

Dielectric properties of water in Triton X-100 (nonionic detergent)–water mixtures

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 376102

(<http://iopscience.iop.org/0953-8984/19/37/376102>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 04:40

Please note that [terms and conditions apply](#).

Dielectric properties of water in Triton X-100 (nonionic detergent)–water mixtures

Koji Asami

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

E-mail: asami@e.kuicr.kyoto-u.ac.jp

Received 24 May 2007, in final form 19 June 2007

Published 27 July 2007

Online at stacks.iop.org/JPhysCM/19/376102

Abstract

Dielectric measurements were carried out for mixtures of Triton X-100 (TX, a nonionic detergent with a poly(ethylene oxide) chain) and water with or without electrolytes over a frequency range of 1 MHz to 10 GHz to study the structure and dynamics of water molecules in the mixtures. Dielectric relaxation was found above 100 MHz, being assigned to the dielectric relaxation of water. The intensity of the dielectric relaxation was proportional to the water content above 0 °C. Below the freezing temperature of bulk water, the relaxation intensity decreased at TX concentrations (C_{TX}) below 50 wt% at -10 °C and below 60 wt% at -20 °C because frozen water shifts the dielectric relaxation to a frequency region far below 1 MHz. This indicated that there is no bulk water at C_{TX} above 50 wt% and that at least two water molecules per ethylene oxide (EO) unit are tightly associated with the ethylene oxide chain. The low-frequency conductivity of the mixtures of TX and electrolyte solutions was well represented by Bruggeman's mixture equation at C_{TX} below 40 wt%, if two water molecules per EO unit form an insulating shell surrounding TX micelles.

1. Introduction

Triton X-100 (TX), a nonionic detergent, has often been used in biological applications such as solubilization of membrane proteins without losing their activity [1], and isolation of membrane rafts [2], and it also forms transparent microemulsions capable of dissolving both water and oil in relatively large amounts. It has a hydrophilic chain of about ten ethylene oxide (EO) units, with which water molecules can be associated by hydrogen bonding. TX–water mixtures form a gel-like structure, related to the hexagonal phase of cylindrical micelles, in a concentration range of 40–60 wt% below about 30 °C, and the lamella phase between 65 and 80 wt% below 5 °C [3, 4]. To understand the molecular organization and functions of TX in water, the structure and dynamics of water associated with TX is important and, therefore, they have been studied by various techniques, e.g. rheological, optical and x-ray synchrotron techniques [3], nuclear magnetic resonance (NMR) [4] and Fourier transform infrared (FT-IR) spectroscopy [5].

Beyer [4] studied TX–water mixtures by NMR over wide ranges of temperature and TX concentration, and found that about two water molecules per EO unit are non-freezing just after freezing of bulk water and that at least one water molecule is tightly bound to one EO unit. Kimura *et al* [5], from their FT-IR study, proposed a molecular model that two water molecules per EO unit are directly associated with the poly(ethylene oxide) (PEO) chain of TX to form the first-nearest neighbours, which are surrounded by three water molecules per EO unit as the second-nearest neighbours.

Dielectric spectroscopy is also a powerful method to study the structure and dynamics of water molecules, as proved in previous studies on microemulsions [6] and aqueous solutions of various polymers [7–11]. Kaatze *et al* [7, 8] studied the dielectric relaxation of water in aqueous solutions of oxygen-containing linear hydrocarbon polymers such as PEO, poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP). The dielectric relaxation was interpreted by assuming two types of water: ‘hydration’ water and ‘free’ water. Shinyashiki *et al* [9] pointed out that PVA–water mixtures have three types of water: bulk water, water gradually squeezed out below the freezing temperature of bulk water, and non-freezing water. Foster *et al* [6] studied nonionic microemulsions (hexadecane–water mixtures with an emulsifier consisting of Tween 60 and *n*-pentanol) and suggested that a shell of about two water monolayers is associated with the oil droplets. As well as dielectric relaxation spectra, the conductivity behaviour of mixtures of polymer and water containing electrolytes also provides information on the hydration water [11–13]. Assuming that the polymer–water mixtures are heterogeneous systems including particles with a hydration shell in a bulk electrolyte solution, the number of water molecules associated with the polymer was estimated using an appropriate mixture equation.

Regardless of its ability, dielectric spectroscopy has never been applied to TX–water mixtures. Hence, in this study, dielectric measurements of the mixtures were carried out over a frequency range of 1 MHz to 10 GHz by varying the TX concentration and temperature. The results were analysed with the previous approaches used for polymer–water mixtures and microemulsions.

2. Materials and methods

Triton X-100 (*p*-(1,1,3,3-tetramethylbutyl)phenoxy polyoxyethyleneglycol) was obtained from Wako Pure Chemical Industries (Japan) and used without further purification. The number of EO units per TX is about ten. TX was dissolved with Milli-Q water or an aqueous electrolyte solution at TX concentrations from 0 to 100 wt%.

Dielectric spectra of TX–water mixtures were measured with a 4191A impedance analyser and an 8791C network analyser (Hewlett-Packard), which cover the frequency ranges from 1 MHz to 1 GHz and from 200 MHz to 13.5 GHz, respectively. Measurements with the 4191A impedance analyser used the coaxial cell described previously [14]. The 8791C network analyser was used together with an 85070A dielectric probe kit (Hewlett-Packard) including an open-ended probe and a set of measurement software. The open-ended probe was immersed in a sample liquid in a bottle, which was maintained at constant temperatures between 25 and -20°C .

3. Results

3.1. Dielectric relaxation of water in the TX–water system

Dielectric spectra of TX–water mixtures have been measured at TX concentrations C_{TX} ranging from 0 to 100 wt% and at temperatures from 25 to -20°C . Figure 1 shows the frequency

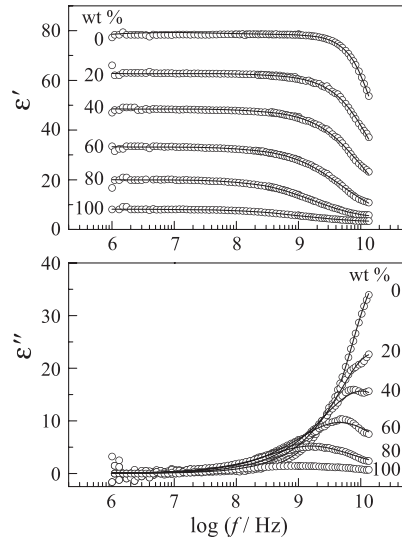


Figure 1. The real part ε' and the imaginary part ε'' of the complex permittivity ε^* of TX–water mixtures as a function of frequency f . The TX concentration is varied from 0 to 100 wt%, as indicated in the figure. The measurement temperature is 25 °C. Open circles are data points and solid curves are calculated from equation (1).

dependence of the real part ε' and the imaginary part ε'' of the complex permittivity ε^* at 25 °C. ε'' has been obtained by subtracting the contribution of the dc conductivity, which is slight but not negligible. Dielectric relaxation is found above 0.1 GHz and is attributed to water relaxation. As C_{TX} increases, the intensity of the dielectric relaxation decreases and the relaxation curve is shifted to lower frequencies and becomes broader. The relaxation curves are symmetric and thus are well represented by the Cole–Cole equation [15]:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + (j\omega\tau)^\beta}, \quad (1)$$

where ε_h is the high-frequency limit of relative permittivity, ε_l the low-frequency limit of relative permittivity, τ the relaxation time, β the Cole–Cole parameter ($0 < \beta \leq 1$), ω angular frequency ($\omega = 2\pi f$), f frequency and $j^2 = -1$. The relaxation intensity $\Delta\varepsilon$ and the characteristic frequency f_c are given by $\Delta\varepsilon = \varepsilon_l - \varepsilon_h$ and $f_c = 1/(2\pi\tau)$, respectively. The dielectric relaxation parameters ε_h , ε_l , τ and β were obtained by fitting equation (1) to the dielectric spectra.

Figure 2 shows the ε_l obtained at 25, 10, 0, –10 and –20 °C as a function of C_{TX} . At temperatures above 0 °C, ε_l decreases almost linearly with increasing C_{TX} , whose slope slightly depends on temperature. Similar relations were reported for various mixtures of water and polymers such as PEO, PVA and PVP [7–9] and nonionic microemulsions [6]. Below the freezing temperature of bulk water, however, ε_l decreases at C_{TX} below 50 wt% at –10 °C and at C_{TX} below 60 wt% at –20 °C because of the freezing of bulk water. Since the dielectric relaxation time of ice is larger than 0.1 μs , (i.e., the relaxation frequency at 0 °C is about 16 kHz) [16], there is no contribution of frozen water to the dielectric spectra in the frequency range above 1 MHz. The decrement of ε_l is proportional to the amount of frozen water and the remaining ε_l is mainly attributed to non-freezing water; the molar ratio of non-freezing water to C_{TX} is roughly constant at $C_{\text{TX}} < 50$ wt% at –10 °C and $C_{\text{TX}} < 60$ wt% at –20 °C. It is clear that water did not freeze at $C_{\text{TX}} \geq 50$ wt% at –10 °C and $C_{\text{TX}} \geq 60$ wt% at –20 °C.

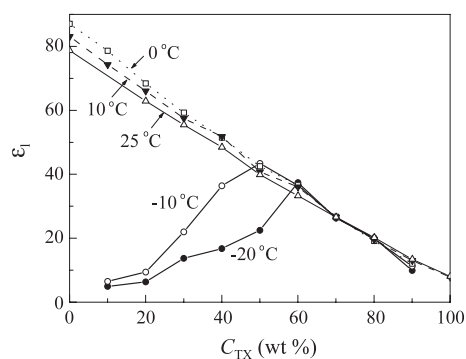


Figure 2. The low-frequency limit of relative permittivity ϵ_1 as a function of TX concentration C_{TX} . The measurement temperature is indicated beside each curve.

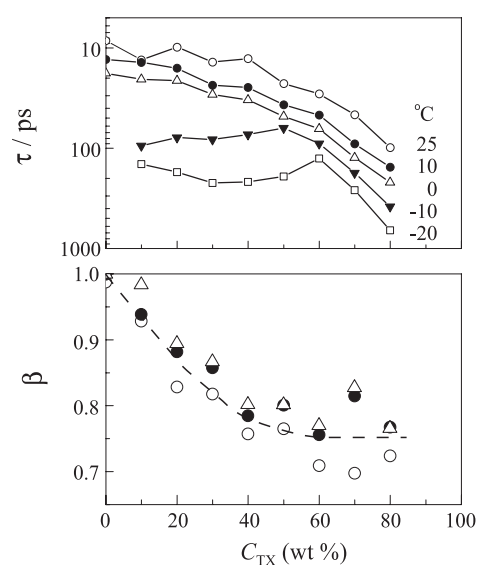


Figure 3. The relaxation time τ and the Cole–Cole parameter β as a function of TX concentration C_{TX} . Measurement temperature: 25 °C(O), 10 °C(●), 0 °C(Δ), –10 °C(▼) and –20 °C(□). In the β – C_{TX} plots, the data at –10 and –20 °C are not shown and the broken line is a guide to the eye.

Since TX has a molecular weight of 647 and ten EO units, the molar ratio of water to EO unit is 3.6 at $C_{TX} = 50$ wt% and 2.4 at $C_{TX} = 60$ wt%.

Figure 3 shows the τ and β obtained at temperatures from 25 to –20 °C as a function of C_{TX} . As C_{TX} increases, τ increases at temperatures above 0 °C. Below the freezing point of bulk water, the relaxation time is rather independent of C_{TX} below 50 wt% at –10 °C and below 60 wt% at –20 °C. The data points of β seem to trace the same curve, irrespective of temperature; β decreases with increasing C_{TX} and then levels off above 60 wt%.

3.2. Conductivity of an TX–aqueous electrolyte system

The conductivity behaviour of mixtures of TX and an aqueous electrolyte solution provides information of water tightly associated with TX as well as the dielectric relaxation. The

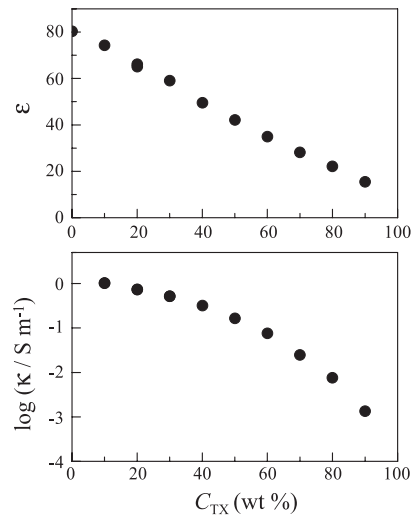


Figure 4. The relative permittivity ϵ and conductivity κ of mixtures of TX and a 100 mM KCl solution as a function of TX concentration C_{TX} . Data were obtained at 5.2 MHz and at 25 °C.

mixtures of TX with KCl and NaCl solutions showed dielectric relaxation above 100 MHz, which was almost the same as that of TX–pure water mixtures; the relationships between the low-frequency relative permittivity and C_{TX} were independent of the presence of electrolytes (cf figures 2 and 4). Hence, our attention is focused only on the conductivity at low frequencies far below the dielectric relaxation. Figure 4 shows C_{TX} dependence of the conductivity of TX–100 mM KCl mixtures at 5.2 MHz, where there is little influence of electrode polarization and no contribution of water relaxation (i.e., the conductivity at 5.2 MHz has been used as the dc conductivity). The relationship between the conductivity and C_{TX} is nonlinear, and the conductivity decreases steeply with C_{TX} , especially above 50 wt%.

In previous studies, the conductivity behaviour of polymer–water and detergent–water mixtures has been analysed using mixture equations for heterogeneous systems [11–13]. The systems are modelled such that particles of conductivity κ_p are dispersed in a conducting medium of conductivity κ_a at volume fraction P . Following Bruggeman’s effective-medium approximation [17] the conductivity κ of the system is given by

$$\frac{\kappa - \kappa_p}{\kappa_a - \kappa_p} \left(\frac{\kappa_a}{\kappa} \right)^{1/3} = 1 - P, \quad (2)$$

which was originally derived by Bruggeman for the relative permittivity of a spherical particle suspension. Alternatively, Looyenga [18] derived a mixture equation that is applicable to the relative permittivity of a binary mixture of arbitrary shape, and its conductivity form is

$$\kappa^{1/3} = (1 - P)\kappa_a^{1/3} + P\kappa_p^{1/3}. \quad (3)$$

Since TX micelles in an aqueous electrolyte solution meet the conditions $\kappa \gg \kappa_p$ and $\kappa_a \gg \kappa_p$, equations (2) and (3) respectively become

$$(\kappa/\kappa_a)^{2/3} = 1 - P \quad (4)$$

and

$$(\kappa/\kappa_a)^{1/3} = 1 - P. \quad (5)$$

If TX micelles have a non-conducting hydration shell, equations (4) and (5) are rewritten as

$$(\kappa/\kappa_a)^{2/3} = 1 - \alpha P \quad (6)$$

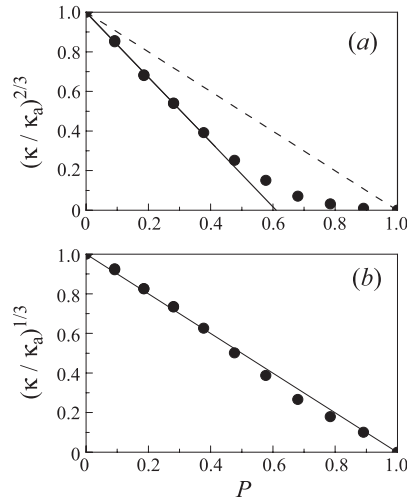


Figure 5. The conductivity ratios $(\kappa/\kappa_a)^{2/3}$ and $(\kappa/\kappa_a)^{1/3}$ as a function of volume fraction P . κ_a is the conductivity at $P = 0$. The data are the same as in figure 4. (a) The solid line and the dotted line are calculated from equation (6) with $\alpha = 1.63$ and $\alpha = 1.0$, respectively, and (b) the solid line is calculated from equation (7) with $\alpha = 1.0$.

and

$$(\kappa/\kappa_a)^{1/3} = 1 - \alpha P, \quad (7)$$

with the volume ratio α of the micelle with the hydration shell to the bare micelle. According to equations (6) and (7), the conductivity ratios $(\kappa/\kappa_a)^{2/3}$ and $(\kappa/\kappa_a)^{1/3}$ are inversely proportional to P and the slope provides the value of α .

In figure 5, the conductivity ratios $(\kappa/\kappa_a)^{2/3}$ and $(\kappa/\kappa_a)^{1/3}$ calculated from the data in figure 4 are plotted against P , which is converted from C_{TX} by assuming $0.908 \text{ cm}^3 \text{ g}^{-1}$ for the specific partial volume of TX [19]. A linear relation between $(\kappa/\kappa_a)^{2/3}$ and P is found at $P \leq 0.4$, whereas $(\kappa/\kappa_a)^{1/3}$ is proportional to P over the whole range of P . The values of α are 1.63 for equation (6) and 1.0 for equation (7). Similar relations were obtained with the electrolyte solutions of 10 mM KCl, 1 M KCl and 100 mM NaCl used as the aqueous phase. The quantity $\alpha - 1$ is the volume ratio of hydration water to TX, being given by

$$\alpha - 1 = \frac{v_w}{v_{TX}} \frac{m_{hw} M_w}{m_{TX} M_{TX}}, \quad (8)$$

where v is specific partial volume, m is molar concentration and M is molecular weight, and subscripts TX, hw and w refer to TX, hydration water and bulk water, respectively. For TX with n EO units, the number of associated water molecules per EO unit n_{hw} is given by

$$n_{hw} = \frac{m_{hw}}{m_{EO}} = \frac{m_{hw}}{n m_{TX}} = (\alpha - 1) \frac{v_{TX} M_{TX}}{n v_w M_w}, \quad (9)$$

where m_{EO} is the molar concentration of EO units. With $M_{TX} = 647$, $n = 10$ and $v_{TX} = 0.908 \text{ cm}^3 \text{ g}^{-1}$, n_{hw} can be calculated from the observed α . Table 1 summarizes the values of α determined using Bruggeman's equation and the n_{hw} calculated from equation (9). The n_{hw} values of 2–3 are in good agreement with the number of non-freezing water molecules per OE unit. The n_{hw} is inversely proportional to the ionic strength of the aqueous solution, suggesting that ions disturb the hydrogen bonding between water molecules and EO units. In contrast to Bruggeman's equation, Looyenga's equation provided $\alpha = 1.0$, indicating that there is no associated water.

Table 1. The number of water molecules n_{hw} associated with an ethylene oxide unit. The values of n_{hw} were calculated from the values of α determined using Bruggeman's equation.

Electrolyte solutions	α	n_{hw}
10 mM KCl	1.80	2.66
100 mM KCl	1.63	2.09
1 M KCl	1.53	1.75
100 mM NaCl	1.57	1.90

4. Discussion

4.1. Number of hydration water molecules per EO unit

The number n_{hw} of hydration water molecules per EO unit for the TX–water systems has been estimated from (i) the amount of non-freezing water measured by dielectric measurements at temperature below freezing point of bulk water and (ii) the analysis of the conductivity behaviour of TX–aqueous electrolyte mixtures. About two water molecules per EO unit are unable to freeze at -20°C . There are about four non-freezing water molecules per EO unit at -10°C , some of which could be loosely bound water that is squeezed out at -20°C . Alternatively, the relationship between the conductivity and C_{TX} was analysed using Bruggeman's mixture equation, suggesting that two to three water molecules per EO unit are tightly associated with the TX micelles. The results are consistent with those obtained for TX–water mixtures by NMR [4] and FT-IR [5].

The values of n_{hw} estimated in this paper are comparable to those reported for PEO–water mixtures and nonionic microemulsions. Kaatze [7, 8] estimated that five hydration water molecules per EO unit from the dielectric relaxation by assuming two types of water having different relaxation times. Foster [6] reported values of two to four molecules of water per EO unit for interfacial water associated with oil droplets in nonionic microemulsions (containing Tween 60 as an emulsifier) [6]. Bordi *et al* [12] analysed the conductivity behaviour of PEO ($\text{MW} = 6 \times 10^3 - 5 \times 10^6$) in aqueous electrolytes using Bruggeman's equation and Looyenga's equation, and found that Looyenga's equation provided a good approximation for not only the conductivity but also other transport properties to yield $n_{\text{hw}} = 0.6$. On the other hand, Bisal *et al* [13] applied Bruggeman's mixture equation to aqueous solutions of PEO and TX, to estimate the values of n_{hw} to be 1–2 for PEO ($\text{MW} = 200 - 1000$) and 0.7 for TX. The analysis of the conductivity behaviour, however, has a drawback that the results depend on the mixture equations used.

In summary, about two water molecules per EO unit are tightly associated, which are non-freezing. A few molecules per EO unit are loosely associated and gradually freeze. TX micelles have a shell of water molecules tightly associated with the EO chain and, as a whole, behave as less-conducting particles in a conducting medium.

4.2. Dielectric relaxation of hydration water

The dielectric behaviour of TX–water mixtures was similar to that observed for various water mixtures of polymers such as PEO, PVA and PVP [7–10] and nonionic microemulsions [6]. As C_{TX} increases, the Cole–Cole parameter β decreases and the principal relaxation time τ increases. The decrease in β (i.e., broadening of the relaxation curve) is correlated with the increase in the principal relaxation time. One possible explanation of the correlation, provided by Kaatze, is that there are at least two types of water: 'free' water and 'hydration' water [7, 8].

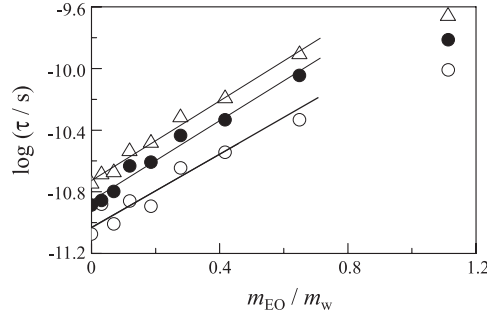


Figure 6. The logarithm of the relaxation time τ as a function of molar ratio of EO unit to water, $m_{\text{EO}}/m_{\text{w}}$. Linear regression lines are obtained for data points at 25 °C (○), 10 °C (●) and 0 °C (△) at $m_{\text{EO}}/m_{\text{w}} < 0.7$ or at $C_{\text{TX}} \leq 60$ wt%.

Table 2. The relaxation times τ_{w} and τ_{hw} of free and hydration water estimated from the linear regression lines shown in figure 6 using equation (12) with $n_{\text{hw}} = 2$.

T (°C)	$\tau_{\text{hw}}/\tau_{\text{w}}$	τ_{w} (ps)	τ_{hw} (ps)
25	3.9	9.3	36.3
10	4.4	13.8	60.7
0	4.4	18.6	81.8

The dielectric spectra observed were decomposed into two relaxation terms of the Debye type, corresponding to the two types of water, as

$$\varepsilon^* = \varepsilon_{\text{h}} + \Delta\varepsilon \left(\frac{1 - x_{\text{hw}}}{1 + j\omega\tau_{\text{w}}} + \frac{x_{\text{hw}}}{1 + j\omega\tau_{\text{hw}}} \right), \quad (10)$$

where x_{hw} is the molar ratio of hydration water to the whole water, and τ_{hw} and τ_{w} are the relaxation times of hydration and free water, respectively. For PEO solutions, the values of n_{hw} and $\tau_{\text{hw}}/\tau_{\text{w}}$ were about 5 and 2, respectively, independent of the number n of EO units for PEO of $n > 10$.

Shinyashiki *et al* [9] found that the logarithm of the relaxation time of PVP–water mixtures was well represented by a linear function of x_{hw} :

$$\log \tau = (1 - x_{\text{hw}}) \log \tau_{\text{w}} + x_{\text{hw}} \log \tau_{\text{hw}}. \quad (11)$$

Since, in the case of TX–water mixtures, x_{hw} is given by $x_{\text{hw}} = n_{\text{hw}}(m_{\text{EO}}/m_{\text{w}})$, equation (11) is rewritten as

$$\log \tau = \log \tau_{\text{w}} + n_{\text{hw}} \frac{m_{\text{EO}}}{m_{\text{w}}} \log \left(\frac{\tau_{\text{hw}}}{\tau_{\text{w}}} \right). \quad (12)$$

Hence, $\log \tau$ is a function of the molar ratio of EO units to water, $m_{\text{EO}}/m_{\text{w}}$. Figure 6 shows plots of $\log \tau$ against $m_{\text{EO}}/m_{\text{w}}$ for the data at 25, 10 and 0 °C. Linear relationships between $\log \tau$ and $m_{\text{EO}}/m_{\text{w}}$ were found as expected from equation (12). The intersection at $m_{\text{EO}}/m_{\text{w}} = 0$ provides the value of $\log \tau_{\text{hw}}$, and the slope is $n_{\text{hw}} \log(\tau_{\text{hw}}/\tau_{\text{w}})$, from which the ratio $\tau_{\text{hw}}/\tau_{\text{w}}$ is obtained if the value of n_{hw} is given. Table 2 shows the τ_{w} , $\tau_{\text{hw}}/\tau_{\text{w}}$ and τ_{hw} , obtained with $n_{\text{hw}} = 2$. If we adopt $n_{\text{hw}} = 5$, the ratio $\tau_{\text{hw}}/\tau_{\text{w}}$ becomes 1.7 at 25 °C, being comparable to that obtained by Kaatze.

Foster *et al* [6] calculated the dielectric relaxation of an oil droplet with interfacial water from that of the microemulsion using Wagner's equation and Hanai's equation. Hanai's equation was derived from Wagner's equation following Bruggeman's effective-medium

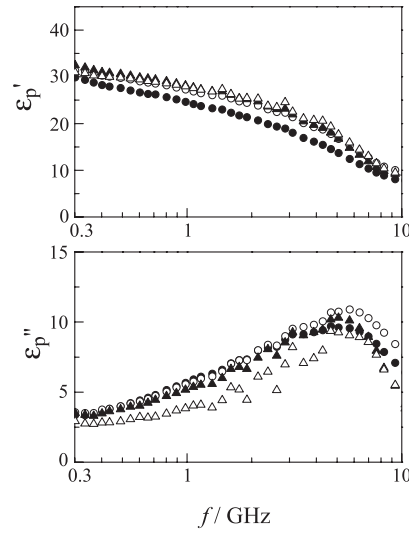


Figure 7. The real ϵ'_p and the imaginary ϵ''_p parts of the complex permittivity ϵ_p^* of a TX micelle with hydration water as a function of frequency f . The value of ϵ'_i was calculated from the dielectric spectra of water and TX–water mixtures measured at 25 °C using Hanai's equation with $n_{hw} = 2$. The effective volume fraction αP is 0.29, 0.44, 0.58 and 0.73 for $C_{TX} = 20(\Delta)$, 30(\blacktriangle), 40 (\circ) and 50 wt% (\bullet), respectively.

procedure. The calculated dielectric relaxation of an oil droplet with interfacial water at 25 °C showed Debye-type relaxation with $f_c = 5\text{--}6$ GHz, and $\Delta\epsilon = 25$, which might be due to the relaxation of the interfacial water. The same analysis has been applied to the dielectric spectra in figure 1 using Hanai's equation [20],

$$\frac{\epsilon^* - \epsilon_p^*}{\epsilon_a^* - \epsilon_p^*} \left(\frac{\epsilon_a^*}{\epsilon^*} \right)^{1/3} = 1 - \alpha P, \quad (13)$$

where ϵ^* , ϵ_p^* and ϵ_a^* are the complex permittivities of the suspension, the droplet and the medium, respectively, and αP is the volume fraction of TX micelles with hydration water. Figure 7 shows the results calculated from equation (13) with $\alpha = 1.6$ corresponding to $n_{hw} = 2$. The dielectric spectra were almost independent of C_{TX} between 20 and 40 wt%, having $\epsilon_1 \approx 30$ and $f_c \approx 5$ GHz (or $\tau \approx 30$ ps). The value of τ is comparable to that of τ_{hw} at 25 °C estimated in table 2 and is similar to that of oil droplets with hydration water reported by Foster *et al* [6]. The ϵ_1 value of 30 corresponds to that of the TX–water mixture of $C_{TX} = 64$ wt% (see figure 2), which yields about two water molecules per EO unit. The analysis using Hanai's equation with $n_{hw} = 2$, therefore, provides self-consistent results.

References

- [1] Tanford C and Reynolds J A 1976 *Biochim. Biophys. Acta* **457** 133
- [2] London E and Brown D 2000 *Biochim. Biophys. Acta* **1508** 182
- [3] Ahir S A, Petrov P G and Terentjev E M 2002 *Langmuir* **18** 9140
- [4] Beyer K 1982 *J. Colloid Interface Sci.* **86** 73
- [5] Kimura N, Umemura J and Hayashi S 1996 *J. Colloid Interface Sci.* **182** 356
- [6] Foster K R, Epstein B R, Jenin P C and Mackay R A 1982 *J. Colloid Interface Sci.* **88** 233
- [7] Kaatz U 1978 *Prog. Colloid Polym. Sci.* **65** 214
- [8] Kaatz U, Göttmann O, Podbielski R, Pottel R and Terveer U 1978 *J. Phys. Chem.* **82** 112

- [9] Shinyashiki N, Matsumura Y, Miura N, Yagihara S and Mashimo S 1994 *J. Phys. Chem.* **98** 13612
- [10] Shinyashiki N, Yagihara S, Arita I and Mashimo S 1998 *J. Phys. Chem. B* **102** 3249
- [11] Foster K R, Cheever E and Leonard J B 1984 *Biophys. J.* **45** 975
- [12] Bordi F, Cametti C and Biasio A D 1988 *J. Phys. Chem.* **92** 4772
- [13] Bisal S, Bhattacharya P K and Moulik S P 1990 *J. Phys. Chem.* **94** 4212
- [14] Asami K 2005 *Langmuir* **21** 9032
- [15] Cole K S and Cole R H 1941 *J. Chem. Phys.* **9** 341
- [16] Davies M 1965 *Some Electrical and Optical Aspects of Molecular Behaviour* (Oxford: Pergamon)
- [17] Bruggeman D A G 1935 *Ann. Phys.* **24** 636
- [18] Looyenga H 1965 *Physica* **31** 401
- [19] Tanford C, Nozaki Y, Reynolds J A and Makino S 1974 *Biochemistry* **13** 2369
- [20] Hanai T 1960 *Kolloid Z.* **171** 23