

## Percolation phenomenon and the study of conductivity, viscosity, and ultrasonic velocity in microemulsions

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The dynamic properties, i.e., conductance, viscosity, and ultrasonic velocity, of water–aqueous NaCl + Tween 20 + propanol + benzene have been studied as a function of volume fraction of water at 30°C. The conductivity results of these microemulsions are discussed in terms of a percolation model. An excellent qualitative agreement is observed between experimental and calculated values. The viscosity passes through a maximum, a local minimum, and again a second maximum. The ultrasonic velocity plots are not significantly influenced by salinity.

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### I. INTRODUCTION

The term microemulsion was first introduced by Hoar and Schulman [1] to describe it as a dispersion of two immiscible liquids, e.g., oil and water, made possible with surfactant molecules. They are droplet type dispersions either of water in oil (w-o) or oil in water (o-w) depending upon the components' nature and the concentration ratio. Because of very small droplet size (100 Å), microemulsion differs from ordinary emulsion in two main respects, namely, (i) lack of turbidity (as small droplets [2] scatter little light) and (ii) thermodynamic stability [3] (due to very low interfacial tension between oil and water). Surfactants alone cannot lower the interfacial tension to such ultralow values. A cosurfactant such as a short chain alcohol is sometimes used for this purpose.

A large electrical conductivity transition has been observed in several water in oil systems [4–11]. As the volume fraction of water increases the electrical conductivity increases sharply by several orders of magnitude. Several reports indicate that this is due to percolation [7,8,10,11] of a phase of spherical globules in the continuum. In this percolation model, the conductivity remains low up to a certain volume fraction of water due to the nonconducting nature of the continuous phase of the w-o system. However, as the volume fraction of water reaches and exceeds percolation threshold, i.e.,  $\phi_c$ , some of these conductive droplets begin to contact each other and form clusters which are sufficiently close to each other. This causes an efficient transfer of charge carriers between the globules by charge hopping or transient merging of connected droplets with communication between the water cores, resulting in the rapid increase of conductance from an almost zero value to some much higher level.

The existence and position of this threshold depend on the interactions between droplets, which control the duration of the collision and the degree of interface overlapping, hence the probability of hopping or merging. Building up of conductivity needs attractive interactions

and  $\phi_c$  decreases when the strength of these interactions increases.

Similarly, the dynamic viscosity of these systems can also be interpreted with reference to the phenomenon of percolation [12–17] and it has also been mentioned in a study of dynamic viscosity in the course of the Winsor  $I \rightarrow III \rightarrow II$  transition [18] as a function of water volume fraction.

The ultrasonic velocity and isentropic compressibility are sensitive to structural changes that occur in solutions and to any interactions between solvent and solute. Micellar formation, stacking, and transformation from spherical to rodlike shapes have been detected from the analysis of these properties [19–22]. Rao and Verrall [23] have shown that the presence of microemulsion may be detected by means of the variation in ultrasonic velocity and isentropic compressibility properties of quaternary systems containing amphiphile.

The present investigation deals with the study of conductivity viscosity, and ultrasonic velocity of Tween 20-propanol-water-oil systems throughout the single phase region as a function of volume fraction of water  $\phi$ . The analysis of the conductivity data allows one to determine the value of percolation threshold  $\phi_c$  for various mixtures. The influence of salinity on the conductivity, viscosity, and ultrasonic velocity has also been studied.

### II. EXPERIMENT

All the chemicals, viz., Tween 20, propanol, and benzene used in the present investigation were supplied by Fluka. The microemulsions were formulated by keeping the ratio of the number of moles of alcohol to the number of moles of the surfactant ( $n_a/n_s$ ) as 2 (constant).

The conductivity  $\sigma$  was measured with a digital conductivity meter (model NDC 732) of Naina Electronics (cell const. = 1.17). Measurements of viscosity were carried out using a suspended level dilution Ubbelohde capillary viscometer. During measurements, the viscometer was placed in a water bath thermostated at  $30.0 \pm 0.1$  °C. The dynamic viscosity  $\eta$  was obtained from the kinematic viscosity data by multiplying by the density of the studied sample. The density  $\rho$  was measured with the help of a high precision Anton Paar automatic densimeter.

For the accurate ultrasonic velocity measurements, the

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ultrasonic time intervalometer (UTI-101) from Innovative instruments based on the pulse-echo-overlap technique (PET) was used. A transducer of frequency 2 MHz was used for the measurement. All the samples were characterized by the volume fraction of water  $\phi$  and the experiments were performed at  $30.0 \pm 0.1^\circ\text{C}$ .

### III. RESULTS AND DISCUSSION

#### A. Conductivity studies

Figure 1 shows the variation of  $\sigma$  versus  $\phi$  at constant temperature and molar ratio. As the water content is increased in the system, we move from a low conductive region to a highly conductive region showing percolation phenomena. It may be noted that  $\sigma$  remains very low while  $\phi$  is less than  $\phi_c$ . Above  $\phi = \phi_c$ , conductivity increases very rapidly. Similar results have also been obtained by other authors [5,6,9].

The influence of salinity on the conductivity has also been investigated. A large increase in the conductivity of the microemulsion is observed above  $\phi = \phi_c$  on addition of salt (Fig. 2).

We have utilized a theoretical model of Grest *et al.* [24], which is based on the dynamic picture of percolation, to analyze the conductivity results of the present studies. According to the model the charge transport occurs through the surfactant on a cluster of water globules. The water globules are mobile and rearrange with time. This process results in an increase in conductance, which continues till an infinite cluster is formed. The theory gives

$$\sigma = \begin{cases} A(\phi_c - \phi)^{-s} & \text{if } \phi < \phi_c \\ B(\phi - \phi_c)^t & \text{if } \phi > \phi_c \end{cases} \quad (1)$$

(2)

Above the percolation transition  $\phi_c$ ,  $\sigma$  varies as Eq. (2). Experimental studies on microemulsion systems [5,8,25–27] and static systems [28,29] and theoretical studies [30,31] have shown that  $t \approx 1.2$ –2.1. Below, the percolation transition [Eq. (1)] is expected to diverge [31,32]. Grannan, Gailand, and Tanner [33] and Song *et al.* [28] have suggested  $s = 0.7$  for static systems. We

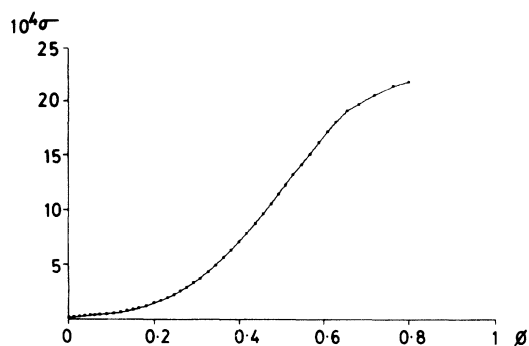


FIG. 1. Variations of the conductivity  $\sigma$  ( $\text{S m}^{-1}$ ) vs volume fraction  $\phi$  for water + Tween 20 + propanol + benzene.

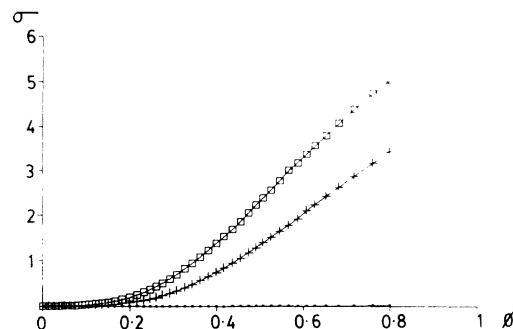


FIG. 2. Effect of salinity on  $\sigma$  ( $\text{S m}^{-1}$ ) values vs volume fraction  $\phi$ : . . . , water; +, 1M NaCl;  $\square$ , 2M NaCl.

have obtained, for the present set of systems, the value of  $s$  as 1.0 and that of  $t$  as 1.2.

The above equations are valid only near  $\phi_c$  and cannot be extrapolated to infinite dilution and unit concentration. Also, these are not applicable at the immediate vicinity of  $\phi_c$ , where there is a continuous variation within a narrow interval around the percolation threshold.

The analysis of our conductance results is shown in Fig. 3. There is a good agreement between calculated and experimental values over the whole range of composition with a mean deviation of 8.9%. Last, the plot of  $d(\log_{10}\sigma)/d\phi$  versus  $\phi$  (Fig. 4) passes through a maximum giving the exact estimate of the magnitude of  $\phi_c$ .

The conductivity of microemulsions has been analyzed using various models by a number of investigators. It has been indicated by Foster *et al.* [34] that water continuous type microemulsions show much more complicated conductivity behavior than do the oil continuous types. The present set of microemulsions is believed to be of the w-o type at low water concentrations. Therefore, we can use the phenomenon of percolation to explain the behavior of conductivity as indicated by Venable and Fang [35].

In general, microemulsion is a single phase fluid of two immiscible liquids, i.e., water and oil, containing amphi-

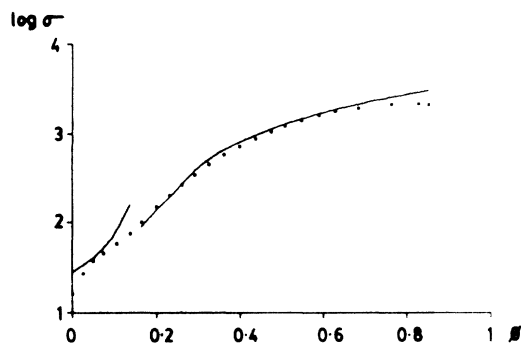


FIG. 3. Variations of the conductivity  $\log_{10}\sigma$  ( $\text{S m}^{-1}$ ) vs volume fraction  $\phi$ . —, theoretical curve [Eqs. (1) and (2)]; . . . , experimental data.

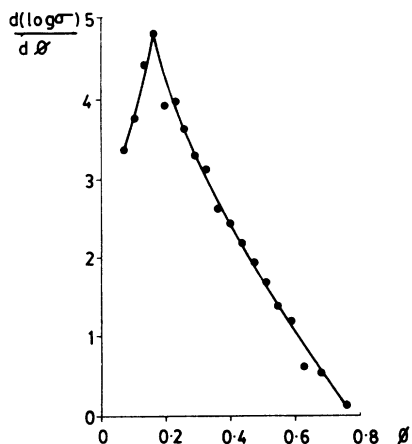


FIG. 4. Variations of  $(d \log_{10} \sigma) / (d \phi)$  vs volume fraction  $\phi$ .

phile molecules as a third component. Many systems require the presence of alcohol and/or salt for their formation. When the volume fraction of water is low, then the oil phase is continuous and all the water is isolated. Thus, the disperse phase consists of water droplets surrounded by amphiphile molecules and these act as the electrical conducting constituent in the microemulsions. Below percolation threshold  $\phi_c$ , the water droplets are isolated from each other and contribute little to conductance. However, for the volume fraction of water above the percolation threshold  $\phi_c$ , some of these conducting droplets begin to contact each other and form clusters, i.e., there exists a continuous path of water reaching from one side of the sample to the other. Hence, the conductivity will start to increase rapidly from an almost zero value to a much higher value. Figure 1 shows such increase in conductivity for the present set of systems.

### B. Viscosity studies

We have represented in Fig. 5 the variation of the dynamic viscosity  $\eta$  as a function of the volume fraction of water  $\phi$ . The viscosity  $\eta$  varies in a nonmonotonic [36–38] way when the water content increases and reaches a local maximum at two composition points. On addition of salt to the microemulsion, the first maximum around  $\phi_c$  increases whereas the second maximum starts decreasing to a large extent as shown in Fig. 6.

The viscosity results of microemulsions in the present study are different from those of conductivity. Microemulsion viscosity goes through two maxima [36–38] as the volume fraction of water increases (Fig. 5). This may be explained in terms of three structural regimes [18]: discontinuous oil in water, bicontinuous [36–39] oil and water, and discontinuous water in oil. The observed double viscosity peak implies three microstructural regimes for microemulsion. One break in the viscosity versus volume fraction of water curve occurs near the water percolation threshold as determined by electrical conductivity and presumably the second break is related to the oil percolation threshold.

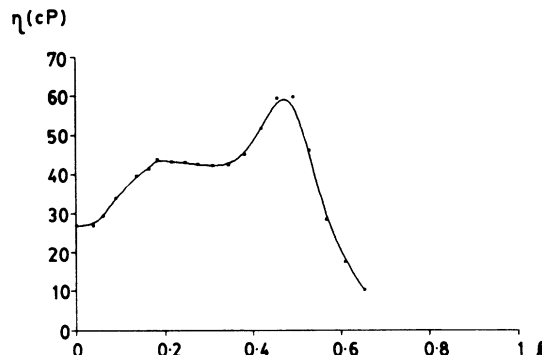


FIG. 5. Variations of the dynamic viscosity  $\eta$  (cP) vs. volume fraction  $\phi$ .

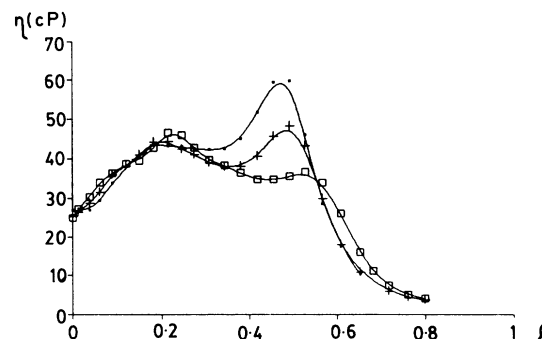


FIG. 6. Effect of salinity on  $\eta$  values vs volume fraction  $\phi$ , ..., water; +, 1M NaCl; □, 2M NaCl.

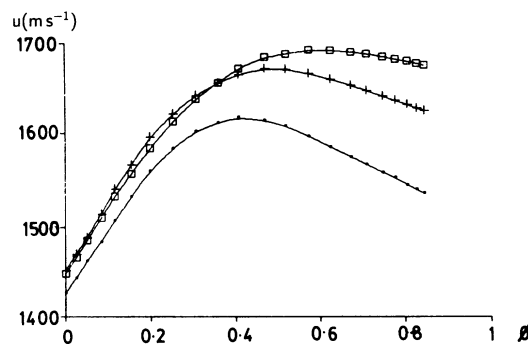


FIG. 7. Variations of the ultrasonic velocity  $u$  ( $\text{ms}^{-1}$ ) values vs volume fraction  $\phi$ , ..., water; +, 1M NaCl; □, 2M NaCl.

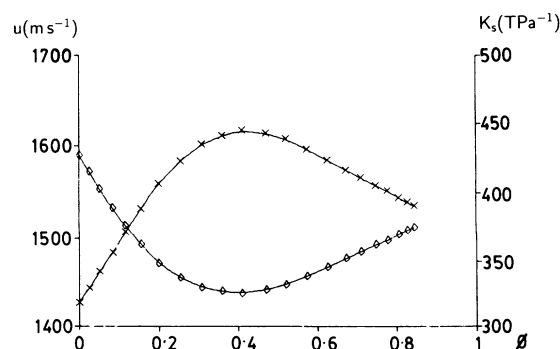


FIG. 8. Variations of  $u$  ( $\text{ms}^{-1}$ ) and  $K_s$  ( $\text{TPa}^{-1}$ ) vs volume fraction  $\phi$ . +,  $u$ ; ◇,  $K_s$ .

### C. Ultrasonic velocity

Figure 7 represents the variations of  $u$  vs  $\phi$ . This curve moves through a flattened maximum near  $\phi \approx 0.3$ . Initially, ultrasonic velocity increases sharply with an increase in  $\phi$  but the increase becomes less and less around  $\phi \approx 0.3$  and finally  $u$  decreases sharply at high water concentrations.

The isentropic compressibility  $K_s$  can be calculated as

$$K_s = 1/u^2 \rho, \quad (3)$$

where  $u$  is the ultrasonic velocity in units of  $\text{ms}^{-1}$  and  $\rho$  is the solution density in  $\text{g cm}^{-3}$ .

The behavior of ultrasonic velocity and isentropic compressibility is quite interesting. The  $u$  versus  $\phi$  shows

that  $u$  increases sharply with addition of water, but at a point corresponding to the first peak in viscosity curve, this increase in  $u$  becomes less and less. The value of  $u$  starts decreasing at a point roughly corresponding to the second viscosity peak. A typical plot of the variation of isentropic compressibility with concentration of water is shown in Fig. 8. At a low volume fraction of water, the isentropic compressibility decreases sharply with increasing  $\phi$ . These results appear to indicate that the addition of water affects the aggregates of oil, surfactant, alcohol by transforming them into loosely packed aggregates. The isentropic compressibility increases sharply at a higher concentration of water, which indicates that structures of higher compressibility are being formed, possibly oil in water microemulsion.

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