

Dielectric analysis of poly(diallyldimethylammonium chloride) aqueous solution coupled with scaling approach†

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Dielectric measurements were carried out on aqueous solution of poly(diallyldimethylammonium chloride) (PDADMAC) with different concentrations at room temperature. Additionally, for selected solutions the temperature dependence of dielectric relaxation spectroscopy (DRS) was examined in the range of 5–70 °C. The dielectric relaxation in the order of around MHz was observed, and the dielectric parameters were determined from the dielectric spectra by fitting data with the Cole–Cole equation. The dielectric parameters showed strong dependences on concentration and on temperature, respectively, and these dependences are analyzed by the scaling theory. From the analysis of concentration dependence of dielectric parameters, the dielectric relaxation is assigned to the localized fluctuation of uncondensed counter-ions over the distance between chains in dilute solution and correlation length in semi-dilute solution, respectively, and the solvent quality parameter for the uncharged polyelectrolyte chain is evaluated. By the analysis of temperature dependence of dielectric parameters, we find that: the physical meanings of the typical lengths of uncondensed counter-ions are not influenced by temperature; in semi-dilute solution, the highly extended length of the chain (correlation length) increases and the end-to-end distance of the chain decreases with increasing solution temperature; in the change process of dielectric relaxation of PDADMAC solution induced by the increase of temperature, the increment of ionic diffusion coefficient and decrement of permittivity of the solvent medium are the major factors. The enthalpy and entropy of activation of the dielectric relaxation are experimentally determined by the dependence of relaxation time on temperature, individually.

Introduction

Charged polymers, namely polyelectrolytes, can dissolve in water or other ionizing solvents and dissociate into polyions that carry multiple charges together with an equivalent amount of counter-ions.¹ Poly(diallyldimethylammonium chloride) (PDADMAC) is one of the typical representatives of polyelectrolytes which has many positive charges and a cyclic structure in its backbone as shown in Fig. 1. Because it is a cationic polyelectrolyte, PDADMAC is often used as a model for studying the interaction with various negatively charged soluble polymers,² colloids¹ and micelles.³ On the other hand, PDADMAC has also been widely used in industrial applications, for example, petroleum extraction, water treatment and cosmetic formulations.⁴ Therefore, PDADMAC has attracted much interest in the last decades and tremendous efforts have been devoted to the study of it,

which involves the kinetics and mechanism of the free radical polymerization of DADMAC,⁵ the determination of molecular parameters,^{6,7} the solution properties,^{8–10} molecular dynamics simulations¹¹ and studies in application fields.⁴ Nevertheless, most of these works do not study the configuration of the PDADMAC chain in solution. Additionally, few previous works investigated the dielectric properties of PDADMAC solution which can reflect dynamics information such as the details of the Coulombic interaction between the counter-ions and the polyion in solution.^{12,13}

Dielectric relaxation spectroscopy (DRS), which measures permittivity and conductivity as a function of frequency, is a powerful method to investigate the dielectric properties of polyelectrolyte solution. Further analysis of the data obtained from DRS, combined with proper theories,¹² can give us useful information, such as the spatial distribution^{14,15} and diffuse situation¹⁶ of counter-ions, the configuration of the chain, the solvent quality parameter¹⁷ and so on. In previous DRS works on polyelectrolyte solution, two adjacent dielectric

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† Electronic supplementary information (ESI) available: Figure A. Temperature dependence of (a) permittivity, (b) conductivity and (c) dielectric loss of 0.008 wt% PDADMAC solution. Data of different temperatures are represented by different symbols as indicated in (a), and the same symbols in (b) and (c) have the same meanings. Figure B. Temperature dependence of diffusion coefficient of uncondensed counter-ions in different selected concentrations represented by different symbols as indicated. Figure C. Temperature dependence of (a) relaxation time and (b) dielectric increment of selected concentrations as indicated. See DOI: 10.1039/b924572c

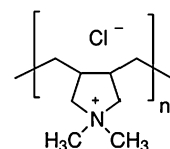


Fig. 1 Structure of poly(diallyldimethylammonium chloride) (PDADMAC).

relaxations have been found in the frequency range from several Hz to 100 MHz. Lots of works have discussed the mechanisms of these two dielectric relaxations: concretely, the low-frequency relaxation which occurs in the order of around kHz is commonly assigned to the fluctuation of the condensed counter-ions along the whole polyion axis.^{18,19} However, the mechanism of high-frequency relaxation in the order of around MHz has not been understood fully until now. Therefore, various models have been used to interpret this dielectric behavior. For example, O’Konski explained some aspects of the high-frequency relaxation based on the Maxwell-Wagner effect,²⁰ but can not account for the main features of this relaxation. On the other hand, in terms of the van der Touw and Mandel’s model,¹⁸ the polyion chain can be represented by a sequence of subunits that are separated by potential barriers opposing the diffusion of the counter-ions, and the counter-ion fluctuation along each of them determines an induced dipole moment along the polymer chain whose dispersion causes the high-frequency relaxation. In the linear lattice models developed by Minakata,²¹ high-frequency relaxation is due to the counter-ion radial diffusion processes which reduce the relaxation time in the longitudinal ion motion. In the polyelectrolyte cell model proposed by Katchalsky,²² the high-frequency relaxation of dilute polyelectrolyte solutions can be explained in two different ways: one way is to characterize this relaxation as counter-ion radial diffusion,²³ another way is to assign this relaxation to the fluctuation of counter-ions spreading over the distance between polyions.^{16,24} Recently, in the scaling model, which is used for describing the configuration of linear flexible polyelectrolytes in solution,^{25,26} the observed power-law behaviors of dielectric properties (relaxation time and dielectric increment) as a function of polyelectrolyte concentration were successfully explained by Bordi *et al.*,^{12,27} and a many works which used the analogous approach have been published since.^{28–30}

The dielectric properties of polyelectrolyte solution are very sensitive to the variation of external environment. The changes of dielectric property of PDADMAC solution caused by the alteration of concentration and temperature can be reflected by the DRS. Further analysis of the concentration and temperature dependence of DRS, with the help of proper theory of polyelectrolyte, will give the internal information of the PDADMAC solution which can not be obtained from other methods. On the other hand, there are not enough DRS studies of positively charged polyelectrolyte solutions³¹ compared with similar studies of organic polymers^{27,30} anionic polyelectrolytes^{17,30} and copolymers^{28–30}, as far as we know.

In this work, DRS has been performed on poly(diallyldimethylammonium chloride) (PDADMAC) solution in a wide mass concentration, c_m , ranging from 0.004 to 0.092 wt% and in the temperature range from 5 to 70 °C. The first purpose of this work is to study the dynamics properties and configuration information of PDADMAC solution through analyzing the dielectric data with the help of the scaling theory. The second aim is to contribute new concentration and temperature dependent dielectric data for the theoretical dielectric analysis by measuring the DRS of a cationic polyelectrolyte which has a cyclic structure in its backbone.

Finally, the activation enthalpies and entropies of the observed relaxation processes will also be obtained from the investigation of temperature dependence of DRS, respectively.

Theory

In the modeling of polyelectrolyte solutions using the modern theoretical approaches, such as the scaling theory,^{25,26} the atomistic details of solvent and polymers are ignored. The solvent molecules are replaced by a continuum with the same permittivity, ϵ_m , and the polyelectrolyte chains are modeled by a chain of electrostatic blobs as shown in Fig. 2. The size of the electrostatic blobs, ξ_e , and the number of monomers inside each of these blobs, g_e , can be expressed as:

$$\xi_e \approx \frac{b^{4/3}}{f^{2/3} l_B^{1/3}} \text{ and } g_e \approx \frac{T_r b}{f^2 l_B} \quad (1)$$

where b is the average spacing between charged groups on the polyion chain, $l_B = e^2/\epsilon_m k_B T$ is the Bjerrum length (e is elementary charge, ϵ_m is permittivity of the solvent medium, k_B is the Boltzmann constant and T is temperature), defined as the distance at which the energy of the Coulomb interaction between two elementary charges is equal to the thermal energy, $k_B T$, $T_r \equiv (\theta - T)/\theta$ is the solvent quality parameter (also called reduced temperature) and θ is the temperature at which the net interaction between uncharged polymer and water is zero. In this scaling theory, there is a lack of a clear phase interface between the dissolved polyelectrolyte chains and the continuum of solvent to assign the dielectric relaxation in polyelectrolyte solution to the interfacial polarization. In addition, in previous studies, the dielectric relaxation which occurs in the order of around MHz is often successfully attributed to an induced dipole moment which is imparted by the counter-ions fluctuating along some typical length (also called fluctuation length).^{16,18,24,27–30} According to these two points, the dielectric relaxation observed in this work may originate from the counter-ion fluctuating along the typical length L (and this assumption can be strongly supported by the analysis for concentration dependencies of dielectric increment and relaxation time as discussed in the results and discussion section). Thus, the relaxation time can be given by eqn (2).¹³

$$\tau \approx \frac{L^2}{6D_{\text{ion}}} \quad (2)$$

where D_{ion} is the diffusion coefficient of the counter-ions in solution. And the dielectric increment is simply the product of the number concentration of the counter-ion, fc (c is the number concentration of monomers), and their polarizability, $\alpha_{\text{ion}} \approx e^2 L^2 / (kT)$.¹³

$$\Delta\epsilon \approx \frac{e^2 L^2}{kT} fc \approx l_B \epsilon_m L^2 fc \approx b \epsilon_m L^2 c \quad (3)$$

In the counter-ion condensation model,³² when the charge density parameter l_B/b is greater than 1, the electrostatic attraction between polyelectrolyte chains and counter-ions in solution can cause a fraction $1 - f = 1 - b/l_B$ of the counter-ions to condense on the ionized polyion groups in order to

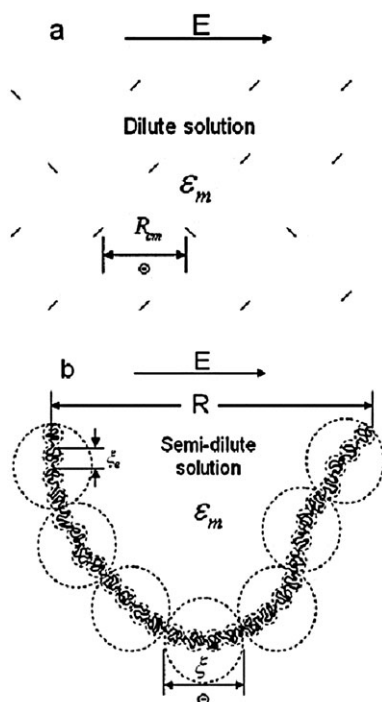


Fig. 2 Schematic representation of the polyelectrolyte chain in (a) dilute solution (b) semi-dilute solution.

reduce the effective charge density of polyelectrolyte chains. This means a fraction $f = b/l_B$ of uncondensed counter-ions are free in solution. These counter-ions are also called loosely bound or free counter-ions in different literatures.^{13,24}

Uncondensed counter-ions are free in solution, but their movements are limited within some typical lengths due to the periodic shielding effect of the condensed counter-ions.²² These typical lengths are likely to be the electrostatic screening length, r_{scr} , probably because r_{scr} is the length which limits the range of motion of ions and is determined by the periodic shielding effect which is determined by the interactions between different charged species existing in the solution. According to the scaling theory, r_{scr} is the distance between chains $R_{cm} \approx (N/c)^{1/3}$ (where N is the degree of polymerization) in dilute solution; and r_{scr} is identical to the correlation length ξ ($\approx [g_e/(\xi_c c)]^{1/2}$) within a prefactor in semi-dilute solution when there is no added salt.²⁶

Experimental

Materials

The poly(diallyldimethylammonium chloride) (PDADMAC) sample with nominal molecular weight of 200 to 350 kD was purchased from Aldrich Chem. Co., as 20 wt% solution in water, residual M-Dadmac $\leq 0.5\%$ wt. The structure of PDADMAC has been shown in Fig. 1. The sample was used as received, without any further purification. Highly deionized water possessing specific resistance higher than $16 \text{ M}\Omega \text{ cm}^{-1}$ was used as the solvent. No additional electrolyte was added to the aqueous solution of PDADMAC. The solutions were kept standing for over two days prior to DRS measurements in order to equilibrate the system. Ten of different

concentrations mentioned above were used for the temperature dependent dielectric measurements.

Dielectric measurement

Dielectric measurements of PDADMAC solution were carried out on 4294A Precision Impedance Analyzer from Agilent Technologies (tested and calibrated in accordance with the procedure recommended by the manufacturer) that allows a continuous frequency measurement from 40 Hz to 110 MHz, controlled by a personal computer. The amplitude of the applied alternating field was 500 mV. A dielectric measurement cell with concentric cylindrical platinum electrodes was employed,³³ and connected to the impedance analyzer by means of a 1607E Spring Clip fixture (Agilent Technologies). The volume of the solutions used in the experiment was 1 mL in order to submerge the electrode. The concentration dependent dielectric measurements were carried at 25 ± 0.1 °C. The temperature dependent dielectric measurements were performed from 5 to 70 °C and the interval is 5 °C. The deviation of temperature was less than ± 0.1 °C. At each measurement temperature, the cell constant and stray capacitance was determined with air, ethanol and pure water. The experimental data were corrected by the cell constant, stray capacitance and residual inductance (arising from the terminal leads) according to Schwan's method.³⁴ The permittivity and conductivity were calculated from the corrected capacitance and conductance.

Determination of the dielectric parameters

In an applied electric field of frequency f , the dielectric properties of a polyelectrolyte aqueous solution can be characterized by the complex permittivity $\varepsilon^*(\omega)$ which is defined as

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j \frac{\kappa(\omega)}{\varepsilon_0 \omega} = \varepsilon'(\omega) - j \varepsilon''(\omega) - j \frac{\kappa_l}{\varepsilon_0 \omega} \quad (4)$$

where $\varepsilon'(\omega)$ is the permittivity, $\kappa(\omega)$ is the conductivity, κ_l is the low-frequency limit of conductivity, ε_0 is the permittivity of vacuum, ω is the angular frequency, $j^2 = -1$, $\kappa(\omega)/\varepsilon_0 \omega$ is the total dielectric loss which includes two parts, namely, dielectric loss, $\varepsilon''(\omega)$, and dc conductivity contribution, $\kappa_l/\varepsilon_0 \omega$. If the dielectric relaxation occurs, it can be characterized by a set of dielectric parameters: ε_l and ε_h are the low-frequency and high-frequency limits of permittivity, respectively, $\Delta\varepsilon = \varepsilon_l - \varepsilon_h$ is the dielectric increment, f_0 is the characteristic frequency, and τ ($\tau = (2\pi f_0)^{-1}$) is the relaxation time. These dielectric parameters can be obtained by fitting the Cole–Cole empirical function to the experimental data:³⁵

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j \varepsilon''(\omega) = \varepsilon_h + \sum_i \frac{\Delta\varepsilon_i}{1 + (j\omega\tau_i)^\beta} \quad (5)$$

where β ($0 < \beta \leq 1$) is the Cole–Cole parameter indicating the dispersion of the relaxation time and i is the number of the dielectric relaxation.

When the continuous phase is conductive, there is a considerable electrode polarization effect (EP) due to the accumulation of spatial charges on the electrode surface, often obscuring the dielectric relaxation in the low-frequency range.

Thus, the electrode polarization term, ε'_{EP} , which can be expressed by the following empirical equation³⁶

$$\varepsilon'_{EP} = A\omega^{-m} \quad (6)$$

(where A and m are adjustable parameters), should be added to the fitting function. Therefore, the final fitting function used here can be got from eqn (4)–(6).

$$\varepsilon^* = \varepsilon_h + \sum_i \frac{\Delta\varepsilon_i}{1 + (j\omega\tau_i)^{\beta_i}} + \frac{\kappa_l}{j\omega\varepsilon_0} + A\omega^{-m} \quad (7)$$

All of the data were eventually fitted with eqn (7). During this process, a satisfactory estimation of the dielectric parameters is obtained by using the nonlinear least-squares method to minimize the sum of the residuals for the permittivity $\varepsilon(\omega)$ and the conductivity $\kappa(\omega)$. The fitting process results in uncertainties of the order of ± 2 to 3% in $\Delta\varepsilon$ and ± 3 to 4% in τ .

Results and discussion

Dependence of dielectric behavior of PDADMAC solution on the concentration

Fig. 3 shows the frequency dependence of the permittivity and conductivity of some PDADMAC solutions with different concentrations when the experiment temperature is fixed at 25 ± 0.1 °C. From Fig. 3a, one dielectric relaxation in the order of around MHz is displayed, which is confirmed by the only one peak represented by the spectra of dielectric loss $\varepsilon''(\omega)$ in Fig. 3c. The dielectric loss, $\varepsilon''(\omega)$, is presented by the logarithmic derivative $\varepsilon''_D = -(\pi/2)(\partial\varepsilon'/\partial \ln \omega)$ on the basis of the logarithmic derivative of raw $\varepsilon'(\omega)$ data. This method has been successfully used for separating the two dielectric relaxation peaks (one corresponding to the electrode, and the other to the relaxations of sample).^{37,38} At the same time, Fig. 3 clearly shows that the dielectric spectra have changed with the increasing of mass concentration.

Now that the number of dielectric relaxation has been determined, according to the method mentioned in ‘‘Determination of the dielectric parameters’’, we use eqn (7) with one dispersion term to fit the experimental data. The fitting curves are in good agreement with the experimental data as shown in Fig. 4, where the symbols represent the experimental data of 0.004 wt% PDADMAC solution at 25 °C, the solid lines represent the best fit curves evaluated from eqn (7). Thus, the dielectric parameters are obtained (listed in Table 1) and synchronously the electrode polarization effect can be eliminated from the data. As shown in Table 1, the dielectric parameters obviously depend on mass concentration, except ε_h .

The dielectric parameters which reflect the dielectric behavior of polyelectrolyte solutions are determined by internal micro-mechanism of the system. They can be related to the micro-structure or some physicochemical quantities of PDADMAC solution through being discussed in light of the scaling theory. This because the conclusions of scaling theory in polymer research field have revealed some acknowledged information about the conformation of the polyelectrolyte chains in different concentration regimes, which can contribute to analyzing the dielectric data of polyelectrolyte solution. Therefore, the dependencies of

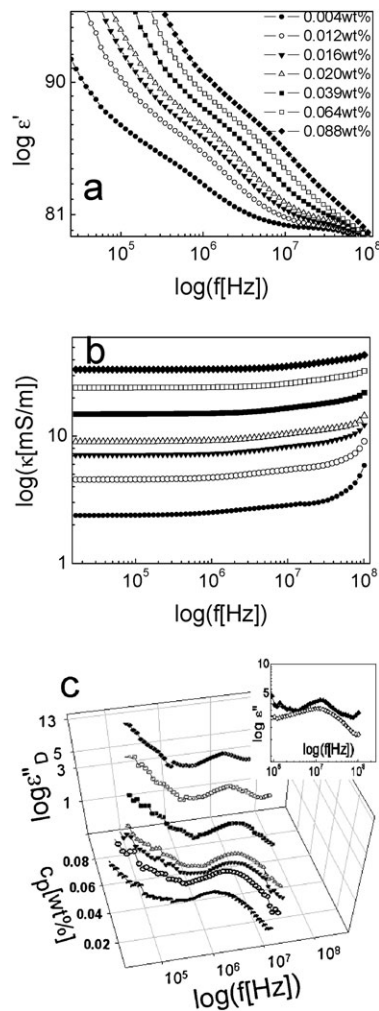


Fig. 3 Concentration dependence of (a) permittivity, (b) conductivity and (c) dielectric loss of the PDADMAC solution. Data of different concentrations are represented by different symbols as indicated in (a), and the same symbols in (b) and (c) have the same meanings. The inset shows the dielectric loss data of 0.0092 wt% PDADMAC solution which were obtained from two different methods: (\blacklozenge): $\varepsilon''_D = -(\pi/2)(\partial\varepsilon'/\partial \ln \omega)$; (\diamond): $\varepsilon'' = (\kappa - \kappa_l)/(\varepsilon_0\omega)$.

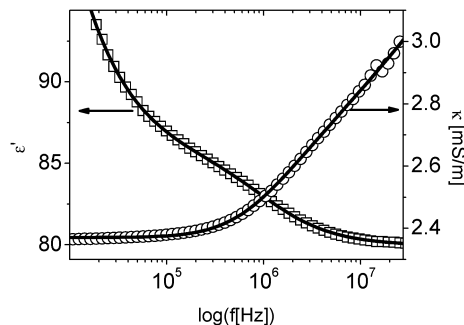


Fig. 4 Comparison between the experimental data of (\square) permittivity and (\circ) conductivity of 0.004 wt% PDADMAC solution at 25 °C and the fitting curves (the solid lines).

dielectric parameters on the concentration will be discussed in light of the scaling theory in the following paragraphs, in order to get the dynamics information of the PDADMAC solution.

Table 1 Dielectric parameters of some mass concentrations of PDADMAC solution obtained by fitting dielectric spectra with eqn (7)

Concn (10^2 wt%)	$\Delta\epsilon$	β	τ/ns	$\kappa/\text{mS m}^{-1}$	ϵ_h
0.6	7.3 ± 0.2	0.77 ± 0.03	153 ± 6	2.96 ± 0.01	79.8 ± 0.2
1.0	9.2 ± 0.2	0.73 ± 0.03	113 ± 4	4.69 ± 0.01	79.4 ± 0.3
1.4	9.6 ± 0.2	0.73 ± 0.04	89 ± 3	5.87 ± 0.01	79.6 ± 0.3
1.8	10.6 ± 0.3	0.70 ± 0.03	80 ± 3	7.08 ± 0.01	80.1 ± 0.3
2.2	11.1 ± 0.3	0.70 ± 0.04	60 ± 2	9.31 ± 0.01	78.9 ± 0.3
2.6	11.4 ± 0.3	0.70 ± 0.04	53 ± 2	10.77 ± 0.01	80.1 ± 0.4
3.0	11.6 ± 0.3	0.69 ± 0.04	48 ± 2	12.25 ± 0.01	79.4 ± 0.4
3.6	11.6 ± 0.4	0.67 ± 0.05	44 ± 2	13.41 ± 0.01	79.1 ± 0.4
4.5	11.6 ± 0.4	0.68 ± 0.05	33 ± 1	18.06 ± 0.01	79.3 ± 0.4
5.4	11.6 ± 0.2	0.67 ± 0.05	28 ± 1	21.18 ± 0.01	79.7 ± 0.5
6.0	11.8 ± 0.2	0.68 ± 0.04	26 ± 1	23.11 ± 0.01	79.9 ± 0.5
6.8	12.2 ± 0.3	0.67 ± 0.05	23 ± 1	27.31 ± 0.01	79.4 ± 0.5
7.6	11.9 ± 0.2	0.68 ± 0.04	21.6 ± 0.8	28.10 ± 0.01	79.2 ± 0.5
8.4	11.5 ± 0.2	0.69 ± 0.05	17.9 ± 0.6	31.60 ± 0.01	79.2 ± 0.5
9.2	12.3 ± 0.2	0.67 ± 0.05	18.1 ± 0.7	33.80 ± 0.01	79.1 ± 0.5

The mechanism of dielectric relaxation in PDADMAC solution

As introduced in the theoretical background section, there are two kind of counter-ions (condensed or uncondensed). The issues of which counter-ions contribute to the dielectric relaxation in this work, and whether the physical meaning for the typical length of these counter-ions is r_{scr} will be discussed by using the data of relaxation time and dielectric increment as follows.

In order to determine which type of counter-ion causes the dielectric relaxation, the most effective way is to estimate their diffusion coefficient by combining eqn (2) and (3):

$$D_{\text{ion}} \approx \frac{\Delta\epsilon}{6\tau b\epsilon_m c} \quad (8)$$

where the value of b is assumed to be 0.5 nm according to the literature,^{6,7} ϵ_m is considered to be that of pure water at 25 °C, being taken as 78.30. Importing the data of relaxation time and dielectric increment listed in Table 1 into eqn (8), the value of the diffusion coefficient of counter-ion, $D(\text{Cl}^-)$, whose fluctuation caused the dielectric relaxation, is obtained. $D(\text{Cl}^-)$ is largely independent of the polymer concentration and the mean value of all observed concentrations is determined to be $10 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Although a direct comparison of $D(\text{Cl}^-)$ with literature is impossible for PDADMAC solution, indirect comparison can be carried out as follows: in the result of the literature,¹⁶ for the polyelectrolyte NaPSS, the value of the diffusion coefficient of counter-ions $D^\infty(\text{Na}^+)$ in bulk water is ten times that of the value of the condensed (bound) counter-ions which caused the low-frequency relaxation. By comparison, our result is that the diffusion coefficient of Cl^- in bulk water, $2.032 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$,³⁹ is just two times that of the counter-ions which caused the high-frequency relaxation. Thus, we can conclude that the uncondensed counter-ions caused the dielectric relaxation in the present work. This conclusion is consistent with the conclusions of previous works.^{12,16,24}

On the other hand, the concentration dependence of relaxation time and dielectric increment can be used to determine the physical meaning of the typical length through the following discussion. According to the scaling theory (introduced in the theoretical background section), the

concentration dependence of relaxation and dielectric increment in dilute solution can be obtained by putting R_{cm} into eqn (2) and (3), respectively.

$$\tau \approx \frac{R_{\text{cm}}^2}{6D} \approx \frac{N^{2/3} c^{-2/3}}{6D} \propto c_m^{-2/3} \quad (9)$$

$$\Delta\epsilon \approx b\epsilon_m R_{\text{cm}}^2 c \approx b\epsilon_m N^{2/3} c^{1/3} \propto c_m^{1/3} \quad (10)$$

In semi-dilute polyelectrolyte solution, similarly, the situation is that the correlation length, ξ , should replace the typical length, L , thus the dependencies below can be found:

$$\tau \approx \frac{\xi^2}{6D_{\text{ion}}} \approx \frac{g_e}{6D_{\text{ion}} \xi_e c} \propto c_m^{-1} \quad (11)$$

$$\Delta\epsilon \approx b\epsilon_m \xi^2 c \approx b\epsilon_m g_e / \xi_e \propto c_m^0 \quad (12)$$

Then, the relaxation time and dielectric increment data listed in Table 1 are plotted against the mass concentration, as shown in Fig. 5: intersection points which can be found simultaneously both in (a) and (b) of Fig. 5 around the same concentration correspond to 0.024 wt%; the solid lines represent the expected results using the scaling laws (eqn (9)–(12)). It can be seen that the scaling laws of concentration dependencies of $\Delta\epsilon$ and τ , obtained from the experimental data, are well described by the prediction of the scaling theory ($\tau \propto c_m^{-2/3}$, $\Delta\epsilon \propto c_m^{1/3}$ below overlap concentration, and $\tau \propto c_m^{-1}$, $\Delta\epsilon \propto c_m^0$ above overlap concentration, respectively), thus the relaxation mechanism can be described as (see Fig. 2): 0.024 wt% is the overlap concentration, the dielectric relaxation is caused by the localized fluctuation of uncondensed counter-ions over the distance between chains in dilute solution (below 0.024 wt%) and correlation length in semi-dilute solution (above 0.024 wt%), respectively.

On the basis of these findings, the dielectric relaxation in PDADMAC solution and the consequent extraction of the dielectric increment and relaxation time provide a simple and unique means to evaluate the interaction of the polyelectrolyte with the solvent medium through estimating the solvent quality parameter, T_r . T_r can be evaluated from the relaxation

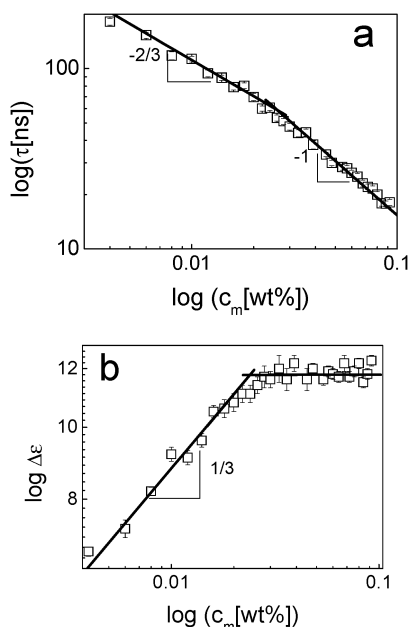


Fig. 5 (a) Log–log plot of τ versus c_m ; the solid straight lines have a slope of $-2/3$ or -1 ; (b) log–log plot of $\Delta\epsilon$ versus c_m ; the solid straight lines have a slope of $1/3$ or 0 .

time or dielectric increment by combining eqn (1), (11) and (12) as

$$T_r = \left(\frac{b}{l_B}\right)^{2/3} \frac{\Delta\epsilon}{\epsilon_m} \text{ or } T_r = 6D\tau c l_B^{-2/3} b^{5/3} \quad (13)$$

The results are plotted against the concentration, as shown in Fig. 6. It can be seen from Fig. 6 that after a rapid increase, T_r finally reaches an unchanged value. The intersection point can also be found around 0.024 wt%. The trend of the concentration dependence of T_r is similar to that of the literature,⁴⁰ namely the strongly charged polyions show a dependence of T_r on concentration, and T_r apparently saturates at high concentration.

The dependence of β and κ_l on concentration

From the above discussion, two concentration regimes are found; this conclusion is also supported to a certain extent by the dependence of β on concentration as shown in Fig. 7:

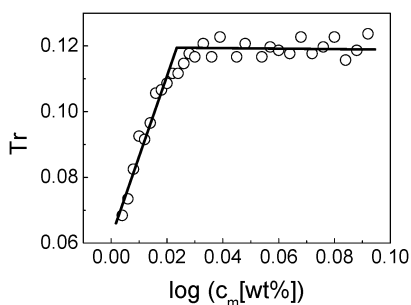


Fig. 6 Mass concentration dependence of solvent quality parameter, calculated from the data in Fig. 5 using eqn (13), the solid line is only to guide the eyes.

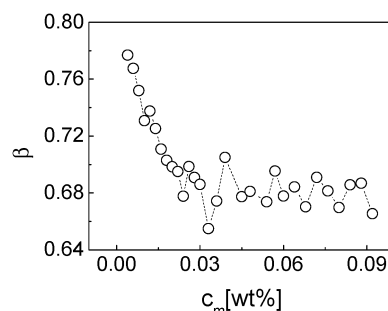


Fig. 7 Mass concentration dependence of the Cole–Cole parameter, β , obtained from the best-fitting of dielectric spectra with eqn (7).

β (indicating the distribution of relaxation time) sharply decreases as the concentration increases until 0.024 wt%; above this concentration, β diminishes rather slowly. This phenomenon can be interpreted as: as concluded above, in dilute solution, the uncondensed counter-ions are likely to fluctuate on the scale of the distance between chains; the distribution of this fluctuation process of uncondensed counter-ions may be less effected by the charges on the polyelectrolyte chains (because the chains are apart from each other) and very sensitive to the increment of concentration, so the beta value is closer to the theoretical value and decreases sharply with increasing concentration. In semi-dilute solution, the uncondensed counter-ions may fluctuate on the scale of the correlation length. The distribution of relaxation may be more affected by the charge of the chains (probably due to the chains being overlapped) and insensitive to the increase of concentration, thus the beta value deviates more from unit 1 and decreases very slow.

Fig. 8 is the plot of the low-frequency limit of conductivity, κ_l , against the mass concentration, which shows that κ_l increases linearly with c_m in the whole experimental concentration range, which agrees with the finding of the literature for another kind of polyelectrolyte.²⁴ This phenomenon can be explained as: because the condensed counterions loses its activity and does not contribute to the electric conductivity⁴¹ and polyelectrolyte chains are stationary compared to the free counter-ions;¹³ the movement of uncondensed counter-ions may contribute to the electric conductivity; the increase of c_m leads to the increment of number concentration of uncondensed counter-ions, finally resulting in an increase of the low-frequency limit of conductivity κ_l .

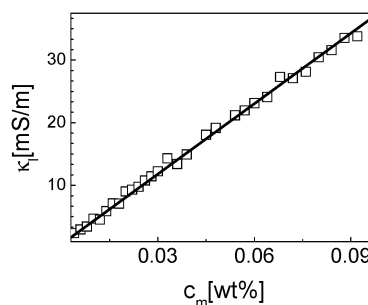


Fig. 8 Mass concentration dependence of low-frequency limit of conductivity κ_l . The line is the linear fitting results of experimental data.

From the above discussion, the overlap concentration (0.024 wt%) of PDADMAC solution is determined, and the dynamic properties for PDADMAC solution can be described as: the uncondensed counter-ions fluctuate in the range of the distance between chains in dilute solution and correlation length in semi-dilute solution, respectively.

Temperature dependent dielectric relaxation of PDADMAC solution

The discussion about concentration dependence of dielectric parameters in light of the scaling theory reveals that the uncondensed counter-ions fluctuate along some typical length whose range is determined by the interactions between different charged species existing in the solution. These dynamic properties and configuration of polyelectrolyte chains are very sensitive to temperature, due to the viscosity and permittivity of the solvent medium, which are closely related to the dielectric properties of system, which may change when the temperature is changed. Moreover, the enthalpy and entropy of activation of the dielectric relaxation can also be obtained from the temperature dependence of DRS. Hence, the dielectric measurements for PDADMAC solution with ten different concentrations (covering the dilute and semi-dilute regimes) were carried out under varying temperature, and the measurement results are shown in figure A in the ESI.†

From figure A of the electronic supplement,† it can be observed that the dielectric relaxation moves to higher frequency when the temperature is raised. It is more clearly seen from part A(c) that the characteristic frequency moves to higher frequency as the temperature increases. For further discussion, the Cole–Cole formula, with one relaxation term and the electrode polarization term, is used to fit the experiment data. The dielectric parameters are then obtained and the best-fitting results of a dilute solution (0.008 wt%) and a semi-dilute solution (0.033 wt%) are listed in Table 2 and 3, respectively.

As a consequent investigation, the dependence of dynamic and dielectric properties of PDADMAC solution on temperature will be displayed and discussed in detail in the following paragraphs, one by one.

Table 2 Dielectric parameters of 0.008 wt% PDADMAC solution under a temperature range of 5 to 70 °C, obtained by fitting dielectric spectra with eqn (7)

T/K	$\Delta\epsilon$	β	τ_i/ns	$\kappa_i/\text{mS m}^{-1}$	ϵ_h
278	9.0	0.75	198	1.58	86.2
283	8.7	0.76	161	2.06	84.4
288	8.6	0.77	137	2.63	82.6
293	8.5	0.77	122	2.96	80.9
298	8.2	0.78	118	3.42	79.7
303	8.2	0.78	98.1	4.06	78.0
308	8.0	0.78	89.2	4.77	76.1
313	8.0	0.78	81.2	5.22	74.2
318	7.9	0.78	70.4	5.60	72.8
323	7.7	0.79	70.2	6.02	70.9
328	7.6	0.79	62.5	6.47	69.1
333	7.3	0.79	56.2	6.92	67.5
338	7.2	0.81	49.1	7.38	66.4
343	7.0	0.82	43.0	7.85	64.9

Table 3 Dielectric parameters of 0.033 wt% PDADMAC solution under a temperature range of 5 to 70 °C, also obtained by fitting dielectric spectra with eqn (7)

T/K	$\Delta\epsilon$	β	τ_i/ns	$\kappa_i/\text{mS m}^{-1}$	ϵ_h
278	12.4	0.70	62.9	9.27	86.5
283	12.4	0.69	59.4	10.60	84.5
288	12.2	0.69	53.4	11.84	82.7
293	12.4	0.69	49.1	13.16	81.2
298	12.0	0.67	43.9	14.31	79.1
303	12.1	0.66	43.1	16.22	77.9
308	11.9	0.66	40.5	17.62	76.2
313	11.7	0.64	35.6	19.19	74.0
318	11.6	0.66	30.0	21.11	73.5
323	11.3	0.67	27.3	22.10	70.9
328	11.3	0.67	23.8	24.17	70.0
333	11.3	0.68	20.6	25.58	68.1
338	11.0	0.69	20.3	27.18	66.7
343	11.0	0.69	19.5	28.93	65.3

Dependence of the diffusion coefficient of uncondensed counter-ions on temperature

Using the data of relaxation time and dielectric increment listed in Table 2 and 3, according to eqn (8), we can calculate $D(\text{Cl}^-)$ of a fixed concentration at different temperatures. The result, shown in Fig. B of the electronic supplement,† show that regardless of whether the solutions are dilute or semi-dilute, $D(\text{Cl}^-)$ increases by 2.4% as the temperature increases by 1 °C, which agrees with the law of the increment of diffusion coefficient in bulk water when the temperature increases. This conclusion can be considered as: according to $D = k_{\text{B}}T/\lambda$, where λ is the drag coefficient of counter-ions, D increases with increasing temperature, which originated from the ease of ionic transport due to the decrease in the viscosity of the liquid medium (that is the decrease of drag coefficient, λ).

Dependence of typical length and end-to-end distance of polyelectrolyte chain on temperature

Fig. 9 shows the dependence of (a) relaxation time and (b) dielectric increment on concentration at three temperatures (\square 5 °C, \bullet 25 °C, \triangle 70 °C). At each temperature, the scaling dependence of relaxation time and dielectric increment are still $\tau \propto c_m^{-2/3}$, $\Delta\epsilon \propto c_m^{1/3}$ and $\tau \propto c_m^{-1}$, $\Delta\epsilon \propto c_m^0$ below and above the intersection point, respectively, as predicted by eqn (9)–(12). This means that changing the temperature of the solution system just bring about the change of diffusion coefficient of uncondensed counter-ions, but does not affect the physical meaning of the typical length of these counter-ions (note that it has been concluded in the discussion for concentration dependence of relaxation time and dielectric increment that the physical meaning of the typical length is the distance of chains in dilute solution and the correlation length in semi-dilute solution). However, as indicated by the arrows in Fig. 9, the intersection point move to higher concentration as the temperature rises. The intersection point represents the overlap concentration according to the scaling theory, and its definition is given as:

$$c^* \approx \left(\frac{g_e}{\xi_e}\right)^3 \frac{1}{N^2} \quad (14)$$

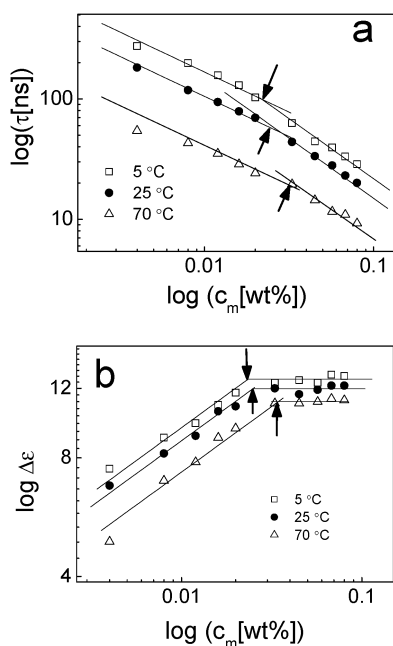


Fig. 9 (a) Doubly logarithmic plot of τ against c_m and (b) doubly logarithmic plot of $\Delta\epsilon$ against c_m at different temperatures as indicated.

From this equation, the increment of c^* indicates that g_e/ξ_e increases with the increase of temperature. Then we can infer that when the concentration is fixed, the correlation length $\xi(\approx [g_e/\xi_e c]^{1/2})$ increases and the end-to-end distance of the polyelectrolyte chain, $R \approx [\xi_e/g_e c]^{1/4} N^{1/2}$, decreases when the temperature of solution became higher. Additionally, the increment of ξ represents the increase of the range of highly extended conformation in chain in the semi-dilute solution.

Dependence of relaxation time and dielectric increment on temperature

Figure C of the electronic supplement† shows that the temperature dependence of (a) relaxation time and (b) dielectric increment for some dilute and semi-dilute PDADMAC solutions, represented by different symbols as indicated in (a), shows that both the relaxation time and the dielectric increment decreased with the increase of temperature. It should be noted that since the mechanisms of dielectric relaxation are different in dilute and semi-dilute solutions, the temperature dependence of relaxation time and dielectric increment may reflect dissimilar change processes of the dielectric relaxation. On the other hand, the increment of temperature results in: the decrease of viscosity and permittivity; the increase of the diffusion coefficient of counter-ions and the typical length of counter-ions in semi-dilute solution, respectively. Since relaxation time and dielectric increment is determined from the above physical quantities, the decrease of dielectric parameters can be used to analyze which quantity is the major influence factor of the dielectric properties of the polyelectrolyte solution. Now that the physical meaning of the typical length is changeless in each temperature, it is possible to use the scaling theory to discuss the temperature dependence of relaxation time and dielectric increment; additionally, the

equations used in the explanation of the concentration dependence of dielectric data have established the relationship between the dielectric parameters and the temperature at the same time. So we will discuss the temperature dependence of relaxation time and dielectric increment at a fixed concentration by eqn (9) to (12) as follows.

In dilute solution, according to eqn (9), the typical length, namely the distance between chains, is not affected by the temperature once the concentration is changeless; thus, the sharp decrease of relaxation time is caused by the increase of diffusion coefficient of counter-ions. On the other hand, according to eqn (10), the decrease of permittivity of the solvent medium caused the rapid decrease of dielectric increase. In semi-dilute solution, when temperature rises, it can be seen from eqn (11) that the increase of $D(\text{Cl}^-)$ and ξ have an opposite effect on the change of relaxation time, respectively. The decrease of relaxation time shows that the increase of $D(\text{Cl}^-)$ is the major factor, and the increase of the typical length just makes the relaxation time in semi-dilute solution decrease slower than that in dilute solution. The situation is similar for the analysis of dielectric increment: from eqn (12) it can be seen that the changes of the permittivity of solvent medium and the typical length also have the opposite effect on the temperature dependence of dielectric increment. The decrease of permittivity of solvent medium is the major influence factor, which is inferred from the decrease of dielectric increment. On the other hand, the increase of the polarization distance, namely typical length, just makes the decrease speed of dielectric increment less than that of dilute solution.

Determination of activation enthalpy and entropy of the relaxation process

Relaxation phenomena are controlled by thermally activated kinetics. The evaluation of activation enthalpy, ΔH^\ddagger , and the corresponding entropy, ΔS^\ddagger , is traced back to the Eyring equation

$$\ln \tau = \ln \left(\frac{h}{k_B T} \right) + \frac{\Delta H^\ddagger}{R} \frac{1}{T} - \frac{\Delta S^\ddagger}{R} \quad (15)$$

h denotes the Planck constant, R the gas constant. For the dielectric relaxations of dilute and semi-dilute solutions, $\ln(\tau T)$ are plotted against $1/T$ as shown in Fig. 10. The variation trends of data are well expressed by straight lines, thus ΔH^\ddagger and ΔS^\ddagger were obtained from slope and intercept of these lines and summarized in Table 4. Plots of ΔH^\ddagger and ΔS^\ddagger against concentration are shown in parts (a) and (b) of Fig. 11, respectively. It can be seen from Fig. 11 that ΔH^\ddagger decreases as the concentration increases, and ΔS^\ddagger does not show a dependence on concentration. The decrease of ΔH^\ddagger can be considered as: the increment of concentration shortens the typical length of uncondensed counter-ions (inferred from the expressions $R_{cm} \approx (N/c)^{1/3}$ and $\xi \approx [g_e/(\xi_e c)]^{1/2}$); thus the energy needed for the movement of uncondensed counter-ions from one end of the typical length to another end reduces with the increase of concentration. $\Delta S^\ddagger < 0$ implies that under the applied field, the directional movement of the counter-ions diminishes the disorder of the solution system.

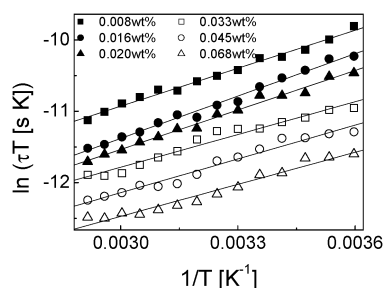


Fig. 10 Plot of $\ln(\tau T)$ against $1/T$ of selected concentrations as indicated by different symbols.

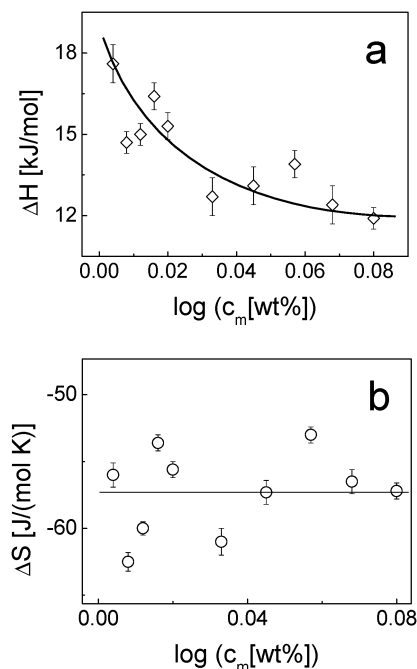


Fig. 11 Plot of the (a) activation enthalpy, ΔH^\ddagger , (b) activation entropy of the relaxation process of PDADMAC solution as a function of the mass concentration; the solid lines are only to guide the eyes.

Conclusions

For the investigated PDADMAC solution, a dielectric relaxation behavior in the order of around MHz is observed. The dielectric spectra exhibited a distinct dependence on concentration and on temperature, respectively. The concentration and temperature dependent dielectric parameters (determined from the fitting process of dielectric spectra by the Cole–Cole equation) were analyzed in light of the scaling theory.

Through estimating the diffusion coefficient of counter-ions by using the data of relaxation time and dielectric increment, it

is shown that the fluctuation of the uncondensed counter-ions cause the dielectric relaxation. Moreover, the analysis of the scaling dependence of relaxation time and dielectric increment on the concentration of PDADMAC solution reveals that the dielectric relaxation can be attributed to the localized movement or fluctuation of uncondensed counter-ions over the distance between chains in dilute solution and correlation length in semi-dilute solution, respectively. From the relaxation time in semi-dilute solution, the solvent quality parameter is evaluated and reaches a saturation value when the concentration is raised. The concentration dependence of β infers that in dilute solution, the distribution of relaxation is less affected by the charges on the polyelectrolyte chains and is very sensitive to the increase of concentration, but in semi-dilute solution, the situation is reversed. On the other hand, several conclusions can be obtained from the discussion of temperature dependent dielectric behavior of PDADMAC solution: diffusion coefficient of uncondensed counter-ions increases by 2.4% as the temperature increases by 1 °C. The fact that scaling laws (which describe the concentration dependence of relaxation time and dielectric increment) do not change at different temperatures shows that the temperature does not have an effect on the physical meaning of the typical length of uncondensed counter-ions. The intersection point, determined simultaneously from the scaling dependence of relaxation time and dielectric increment on concentration, moved to higher concentration when temperature increased, which indicates that higher temperature enlarges the correlation length and diminishes the end-to-end distance of the PDADMAC chain. Through the analysis of the dependence of relaxation time and dielectric increment on temperature, it is concluded that the changes of diffusion coefficient of uncondensed counter-ions and the permittivity of the solvent medium are the major factors during the change of the dielectric relaxation in dilute and semi-dilute solutions, respectively, caused by the increment of temperature. Finally, the enthalpy and entropy of activation of the relaxation process of PDADMAC solution is determined by the dependence of relaxation time on temperature. The activation enthalpy may be the energy needed during the movement of uncondensed counter-ions from one end of the typical length to another end. $\Delta S^\ddagger < 0$ implies that the disorder of the solution system is reduced by the directional movement of the uncondensed counter-ions under the applied field.

It can be concluded from our dielectric discussion that dielectric relaxation spectroscopy can be used to study the influence of concentration and temperature on the configuration and dielectric properties of polyelectrolyte chains in solution, and reflect the dynamics information of PDADMAC solution, such as the diffusion coefficient and typical length of the uncondensed counter-ions.

Table 4 Activation parameters, ΔH^\ddagger and ΔS^\ddagger , of selected dilute and semi-dilute solutions

Concn ($\times 10^2$ wt%)	0.4	0.8	1.2	1.6	2	3.3	4.5	5.7	6.8	8
ΔH^\ddagger /kJ mol ⁻¹	17.6 ± 0.7	14.7 ± 0.4	15.0 ± 0.4	16.4 ± 0.5	15.3 ± 0.5	12.7 ± 0.7	13.1 ± 0.7	13.9 ± 0.5	12.4 ± 0.7	11.9 ± 0.4
ΔS^\ddagger /J mol ⁻¹ K ⁻¹	-56.0 ± 0.9	-62.5 ± 0.7	-60.0 ± 0.5	-53.6 ± 0.6	-55.6 ± 0.6	-61 ± 1	-57.3 ± 0.9	-53.0 ± 0.6	-56.5 ± 0.9	-57.2 ± 0.6

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