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Dynamics in Propylene Carbonate and Propylene Carbonate containing LiPF_6

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by

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13. ABSTRACT (Maximum 200 words)

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DYNAMICS IN PROPYLENE CARBONATE AND PROPYLENE CARBONATE CONTAINING LiPF_6

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Electrical conductivity and differential scanning calorimetry studies (DSC) have been carried out on 1 M LiPF_6 in propylene carbonate (PC) from 187 to 296K. The electrical conductivity data are analyzed in terms of Vogel-Tammann-Fulcher (VTF), Williams-Landel-Ferry (WLF) and Bendler-Shlesinger (BENSH) formalisms. In addition, literature data for viscosity and relaxation times for PC (not containing salt) are analyzed using the same formalisms. Large, systematic variations are found in both the VTF and WLF fitting parameters with temperature interval. The large variation of the parameters with temperature demonstrates the failure of both formalisms and shows that care must be taken when utilizing the VTF/WLF parameters to draw conclusions concerning the behavior of systems. One conclusion which can be reached is that the VTF results indicate a significant difference between the molecular motions in PC and PC containing LiPF_6 . Another is that the WLF parameter C_1 is about 11 for low temperature data referenced to the DSC glass transition temperature, T_g , which shows that for PC and PC-based liquids the value of all three dynamical quantities at T_g is about 11 decades smaller than the value predicted for very high temperatures. Finally, all data are found to be better fit by the BENSH equation.

Keywords: Electrical Conductivity, Nuclear Magnetic Resonance,
Lithium Hexafluorophosphate, Propylene Carbonate

INTRODUCTION

Propylene carbonate (PC) is a liquid of both applied and fundamental interest. The applied interest is centered around its use in battery electrolytes both in the pure form and in combination with other liquids.¹ The fundamental interest is because it is a glass-forming liquid resisting the tendency to crystallize.²⁻¹⁰ In order to learn more about PC, differential scanning calorimetry (DSC) and electrical conductivity studies have been undertaken. Complex impedance studies were performed at frequencies from 10 Hz to 100 MHz and at temperatures from 187 to 296K. The DSC studies were performed on both pure PC and PC:LiPF₆ while the electrical conductivity measurements were carried out on PC:LiPF₆ only. The results are compared with data from the literature for viscosity and structural relaxation times.

EXPERIMENT AND RESULTS

1 M LiPF₆ in PC was prepared using LiPF₆ from Alfa Aesar and 99.7% anhydrous PC from Aldrich Chemical Company. All sample preparation and subsequent loading of the samples into various sample holders were carried out in a Vac Atmospheres glove box with less than 0.08 ppm water. All measurements were carried out as described elsewhere for various solutions of PC and ethylene carbonate (EC) and PC and dimethyl carbonate (DMC).¹⁰

The electrical measurements were analyzed via complex impedance diagrams, all of which are typical of those shown for other ion-conducting systems with blocking electrodes.¹¹⁻¹⁹ The usual slightly depressed semicircular arc was found which represents the effective parallel bulk resistance and capacitance of the sample. In addition, a slanted line was observed at the lowest frequencies which is

attributed to the blocking electrodes. The bulk resistance, R , was obtained from the intercept of the arc (or position of the minimum value of Z'') or slanted line with the Z' axis. The conductance, $G=1/R$, was calculated from the intercept and transformed to the electrical conductivity, σ , via the usual equation:

$$\sigma = GL/A \quad (1)$$

where A is the cross-sectional area of the sample and L is the length.

The electrical conductivity of PC:LiPF₆ at room temperature (approximately 23°C) was found to be 5.94 mS/cm which is close to the value of 5.64 mS/cm quoted for a closely related material, 15% EC and 85% PC at 20°C.¹ Also, the value is lower than the values for EC:DMC:LiPF₆ (11.5 mS/cm) and EC:PC:LiPF₆ (6.8 mS/cm).¹⁰ Values of the electrical conductivity at other temperatures were obtained by assuming that the relative change in electrical conductivity is the same as the relative change in electrical conductance, i.e. no correction was made for changes in the dimensions of the sample. The results for the variation of the conductivity with temperature are shown in Fig. 1 and typical DSC runs are shown in Fig. 2.

DISCUSSION

I. VTF Formalism

It is clear from Fig. 1 that the temperature variation of the electrical conductivity of PC:LiPF₆ exhibits smooth, non-Arrhenius behaviour. This is not surprising since it is well-known that pure PC is a glass-forming liquid and the related smooth variation with temperature of such properties as viscosity, electrical conductivity or relaxation times is well-documented.²⁻⁹ That PC:LiPF₆ is a glass at

low temperature is confirmed by the DSC results shown in Fig. 2 since a single endothermic event typical of a glass transition is observed at about 178K.

The smooth variation of the electrical conductivity with temperature allows a quantitative treatment via the Vogel-Tammann-Fulcher (VTF) [20] equation:

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right) \quad (2)$$

or the modified VTF equation:

$$\sigma = \frac{A}{\sqrt{T}} \exp\left(\frac{-B'}{T - T_0'}\right) \quad (3)$$

A non-linear least squares procedure was carried out as described elsewhere.²¹ An error was found in the discussion of Ref. 21. Both for that paper and the present work, one of the conditions used in the minimization of the sum of the squares of the deviations, S , for equation (2) was $dS/d(\log_{10}\sigma_0)=0$ rather than $dS/d\sigma_0=0$. The other two conditions, $dS/dB=0$ and $dS/dT_0=0$ were used as stated in Ref. 21. The resultant best-fit parameters are listed in Table 1 along with the RMS deviation. In order to show the goodness of fit, the deviations of the datum points from the best-fit of equation (2) are shown in Fig. 3.

As seen by a comparison of lines I and II of Table 1, the value of $T_0=151.7\text{K}$ for PC:LiPF₆, is somewhat lower than the results of Barthel et al.⁸ who quote a value of 164.01K for an approximately 1M solution PC:LiPF₆. Correspondingly, $B=652\text{K}$ is larger than their value of $B=438\text{K}$. The difference is due to the different temperature ranges involved since the entry in line I is for a temperature range of 187-296K while that of Barthel et al. is for 228-298K. Specifically, it is well known that values of VTF parameters depend upon the temperature range of the data.⁴⁻

6,21-23 In order to show that this accounts for the difference between the VTF parameters of Barthel et al.⁸ and those of the present work, the VTF equation was best-fit to the present data for the temperature interval 228-296K (which approximates that of Barthel et al.) and the results are listed in line III of Table 1. It is clear that the new values are close to the values quoted by Barthel et al. and thus the apparent discrepancy is explained.

In order to investigate this effect more fully, the present ionic conductivity data were separated into successive 65°C intervals and the VTF equation was refit to those intervals. Fig. 4 shows a plot of the resultant fitting parameters vs. the temperature at the middle of each interval. It is clear that B and $\log \sigma_0$ decrease and T_0 increases as the temperature interval occurs at successively higher temperatures. This trend has been observed previously for PDMS-EO₈-NaCF₃COO as can be seen in Table III of Ref. 21.

This shows that care must be taken when considering the VTF parameters. For example, T_0 , which is sometimes referred to as the "ideal glass transition temperature" and which is interpreted as the limiting value of T_g as the cooling rate becomes infinitely slow,²⁴ has received a great deal of attention in the literature. Clearly, a unique value of T_0 , at least for PC containing LiPF₆, does not exist. In addition, the logarithm of the preexponential, $\log(\sigma_0)$, is sometimes considered to be related to the concentration of charge carriers.²⁵ In fact, the decrease in $\log(\sigma_0)$ as temperature increases is not associated with a decrease in the concentration of charge carriers, but is an artifact of the VTF formalism. This will be confirmed below since the preexponential for the viscosity of PC, where no ions are present, exhibits the same behavior.

It is of interest to compare the electrical conductivity results with those for viscosity and relaxation times. Viscosity and electrical relaxation data for PC containing salt do not seem to be available. Nonetheless, some insight can be

gained by considering those for pure PC. VTF analysis of various types of data for pure PC has been carried out by several authors^{4-6,8,9} and the resultant parameters are listed in Table 1. In addition, an analysis of combined data^{5,8} for the viscosity of PC was carried out in order to include data at temperatures where none existed for Ref. 5 and to specify the RMS deviation. In order to check for temperature dependence of the parameters, the VTF equation was fit to the viscosity data in approximately 109°C intervals, which matches the widest interval for the ionic conductivity studies. The results for the fitting parameters, plotted vs. the middle temperature of the 109°C intervals, are shown in Fig. 5.

As can be seen in Fig. 5, for viscosity, decreases in B and and the logarithm of the preexponential and an increase in T_0 are observed as the temperature of the temperature interval increases (similar to that observed for the ionic conductivity) for temperatures below about 260K. As the temperature increases beyond about 260K the reverse is observed for all parameters. The latter trend is probably associated with the exponential behavior which dynamical quantities such as σ and η for PC exhibit at high temperature⁴ since, for example, for Arrhenius behavior, $T_0=0$.

There is an added complication associated with comparing the electrical conductivity and viscosity and relaxation times which is that the glass transition temperatures for the pure material (viscosity and relaxation times) and ion-containing materials (electrical conductivity) are different. As can be seen from Table 2, the DSC T_g for PC is 166K which is about 12°C lower than the value of 178K for 1M PC:LiPF₆. The shapes of the curves shown in Fig. 1 suggest that the most appropriate temperature intervals for comparison are approximately equal intervals above a glass transition temperature such as the DSC T_g .

For example, lines I and IV in Table 1 represent conductivity for PC:LiPF₆ and viscosity for PC, respectively, over roughly the same temperature interval,

about 190-296K. It is apparent that the values of both B and T_0 are lower for viscosity ($B=480K$ and $146.2K$) than for conductivity ($B=652K$ and $151.7K$). At first sight, the value of T_0 would appear to be meaningful, being lower for viscosity and thus reflecting the trend in the DSC T_g . Even though it might be expected that the values of B should be the same (assuming the same dynamics) the value of B for conductivity is much higher. However, because of the DSC T_g 's for PC and PC:LiPF₆, there is a better match if the interval for viscosity is 175-283K. The resultant VTF parameters for that interval, which are not listed in Table 1 but which can be seen in Fig. 5, are $B=434.7K$, $T_0=150.1K$, and $\log(\eta_0^{-1})=3.88$. Interestingly, the difference between the values of B is even greater and the values of T_0 are close to one another.

In order to confirm that there is a difference between the liquids, the data for the conductivity of PC:LiPF₆ and viscosity of PC are plotted in Fig. 6 vs. reduced temperature, $T-T_g$. The data are shifted so that they overlap at the highest temperatures. Clearly, they also overlap at the lowest temperatures and there is a difference in the middle which is responsible for the different VTF parameters.

These results imply that there is a fundamental difference between the dynamics of pure PC and a 1M solution of PC with LiPF₆. i.e. there is a difference in molecular motions beyond a simple change in the rate of the processes due to a shift in glass transition temperature. First, the larger value of B for 1M PC:LiPF₆ shows that the motions in 1M PC:LiPF₆ respond more strongly to temperature changes above T_0 than those in PC i.e. the ions behave as if there is a larger "average energy barrier to motion above T_0 ." That follows from the fact that B can be thought of a "reduced temperature activation energy" since it represents the slope of the curve on a reduced-temperature Arrhenius plot ($\log(x)$ vs. $1/(T-T_0)$). Furthermore, B represents the high temperature limiting slope on a true Arrhenius plot. Second, the fact that T_0 is lower than expected on the basis of the DSC results shows that

the motions result in a difference in the dynamics of the glass transition of the two liquids, the difference between T_0 and T_g being larger in the case of 1M PC:LiPF₆. It would be of interest to carry out molecular dynamics calculations in an attempt to simulate the motions in the two liquids.

Finally, it is of interest to compare the present results for 1M PC:LiPF₆ with those recently reported for 1 M EC:PC:LiPF₆.¹⁰ Again, care must be taken in comparing the results because the glass transition temperatures are different, the DSC T_g 's being about 178K for PC:LiPF₆ and 183K for EC:PC:LiPF₆.¹⁰ The best match that can be made to the data was to carry out a fit to the PC:LiPF₆ data over the temperature interval of approximately 190-290K, which is 6°C lower than the interval of 196-296K for EC:PC:LiPF₆. The results are that $B=633K$ and $T_0=152.9K$ for PC:LiPF₆ which are to be compared with the values of $B=530K$ and $T_0=161.6K$ reported for EC:PC:LiPF₆.¹⁰ The difference in T_0 is larger than the difference in glass transition temperatures which may indicate a difference in the dynamics of the glass transition due to the presence of EC. In addition, the smaller value of B for ionic conductivity in EC:PC:LiPF₆ implies that the presence of EC may reduce the "average energy barrier to motion above T_0 ." Again, theoretical calculations would be of interest.

II. WLF Formalism

An alternative formalism which is often used to characterize glass-forming liquids is the Williams-Landel-Ferry (WLF) equation:²⁶

$$\log_{10} \left(\frac{\sigma(T)}{\sigma(T^*)} \right) = \frac{C_1(T - T^*)}{C_2 + (T - T^*)} \quad (4)$$

The adjustable parameters are C_1 , C_2 and $\log_{10}\sigma(T^*)$ where T^* is a reference temperature. Since this equation is mathematically equivalent to equation (2),²⁷ no

improvement over the VTF formalism in a fit to the data will be achieved. However, because of some recent work by Angell³ concerning the physical interpretation of the adjustable parameters, it is useful to consider the implications of the WLF equations. (Equation (1) in the paper by Angell³ differs from equation (4) by a minus sign. The reason is that equation (4) above is for ionic conductivity which increases as temperature increases while equation (1) of Angell is for electrical relaxation time which decreases as temperature increases. One consequence is that equation (1) of Angell yields negative values of C_1 .)

1. $T^*=T_g$

In order to apply the WLF equation to the data, a value of T^* must be chosen. Usually, T^* is taken to be T_g , the glass transition temperature measured by DSC^{11-13,28-33} and thus the first value of T^* used in the present work is the value of the T_g from DSC measurements performed at 10K/min. The DSC T_g quoted is midway between the onset and end of the glass transition and thus corresponds to the "central" T_g in previous papers by the authors.^{11-13,28-33} The best-fit WLF parameters corresponding to the VTF parameters listed in Table 1 are listed in Table 2. In addition, WLF parameters were calculated for the temperature intervals in Figs. 4 and 5 and the results are plotted in Figs. 7 and 8. Finally, for comparison, electrical conductivity data for 1M EC:PC:LiPF₆ and Film:EC:PC:LiPF₆¹⁰ were also analyzed and the best-fit parameters for equation (4) are listed in Table 2.

a. C_1

It is apparent from a comparison of Tables 1 and 2 or Figs. 5 and 8 that a large number of the values of C_1 are relatively constant at about 10.5-11 even

though there is a wide variation in the VTF parameters. The mathematical reason for this can be seen from the transformation equation:

$$C_1 = \frac{B}{2.3(T^* - T_0)} \quad (5)$$

If T^* is constant and B increases while T_0 decreases both the numerator and denominator in equation (5) increase thus preserving the constancy of C_1 . However, this applies only to limited values of B , T^* and T_0 . That is clear from Table 2 and Figs. 7 and 8 where mostly larger values are reported. In fact, the reason for the large values of C_1 are the high values of T_0 (close to T_g) which make the denominator in equation (5) small thus resulting in large values of C_1 . For example, this explains the value $C_1=13.6$ calculated from the data of Barthel et al.⁸ and $C_1 = 15.1$ of the present work.

However, it is clear from Figs. 7 and 8 that while C_1 takes on a range of values, the values of C_1 for the temperature intervals at the lowest temperatures converge to a value of about 11 for both the ionic conductivity and the viscosity. In addition, the C_1 values for the relaxation times, listed in Table 2, fall in the range 9-12.

Angell has pointed out how to interpret these results. Specifically, he has shown that:³

$$C_1 = \log_{10} \left(\frac{\tau_0^{-1}}{\tau^{-1}(T^*)} \right) \quad (6)$$

and

$$C_1 = \log_{10} \left(\frac{\eta_0^{-1}}{\eta^{-1}(T^*)} \right) \quad (7)$$

A similar equation can be written for the electrical conductivity:

$$C_1 = \log_{10} \left(\frac{\sigma_0}{\sigma(T^*)} \right) \quad (8)$$

Angell pointed out that because of the Maxwell relation:

$$\eta = G_\infty \tau_s \quad (9)$$

where G_∞ is the high frequency shear modulus and τ_s is the shear relaxation time, C_1 in equations (6) and (7) are related. If G_∞ is temperature independent, the relaxation time and viscosity C_1 's are predicted to be the same. In addition, the electrical conductivity can be related to the shear viscosity via:^{4,34}

$$\sigma = \eta^{-1} \frac{ne^2}{6\pi r} \quad (10)$$

where n , e and r are the number, charge and radius of the spherical particles, respectively. Consequently, if the reference temperatures are the same, the values of C_1 for the electrical conductivity should also be the same as for viscosity, provided that n , e and r are temperature independent. However, the reference temperatures are not the same because the glass transition temperatures are different for PC, PC:LiPF₆ and EC:PC:LiPF₆. Nonetheless, it is clear from the data that when referenced to the DSC T_g , all three dynamical quantities, electrical relaxation, viscosity and ionic conductivity in PC based liquids, lead to a value of $C_1 \approx 11$, particularly when the data are restricted to a range close to T_g .

The value of C_1 of about 11 is on the order of the values reported by two of the authors for a wide variety of materials including PPO₈NaB(C₆H₅)₄,¹³ PDMS-EO₈NaCF₃COO,^{11,12,28} PPO containing lithium salts,^{29,30} PPO containing NaClO₄,³¹ PEO containing sodium salts³² and MEEP₄NaCF₃SO₃.³³ The average of the values of C_1 is about 11.5. Further, the value of C_1 for relaxation times in PPO

(no ions) has been reported to be 11.5.²⁹ Finally, Hubbard et al.²⁵ have shown that a large number of polymer electrolytes exhibit a value of about 11.5 for C_1 . In the last paragraph of a recent paper, Angell has suggested that values of C_1 approximately equal to 11 frequently reported for ion-conducting polymers may be due to ion-pairing.³ On the basis of the large body of data which yield values of C_1 approximately equal to 11, including data for materials which contain no salt,²⁹ it cannot be concluded that ion-pairing, while it may exist, is responsible for the values of C_1 approximately equal to 11. Rather, the value of 11 is a due to the choice of reference temperature as will be discussed in Section II.2.

b. C_2 and $\log_{10}(x(T^*))$

As can be seen from Figs. 7 and 8, the remaining WLF parameters C_2 and $\log_{10}(x(T^*))$, where x represents conductivity, reciprocal viscosity or relaxation time, also vary with the temperature of the temperature interval. In fact, $\log_{10}(x(T^*))$ varies approximately opposite to C_1 . This is expected from the transformation equation:

$$\log_{10}(x(T^*)) = \log_{10}(x_0) - C_1 \quad (11)$$

since $\log_{10}(x_0)$ exhibits only a weak variation with temperature as can be seen in Figs. 4 and 5. More importantly, it is clear from a comparison of Figs. 4 and 7 and Figs. 5 and 8, that C_2 varies opposite to T_0 . The reason is clear from the final transformation equation:

$$C_2 = T^* - T_0 \quad (12)$$

In contrast to C_1 , it is apparent from Figs. 7 and 8 that C_2 does not converge to a characteristic value. The significance of the non-uniqueness of C_2 will be discussed at the end of section II.3.

2. $T^* = T_{100}$

Angell has suggested that a more appropriate reference temperature is the temperature at which the relaxation time is 100s i.e. $\tau(T^*)=100\text{s}$.³ This temperature will be referred to as T_{100} . Stickel et al.⁴ have reported dielectric relaxation data for PC which extend to 165K and hence overlap the DSC T_g of 166K. On the basis of that data, T_{100} for PC is calculated to be 156.8K which is about 9°C lower than the measured DSC T_g . Stickel quotes a value of $T_{100}=157\text{K}$.⁴ Unfortunately, no relaxation data exist for LiPF_6 in PC or EC:PC. Alternatively, the electrical conductivity data were reanalyzed using reference temperatures scaled using the DSC T_g 's. Specifically, since T_g for PC: LiPF_6 is about 12°C higher than for PC, a value of $T_{100}=168.8\text{K}$ was used for that material and a similar scaling gave a value of $T_{100}=173.8\text{K}$ for EC:PC: LiPF_6 . The new WLF parameters were calculated using the various values of $T^*=T_{100}$ and are listed in Table 3. Finally, the WLF parameters were recalculated for the various temperature intervals of Figs. 7 and 8 and the results are plotted in Figs 9 and 10.

It is apparent from Table 3 and the figures that, in general, use of $T^*=T_{100}$ results in larger values of C_1 and smaller values of C_2 than for $T^*=T_g$. For example, for the ionic conductivity, values of C_1 range from about 16 to 50 (using $T^*=T_{100}$) as compared with about 11 to 15 (using $T^*=T_g$) and C_2 ranges from about 21 to 4K as compared with about 30 to 13K. In addition, the values of both C_1 and C_2 at two temperatures for the viscosity are negative. The reasons for these results are obvious from equations (5) and (12), both of which contain the quantity T^*-T_0 . This quantity is smaller for the lower values of $T^*=T_{100}$ and becomes negative when T_0 is greater than T^* thus resulting in the observed general trends.

In the original work,²⁶ two reference temperatures were also used, the glass transition temperature determined by thermal expansion or heat capacity measurements and a second, higher temperature. The conclusions of the original

work were that T_g resulted in "universal" values of $C_1=17.4$ and $C_2=51.6$ while the use of the higher reference temperature gave value of $C_1=8.86$ and $C_2=101.6$. Consequently, while the absolute numbers are significantly different e.g. $C_1=17.4$ vs. about 11, the variation with reference temperature, lower T^* giving rise to a larger C_1 and smaller C_2 , etc. is consistent.

In addition to the shift with reference temperature, it is clear from Figs. 9 and 10 that the values of C_1 and C_2 again exhibit a strong dependence upon temperature interval. Nonetheless, for the temperature intervals at the lowest temperatures, C_1 tends towards a value of about 16. On the other hand, C_2 again does not appear to converge to a characteristic value, at least for the temperature intervals of the present work.

3. Implications of the WLF formalism

a. C_1

Equations (6)-(8) lead to the physical interpretation of C_1 as a measure of the difference between extreme values of the dynamical quantities. Specifically, C_1 is the difference between the logarithm of the dynamical quantity at very high temperatures (logarithm of the VTF preexponential) and the value at the reference temperature (logarithm of the WLF preexponential).

The first implication of the WLF formalism, then, is that for PC and PC based liquids (and traditional ion-conducting polymers) the value of the dynamical quantity at the DSC glass transition temperature should be about 11 decades smaller than the value predicted for very high temperatures since C_1 approaches 11 at low temperatures when referenced to $T^*=T_g$. For example, since $\log(\sigma_0)\approx-0.3$, it is predicted that $\log(\sigma(T_g))\approx-11.3$. It would be of interest to carry out electrical conductivity measurements nearer T_g in order to check this prediction.

On the other hand, when referenced to T_{100} , the limiting value of C_1 is about 16. Referencing to T_{100} has been discussed in detail by Angell.³ He pointed out that the relaxation time preexponential, τ_0 , which is sometimes known as the reciprocal frequency factor³⁵⁻³⁷ should be on the order of a reciprocal lattice vibrational frequency, $\tau_0 \approx 10^{-14}$ s, so that $\log(\tau_0^{-1}) \approx 14$. That condition holds for PC since the data of Stickel et al.⁴ give rise to a value of $\log_{10}(\tau_0^{-1}) = 13.9$ for the temperature interval 165-200K. (Note that the data in Table 1 are for the f_{\max} , the frequency in Hz. Consequently, $\tau^{-1} = 2\pi f_{\max}$.) Since $\log_{10}(\tau^{-1}(T_{100}))$ is fixed at -2, equation (6) predicts that C_1 should be approximately 16 for relaxation times. Finally, Angell pointed out that the temperature dependence of G_∞ in equation (9) should increase C_1 to about 17 for viscosity.³ Since it was shown above that C_1 for electrical conductivity should be about the same as for viscosity, a value of $C_1 \approx 17$ is expected. While some of the values of C_1 in Table 3 for the ionic conductivity are close to 17, it has been shown that the low temperature limiting value of C_1 for both conductivity and viscosity is approximately 16.

As regards referencing, no new information is obtained by using T_{100} rather than the DSC T_g when the relaxation time is known. In fact, the auxiliary relaxation information necessary for defining reference temperatures such as T_{100} is not always available. The present work is an example since relaxation data are not available for PC:LiPF₆ or EC:PC:LiPF₆. In fact, in general this is true for ion-conducting systems since it is usually difficult to observe dielectric relaxation in such systems. In addition, it should be clear from section II.2 that referencing to the lower temperature T_{100} leads to larger fluctuations in the values of C_1 and C_2 than when referenced to the DSC T_g . For these reasons, then, referencing to the DSC T_g is preferable.

Finally, the consequences of attempting to use C_1 or C_2 in a theory are considered. Clearly, it must be carefully specified which data interval should be

used. Based upon the results discussed above, the intervals of choice for C_1 are those at the very lowest temperatures. Fortunately, this is consistent with the requirement emphasized by Angell³ that the theory must properly represent the data near the glass transition temperature. The drawback to using only the low temperature data, of course, is that the high temperature data are ignored. In fact, the behavior at high temperatures is different for different liquids. For example, Stickel et al.⁴ have pointed out that PC exhibits a transition to Arrhenius behavior at high temperatures while many liquids do not. Consequently, limiting the analysis to data near the glass transition temperature results in only a partial characterization of a liquid. Next, C_2 does not appear to have a unique value which, of course, impacts any related theoretical considerations. For example, C_2 is sometimes used to estimate the "fragility" of a liquid.³ Clearly, care must be taken in basing materials characterization on an imperfect formalism such as those provided by the VTF or WLF equations.

III. Formalism of Bendler and Shlesinger

In fact, the inadequacy of the VTF and WLF equations is not surprising because, despite their widespread application, they have no rigorous theoretical basis.^{4,40} Fortunately, other formalisms are available. For example, one recent phenomenological model⁴¹⁻⁴³ gives rise to the following equation:

$$\sigma = D \exp\left(\frac{-B''}{(T - T_c)^{1.5\gamma}}\right) \quad (11)$$

which contains four adjustable parameters D , B'' , T_c and γ . In order to make a direct comparison with the three parameter VTF and WLF equations the mean-field

limit, $\gamma=1$, was used. Equation (11), known as the BENSHE equation,²¹ was best-fit to the data and the resultant parameters are listed in Table 4.

It is seen that the RMS deviation for the BENSHE equation for all of the materials is on the order of half that for the VTF equation and thus the data are better fit by the BENSHE equation. This is similar to the findings reported in a previous paper²¹ where the BENSHE equation was fit to the data for ion-conducting polymers. In that paper, it was shown that the best data were better-fit by the BENSHE equation. That is particularly interesting as the BENSHE equation has a straightforward physical interpretation.²¹

Further insight can be gained into the applicability of the BENSHE equation by fitting different portions of the data. Specifically, it was noted during the analysis that if the two lowest temperature datum points are omitted for PVdF:EC:PC:LiPF₆ the superiority of the BENSHE equation decreases. This trend can also be seen in Table III of Ref. 21 where the VTF and BENSHE parameters are listed for conductivity data for PDMS-EO₈-NaCF₃CO over different temperature ranges. Further, it needs to be kept in mind that the BENSHE equation has still another adjustable parameter, γ . It will be of interest to investigate the extent to which inclusion of that parameter affects the goodness of fit.

SUMMARY

In summary, several results have been obtained via electrical conductivity and DSC studies on 1 M LiPF₆ in propylene carbonate. The electrical conductivity data and literature data for viscosity and relaxation times for PC not containing salt are analyzed in terms of VTF, WLF and BENSCH formalisms. Large variations are found in both the VTF and WLF fitting parameters with temperature interval. In general this is not due to inaccuracy in the data but rather to the systematic deviation of the VTF or WLF formalisms from the data. Using the DSC T_g, C₁ ranges from about 10 to 30 though the temperature intervals at the lowest temperatures is about 11. This is approximately that observed for traditional ion-conducting polymers. When referenced to the temperature where $\tau=100s$, C₁ ranges from about -100 to 50 though the value for the temperature intervals with the lowest central temperatures is about 16. In neither case does C₂ exhibit a unique value. This shows that care must be taken when utilizing the VTF/WLF parameters to draw conclusions concerning the behavior of systems. Finally, it is shown that all data are better fit by the BENSCH equation.

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Table 1. Best-fit VTF parameters. The results are for electrical conductivity data unless otherwise indicated.

| Material | Temperature Range (K) | $\log_{10}(x_0)$ | B (K) | T_0 (K) | RMS dev |
|------------------------------------------------|-----------------------|-------------------------------------------|---------|------------|---------|
| Electrical Conductivity | | | | | |
| $x = \sigma_0(\text{S/cm})$ | | | | | |
| I. PC:LiPF ₆ | 187-296 | -0.27 | 652 | 151.7 | 0.0328 |
| II. PC:LiPF ₆ ^a | 228-298 | -0.85 | 438 | 164.01 | |
| III. PC:LiPF ₆ | 228-296 | -0.71 | 474 | 164.4 | 0.00095 |
| Viscosity | | | | | |
| $x = \eta_0^{-1}(\text{Pa}\cdot\text{s})^{-1}$ | | | | | |
| IV. PC ^b | 193-298 | 3.99 | 480 | 146.2 | 0.0328 |
| V. PC ^b | 157-343 | 4.60 | 707 | 136.9 | 0.189 |
| VI. PC ^c | 157-343 | 4.55 | 702 | 137 | |
| VII. PC ^c | 175-343 | 3.91 | 440 | 150 | |
| VIII. PC ^c | 157-193 | 8.92 | 1532 | 122 | |
| IX. PC ^a | 238-313 | 3.82 | 411 | 152.11 | |
| Dielectric Relaxation | | | | | |
| $x = f_0^{\text{max}}(\text{Hz})$ | | | | | |
| X. PC ^d | 200-290 | 10.7 | 363 | 153 | |
| XI. PC ^d | 165-200 | 13.1 | 897 | 132.3 | |
| Relaxation times | | | | | |
| $x = \tau_0^{-1}(\text{s}^{-1})$ | | | | | |
| XII. PC ^e | 160-290 | 12.7 | 435 | 145 | |
| | Temperature Range (K) | $\log_{10}(A(\text{K}^{1/2}\text{S/cm}))$ | B' (eV) | T_0' (K) | RMS dev |
| PC:LiPF ₆ | 187-296 | 1.04 | 681 | 150.8 | 0.0302 |
| PC (Viscosity) | 193-298 | 2.66 | 441 | 148.2 | 0.0339 |
| PC (Viscosity) | 157-343 | 3.31 | 684 | 137.3 | 0.198 |

a. Ref. 8

b. Analysis of the combined data of Refs. 5 and 8.

c. Ref. 5.

d. Ref. 4.

e. Ref. 9.

Table 2 Best-fit WLF parameters using the DSC T_g as the reference temperature.

The electrical conductivity data are either from the present work or Ref. 10.

| | Temperature Range (K) | $T^*=T_g$ (K) | $\log_{10}(x(T_g))$ | C_1 | C_2 (K) | RMS dev |
|---------------------------------------|--------------------------|------------------|---------------------|-------|--------------|------------|
| Electrical Conductivity | | | | | | |
| $x = \sigma(T^*)(S/cm)$ | | | | | | |
| Film:EC:PC:LiPF ₆ | 196-296 | 183 | -11.2 | 10.2 | 25.7 | 0.0137 |
| EC:PC:LiPF ₆ | 196-296 | 183 | -11.2 | 10.8 | 21.4 | 0.0211 |
| EC:PC:LiPF ₆ | 190-296 | 183 | -10.6 | 10.3 | 24.3 | 0.0354 |
| I. PC:LiPF ₆ | 187-296 | 178 | -11.0 | 10.8 | 26.3 | 0.0328 |
| II. PC:LiPF ₆ ^a | 228-298 | 178 | -14.4 | 13.6 | 14 | |
| III. PC:LiPF ₆ | 228-296 | 178 | -15.8 | 15.1 | 13.6 | 0.00095 |
| Viscosity | | | | | | |
| $x = \eta^{-1}(T^*)(Pa-s)^{-1}$ | | | | | | |
| IV. PC ^b | 193-298 | 166 | -6.57 | 10.6 | 19.8 | 0.0328 |
| V. PC ^b | 157-343 | 166 | -5.94 | 10.5 | 29.1 | 0.189 |
| VI. PC ^c | 157-343 | 166 | -5.96 | 10.5 | 29 | |
| VII. PC ^c | 175-343 | 166 | -8.03 | 11.9 | 16 | |
| VIII. PC ^c | 157-193 | 166 | -6.2 | 15.1 | 44 | |
| IX. PC ^a | 238-313 | 166 | -9.03 | 12.8 | 13.9 | |
| Dielectric relaxation | | | | | | |
| $x=f_{max}(T^*)(Hz)$ | | | | | | |
| X. PC ^d | 200-290 | 166 | -1.45 | 12.1 | 13 | |
| XI. PC ^d | 165-200 | 166 | 1.54 | 11.6 | 33.7 | |
| Relaxation times | | | | | | |
| $x = \tau^{-1}(T^*)(s^{-1})$ | | | | | | |
| XII. PC ^e | 160-290 | 166 | 3.70 | 9.0 | 21 | |

a. Ref. 8

b. Analysis of the combined data of Refs. 5 and 8.

c. Ref. 5.

d. Ref. 4.

e. Ref. 9.

Table 3. Best-fit WLF parameters using the reference temperature proposed by Angell³ for dielectric relaxation and viscosity. The reference temperature for the electrical conductivity is scaled via the DSC T_g .

| | Temperature Range (K) | $T^*=T_{100}$ (K) | $\log_{10}(x(T_{100}))$ | C_1 | C_2 (K) | RMS dev |
|---------------------------------------|-----------------------|-------------------|-------------------------|-------|-----------|---------|
| Electrical Conductivity | | | | | | |
| $x = \sigma(T^*)(S/cm)$ | | | | | | |
| Film:EC:PC:LiPF ₆ | 196-296 | 173.8 | -16.9 | 15.8 | 16.5 | 0.0137 |
| EC:PC:LiPF ₆ | 196-296 | 173.8 | -19.3 | 18.9 | 12.2 | 0.0211 |
| EC:PC:LiPF ₆ | 190-296 | 173.8 | -16.9 | 16.6 | 15.1 | 0.0354 |
| I. PC:LiPF ₆ | 187-296 | 168.8 | -16.8 | 16.6 | 17.1 | 0.0328 |
| II. PC:LiPF ₆ ^a | 228-298 | 168.8 | -40.6 | 39.7 | 4.8 | |
| III. PC:LiPF ₆ | 228-296 | 168.8 | -47.5 | 46.8 | 4.4 | 0.00095 |
| Viscosity | | | | | | |
| $x = \eta^{-1}(T^*)(Pa-s)^{-1}$ | | | | | | |
| IV. PC ^b | 193-298 | 156.8 | -15.7 | 19.7 | 10.6 | 0.0328 |
| V. PC ^b | 157-343 | 156.8 | -10.8 | 15.4 | 19.9 | 0.189 |
| VI. PC ^c | 157-343 | 156.8 | -10.8 | 15.4 | 19.8 | |
| VII. PC ^c | 175-343 | 156.8 | -24.2 | 28.1 | 6.8 | |
| VIII. PC ^c | 157-193 | 156.8 | -10.2 | 19.1 | 34.8 | |
| IX. PC ^a | 238-313 | 156.8 | -34.2 | 38.1 | 4.7 | |
| Dielectric relaxation | | | | | | |
| $x=f_{max}(T^*)(Hz)$ | | | | | | |
| X. PC ^d | 200-290 | 156.8 | -30.8 | 41.5 | 3.8 | |
| XI. PC ^d | 165-200 | 156.8 | -2.8 | 15.9 | 24.5 | |
| Relaxation times | | | | | | |
| $x=\tau^{-1}(T^*)(s^{-1})$ | | | | | | |
| XII. PC ^e | 160-290 | 156.8 | -3.31 | 16.0 | 11.8 | |

a. Ref. 8

b. Analysis of the combined data of Refs. 5 and 8.

c. Ref. 5.

d. Ref. 4.

e. Ref. 9.

Table 4. Best fit BENSH parameters.Three parameter fit ($\gamma=1$)

| | Temperature Range (K) | $\log_{10}(D(\text{S/cm}))$ | B'' ($\text{K}^{3/2}$) | T_c (K) | RMS dev |
|-----------------------------------------------------|--------------------------|-----------------------------|-------------------------------|--------------|------------|
| Film:EC:PC:LiPF ₆ | 196-296 | -1.62 | 5856 | 140.5 | 0.0088 |
| EC:PC:LiPF ₆ | 196-296 | -0.99 | 4944 | 146.2 | 0.0110 |
| EC:PC:LiPF ₆ | 190-296 | -0.93 | 5262 | 144.1 | 0.0199 |
| I. PC:LiPF ₆ | 187-296 | -0.93 | 6202 | 135.7 | 0.0183 |
| Viscosity $x = \eta^{-1}(T_g)(\text{Pa-s})^{-1}$ | | | | | |
| III. PC ^a | 193-298 | 3.58 | 5028 | 126.7 | 0.0300 |
| IV. PC ^a | 157-343 | 3.80 | 5932 | 125.1 | 0.127 |

Four parameter fit

| | Temperature Range (K) | $\log_{10}(D(\text{S/cm}))$ | B'' (K) | T_c (K) | γ | RMS dev |
|-----------------------------------------------------|--------------------------|-----------------------------|--------------|--------------|----------|------------|
| Film:EC:PC:LiPF ₆ | 196-296 | -1.62 | 5856 | 140.5 | | 0.0088 |
| EC:PC:LiPF ₆ | 196-296 | -0.99 | 4944 | 146.2 | | 0.0110 |
| EC:PC:LiPF ₆ | 190-296 | -0.93 | 5262 | 144.1 | | 0.0199 |
| I. PC:LiPF ₆ | 187-296 | -0.93 | 6202 | 135.7 | | 0.0183 |
| Viscosity $x = \eta^{-1}(T_g)(\text{Pa-s})^{-1}$ | | | | | | |
| III. PC ^a | 193-298 | 3.58 | 5028 | 126.7 | | 0.0300 |
| IV. PC ^a | 157-343 | 3.80 | 5932 | 125.1 | | 0.127 |

a. Analysis of the combined data of Refs. 5 and 8.

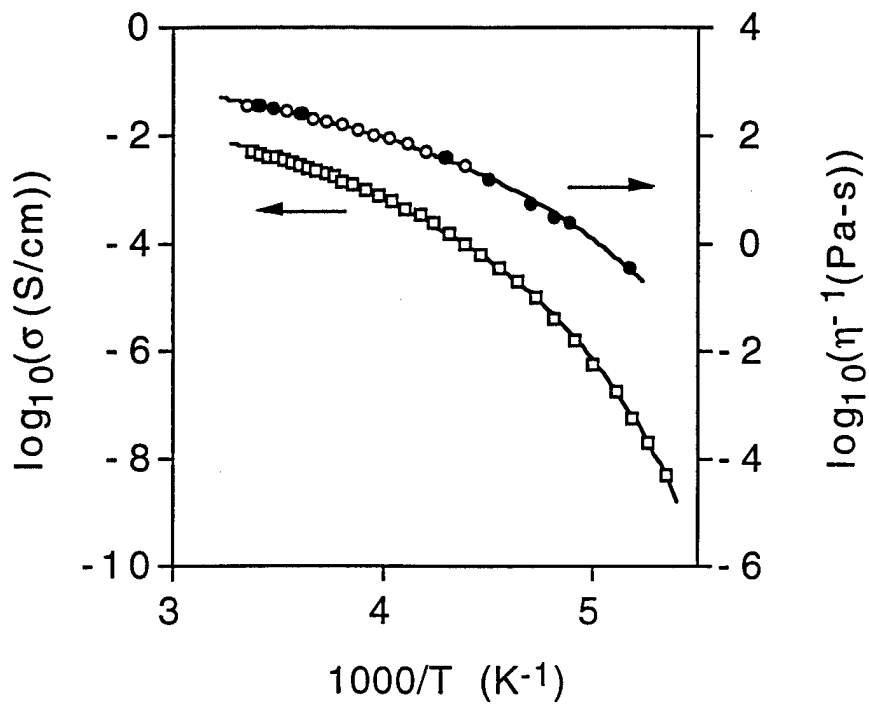


Figure 1. Electrical conductivity for PC:LiPF₆ (open squares) and reciprocal viscosity for pure PC vs. reciprocal temperature. The open circles are from Ref. [8] and the closed circles are from Ref. [5]. Also shown is the best-fit WLF (VTF) curve for each set of data.

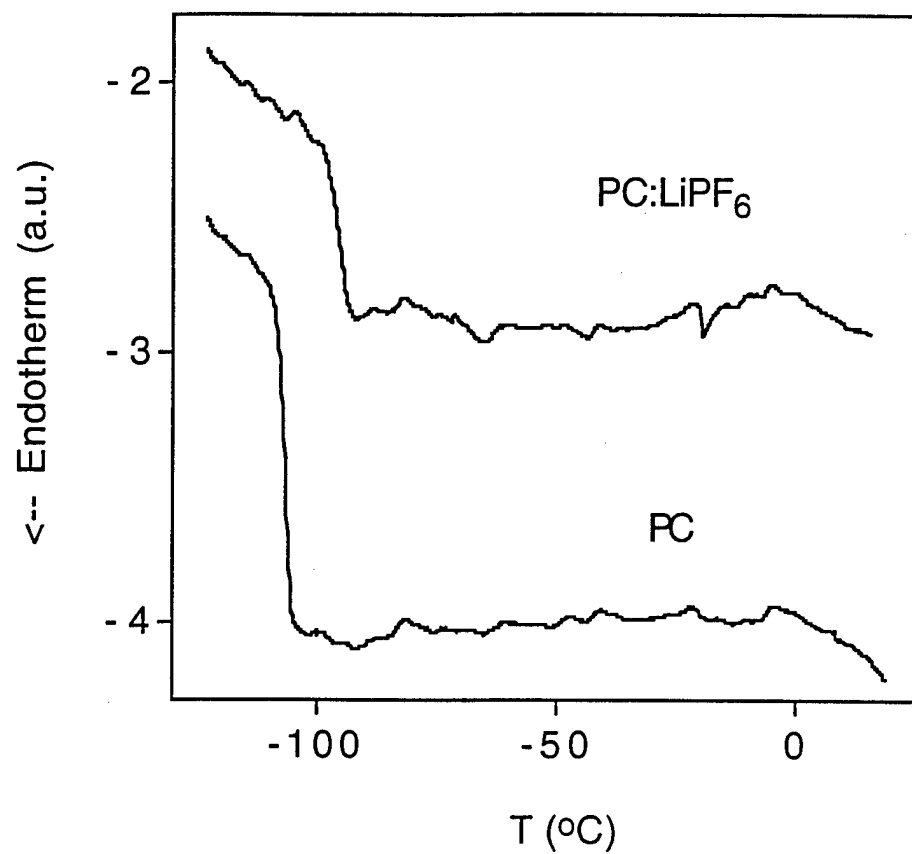


Figure 2. DSC thermograms for PC and 1M PC:LiPF₆. The scanning rate is 10 K/min.

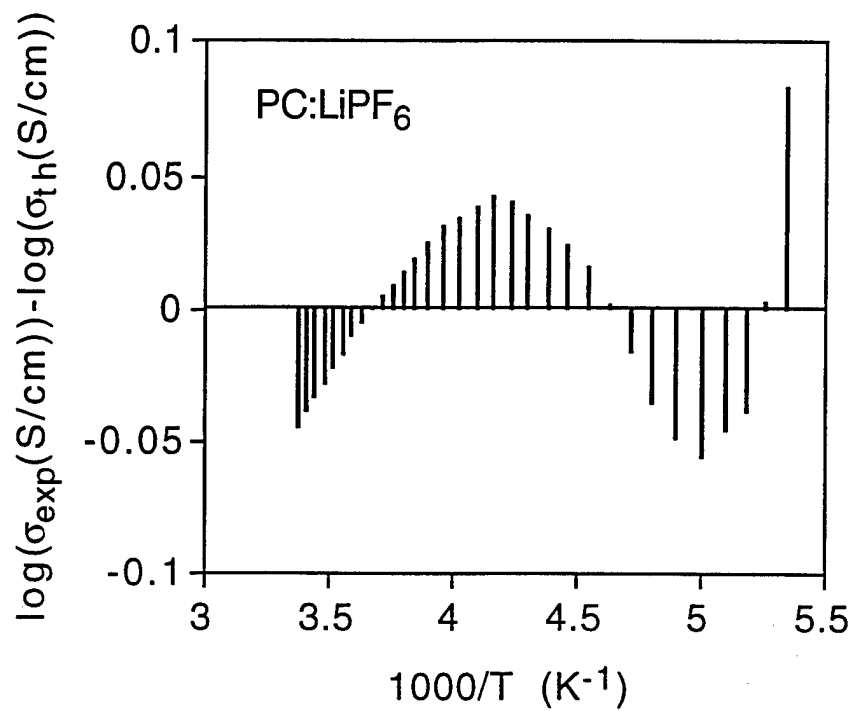


Figure 3. Deviation of the VTF (WLF) equation from the data vs. reciprocal temperature for the electrical conductivity of PC:LiPF₆.

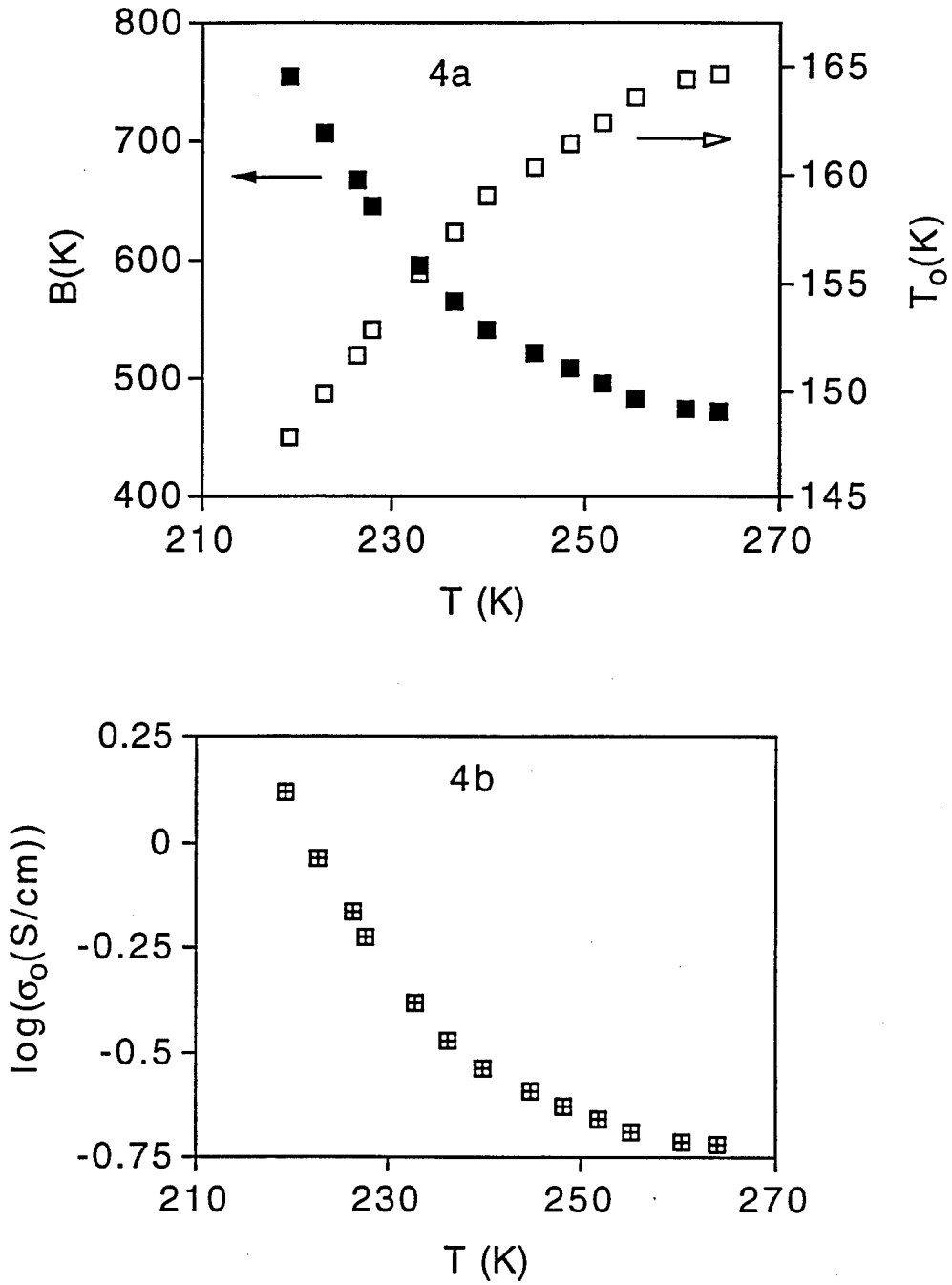


Figure 4. VTF parameters for 65°C intervals of electrical conductivity data for PC:LiPF₆. The temperature is the temperature at the middle of the interval.

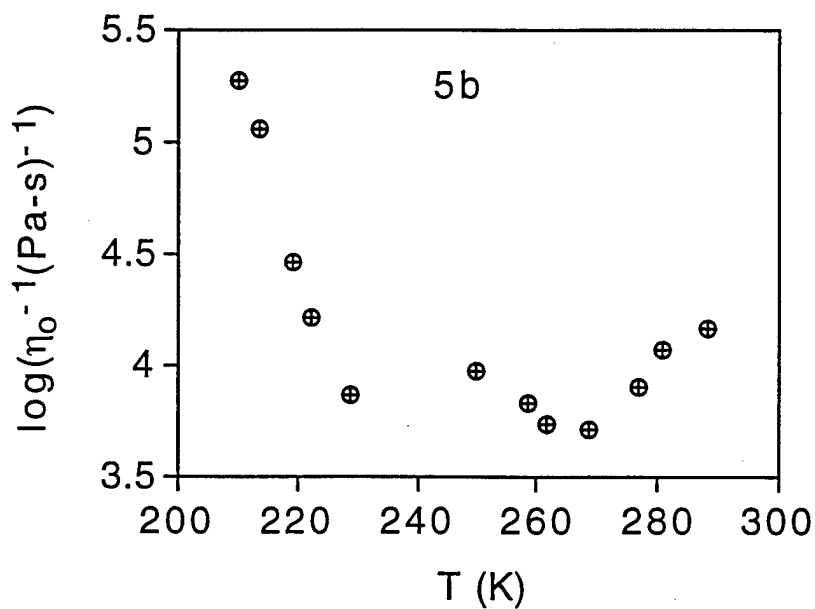
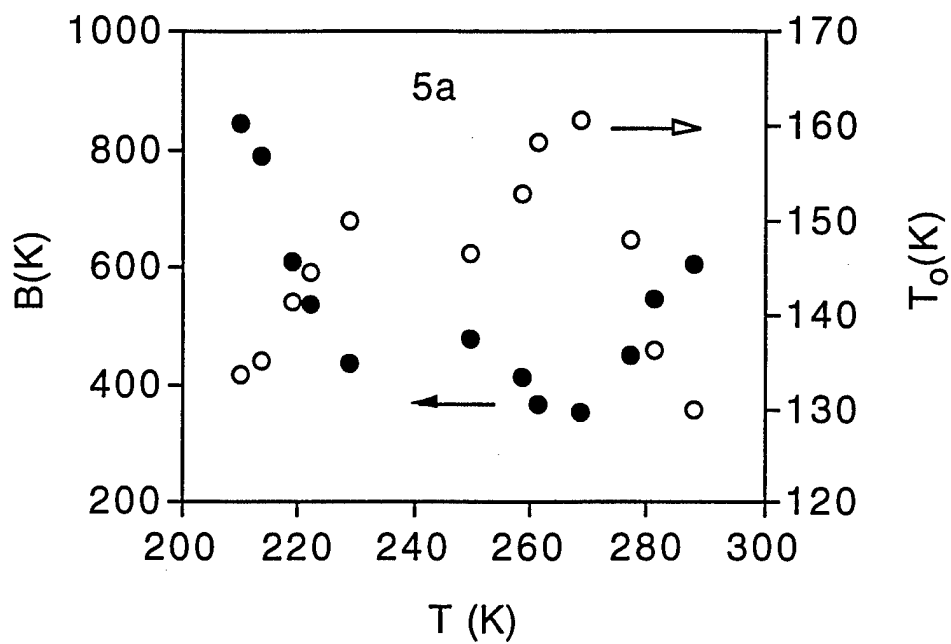


Figure 5. VTF parameters for 109°C intervals of viscosity data for PC. The temperature is the temperature at the middle of the interval. The data are the combined data of Refs. 5 and 8.

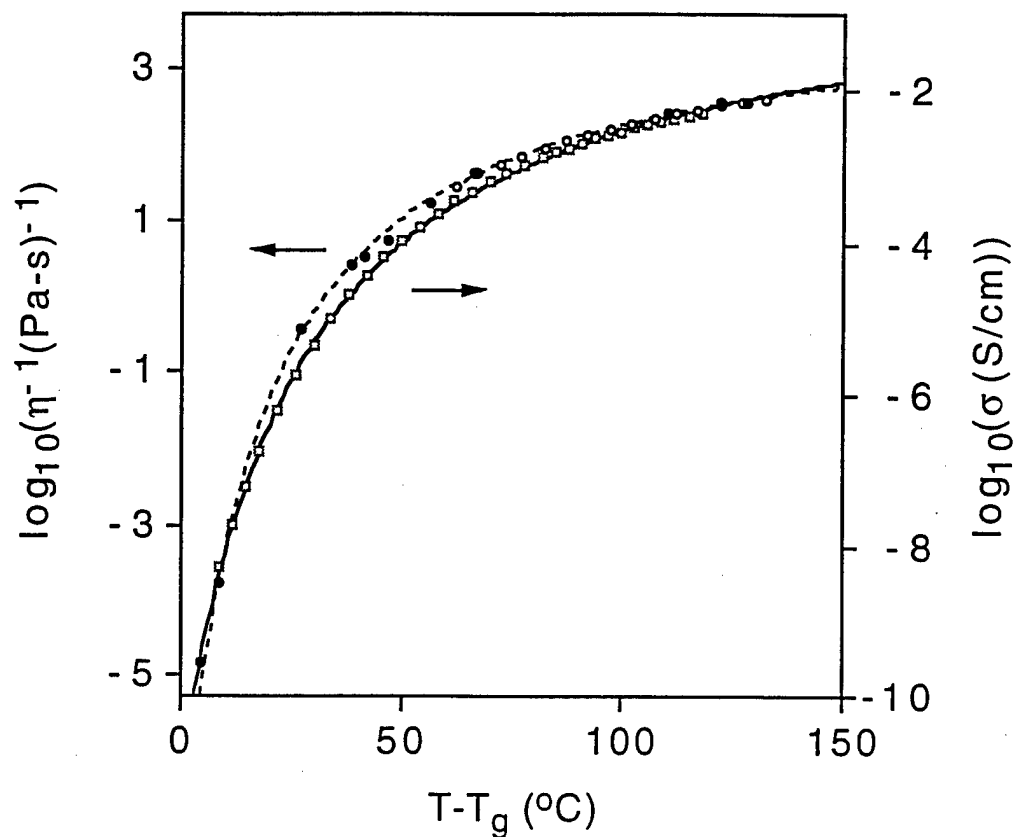


Figure 6. Electrical conductivity for PC:LiPF₆ and reciprocal viscosity for pure PC vs. reduced temperature. The open circles are from Ref. [8] and the closed circles are from Ref. [5]. Also shown is the best-fit WLF (VTF) curves for the electrical conductivity data over the temperature range 187-296K and the viscosity over the temperature range 175-283K.

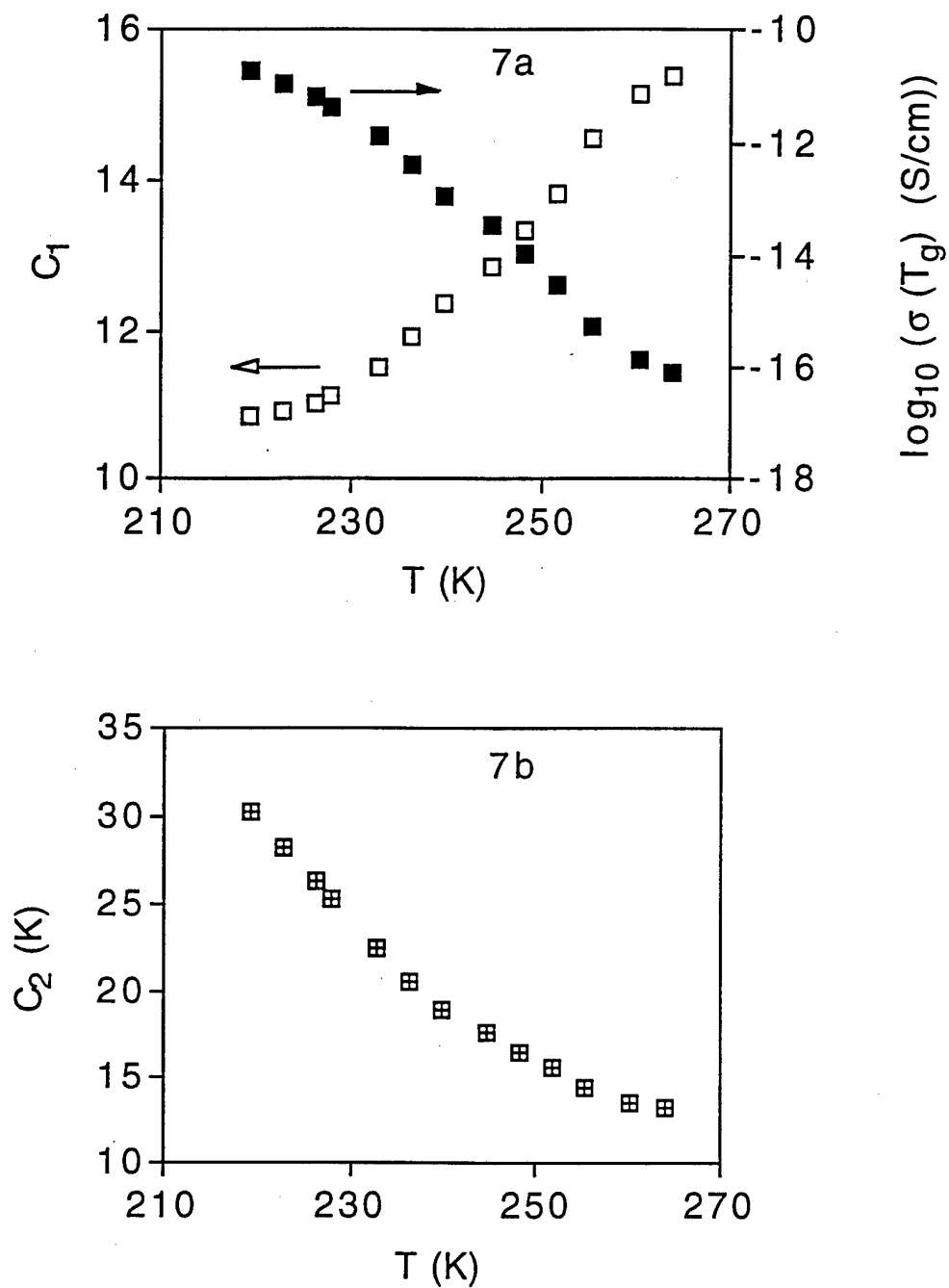


Figure 7. WLF parameters for 65°C intervals of electrical conductivity data for PC:LiPF₆. The temperature is the temperature at the middle of the interval. The reference temperature is the DSC T_g .

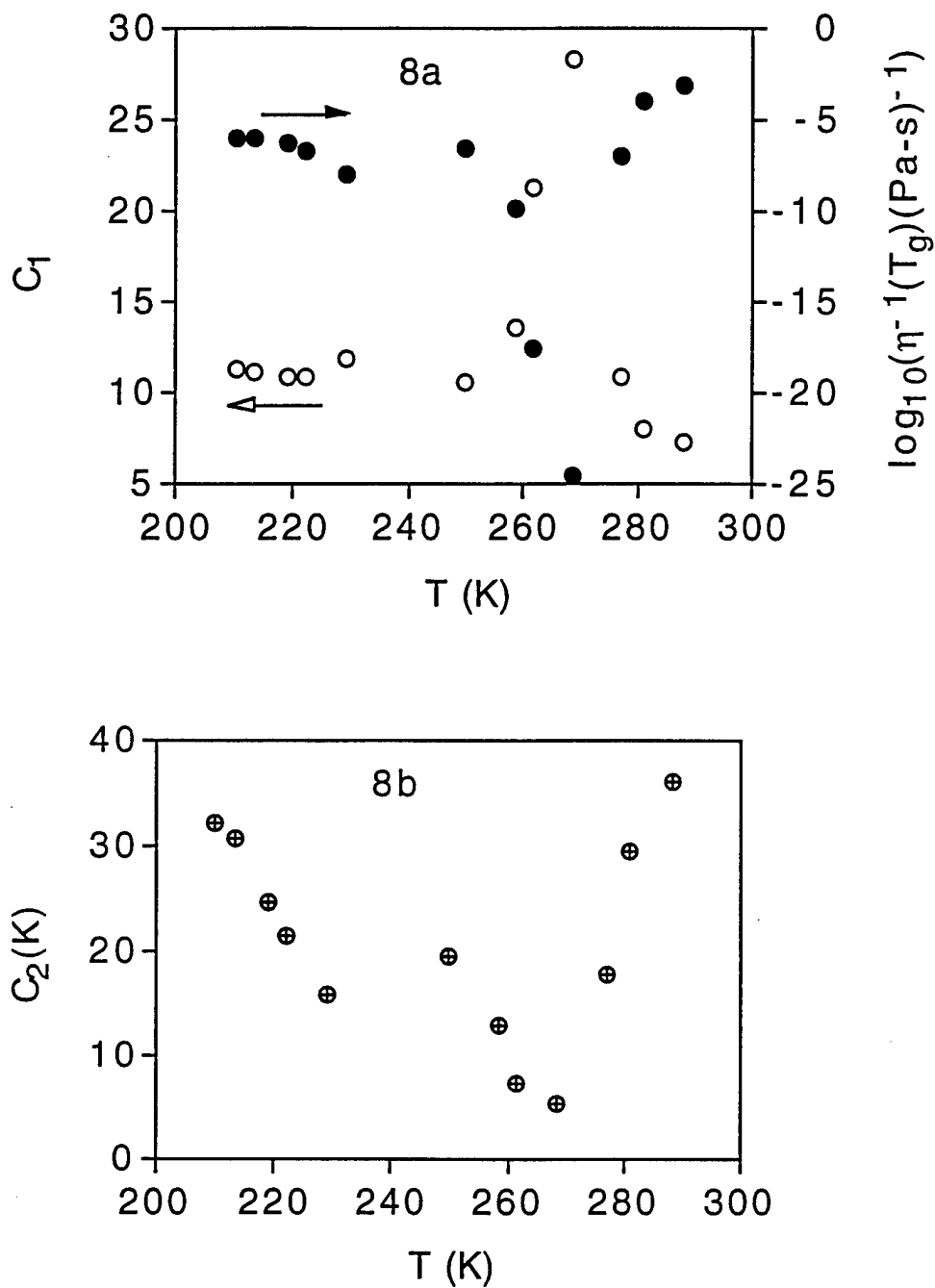


Figure 8. WLF parameters for 109°C intervals of viscosity data for PC:LiPF₆. The temperature is the temperature at the middle of the interval. The data are the combined data of Refs. 5 and 8. The reference temperature is the DSC T_g .

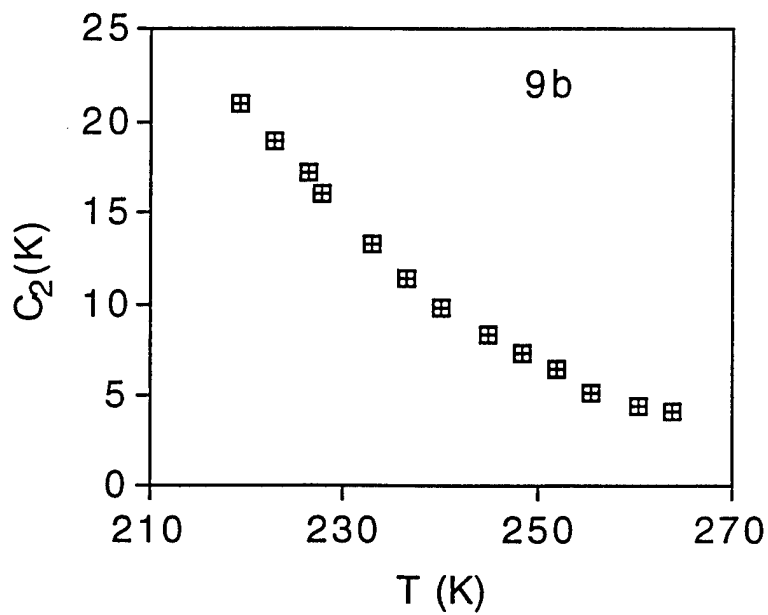
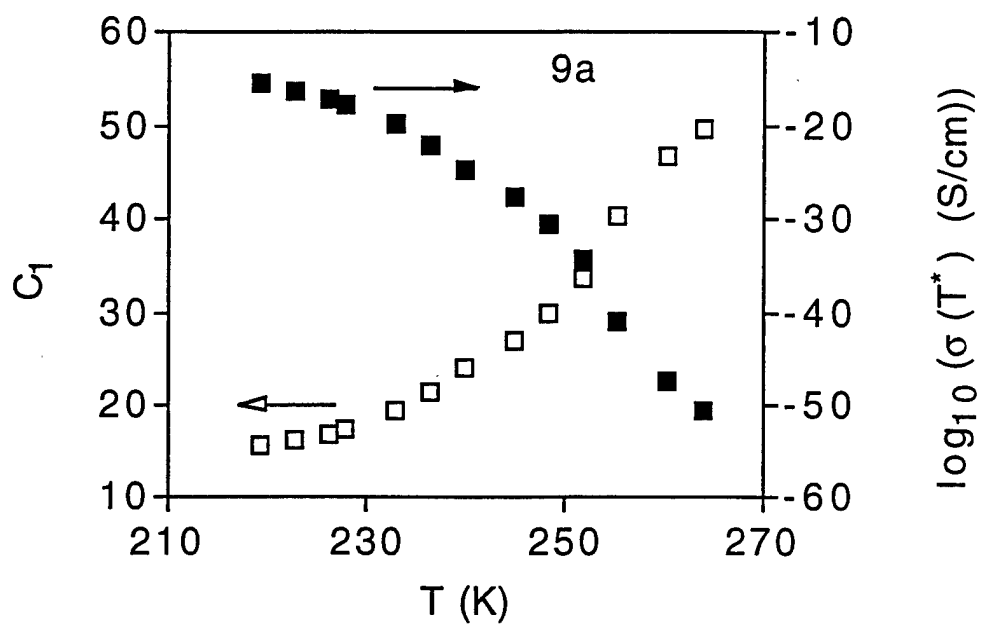


Figure 9. WLF parameters for 65°C intervals of electrical conductivity data for PC:LiPF₆. The temperature is the temperature at the middle of the interval. The reference temperature is the temperature at which $\tau=100$ s.

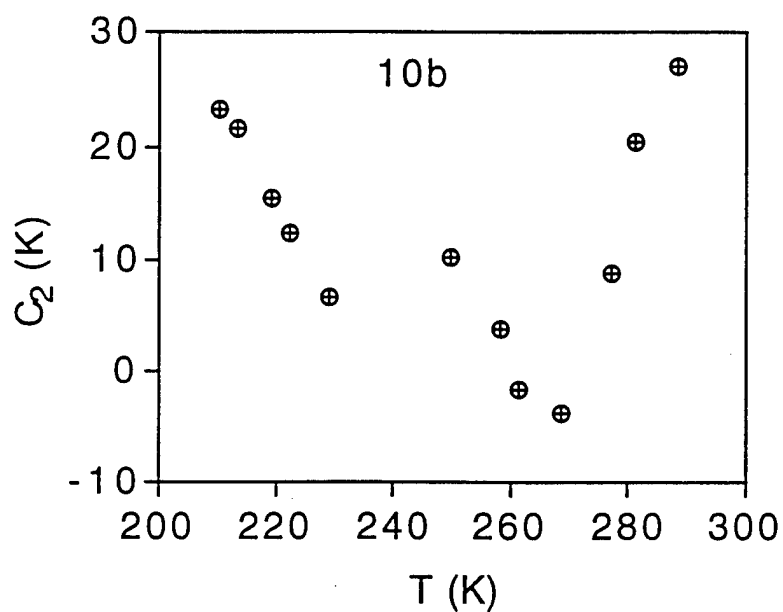
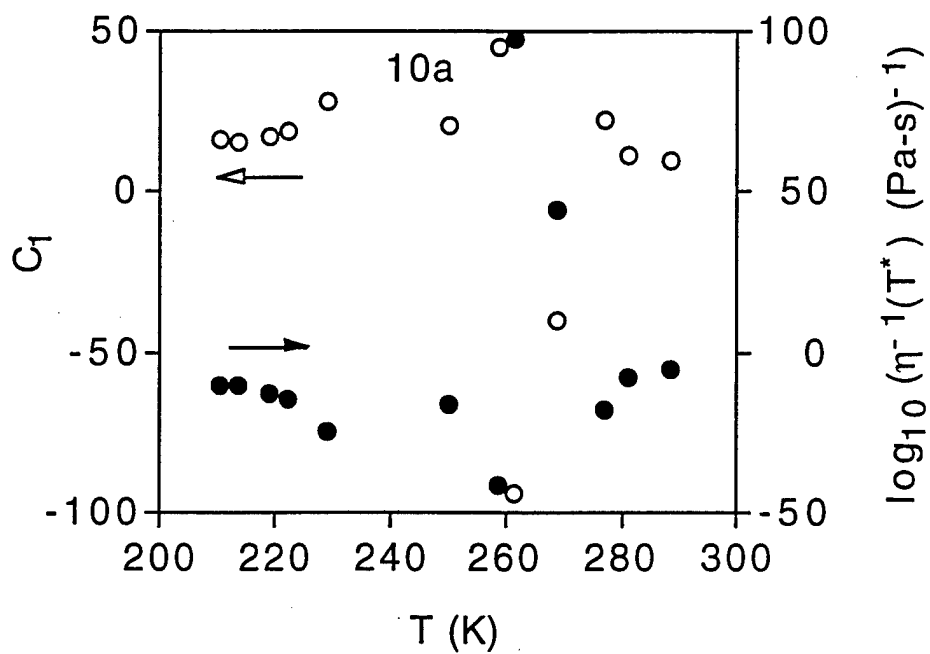


Figure 10. WLF parameters for 109°C intervals of viscosity data for PC:LiPF₆. The temperature is the temperature at the middle of the interval. The data are the combined data of Refs. 5 and 8. The reference temperature is the temperature at which $\tau=100$ s.