

Influence of Different Cosurfactants on Conductance, Viscosity and Ultrasonic Velocity in Water in Oil Microemulsion

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Conductance, viscosity and ultrasonic velocity measurements have been carried out on microemulsions containing water, STS as surfactant and different alkanols (C_4 – C_{10}) as cosurfactant and hexane as oil. A drastic decrease in conductance is observed when hexanol/octanol/decanol are substituted for butanol/pentanol as cosurfactant. Similarly in case of viscosity, no sharp break is observed when higher alkanols (C_4 – C_{10}) are employed as cosurfactant. However in case of ultrasonic velocity, when hexanol is used as cosurfactant, a minima is observed instead of maxima as in case of butanol and pentanol. With heptanol, there is no maxima or minima and with octanol and decanol first there is an increase in velocity, which then levels to a constant value.

Key Words: Conductance, Viscosity, Ultrasonic velocity, Oil, Microemulsion.

INTRODUCTION

Microemulsions^{1,2} differ from emulsions in their lack of turbidity and thermodynamic stability. These microemulsions were in commercial use long before the term was used. So, microemulsion is isotropic, clear, thermodynamically stable oil/water dispersion with or without cosurfactant. A number of studies have been carried out on microemulsions with alkanols as cosurfactants^{3–6}.

The alkyl chain-lengths of oil and cosurfactant are known to strongly influence the interfacial composition and distribution of cosurfactant in the oil and interface^{7,8}. Morphological changes in microemulsion systems have been shown to occur by using fluorescence technique⁹. Small Angle Neutron Scattering (SANS) studies show the dependence of structure of microemulsion droplets on alkyl chain length of oil phase¹⁰. At high water content, the existence of a dynamic equilibrium between the breaking and reforming of droplets was suggested¹¹. The isotropic region in which both oil and water show rapid diffusion is referred to as bicontinuous¹². A percolation mechanism has been involved to account for electrical conductance of microemulsions¹³. In all surface chemical systems where surfactant molecules are used, it has always been a practice to measure the effect of alkyl chain-length on free energy of the system¹⁴. In recent years, water-in-oil (w/o) microemulsions have been found useful in preparing small particles of metals and in organic salts. Microemulsions (w/o) have been evaluated as a reaction

medium^{15,16}. The conductivity of water-in-oil microemulsion was found out by adding a number of surfactants and the amount which would stabilize the microemulsion¹⁷. Lynn *et al.*¹⁸ found that the system consisting of water-SPS and cosurfactant pentanol is much more effective at solubilizing water than hexanol.

EXPERIMENTAL

STS and different alkanols (C₄-C₁₀) were provided by Fluka AG, Bucks and hexane by Sisco Research Lab, Bombay. Conductance measurements were made with a digital conductivity meter (Model No. 732) from Naina Electronics, Chandigarh. The viscosity measurements were carried out at constant temperature using suspended level dilution Ubbelode viscometer for maintaining accuracy and reproducibility of results. The viscometer was cleaned with warm chromic acid and washed several times with double distilled water. Finally, the viscometer was rinsed with alcohol followed by acetone and dried under vacuum. The initial microemulsion sample was prepared in the viscometer itself after mixing STS, hydrocarbon, alkanol and water in required ratio, keeping n_a/n_s ratio constant. The viscometer containing the microemulsion was placed in a water bath maintained at 303.15 K. The time of flow was measured accurately using electronic digital display stop watch up to ± 0.01 sec. The measurements were repeated to get concordant readings. Further dilutions were made to cover a wide range of water concentration. In the present investigation, Martin's equation was used for the determination of viscosity of microemulsions. Martin's equation is as under:

$$\eta = A\rho t - B\rho/t$$

where $A = \pi r^4 hg/8v(L + nr) = \text{const}$, $B = mv/8\pi(L + nr) = \text{const}$.

A and B may be treated as viscometer constants.

Density of liquid = ρ , coefficient of viscosity = η , radius of capillary = r , volume of liquid = v , time of flow = t , length of capillary = L .

The viscometer constants A and B for the viscometer used were determined from the measured efflux times and densities of two or more liquids of known viscosity.

Ultrasonic velocity measurements are made on an oscilloscope. The principle of measurement is to make two signals of interest overlap on the oscilloscope. The oscilloscope intensity is turned down so that only two signals of interest are visible. To make measurements, one first sets the oscilloscope on the triggered mode of operation. The delays and widths of intensity pulse are then adjusted to cover the signals of interest. Densities of pure components and various microemulsions have been determined by making use of an Austrian precision densimeter Anton Paar (Model DMA 60). Before carrying out measurements of an unknown sample, the instrument is calibrated with a calibrating liquid of known density.

For an unknown liquid, density is given by the equation

$$\rho = T^3 - B/A$$

$B = 21.25713$, $A = 28.16227$.

For a liquid or mixture of unknown density, the same operation is repeated and T is noted and ρ is calculated.

Microemulsions containing water, hexane and oil as surfactants and different alcohols (C_4 – C_{10}) as cosurfactants were prepared. In a particular emulsion, the ratio of number of moles of alcohol (n_a) to the number of moles of soap (n_s) was kept constant. Experiments were carried out with 1.0 g STS mixed the 5 mL of oil and the required amount of alcohol in a container, which was placed at constant temperature. Water was added in instalments from a microburette and the mixture was shaken vigorously. For attainment of constant temperature, all experiments were performed at 303.15 K. By varying different aliphatic alcohols as cosurfactant, different microemulsions were prepared.

RESULTS AND DISCUSSION

Conductance, viscosity and ultrasonic velocity measurements have been carried out on microemulsions containing water, STS as surfactants, different alkanols (C_4 – C_{10}) as cosurfactants and hexane as oil.

The mole ratio of alcohol to surfactant (n_a/n_s) was kept constant in all the systems. The variation of conductance with volume fraction of water (ϕ). For the microemulsions containing STS, water, hexane and the cosurfactant butanol/pentanol/hexanol/heptanol/octanol/decanol has been shown in Fig. 1. When hexanol/heptanol/octanol/decanol are substituted for butanol/pentanol as cosurfactant, a drastic decrease in conductance is observed. Another notable change is that the height of maxima is also very much suppressed. Surprisingly, with decanol as the cosurfactant the height of maxima again becomes very high and it also becomes very sharp. The overall conductance values are quite low even in the decanol case.

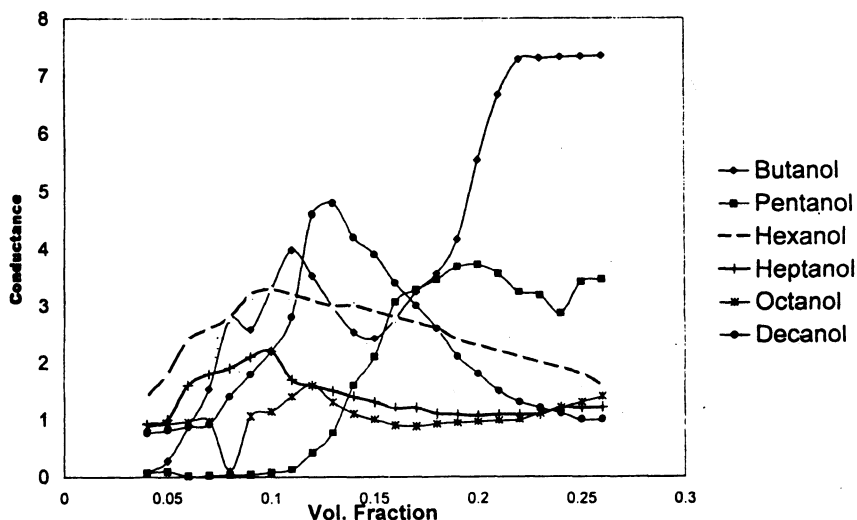


Fig. 1. Conductance vs. volume fraction for different microemulsion systems

The viscosity vs. volume fraction curves microemulsion system containing STS (1 g) water + hexane and cosurfactant butanol/pentanol/hexanol/octanol/decanol is shown in Fig. 2.

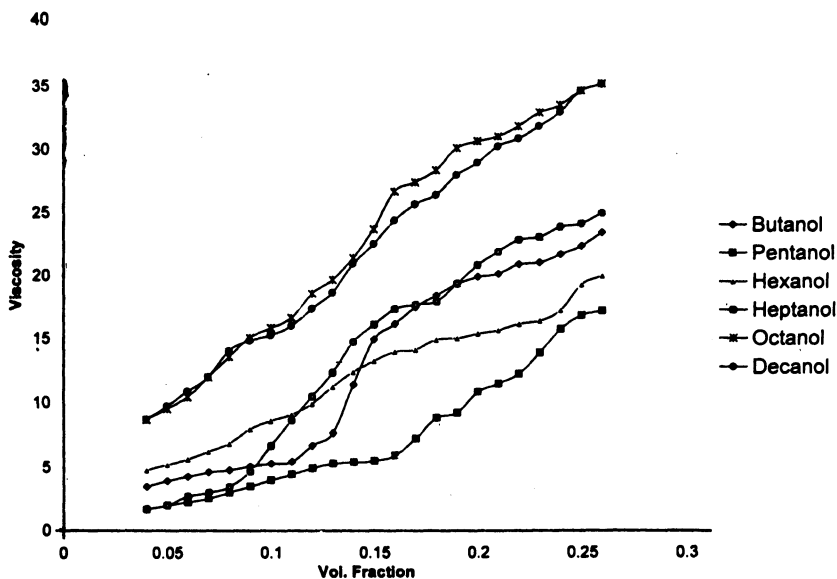


Fig. 2. Viscosity vs. volume fraction for different microemulsion systems

As in conductance vs. ϕ curves, difference in the viscosity behaviour is observed when the cosurfactant hexanol/heptanol/octanol/decanol are substituted for butanol/pentanol. No sharp break indicating a sharp increase in viscosity is observed.

When higher alkanols (C_4 – C_{10}) are employed as cosurfactant, the viscosity goes on increasing with the increase in value of $\phi = 0.18$, a break is observed.

The ultrasonic velocity vs. ϕ curves showing the effect of increase of chain length of the alkanol used as a cosurfactant (C_4 – C_{10}) are shown in Fig. 3. It is evident that the increase in chain length of the alkanol being used as a cosurfactant causes distinct changes in the behaviour of ultrasonic velocity with increase in value of ϕ .

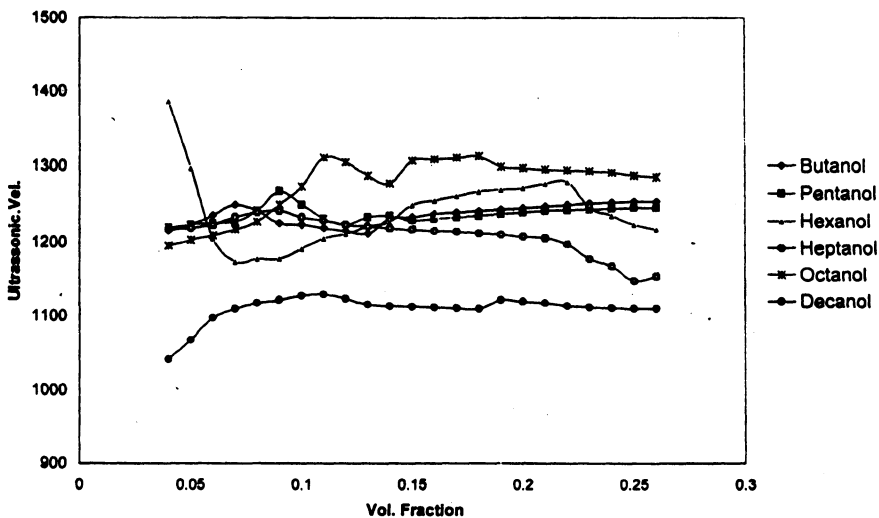


Fig. 3. Ultrasonic velocity vs. volume fraction for different microemulsion systems

With hexanol as cosurfactant, a maximum is observed in case of butanol and pentanol; there appears a minimum at $\phi = 0.25$ with a broad maximum at $\phi = 0.18$. When heptanol is used as co-surfactant, the conductance goes on decreasing gradually without showing any maxima or minima, a very faint maximum being observed at $\phi = 0.18$. Ultrasonic velocity vs. ϕ curve with that of octanol and decanol, as cosurfactant appears very similar, showing increase in ultrasonic velocity in the beginning, which then levels off to a constant value. With decanol, the ultrasonic velocity values are lower as compared to the values obtained in case of octanol.

Conclusion

In a nutshell, there is a drastic decrease in conductance when hexanol/heptanol/octanol/decanol are substituted instead of butanol/pentanol as cosurfactants, along with the suppression of maximum height. Like conductance a difference in the viscosity is also observed when the above mentioned substitution is affected. No sharp break indicating a sharp increase in viscosity is observed. Distinct changes in the behaviour of ultrasonic velocity with increase in value of ϕ are also observed as the chain length of alkanol used as cosurfactant is increased.

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