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## Effect of counterions on anionic fluorocarbon surfactant micelles by dielectric spectroscopy

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The dielectric spectra of sodium perfluorooctanoate (NaPFO), ammonium perfluorooctanoate (APFO) and tetraalkylammonium perfluorooctanoate ( $C_7F_{15}COON(C_nH_{2n+1})_4$ ,  $n = 1, 2, 3, 4$ , namely, TMPFO, TEPFO, TPPFO and TBPFO) were studied in the frequency range from 40 Hz to 110 MHz. An obvious dielectric relaxation was observed in each aqueous system whose low-frequency limit of relative permittivity ( $\epsilon_1$ ) was divided into two groups based on their dependence on concentration, except there were two relaxations for TBPFO. Furthermore, their relaxation mechanism was analyzed and attributed to the radial diffusion of the free counterions in the diffuse layer. What's more, combined with the average radius  $\bar{R}$  of these micelles obtained on the basis of the Grosse's model, the difference between these two groups and their structural information were speculated. It was proved that the type of counterion has an important influence on the structure and properties of fluorocarbon surfactants.

### 1. Introduction

With the increasingly widespread application of surfactants in industrial production, research and daily life, fluorocarbon surfactants have gradually become the focus of industrial research.<sup>1–5</sup> Because the introduced fluorine completely or partially replaces the hydrogen in the conventional hydrocarbon chain, it forms a special surfactant with a fluorocarbon chain as a hydrophobic and oleophobic group, which endows it with superior hydrophobic oleophobicity, high surface activity and other special properties.<sup>1,2,4,5</sup> However, since they are hard to be degraded in the environment and have been listed as persistent organic pollutants (POPs), it is urgent to find alternatives and ways to offset or degrade their toxicity and bioaccumulative properties, which requires a comprehensive understanding of the properties of such surfactants.<sup>4,6–11</sup>

Micelle solutions would experience remarkable structure changes (from spherical to rodlike, wormlike or more complex morphologies) with changing exterior conditions including concentration,<sup>12,13</sup> which has attracted much attention from the field of molecular aggregates and self-assembly.<sup>13–16</sup> And there have been manifold methods and techniques applied such as the thermodynamic method,<sup>17</sup> nuclear magnetic resonance (NMR),<sup>18–20</sup> static or dynamic light scattering (SLS or DLS),<sup>21,22</sup> fluorescence,<sup>23</sup> small-angle neutron scattering (SANS) and Raman spectroscopy,<sup>24</sup> and small-angle X-ray measurement (SAXS)<sup>25</sup> and many others.<sup>26–29</sup>

It is generally believed that the counterions of hydrocarbon surfactants mainly affect the solubility of surfactants, but have little impact on surfactivity.<sup>12,30,31</sup> Zana *et al.*,<sup>32</sup> in one of their articles about the counterions of surfactants, have pointed out that there is very little change for the critical micelle concentration (cmc) of surfactants when their counterions change from  $Li^+$  to  $Cs^+$ , and even to divalent counterions, such as  $Mg^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$ . However, take ammonium perfluorooctane (APFO) and sodium perfluorooctanoate (NaPFO) as an example. The surfactivity of the former is higher than that of the latter,<sup>33</sup> which is well-known. An explanation of this is a small amount of perfluorooctanoic acid generated by the hydrolysis of APFO (a strong acid and weakly alkaline salt) involved in the surface adsorption and micellation of APFO.<sup>33</sup> In addition, Tabor *et al.*<sup>34,35</sup> and other groups<sup>36–38</sup> argued that surfactant counterions, whether inorganic, such as sodium and potassium, or organic ions, like alkylammonium, have an obvious influence on the behavior and properties of surfactants including solubility and surfactivity.

Dielectric relaxation spectroscopy (DRS) is a kind of non-invasive method, which can be used to monitor the structural changes and orientation motion *in situ* and provide insights into mechanisms and electrical properties on the molecular and macroscopic levels over an extremely wide range of characteristic frequencies ( $10^{-6}$ – $10^{11}$  Hz).<sup>39–42</sup> Furthermore, DRS has been applied to analyze the physical and chemical properties of heterogeneous systems such as colloidal particles,<sup>43–45</sup> micelles,<sup>46–52</sup> microemulsions,<sup>52–55</sup> vesicles,<sup>56</sup> and biological cell dispersions.<sup>57</sup>

It is widely known that low-frequency dielectric relaxation and Maxwell–Wagner dielectric relaxation are the two typical mechanisms for suspensions, which are sensitive to the polarization

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of the electric double layer of the disperse particles. A theoretical explanation of the low-frequency relaxation was first given by Schwarz,<sup>58</sup> based on which Dukhin and Shilov<sup>59,60</sup> put forward the concept of a diffuse double layer. Later, experiencing the development of O'Konski,<sup>61</sup> who applied the Maxwell-Wagner<sup>62,63</sup> interfacial polarization theory of spherical particles to the presence of a conducting shell, a concise model for the electrolyte suspension has been given by Grosse.<sup>64</sup> And it has been successfully applied to explain the relaxation mechanisms of suspensions of colloidal particles<sup>65-67</sup> (including the micelle aqueous solution<sup>49</sup>).

The TBPFO aqueous solution, which could experience obvious phase and structure transition with the change of temperature or concentration, is appropriate for being monitored by DRS theoretically and has been confirmed by our previous work.<sup>68</sup> Here, we want to extend this kind of insight into other effect factors on the properties of anionic fluorocarbon surfactants, namely, this work aims at the effect of the types of counterions on the properties of perfluorooctanoate by dielectric spectroscopy in the frequency range of 40 Hz to 110 MHz. The change in counterions is very obvious, not only for the size of ions, but also for their hydrophobicity and other properties, in which case, the change of dielectric spectrum is worth being paid attention. Furthermore, the mechanism and cause of relaxation in these systems was presented, which is based on the characteristics of these ions and the structural characteristics of micelles formed by them and Grosse's model.

## 2. Experimental section

### 2.1. Materials

Perfluorooctanoate acid ( $C_7F_{15}COOH$ ) and tetraalkylammonium hydroxides ( $N(C_nH_{2n+1})_4OH$ ,  $n = 1, 2, 3, 4$ ) were purchased from

Acros Organics. Ammonium perfluorooctanoate ( $C_7F_{15}COONH_4$ , APFO) was a product of Sigma. Tetraalkylammoniumperfluorooctanoate  $C_7F_{15}COON(C_nH_{2n+1})_4$  ( $n = 1, 2, 3, 4$ ) (TMPFO, TEPFO, TPPFO and TBPFO, respectively) were prepared by neutralizing perfluorooctanoic acid with tetrabutylammonium hydroxides, as previously described.<sup>69,70</sup> All of their structural formula are shown in Fig. 1. The critical micelle concentrations (cmc) of NaPFO, APFO, TMPFO, TEPFO, TPPFO and TBPFO are 31.2, 27.3, 12.1, 6.6, 3.8 and 2.3  $mmol L^{-1}$  at 25 °C, respectively.<sup>71</sup> In order to compare with the previous investigations,<sup>68</sup> the experimental concentration of these surfactants ranged from 20 to 87  $mmol L^{-1}$ , all exceeding the cmc except for NaPFO and APFO.

### 2.2. Dielectric measurement

Dielectric spectra with frequency from 40 Hz to 110 MHz were obtained by an HP 4294A Precision Impedance Analyzer with a 16047E Spring Clip fixture (Agilent Technologies). All the tested specimens were placed in a dielectric measurement cell with concentric cylindrical platinum electrodes<sup>72</sup> with the same volume of the solutions, namely 1 mL. The experimental data were corrected for deducting the residual inductance arising from the terminal leads and measurement cell by using Schwan's method.<sup>73</sup> The experiment temperature was 20 °C.

### 2.3. Determination of the relaxation parameters

The parameters of dielectric relaxation such as the limiting values of low- and high-frequency of permittivity ( $\epsilon_l, \epsilon_h$ ) and conductivity ( $\kappa_l, \kappa_h$ ) and the characteristic relaxation frequency ( $f_0$ ) can be obtained by fitting the Cole-Cole empirical equation,<sup>74,75</sup> which includes one ( $i = 1$  for NaPFO, APFO,

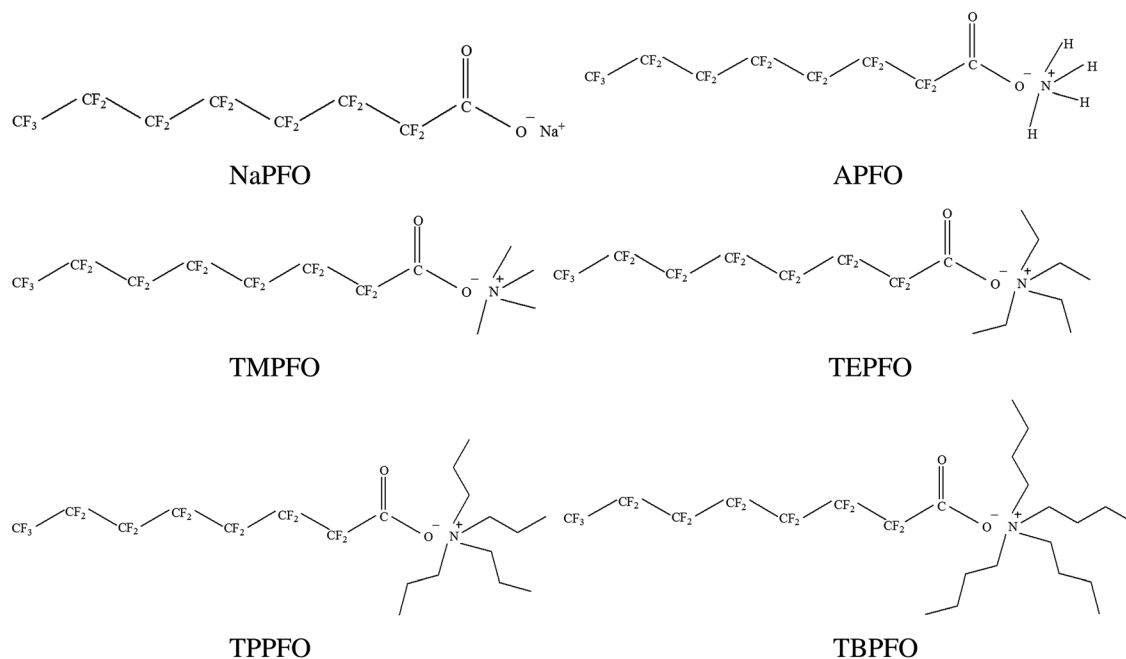


Fig. 1 The structural formula of NaPFO, APFO, TMPFO, TEPFO, TPPFO and TBPFO.

TMPFO, TEPFO and TPPFO) or two ( $i = 1, 2$  for TBPFO) Cole-Cole's terms.

$$\varepsilon^* = \varepsilon_h + \sum_i \frac{\Delta\varepsilon_i}{1 + (j\omega\tau_i)^{\beta_i}} + A\omega^{-m} \quad (1)$$

where  $\varepsilon^*$  is the complex permittivity,  $\varepsilon''(=\kappa - \kappa_1)/\omega\varepsilon_0$  is the dielectric loss,  $\omega (=2\pi f)$  is the angular frequency,  $\kappa_1$  is the low-frequency limit of conductivity,  $\Delta\varepsilon(=\varepsilon_1 - \varepsilon_h)$  is the permittivity increment,  $\varepsilon_0 (=8.854 \times 10^{-12} \text{ F m}^{-1})$  is the permittivity of vacuum,  $\tau (=2\pi f_0^{-1})$  is the relaxation time,  $\beta(0 < \beta \leq 1)$  is the Cole-Cole parameter indicating the dispersion of the relaxation time  $\tau$ , and  $J = \sqrt{-1}$ .  $A$  and  $m$  are adjustable parameters determined by fitting the experimental data simultaneously.

### 3. Results and discussion

#### 3.1. Dielectric behavior of anionic fluorocarbon surfactants in aqueous solutions

Fig. 2 shows 3D representations of the dielectric loss spectra of NaPFO, APFO, TMPFO, TEPFO, TPPFO and TBPFO aqueous solutions. The number of dielectric relaxations can be determined from the number of peaks represented in Fig. 2. It can be seen from Fig. 2 that, therefore, there is one relaxation in these systems except for the TBPFO system in which two relaxations were found. The

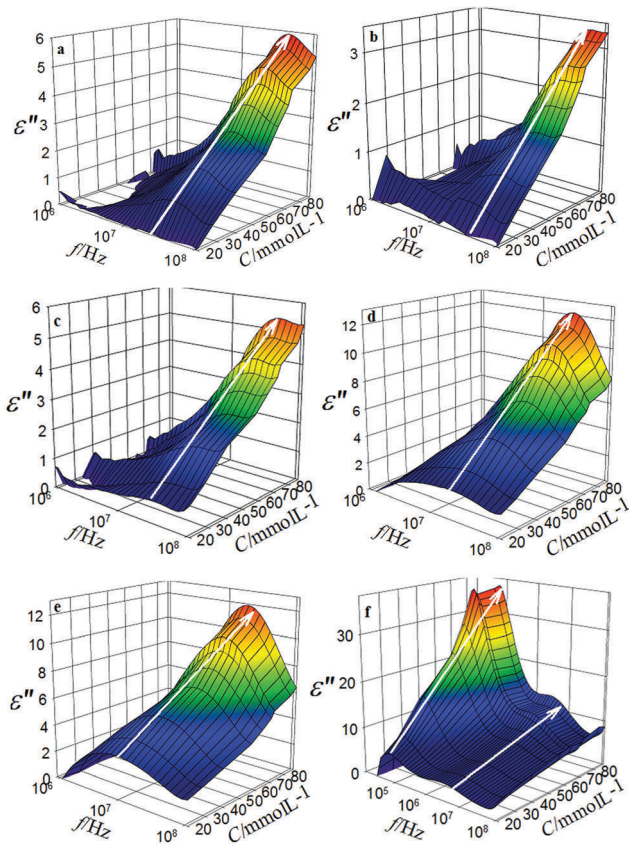


Fig. 2 Three-dimensional representations of the dielectric loss spectra of (a) NaPFO, (b) APFO, (c) TMPFO, (d) TEPFO, (e) TPPFO and (f) TBPFO aqueous solutions.

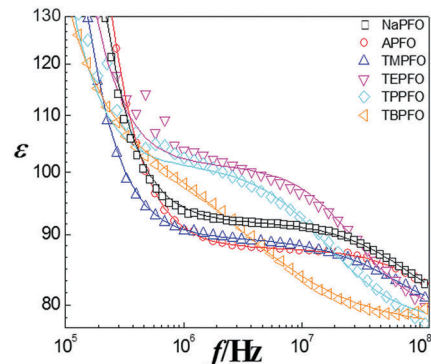


Fig. 3 Relative permittivity spectra extracted from each figure in Fig. 1 at the same concentration of  $70 \text{ mmol L}^{-1}$ . The solid lines represent the best fitting curves evaluated from eqn (1).

reason is that the aggregates of TBPFO are rodlike micelles when the temperature is  $20 \text{ }^\circ\text{C}$  in aqueous solution,<sup>69</sup> whereas the aggregates of other fluorocarbon surfactants are spherical micelles.

In order to discern the variety of the dielectric relaxation in different surfactant solutions, relative permittivity spectra of these solutions are exhibited in Fig. 3 when the concentration is  $70 \text{ mmol L}^{-1}$  in which the best-fit results were also shown simultaneously and were in good agreement with the experimental data. Furthermore, these dielectric parameters represented the real properties of the whole system because the effect of the electrode polarization has been eliminated. All the above also indicate that the determination of the number of relaxations is reasonable.

The dependency of several dielectric parameters on the concentration of different surfactants is shown in Fig. 4. It can be seen that  $\varepsilon_1$  and  $\kappa_1$  increase with the concentration in all systems (Fig. 4a and b). The characteristic relaxation frequency  $f_0$  (Fig. 4c) approximately keeps constant with concentration except for APFO aqueous solution in which  $f_0$  increases a little but not obviously. Cole-Cole parameter  $\beta$  (Fig. 4d) is relatively large, which indicates that the dispersion of the relaxation is single, close to Debye-type relaxation. Comparing the dependence of these parameters on the concentration, however, it seems to follow different regularity for these parameters with the variety of surfactants, which may result from the properties of the micelles and the characteristics of the dielectric relaxation changing with the variety of the counterions of the surfactants. The essential reason of these differences and the relationship of the variational regularity with the micellar structures and properties will be discussed in the next part in detail.

#### 3.2. The reason for the effect of counterions on the dielectric properties of anionic fluorocarbon surfactants

In our previous work,<sup>68</sup> the dielectric relaxations of TBPFO aqueous solution have been investigated, and the essential mechanism of relaxations has been analyzed reasonably which is attributed to the radial diffusion of the free counterions surrounding the rodlike micelles in the diffuse layer. It can be seen from Fig. 1 that  $f_0$  changes parallelly with the variety of

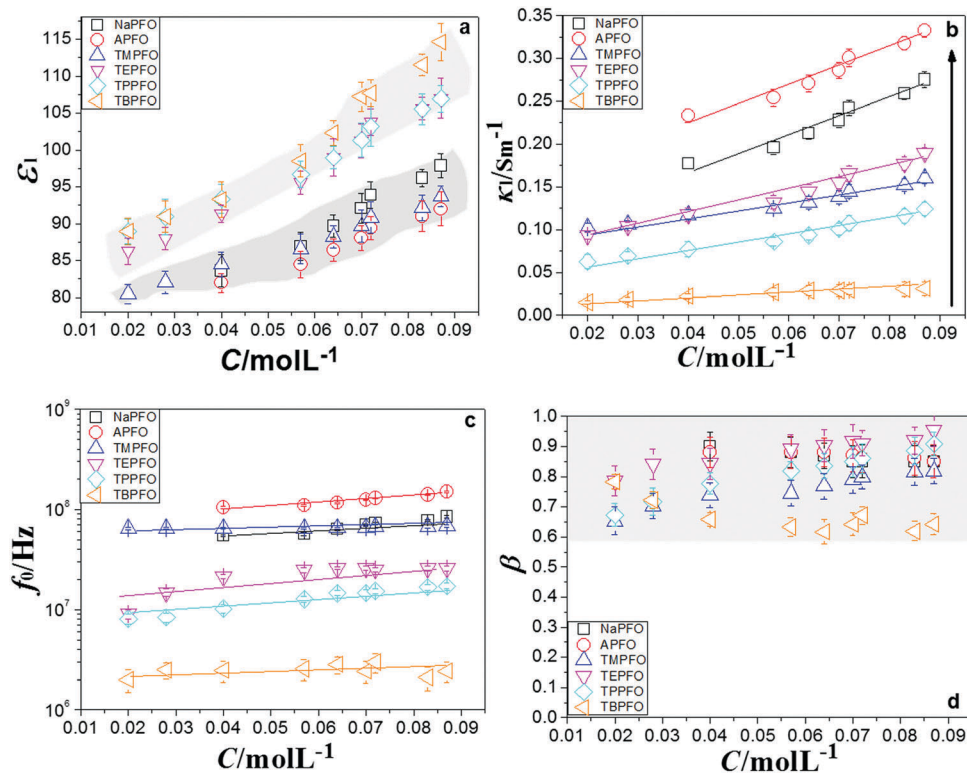


Fig. 4 Concentration dependence of several dielectric relaxation parameters obtained by fitting eqn (1): (a) low-frequency limit of the relative permittivity  $\epsilon_l$ , (b) low-frequency limit of the conductivity  $\kappa_l$ , (c) characteristic relaxation frequency  $f_0$ , and (d) Cole-Cole parameter  $\beta$ .

surfactants, so the mechanism of relaxation in these similar systems may be unvaried basically, which also enhances the possibility of contrast. Therefore, the relaxation of all investigated systems is ascribed to the radial diffusion of free counterions surrounding the micelles which can be interpreted by Grosse's model.<sup>64</sup>

The relaxation time in Grosse's model,<sup>64</sup> originated from the radial diffusion of the free counterions surrounding the micelles in the diffuse layer, can be represented by the following equation:

$$\tau = R^2/D_t \quad (2)$$

where  $D_t$  is the diffusion coefficient of the counterions, and  $R$  is the radius of a spherical particle.

The diffusion coefficient  $D_t$  of these counterions in the aqueous solutions are about  $1.34 \times 10^9 \text{ m}^2 \text{ s}^{-1}$  for  $\text{Na}^+$ ,<sup>76</sup>  $1.96 \times 10^9 \text{ m}^2 \text{ s}^{-1}$  for  $\text{NH}_4^+$ ,<sup>77</sup>  $1.38 \times 10^9 \text{ m}^2 \text{ s}^{-1}$  for  $\text{TMA}^+$ ,<sup>78</sup>  $1.00 \times 10^9 \text{ m}^2 \text{ s}^{-1}$  for  $\text{TEA}^+$ ,<sup>78</sup>  $0.70 \times 10^9 \text{ m}^2 \text{ s}^{-1}$  for  $\text{TPA}^+$ <sup>78</sup> and  $0.63 \times 10^9 \text{ m}^2 \text{ s}^{-1}$

for  $\text{TBA}^+$ ,<sup>78</sup> respectively. Thus, with them, the radius ( $R$ ) of these micelles can be calculated from the obtained relaxation time  $\tau$  by eqn (2). The detailed results are listed in Table 1 except for TBPFO systems, because the lengths of the long half-axis and the short half-axis of the rodlike micelles in TBPFO solutions have been reported in our previous work.<sup>68</sup> Although these results cannot be compared with those of other measurements for the reason that they have not been reported before, it can be found from Table 1 that these data are quite reasonable. It is well-known that the radius of the micelles is in the range of nanometers which is consistent with the results shown in Table 1.

Moreover, the average radius  $\bar{R}$  can be obtained as well in order to contrast with each other. They are 1.77 nm for the NaPFO system, 1.59 nm for the APFO system, 1.82 nm for the TMPFO system, 2.80 nm for the TEPFO system and 3.00 nm for the TPPFO system. The average radius  $\bar{R}$  of TBPFO is larger than that of the others, and there are two directions of  $\bar{R}$  ( $R_a$  and  $R_b$ ),

Table 1 The radius  $R$  of micelles at different concentrations of NaPFO, APFO, TMPFO, TEPFO, TPPFO and TBPFO aqueous solutions

$C$ (mmol L <sup>-1</sup> )	20	28	40	57	64	70	72	83	87
$R_{\text{NaPFO}}$ (nm)	—	—	1.97	1.93	1.82	1.74	1.71	1.65	1.58
$R_{\text{APFO}}$ (nm)	—	—	1.72	1.68	1.63	1.58	1.55	1.49	1.44
$R_{\text{TMPFO}}$ (nm)	1.84	1.84	1.84	1.83	1.83	1.81	1.80	1.80	1.79
$R_{\text{TEPFO}}$ (nm)	4.20	3.27	2.73	2.53	2.48	2.48	2.518	2.488	2.48
$R_{\text{TPPFO}}$ (nm)	3.71	3.66	3.30	2.96	2.77	2.75	2.70	2.58	2.54
$R_{\text{TBPFO}}$ (nm)	$R_a$	23.66	22.69	19.86	14.14	13.47	9.20	12.18	14.93
	$R_b$	2.69	2.15	1.89	1.70	1.65	1.61	1.62	1.62



because the micelles formed in TBPFO aqueous solution are rodlike.<sup>68</sup>

The results of such an average radius are closely related to the properties of the micelles and that of the counterions because the surfactants we studied here are the same except for their counterions. Furthermore, there have been some reports revealed:<sup>79</sup> when the counterion is  $\text{Na}^+$ ,  $\text{NH}_4^+$  or  $\text{TMA}^+$ , the area ( $\sigma$ ) of each surfactant occupied and the saturated adsorption capacity ( $\Gamma_{\text{cmc}}$ ) change very little; while the counterion is  $\text{TEA}^+$ ,  $\text{TPA}^+$  or  $\text{TBA}^+$ , the values of their  $\Gamma_{\text{cmc}}$  decrease and  $\sigma$  increases with the size of the counterions increasing. If the counterions did not insert into the surface adsorption layer, the values of all these  $\sigma$  should be very close. On the contrary, if there are counterions occupying the surface adsorption layer, the corresponding  $\sigma$  values will show a growing trend with the size of the counterions increasing. Obviously, due to the strong hydrophilicity of  $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{TMA}^+$ , they are not or rarely inserted into the surface adsorption layer (report indicated that only part of the  $\text{TMA}^+$  can insert into the surface adsorption layer of lauryl sulfate.<sup>42</sup> But, because of its relatively small volume, the overall impact on  $\sigma$  is very small); nevertheless,  $\text{TEA}^+$ ,  $\text{TPA}^+$  and  $\text{TBA}^+$  all have a certain degree of hydrophobicity, as a result they are more likely to insert into the surface adsorption layer. In addition, the longer the carbon chain of the counterion is, the greater the steric hindrance is, which will result in a larger  $\sigma$  and a smaller  $\Gamma_{\text{cmc}}$ . According to the analyses above, it can be roughly estimated for the size of their micelles on the basis of the hydrophobicity and space structure of these six ions. Because of the very small hydrophobicity of  $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{TMA}^+$ , they do not insert into the surface adsorption layer (like lower left in Fig. 5), consequently, the sizes of their micelles are only equal to the size of perfluorooctanoic acid, that is to say, the average radius  $\bar{R}$  of

these micelles is relatively small. While the hydrophobicity of  $\text{TEA}^+$ ,  $\text{TPA}^+$  and  $\text{TBA}^+$  is very strong, so the perfluorooctanoic acid ions and counterions partially entwined closely together (see lower right in Fig. 5), in which case, the size of the micelles contains both of them, so  $\bar{R}$  of these micelles is a little larger. Besides, with the carbon chain becoming longer, the average radius of the micelles will also grow greater. It is worth mentioning that these above analyzed theoretical results are in accordance with the results we have calculated from our experimental data.

According to the calculated average radius  $\bar{R}$  of the micelles, the structural information of these systems can be speculated. And the irregular variation of the dielectric parameters with the variety of surfactants in the above Fig. 4 also can be interpreted on the basis of this information.

It is known that counterions dissociate in micelle solutions. Some of them form counterion clouds that cover the surface of the micelles. If the shapes of the counterion clouds deviate from symmetry, then a dipole moment  $\mu_0$  will be induced.<sup>46</sup> Therefore, micelles with counterion clouds can be regarded as a dipole to some extent. The permittivity characterizing the polarization capability of materials is related to the dipole moment  $\mu_0$  and the molecular number  $n$  in unit volume.<sup>80</sup> At the beginning of the relaxation,  $\varepsilon_1$  is close to the whole permittivity  $\varepsilon$  of the solution. When  $n$  keeps constant at the same concentration of surfactants,  $\varepsilon_1$  is mostly influenced by  $\mu_0$ . It can be known from Table 1 and the analysis above that the scales of micelles are divided into two groups according to  $\bar{R}$ . They are the small-scaled group of  $\bar{R}$  composed of NaPFO, APFO and TMPFO and the big-scaled group of  $\bar{R}$  consisting of TEPFO, TPPFO and TBPFO. As a result of the dependence of  $\mu_0$  on the  $\bar{R}$  of micelles,  $\mu_0$  increases with the  $\bar{R}$ , which shows the reason why  $\varepsilon_1$  increases with the concentration increasing and the values of  $\varepsilon_1$  are also separated into two groups as shown in Fig. 4a. Walden's<sup>80</sup> law points out that the conductivity and the viscosity of a substance is a fixed value for a confined dielectric liquid. It has been found that the viscosity of these solutions increases with the counterions in the experiments. The increasing order is APFO, NaPFO, TMPFO, TEPFO, TPPFO and TBPFO. So  $\kappa_1$  also increases with the counterions in that order, as shown in Fig. 4b. In each micellar solution of surfactant, however,  $\varepsilon_1$  and  $\kappa_1$  both increase with the concentration because of the increase of  $n$ . All above explained why the variational tendency of  $\varepsilon_1$  and  $\kappa_1$  is different in Fig. 4a and b and indirectly confirmed the above mentioned results (Fig. 5).

For the relaxation frequency  $f_0$  in Fig. 4c, since the mechanism of the relaxation is already known, the variety of  $f_0$  can be explained by the diffusion coefficient  $D_t$  of these counterions and the average radius  $\bar{R}$  of these micelles with eqn (2). It is interesting that  $D_t$  of APFO is the biggest one and  $\bar{R}$  is the smallest one, so  $f_0$  of APFO is bigger than that of any other in these six systems. Because  $D_t$  and  $\bar{R}$  of NaPFO are both in the middle of the values and similar to those of TMPFO, their  $f_0$  values are in-between values, too. For TEPFO, TPPFO and TBPFO,  $f_0$  will be proportional to the increase of  $D_t$  and the decrease of  $\bar{R}$ .

Fig. 6 shows the dependence of the permittivity increment  $\Delta\varepsilon$  calculated by fitting the experimental data on the

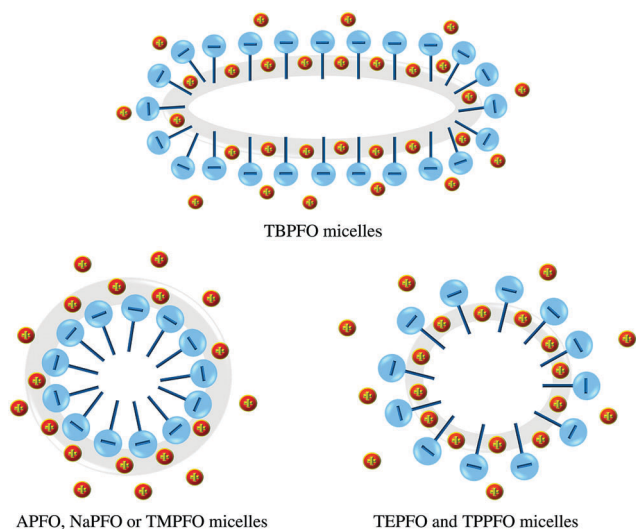


Fig. 5 Schematic representation of two groups of surfactants micelles (APFO, NaPFO and TMPFO, and TEPFO, TPPFO and TBPFO) in which that of TBPFO is presented separately due to its distinct structure (● and — represent the positive counterions of the respective fluorocarbon surfactants, individually.).

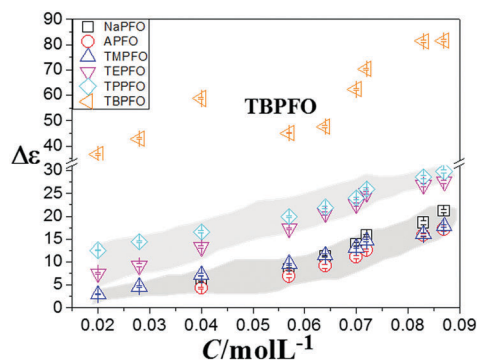


Fig. 6 Relationship between permittivity increments and the concentration of surfactants estimated with the curve-fitting technique.

concentration of surfactant. This relationship has also been discussed in the previous work in detail.<sup>68</sup> The conclusion is that the permittivity increment  $\Delta\epsilon$  of dielectric relaxation will increase with the concentration, which can be interpreted by Grosse's model. From Fig. 6, it can be seen that the  $\Delta\epsilon$  increases with the concentration in each system, which is consistent with the previous result. This further proves that the mechanism of relaxation of these systems has hardly changed, which is ascribed to the radial diffusion of the free counterions.

## 4. Conclusions

In this work, the dielectric relaxation spectra of six surfactant aqueous solutions (NaPFO, APFO, TMPFO, TEPFO, TPPFO and TBPFO) were investigated at different concentrations. Only one dielectric relaxation was observed in each system except for TBPFO with two relaxations. When the concentration of surfactants was fixed, the values of  $\epsilon_1$  were divided into two groups: (1) NaPFO, APFO and TMPFO; (2) TEPFO, TPPFO and TBPFO. While  $\kappa_1$  just decreased gradually with the variety of surfactants in the order of APFO, NaPFO, TMPFO, TEPFO, TPPFO and TBPFO. The changes in these parameters, mainly depending on the structures and properties of the micelles, and the size and the diffusion coefficient of counterions, provided evidence for the effect of counterions on the micelles.

Meanwhile, according to the equation of relaxation time in Grosse's model, the structural information of these micelles was obtained: the shape of these micelles was spherical except for TBPFO with ellipsoid shape and the average radius  $\bar{R}$  of them was evaluated. The average radius  $\bar{R}$  increased with the variety of surfactants in the order of APFO, NaPFO, TMPFO, TEPFO, TPPFO and TBPFO and can be divided into two groups approximately, which presented reasonable and powerful testimony for the results of our dielectric analysis.

In summary, the dielectric study of the micelle solutions of several fluorocarbon surfactants proved once again that DRS is an effective method of detecting the inner properties and the structural characteristics of this kind of system. The dynamic information and the structural properties obtained by DRS like above presented will provide the theoretical foundation and

application for other related studies including the treatment of toxic and refractory fluorinated surfactants.

## Conflicts of interest

There are no conflicts of interest to declare.

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