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Aggregation behavior and electrical properties of amphiphilic pyrrole-tailed ionic liquids in water, from the viewpoint of dielectric relaxation spectroscopy

Xiaoqing Fan and Kongshuang Zhao*

The self-aggregation behavior of amphiphilic pyrrole-tailed imidazolium ionic liquids (Py(CH₂)₁₂mim⁺Br⁻: Py = pyrrole, mim = methylimidazolium) in water is investigated by dielectric spectroscopy from 40 Hz to 110 MHz. Dielectric determination shows that the critical micelle concentration (CMC) is 8.5 mM, which is lower than that for traditional ionic surfactants. The thermodynamic parameter of the micellization, the Gibbs free energy ΔG , was calculated for Py(CH₂)₁₂mim⁺Br⁻ and compared to those of the corresponding $C_n \min^+ Br^-$ (n = 12, 14). It was found that the main driven forces of the Py(CH₂)₁₂mim⁺Br⁻ aggregation were hydrophobic interaction and π - π interactions among the adjacent Py groups. Further, the structure of aggregation was speculated theoretically that Py groups partially insert into the alkyl chains and the staggered arrangement in micelles is formed. When the concentration of Py(CH₂)₁₂mim⁺Br⁻ is higher than CMC, two remarkable relaxations which originated from diffusion of counterions and interfacial polarization between the micelles and solution, were observed at about 1.3 MHz and 55 MHz. The relaxation parameters representing the real properties of the whole system were obtained by fitting the experimental data with Cole-Cole equation. A dielectric model characterizing the structure and electrical properties of spherical micelles was proposed by which the conductivity, permittivity and the volume fraction of micelles as well as electrical properties of solution were calculated from the relaxation parameters. An intriguingly high permittivity of about 150 for the micelle was found to be a direct consequence of the strong orientational order of water molecules inside the core of micelle, and essentially is attributed to the special structure of the micelle. Furthermore, the calculation of the interfacial electrokinetic parameters of the micelles, *i.e.*, the surface conductivity, surface charge density and zeta potential, were also achieved based on the relaxation parameters and phase parameters from higher frequency relaxation. On the basis of the results obtained, the aggregation behaviours and interfacial electrokinetic properties of the special micelles are discussed.

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1. Introduction

In recent years, ionic liquids (ILs), as a new soft matter, are receiving more attention due to their special properties, such as low volatility, nonflammability, high thermal stability and high ionic conductivity.^{1,2} A large amount of research has focused on the self-aggregation behavior of ILs in aqueous solution.³ An interesting characteristic of ILs is that the cations, such as 1-alkyl-methylimidazolium ($C_n mim^+$), 1-alkyl-pyrrolidinium ($C_n Pyrr^+$), which possess an inherent amphiphilicity, can self-assemble to form a special structure and properties of aggregates. The structural features of the amphiphilic ionic liquids offer mainly three types of variations, namely, hydrophobicity by variation of chain length in the alkyl branch, type of

headgroup and the nature of the anion. The diversity of ILs in structure makes it widely applicable in various fields, and this is the reason why research on the synthesis and properties of new ionic liquids with varying functionalities has drawn extensive attention recently.^{4,5}

Aggregation behaviors of amphiphilic ILs play a key role in the potential applications of synthetic, catalytic, and separation science. For example, ILs can serve as structure-directing templates for the synthesis of mesoporous silica nanoparticle materials with various particle morphologies.⁶ Brezesinski *et al.*⁷ generated a bimodal pore system of deformed spherical mesopores using a suitable block copolymer and an amphiphilic ionic liquid C₁₆mimCl as template. Pino *et al.*⁸ applied dicationic imidazolium ILs aggregates in the determination of partition coefficients by the utilization of the solid phase microextraction-gas chromatography method, and they also⁹ extracted polycyclic aromatic hydrocarbons from sediments



College of Chemistry, Beijing Normal University, Beijing, China. E-mail: zhaoks@bnu. edu.cn; Tel: +86-010-58805856

using aqueous solution containing ILs (1-hexadecyl-3-methylimidazolium bromide) aggregates as the extracting medium. In short, the applications of the amphiphilic ionic liquid as templates in synthesis and as extracting medium in separation are closely related to the structure and properties presented when the amphiphilic ILs aggregate. Therefore, it is essential to understand how ILs aggregate in different solvents and the properties of the aggregation.

Bowers et al.¹⁰ and Miskolczy et al.¹¹ studied the aggregation of a series of amphiphilic ILs with different lengths of alkyl chain in water. Since then, numerous work has focused on the self-assembly of amphiphilic ILs because the amphiphilic ILs have the ability to form a variety of aggregates such as vesicles,12 liquid crystal13 and microemulsions.14,15 Meanwhile, some fundamental studies about the physicochemical property and aggregation structure by a variety of traditional physical techniques have been also reported. They include the determination of CMC of the amphiphilic imidazolium ILs by surface tension and electrical conductivity measurements,16 the estimation of micellar aggregation number (N_{agg}) and the thermodynamic parameters for micelle formation by fluorescence quenching and small angle neutron scattering methods.¹⁷ In addition, many attempts¹⁸ have been made to explore functional ILs by incorporating additional functional groups into hydrophobic chain or headgroup of amphiphilic ILs to make ILs have special functionality according to different application needs. Some research focuses on ILs with targeted functionality, designs including heterocyclic aromatic molecules as well as ions with structurally and functionally complex side chains. For example, Davis et al.¹⁹ synthesized a range of acidic ionic liquids with an alkane sulfonic acid group which provide good product selectivity. A series of hydrophobic task-specific ILs designed to extract Hg²⁺ and Cd²⁺ from water were prepared by appending urea-, thiourea-, and thioether-substituted alkyl groups to the imidazole ring. Firestone et al.²⁰ described the self-aggregation of thiophene-tailed imidazolium ILs in aqueous solutions, where the IL is changed to be more electroactive due to the tether of a thiophene moiety at the terminal of the hydrocarbon chain. Recently, Zheng et al.21 studied the surface activity, aggregation behavior, and thermodynamics of micelle formation of carbazole-tailored imidazolium-based ionic liquids in aqueous solutions by surface tension, electrical conductivity, and ¹H NMR spectroscopy, and indicated that the incorporation of a bulky organic ring leads to lower CMC and higher micellar aggregation number. From the above studies, it can be concluded that special groups in amphiphilic ILs played a key role in the formation of micellar aggregation with different structures, which highlights the need to investigate these properties of special aggregation. However, there are few reports on the physicochemical properties which possess dual characteristics of ILs and surfactant, such as the dispersion for aggregates in medium, the properties inside the aggregates, the electric properties in the interface between the aggregation and solution, and diffusion of counterions in the electric double layer (EDL) surrounding the aggregation.

On the other hand, much of the fundamental research on the self-aggregation behaviors of amphiphilic molecules, including

amphiphilic ILs, has been done from the perspective of thermodynamics and molecular interactions. These studies focused on a fact that liquids confined to hydrophobic region behave differently than their bulk counterparts. Due to the interactions between confined water and hydrophobic region, there were clear variations in some basic dynamic properties²² and the structure of aggregate.23 Hence, the arrangement and the relaxation dynamics of water molecules surrounding a hydrophobe were also explored theoretically.24 In this research, one major concern is the permittivity that reflects the polarity of the medium environment. Therefore, studying the dielectric properties of the aggregation formed from amphiphilic ILs and giving determined parameters about the aggregation will play a greater role in their application. Additionally, from the viewpoint of dielectric materials research, for the amphiphilic ILs which have special group and geometric structure, as the new substance, understanding their dielectric properties has theoretical significance and practical value. However, some basic properties such as permittivity, the density of aggregate, and molecule arrangements within the aggregate, which are closely related to the aggregate, can not readily be characterized in situ yet.

It is generally known that dielectric relaxation spectroscopy (DRS), owing to its sensibility to all kinds of polarization, has been extensively applied to research the dynamic and structural properties of materials.²⁵ It has also been used recently to study micellar aggregations with various geometrical structures.^{26–28} Moreover, valuable electrical and structural information inside the constituent phases in the aggregation solution systems can be obtained by analyzing DRS based on appropriate electrical models.²⁹ Thereby, it is totally possible to analyze dielectric spectra of a complex system like micellar aggregation systematically and completely. An increasing number of papers^{30,31} have been published concerning dielectric properties of colloidal particles including our research. For this reason, DRS has the potential of becoming an important new alternative method to study the amphiphilic ILs.

In the present study, amphiphilic pyrrole-tailed imidazolium ILs $Py(CH_2)_{12}mim^+Br^-$ aggregation behavior in water is investigated because of its special structure as shown in Scheme 1. The applications³² of $Py(CH_2)_{12}mim^+Br^-$ as structure-directing agent for the formation of mesoporous silica spheres have been reported. However, its aggregation behavior still has not been studied in detail, and few studies have been devoted to the electrical properties inside the micellar aggregation. Here, our basic interest lies in finding out how the pyrrole-tailed imidazolium ionic liquids influence the microstructure in the micelle, and give physical chemistry parameters related to the



Scheme 1 Chemical structures of the surface active imidazolium ILs used in this study.

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micelle by analyzing the data acquired from dielectric spectra. We observed two dielectric relaxations markedly dependent on the concentration of $Py(CH_2)_{12}mim^+Br^-$ solution and attributed to Maxwell–Wagner polarization and counterion polarization mechanisms, respectively. The relaxation parameters are obtained by fitting the experimental data with proper equations. Based on the dielectric model proposed, the relaxation at higher frequency was analyzed theoretically by using observed relaxation parameters. It was found that an abnormal permittivity of micellar aggregation is closely related to the microstructures of micelle core. Further, some electrokinetic parameters, which gave some valuable information on EDL, were also calculated from the relaxation parameters and phase parameters.

2. Materials and methods

2.1. Materials

Py(CH₂)₁₂mim⁺Br⁻ was prepared and purified by using the procedures previously described.³² C_nmim⁺Br⁻ (n = 6, 10, 12, 14) (purity > 99%) was purchased from Shanghai Cheng Jie Chemical Co. Ltd., China. The water content was less than 1000 ppm. The molecular structure of the ILs used in this work is depicted in Scheme 1. A series of concentrations of Py(CH₂)₁₂mim⁺Br⁻ aqueous solution were prepared from 2.5 to 28.3 mM. Doubly distilled water was used for all experiments.

2.2. Dielectric measurements

Dielectric measurements of Py(CH₂)₁₂mim⁺Br⁻ aqueous solution were carried out with HP4294A Precision Impedance Analyzer (Agilent Technologies) over a frequency range from 40 Hz to 110 MHz, controlled by a personal computer. The applied alternating field was 500 mV, and a measurement cell with concentrically cylindrical platinum electrodes was employed.³³ All measurements were maintained at 25 ± 0.5 °C. To eliminate the errors from the residual inductance (L_r) and stray capacitance (C_r) (the values of C_r , L_r and cell constant C_1 have been determined by using several standard substances (air, pure ethanol, pure water) and KCl solution with different concentrations were -0.02 pF, 9.3 nH, and 0.07 pF, respectively), the raw experimental data, capacitance C_x and conductance G_x were corrected applying the following equations:³⁴

$$C_{\rm s} = \frac{C_{\rm x}(1+\omega^2 L_{\rm r} C_{\rm x}) + L_{\rm r} G_{\rm x}^2}{(1+\omega^2 L_{\rm r} C_{\rm x})^2 + (\omega L_{\rm r} G_{\rm x})^2} - C_{\rm r}$$
(1a)

$$G_{\rm s} = \frac{G_{\rm x}}{\left(1 + \omega^2 L_{\rm r} C_{\rm x}\right)^2 + \left(\omega L_{\rm r} G_{\rm x}\right)^2}$$
(1b)

where ω ($\omega = 2\pi f$, f is the measurement frequency) is the angular frequency. Then the permittivity ε and conductivity κ were determined by equations $\varepsilon = C_s/C_1$ and $\kappa = G_s \varepsilon_0/C_1 (\varepsilon_0$ is the permittivity of vacuum).

2.3. Dielectric analysis

The complex permittivity ε^* of a substance or system under an applied electric field with angular frequency ω can be expressed as:

$$\varepsilon^* = \varepsilon - j\varepsilon'' = \varepsilon - j\frac{\kappa - \kappa_1}{\varepsilon_0\omega}$$
 (2)

here ε'' is the dielectric loss, κ_1 denotes low-frequency limits of conductivity (called the dc conductivity) and $j = \sqrt{-1}$. The conductivity of the whole system will contain two contributions, one from the d.c. conductivity and the second one from the dielectric loss. The dielectric loss was calculated from the conductivity spectra through the equation $\varepsilon'' = \frac{\kappa - \kappa_1}{\varepsilon_0 \omega}$, where κ_1 was read out from the conductivity spectra at low frequency.

Generally, the dielectric spectra over the whole measuring frequency range can be described by an empirical eqn (3) including the Cole–Cole function and the electrode polarization (EP) term $A\omega^{-m}$ (where *A* and *m* are adjustable parameters).

$$\varepsilon^* = \varepsilon_{\rm h} + \sum_i \frac{\Delta \varepsilon_i}{1 + (j\omega \tau_i)^{\beta_i}} + A\omega^{-m}$$
(3)

where $\varepsilon_{\rm h}$ is the high frequency limit of permittivity, *i* is the number of dielectric relaxations, $\Delta \varepsilon$ is the dielectric increment, $\tau = 1/2\pi f_0$ is the characteristic relaxation time (f_0 is the characteristic relaxation frequency) and $\beta(0 < \beta \leq 1)$ is the shape parameter indicating the distribution of relaxation time. In this work, the dielectric relaxation parameters were obtained by fitting eqn (3) which includes two Cole–Cole's terms (i = 1, 2) to the experimental data.

The derivative dielectric loss $\varepsilon_{\text{LD}}^{"}$, is presented on the basis of the logarithmic derivative of raw ε data to determine the characteristic frequency:³⁵

$$\varepsilon_{\rm LD}'' = -\frac{\pi}{2} \frac{\partial \varepsilon}{\partial \ln \omega} \tag{4}$$

This method has been successfully used for separating the two or more overlapping dielectric relaxation peaks. By introducing the real part of eqn (3) into the derivative expression (eqn (4)), we get the following expression:³⁶

$$\varepsilon_{\rm LD}'' = \frac{\pi}{2} \left(\sum_{i} \frac{\beta_i (\Delta \varepsilon_i) (\omega \tau_1)^{\beta_i} \cos\left[\frac{\beta_i \pi}{2} - (1 + \beta_i)\theta_i\right]}{1 + 2(\omega \tau_i)^{\beta_i} \cos\frac{\beta_i \pi}{2} + (\omega \tau_i)^{2\beta_i}} \right) + A\omega^{-m}$$
$$\theta_i = \arctan\left[\frac{\sin\left(\frac{\beta_i \pi}{2}\right)}{(\omega \tau_i)^{\beta_i} + \cos\left(\frac{\beta_i \pi}{2}\right)}\right] \tag{5}$$

This equation has the same set of variables as that in eqn (3) and can be used to fit the derivative dielectric loss curve. In order to identify these relaxation processes more clearly, strict analysis of the dielectric spectra at concentrations of 28.3 mM was performed according to the described method in Fig. 1. Fig. 1 shows the frequency dependence of the permittivity (inset) and its derivative dielectric loss. As can be clearly seen, two relaxations can be observed in the permittivity and derivative dielectric loss spectrum. The red solid line in derivative



Fig. 1 Frequency dependence of the derivative dielectric loss of 28.3 mM $Py(CH_2)_{12}mim^+Br^-$ aqueous solution. The inset shows the fitting result of the permittivity with eqn (3).

dielectric loss spectrum represents the best fitting line with eqn (5), which contains three parts: the EP effect and the contributions from the lower and higher frequency relaxations (relaxation-1 and relaxation-2, respectively).

As the $Py(CH_2)_{12}mim^+Br^-$ solution is conductive, a considerable EP effect dominates at low frequency range due to the accumulation of spatial charge at the electrode solution interface. It is the important step to eliminate the contribution of EP from the dielectric spectra which may mask the relaxation behavior at low frequency range. A simultaneous fit of the ε curve and ε''_{LD} curve was made, by which A and m were determined. Thus, new permittivity and derivative dielectric loss curves free of the EP effect were derived by mathematically subtracting the $A\omega^{-m}$ from the raw permittivity according to the method described in the literature.37 The permittivity and derivative dielectric loss of Py(CH₂)₁₂mim⁺Br⁻ solution after eliminating the EP effect are shown in Fig. 2. It should be noted in Fig. 2 that the EP effect at the low frequency range is well eliminated, the corrected permittivity (black squares) shows a clear-cut platform of the low frequency relaxation, and the corrected derivative dielectric loss (blue squares) shows a clearcut peak of the low frequency relaxation.

3. Results and discussion

3.1. Aggregation behavior of $Py(CH_2)_{12}mim^+Br^-$ in water

3.1.1 Dielectric spectra of $Py(CH_2)_{12}mim^+Br^-$ **aqueous solution.** Fig. 3 shows three-dimensional representations for the concentration dependence of the dielectric spectra and derivative dielectric loss spectra for $Py(CH_2)_{12}mim^+Br^-$ aqueous solution in the concentration range of 11.3–28.3 mM. It should be noted here that the effect of EP has been eliminated as described in Section 2.3. Remarkably, both permittivity and derivative dielectric loss spectra show two dielectric relaxation processes located at around 1.3 MHz (called relaxation-1) and 55 MHz (called relaxation-2), respectively. It is also clear from Fig. 3 that whether for permittivity and derivative dielectric loss, they increase markedly with the increment in the concentration



Fig. 2 Frequency dependence of permittivity (black circles) and derivative dielectric loss (blue circles) of 28.3 mM Py(CH₂)₁₂mim⁺Br⁻ aqueous solution. The squares are the corrected curves after subtraction of the EP effect, and the solid lines represent the best fits.

of $Py(CH_2)_{12}mim^+Br^-$ solution indicated by the arrows, implying the formation of aggregated micelles of the ILs, which will be discussed in detail in the following sections.



Fig. 3 Three-dimensional representations for the concentration dependence of the dielectric spectra (a), and derivative dielectric loss (b), of $Py(CH_2)_{12}mim^+Br^-$ solution after eliminating the effect of electrode polarization.

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3.1.2 The micellisation process of $Py(CH_2)_{12}mim^+Br^-$. The CMC of amphiphilic ILs is especially important for their application because it is often used as a considerable measure of the surface activity and reflects the tendency of micellisation. A measurement of electrical conductivity is the most popular method to determine the CMC of ionic surfactant. In order to understand the difference between the amphiphilic ILs $Py(CH_2)_{12}mim^+Br^-$ and ordinary surfactant molecule in micellisation process, we surveyed the conductivity data obtained by analyzing the imaginary part of the complex permittivity. Fig. 4(a) shows the frequency dependences of the conductivity κ of Py(CH₂)₁₂mim⁺Br⁻ solution with different concentrations. As can be seen, in the low frequency range below 10^3 Hz, the conductivities are influenced by EP effect, which reflected in the sharp decrease of conductivity with frequency decrease. In the frequency range of $10^4 \sim 10^7$ Hz, the κ is almost independent of measuring frequency for Py(CH₂)₁₂mim⁺Br⁻ solution of all concentrations. The conductivity κ of the system was read at 7×10^5 Hz and is plotted in Fig. 4(b). It is obvious from Fig. 4(b) that the gradual increase of concentration leads to two readily distinguishable linear dependencies. An abrupt change in the conductivity-concentration curve can be observed at the concentration of about 9 mM, which is considered to the CMC of $Py(CH_2)_{12}mim^+Br^-$. That is, micellar aggregations form when



Fig. 4 Frequency dependence of conductivity (a), and plots of conductivity and permittivity of Py(CH₂)₁₂mim⁺Br⁻ (b), aqueous solution with different concentrations at the 7 × 10⁵ Hz.

the concentration of $Py(CH_2)_{12}mim^+Br^-$ is larger than 9 mM. In the low concentration domain below 9 mM, κ linearly increases with the concentration due to the growing number of free Py(CH₂)₁₂mim⁺ and Br⁻ ions, whereas the increase was inhibited in the plot originates from the onset of micellization. This is because that the partial anions Br⁻(counterions) serves as charge transport are confined to the micellar surface and results in an effective loss of ionic charges. The micelles can contribute to the charge transport to a lesser extent than the free ions owing to their lower mobility. On the other hand, it was found that the permittivity of the $Py(CH_2)_{12}mim^+Br^-$ solution rises from 80 to 90 with increasing concentration. A possible explanation for this fact could be the presence of aggregation with larger dipole in the Py(CH₂)₁₂mim⁺Br⁻ aqueous solution. Interestingly, when the permittivity of the system was read at 7×10^5 Hz, the permittivity-concentration curve shows a surprising consistency inflection point with that given by the κ -*c* curve as shown in Fig. 4(b).

In order to confirm the micelle formation, the CMC values and the slopes were obtained from the nonlinear least-squares fit of the experimental results to eqn (6), as described by Carpena *et al.*³⁸

$$\kappa = S_1 C + p(S_2 - S_1) \ln\left(\frac{1 + \exp[(C - \text{CMC})/p]}{1 + \exp(-\text{CMC}/p)}\right)$$
(6)

where, S_1 and S_2 are the gradient of the κ -c curve below and above the CMC, respectively, p is the width of the transition, C is the concentration of Py(CH₂)₁₂mim⁺Br⁻, and CMC represents the central point of the transition. The ratio S_2/S_1 provides an estimate for the degree of counterion dissociation (γ). The fitted parameters are summarized in Table 1. The standard free energy of micelle formation for ionic uni-univalent surfactants, $\Delta G_{\rm CMC}^0$, was calculated by eqn (7):³⁹

$$\Delta G_{\rm CMC}^0 = (2 - \gamma) RT \ln(x_{\rm CMC}) \tag{7}$$

where, $x_{\rm CMC}$ is the CMC in mole fraction unit, and γ is the degree of ionic dissociation of the micelle. The $\Delta G^0_{\rm CMC}$ for the Py(CH₂)₁₂mim⁺Br⁻ was calculated according to eqn (7) using the values of CMC and γ listed in Table 1. Meanwhile, the dielectric measurements of C₁₂mim⁺Br⁻ and C₁₄mim⁺Br⁻ solution have also been carried out under the same condition and the parameters obtained by the conductivity data are also summarized in Table 1.

As listed in Table 1, the value of CMC for $Py(CH_2)_{12}mim^+Br^-$ (8.54 mM) is very close to that obtained experimentally, and the CMC for three ILs are found to decrease with increasing alkyl chain length. The values of ΔG^0_{CMC} for three ILs are all negative. This means micellization of three ILs in aqueous solution is a spontaneous process. It can be seen that the longer the alkyl chain of ILs, the more negative the standard Gibbs energy of aggregation, indicating that the aggregation comes more easily with the increase of the alkyl chain length of ILs. Therefore, it may be concluded that the aggregation is driven by hydrophobic interaction force. Further, compared to the values of ΔG^0_{CMC} of $Py(CH_2)_{12}mim^+Br^-$ and $C_{12}mim^+Br^-$, it can be confirmed that the $Py(CH_2)_{12}mim^+Br^-$ molecule is slightly easier to form

Table 1 Parameters calculated from conductivity measurements

	CMC/mM	S_1/S cm ² mol ⁻¹	$S_2/S m cm^2 mol^{-1}$	$x_{ m CMC} imes 10^4$	γ	$\Delta G_{ m CMC}^0/{ m kJ}$ mol $^{-1}$	$N_{ m agg}$
$Py(CH_2)_{12}mim^+Br^-$	8.54	89.1	25.2	1.54	0.246	-38.05	50
C_{12} mim ⁺ Br ⁻	9.63	93.4	22.9	1.74	0.250	-37.44	45 (ref. 41)
C ₁₄ mim ⁺ Br ⁻	2.50	87.1	23.1	0.454	0.265	-42.90	60 (ref. 41)

aggregation than $C_{12}mim^+Br^-$ just because of the slightly different hydrocarbon chain length. More importantly, it may be interpreted as the incorporation of Py group extended the hydrophobic region and increased hydrophobicity. However, on the other hand, the higher polarity of Py group reduced the hydrophobicity of hydrocarbon chains of $Py(CH_2)_{12}mim^+Br^-$, which is not favorable for micelle formation. In addition, from microcosmic aspect, the incorporation of Py group produced π - π interactions among the adjacent Py groups and influenced the $Py(CH_2)_{12}mim^+Br$ molecules to pack more compactly.⁴⁰ The balance between these opposite factors determines the aggregation character of $Py(CH_2)_{12}mim^+Br^-$ molecules.

With regard to the dynamics of the micellisation process of $Py(CH_2)_{12}mim^+Br^-$, we further analyse as below: the Gibbs energy ΔG^0_{CMC} of aggregation may be considered to contain the contributions from transfer of the IL segments from bulk water to the aggregates, *i.e.*, the ΔG^0_{CMC} can be divided into three contributions from the terminal group of the alkyl chain $(\Delta G^0_{CMC,terminal\ group})$, the methylene group of alkyl chain $(n_{CH_2}\Delta G^0_{CMC,CH_2})$, and the headgroup $(\Delta G^0_{CMC,headgroup})$, respectively. Therefore, ΔG^0_{CMC} can be calculated by:

$$\Delta G_{\rm CMC}^0 = \Delta G_{\rm CMC,head\ group}^0 + \Delta G_{\rm CMC,terminal\ group}^0 + n_{\rm CH_2} \Delta G_{\rm CMC,CH_2}^0$$
(8)

where, n_{CH_2} is the number of $-\text{CH}_2-$ group. According to previous reports,⁴² $\Delta G^0_{\text{CMC,CH}_2}$ should be independent of headgroup structure for homologous salts. So, deciding the difficulty of their aggregation is the terminal group of Py(CH₂)₁₂mim⁺Br⁻. According to the values of Gibbs energy listed in Table 1 and eqn (8), the values of $\Delta G^0_{\text{CMC,CH}_3}$ (with $-\text{CH}_3$ group in the terminal) and $\Delta G^0_{\text{CMC,Py}}$ (with Py group in the terminal) are all negative, and the absolute value of $\Delta G^0_{\text{CMC,CH}_3}$ is larger than that of $\Delta G^0_{\text{CMC,Py}}$. This means the methyl group is more hydrophobic than the Py group as described above. Therefore, it may be concluded that the driving force of the micellization process is the transfer of alkyl chain from bulk solution to interior of the micellar aggregation. The contribution of Py group to the hydrophobic effect is relatively weak, but the π - π interaction among Py groups is favorable for micelle formation.

3.1.3 The micellar shape and the aggregation number. As is well known, the size of amphiphile aggregates and their specific structures are restricted to depending on many factors, chiefly the geometry of amphiphile. The micellar packing parameter equation proposed by Israelachvili⁴³ is utilized to help predict molecular self-assembly in surfactant solutions.

$$P = \frac{V}{l_{\rm c}A_0} \tag{9}$$

where, *V* is the effective hydrophobic chain volume, A_0 is the effective headgroup area of the surfactant molecules and was obtained referring to literature⁴⁴ in this work, and l_c is the alkyl chain length in the micellar core. The values of *V* and l_c are given by Tanford's formulas (*n* is the number of carbon atoms in the alkyl chain):

$$V = (27.4 + 26.9n) \times 10^{-3} \text{ nm}^3$$
 (10a)

$$l_{\rm c} = (0.15 + 0.1265n) \,\rm nm$$
 (10b)

For a homologous series of single-chain amphiphiles, the CMC follows the empirical Stauff-Klevens rule, which indicates a logarithmic relationship between CMC and the number of carbon atoms in the alkyl chain as shown in the following equation:⁴⁵ lg CMC = A + Bn (where A is a constant relevant to the nature and number of hydrophilic groups, B is a measurement of the effect of each additional methylene group on CMC and the equal of the free energy transferring a methylene unit from aqueous solution to micelle). After determining the CMC of $C_n mim^+Br^-$ with different alkyl chain length (carbon atoms n = 6, 10, 12, 14) by dielectric measurements as described in Section 3.1.2, the values of A and B were determined. Such, the Stauff-Klevens relation becomes: $\lg CMC = 4.847 +$ 0.316n. Based on this relation, according to the CMC of $Py(CH_2)_{12}mim^+Br^-$ obtained from Fig. 4, the number of carbon atom in the alkyl chain of $Py(CH_2)_{12}mim^+Br^-$ is determined to be 12.4. As a consequence, the micellar packing parameter P for $Py(CH_2)_{12}mim^+Br^-$ is 0.24 calculated from eqn (9). According to the relationship between P and shapes of surfactant molecule, micelles are approximately spherical in shape when $0 < P \le 1/3$. The *P* of $Py(CH_2)_{12}mim^+Br^-$, in this work, is smaller than 0.33, this clearly indicates the formation of sphere micelles.

Further, the value of the average aggregation number (N_{agg}) for Py(CH₂)₁₂mim⁺Br⁻, a fundamental parameter of micellar aggregation, was estimated by eqn (11) and also listed in Table 1.

$$N_{\rm agg} = \frac{4\pi l_c^3}{3V} \tag{11}$$

So far, we have discussed the aggregation process and the aggregation structure of single chain molecules with Py group $Py(CH_2)_{12}mim^+Br^-$, and obtained the micellar aggregation number. The aggregation number of $Py(CH_2)_{12}mim^+Br^-$, 50, is slightly larger than that of $C_{12}mim^+Br^-$ ($N_{agg} = 45$).⁴¹ Then what the microstructure of micelle is? The number of carbon atoms in the hydrocarbon chain of $Py(CH_2)_{12}mim^+Br^-$ determined above is 12.4. Compared with $C_{12}mim^+Br^-$, $Py(CH_2)_{12}mim^+Br^-$

is just one more Py group. This means the effect of Py group in the hydrophobic group is equivalent to that of about 0.4 methyl group. The bulky Py group in the hydrocarbon chain of Py(CH₂)₁₂mim⁺Br⁻ influences the micellization due to its steric hindrance effect. So we consider the Py group was not fully stretched but curved in the micelle, penetrated into the inner of the micelle and overlapped with the middle few methylenes in the alkyl chains. It may be interpreted in accordance with the Gibbs energy of aggregation as following: the tendency that Py group escapes water environment to form aggregates is not stronger than -CH₃ group, *i.e.*, when the Py group located in water medium, it will be close to the core of micelle and result in bending towards the hydrophobic chain. On the basis of the above discussion, a possible packing structure of $Py(CH_2)_{1,2}mim^+Br^-$ molecules in a micelle is depicted in Fig. 5. This staggered arrangement favors the compact stacking of hydrophobic parts of Py(CH₂)₁₂mim⁺Br⁻ inside the micelle and decreases the unfavorable contact with water.46

3.2. Dielectric properties of $Py(CH_2)_{12}mim^+Br^-$ aqueous solution

3.2.1 Determination of relaxation parameters. To characterise the two relaxation processes in Fig. 3 in detail, it is necessary to determine the relaxation parameters. All these parameters were obtained by fitting the eqn (3) including two Cole–Cole's terms and are summarized in Table 2. The ε_1 , ε_m and ε_h indicate the values of permittivity at low, middle and high frequency range, respectively. $\Delta \varepsilon_i$ and τ_i are the dielectric increment and the relaxation time for each dielectric relaxation *i* (*i* = 1, 2), respectively. The uncertainties of these parameters we calculated are within 5.5%.

It should be pointed out that the conductivity values (κ_h and κ_m) at high and middle frequency are estimated from eqn (12):⁴⁷

$$\kappa_{\rm h} = ((\varepsilon_{\rm m} - \varepsilon_{\rm h}) \times 2 \times \pi \times f_0 \times \varepsilon_0) + \kappa_{\rm m}$$
(12a)

$$\kappa_{\rm m} = ((\varepsilon_{\rm l} - \varepsilon_{\rm m}) \times 2 \times \pi \times f_0 \times \varepsilon_0) + \kappa_{\rm l}$$
(12b)

From Table 2, it can be seen that both of β_1 and β_2 are around 0.8, indicating that the dielectric relaxation is not the



Debye-type relaxation. The small distributions of these two relaxations probably indicate the heterogeneity in the size or electrical property of micelle. It also will be involved and discussed later.

3.2.2 The relaxation mechanisms. It is well known that the relaxation time (τ) is the most effective criterion to describe the characteristics of relaxation and determine the relaxation mechanism and dynamics. Two relaxation mechanisms known as counterion polarization and interfacial polarization, in general, are typically responsible for the dielectric dispersion of aqueous colloidal suspensions.48 We think the relaxation-1 may be caused by the counterion polarization which is associated with the setup of ionic concentration gradient around the particle, while the relaxation-2 can be due to the famous Maxwell–Wagner effect. The relaxation time τ can be used to ascertain the mechanisms of these relaxation processes. According to Schwarz,⁴⁹ the relaxation time of the counterion polarization corresponds to the time for the counterions to transport from one side of the spherical particle to the other side, and relates to the migration distance of counterions which is on the order of $l \approx 2(a + \chi^{-1})^{50}$ and the diffusion coefficient of counterion by the equation:

$$\tau_{\rm low} = \frac{l^2}{D_{\rm Br^-}} \tag{13}$$

where, $D_{\rm Br}$, the counterion in this work, is estimated to be 2.1 × 10⁻⁹ m² s⁻¹,⁵¹ *a* is the radius of the particle (approximately 2.5 nm (ref. 52 and 53)), and χ^{-1} is a measure of the EDL thickness, also known as the Debye length characterizing the size of the diffuse ion cloud, is approximately given by eqn (14):⁵⁴

$$\chi^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_a D_{\mathrm{Br}^-}}{\kappa_1}} \tag{14}$$

where, the permittivity of solution ε_a is considered as a constant value 78.36 at 298.15 K. From eqn (13) and (14), low frequency relaxation time was estimated and it has an order of 10^{-8} s, being in good agreement with the order of τ_1 listed in Table 2. This confirmed that the low frequency dielectric relaxation observed in the system is caused by the counterion polarization.

Maxwell–Wagner polarization occurs because of the different permittivity and conductivity between the micelle particle and the surrounding medium. According to the Maxwell–Wagner's theory, the relaxation time corresponds to the time that counterions are shaking back and forth in the EDL and can be estimated by the well-known Einstein equation:⁴⁸

$$\tau_{\rm high} = \frac{\chi^{-2}}{D_{\rm Br^-}} \tag{15}$$

By this equation, the relaxation time of relaxation-2 was calculated and the values of different concentrations are in the range of 5.2–8.4 ns, which is the same order of τ_2 observed experimentally (see Table 2). Similarly, the mechanism of relaxation-2 at high frequency is also assigned to be caused by the Maxwell–Wagner polarization.

Table 2 Relaxation parameters of the relaxations in $Py(CH_2)_{12}mim^+Br^-$ solution with different concentrations, obtained by fitting eqn (3) to the dielectric spectra

C/mM	$\Delta \epsilon_1 = \epsilon_l - \epsilon_m$	$\Delta \epsilon_2 = \epsilon_m - \epsilon_h$	$\varepsilon_{\rm h}$	β_1	β_2	τ_1/ns	τ_2/ns	$\kappa_{\rm l}/{\rm S~m^{-1a}}$
11.3	1.3 ± 0.07	0.5 ± 0.05	80.5 ± 0.2	0.806 ± 0.03	0.817 ± 0.04	117.6 ± 5	4.31 ± 0.3	0.078
12.1	1.4 ± 0.08	0.9 ± 0.05	80.4 ± 0.2	0.805 ± 0.04	0.846 ± 0.05	117.0 ± 0 115.1 ± 2	3.96 ± 0.3	0.081
13.1	1.8 ± 0.07	0.9 ± 0.03	80.7 ± 0.4	0.822 ± 0.05	0.855 ± 0.04	113.4 ± 2	3.87 ± 0.1	0.082
14.0	2.0 ± 0.07	1.3 ± 0.03	80.7 ± 0.3	0.859 ± 0.03	0.864 ± 0.03	110.3 ± 2	3.56 ± 0.2	0.084
15.5	2.1 ± 0.1	1.6 ± 0.05	80.8 ± 0.5	0.849 ± 0.05	0.846 ± 0.05	105.9 ± 3	3.42 ± 0.3	0.087
17.0	2.7 ± 0.2	1.3 ± 0.1	81.1 ± 0.4	0.815 ± 0.06	0.897 ± 0.04	102.5 ± 1	3.34 ± 0.1	0.091
18.9	2.5 ± 0.2	1.9 ± 0.04	81.2 ± 0.5	0.862 ± 0.05	0.816 ± 0.02	100.2 ± 2	3.26 ± 0.2	0.095
21.3	3.1 ± 0.2	3.3 ± 0.1	80.1 ± 0.6	0.829 ± 0.02	0.899 ± 0.06	87.2 ± 5	2.89 ± 0.2	0.100
24.3	3.9 ± 0.2	2.5 ± 0.1	81.3 ± 0.5	0.811 ± 0.05	0.865 ± 0.02	79.7 ± 2	2.75 ± 0.1	0.106
28.3	4.2 ± 0.2	3.9 ± 0.2	80.6 ± 0.4	0.795 ± 0.03	0.814 ± 0.02	75.9 ± 3	2.53 ± 0.1	0.114
^{<i>a</i>} The val	lues of κ_l were read	from conductivity s	pectra.					

Both of the relaxation times listed in Table 2 are plotted as a function of the concentration of $Py(CH_2)_{12}mim^+Br^-$ solution in Fig. 6. Fig. 6 shows that τ_2 remains virtually unchanged in the experimental concentration range, while τ_1 decreases monotonously with concentration of $Py(CH_2)_{12}mim^+Br^-$, implying the migration distance of counterions l decrease by eqn (13). On the other hand, the radius of micelles was calculated by eqn (14) and $l \approx 2(a + \chi^{-1})$. It shows the difference in the micellar radius between $Py(CH_2)_{12}mim^+Br^- C = 28.3 \text{ mM}$ and C = 11.3mM is 8 Å. In other words, increasing the concentration of $Py(CH_2)_{12}mim^+Br^-$ shortened migration distance of counterions l and led to the smaller micellar radius. This change of radius is due to the fraction of water in micelles because micellar size is sensitive to the amount of water trapped in the micelle core. When the concentration of Py(CH₂)₁₂mim⁺Br⁻ solution is lower, the micelle will adopt a comparatively looser structure and will include a certain amount of water molecules, while the tightly aggregated micelle structure will be formed with an increase of the concentration. This suggests that the aggregation was accompanied by the decrease in amount of water, and the conclusion is supported by the literature.55 Thus, by analyzing dielectric spectra we found the small variations of water in the micelle that are hard to detect by other traditional methods.



Fig. 6 Relaxation time of low and high frequency dielectric relaxation as a function of $Py(CH_2)_{12}mim^+Br^-$ concentration.

3.2.3 Dielectric model. As mentioned in Section 3.1, it has been confirmed that spherical micelles form when the concentration of $Py(CH_2)_{12}mim^+Br^-$ solution exceeds 9 mM. To obtain the detailed information about inner structure, electrical properties of micelles and interfacial electrokinetics, it is necessary to calculate the parameters of the constituent phase of the micelle solution system (named phase parameters in this work). The present micelle system can be modeled as a particle suspensions with complex permittivity ε^* , *i.e.*, the spherical micelle particles with radius *a* and complex permittivity ε^*_p dispersed in a continuous media of permittivity ε^*_a in a volume fraction ϕ as illustrated in Fig. 7(a-c).

Based on above model, the following Maxwell–Wagner equation (eqn (16)) which is applicable to the dilute suspension can be used to calculate the phase parameters:

$$\varepsilon^* = \varepsilon_{\rm a}^* \frac{2(1-\phi)\varepsilon_{\rm a}^* + (1+2\phi)\varepsilon_{\rm p}^*}{(2+\phi)\varepsilon_{\rm a}^* + (1-\phi)\varepsilon_{\rm p}^*} \tag{16}$$

It should be noted that the phase parameters, ε_a , ε_p , κ_a , κ_p and ϕ , are those of the bulk materials of respective phases without considering the volume charge distribution at the interfaces. By means of a systematic numerical method for computing the phase parameters from the relaxation parameters, ε_m , ε_h , κ_m and κ_h , developed by Hanai as follows:⁵⁶

$$H(\kappa_{\rm a}) \equiv \sqrt{\frac{\kappa_{\rm m}\varepsilon_{\rm a} - \kappa_{\rm a}\varepsilon_{\rm m}}{\kappa_{\rm h}\varepsilon_{\rm a} - \kappa_{\rm a}\varepsilon_{\rm h}}} - \frac{\kappa_{\rm a}}{\varepsilon_{\rm a}} \frac{\varepsilon_{\rm m} - \varepsilon_{\rm h}}{\varepsilon_{\rm h} - \kappa_{\rm m}} = 0$$
(17a)

$$\phi = \frac{\varepsilon_{a}\varepsilon_{h}(\kappa_{m} - \kappa_{a})^{2} + (\varepsilon_{a} - \varepsilon_{h})(\varepsilon_{a}\kappa_{m}^{2} - \varepsilon_{m}\kappa_{a}^{2})}{(\varepsilon_{a}\kappa_{m} - \varepsilon_{h}\kappa_{a})^{2} + (\varepsilon_{m} - \varepsilon_{h})(2\varepsilon_{a} + \varepsilon_{h})\kappa_{a}^{2}}$$
(17b)

$$\varepsilon_{\rm p} = \varepsilon_{\rm a} \frac{\phi(2\varepsilon_{\rm a} + \varepsilon_{\rm h}) - 2(\varepsilon_{\rm a} - \varepsilon_{\rm h})}{\phi(2\varepsilon_{\rm a} + \varepsilon_{\rm h}) + \varepsilon_{\rm a} - \varepsilon_{\rm h}} \tag{17c}$$

$$\kappa_{\rm p} = \kappa_{\rm a} \frac{\phi(2\kappa_{\rm a} + \kappa_{\rm m}) + 2(\kappa_{\rm m} - \kappa_{\rm a})}{\phi(2\kappa_{\rm a} + \kappa_{\rm m}) - (\kappa_{\rm m} - \kappa_{\rm a})}$$
(17d)

the values of ϕ , $\varepsilon_{\rm p}$ and $\kappa_{\rm p}$ were calculated in sequence after a cumbersome mathematical treatment, and are listed in Table 3. The permittivity of solution medium $\varepsilon_{\rm a}$ is considered to be a



constant, 78.36, at the experimental temperature. The value of κ_a was obtained by computer-searching eqn (17a).

The observed relaxation time τ_2 given in Table 2 can be used to ascertain the relaxation mechanism. According to Maxwell– Wagner theory, τ_{MW} is given by the following equation:

$$\tau_{\rm MW} = \frac{2\varepsilon_{\rm a} + \varepsilon_{\rm p} + \phi(\varepsilon_{\rm a} - \varepsilon_{\rm p})}{2\kappa_{\rm a} + \kappa_{\rm p} + \phi(\kappa_{\rm a} - \kappa_{\rm p})}\varepsilon_0 \tag{18}$$

Using $\varepsilon_a = 78.36$, τ_{MW} of different Py(CH₂)₁₂mim⁺Br⁻ concentrations were calculated to be in the range of 2.5–6.2 ns, which is in good agreement with the measured τ_2 . This indicates that it is reasonable and credible to deal with the micelle system with the dielectric model of particle dispersion.

It is obvious from Table 3 that the volume fraction of micelles ϕ increases from about 0.03 to 0.05 with the increment of concentration of Py(CH₂)₁₂mim⁺Br⁻ solution. Combining the concentration dependence of the low frequency relaxation time τ_1 given in Table 2 and Fig. 6, we found τ_1 decreases slightly as Py(CH₂)₁₂mim⁺Br⁻ concentration increases. It may be concluded that the increase in the volume fraction of micelles is because the number of micelles increased with the enhancement of the concentration and not because the volume of the micelle particle became turgid.

3.2.4 The unusual permittivity and conductivity of micelle. We also got an interesting finding from the analyzing results shown in Table 3, the permittivity of the micelle particles are

Table 3	Phase parameters of $Py(CH_2)_{12}mim^+Br^-$ system					
C/mM	$\kappa_{\rm a}/{\rm S}/{\rm m}$	ϕ	ε_{p}	$\kappa_{\rm p}/{ m S}~{ m m}^{-1}$		
11.3	0.0784	0.0336	163	0.297		
12.1	0.0806	0.0363	152	0.332		
13.1	0.0818	0.0386	157	0.363		
14.0	0.0838	0.0400	157	0.416		
15.5	0.0868	0.0419	156	0.459		
17.0	0.0921	0.0437	161	0.467		
18.9	0.0952	0.0501	153	0.497		
21.3	0.0995	0.0505	130	0.586		
24.3	0.1056	0.0519	147	0.606		
28.3	0.1138	0.0535	129	0.813		

130 to 160 levels. It is much higher than either of those of the alkyl chain of micelle (2, 25 °C (ref. 57)) and the water including in the micelle ($\varepsilon_a = 78.36$, 25 °C). This unusual dielectric property of the micelle must have something to do with the materials that make up the micelle, amphiphilic pyrrole-tailed imidazolium ILs Py(CH₂)₁₂mim⁺Br⁻ and their molecular arrangements in the micelle core.

The bulky methylimidazolium and Py group in the Py(CH₂)₁₂mim⁺Br⁻ molecule increase the steric hindrance and make the molecule in the micelle core well-organized.40 Meanwhile, Vanyúr et al.41 showed that the larger size of methylimidazolium headgroups allows more facile water penetration than in other traditional micelles such as alkyltrimethylammonium bromides (C_n TAB), and the water in micelle core strongly influences the properties of the micelle. In addition, the research of Allen⁵⁸ and Ballenegger⁵⁹ also shows that the image charge interactions arise on the mesoscopic scale because of the dielectric discontinuity between the polar fluid and interface, and the first layer of molecules align their dipoles parallel to the interface in terms of electrostatic interactions of these dipoles with their images. Similarly, there is a large dielectric discontinuity between water and alkyl chains in the micelle core, therefore the water alongside the alkyl chain aligns their dipoles parallel to the hydrophobic chain. Such orientations would favor larger values of dipole-dipole correlations as shown in Fig. 7(d). This description about water molecule orientation is well supported by the findings of Martí⁶⁰ in which a lager permittivity of about 172 for the confined water in graphite slabs was observed and was attributed to the strong orientational order of water in the slabs surface, which have been proved by molecular dynamics simulations. On the other hand, because the Py group in the terminal of hydrocarbon chain of Py(CH₂)₁₂mim⁺Br⁻ is dipolar due to the less symmetrical molecular structure, the dipole-dipole attractions generated between water and Py group⁶¹ (see Fig. 7(d)), and the attraction is lower in energy than the dipole-dipole repulsion. The coupling of the dipoles of the water molecules nearest Py group creates a relatively long-lived dipole pair, giving rise to the increase of the global permittivity of the micelle. As mentioned above, the larger permittivity ε_p contains two major contributions from two segments of water that can be expressed as:

$\varepsilon_{\rm p} = \varepsilon_{\rm alkyl\ chain-water} + \varepsilon_{\rm py-water}$

In conclusion, the reorientation of water molecules in the interfaces of alkyl chain and near Py group induced a stronger correlation between the molecular dipole moments, resulting in the larger values of $\varepsilon_{\rm p}$. Alternatively, the unusual apparent permittivity provided the unique information about the orientation of water molecules confined in micelle and interactions with the hydrophobic regions.

In addition, it is also obvious from Table 3 that the conductivity of micelle particle κ_p is much bigger than the conductivity κ_a of continuous medium. It is easy to understand why the micelle particle has higher conductivity from its structure: the counterions Br⁻ in the micelle suspension are mostly condensed near the micelle surface due to the electrostatic attraction from methylimidazolium headgroups positively charged, and their migration led to the higher conductivity. This can also be interpreted from the counterion ionization degree γ of Py(CH₂)₁₂mim⁺Br⁻ micelle given in Section 3.1 (see Fig. 4(b)). The ratio of two conductivity gradients S_2/S_1 (*i.e.*, $\gamma = 0.246$) is lower, which exhibits lower ion conductivity in the micelle suspension. In other words, most Br⁻ as counterions were trapped inside the micelle and moved around the methylimidazolium headgroups as depicted in Fig. 7(c), and the ion mobility from the excess Br^{-} in the micelle created the higher conductivity.

3.2.5 The electrical parameter of electrode double layer. According to the result of Maxwell–Wagner theory, the surface conductivity λ , existing near the micelle surface covered with EDL containing a lot of counterions Br⁻ with thickness of χ^- (see Fig. 7(b)), can be obtained by using the following equation from the relaxation parameters (Table 2) and the electrical parameters of micelle particles (Table 3):⁶²

$$\Delta \varepsilon_{2} = 9\phi \frac{\left(\varepsilon_{p}\kappa_{a} - \varepsilon_{a}\left(\kappa_{p} + 2\lambda/a\right)\right)^{2}(1-\phi)}{\left[(1-\phi)\varepsilon_{p} + (2+\phi)\varepsilon_{a}\right]\left[(1-\phi)\left(\kappa_{p} + 2\lambda/a\right) + (2+\phi)\kappa_{a}\right]^{2}}$$
(19)

where $\Delta \varepsilon_2$ is the dielectric increment of the relaxation-2 that is ascribed to interfacial polarization as mentioned above. Other symbols have the same meaning as mentioned above. The calculated results of λ for micelle suspensions of different Py(CH₂)₁₂mim⁺Br⁻ concentrations are listed in Table 4.

Further, the surface charge density σ of the micelle and zeta potential ζ for these suspensions were also calculated by the following equation:⁶³

$$\sigma = \frac{\lambda}{z^2 u} = \frac{4C_{\rm e}e}{\chi} \sinh\left(\frac{e\zeta}{2k_{\rm B}T}\right) \tag{20}$$

where, *u* is the mobility of counterion Br⁻ and *z* is the valence of free charge, *e*, *C*_e, χ , *k*_B and *T* are the quantity of elementary free charge, number concentration of free charge, reciprocal of the EDL thickness, Boltzmann constant and absolute temperature, respectively. The calculated results for the parameters σ and ζ are also summarized in Table 4.

It is evident from Table 4 and Fig. 8 that all the three electrical parameters change with the enhancement of

Table 4The interfacial electrokinetic parameters calculated by eqn(19) and (20)

C/mM	$\lambda/10^{11}$ S	$\sigma/10^3 \mathrm{~C~m^{-2}}$	ζ/mV
11.3	7 34	8 0/	236
12.1	8.19	9.98	238
13.1	11.7	14.3	253
14.0	13.7	16.7	259
15.5	16.6	20.2	265
17.0	18.0	22.0	265
18.9	25.1	30.5	272
21.3	24.4	29.8	278
24.3	36.0	43.9	283
28.3	37.6	45.8	287

concentration. The values of λ and σ increase proportionally to the concentration of Py(CH₂)₁₂mim⁺Br⁻, whereas ζ increases first with the increment of Py(CH₂)₁₂mim⁺Br⁻ concentration, and then remains stable. Zana *et al.*⁶⁴ found the mean micellar aggregation number increases with surfactant concentrations by fluorescence probing method. In our system, as the concentration of Py(CH₂)₁₂mim⁺Br⁻ increases the N_{agg} increases. As a result, the number of positive charges in the micelle surface increase and it exhibits the increment of σ as



Fig. 8 Concentration dependence of surface conductivity λ , surface charge density σ and zeta potential ζ .

macro-characteristics. On this basis, under the external applied electric field, the ions accumulate on the interface as polarized charges and lead to the transferring of more counterions in diffuse layer to keep the charge balance. Hence, the surface conductivity λ also increases with Py(CH₂)₁₂mim⁺Br⁻ concentrations. From the viewpoint of the surface conductivity λ and the surface charge density σ , it was found that there are many condensed counterions Br⁻ near micelle surface with mobility around the micelle. These also explain the reason of the unusually large conductivity of the micelles.

It is well known that zeta potential is related to the surface charge of micelle, the positive charge in this work, and absorbed Br⁻. With increasing concentration of Py(CH₂)₁₂mim⁺Br⁻, the positive charges in the micelle surface increase and the cumulation of Br⁻ also gradually increases, leading to the increase of ζ . While the concentration is higher than 18 mM, the aggregation of ILs monomer and adsorption of Br⁻ reached the saturation. Therefore, the value of ζ gradually tended to be stable and these values in the experimental concentration range are comparable to that of micelles measured by electrophoresis method:⁶⁵ $\zeta = 56.5$ mV for C₁₀N(CH₃)₃C1 at 61.1 mM, 75 mV for C₁₂N(CH₃)₃C1 at 17.2 mM and 116 mV for C₁₄N(CH₃)₃C1 at 4.5 mM. The zeta potential we obtained is larger than other values measured by electrophoresis method. It can be understood from larger charge density originating from the special structure headgroup. Considering the special structure and multiple computing from dielectric spectra data, the difference in the ζ values is not significant. However, the electrokinetic parameters of micelle surface acquired above by analyzing dielectric spectroscopy may provide a valuable reference, especially the surface charge density σ , which is hardly to be estimated directly in any other methods.

4. Conclusions

The special ionic liquid surfactant with a terminal polymerizable unit, as structure-directing agent has important applications in the preparation of nanoparticles and drug carriers. Its special aggregation behavior caused by the terminal group is one of the most important reasons to use it as the template. The aggregation behavior of Py(CH₂)₁₂mim⁺Br⁻ was studied in detail by dielectric spectroscopy. The CMC of Py(CH₂)₁₂mim⁺Br⁻ micelle and its spherical structure were affirmed from the dielectric measurements, and the dynamics of the aggregation are also discussed. It is revealed that the Py(CH₂)₁₂mim⁺Br⁻ molecular spontaneously formed spherical micelle at the concentration range higher than CMC, and the incorporation of Py group has a significant influence on the surface activity, thermodynamics, and mechanism of micelle formation.

A couple of dielectric relaxations were firstly observed in micelle system in radio frequency ranges and their relaxation mechanisms are identified. The relaxation at lower frequency originated from the diffusion of counterions at the micelle surface and the one at higher frequency is attributed to the interfacial polarization between micelles and medium solution. The inner parameters of micelle suspension were calculated based on the Maxwell–Wagner theory and a dielectric model proposed. As one of the results of dielectric analyzing, an unusual apparent permittivity of the whole spherical micelle was discussed from a microstructure point. A possible arrangement of the water molecules trapped in micellar core is suggested. This finding is important because of the little information available from experimental, or computer simulation research into the dielectric properties of confined water, especially in the micellar core. Further, the three electrokinetic parameters, surface conductivity, surface charge density and zeta potential, that control the electric properties of $Py(CH_2)_{12}mim^+Br^-$ micelle surface and EDL were estimated. These three electrokinetic parameters of special aggregation can be used as the reference in the fundamental research.

The micellar structure and dielectric properties of $Py(CH_2)_{12}mim^+Br^-$ in water explored in this paper will help to understand the aggregation behavior of surfactant incorporated a special group at the terminal of the hydrocarbon chain. The specific dielectric properties obtained in this system can provide information on arrangements and stability of water molecules confined in nanoscale hydrophobic environments as well as the polarity of ordered microregions. The present study also shows the advantage and the feasibility of evaluating the physical chemistry properties of particle interior and the external medium of dispersion system by DRS.

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