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Dielectric Behavior of Middle Phase Microemulsion

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Abstract: Dielectric measurements were performed on middle phase microemulsions composed of sodium dodecylsulfate(SDS), cetyltrimethylammonium bromide(CTAB), n-butanol, n-heptane and brine. Distinct and unique dielectric behavior, with characteristic frequency dependence regularity on the salinity of the microemulsions, was observed in the low-frequency range from $10\text{-}10^3$Hz. It can be considered to be an interfacial polarization mechanism.

Keywords: Middle phase microemulsions, dielectric spectroscopy, relaxation time.

Introduction

Microemulsions are transparent and fluid systems composed of water, oil and amphiphilic molecules. They form spontaneously with simple mixing. Microemulsions may be water- or oil- continuous and bicontinuous under some conditions of temperature or composition. Middle phase microemulsions(MPME) is called the 'bicontinuous state' which is considered to be a sponge-like random network. Owing to its ultralow interfacial tensions against the excess water and oil phase with which they are in equilibrium, the MPME has important applications in chemically enhanced oil recovery, chemical reaction and fine chemistry. But there is no general agreement the interpretation of internal structure of MPME, because of its complicated chemical system consisting of, in general, three to five components with internal association structures.

The dielectric relaxation spectroscopy method (DRS) provides a non-invasive technique[1] by which the electrical and structural properties of the heterogeneous systems, such as emulsion and colloidal particles, can be obtained. Microemulsion systems exhibit marked frequency dependence of dielectric constant and conductivity, so-called dielectric relaxation, being due to the interfacial polarization between the oil/water phases. Thee pattern of the relaxation is associated with the internal structures and electrical properties of the microemulsion, the relaxation processes provide us some dynamic information. Therefore, there has been considerable interest in the dielectric approach of microemulsion in recent years[2,3]. However, the studies on the MPME have rarely been reported. In this study, we have attempted to apply frequency domain dielectric spectroscopy to the MPME system composed of SDS, CTAB, n-butanol, n-heptane and brine coupled with salinity scanning, and discussed the dielectric relaxation pattern by means of Cole-Cole equation.

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Experimental

Chemicals: sodium dodecylsulfate (SDS), cetyl trimethylammonium bromide(CTAB), n-butanol, n-heptane and NaCl were A.R. Grade. Water was deionized water.

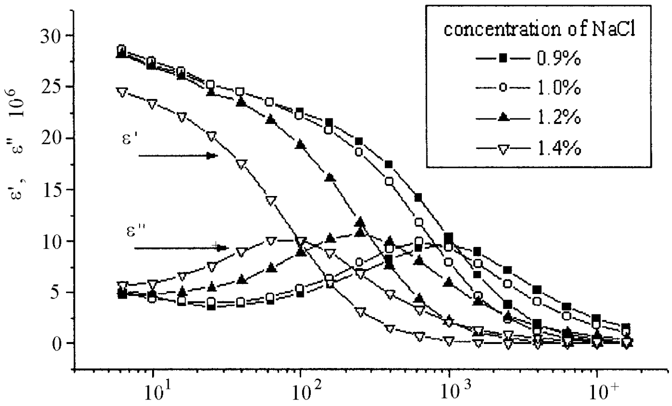
Preparation of MPME: The middle phase microemulsions were prepared by mixing appropriate weight fractions of the above six components.

Dielectric measurements: The dielectric measurements were carried out with 5201Loke-Amplifier coupled to a 273PAR potentiogalvanostat in the frequency range from 10 Hz to 10^5 Hz. A measuring cell consisted of two concentric platinum cylinderal electrodes fixed at the bottom of a glass vessel. The measuring cell was charged with MPME up to a level above the electrodes. All experiments were carried out at 40 ± 0.1 ℃.

Results and discussion

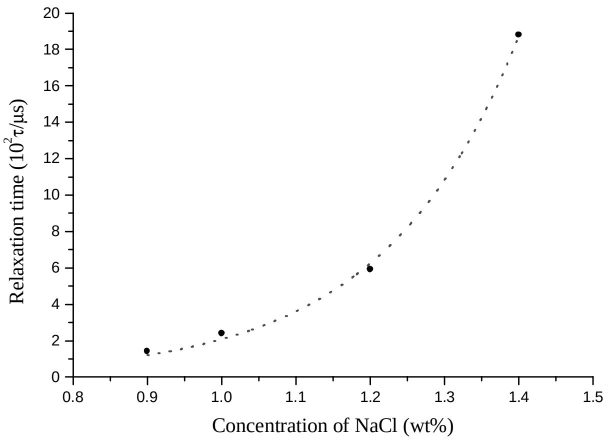
Figure 1 shows remarkable frequency dependence of the dielectric constant ε' and dielectric loss ε'' for the MPME. This kind of frequency dependency is called dielectric relaxation, being characterized by a relaxation time τ or relaxation frequency f_o corresponding to $\Delta\varepsilon/2$. The relaxations shift to lower frequencies with the increasing of NaCl content. The plots of relaxation time against the salinity of microemulsion are shown in **Figure 2**. The values of τ vary from 1.4×10^{-4}s to 1.9×10^{-3}s, which is very large in magnitude. As a consequence it is supposed that the set

Figure 1. Frequency dependence of ε' and ε'' for MPME on different NaCl concentration



up of electrical polarization in the interface of oil and water phases is a slow process. The value of τ rising steeply above 1.2 (wt%), which may be due to some change in the inner structure, *i.e.* the transitions between water or oil and bicontinuous structures. It can be explained as follows: When the concentration of NaCl is increased, the dissociation of surfactant molecule SDS is restrained and gather of water is impelled, resulting in structural evolution of MPME from bicontinuous to microemulsion and surplus water[4].

Figure 2. Relation between relaxation time τ and NaCl concentration



From a dielectric point of view, in order to examine the relaxation mechanism, a numerical calculation is carried out using the Cole-Cole type distribution Equation 1. Where ε_l and ε_h are the limiting values at low and high frequencies, $\omega=2\pi f$ is the

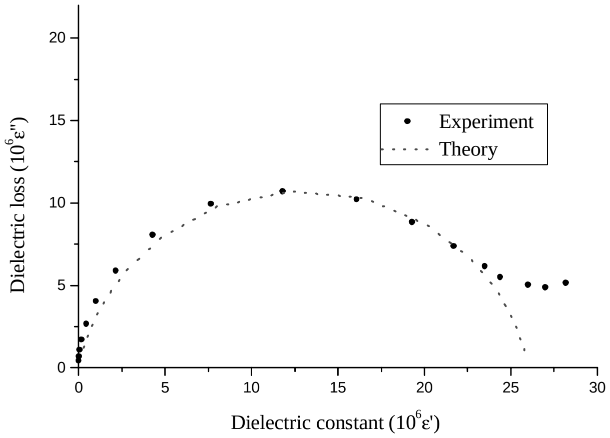
$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + (j\omega\tau)^{1-\alpha}} \qquad (1)$$

angular frequency, $j^2=-1$, and $\varepsilon^* = \varepsilon' - j\varepsilon''$. The parameter α can be interpreted as a measure of a relaxation time distribution.

Numerical calculation was carried out with the following set of parameters: $\varepsilon_l=28.6\times10^6$, $\varepsilon_h=3508$, $\tau=2.5\times10^{-4}$s, $\alpha=0.2$. The results are shown in **Figure. 3** in dashed line together with the observed points. The experimental and calculated values are all in good agreement over the whole measuring range.

Moreover, from the **Figure 3**, it is also seen that the graph is a symmetrical circle arc, obeying the Cole-Cole equation. This suggests that the relaxation is not a single relaxation process and is caused by the Maxwell-Wagner effect, being attributed to the interfacial polarization mechanism[5] because of the bicontinuous phase structure of the MPME. Although the relaxation time by itself does not tell us anything definite about the detailed mechanism(s) and architecture of the MPME, the degree of distribution in the Cole-Cole diagram has been empirically interpreted in terms of heterogeneity in the electrical parameters and structural complexity in the inner of the MPME[6].

Figure 3. Complex plane plots of the dielectric data (1.0wt% NaCl) shown in Fig.1. The full blacks circle(●) and the dashed line (-----) are observed and calculated from Eq1 respectively.



The present work provides us a new approach of studying microemulsion by means of DRS, and leads to a better understanding for the information about internal structure of middle phase microemulsion. A paper concerning theoretical analysis of inner electrical and structural properties of the MPME is now in preparation for publication. The present method can also be expanded to various heterogeneous systems, such as micelle, lipid vesicle suspension and biological cell.

Acknowledgments

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