Effect of butanol and cholesterol on the conductance of AOT-aided water/xylene microemulsion

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The conductance behaviour of water-in-oil (W/O) microemulsions formed by xylene and AOT has been studied at different temperatures in the presence of cholesterol, butanol, benzyl alcohol and crown ether. The dependence of conductance on the degree of rigidity of the interface between water and oil in the microemulsion as affected by the additives has been analysed. The increased conductance at higher temperatures is explained in terms of the coalescence of dispersed water particles of microdimensions, followed by exchange of Na\(^+\) ions. Two distinct values of energy of activation for conductance have been obtained in the temperature range below and above 35°C. The temperature-dependent viscosity behaviour of the microemulsion has also been studied.

Microdispersions of water in oil stabilized by ionic amphiphiles, termed as water-in-oil microemulsions (W/O) exhibit poor conductance so long as the water/amphiphile mole ratio (\(\omega\)) is low. The observed low conductance is due to charge fluctuation in the dispersed particles\(^1\). At higher \(\omega\), as well as at moderate \(\omega\) but higher temperatures, the conductance rises sharply by several orders of magnitude\(^1-4\). It is considered that the microparticles come closer and either the surfactant ions ‘hop’ from one particle to another\(^5-10\) or the particles undergo ‘transient fusion and separation’ with exchange of the counterion\(^11-18\). Both the processes result in efficient migration of ions which increases the conductance. A sharp rise in either a narrow range of volume fraction of the dispersed phase or temperature, termed as ‘percolation’, has been an important topic of investigation in recent years. In the post-percolation stage, the system becomes bicontinuous having water filled conduits (channels) to maintain high conductance of the system\(^16-19\). In a previous study\(^13\), we have given evidence supporting the ‘transient fusion’ model for percolation.

Whatever be the mechanism of increase in conductance, ‘hopping’ or ‘fusion and separation’, the change in conductance is primarily determined by the rigidity or flexibility of the amphiphilic coat of the dispersed particles. By altering the consistency of the skin, the conducting property may be affected; a rigid skin would hinder while a soft skin would assist the process.

It is known that butanol softens the amphiphilic interphase between water and oil\(^20\), while cholesterol and its derivatives make it rigid\(^13-21\). It has been reported that toluene can block the passage of transfer of the charge carriers, thus suppressing the enhancement in conductance\(^12\). It was, therefore, worthwhile to investigate the combined effect of butanol and cholesterol, taken in different ratios, on the conductance of W/O microemulsion. In this paper, the results of conductivity and viscosity studies of water-AOT-xylene system in presence of butanol and cholesterol have been presented. The system shows moderate conductance change with increase in temperature. Microemulsion systems showing similar behaviour have been rarely studied in the past\(^22\).

Materials and Methods

The purity of AOT (Sigma) and xylene (AR grade, BDH) used was 99%. Butanol (Bu), benzyl alcohol (BA) and cyclohexyl-18-crown (CE) were similar to those used in a previous study\(^13\). Cholesterol monohydrate (Ch) used was purified as given in literature\(^21\). Diphenyl hexatriene (DPH) was a product of Aldrich, USA. Doubly distilled water (sp. cond. 2-4 \(\mu S \text{ cm}^{-1}\)) was used for all sample preparations. A conductivity meter (Jenway, England) and Perkin-Elmer IS-3 fluorescence polarisation spectrometer were used for conductivity and fluorescence depolarization measurements respectively.

A number of ternary mixtures of xylene (with 20% w/w cholesterol)/AOT/water in weight per cents 40/50/10, 40/45/15, 40/40/20, 40/35/25 and 40/30/30 were prepared. Another sample containing xylene/AOT/water/additive (Bu or Ch or Bu + Ch or
CE + Ch or BA + Ch) in weight per cents 42/34/10/14 was also prepared. These mixtures were found to be isotropic and stable in the temperature range 10-70°C; their stability at higher temperature was not tested.

In an actual experiment, a sample was taken in a well-stoppered conductivity cell with a cell constant 1.10 cm⁻¹, and the conductance was measured at 1 kHz at different temperatures between 10 and 60°C at 10°C intervals, allowing 30 min for equilibration. Conductance measurements were also made in the presence of the additives, Bu, Ch, CE and BA at concentration levels 0 to 14% (w/w).

The viscosity and density of xylene and the microemulsion samples with and without additives were measured at different temperatures following the procedure described earlier.

Fluorescence depolarization was measured using diphenyl hexatriene (DPH) as the probe. The measurements were taken at 37°C using excitation and emission wavelengths of 365 and 430 nm respectively. Along with the microemulsion samples [xylene/AOT/Bu/water in the wt % 42/34/14/10 (sample A); xylene/AOT/Bu/Ch/water in the wt % 42/34/14/10 (sample A)], corresponding samples without water were also used for fluorescence measurements. To each sample, DPH was added to the extent of 1 μmol l⁻¹ and the fluorescence intensities for parallel and perpendicular polarized excited light were measured. Each run was duplicated to ascertain reproducibility and the average values were used in the calculation of fluorescence anisotropy.

Results and Discussion
Temperature induced conductance at different H₂O/AOT ratio
The conductance-temperature profiles at various H₂O/AOT mole ratios of xylene-water-AOT system at a constant level of AOT are presented in Fig. 1. The oil contained 20% (w/w) Ch. Below 45°C, the conductance was low and remained unchanged. The charge fluctuation in the AOT surrounded interface of the microwater particles is the cause of the initial low conductivity. Above 45°C, the conductance increased with increase in proportion of water. At constant oil/water ratio (O/W), perceptible rise in conductance commenced at 40°C, which was steep above 45°C. For samples with different W/O ratio, the level of Ch varied between 6 and 10% (w/w). All the solutions showed moderate increase in conductance with temperature; nearly 2.5 to 8.5 fold increase was observed. With increase in proportion of the microwater particles (sample 5 to sample 1), conductance increased due to efficient transfer of ions among them. At higher O/W ratio, increase in cholesterol content made the interphase rigid, so that transfer of ions among the particles was hindered.

Combined effects of butanol and cholesterol on conductance
The combined effect of Bu and Ch (total concentration 14% (w/w)) on water/AOT/xylene system (10/34/42, w/w) is shown in Fig. 2. There is minor change in conductance at 0% Bu and 14% Ch (curve 1) as long as the temperature is below 45°C; an overall lowering effect compared to others is observed. In the reverse mixture, 14% Bu and 0% Ch (curve 2), there is considerable increase in the overall conductance. An overall transition in conductance for most situations is witnessed at 35°C. For samples having 5% Bu + 9% Ch (curve 8) and 3% Bu + 11% Ch (curve 9), the transitions are at 37°C and 45°C respectively.

Alkanols have been reported to increase the conductance of W/O microemulsions. It has been pointed out that alkanols make the interphase flexible with enhanced charge fluctuations, thereby increasing the conductance. The conductance variations with respect to Bu at 10°C (starting temperature), 35°C (transition temperature) and 60°C (maximum studied temperature) are presented in Fig. 3. Transitions were observed at 91% Bu (X_Bu = 0.91). Up to 61% Bu and 39% Ch, the conductance...
remains practically unaffected. The considerable decrease in conductance due to Ch is compensated by a significant enhancement in conductance by Bu. In the inset, the effect of temperature on the conductance of aqueous AOT solution is depicted. The conductance ratio at 60°C and 10°C (σ°/σ°C) of aqueous AOT was 1.21. In 14% Bu (corresponding to \( X_{Bu} = 1 \) in Fig 3) the \( σ°/σ°C \) ratio in microemulsion was 3-4 times in the whole range of Bu addition.

The Bu-induced conductance behaviour at different temperatures is presented in Fig. 4. The sigmoid curves at all temperatures exhibit an inflexion at 11% Bu and 3% Ch. The results show that irrespective of the thermal state, conductance is a direct function of the interphase modulating agent, Bu. The proportion of this skin softening agent is important for the effective increase in the conductance of the studied W/O microemulsion system. The results are in conformity with those discussed with reference to Fig. 3, where a transition is observed at \( X_{Ch} = 0.91 \) (i.e., 11% Bu + 3% Ch).

**Cholesterol induced rigidity of the AOT interphase between oil and water**

It is known that cholesterol imparts rigidity to liposomal membranes and cell membranes. The interphase constituted by the surfactants in microemulsion is also stiffened by the presence of Ch and its derivatives. This is supported by fluorescence depolarization measurements. The fluorescence intensities of the blanks with and
without Ch are similar; the microemulsions without Ch show similar intensities whereas those with 7% Ch + 7% Bu exhibit increased fluorescence, which is made more perceptible in presence of 14% Ch. The DPH fluoresced more, remaining in the organised hydrophobic interphase provided by AOT and Ch. The interphase in the microemulsions provides a zone where the weakly polar cholesterol molecules are oriented with hydroxyl groups projecting towards the microaqueous phase.

The fluorescence anisotropy (r) for the microemulsion samples was calculated\(^2\) using the relation \(r = (I_\| - I_\perp) / (I_\| + 2I_\perp)\), where \(I_\|\) and \(I_\perp\) are the parallel and perpendicular intensities respectively relative to the exciting radiation. The \(r\) values for the samples A, B, and C are 0.02, 0.03 and 0.05 respectively. The increased \(r\) values are indicative of increased microviscosity\(^2\) of the interphase between oil and water. These results support stiffening of the interphase by Ch. Relative to sample A (without Ch), there was a 250% increase in \(r\) in sample C containing 14% Ch; this increase was 150% in sample B with 7% Ch and 7% Bu. The results indicate that the softened particle skin in presence of Bu was made rigid by Ch.

### Activation energy for conduction

The Arrhenius type equation, \(\sigma = \text{constant} e^{-\Delta E_{\text{cond}} / RT}\) where \(\Delta E_{\text{cond}}\) is the activation energy for conductance has been used for the evaluation of \(\Delta E_{\text{cond}}\) from the slopes of the straight line plots of \(\log \sigma\) versus \(1/T\) (Fig. 5). Two sharp and unambiguously intersecting straight lines yielding two distinct \(\Delta E_{\text{cond}}\) values have been obtained. The values for the primary and secondary stages in different environments are presented in Table 1.

In the primary region, the \(\Delta E_{\text{cond}}\) values are virtually constant except for samples with 14% Bu and 9% Bu + 5% CE. The \(\Delta E_{\text{cond}}\) values are comparable with the \(\Delta E_{\text{cond}}\) of electrolytes\(^2\). In the secondary region (between 35°C and 60°C), \(\Delta E_{\text{cond}}\) values are lower in the presence of 14% Bu as well as in the presence of 9% Bu + 5% CE. Bu softens the interphase (as shown by fluorescence depolarisation measurements) and consequently lowers the \(\Delta E_{\text{cond}}\). It also assists better electrical transport by way of its solubility in the oil phase\(^1\). With increased percentage of Ch, the \(\Delta E_{\text{cond}}\) systematically increases. The stiffening of the interphase between oil and water due to the presence of Ch acts as a greater barrier to the charge transport through the medium. The counter Na\(^+\) ions present in the water droplets form complex with CE during skin adherence (fusion), resulting in facilitated transfer with lowering of \(\Delta E_{\text{cond}}\). BA forms channels through the

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**Table 1—Activation energy of conduction in the primary and secondary regions of the microemulsion system (water/AOT/xylene, 10/34/42) under various environments**

<table>
<thead>
<tr>
<th>% Additive (w/w)</th>
<th>(\Delta E_{\text{cond}}), kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primary region</td>
</tr>
<tr>
<td>0</td>
<td>12.4</td>
</tr>
<tr>
<td>Bu (14%) + Ch (0%)</td>
<td>12.6</td>
</tr>
<tr>
<td>Bu (12.5%) + Ch (1.5%)</td>
<td>14.0</td>
</tr>
<tr>
<td>Bu (11%) + Ch (3%)</td>
<td>14.4</td>
</tr>
<tr>
<td>Bu (9%) + Ch (5%)</td>
<td>14.4</td>
</tr>
<tr>
<td>Bu (7%) + Ch (7%)</td>
<td>16.0</td>
</tr>
<tr>
<td>Bu (5%) + Ch (9%)</td>
<td>14.4</td>
</tr>
<tr>
<td>Bu (3%) + Ch (11%)</td>
<td>14.0</td>
</tr>
<tr>
<td>Bu (0%) + Ch (14%)</td>
<td>15.0</td>
</tr>
<tr>
<td>Bu (9%) + Ch (5%)</td>
<td>15.0</td>
</tr>
<tr>
<td>Bu (9%) + Ch (5%)</td>
<td>12.6</td>
</tr>
</tbody>
</table>

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![Fig. 5 —Log \(\sigma\) versus \(1/T\) profile of water/AOT/xylene system (10/34/42, w/w) in presence of additives]
interphase for favourable ion transport. The results thus supported the coalescence and mass exchange mode of ion-transport (or conduction) in microemulsion.

In the secondary region, $\Delta E_{\text{cond}}$ versus $X_{\text{Ch}}$ profile (Fig. 6a) exhibits systematic increase with the maximum at $X_{\text{Ch}} = 0.4$. The skin stiffening effect reaches a maximum at 40 mole % Ch in combination with Bu. In the plot of $\Delta E_{\text{cond}}$ versus $X_{\text{Ch}}$, $\sigma^{60}/\sigma^{10}$ values are also presented as a function of $X_{\text{Ch}}$ (Fig. 6a). A sharp maximum occurs at $X_{\text{Ch}} = 0.16 (7\% \text{ Ch } + 7\% \text{ Bu})$. The conductance in the secondary region increases more rapidly than the increase in the primary region with addition of Ch + Bu from 0% + 14% to 7% + 7% (w/w); further increase in Ch concentration led to a decrease in the conductance. The amphiphilic interphase (between oil and water) becomes strikingly rigid in the presence of higher Ch at a concentration higher than 16 mole % in combination with Bu.

The $\Delta E_{\text{cond}}$ values for truly percolative W/O microemulsions fall in the range 500-600 kJ mol$^{-1}$. The values for the present system are strikingly lower. The samples on an average contained $\omega = 7.3$. That W/O microemulsion systems of such a low water/amphiphile mole ratio are seldom percolative is supported by the present study. The population of the dispersed phase is insufficient (higher mole ratios between water and AOT was not permitted in xylene) for easy ion transport by transient fusion although the energy barrier is low. The additives, however, modify the amphiphilic interphase and alter the energy barrier; this is reflected in the conductance-temperature profile. Like toluene, xylene molecules from the oil itself could have a blocking effect on conductance to show mild percolation.

**Viscosity of microemulsion**

Viscosity of the microemulsions varies systematically with increase in temperature; a decrease is observed for all the studied compositions (Fig. 6b). The sample containing 14% Ch shows maximum viscosity and a rapid decrease with increase in temperature. The viscosity profiles of the other three samples are parallel, the sequential order being 14% Ch > zero additive > 5% Ch + 9% Bu > 14% Bu. Ch made the sample more viscous while Bu made it more fluid. The activation energies for the viscous flow were computed from the slopes of the log $\eta$ versus $T^{-1}$ plots (Table 2). The activation energies follow a trend similar to that of conductance. They reflect the consequence of local rigidity and softness contributed by Ch and Bu in the medium.

A comment on the overall geometry of the dispersed phase in terms of viscosity may not be out of place. The specific viscosities per unit concentration of the disperse phase ($\eta_{\text{isp}}/c$) expressed in ml gm$^{-1}$ of the studied system under varied environments at 25°C range between 4.0 and 25.0 ml gm$^{-1}$, which suggest an overall non-spherical geometry of the dispersed phase. This is likely to be a simplified view. Conclusion should be drawn on the basis of the intrinsic viscosity, $[\eta]$, i.e., $L_c = \eta_{\text{isp}}/C$, where $\eta_{\text{isp}}$ is the specific viscosity of the microemulsion at concentration $c$ (gm/ml). Further experimentations are necessary for structure elucidation.

**Intrinsic roles of butanol and cholesterol**

For a percolative system (AOT/isooctane/water), methanol, ethanol and propanol systematically decrease the transition temperature whereas butanol and higher alkanols increase it. It has been proposed that in the kinetic process the particles

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Fig. 6a—The ratio of conductance at 60°C and 10°C ($\sigma^{60}/\sigma^{10}$) and the activation energy for conduction ($\Delta E_{\text{cond}}$) of microemulsion in the secondary region as a function of mole fraction of cholesterol.

Fig. 6b—Viscosity of water/AOT/xylene system (42/10/34) as a function of temperature. 1, 14% cholesterol; 2, no additive; 3, Ch (5%) + Bu (9%); 4, Bu (14% w/w).
Table 2—Activation energies for flow of W/O microemulsion
(water/AOT/xylene, 10/34/42) in presence of additives

<table>
<thead>
<tr>
<th>Additives</th>
<th>$\Delta E_{\text{mol}}$ (kJ mol$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>17.7</td>
</tr>
<tr>
<td>Bu (14%) + Ch (0%)</td>
<td>24.5</td>
</tr>
<tr>
<td>Bu (9%) + Ch (5%)</td>
<td>26.0</td>
</tr>
<tr>
<td>Ch (14%)</td>
<td>32.7</td>
</tr>
</tbody>
</table>

fuse$^{2-3,11}$ and by way of opening of the interfacial skin, exchange of counterions takes place and conductance increases sharply. The alkanols (cosurfactants) are considered to soften the interfacial region between oil and water, and efficient conduction is favoured by easier formation of transient channels. The effective sizes of the dispersed particles increase in the presence of higher alkanols. As a consequence, transient fusion, forming water channels becomes difficult. In the fused state, the water pools remain separated by the alkanol barrier and easy communication or transport of counterions becomes less favourable$^{13}$. In the present context, both Ch and Bu have sizes comparable with AOT. The dimension of the interphase was hardly affected by their presence, only the flexibility of the skin was altered. The fluorescence depolarization results support the rigidity and flexibility of the interphase by cholesterol and butanol respectively. This is also reflected in the activation energy data. About two-fold increase in the activation energy was observed with addition of 14% (w/w) cholesterol; both 14% (w/w) butanol and 9% Bu + 5% CE decreased the $\Delta E_{\text{cond}}$ by about 1.2 fold.

Acknowledgement

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References