Supplementary Material

Variation of water content

The transition from a low to high conducting state, occurring in reverse micelles with the increase in water content at 310.15 K for different hp-β-CD concentrations (1, 2.5 and 5 mM) in ME-I have been depicted in Fig. I (A) (Supplementary material). The critical value of the percolation has been determined from dlogσ /dω vs ω plot, where maxima corresponds to percolation threshold, $\omega_{p.}$ The values of ω_p follow the order 1 mM < without < 2.5 mM < 5mM for the constant composition of the studied formulation. The results have been depicted in Table 3.

The curves in the Fig. I (A) (Supplementary material) can be divided into two sections due to different conducting mechanisms. The conductance behavior before the rapid increase is considered to be caused by the motion of charged droplets in the electric field[1,2], while in the portion after the critical point is due to percolation phenomenon .[3,4] The behavior of conductivity as presented is due to two antagonistic effects. On one hand, the increase in water content increases the mobility of surfactant ions during the "fusion-fission" process, which tends to increase the electrical conductivity. At low water content, water disperses in the continuous phase in nanosized domains. Most water molecules tend to associate with the surfactant molecules that make the interface rigid. There are relatively few bulk-like water molecules to supply a diffusion environment for the hydrated Na^+ counterions. In such case, the conductivity of reverse micelles is thought to be the result of electrophoretic moment of charged droplets in electric field.[5-7] The addition of water in AOT reverse micelles favors the charging process and tends to increase the electrical conductivity. On the other hand, the size of surfactant aggregates increase accordingly with more water solubilizing in AOT microemulsions[6], which results in slow migration of droplets under electric field. The increased size of the droplets leads to a tendency of decreasing electrical conductance. The two antagonistic effects counteract each other and result in maximum conductivity with the increase in water content. The modifications in the interfacial composition of the surfactant aggregates and the aqueous water pool cause a remarkable shift of percolation limit. The interactions of hp-β-CD, surfactant ions and the water molecules affect the distribution of different water species and electron density of H-atoms of water. Addition of water to the system beyond the hydration capability of counterions and head groups is in fact a dilution process inside the aqueous core. The hp-β-CD molecules are water-insoluble entities and fervently reside in the interface of the reverse micelle. This results in the decrease in droplet size thereby allowing the unfavorable overlap of the two colliding droplets and hence delaying percolation. This has also been supported by the particle size estimations reported above where the particle size has been found to decrease with the incorporation of hp-β-CD. Similar studies could not be preformed for ME-II as the nanoemulsion turns turbid with the incorporation of water as it is formed over a low ω range.

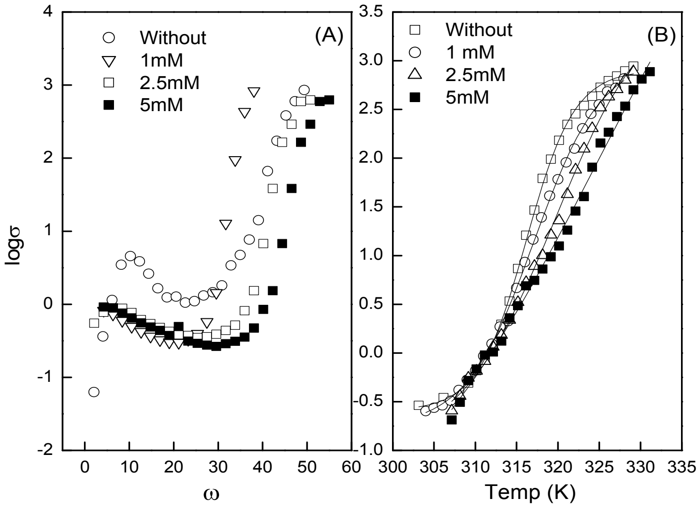

Fig. I. Variation of electrical conductivity as a function of temperature at different hp-β-CD concentrations for ME-I.

FTIR Spectroscopy

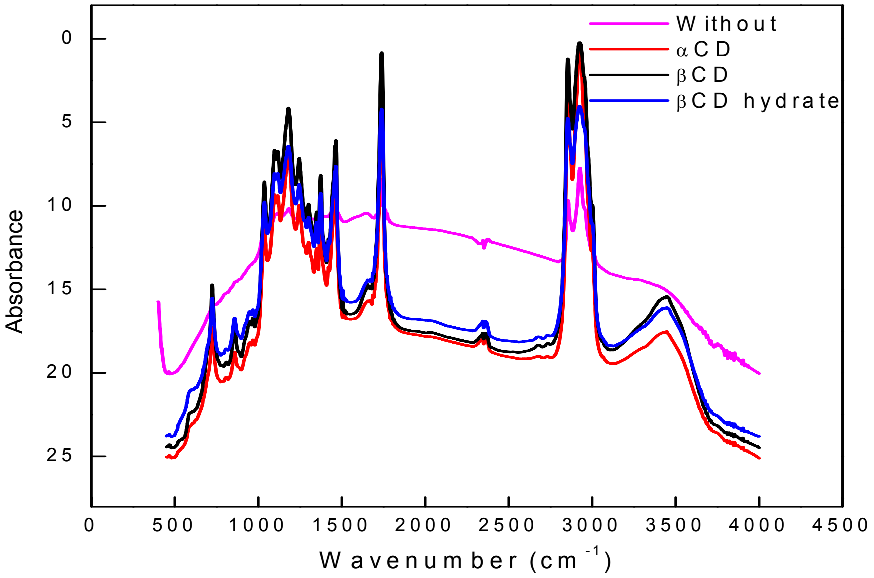

Fig. II Representative FTIR spectra of ME-I

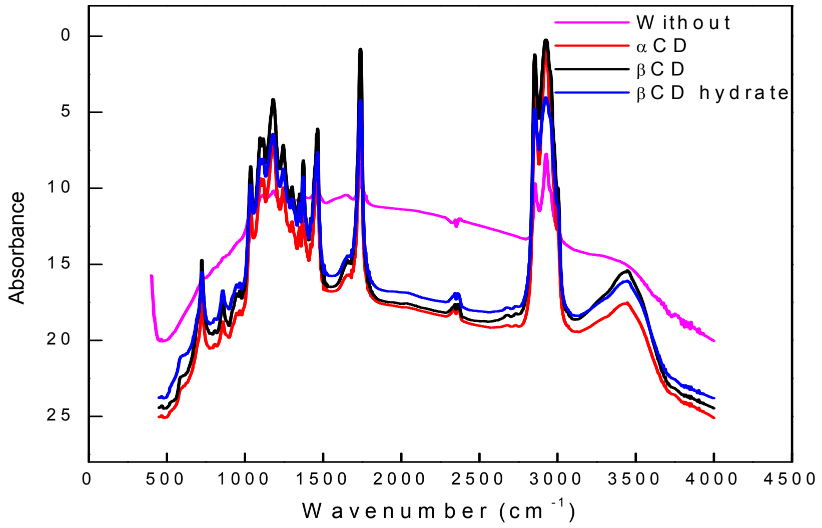

Fig. III Representative FTIR spectra of ME-II

Solvatochromic Studies

To elucidate the behavior of microemulsions/nanoemulsions, solvatochromic studies have also been carried out. Solvatochromism represents the solvent-induced spectral band shift, which is due to changes in the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition energy because of differential solvation of ground and excited states of the probe.[9] With increasing polarity of the solvent, the spectral band can undergo a hypsochromic or a bathochromic shift depending on the electronic structure of the probe and its interaction with the environment given by the solvent shell. Accordingly, a negative or positive solvatochromism can be found, which gives qualitative and quantitative conclusions about the energetics of the dye solvation. Solvatochromic dyes generally exhibit steady bathochromic (positive solvatochromism) or hypsochromic (negative solvatochromism) band shifts in solvents with a change in polarity.

To have a quantitative picture of the above observations, the Strokes spectral shifts, $\Delta\nu = (\nu_a - \nu_f)$ where ν_a and ν_f refer to absorption and emission frequencies respectively, has been correlated with solvent polarity parameters $E_{T(30)}$. The $E_{T(30)}$ parameter developed by Reichardt[9] is reported to be the most appropriate to explain the electronic transition of various organic compounds. The parameter has been generated from a pyridinium N-phenolate betaine dye. Because of the analogy of functional group of the dyes with the betaine, $E_{T(30)}$ parameter has been considered to explain the effect of solvents. MB has been found to show positive solvatochromic with the increase in solvent polarity. Positive solvatochromism is more sensitive to changes in solvent polarity than the corresponding absorption band in suitable cases. The correlation of $\Delta\nu$ with $E_{T(30)}$ is decreasing linear (Fig. IV). The results suggest that increased population of head group has a reverse effect on the Stokes shift and solvent parameter. This may be due to a modification of water-dye hydrogen bonding interactions by the hydrogen bonded network present in liquid water. Such an anomalous hydrogen bonding behavior for water and aprotic solvents has also been observed for other solutes.[9] The relationship could not be evaluated for ME-II as the system shows the absence of sharp peaks at higher ω.

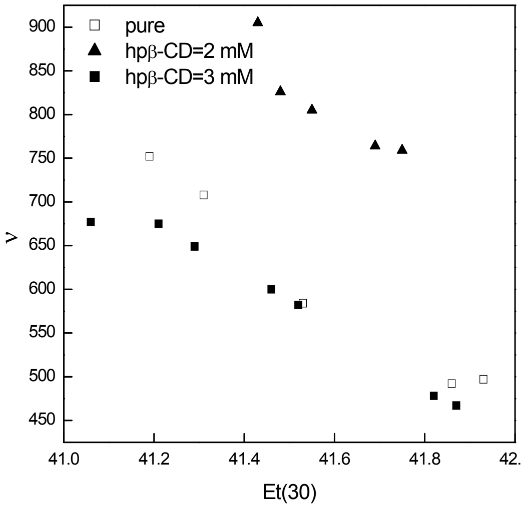

Fig. IV. Linear relationship between $E_T(30)$ and strokes shift.

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