Effect on Conductance, Viscosity and Ultrasonic Velocity Using Sodium Tetradecyl Sulphate as Surfactant with Butanol/Pentanol/Hexyl amine as Co-surfactant and Heptane/Hexane as Oil

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In the present investigation, water in oil microemulsions have been prepared with sodium tetradecyl sulphate (STS) as surfactant and butanol/ pentanol/hexyl amine as co-surfactant, the continuous phase being hexane/heptane. Various physical measurements such as conductance, viscosity and ultrasonic velocity have been carried out in these microemulsions. With these co-surfactants there is a change in conductance as compared to pentanol. With the change of oil there is a notable difference in conductance behaviour in case of butanol but in case of pentanol with change of oil the conductance behaviour is similar; only the use of hexane causes conductance value to suppress. This is also the case if hexylamine is used as co-surfactant; only the constant value of conductance is lower as compared to hexane case. In case of hexane there are two maxima as compared to one in heptane; the viscosity behaviour is not much affected by change of oil; only sharp increase in viscosity is exhibited at a lower volume fraction in case of hexane as compared to heptane. The value of ultrasonic velocity shifts to a lower value when hexane is replaced with heptane when butanol is the co-surfactant. This is also the case when butanol is replaced by pentanol as co-surfactant. Surprisingly, when hexyl amine is used as cosurfactant its ultrasonic behaviour is very similar to the one shown by microemulsions containing butanol/pentanol as co-surfactant.

Key Words: Sodium tetradecyl sulphate, Surfactant, Conductance, Viscosity, Ultrasonic velocity, Microemulsion.

INTRODUCTION

Microemulsions were in commercial use long before^{1, 2} the term was coined by Schulman *et al.*³ A microemulsion is an isotropic, clear, thermodynamically stable oil/water/emulsifier dispersion with or without co-solvent or co-surfactant. Microemulsions are of water in oil (w/o) type or oil in water (o/w) type and inversion from one type to another can be achieved by adding more of dispersed phase. Different methods have been used to investigate these microemulsions^{4–8}. Bellocq *et al.*⁹ have studied the wide single phase region of SDS-*n*-butanol-toluenewater system using high resolution NMR, viscosity and electron microscope. These studies show that water-containing microemulsion droplets are bonded by a film essentially constituted by low solubility surfactant molecules. Likewise, Lagues¹⁰ has measured the electrical conductivity of water-in-oil microemulsions containing hexane-SDS-pentanol systems. Singh *et al.*¹¹ have studied the formation of water-

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in-oil microemulsions using SDS with different alcohols showing that surfactant concentration affects the distribution of alcohol in bulk phase. Raymond and coworkers 12 have found that medium chain length alkyl amines are more effective as co-surfactant for microemulsion formation than medium chain length alcohols, at high hydrocarbon levels with SDS as surfactant. Lynn 13 found that systems consisting of water-SDS and co-surfactant pentanol or hexyl amine are more effective for solubilising water than hexanol.

The results of measurement of viscosity as a function of temperature and volume fraction have been reported by Majoline et al. 14 in three component Aot-decanewater microemulsion. Albuin et al. 15 found water-in-oil microemulsions' dependence on minimum amount of alcohol which is required to produce a microemulsion. The conductivity of water-in-oil microemulsion system was found by using mixed surfactant by Bumagid et al. 16 Gonnella and Ruggieri 17 found the rheological behaviour of microemulsions.

EXPERIMENTAL

Sodium tetradecyl sulphate, butanol, pentanol and hexylamine were provided by Fluka AG, Bucks; hexane and heptane by Sisco Research Lab, Mumbai. Conductance measurements were made with a digital conductivity meter (Model 732) from Naina Electronics, Chandigarh. The viscosity measurements were carried out at constant temperature using suspended level dilution Ubbelode viscometer was used 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 sodium tetradecyl sulphate with hexane/heptane, hydrocarbon, butanol/pentanol/hexylamine 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 upto ±0.01 s. 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:

$$\eta = A\rho t - \frac{B\rho}{I}$$

where $A = \pi r^4 hg/8v(L + nr) = constant$, $B = mv/8\pi(L + nr) = constant$ (A and B may be treated as viscometer constants); density of liquid = p; co-efficient 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 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 measurement, 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 densimenter 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

$$\rho = T^2 - \frac{B}{A}$$

where B = 21.25713, A = 28.16227.

For a liquid or mixture of unknown density the same operation is repeated; T is noted and ρ is calculated. Microemulsion containing water, hexane/heptane as oil (surfactant) and butanol/pentanol/hexylamine as co-surfactant was 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 0.5 g sodium tetradecyl sulphate mixed into 5 mL of oil and required amount of alcohol in a container, which was placed at a 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 butanol/pentanol/hexylamine as co-surfactant and hexane/heptane as oil different micro-emulsions were prepared.

RESULTS AND DISCUSSION

The mole ratio of alcohol to surfactant (n_a/n_s) was kept constant in all the systems. The concentration of sodium tetradecyl sulphate was taken as 0.5 g in microemulsions using butanol/pentanol/hexylamine as co-surfactant and hexane/heptane as oil. With butanol as co-surfactant (Fig. 1), the change of oil does appear to cause a noticeable difference in conductance vs. volume fraction curves. In the hexane case, two maxima are observed as compared to one obtained in heptane case. With pentanol as co-surfactant, the conductance vs. volume fraction

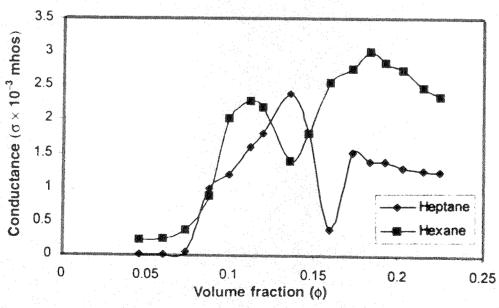


Fig. 1. Conductance vs. volume fraction containing butanol as co-surfactant and heptane/hexane as oil

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curves are similar for hexane and heptane case but use of hexane as an oil does appear to suppress the value at which the maxima appears as shown in Fig. 2. The

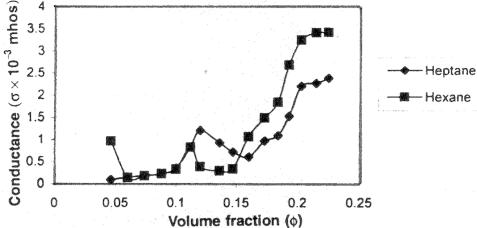


Fig. 2. Conductance vs. volume fraction containing pentanol as co-surfactant and heptane/ hexane as oil

constant value of conductance is quite high in hexane case as compared to heptane. With hexylamine as co-surfactant and hexane as oil the conductance at first sharply increases, then becomes constant and then there is a sharp fall. Similar behaviour is exhibited when heptane is used as oil but the constant value of conductance is lower as compared to hexane as shown in Fig. 3.

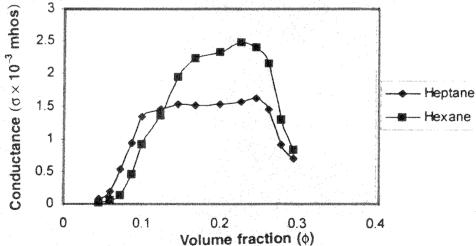


Fig. 3. Volume fraction vs. conductance containing hexylamine as co-surfactant and heptane/hexane as oil

For the microemulsion systems containing 0.5 g STS the change of oil from heptane to hexane does cause a noticeable change in viscosity behaviour. With butanol as co-surfactant a sharp increase takes place at a lower value of volume fraction when hexane is used as an oil (Fig. 4). The same is true when pentanol is the co-surfactant (Fig. 5). With hexylamine as co-surfactant and sodium tetradecyl sulphate as surfactant the change in oil from heptane to hexane pushes the volume fraction value and the maximum of the curve to a higher value as shown in Fig. 6. The viscosity vs. volume fraction curves were similar, otherwise showing the maximum in case of heptane as well as hexane.

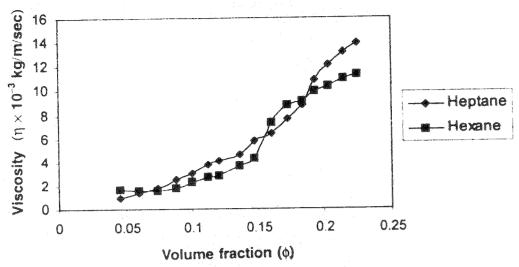


Fig. 4. Viscosity vs. volume fraction containing butanol as co-surfactant and heptane/hexane as oil

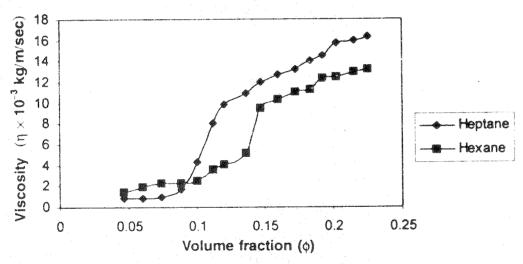


Fig. 5. Viscosity vs. volume fraction containing pentanol as co-surfactant and heptane/hexane as oil

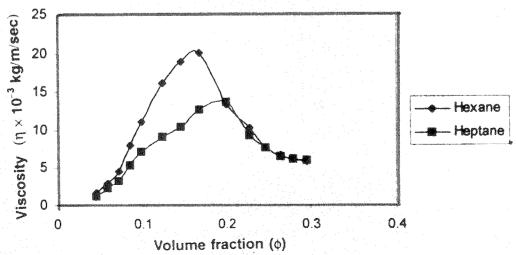


Fig. 6. Viscosity vs. volume fraction containing hexyl amine as co-surfactant and heptane/hexane as oil

For the microemulsion systems containing 0.5 g sodium tetradecyl sulphate, the ultrasonic velocity vs. volume fraction curves show a maximum and a minimum when butanol is the co-surfactant while only a minimum is observed in the pentanol case. This is in sharp contrast to conductance results where only a maximum is observed with the appearance of no minima in butanol case. With pentanol as the co-surfactant the conductance maxima is observed at a lower value while the ultrasonic velocity minima appears at a higher value. However, when heptane is replaced by hexane, the minima is shifted to a lower value as seen in Figs. 7 and 8.

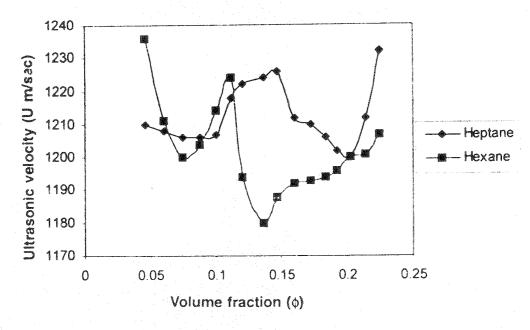


Fig. 7. Ultrasonic velocity vs. volume fraction containing butanol as co-surfactant and heptane/hexane as oil

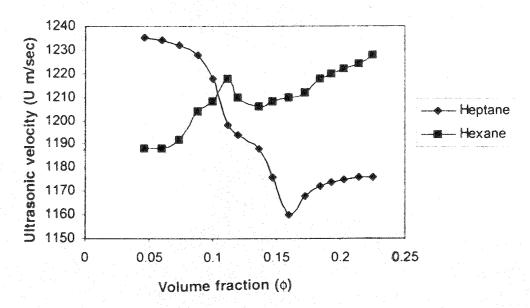


Fig. 8. Ultrasonic velocity vs. volume fraction containing pentanol as co-surfactant and heptane/hexane as oil

Surprisingly, when hexylamine is used as co-surfactant, its ultrasonic behaviour is very similar to the one shown by microemulsions containing butanol/pentanol as the co-surfactant. However, the substitution of heptane as an oil in place of hexane causes a shift in maxima and minima to higher values as seen in Fig. 9.

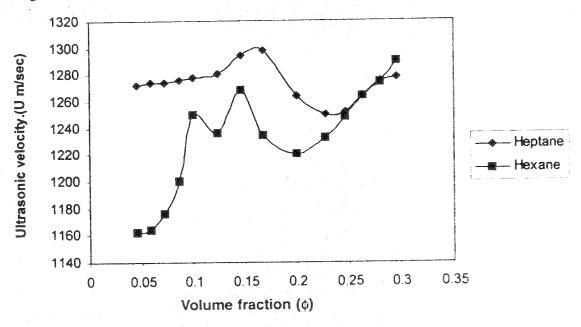


Fig. 9. Ultrasonic velocity vs. volume fraction containing hexyl amine as co-surfactant and heptane/hexane as oil

Conclusion

The change of oil from heptane to hexane does not cause any perceptible change in conductance behaviour with maxima and minima appearing nearly at same value of volume fraction as seen in case of pentanol. The viscosity behaviour is also not affected by the change of oil; only sharp increase in viscosity is exhibited at a lower value of volume fraction in case of hexane as compared to that of heptane in both pentanol and butanol. The ultrasonic velocity vs. volume fraction curves with maxima, minima get shifted to lower value of volume fraction when hexane is substituted for heptane in butanol as co-surfactant, but in pentanol only minima is observed.

The addition of co-surfactant hexylamine resulted in completely different conductance and viscosity behaviour in microemulsions replacing the maximum in the conductance curve with a straight line and showing the maxima in the viscosity vs. volume fraction curve instead of a simple monotonic increase. The ultrasonic behaviour, on the other hand, is very similar to the one shown by microemulsions containing butanol/pentanol as co-surfactant, showing both a maxima and a minima.

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