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# Measurement scheme to detect $\alpha$ relaxation time of glass-forming liquid*

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A measurement scheme for detecting the $\alpha$ relaxation time ($\tau$) of glass-forming liquid is proposed, which is based on the measured ionic conductivity of the liquid doped with probing ions by low- and middle-frequency dielectric spectroscopy and according to the Nernst–Einstein, Stokes–Einstein, and Maxwell equations. The obtained $\tau$ values of glycerol and propylene carbonate by the scheme are consistent with those obtained by traditional dielectric spectroscopy, which confirms its reliability and accuracy. Moreover, the $\tau$ of 1,2-propanediol in a larger temperature range is compared with existing data.

**Keywords:** $\alpha$ relaxation, ionic conductivity, glass-forming liquid, dielectric spectroscopy

**PACS:** 66.10.–x, 77.22.Gm, 64.70.P–, 82.56.Na **DOI:** 10.1088/1674-1056/28/8/086601

## 1. Introduction

The glass transition is the crossover between the $\alpha$ relaxation time ($\tau$) of the glass-former and the observation time.[1,2] Therefore, the measurement of $\tau$ as well as its mechanism is one of the key issues of the glass transition.[3–10] So far, there has been no widely accepted theory of glass transition,[3–6,11] which has led to no exact relationship between $\tau$ and temperature ($T$). Based on available experimental data on $\tau$, a few empirical laws have been put forward, such as the Vogel–Fulcher–Tammann law[12–15] (VFT) ($\tau = \tau_0 \exp[A/(T-T_0)]$), critical-like behavior[16] ($\tau = \tau_0 [(T-T_C)/T]^{-\phi}$) , the Waterton–Mauro equation[8] (WM) ($\tau = \tau_0 \exp[(B/T)\exp(C/T)]$), and the Avramov–Milchev equation[17] (AM) ($\tau = \tau_0 \exp[(L/T)^m]$), where $\tau_0$, $A$, $T_0$, $T_C$, $\phi$, $B$, $C$, $L$, and $m$ are all temperature-independent fitting parameters. The $\tau$ values of the VFT and critical-like laws diverge at $T_0$ and $T_C$, respectively, which indicates that there is a phase transition at the temperatures,[3,6] but the $\tau$ values of WM and AM only tend to be infinite at 0 K, giving no phase transition above 0 K.

Up to now, the non-zero temperature divergence of $\tau$ is still under controversy. For example, Hecksher *et al.*[5] found that there was not enough evidence of divergence by analyzing 42 glass-formers. However, Drozd-Rzoska *et al.*[4] showed that the $\tau$ value of some glass-forming liquids has a critical behavior. Martinez-Garcia *et al.*[3] also showed the existence of divergence and a relationship between the glass transition and critical phenomena. Therefore, more systematic experimental data are needed to further understand $\tau$. At present, the wide range of $\tau$ is mainly measured by the dielectric spectroscopy,[18–20] viscosity,[21–24] and diffusion coefficient[22–25] methods, and each kind of method contains a combination of a set of technologies. The different techniques have different measurement errors; for instance, high-frequency (greater than about 10 MHz) dielectric spectroscopy has larger errors than low- and middle-frequency dielectric spectroscopy. Moreover, the measurement data of the different techniques have different deviations. So, it is necessary and valuable to explore new measurement methods or schemes for detecting the value of $\tau$.

Consider that the relation between the shear relaxation time (nearly the same as $\tau$ in small-molecular liquids) and the viscosity ($\eta$) is subject to the Maxwell equation,[1,24]

$$\tau = \frac{\eta}{G_\infty}, \tag{1}$$

where $G_\infty$ is the high-frequency shear modulus of the liquid; the relation between $\eta$ and the diffusion coefficient ($D$) of ions in liquids satisfies the Stokes–Einstein equation,[26–28]

$$\eta = \frac{k_B T}{6\pi a D}, \tag{2}$$

where $a$ is the effective radius of the ions, and $k_B$ the Boltzmann constant; and the relation between $D$ and the conductivity ($\sigma$) of ions in liquids obeys the Nernst–Einstein equation,[28–30]

$$D = \sigma k_B T / n q^2, \tag{3}$$

where $n$ is the number density of ions, and $q$ the electric charge quantity of the ions.

From Eqs. (1)–(3), it is obtained that

$$\tau = c/\sigma, \tag{4}$$

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where $c \equiv nq^2/6\pi aG_\infty$, which is a nearly temperature-independent constant.

So in theory, $\tau$ can be obtained by calculating the value of $\sigma$. In fact, the experimental results of several materials show that the temperature dependence of $\tau$ is the same as that of $1/\sigma$ for impurity ions in a large range.[31–34] However, both the type and the quantity of impurity ions are unknown; hence it is impossible to control the amplitude of $\sigma$ and the process of $\sigma$ will be affected by the $\alpha$ relaxation when $\sigma$ is small.

In this paper, a measurement scheme is designed to detect the $\tau$ of glass-forming liquids by doping an appropriate quantity of given probing ions into the liquids and by using Eq. (4). The $\tau$ value of glycerol and propylene carbonate obtained by the scheme is consistent with that obtained by traditional methods. Moreover, the $\tau$ value of 1,2-propanediol in a larger time range is given.

## 2. Measurement scheme

The scheme for detecting the $\tau$ value of glass-forming liquids covers three steps as follows.

(i) Dope probing ions (ionic materials, *e.g.*, electrolytes) into glass-forming liquids, and the ion concentration should be low enough, which has no obvious effect on the $\alpha$ relaxation of the liquid.

(ii) Measure the ionic conductivity ($\sigma$) of the liquid by low- and middle-frequency dielectric spectroscopy (LMF-DS), which has a high measurement accuracy. Specifically, the imaginary part ($\varepsilon''$) of the complex permittivity of the liquid with ions can be expressed as[35–37]

$$\varepsilon'' = \varepsilon''_R + \sigma/\varepsilon_0\omega. \tag{5}$$

In other words,

$$\sigma = \omega\varepsilon_0\left(\varepsilon'' - \varepsilon''_R\right), \tag{6}$$

where $\varepsilon''_R$ is the imaginary part of the dipole orientation polarization, $\varepsilon_0$ is the permittivity of vacuum, and $\omega$ is the angular frequency of a sine alternating external electric field. As shown in Section 3 (Fig. 5 and 6),

$$\sigma \approx \omega\varepsilon''_0 \tag{7}$$

in the region where the conductivity plays a dominant role[37] and the electrode effect could be neglected.[38]

(iii) Calculate $\tau$ from $\sigma$ according to Eq. (4), in which $c$ is a reduced constant and is determined on condition that the translation and rotation relaxation times are the same at a certain temperature.

## 3. Experiments

The typical small-molecule glass-forming liquids, the ionic probe materials, and the concentration ($x$) values of the ionic probe in the liquids are shown in Table 1.

The parallel-plate capacitor method is used to measure $\varepsilon''$ by a Novocontrol Beta-NB impedance analyzer. The measurement frequency ($f$) values are 1, 10, 100, $10^3$, $10^4$, $10^5$, and $10^6$ Hz. The cooling rate is 1.5 K/min. The $\varepsilon''$ values of samples at high frequencies (1 MHz–1 GHz) near the room temperature are obtained by a Keysight E4991B impedance analyzer.

**Table 1.** Glass-forming liquids, ionic probe materials, and concentration ($x$) values.

| Liquid (abbr. of the name) | Content | Ionic probe material (chemical formula) | Content | $x$ |
|---|---|---|---|---|
| Glycerol (GLY)[a] | 99% | potassium hydroxide (KOH)[b] | 85% | 0.1‰ and 0.3‰ |
| | | sodium chloride (NaCl)[a] | 99.5% | 1‰ and 3‰ |
| Propylene carbonate (PC)[a] | 99.7% | sodium iodide (NaI)[a] | 99.5% | 0.2‰ and 0.6‰ |
| 1,2-propanediol (PDO)[a] | 99% | magnesium chloride ($MgCl_2$)[a] | 99.9% | 0.1‰ and 0.3‰ |

In Table 1, $x$ is the mass percent. The original samples are produced by Aladdin Industrial Corporation (a) and Tianjin Fuchen Chemical Reagent Factory (b).

## 4. Results and discussion

Figures 1–4 show the $\varepsilon''$ of GLY, PC, and PDO doped with probing ions *versus* $T$ at a series of $f$ values on cooling. It can be seen that there are two processes in each sample, marked $P_\alpha$ and $L_\mathrm{d}$. The $P_\alpha$ peaks reflect the $\alpha$ relaxation of the liquid, which corresponds to the molecular orientation movement, while the process marked $L_\mathrm{d}$ corresponds to the ion diffusion in the liquid. $C_0$ in Figs. 1–4 is the capacitance of the parallel-plate capacitor without liquid.

The insets of Figs. 1–4 show plots of $\varepsilon''$ *versus* $T$ of GLY, PC, and PDO with different $x$ values at $f = 10^3$ Hz, and the data at the other $f$ values have the same characteristics. Moreover, all $\varepsilon''$ data of each liquid with different $x$ values at the same $f$ coincide well with each other at temperatures both below and near the temperature ($T_\mathrm{p}$) of the maximum of the $\alpha$ relaxation peak, which indicates that the probing ions doped have almost no effects on $\alpha$ relaxation, but obvious differences at temperatures well above $T_\mathrm{p}$. The value of $\varepsilon''$ is larger when $x$ is larger, which shows that the $L_\mathrm{d}$ process is caused by the movement of the probing ions in the liquid.

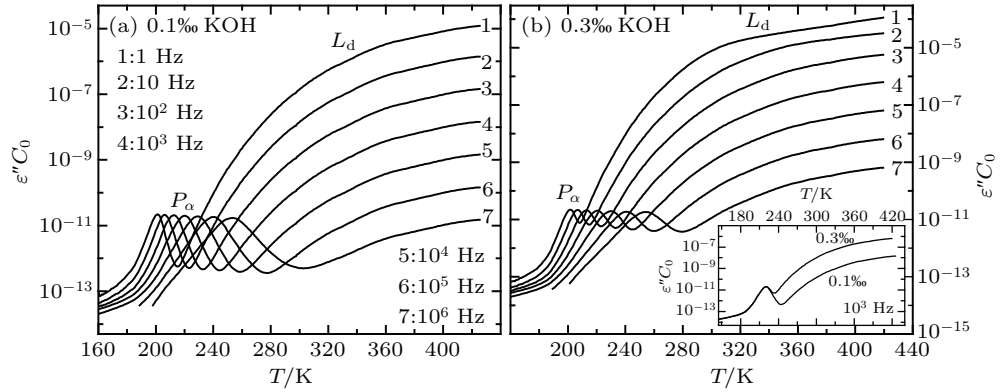



**Fig. 1.** Plots of $\varepsilon''$ of GLY doped with 0.1‰ and 0.3‰ KOH *versus T* on cooling.

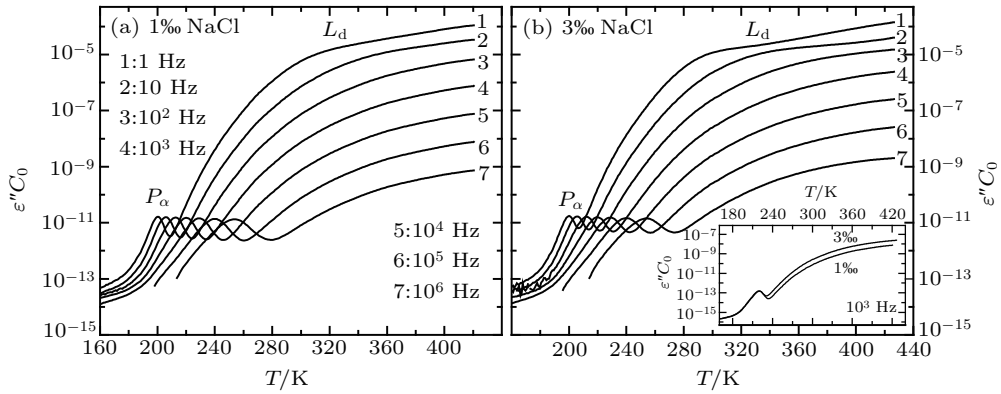



**Fig. 2.** Plots of $\varepsilon''$ of GLY doped with 1‰ and 3‰ NaCl *versus T* on cooling.

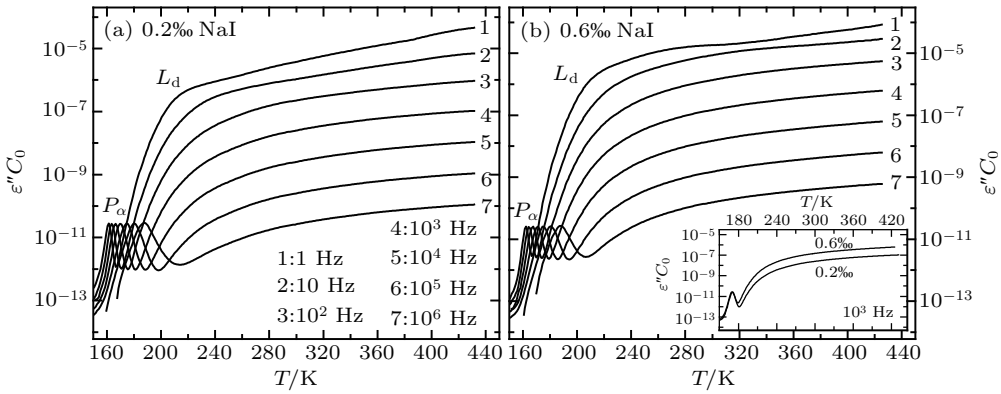



**Fig. 3.** Plots of $\varepsilon''$ of PC doped with 0.2‰ and 0.6‰ NaI *versus T* on cooling.

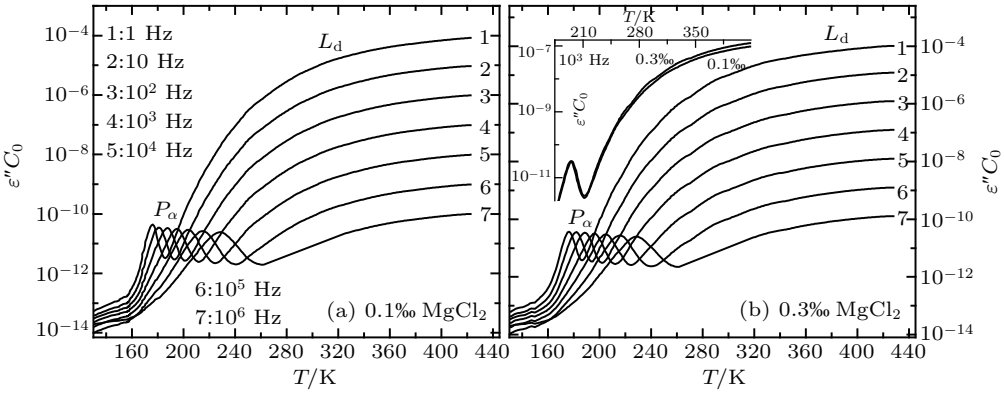



**Fig. 4.** Plots of $\varepsilon''$ of PDO doped with 0.1‰ and 0.3‰ $MgCl_2$ *versus T* on cooling.

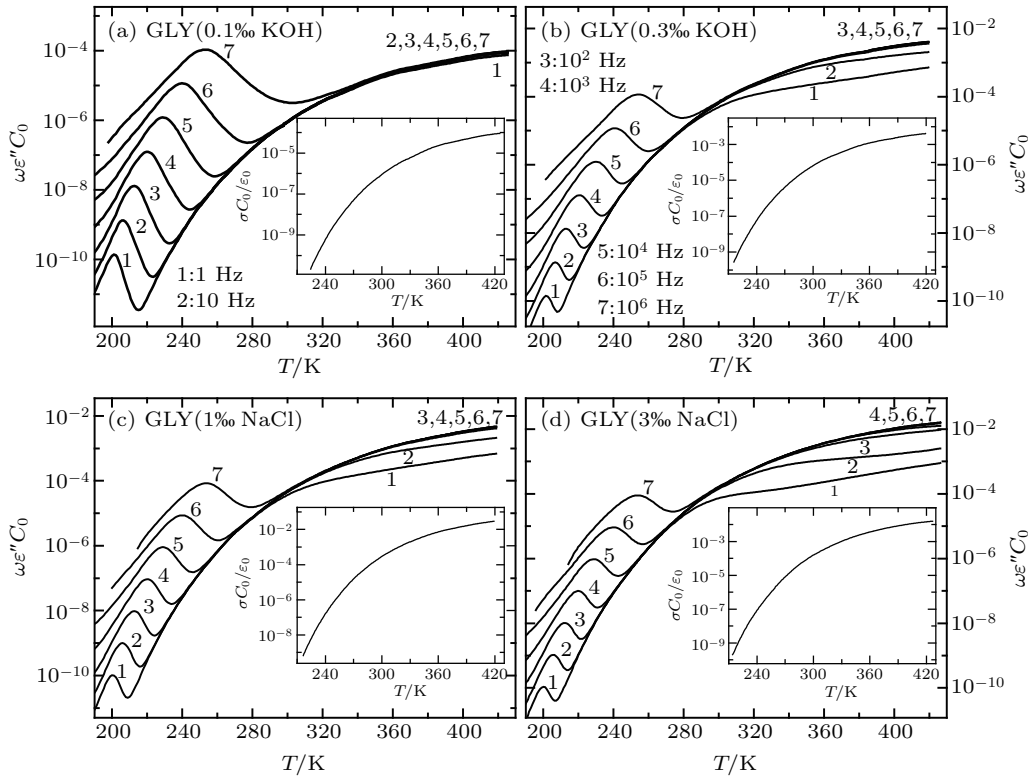



**Fig. 5.** Plots of $\omega\varepsilon''$ *versus* $T$ of GLY doped with ions, with inset showing plot of $\sigma$ *versus* $T$.

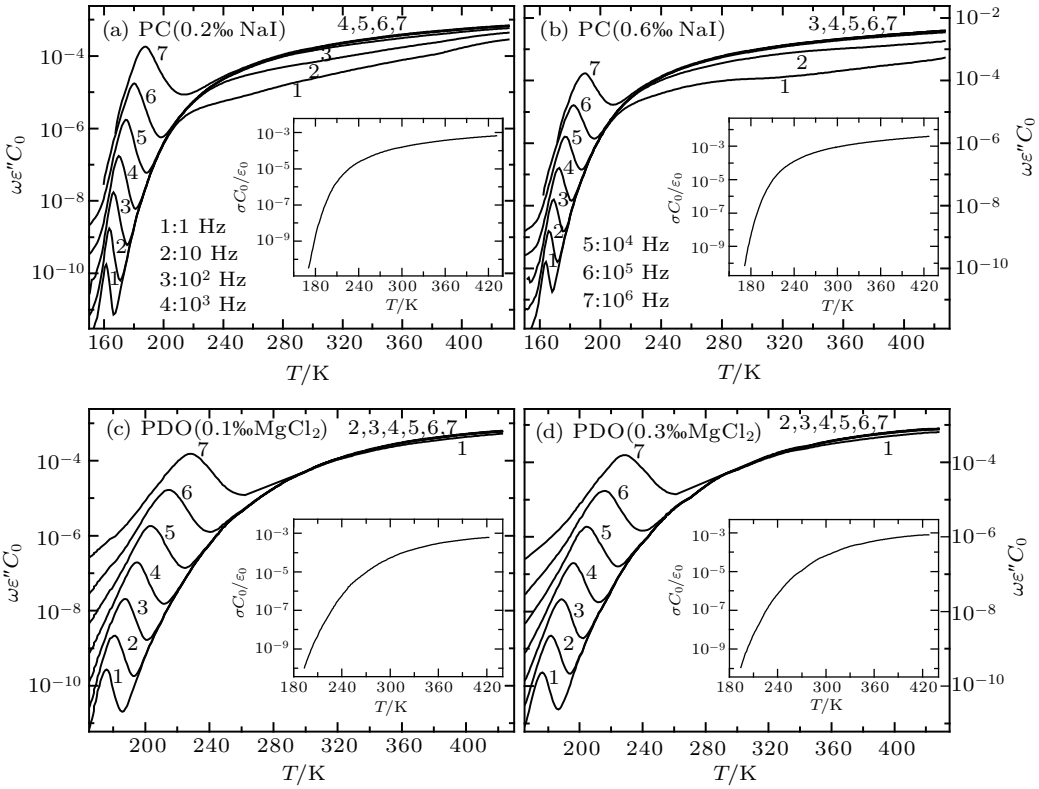



**Fig. 6.** Plots of $\omega\varepsilon''$ *versus* $T$ of PC and PDO doped with ions, with inset showing plot of $\sigma$ *versus* $T$.

Based on the data in Figs. 1–4, plots of $\omega\varepsilon''$ *versus* $T$ are obtained (Figs. 5 and 6). According to Eq. (6), it can be seen that the overlapping part of $\omega\varepsilon''$ in the figures originates from the ionic conductivity,[37] and in the higher-temperature range, the deviations at lower frequencies (curve 1 in Fig. 5(a), curves 1–2 in Figs. 5(b) and 5(c), and curves 1–3 in Fig. 5(d), as well as curves 1–3 in Fig. 6(a), curves 1–2 in Fig. 6(b), and curve 1 in Figs. 6(c) and 6(d)) are due to the electrode effect,[38]

*i.e.*, the charge accumulation near electrodes in a period when the probing ions move rapidly at high temperature. Whether the electrode effect is obvious depends on the speed of ion motion and the period $(1/f)$ of the external electric field.[38] Only when the period is much longer than the time required for a large number of ions to move to the vicinity of the plate does $\varepsilon''$ not satisfy Eq. (7) distinctly. At high temperatures, the electrode effect of low-frequency $\varepsilon''$ may be obvious, but when the temperature is lower, the movement of ions will become slower and the electrode effect will be very weak. So low-frequency $\varepsilon''$ can also be used to calculate $\sigma$ as long as it can coincide with those of other frequencies at a certain temperature, *i.e.*, $\varepsilon''$ satisfies Eq. (7). From the overlapping parts of $\omega\varepsilon''$, the $\sigma$ data of the liquids, shown in the insets of Figs. 5 and 6, are given according to Eq. (6).

The solid symbols in Fig. 7 are the relaxation time ($\tau_r$) of molecule rotations in the liquid (calculated from $\tau_r(T_p) = 1/2\pi f$), and the lines in Fig. 7 represent the $\tau$ of GLY, PC, and PDO in a series of $x$, with $c$ in Eq. (4) chosen under the condition of $\tau = \tau_r$ at low temperature. The $\tau_r$ data of GLY (295 K) and PDO (299 K) (solid squares in Fig. 7) are obtained by the radio-frequency impedance analyzer. For GLY and PC, the data on $\tau_r$ from Ref. [18] are also given in Fig. 7 as empty symbols. From Figs. 7(a) and 7(b), it can be seen that the $\tau$ value obtained from the ionic conductivity is consistent with the $\tau_r$ and $\tau$ values in Ref. [18], independently of the $x$ value and the types of probing ions, which shows that the scheme proposed here is reliable and accurate. By this scheme, the $\tau$ value of PDO in a larger time range than those in Refs. [39]–[44] is given and it is coincident with the $\tau_r$ value near room temperature, thus further verifying the feasibility of this scheme.

It is worth pointing out that the measurement scheme proposed in this paper can detect $\tau$ values in a larger time range ($10^{-11}$ s–$10^{-4}$ s) only by the LMF-DS technique and ionic conductivity mechanism. By contrast, to measure $\tau$ values in the same range, dielectric spectroscopy requires the combination of frequency response analysis ($\sim 10^{4}$ s–$10^{-7}$ s) (or an AC bridge, $\sim 10^{-2}$ s–$10^{-8}$ s), coaxial transmission and reflection ($\sim 10^{-7}$ s–$10^{-10}$ s), and quasi-optics ($\sim 10^{-10}$ s–$10^{-12}$ s).[18] The viscosity method needs a combination of rotating (including a few apparatuses, $\sim 10^{-13}$ s–$10^{-5}$ s), capillary-flow ($\sim 10^{-13}$ s–$10^{-8}$ s), and parallel-plate ($\sim 10^{-7}$ s–$10^{-1}$ s) viscometers.[22,45–47] And the diffusion coefficient method requires the combination of diaphragm cell, capillary cell, and refractive index techniques. In these combination measurements, there are some deviations between the data caused by the different techniques or apparatuses. Therefore, the measurement scheme proposed here will be a useful supplement to the above methods.

In the theoretical part of this scheme, equation (1) is derived in Newtonian fluid,[1] and the experimental results are also well consistent with the theoretical results for small-molecule glass-forming liquids.[1,24] Equation (2) requires the diffused particles to be nearly spherical,[24] and equation (3) needs the conductivity to originate from ion diffusion.[48,49] Therefore, in the scheme, both the molecules and the doped ions in the measured liquid will be spherical as far as possible. Moreover, we should point out that $a$ and $G_\infty$ will significantly change if a liquid–liquid phase transition occurs in the system, i.e., the interaction between molecules varies obviously. In this case, whether the scheme in this paper is applicable still needs further investigating. Of course, the scheme in this paper also needs more experimental work to further ascertain applicability.

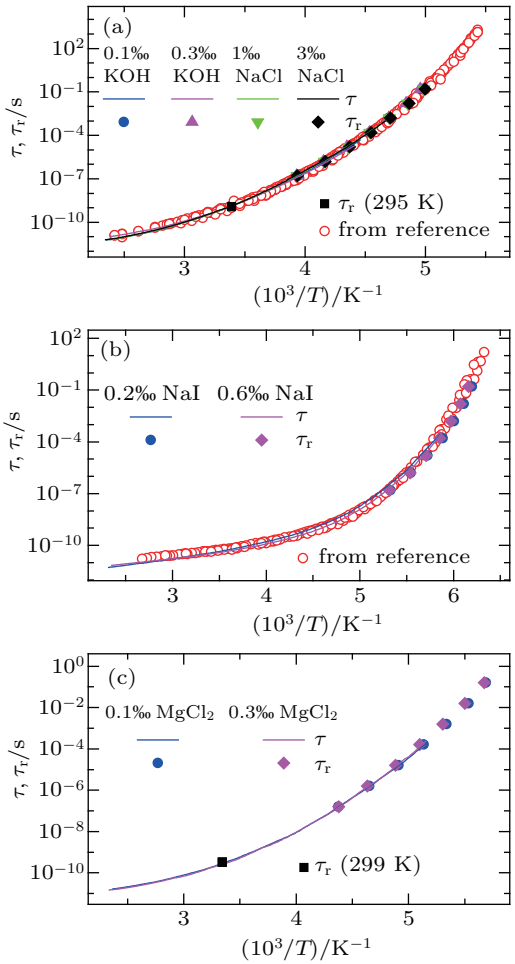



**Fig. 7.** Plots of $\tau$ and $\tau_r$ *versus* $T$ of (a) GLY, (b) PC, and (c) PDO.

From Eq. (7), the measurement error of this scheme mainly depends on the electrode effect and $\alpha$ relaxation. Compared with $\sigma/(\varepsilon_0\omega)$ in Eq. (5), the weaker the electrode effect and $\alpha$ relaxation are, the smaller the error will be. In the experimental analysis, the error is mainly reflected in the coincidence degree of $\omega\varepsilon''$ of each frequency used to calculate the $\sigma$ value. The error of the final experimental data is also related to the measurement error of the instrument.

## 5. Conclusions

According to the Nernst–Einstein, Stokes–Einstein, and Maxwell equations, a measurement scheme for detecting the $\alpha$ relaxation time ($\tau$) of glass-forming liquids is proposed, which is based on the measured ionic conductivity of the liquid doped with probing ions by LMF-DS. The obtained $\tau$ values of glycerol and propylene carbonate by the scheme are consistent with those obtained by traditional dielectric spectroscopy, which confirms its reliability and accuracy. Moreover, the $\tau$ value of 1,2-propanediol in a larger time range than that of existing data is given. The scheme can measure $\tau$ values in a larger time range ($10^{-11}$ s–$10^{-4}$ s) only based on LMF-DS and the ionic conductivity mechanism. By contrast, to measure $\tau$ values in the same range, traditional methods require the combination of a few techniques, and there are some deviations between the data of the different techniques. Therefore, the measurement scheme proposed here will be a useful supplement to existing methods.

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