SUMMARY
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Conductivity, ultrasonic velocity and viscosity studies have been carried out on the following prepared microemulsion systems as a function of volume fraction of water throughout the single phase region at 303.15 K keeping the ratio of number of moles of alcohol to number of moles of surfactant \( \frac{n_a}{n_s} \) constant.

These may be divided broadly into four main categories. These are:

I. Systems involving Tween 20 as surfactant

II. Systems involving mixture of surfactant i.e. Tween 20 with different Span’s (Span 20, Span 40, Span 60, Span 80).

III. Systems involving (Tween 20 + Span 80 only).

IV. Systems involving Tween 80 as surfactant.
As the volume fraction of water increases the electrical conductivity changes exponentially. These changes have been attributed to the occurrence of a percolation transition. In this percolation model, the conductivity remains low up to a certain volume fraction of water i.e. $\phi_c$. These conducting w/o droplets, below $\phi_c$, are isolated from each other embedded in non-conducting continuum oil phase and hence contribute very little to the conductance. However as the volume fraction of water reaches the percolation threshold $\phi = \phi_c$, some of these conductive droplets begin to contact each other and form clusters which are sufficiently close to each other. The number of such clusters increases very rapidly above percolation threshold (between $\phi = \phi_c$ to $\phi = 0.5$), giving rise to increase of electrical conductivity. The $\sigma$ above $\phi_c$ has been attributed to either hopping of surfactant ions from droplet to droplet within droplet clusters or transfer of counterions from one droplet to another through water channels opening between droplets during sticky collisions through transient merging of droplets.

The ultrasonic velocity increases with the addition of water, but starts decreasing after $\phi = 0.4$. The systems have been analyzed in terms of isentropic compressibility $K_s = 1/u^2 \rho$, as $K_s$ is much more sensitive than the velocity to structural changes. The origin of the maximum in ultrasonic velocity and minimum in $K_s$ with the increase in volume fraction of water is believed to be due to the formation of clusters of water globules (W/O) which are significantly close to each other. The creation of more compact structure with increasing number of water
droplets first produces an increase in sound velocity but at very high $\phi = 0.4$ the usual volume expansion property tends to dominate forming bicontinuous structure which leads to a decrease in the ultrasonic velocity and an increase in isentropic compressibility. The plot of $K_{s,m}$ i.e. compressibility of micellar phase w.r.t. $\phi$ shows a more water like character of micelles with the increase in volume fraction of water $\phi$. The calculation of micellar density $\rho_m$ also indicates that with increase in $\phi$, the $\rho_m$ decreases from about the surfactant density $\rho_{\text{Tween}} = 1095 \text{ Kgm}^{-3}$ towards the water value ($\rho_w = 997 \text{ Kgm}^{-3}$), clearly confirming the increased water like character of the micelles.

The viscosity results of microemulsions in the present study are quite different from those of conductivity. $\eta$ values vary in a nonmonotonic way w.r.t. volume fraction of water $\phi$ and go through a maxima, a minima and again a second maxima. The first peak in the curve coincides with the water percolation threshold as determined by electrical conductivity. Second maxima occurs at $\phi = 0.4$. On further addition of water, there is a sharp decrease in after second maxima which may be due to the appearance of a bicontinuous stage. The viscosity minima do not correlate with features of other studied physical properties.

It was observed that variation in the constituents of microemulsions (change in oil/brine concentration/alcohol chain length/ and surfactant) produces some changes in the behaviour of measured properties such as conductance, viscosity and ultrasonic velocity quantitatively, but the general behaviour remains the same.
The conductance values are not significantly affected by change of oils, as oils are nonconducting in nature. The change of oil does not affect the first peak in the viscosity curve but the second peak grows in the order benzene < toluene < o-xylene < ethyl benzene.

The effect of addition of salt is very prominent on the conductance behaviour. The conductivity values increase about 200 folds when 2M NaCl ($\sigma^c = 7 \text{sm}^{-1}$) is used instead of water ($\sigma^c = 0.03 \text{sm}^{-1}$). Ultrasonic velocity values also increase in the order water > 1M NaCl > 2M NaCl. In viscosity first maxima remains almost unaffected whereas the second maxima starts decreasing to a large extent in the order water > 1M NaCl > 2M NaCl.

The change of cosurfactant from propanol to octanol and decanol shows percolation behaviour up to microemulsions containing n-heptanol (C$_3$-C$_7$) as cosurfactant. The systems with n-octanol and n-decanol as cosurfactant also show same features of percolation but only up to $\phi = 0.3$. After that viscoelastic gel stage is reached which restricts the further measurement of conductance. The ultrasonic velocity values decrease (not significantly) in the order propanol > butanol > pentanol > hexanol > heptanol. The first peak in two peaked plots of viscosity remains almost unaffected but the second peak grows in magnitude in the order octanol > propanol > heptanol > hexanol > pentanol > butanol, showing propanol as an exceptional case.

A decrease in conductance is observed for the systems containing mixture of Tween 20 with different Span’s (Span 20, 40, 60, 80) in the order Span 20 > Span 40 > Span 60 > Span 80.
The ultrasonic velocity show the trend $u_{\text{Span 80}} > u_{\text{Span 20}}$ up to $\phi = 0.5$. But after $\phi = 0.5$ $u_{\text{Span 80}} = u_{\text{Span 20}}$. In viscosity first peak shows same behaviour as is shown by conductance, but second peak shows a reverse trend i.e. $u_{\text{Span 60}} > u_{\text{Span 80}} > u_{\text{Span 40}}$.

Microemulsions containing Tween80 as surfactant show a gap between $\phi = 0.2$ to $\phi = 0.35$ which may be attributed to viscoelastic gel stage. Viscosity curves also show a miscibility gap for these systems.

From a graphical variation of $\gamma$, $\sigma^-$, and $u$ together as a function of volume fraction of water, some similarity can be observed among these three properties. Below $\phi_c$, the addition of water results in the creation of more compact structure with increasing number of water droplets responsible for the initial increase in ultrasonic velocity and viscosity. It may be emphasised that these conducting droplets, below $\phi_c$, do not change much in size and are isolated from each other embedded in a non-conducting continuum oil phase and hence contribute very little to the conductance. At $\phi_c$ some of these conducting droplets begin to contact each other and form clusters. The number of such clusters increases very rapidly above percolation threshold (between $\phi = \phi_c$ to $\phi \approx 0.5$) giving the observed changes in the properties, in particular the increase in conductivity and ultrasonic velocity. A slight minimum observed in the viscosity behaviour may be the result of possibly the rearrangement of rapidly growing droplets forming clusters. At very high $\phi$ ($\approx 0.5$) the usual volume expansion property tends to dominate, forming
bicontinuous structure that leads to a decrease in the ultrasonic velocity and viscosity. The analysis of the results in terms of density $\rho_m$ and isentropic compressibility $K_{s,m}$ of the micellar phase also predicts a trend towards an enhanced water like character of the dispersed phase of the studied microemulsions. However, at present, the non-correlation of two peaked plots of viscosity with features of other studied physical properties is not clearly understood and requires further probe.