

Studies on the Phase Properties of Winsor I-III Type Microemulsions with Dielectric Relaxation Spectroscopy

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Abstract: The dielectric relaxation spectroscopy (DRS) of Winsor I ~III microemulsions for nonionic surfactant octyl polyglucoside C₈G_{1.46}/1-butanol/cyclohexane/water system was studied. The experiment shows that the permittivity decreases with the increase in the frequency and clear dielectric relaxation phenomena were observed. Permittivity obviously decreases with the change of the microstructure of the microemulsion, W/O, B.C. and O/W can be distinguished by the permittivity.

Keywords: Phase property, microemulsion, dielectric relaxation spectroscopy.

Microemulsions are thermodynamically stable, isotropic mixtures of water, oil, surfactant and cosurfactant that exhibit wide variety of microstructure. Winsor identified four general types of phase equilibria: Type I (O/W), II (W/O), III (B.C.) and IV (isotropic micellar solution)¹. Type I and II are two-phase systems, type III a three-phase system, and type IV a single-phase system. Depending on surfactant type and sample environment, types I, II, III or IV form preferentially, the dominant type being related to the molecular arrangement at the interface. Conductivity measurement is a simple method to determine the different microstructures of microemulsions for an ionic surfactant system, but can not be applied to a nonionic surfactant system.

Dielectric relaxation spectroscopy (DRS) is a noninvasive and rapid method for the structural characterization². It has been successfully used to determine the structural, dynamic, and electric properties of some molecular organized assemblies³. By now the DRS method has also been used in the systems of micelle³, vesicles⁴ and single-phase microemulsions⁵⁻⁷. It seems that it has not been used in the Winsor type microemulsion systems. In fact Winsor microemulsion measurements are more suitable with DRS method, since the sample can be measured directly, without separation of the phases.

In this paper, a modified fishlike phase diagram for nonionic surfactant octyl polyglucoside C₈G_{1.46}/1-butanol/cyclohexane/water Winsor microemulsion system was plotted, and the DRS of Winsor I~III region of this diagram was studied.

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Experimental

Chemicals: Octyl polyglucoside, its composition was determined by chromatography to be $C_8G_{1.46}$ (monoglucoside 70.0%, diglucoside 19.0%, triglucoside 6.0%, tetraglucoside and more 5.0%). The other chemicals used in this study are all A. R. grade. Water was doubly distilled.

Instrument: HP 4192A LF Impedance analyzer, made by Hewlett Packard Co. Ltd.

Procedures: For a quaternary system water (W)/cyclohexane (O)/1-butanol (A)/ $C_8G_{1.46}$ (S), defined $\alpha = O/W+O$, $\beta = S/(W+O+A+S)$, and $\varepsilon = A/(W+O+A+S)$. If a water-to-cyclohexane mass ratio of unity is preferred, 1-butanol varies monotonically, while $C_8G_{1.46}$ concentration is fixed at different values, the values of the middle-phase microemulsions were recorded, then the modified fishlike phase diagram can be obtained.

The samples were placed in the light channel of above instrument. The dielectric measurements were carried out directly at $40 \pm 0.1^\circ\text{C}$. The dielectric response was measured in a frequency range of $2 \sim 10^5 \text{ Hz}$. The data were collected in the form of parallel connection of capacitance (C) and conductance (G) as functions of frequency.

Results and Discussion

The modified phase diagram for water/cyclohexane/1-butanol/ $C_8G_{1.46}$ system is shown in **Figure 1**.

It can be seen that increasing ε at constant β causes a series of phase inversions Winsor I \rightarrow III \rightarrow II. In Winsor I, the surfactant is preferentially soluble in water and oil-in-water (O/W) microemulsions form, the surfactant-rich water phase coexists with the oil phase where surfactant is only present as monomers at small concentration. In Winsor II, the surfactant is mainly in the oil phase and water-in-oil (W/O) microemulsions form, the surfactant-rich oil phase coexists with the surfactant-poor aqueous phase. Winsor III is a three-phase system where a surfactant-rich middle-phase coexists with both excess water and oil surfactant-poor phases (see **Figure 1**).

According to the compositions of points a~g in **Figure 1**, seven solutions were prepared and their DRS were measured. **Figure 2** shows the permittivity~ frequency relation of points a~g in Winsor I, III and II regions.

Figure 1 The modified fishlike phase diagram of the quaternary system water/cyclohexane/1-butanol/ $C_8G_{1.46}$ at 40°C

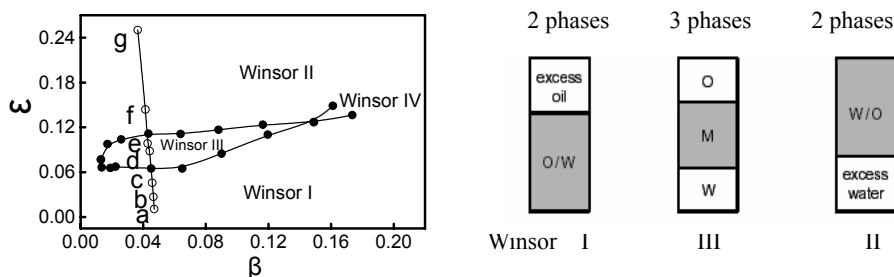


Figure 2 Frequency dependence on permittivity for the microemulsion of Winsor type $C_8G_{1.46}$ /1-butanol/ cyclohexane/water system

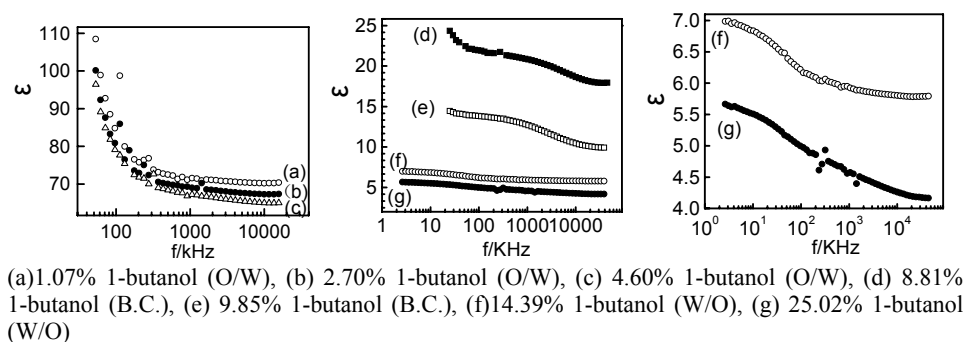


Table 1 Dielectric parameters obtained by fitting for $C_8G_{1.46}$ /1-butanol/ cyclohexane/water system

1-butanol (%)	ϵ_l	ϵ_h	f_0/Hz	$10^4 \tau_0/\text{s}$	$10^5 \kappa_1 / (\text{S/m})$
a-1.07 (O/W)	72.66	69.98	1321.3	1.20	37.33
b-2.70 (O/W)	71.82	67.19	762.0	2.09	34.39
c-4.60 (O/W)	69.39	64.63	1297.4	1.23	31.18
d-8.81 (B.C.)	21.51	17.51	4483.1	0.36	3.60
e-9.85 (B.C.)	14.03	9.55	2494.7	0.64	0.99
f-14.39 (W/O)	6.15	3.98	82.4	19.31	0.03
g-25.02 (W/O)	7.17	5.79	40.7	39.10	0.04

Figure 3 Relaxation time τ_0 as a function of C_4H_9OH content for $C_8G_{1.46}$ /1-butanol/ cyclohexane/water system

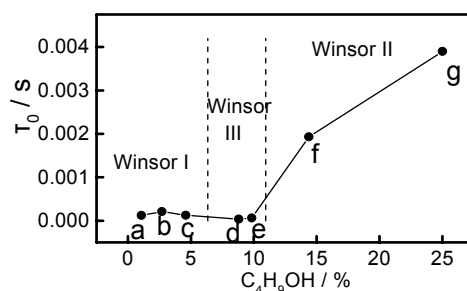


Figure 2 shows that the permittivity decreases obviously with the change of the microstructure of the microemulsion from Winsor I, *via*. Winsor III, to Winsor II, so W/O, B.C. and O/W can be distinguished by the permittivity. The permittivity decreases also with the increase in the frequency and clear dielectric relaxation phenomena were observed, especially in Winsor II and III regions.

Some dielectric parameters are obtained by non-linear curve fitting of **Figure 2** and listed in **Table 1**. As can be seen in **Table 1** that the dielectric parameter group (ϵ_l ,

low-frequency permittivity; ϵ_h : high-frequency permittivity; f_0 : characteristic relaxation frequency; τ_0 : relaxation time and κ_l low-frequency conductivity) was different in different microemulsion regions, this reflects the effect of the different microstructures of the different microemulsions. In **Figure 3**, for example, the relaxation time τ_0 as a function of C_4H_9OH content shows that τ_0 values are small in Winsor I and III regions, and large in Winsor II region. This may be explained by the movement of the droplets in systems. There exists a little water in Winsor II microemulsion, which restricts the movement of the droplets, resulting in a slower relaxation process and a longer relaxation time (points f, g, in **Figure 3**). In Winsor I region, the existence of lots of water speeds up the movement of the droplets, leading to a faster relaxation process compared with that in Winsor II region. In Winsor III region, because of the existence of the special pipeline structure, the movement of the droplets is free, so the structural relaxation time is shortest in three microemulsion regions.

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