left[ \frac{1 - 0.1 V \phi_d}{1 - 1.35 V \phi_d} \right]^2 \quad \dots (8)$$

where  $V$  is the voluminosity (defined as the ratio of the hydrated to anhydrous volumes of the droplets) and  $\phi_d$  is the volume fraction of the anhydrous droplet.

The viscosity of microemulsion systems referred to above have also been tested in terms of the equations of Vand<sup>134</sup> eq. (5), Thomas<sup>139</sup> eq. (9) and Moulik<sup>140</sup> eq. (11).

Thomas equation,

$$\eta_r = 1 + 2.5 \phi + A \phi^2 \quad \dots (9)$$

where  $A$  is the third virial coefficient.

A virial equation of the form,

$$\eta_r = 1 + 2.5 \phi + 10.05 \phi^2 + A' \exp(B \phi) \quad \dots (10)$$

where  $A'$  and  $B$  are constants, has also been used by Thomas for concentrated dispersions<sup>141</sup>.

Moulik equation,

$$\eta_r^2 = I + M \phi^2 \quad \dots (11)$$

where  $I$  and  $M$  are empirical constants ( $1.5 < I > 1.0$  and  $M$  large).

The microemulsion systems both aqueous and waterless studied by Ray *et al.*<sup>137</sup>, and Ray and Moulik<sup>108</sup> have exhibited striking validity of all the three eqs. (8), (9), (11) at constant  $\omega$ . The viscosity results have also been well correlated by the combined unified viscosity equation of Moulik<sup>142,143</sup>,

$$(\eta_r/\phi)(1 - \eta_r/\tau\phi)^{1/2} = (12.5 - m/v)^{1/2} - (12.5 - m/v)^{1/2} Q \phi \quad \dots (12)$$

where the new terms  $\tau = M/2.5$  and  $m = A/(2.5)^2$ . The validity of eq. (12) has been exemplified in Fig. 6

The eq. (12) has been observed to be valid for  $\phi > 0.05$ . The slopes at lower  $\phi$  are positive except for octane and decane containing microemulsions

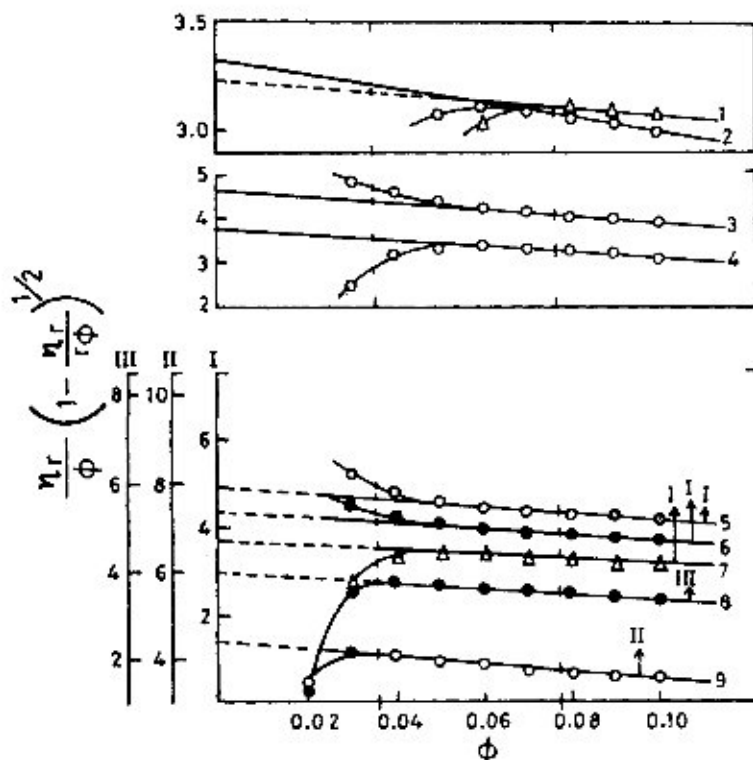


Fig. 6  $\eta_r/\phi (1 - \eta_r/\tau\phi)^{1/2}$  vs.  $\phi$  profiles for w/o microemulsions at constant  $\omega$  at 303 K. Curves 1-9, Hp ( $\omega = 15$ ), Hx ( $\omega = 15$ ), Dc ( $\omega = 15$ ), i-Oc ( $\omega = 15$ ), Dc ( $\omega = 7$ ), Oc ( $\omega = 7$ ), Hx ( $\omega = 15$ ), Hp ( $\omega = 7$ ) and i - Oc ( $\omega = 7$ )<sup>137</sup>.

at  $\omega = 7$ . All the equations (8 - 12) have shown good validity at constant  $\omega$  but have failed to corroborate results at variable  $\omega$ . The correlation of the parameters ( $Q$ ,  $M$  and  $A$ ) of different equations with the carbon number and molar masses of the oils and  $\omega$  has been attempted. The results are exemplified in Fig. 7A and B.

The effect of salt (sodium cholate, NaC and NaCl) on the viscosity behaviours of microemulsions containing different kinds of oil has also been examined<sup>137</sup>. A distinct difference between the behaviours of microdispersions in open chain and cyclic hydrocarbon continuum has been observed. For the evaluation of droplet

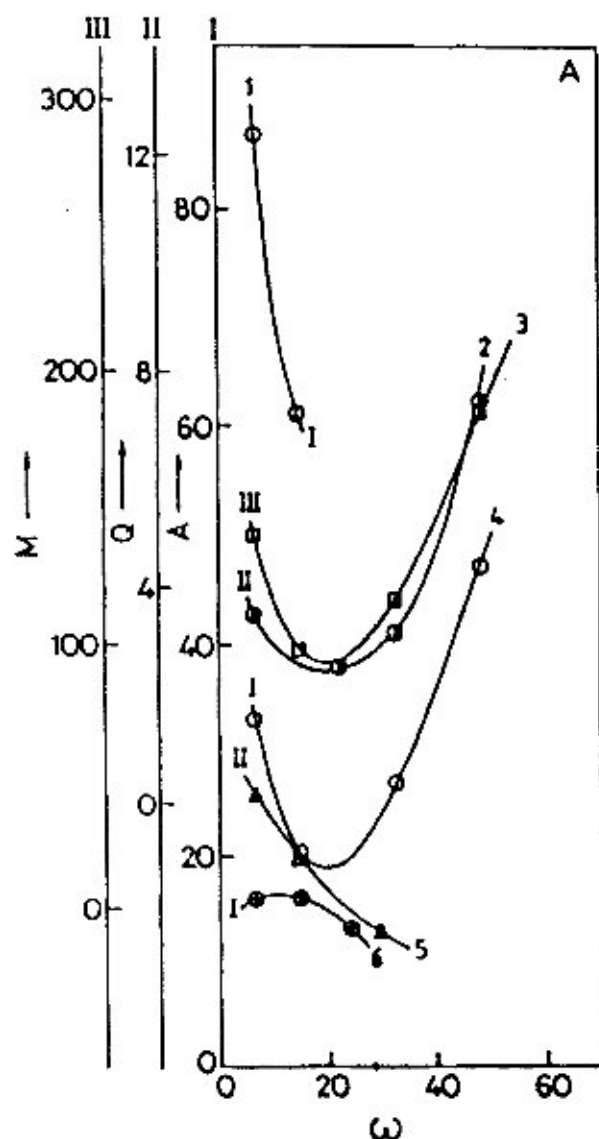


Fig. 7A M, Q, A vs.  $\omega$  plots for w/o microemulsions at 303 K. Curves 1, 2-4, 5, 6, Dc, Hp Hx, Cy.<sup>137</sup>

geometry and solvation of w/o microemulsions, the following equation has been used<sup>144-146</sup>

$$[\eta] = v(\bar{v}_d + \delta\bar{v}_o), \quad \dots (13)$$

where  $\eta$  is the intrinsic viscosity of the microemulsion, and  $\bar{v}_d$  and  $\bar{v}_o$  are the partial specific volumes of the dispersed phase and the dispersion medium respectively, and  $\delta$  is the gm/gm oil bound to the dispersed phase. The shape factor is,  $v = 2.5$  for spheres and it is greater than 2.5 for spheroids.

In terms of viscosity data, negligible solvation of the dispersed amphiphile coated water droplets by oil has been observed<sup>137</sup>. Viscometry is a dynamic method of probing; there may be solvation under static or equilibrated condition. Based on  $\delta = 0$ , the shape factor ( $v$ ) and the droplet geometry (axial ratio,  $a/b$  for spheroids) at different  $\omega$  at 303K have been evaluated. A typical set of results is given in Table I.

It is seen from the Table that the  $v$ -values are only moderately higher than 2.5, the droplet shapes are thus minorly spheroidal. The dispersed droplets of formamide, ethylene glycol and dimethyl formamide in waterless microemulsions with AOT and isooctane reported by Ray and Moulik<sup>108</sup> are also spheroidal in shape having low intrinsic viscosity and negligible solvation. Such microemulsions have also obeyed the viscosity equations of Eiler, Vand, Thomas and Moulik. Similar detailed viscosity studies on microemulsions are rarely found in literature warranting scope for further investigation.

The structural and dynamic properties of microemulsion have been studied by Olsson *et al.*<sup>147</sup> using a combination of SANS, static and dynamic scattering, pulsed-gradient NMR self diffusion and low shear viscosity measurements for the pentaethylene glycol dodecyl ether ( $C_{12}E_5$ )/water/decane system. The low shear-viscosity,  $\eta$  has been measured using capillary, and at high concentrations, a cone-plate rheometer has been used. The two techniques have given equivalent results at intermediate concentrations. According to the Quemada expression<sup>148</sup>,

$$\eta_r = (1 - \phi_{HS}/\phi_m)^2 \quad \dots (14)$$

the variation of the relative viscosity (with water as the solvent) with the hard-sphere volume fraction  $\phi_{HS}$  has been plotted and  $\phi_m$  has been found to be

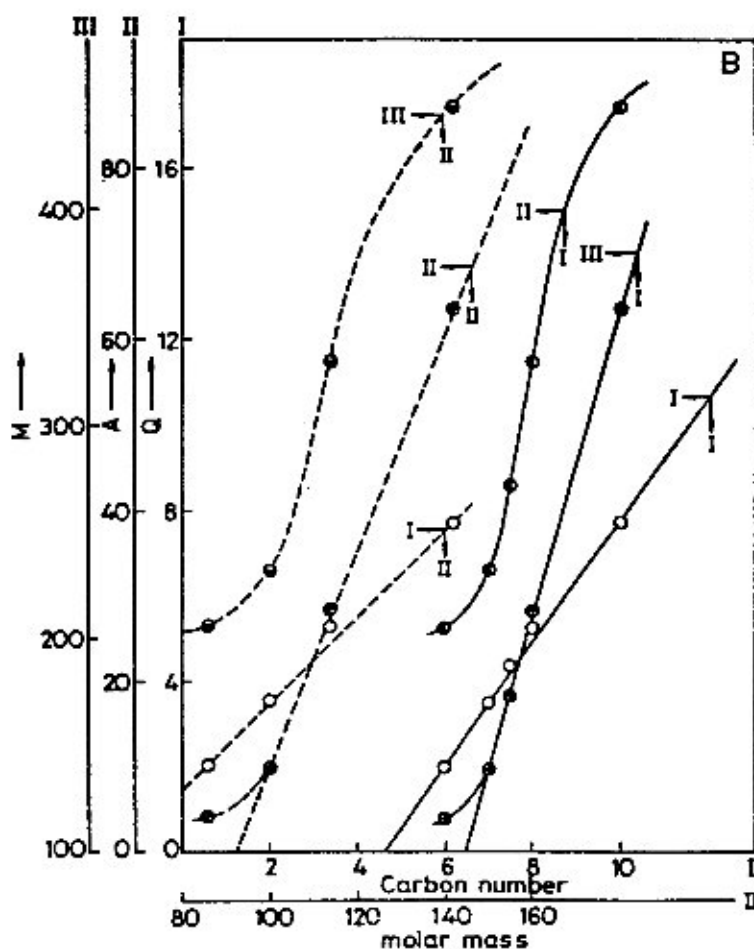


Fig. 7B Dependence of M, A, Q on carbon number and molar mass of the oil for w/o microemulsions at  $\omega = 7$  at 303 K<sup>157</sup>

**Table I**  
The shape factor ( $v$ ) and the axial ratio ( $a/b$ ) of different AOT derived w/o microemulsions in different oils at four different  $\omega$  values at 303K

$\omega$	$v, a/b$					
	Hx	Hp*	i-Oc	Dc	Cy	Xy
7	2.71, 1.37	2.75, 1.43	2.63, 1.20	-	2.79, 1.47	2.66, 1.22
15	2.58, 1.12	2.63, 1.21	2.96, 1.78	2.32	2.86, 1.58	-
25	-	2.81, 1.47	-	-	2.79, 1.47	-
30	2.95, 1.67	-	3.11, 1.91	-	-	-

\* For Hp at  $\omega = 15$ , in 0.05 mol dm<sup>-3</sup> NaCl,  $v = 2.78$  and  $a/b = 1.47$  and in 0.05 mol dm<sup>-3</sup> NaCl,  $v = 2.88$  and  $a/b = 1.58$ . For Hp at  $\omega = 33$ ,  $v = 2.90$  and  $a/b = 1.66$ .

0.63. The results obtained from self-diffusion measurements have followed the model of hard sphere colloidal system<sup>149</sup> and the relation between self-diffusion coefficients and the viscosity derived parameters  $\phi_{HS}$  and  $\phi_m$  according to the relation,

$$D_s/D_o = (1 - \phi_{HS}/\phi_m)^2 \quad \dots (15)$$

where  $D_s$  = self-diffusion coefficients of the droplets, and  $D_o$  = diffusion coefficient extrapolated to infinite dilution.

Steytler *et al.*<sup>82</sup> have applied Einstein's equation<sup>150</sup> (for spheres in the condition of infinite dilution,  $\phi \rightarrow 0$ ) for w/o microemulsions formed by ammonium bis (2-ethyl hexyl) phosphate



(NH<sub>4</sub>DEHP) in cyclohexane. They have shown that the reduced viscosity,  $\eta_{red}$ , approaches a limiting value of 2.5;

$$(\eta_{red})_{\phi \rightarrow 0} = \left\{ \frac{\eta_{sp}}{\phi} \right\}_{\phi \rightarrow 0} = 2.5 \quad \dots (16)$$

where  $\eta_{sp}$  is called the specific viscosity ( $\eta_r - 1$ ).

They have also applied the equation proposed by Frish and Shima<sup>65</sup> to viscosity data for measuring the axial ratio  $J$  of anisotropic, ellipsoidal particles as follows:

$$(\eta) = 2.5 + 0.4075(J-1)^{1.508} \quad \dots (17)$$

The viscosity results displayed as  $\eta_{red}$  vs  $\phi$ , in Fig. 8 are for reverse micelles and w/o microemulsions formed with the surfactant NH<sub>4</sub>DEHP in cyclohexane. The response of the system to water compares that of the SANS data. The intrinsic viscosity at low  $\omega$ -values decreases with increasing  $\omega$  and the length of the rod shaped cluster decreases with  $\omega$ . This general pattern of

behaviour was also observed for NaDEHP, for which the magnitude of the viscosity at low  $\omega$  values was considerably higher<sup>151</sup>.

In principle, eq. (17) can be applied to viscosity data to extract information concerning the length of rod-shaped micelles, provided an estimate of the radius or its independent measurement is available. However, in applying eq. (17) it is assumed that the micellar size and shape are independent of surfactant concentration over the concentration range in which the extrapolation to infinite dilution was conducted. Since SANS measurements clearly demonstrated that the length of the rod was not independent of concentration, a quantitative analysis of viscosity data has not been attempted. Above  $\omega = 4$ , the viscosity data were characteristics of spherical droplets, giving intrinsic viscosities close to 2.5, which was in good agreement with Einstein prediction for hard spheres.

The solubilization of water by the single ionic

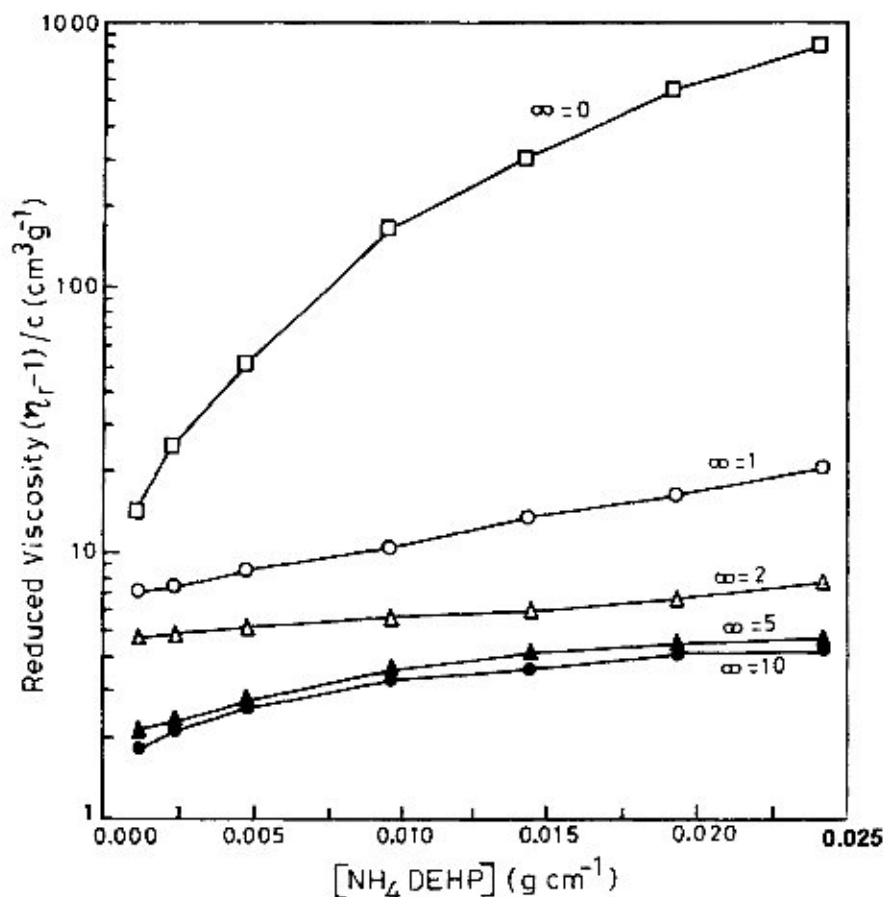


Fig. 8 Dependence of reduced viscosity on concentration for micelles and w/o microemulsions formed by NH<sub>4</sub>DEHP in cyclohexane at 298 K<sup>82</sup>.

amphiphile bis (2-ethylhexyl) phosphoric acid (D2EHPA) and single nonionic surfactant, Span 80 in a nonpolar medium has been investigated by Bart *et al.*<sup>152</sup> with a view to assess the potentiality of the liquid surfactant membrane (LSM) for solving numerous separation problems in various branches of industries and biotechnology. The hydrodynamic, optical and various other analytical techniques were extensively employed to study the physicochemical nature of the microstructures formed in D2EHPA/n-dodecane/water, and Span 80/n-dodecane/water systems. An analytical model based on geometrical assumptions of the spherical shape of the reversed micelles has been developed. The proposed model correlated, among several others, the aggregation number and thus the size of the microstructures with parameters such as the hydrocarbon chain length of the surfactant molecule, its concentration and volume fraction occupied by the reversed micelles etc.; the latter was estimated from the Einstein viscosity equation and its two modified versions reported by Guth and Simha<sup>39a</sup> and Vand<sup>134</sup> as follows;

$$\eta_{sp}=2.5\phi+14.1\phi^2 \quad \dots (18)$$

and,

$$\eta_{sp}=2.5\phi+7.35\phi^2 \quad \dots (19)$$

where  $\eta_{sp}$  = the specific viscosity and  $\phi$  = the volume fraction of the solution taken up by the solute. The Einstein equation has been found to fit the experimental data of the D2EHPA solutions very well; however, Vand's equation has been observed to be more suitable to fit those of Span 80 solutions. The molecular associates formed by D2EHPA were mostly dimers, relatively large microstructures were formed by Span 80; the higher the concentration, the smaller is the size with a tendency to levelling off, and the shapes are nonspherical. The basic structural parameters, i.e., the aggregation number of the reverse micelles, and their water pool radii were derived, and a good agreement between the experimental and the predicted values from the model was observed.

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