Study on dielectric relaxation Spectra of Surfactant-free Microemulsion composed of Water / Ethanol / Triethyl Citrate

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Abstract: In this paper, the dielectric relaxation behavior of surfactant-free microemulsion composed of pure water / ethanol / triethyl citrate (TEC) from 40Hz to 110MHz was studied. There is an obvious relaxation phenomenon between $10^3$ and $10^5$Hz in the selected experimental path, which is presumed to be interfacial polarization relaxation, indicating that there is a microscopic phase region in the system. The dielectric relaxation parameters fitted by a dispersion term Cole-Cole formula, that is, relaxation intensity $\Delta \varepsilon$ and relaxation time $\tau$, obviously vary with the phase composition of the system, and different trends can indicate that the system is in different microemulsion phase regions. It is proved that the dielectric spectrum technique can accurately characterize the surfactant-free microemulsion.

1. Introduction
Although microemulsion systems have been widely used in industrial processes such as separation, chemical reaction, preparation of nanomaterials, and drug delivery and release in recent years,[1,2] the disadvantage is that a large number of surfactants (Wt. > 10%) are usually required to obtain a single Winsor IV phase region (microemulsion region)[3]. Fortunately, in 1976, Smith et al[4] discovered a surfactant-free microemulsion formed only by ternary systems of n-hexane, isopropanol and water. Through the study of the microstructure, properties and formation mechanism of surfactant-free microemulsion,[5,6] it is preliminarily proved that there are some similarities in microstructure and properties between surfactant-free microemulsion and traditional surfactant microemulsion. Surfactant-free microemulsions can also exhibit three structures similar to those of traditional surfactant microemulsions: oil-in-water (O/W), bicontinuous (BC) and water-in-oil (W/O) structures[7], which can be transformed into each other with the change of system composition.[8]

According to what we know, dielectric relaxation spectroscopy has become one of the most effective methods to characterize all kinds of materials.[9] Because it has many unique characteristics, such as non-invasive, high sensitivity to dipole moment and ion motion, wide frequency coverage and so on. Dielectric measurement is also a powerful means to explore the structure and dynamic characteristics of microemulsions, although it is not new to use dielectric relaxation spectroscopy to study microemulsions.[10] However, so far, no article on surfactant-free microemulsion has been published, which allows us to find the motivation for our research. Because in previous studies, it has been proved that the microstructure of surfactant-free microemulsion is similar to that of traditional surfactant microemulsion. Since dielectric spectroscopy can be applied to traditional surfactant microemulsions, it is possible to have a good performance in the study of surfactant-free microemulsions. The results are satisfactory. There is an obvious relaxation phenomenon between $10^3$ and $10^5$Hz, which indicates that the application of dielectric spectroscopy to this kind of microemulsion is successful. The dielectric
relaxation parameters fitted by a dispersion term Cole-Cole formula, that is, relaxation intensity $\Delta \varepsilon$ and relaxation time $\tau$, obviously vary with the phase composition of the system, and different trends can indicate that the system is in different microemulsion phase regions. The results show that the surfactant-free microemulsion also has the same structure as the traditional microemulsion, such as oil-in-water, bicontinuous (BC) and water-in-oil.

2. Materials and methods

2.1. Materials and sample preparation
Ethanol (purity $\geq 99.7\%$) and triethyl citrate (purity $\geq 99.0\%$) were purchased from Sinopharmaceutical Group Chemical Reagent Co., Ltd. (China), and pure water was prepared from the portable ultra-pure water system in our laboratory. all chemicals are used without further purification.

The surfactant-free microemulsion is composed of proper volume fraction of ethanol, pure water and triethyl citrate. The experimental path is shown in figure 1, where the dividing line is drawn according to the work of Sebastian Krickl et al. The composition of path an is as follows: The volume content of ethanol remained unchanged when the content of triethyl citrate was 0.25, while the volume of pure water decreased with the content of triethyl citrate, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70 respectively.

2.2. Dielectric measurement
In this experiment, the dielectric measuring instrument used is WK6500B precision impedance analyzer (Agilent Technologies). The sample cell composed of platinum electrodes in the coaxial cylinder described and used in the previous work was used in the experiment$^{[11]}$, which was connected to the impedance analyzer through the 1011 spring clip fixing device (Agilent Technologies). In order to immerse the electrode, the volume of the microemulsion measured here is 4ml. Through the measurement of air, acetone, ethanol and pure water, it is concluded that the cell constant of the sample cell is 1.72 $\times$ $10^{-12}$F and the planktonic capacitance is 4.31 $\times$ $10^{-12}$F. According to the Schwan's method, the measured dielectric data are corrected by cell constant, floating capacitance and residual inductance. The dielectric constant and dielectric loss at each measured frequency are calculated from the corrected capacitance and conductance.

2.3. Determination of dielectric parameters
In the applied electric field with frequency $f$, the dielectric properties (dielectric constant $\varepsilon$ and conductivity $k$) of the microemulsion can be obtained by fitting the measured experimental data by Cole-Cole empirical formula$^{[12]}$

$$
\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_H + \sum_l \frac{\varepsilon_l - \varepsilon_H}{1 + (j\omega\tau_l)^\beta}
$$

The symbol in the formula means: $\varepsilon^*$ is the complex permittivity; $\varepsilon'$ is the dielectric constant; $\varepsilon''$ is the dielectric loss; $\varepsilon_l$ and $\varepsilon_H$ are the low and high frequency limits of the relative dielectric constant, respectively; $\omega$ is the angular frequency ($\omega = 2 \pi f$ is the electric field frequency); $\tau$ is the relaxation time; $\beta (0 < \beta \leq 1)$ is the Cole-Cole parameter, indicating the dispersion of the relaxation time $\tau$; $j^2 = -1$. Where $\varepsilon'' = (k-k_l)/\omega\varepsilon_0$ and $\tau = (2\pi f_0)^{-1}$, $k$ is the conductivity, $k_l$ is low frequency limit of conductivity, the vacuum permittivity $\varepsilon_0$ is 8.854$\times$10$^{-12}$Fm$^{-1}$, $f_0$ is the characteristic frequency.
3. Results and discussion

The dielectric relaxation behavior of path a:

Figure 2: Fitting result of dielectric loss curve of path a

Figure 2 reflects the dielectric loss curve of path a, and it is obvious that there are two relaxations in this system, in which the black circle is the measured data, the blue curve is the fitting relaxation 1, and the orange curve is the fitting relaxation 2. When we compare the changing trend of relaxation 1 as a whole, we do not find any interesting results, but the results of relaxation 2 are unexpected, so we only discuss relaxation 2 in this paper. Figure 3 shows the fitting result.
Figure 3: The frequency dependence of (A) dielectric constant and (B) dielectric loss after subtraction of dc conductivity of surfactant-free microemulsion with different Triethyl citrate content. The solid lines are best fits.

Table 1: Dielectric parameters of surfactant-free microemulsion (water/ethanol/ TEC) line a

| Wt (TEC) % | ε∞ | εh | εl | Sigma DC (10^5 xS/cm) | β   | Δε  | Log τ(s) |
|------------|----|----|----|------------------------|-----|-----|---------|
| 5          | 54.593 | 54.793 | 108.733 | 201 | 0.8899 | 53.94 | -5.341 |
| 10         | 51.263 | 51.563 | 85.743  | 132 | 0.8899 | 34.18 | -5.331 |
| 15         | 48.263 | 48.663 | 65.933  | 90.483 | 0.8649 | 17.27 | -5.323 |
| 20         | 27.933 | 28.333 | 37.833  | 72.782 | 0.8499 | 9.5  | -5.32   |
| 25         | 43.383 | 43.783 | 52.433  | 65.259 | 0.8549 | 8.65 | -5.31   |
| 30         | 38.233 | 38.533 | 42.883  | 49.489 | 0.8349 | 4.35 | -5.481  |
| 35         | 35.393 | 35.693 | 39.343  | 43.699 | 0.8249 | 3.65 | -5.484  |
| 40         | 15.393 | 15.693 | 19.243  | 36.709 | 0.8199 | 3.55 | -5.481  |
| 45         | 29.853 | 30.053 | 33.603  | 30.939 | 0.8298 | 3.55 | -5.484  |
| 50         | 26.363 | 26.463 | 31.813  | 26.409 | 0.8199 | 5.35 | -5.118  |
| 55         | 23.023 | 23.123 | 26.773  | 16.599 | 0.8199 | 3.65 | -5.118  |
| 60         | 21.323 | 21.423 | 24.273  | 13.859 | 0.9591 | 2.85 | -5.118  |
| 65         | 17.823 | 17.923 | 18.073  | 8.319  | 0.9591 | 0.15 | -5.118  |
| 70         | 14.873 | 14.973 | 15.173  | 5.019  | 0.9591 | 0.2  | -5.12   |

According to the previous work and the properties of surfactant-free microemulsion\[13,14\], it can be determined that this relaxation is caused by the mechanism of interfacial polarization. Figure 4 can be obtained by mapping the relaxation intensity Δ ε and TEC content. Rooted in the different changing trends of Δ ε, the measured results can be divided into three regions, namely I, II, and III regions.

In region I, according to the structural characteristics and component content of surfactant-free microemulsion, it can be known as Omax W region. Δ ε decreases gradually with the increase of TEC content, which can be considered as the formation of O/W microemulsion droplets. Triethyl citrate molecules enter into the interfacial membrane formed by hydrogen bonding of water and ethanol, which leads to the decrease of polarity.

In region II, Δ ε remains constant with the change of TEC content, which is consistent with the characteristics of BC phase region. In the BC phase, the interfacial film area of the microemulsion remains unchanged, which leads to the constant amount of charge accumulated on the interfacial film, so Δ ε remains unchanged.

In region III, the W/O phase region. From figure 3-3, we can see that the sample point corresponding to the W/O phase region is gradually away from the boundary between the single phase region and the multiphase region, which means that the radius R of the microemulsion droplet is gradually decreasing, that is, the interface film area of the droplet is gradually smaller, which leads to a gradual decrease in the amount of charge that can be accumulated, so Δε shows a downward trend.
Figure 4: Dependence of relaxation intensity on TEC content in water/ethanol/TEC ternary system surfactant-free microemulsion in line a measurement.

Figure 5 shows the dependence of relaxation time $\tau$ on TEC content. The relaxation time $\tau$ increases gradually with the increase of TEC (the viscosity of TEC is 35.2 mPa·s is much higher than that of water at 25 °C), because the increase of viscosity leads to the decrease of charge mobility and the increase of relaxation time $\tau$.

Region II is the BC phase region, and the relaxation time $\tau$ is unchanged. From the composition of the sample points, it is known that the content of water is higher than that of TEC, so the channel in the BC region is an oil channel, which shows that the physical and chemical properties of the phase interface are the same, so the value of $\tau$ does not change.

The region III is the W/O phase region, and the change trend of relaxation time $\tau$ remains unchanged, indicating that the mobility of charged particles in the microemulsion remains unchanged, and the specific reasons need to be further studied.

Figure 5: Dependence of relaxation time on TEC content in water/ethanol/TEC ternary system surfactant-free microemulsion in line a measurement

4. Conclusion:
In this work, our main purpose is to study the dielectric relaxation behavior of surfactant-free microemulsion composed of pure water/ethanol/triethyl citrate ternary system in the frequency range from 40Hz to 110MHz. A path near the dividing line between single-phase region and multiphase region is mainly selected.
By analyzing that the relaxation time \( \tau \) and relaxation intensity \( \Delta \varepsilon \) of this path change with the change of component content, and there is a break point between micro phase regions, it can be known that both \( \tau \) and \( \Delta \varepsilon \) can be used to identify the changes of microstructure and phase region of anhydrous surfactant-free microemulsions, and the positions of \( \tau \) and \( \Delta \varepsilon \) breakpoints of this path are consistent. This further proves that \( \tau \) and \( \Delta \varepsilon \) are reliable and effective in characterizing the properties of anhydrous and surfactant-free microemulsions, and they can also be compared with each other.

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