

Insight into the structure of oppositely charged surfactant–polymer system by dielectric spectroscopy

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Abstract The interaction between polymer (poly(acrylic acid)) and surfactant 12-2-12 (ethanediyl-1,2-bis(dimethyl dodecylammonium bromide)) in aqueous solution was investigated by dielectric relaxation spectroscopy (DRS) over a frequency range from 40 Hz to 110 MHz. To better understand the interaction, the dielectric behaviors of surfactant 12-2-12 solution and PAA solution were also separately studied. For surfactant 12-2-12 solution, one dielectric relaxation was observed above the critical micellar concentration, which was attributed to the interface polarization. For polymer PAA solution, two dielectric relaxation processes were evident which were ascribed to the counterion fluctuation along the whole chain and within the scale of correlation length of PAA polymer respectively. For the mixture of PAA and surfactant 12-2-12 solution, the dielectric behavior was discussed through comparing it with that of PAA and surfactant 12-2-12 solution. The possible interaction pattern and the structure of surfactant 12-2-12/PAA complex were proposed on the basis of the dielectric behavior.

Keywords Surfactant 12-2-12 · PAA · Dielectric relaxation

Introduction

The complexes formed by polymer and surfactant in aqueous solutions have been widely applied in many industrial areas such as detergents, cosmetics, food, and mineral recovery and

thus have attracted great interest in scientific research for many decades [1–3]. Numerous research groups have devoted their attention to advancing the fundamental understanding of the physics governing these interactions that control their structure [4–6].

Over a few past decades, many research groups have contributed significantly to a deeper understanding of interaction pattern and the structure of the complexes formed by polymer and surfactant [4, 7–10]. Surfactant aggregates bind with the polymer chain in a “necklace and bead”-like morphology below their critical micellar concentration and are mainly governed by hydrophobic, electrostatic, or dipolar forces. Earlier, two distinct types of structures for polymer–surfactant complexes have been proposed. Type I as shown in Fig. 1a: the surfactant aggregates nucleate binds at the hydrophobic sites of the polymer chain, where the head groups of surfactant are exposed to surrounding water. Type II as shown in Fig. 1b: the chain of polymer wrapped around the surfactant aggregates, where the head groups of surfactant are associated with the chain of polymer. Although there were a lot of significant researches about the possible interaction pattern and the structure of the polymer/surfactant complex, the structure of complex about how surfactant arranges on the chain of polymer still remains controversial at the molecular level. For example, Shen et al. [8] have claimed that, for PVP–SDS system, the nucleate of the aggregates formed by SDS binds at the hydrophobic sites of PVP chain by using surface tension and XRD, which leads to the type I structure. While, as for SDS–PVP complex system mentioned above, M Prasad et al. [9] have proposed that the structure of SDS–PVP complex in aqueous solution is that SDS binds to a positive nitrogen centers on the pyrrolidone rings of PVP, resulting in the formation of type II. Similar contradictory results have been reported for the LiPFN–PVP system. Hou et al. [11] have proposed type I structures for the PVP–LiPFN system, where the PVP chain

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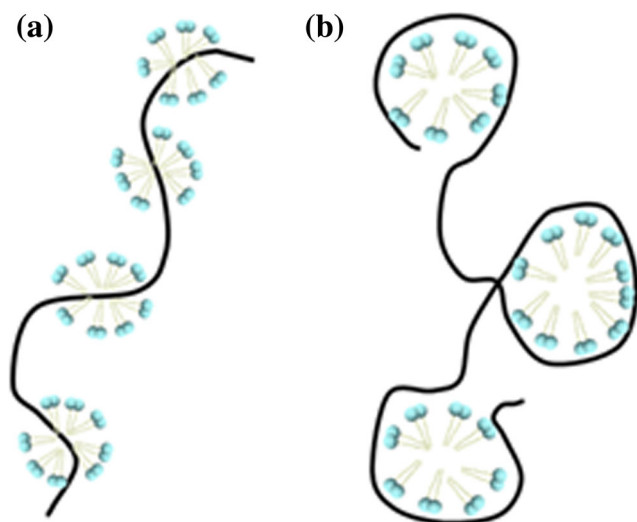


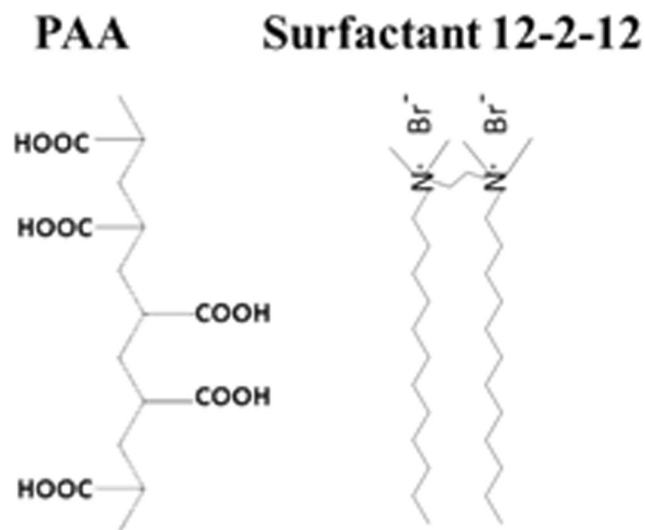
Fig. 1 A schematic representation of the two possible structures of polymer–surfactant complexes. **a** Type I structure. **b** Type II structure

penetrates because of hydrophobic interactions. However, Segre et al. [12] have proposed that, for the PVP–LiPFN system, the chain of PVP wraps the aggregates formed by LiPFN to form type II structures because of electrostatic interactions. The understanding as to how the structure of polymer–surfactant complexes was formed is still under development.

The interaction process is usually accompanied by changes in various physicochemical properties such as viscosity and surface tension. Characterization of these properties is able to offer valuable information on the interaction mechanism and the structure of the polymer/surfactant complex. To this end, a wide variety of characterization methods, such as surface tension [13], zeta potential [9], NMR [14], and light and neutron scattering [15], have been employed. Among these properties, however, the dielectric properties of a matter are essentially related to the fluctuation of the dipole moments and the motions of charges, characterization of which is able to provide important information on the dynamics and structure of the dipole moment, intermolecular interactions, and so on. As the suitable method to characterize the dielectric properties, dielectric relaxation spectroscopy (DRS), owing to its sensibility to all kinds of polarization, and the dynamics of dipoles can be obtained by analyzing the dielectric relaxation. DRS has been extensively applied to research the dynamic interaction between molecules and structural properties of materials and used in physical and chemical analyses of all kinds of materials [16]. Until now, there have been many research studies on micellar solution [17–19]. For example, Fan and Zhao studied on confined water molecules around micelles, aggregation behavior, and other properties of micelles using dielectric relaxation spectrum [20]. Shikata and Imai studied the movement of counterion around spherical micelles [21]. Also, DRS has been extensively applied to polymer solutions for decades, successfully revealing the charge distribution and

polymer structure on the basis of the dielectric relaxations at different frequency ranges [22–26]. However, dielectric relaxation spectrum study on the mixture of oppositely charged polymer and surfactant in aqueous solutions had rarely been reported as yet [27, 28]. If the analysis of DRS combines with appropriate theories, it is possible to have insight into how the interaction between polymer and surfactant is and what the complex structure is. And we believe that it is worthwhile to study polymer–surfactant complexes by dielectric relaxation spectrum.

This study is concerned with the interaction between a negatively charged polymer PAA (Poly(acrylic acid)) and a positively charged Gemini surfactant 12-2-12 (ethanediyl-1,2-bis(dimethyldodecylammonium bromide)) in aqueous solution. This special surfactant, surfactant 12-2-12 (as shown in Scheme 1), can form a variety of micellar aggregates with concentration increasing. Until now, surfactant 12-2-12 was studied very well [29]. Polymer PAA (as shown in Scheme 1) is a water soluble polyelectrolyte; PAA has been so far used widely in various fields of engineering and technology and studied very well by a large number of method [30]. It's worthwhile to study the mixture of surfactant 12-2-12 and polymer PAA. Therefore, in this present work, we carried out dielectric measurements on surfactant 12-2-12, polymer PAA, and the mixture of them respectively over a frequency range from 40 Hz to 110 MHz. Furthermore, we analyzed the dielectric behaviors of surfactant 12-2-12, polymer PAA, and the mixture based on the interface polarization theory and Mandel's theory. The results of dielectric measurements suggested that the structure of the complexes formed by surfactant 12-2-12 and polymer PAA is that surfactant 12-2-12 molecules bind at the hydrophobic sites of polymer PAA chain through hydrophobic interactions. We hope that our present results can advance our understanding on binding mechanism in oppositely charged polymer and surfactant systems.



Scheme 1 Chemical structures of PAA and surfactant 12-2-12

Experimental section

Materials

Surfactant 12-2-12 was prepared and purified using the procedure previously described in the literature [31]. The reaction of alkanediyl-*a,w*-bis(dimethyl-amine) with 1-bromo-*n*-dodecane for surfactant 12-2-12 was performed in dry ethanol under reflux ($T = 80\text{ }^{\circ}\text{C}$) for 48 h in the presence of a 5–10% excess of alkyl bromide to ensure complete biquaternization as much as possible. Surfactant 12-2-12 was recrystallized in various solvent mixtures (ethanol-ethyl acetate), and the purity of surfactant 12-2-12 was checked by elemental analysis. The molecular structure of surfactant 12-2-12 is depicted in Scheme 1. Poly(acrylic acid) PAA aqueous solution (weight fraction 35%, Mw 2.5×10^5 g/mol) from Sigma-Aldrich was used without further purification. A series of concentrations of surfactant 12-2-12 in aqueous solution were prepared from 0.01 to 29 mM and PAA in aqueous solution were prepared from 0.08–05%. Doubly distilled water was used for experiments.

Dielectric measurements

The dielectric measurements of the samples were carried out with a HP 4294A Precision Impedance Analyzer (Agilent Technologies) over a frequency range from 40 Hz to 110 MHz. All measurements were maintained at $25.0 \pm 0.1\text{ }^{\circ}\text{C}$. A measurement cell with concentric cylindrical platinum electrodes was employed [32]. By using several standard substances (air, pure ethanol, and pure water), the determined cell constant C_b , stray capacitance C_s , and residual inductance L_r were 0.014 pF, 0.812 pF, and 3.19×10^{-8} (F/S²), respectively. The experimental data errors arising from the residual inductance and measurement cell were corrected by Schwan method [33]. Then, the corrected data of capacitance C_s and conductance G_s at each frequency were converted to permittivity and conductivity, using the equations: $\varepsilon = C_s/C_l$ and $\kappa = G_s\varepsilon_0/C_l$ ($\varepsilon_0 = 8.8541 \times 10^{-12}$ F/m) is the vacuum permittivity).

Dielectric analysis

Dielectric response of a substance or system to applied AC electric field can be characterized by the complex permittivity ε^* which is defined as [34]:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j \frac{K(\omega)}{\varepsilon_0 \omega} = \varepsilon'(\omega) - j \left(\varepsilon'' \left(\omega + \frac{K_l}{\omega \varepsilon_0} \right) \right) \quad (1)$$

$K'' = \varepsilon_0 \omega (\varepsilon' - \varepsilon_h)$ where $\varepsilon'(\omega)$ and $\kappa(\omega)$ are the frequency-dependent real part of $\varepsilon^*(\omega)$ and complex conductivity $\kappa^*(\omega)$, respectively, $\varepsilon''(\omega)$ is the frequency-dependent dielectric loss, $\omega = 2\pi f$ (f is measuring frequency), $j^2 = -1$, ε_0 is the

permittivity of vacuum, and κ_l is the LF conductivity. The imaginary part of the conductivity, κ'' , can be calculated from the eq. with ε (where ε_h represents the permittivity at high frequency (HF)). The conductivity of the polymer system contains two contributions, one from LF conductivity κ_l related to EP and other a middle frequency (MD) related to the pure ohmic conduction, which is calculated from the conductivity spectra through the equation. For aqueous $\varepsilon''(\omega) = (K(\omega) - H_l)/\omega \varepsilon_0$ solution systems with higher electrolyte contents like our samples, generally, a considerable electrode polarization (EP) occurs in the LF range. The EP is originated by the accumulation of charges at the electrode interface. Additionally, at higher frequencies, the Maxwell–Wagner–Sillars (MWS) relaxations, related to the build-up of charges at the interfaces between the components of the heterogeneous systems, can be observed.

In order to analyze the experimental spectra, a combination of the i empirical Cole–Cole functions ($i = 1, 2$ or 3) and an EP term $A\omega^{-m}$ were used:

$$\text{Re}[\varepsilon^{*}] = \text{Re} \left[\varepsilon_h + \sum_i \frac{\Delta \varepsilon_i}{1 + (j\omega\tau_i)^{\beta_i}} \right] + A\omega^{-m} \quad (2)$$

where ε_l and ε_h are the low- and high-frequency limits of permittivity, respectively. $\Delta\varepsilon = \varepsilon_l - \varepsilon_h$ indicates relaxation strength (or dielectric increment). $\tau = 1/(2\pi f_0)$ is relaxation time. β is Cole–Cole parameter ($0 < \beta \leq 1$) indicating the distribution of relaxation times. A and m are the empirical parameters; m is related to electrical phase angle δ $\delta = \pi(1 - m)/2$ to characterize electrode polarization, and its value is around 0.8–1 [35]. These relaxation parameters $\varepsilon_l, \varepsilon_h, \kappa_l, \tau,$ and β are all called dielectric parameter (or relaxation parameter) and can be obtained by fitting the dielectric data using the Cole–Cole and the EP term.

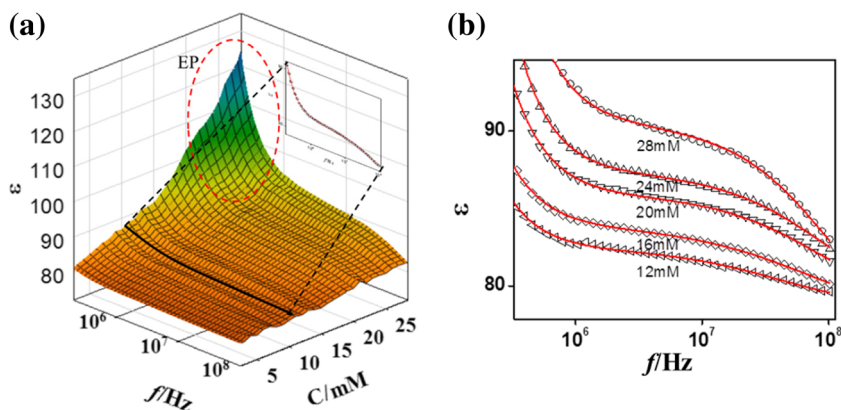
Results and discussion

Surfactant 12-2-12 aqueous solutions

Determinantion of relaxation parameters

While dielectric measurement was performed on all prepared surfactant 12-2-12 solutions, no relaxation was observed for solutions with surfactant concentration lower than 3 mM. When surfactant concentration is more than 3 mM, only one relaxation was observed at about 10^7 Hz, which is obvious from the inset of Fig. 2a. This only relaxation was discussed detailedly in previous work [36]. To examine the dielectric spectra in detail and obtain more information on micelles formed by surfactant 12-2-12, the dielectric relaxation parameters characterizing the dielectric behaviors of the systems were obtained by fitting Eq. 2 to the experimental dielectric

Fig. 2 **a** ϵ versus frequency and concentration in a three-dimensional representation of surfactant 12-2-12 aqueous solution. **b** Frequency dependence of the permittivity of an aqueous solution of surfactant 12-2-12 at certain concentrations. The hollow circles, triangles, and parallelograms are corrected data, and the solid red line represents the best fit



data. These dielectric spectra given in Fig. 2a were well represented by Eq. 2 with the best-fit relaxation parameters, as can be seen in Fig. 2b. The obtained relaxation parameters relaxation time τ , dielectric increment, $\Delta\epsilon$ and distribution coefficient β are summarized in Table 1.

Table 1 Relaxation parameters of the relaxations in surfactant 12-2-12 solution with different concentrations

C/mM	ϵ_l	ϵ_h	$\Delta\epsilon$	β	τ_{MW} (ns)	τ_{exp} (ns)
3.00	79.47	78.27	1.2	0.76	7.32	8.38
4.00	79.87	78.30	1.57	0.53	6.95	7.16
5.00	80.18	78.15	2.03	0.48	6.71	7.83
6.00	80.51	78.25	2.26	0.66	6.35	6.83
7.00	80.66	78.31	2.35	0.70	6.22	7.14
8.00	81.42	78.60	2.82	0.69	4.55	5.03
9.00	81.92	78.51	3.41	0.75	4.19	4.98
10.0	82.31	78.57	3.74	0.71	4.02	3.89
11.0	81.99	78.45	3.54	0.72	3.52	3.39
12.0	82.34	78.45	3.89	0.75	3.21	3.95
13.0	82.61	78.51	4.1	0.71	2.85	3.31
14.0	83.01	78.10	4.91	0.69	2.95	3.12
15.0	83.28	78.12	5.16	0.54	2.78	2.94
16.0	84.64	78.38	6.26	0.67	2.21	2.42
17.0	84.27	78.10	6.17	0.72	2.04	2.38
18.0	84.80	78.42	6.38	0.77	1.99	2.37
19.0	84.67	78.36	6.31	0.75	1.93	2.30
20.0	85.81	78.31	7.5	0.76	1.87	1.96
21.0	86.60	78.31	8.29	0.71	1.78	1.91
22.0	86.75	78.35	8.4	0.69	1.74	1.77
23.0	86.96	78.15	8.81	0.70	1.51	1.77
24.0	87.35	77.96	9.39	0.72	1.42	1.75
25.0	87.90	77.45	10.45	0.75	1.37	1.74
26.0	89.45	77.71	11.74	0.58	1.31	1.74
27.0	89.75	76.82	12.93	0.67	1.23	1.73
28.0	90.61	75.76	14.85	0.69	1.17	1.71
29.0	92.13	74.51	17.62	0.72	1.10	1.71

The relaxation mechanism of micellar solution

It is clear that from Table 1, the relaxation time distribution coefficient β is from 0.5–0.8, which suggests that the mechanism of the dielectric relaxation at about 10^7 Hz may contain some polarization processes that have similar relaxation time. This can be attributed to the distributions of the sizes and charges of the micelle aggregates in the suspension. In spite of the distributions, the mechanism of the distributed dielectric relaxation can be determined to be caused by Maxwell–Wanger polarization. As we all know that for aqueous colloidal suspensions, the high frequency relaxation generally is caused by the famous Maxwell–Wagner polarization. Maxwell–Wagner polarization results from the difference of the permittivity and conductivity between the micelle particle and the surrounding medium. According to the Maxwell–Wagner theory, the relaxation time corresponds to the time that counterions are shaking back and forth in the electric double layer surrounding the aggregation as shown in Fig. 3a. In addition, the theoretical relaxation time can be estimated by the well-known Einstein equation [37]:

$$\tau = \frac{\chi^{-2}}{D_{Br^-}} \tag{3}$$

where the diffusion coefficient of Br^- anion, D_{Br^-} , is estimated to be $2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [21]. χ^{-1} is the Debye length which is characterizing the size of the diffuse ion cloud and is approximately given by Eq. (4) [38]:

$$\chi^{-1} = \sqrt{\frac{\epsilon_0 \epsilon_a D_{Br^-}}{\kappa_l}} \tag{4}$$

By using Eqs. (3) and (4), the theoretical relaxation time of micelles solution was calculated and the values of different concentrations are in the range of 1.1–7.3 ns as shown in Table 1. The theoretical relaxation times are plotted as a function of surfactant concentration in Fig. 4, it is obvious from Fig. 4 that the theoretical value of relaxation time τ_{MW} shows

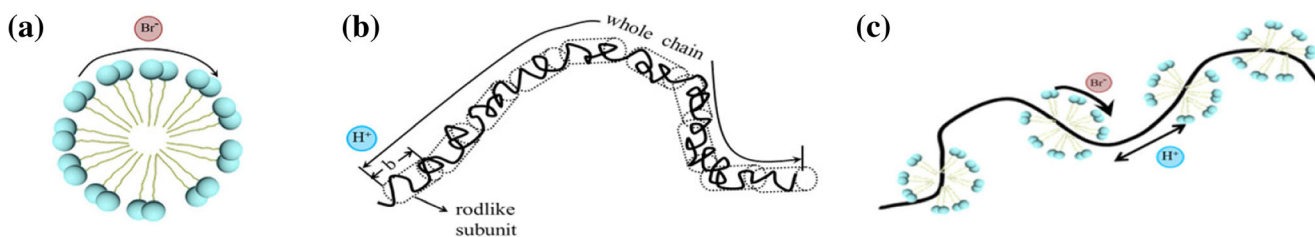


Fig. 3 **a** The counterions Br^- fluctuate around the micelles solution, **b** the counterions H^+ fluctuate along the subunit and the whole chain of polymer PAA in aqueous solution, and **c** the motions of counterions in the complex solution

the same trend with the experimental relaxation time τ_{exp} observed. It is generally known one of the effective standards of determining the mechanism and describing the characterization of dielectric relaxation is relaxation time τ . It suggested that the mechanism of this relaxation is considered as the Maxwell–Wagner polarization.

Polymer PAA aqueous solutions

Mandel's theory

Polymer physics is always closely related to counterions. In the frequency range investigated, dielectric relaxation is expected to reveal the ion movements induced by the external electric field. Generally speaking, the dielectric relaxation of the polymer solution shows two relaxation processes: the high-frequency relaxation in the megahertz frequency range and the low-frequency relaxation in the kilohertz range [25]. For the mechanism of these two relaxations, there are a lot of researches about the mechanism of dielectric relaxation in polymer solution. In fact, as early as 1974, Mandel et al. [39] had proposed a semi-quantitative model to describe these two relaxation processes in terms of the fluctuation of counterions along the polymer chain and suggested that the dielectric relaxation in the kilohertz frequency range is due to the motion of counterion along the whole polymer chain, while the high

frequency relaxation in the megahertz frequency arises from the fluctuation of counterion within the rod-like subunit. In Mandel's model [39], the polymer chain represented as a sequence of charged rod-like subunits of length b . For long enough polymer molecule, the value of b is independent of the molecular weight.

Determination of relaxation parameters

In this work, two dielectric relaxation processes at around kilohertz and megahertz, respectively, are obvious in PAA aqueous solution. For simplicity, in the following discussion, we refer them to low-frequency (LF) relaxation and high-frequency (HF) relaxation, respectively. To accurately characterize these two relaxation processes and understand their relaxation mechanism, it is necessary to determine the relaxation parameters, i.e., the dielectric increments $\Delta\epsilon$ and relaxation time τ of LF and HF relaxations. The dielectric relaxation parameters characterizing the dielectric behaviors of the systems were obtained by fitting Eq. 2 to the experimental dielectric data. And all these dielectric relaxation parameters are shown in Table 2.

The relaxation mechanism

The mechanism of LF relaxation at around kilohertz is often attributed to the fluctuation of counterions along the whole polymer chain. And this view is widely observable. For instance, the study [40] on xanthan solutions indicated that the LF relaxation is characterized by an

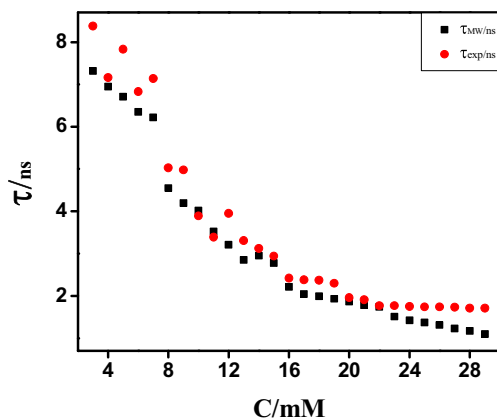


Fig. 4 MW polarization relaxation time τ_{MW} and experimental relaxation time τ_{exp}

Table 2 Relaxation parameters of the relaxations in PAA solution with different concentrations

C/wt%	$\Delta\epsilon_l = \epsilon_l - \epsilon_m$	$\Delta\epsilon_h = \epsilon_m - \epsilon_h$	β_1	β_2	τ_l (μs)	τ_h (ns)
0.08	14.12	3.88	0.73	0.81	30.49	159.31
0.10	15.03	4.98	0.71	0.84	29.05	117.96
0.20	15.11	5.32	0.74	0.85	28.57	81.87
0.30	15.58	6.12	0.75	0.86	28.62	55.56
0.40	16.07	6.16	0.74	0.84	28.87	37.42
0.50	16.52	6.31	0.75	0.81	27.58	5.53

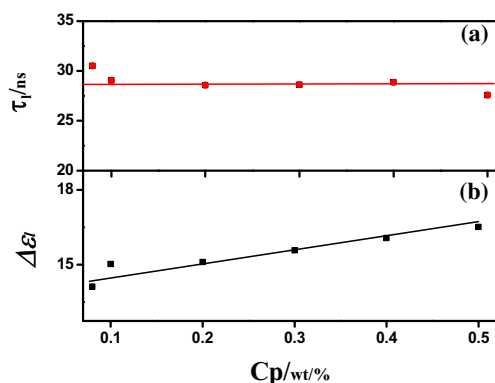


Fig. 5 Relaxation time (a) and dielectric increment (b) of LF relaxation of PAA solutions as a function of the polymer concentration

increasing $\Delta\epsilon$ and a relatively constant τ with concentration of polymer increasing and suggested that LF relaxation was thought to be ascribed to the fluctuation of counterions along the whole polymer chain. In this work, it is clear from Fig. 5 that $\Delta\epsilon_l$ increases and τ_l was substantially retained with concentration of increasing PAA aqueous solution. Therefore, we consider the mechanism of LF relaxation as the motion of counterion along the whole polymer chain as shown in Fig. 3b.

As for the mechanism of HF relaxation of PAA aqueous solution at around megahertz, there exists a lot of related explanation about that mechanism. As early as 1974, Mandel et al. [22] investigated the dielectric behaviors of PAA, PMA, and PSSNa aqueous solutions in the frequency range from 5 kHz to 110 MHz; two dielectric relaxation processes were observed. And they believed that the higher frequency one around megahertz originated from the counterion fluctuation within the subunits. Therefore, in this work, we attributed the mechanism of HF relaxation of PAA solution around megahertz to the fluctuation of counterion within the subunits. The values of subunit b can be calculated by the following Eq. [28]:

$$f = \pi kTu / 2b^2 \tag{5}$$

where f is the HF relaxation frequency, k is the Boltzmann constant, and u is the mobility of the counterions along the subunit of length b . Thus, the value of b was calculated from Eq. (5), and b is about 4 nm long which is in a reasonable range. This also indicates that it is correct to consider the mechanism of HF relaxation as motion of counterions within the subunit of polymer chain.

Table 3 Relaxation parameters of the relaxations in complex solution with different concentrations of surfactant and polymer

$C_{\text{polymer}}/\text{wt}\%$	$C_{\text{surfactant}}/\text{mM}$	$\Delta\epsilon_l = \epsilon_l - \epsilon_m$	$\Delta\epsilon_h = \epsilon_m - \epsilon_h$	β_1	β_2	τ_1 (ns)	τ_h (ns)
0.10	4.00	8.21	2.88	0.75	0.84	94.14	6.59
0.20	8.00	10.15	3.31	0.79	0.81	60.58	4.12

Interaction between surfactant 12-2-12 and PAA in aqueous solution

Determination of relaxation of relaxation parameters of complex system

Subsequently, the dielectric behavior of PAA–surfactant 12-2-12 complex was investigated. Two relaxation processes were found in the frequency range from 40 Hz to 110 MHz. To accurately characterize these two relaxation processes and understand their relaxation mechanism, it is necessary to determine the relaxation parameters, i.e., the dielectric increments $\Delta\epsilon$ and relaxation time τ of the low-frequency and the high-frequency relaxations. All these dielectric relaxation parameters (as shown in Table 3) were obtained by fitting the dielectric spectra as we dealt with the surfactant 12-2-12 solutions before.

The structure of complex between surfactant and polymer

As mentioned in the “Introduction,” the possible structure of complex formed by surfactant and polymer may be type I or type II. In this work, on the basis of two different structures of complex formed by PAA and surfactant 12-2-12, two hypotheses were proposed. One hypothesis is that the structure of complex is that the surfactant 12-2-12 aggregates nucleate binds at the hydrophobic sites of the PAA chain, where the head groups of surfactant 12-2-12 are exposed to surrounding water (type I). Therefore, from the dielectric viewpoint, this hypothesis suggests that two dielectric relaxation processes may occur: one relaxation process is the motion of counterions around the absorbed micelles in megahertz (as shown in Fig. 3c), and the other is the fluctuation of counterion within the distance between absorbed micelles on the polymer chain at 40 MHz (as shown in Fig. 3c). From Table 3, this hypothesis squares with the results of this work.

The other hypothesis is that the chain of PAA wrapped around the surfactant 12-2-12 aggregates, where the head groups of surfactant are associated with the chain of polymer (type II). This hypothesis implies the occurrence of two relaxation processes: one relaxation process in kilohertz ascribed to the fluctuation of counterions along the whole polymer chain, and the other relaxation process in megahertz arose from the fluctuation of counterion within the subunit of polymer chain. It can be seen from Table 3 that this hypothesis is not consistent with experiments. Therefore, the experimental evidence supports that the surfactant 12-2-12 aggregates nucleate binds

on the hydrophobic sites of the PAA chain in the process of the formation of the complex.

Moreover, according to the relation Mandel proposed [41], for the low-frequency relaxation caused by the fluctuation of counterions within the distance b which is between two micelles adsorbed onto the polymer, the values of b can be obtained. Calculations indicate b values to be about 26 nm, which is greater than the b of polymer solution without surfactant. It suggested that the addition of the surfactant reduces the polymer chain stiffness.

Conclusions

In summary, information arising from dielectric experiments indicates the occurrence of interactions between surfactant 12-2-12 and polymer PAA. Two hypotheses were proposed: one hypothesis is that the structure of complex fits type I; the experimental evidence supports this hypothesis. While other hypothesis is that the structure of complex fits type II, the occurrence of relaxation processes at frequencies in the range of kilohertz and megahertz is expected, which is not satisfactory with experimental results. Therefore, the results of this work suggested that in this work, the structure of complex formed by PAA and surfactant 12-2-12 fits a model with type I that is to say the structure of the complex is that the surfactant 12-2-12 aggregates nucleate binds on the hydrophobic sites of the PAA chain through their hydrocarbon tails.

Although DRS measurement can cover a frequency range of more than 12 orders, the present study is limited to just a narrow frequency window. If a higher frequency range is covered, much more information can be obtained. Since the information obtained in different frequency ranges is complementary to each other, deeper insight into interaction mechanism by means of DRS is a worthy expectation.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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