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# Poly(ethylene oxide) Solubilization in Reverse Microemulsion: Conductivity and UV-Vis Spectra Studies

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**Abstract:** The effect of poly (ethylene oxide) (PEO) on the w/o microemulsion is studied. The addition of PEO induces a decrease of attractive interaction between droplets in reverse microemulsion. Due to the absence of interaction between cationic surfactant and neutral polymer, the polymer molecules are forced into the interior of water core, avoiding the interfacial region.

**Keywords:** Reverse microemulsion, cationic surfactant, electrical percalation, PEO.

A large number of biologically and industrially important dispersion is made from polymers and surfactants[1,2], while the interaction between water-in-oil microemulsion and water-soluble polymer is of current interest. Up to now, in these studies, most w/o microemulsions have been investigated with Bis(2-ethylhexyl sodium sulfosuccinate) (AOT) as a surfactant[3], however to better understand such microemulsion systems, it is necessary to study the interaction between the microemulsions made from the other surfactants and simple polymers.

Microemulsion is single-phase transparent thermodynamically stable mixture of oil, surfactant and cosurfactant, while w/o microemulsion can form water droplets enclosed with interface built by surfactant and cosurfactant. For high oil content, the nanometer-size water droplets are dispersed in oil continuous phase. Due to a selective solubility, water-soluble polymers like PEO are confined to the water core of these nanodroplets[4].

The present paper concerns the question whether and to what extent, the unusual effect of PEO on the percolation behavior in cationic surfactant systems. Because polymer chain together with the presence of surfactant at droplet surface can lead to interaction which includes two situations (1) a very weak interaction (*e.g.* nonionic surfactants and PEO). (2) a strong interaction (*e.g.* anionic surfactants and PEO), so it is very interesting to study the solubilization location of PEO molecules in w/o microemulsion. In this paper, we obtain information on possible structure changes when polymer is added to w/o microemulsion.

## Experimental section

Cetyltrimethylammonium bromide (CTAB) was purchased from Beijing Chemical Reagents Co. It was twice crystallized from ethanol. 1-Butanol, n-hexanol and n-decane from Fluka were A.R and used without further purification. The poly (ethylene oxide) (PEO) was obtained from Merck (a quality for G. C). Methyl orange(MO) was A.R grade of Beijing Chemical Co.

Surfactant, cosurfactant, oil (n-decane) and the solution of PEO in water were weighed according to calculation. The ratio of surfactant to cosurfactant is 3:7 (weight), $W_o$ was expressed as follows:

$$W_o = n_{H2O}/n_{(surfactant)} \text{ ( molar ratio)}$$

Oil content is 50% (weight) in all samples. Cp(g/100mL) is the polymer concentration.

The absorption probe (MO, a $2.0\times10^{-3}$ mol/L solution in methanol ) was prepared in order to introduce quantitatively the absorption probe (MO) into the reverse microemulsion. First, appropriate amount of the methanolic solution of MO was transferred into a graded tube, and then methanol was evaporated to dryness. The w/o microemulsion was added to the residue with shaking, and MO was solubilized in the corresponding reverse microemulsion, the desired overall concentration of the dye (MO) was obtained.

The conductivity measurement was made with a DDS-11D conductometer (Shanghai Leizi Instrumental Factory) at 25℃±0.5. The UV-Vis spectral measurements were performed with HP 8452A diode array spectrophotometer at room temperature (about 25 ℃).

## Results and Discussion

### *Conductivity Measurements*

**Figure 1** The variation of conductivity with $W_o$ values in different microemulsion. Solid points: CTAB/1-butanol/decane/water microemulsion. Open points: CTAB/1-hexanol/decane/water microemulsion

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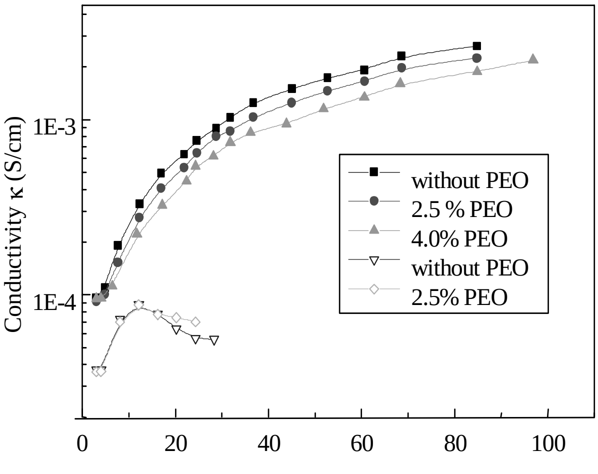


The **Figure** exhibit several features. (1) All κ *verus* $W_o$ variations exhibits electrical percolation phenomena (the steep increase in conductivity with $W_o$ values increasing.). (2) The electrical conductivity ($\kappa$) decreases as the alcohol chain increases for the same $W_o$ values in reverse microemulsions. (3) the electrical threshold increases as PEO concentration increases when the $W_o$ values keep constant.

It is known that from the electrical conductivity $\kappa$ the information of interaction between droplets in w/o microemulsions can be obtained. Several studies[5,6] have shown that when the electrical percolation threshold occurs, the interaction between droplets in w/o microemulsion increases. This means the attractive interaction between droplets decreases as the alcohol chain length increases. The addition of PEO also induces the interaction between droplets to decrease. At the value of $W_o$ above threshold, the same conclusion can be obtained because a lower conductivity value is observed at the same $W_o$ values as in **Figure 1**.

### *UV-Vis spectra studies*

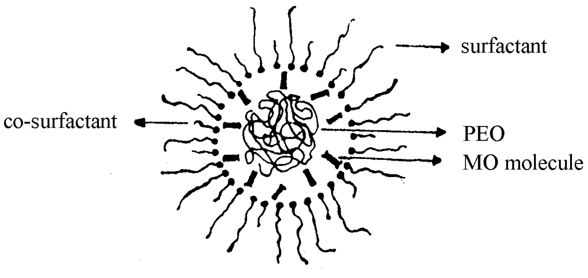
In order to determine the solubilization location of PEO in droplets of w/o microemulsion, we use MO as an absorption probe to study the spectral changes caused by the addition of polymer. First, the dependence of $\lambda_{max}$(the maximum absorbance wavelength of MO in system) on different solvents is monitored. The $\lambda_{max}$ values in solvents are listed in **Table 1**. It is found that a wide variation in $\lambda_{max}$ is observed for different solvent media, with values of 414 nm in nonpolar solvent like heptane to 418 nm and 462 nm in ethanol and water respectively. Based on the above results, MO can be used to investigate the "polarity" of the local microenvironment of the probe [7,8].

**Table 1** The dependence of $\lambda_{max}$ of methyl orange absorption on solvent

| Solvent | $\lambda_{max}$ (nm) |
|---|---|
| n-butanol | 414 |
| ethanol | 418 |
| ethanol | 420 |
| water | 464 |

Because MO molecules with negatively charged sulfonate can strongly interact cationic surfactant with positive charged polar groups by electrostatic interaction, it is expected that MO-surfactant association occur, which enhance a location of MO molecules within the polar region of hydrated surfactant cationic head group in the droplets. The state of MO in the w/o microemulsion has been shown in **Figure 2**.

**Figure 2** The state of MO in the w/o microemulsion. MO is considered to absorb at the surface of hydrated surfactant head groups.



As discussed above, MO can be used as probe to monitor the local micropolarity in droplets. So it is expected that if PEO molecules are absorbed in interfacial layer, the spectra would change due to the change of micropolarity. But in our experiments, at $W_o$=25.1, $\lambda_{max}$ values keep unchanged (418 nm) in w/o microemulsion when PEO concentration increases up to 6 g/100mL. This implies that the addition of PEO did not influence the local micropolarity. Because for PEO molecules (Mw=12,000), the radius of gyration $R_G$ of isolated PEO molecules in water is about 32Å, and the droplet dimension is in the range of the $R_G$. So PEO not only can fit into droplets, but also is forced into the droplet interior and avoids the interfacial region. In consideration of the absence of interaction between cationic surfactant and neutral polymer, above conclusion is rational.

## Conclusion

The influence of water-soluble polymer like PEO on percolation behavior of w/o microemulsion could be shown to be the results of interaction between droplets. The addition of PEO induces a decrease of this interaction. PEO molecules can fit into the droplets in w/o microemulsion. For the system studied in this work, the polymer is forced into interior of water core, avoiding the interfacial region, which results from the absence of interaction between cationic surfactant and neutral polymer.

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