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Correlation Between Ionic Conductivity and ^{7}Li-NMR of Polyether-polyurethane Networks Containing Lithium Perchlorate

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Summary

The effect of temperature on the ionic conductivity and the ^{7}Li NMR line width of a polyether-polyurethane network containing lithium perchlorate was studied. A treatment of the results based on free-volume principles yielded a linear correlation between the logarithm of the reduced conductivity, σ_T/σ_{T_0}, and the logarithm of the reduced ^{7}Li NMR line width, δ_T/δ_{T_0}, for a given reference temperature, T_0=323 K.

Introduction

The field of ion-containing polymers is experiencing an increasing interest both in fundamental studies and in applied science and technology(KILLIS et al.1981). Polyether-polyurethane networks containing alkali metal salts have been studied in our laboratory and their mechanical and electrical properties described and discussed (KILLIS et al. 1981). In particular, it was demonstrated that a direct experimental correlation exists between the ionic conductivity of such materials and their viscoelastic properties. A WLF relationship was found to hold both for the viscoelastic and the ionic conduction (diffusion) processes. It is however still difficult to obtain a clear understanding of the mechanism of ion diffusion on a molecular scale and to determine the parameters actually involved in the conduction process. Lithium nuclei are well suited to studies of ion diffusion because of their good sensitivity (natural abundance of ^{7}Li 92.57%). Their electric quadrupole moment may be exploited to investigate the electrical environment in favourable situations. Also, lithium ions are not paramagnetic and diffusion properties are therefore not screened by electron spin relaxation processes. It is not the purpose of this paper to give an extensive description of nuclear magnetic relaxation processes of lithium nuclei in the polymer network structure. Its aim rather is to show that the relaxation of the transverse magnetic component of lithium nuclei exhibits a motional narrowing effect clearly reflecting a diffusion process of the

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lithium ions and to prove the existence of a correlation between the conductivity and the ^{7}Li NMR line width.

Experimental

A. Preparation of the Membranes

Polyoxyethylene diol of molecular weight 400 (Merck) was vacuum dried at 363 K before dissolving into it anhydrous lithium perchlorate in a dry nitrogen atmosphere to give a concentration of about 8% w/w. Small amounts of dry methylene chloride were added to accelerate the salt dissolution. The second stage of the preparation consisted in cross-linking the polyether diol in a dry nitrogen atmosphere with a trifunctional isocyanate p,p',p"-triphenyl(methane)triisocyanate, added as a methylene chloride solution (Desmodur R, BASF). The mixture was quickly moulded between two glass plates separated by a 1 mm rubber joint. Gellation was allowed to take place at room temperature under dry nitrogen and was completed at about 333 K under vacuum (0.01 Torr) for several days before the membrane was removed, ready for measurements.

B. Conductivity Measurements

These were carried out following the complex impedance diagram principle (RAVAINE, SOUQUET 1974)on a SOLARTRON 1174 frequency analyser, adapted for impedance measurements. The membrane was kept in a specially designed glass cell, under 0.001 Torr, operating between 323 and 423 K,and pressed between two cylindrical stainless-steel electrodes.

C. ^{7}Li NMR Line Width Measurements

Spectra were taken with a WP 100 Bruker instrument and the number of scans was 10^2 to 10^5 depending upon the temperature. Samples were cut from the original membrane in discs of 4 mm diameter which were tightly packed into the NMR tubes. The samples were then outgassed for at least 24 h at about 363 K on a vacuum line before sealing off the tubes.

Results and Discussion

1. Motional Narrowing Effect

A. Line Width Temperature Effect

The motional narrowing of resonance lines is a well established NMR property arising from the relaxation process of the transverse component of the magnetization (GUTOWSKY, McGARVEY 1952). This relaxation is known to be more sensitive to the quantum coherence of nuclear spins than to resonant energy exchanges at the Larmor frequency ($\sim 10^8$ rad/sec) between the spin system and the thermal bath. Accordingly, molecular processes characterised by low relaxation frequencies may be perceived through the transverse magnetisation relaxation function. The motional narrowing effect is well understood but cannot be described quantitatively in the absence of a suitable molecular **diffusion** model.

The temperature dependence of the resonance line width, δ , observed for Li^+ is shown in Fig. 1

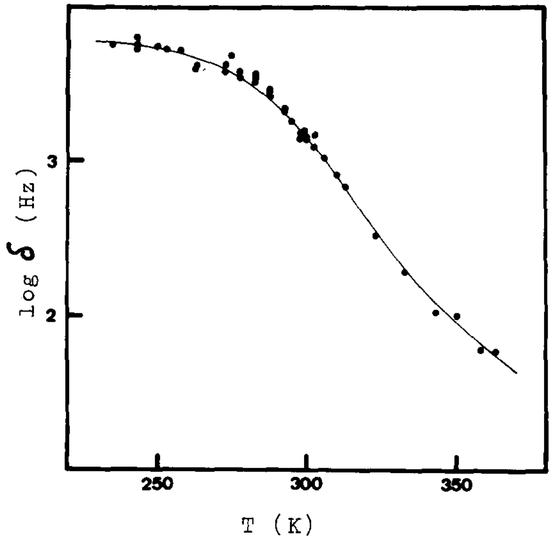

Fig. 1

Variation of the ^{7}Li line width with temperature

A motional narrowing effect is clearly visible at the higher temperatures. A strong deviation occurs at the glass transition temperature, T_g=282 K. It is interesting to note that the line width observed in the plateau range is $\delta_0 \simeq 6 \times 10^3$ Hz, i.e. about the same as that of metallic lithium at 230 K (HOLCOMB, NORBERG 1955), well below its melting point of 455 K. It may be assumed that the motional narrowing condition, $2\pi\delta_0\tau_c \simeq 1$, is approximately fulfilled in the frame rotating at the Larmor frequency at about 320 K (see inflection in Fig. 1). τ_c is a correlation time characterising the random motion of lithium ions, independent of its exact nature. We assume therefore that

$$\tau_c \simeq (2\pi\delta_0)^{-1} \simeq 3 \times 10^{-5} \text{ sec}$$

is a rough estimate for this correlation time at 320 K.

B. Arrhenius Representation

Fig. 2 gives an Arrhenius plot for the line width in the range 230-360 K. From it an activation energy, E=11.2 kcal/mole, is obtained. An estimate of the diffusion constant at 320 K can also be made from $D \simeq \langle a^2 \rangle / \tau_c$, $\langle a^2 \rangle$ being the mean square elementary jump distance. Taking $\langle a^2 \rangle \simeq 10$ Å^2, $D \simeq 5 \times 10^{-11}$ cm^2/sec.

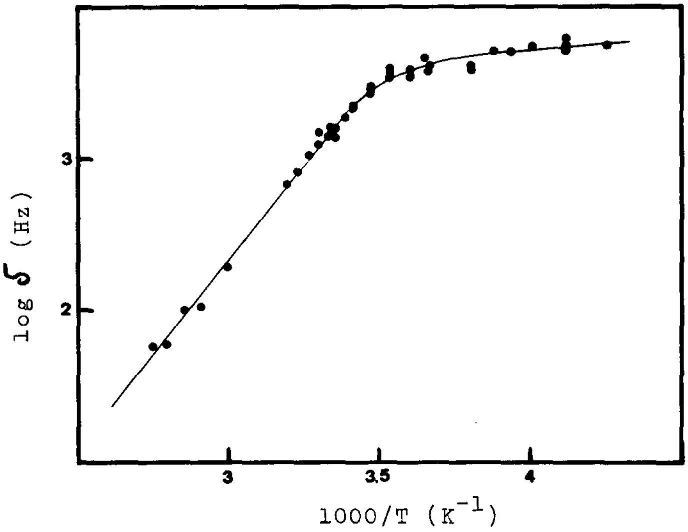

Fig. 2. Arrhenius plot for the ^{7}Li line width

C. Free volume Representation

Most diffusion processes of small molecules through polymeric systems are known to follow a free-volume law (FERRY 1970). A representation of this type is shown in Fig. 3, where the reference temperature, T_o, was set to 323 K. The value of the line width is supposed to be directly proportional to $\delta_o \tau_c^f$ with

$$\tau_c^{f}/\tau_c^{f_o} = \exp\,(f^{-1} - f_o^{-1}) \qquad \text{(I).}$$

Here f_o is the free volume fraction of the polymer network-lithium perchlorate system at 323 K. The free volume fraction, f, for the same system at any temperature other than T_o reads

$$f = f_o + \alpha(T - T_o) \qquad \text{(II)}$$

and

$$\left[\log(\tau_c^{f_o}/\ \tau_c^{f}\right]^{-1} = \frac{C_2 + T - T_o}{C_1\ (T - T_o)} \qquad \text{(III),}$$

with $C_1 = B/2.3f_o$ and $C_2 = f_o/\alpha$. The numerical factor B is usually close to unity. It follows that, from the data in Fig.3, C_1=4.2 and C_2=160. Therefore, f_o/B=0.1 and $\alpha/B = 1/(2.3C_1C_2) = 6.4 \times 10^{-4}$ K^{-1}.

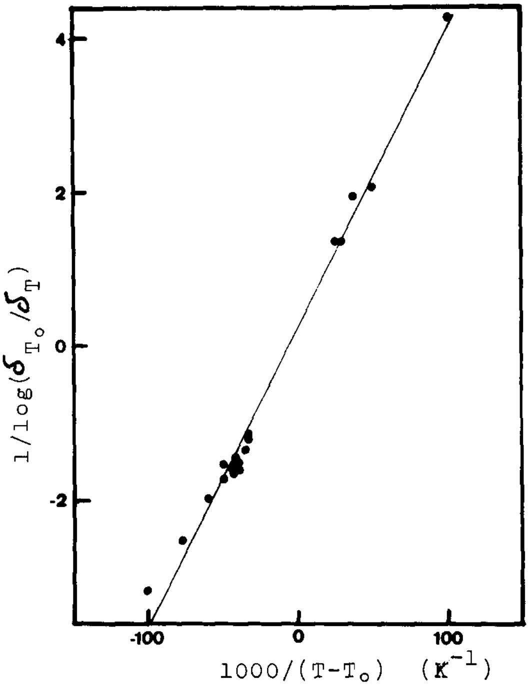

Fig.3.

Free-volume plot of ^{7}Li line width, with T_o=323 K

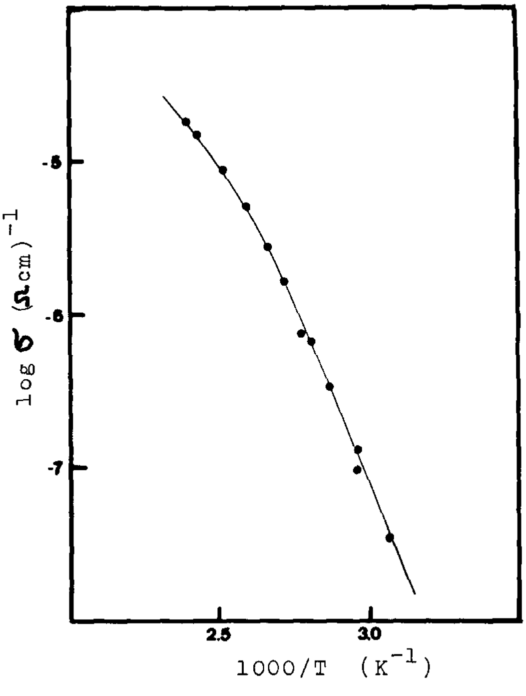

Fig. 4.

Arrhenius plot for the ionic conductivity

2. Temperature Dependence of Conductivity

Fig.4 shows the conductivity results in the form of an Arrhenius plot. Two regions are discernible: in the temperature range 310-380 K the apparent activation energy is 21 kcal/mole, while above 380 K the apparent activation energy becomes about 11 kcal/mole. The fact that the activation energy is a decreasing function of temperature at the higher temperatures suggests the occurrence of cooperative effects in the mechanism of ionic conduction. Thus the phenomena under investigation do not arise solely from activated processes and cannot therefore be interpreted adequately by a simple Arrhenius law.

An alternative way to rationalise the mechanism of ionic conduction consists in applying free volume concepts to the results (CHERADAME 1981). This treatment has given satisfactory correlations and is briefly discussed here. The lithium cations dissolved in our networks are solvated by the ether functions and move from one of these sites to another through a jump process promoted by the polyether segmental movements. In terms of the free volume theory, the lithium cation jumps are only allowed above a critical value of the free volume fraction in the network. The latter is a consequence of the polyether segmental movements, the importance of which is governed by the magnitude of the reduced temperature parameter, $T-T_g$. The WLF relation adequately describes this segmental mobility for ion-containing polymer networks (KILLIS et al. 1981, CHERADAME 1981). In the present situation a free-volume law representation of the ionic conductivity is shown in Fig.5, with a reference temperature of 323 K, i.e. the same as for the NMR determinations. From the linear plot obtained we calculated $C_1'=6.3$ and $C_2'=110$.

It follows that (see section 1.C. above) $f_o'/B=0.07$ and $\alpha'/B=6.2 \times 10^{-4} K^{-1}$. While f_o' differs slightly from the f_o obtained from ^{7}Li NMR data, α and α' are in good agreement.

The two free-volume law representations associated with NMR and conductivity measurements respectively can obviously be correlated to each other through the $(T-T_o)$ variable:

$$\log (\sigma_T / \sigma_{T_o}) = \frac{C_2 \; C_1'}{C_2' \; C_1} \log (\delta_{T_o} / \delta_T) \qquad \text{(IV)}$$

with $\frac{C_2 \; C_1'}{C_2' \; C_1} = (f_o/f_o')^2 = 2.1$. This correlation is shown in Fig.6.

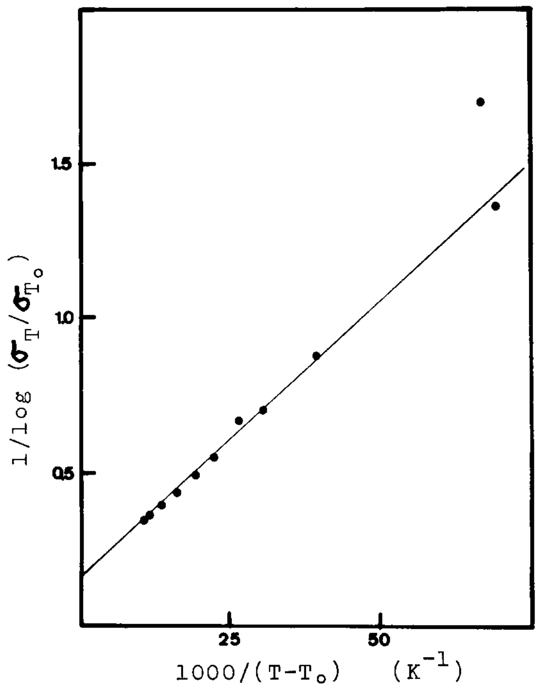

Fig. 5.

Free-volume plot of ionic conductivity, with T_o=323 K

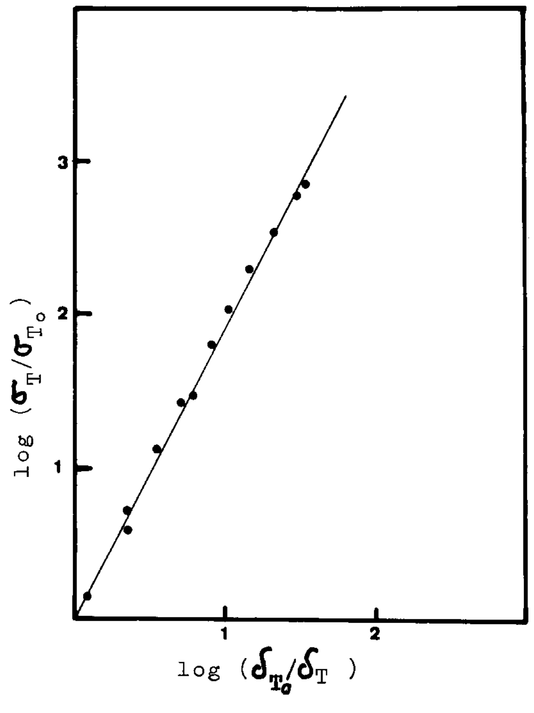

Fig. 6.

Correlation between the reduced ionic conductivity and the reduced line width. T_o=323 K

Conclusions

The results gathered in this study strongly suggest that the elementary diffusion processes involved in ionic conduction and deduced from NMR measurements on the dissolved cations reflect essentially the same phenomenon since they can both be described within a free-volume framework characterised by the same thermal expansion factors, with however slightly different free volume references. The latter inequality leads to different values of the apparent activation energy. We tentatively attribute this slight difference to the existence of a translational diffusion process involved in the ionic conductivity measurements.

The comparable values of line width observed for Li^+ in our networks and for metallic lithium at low temperatures suggest that the lithium cation and the perchlorate anion might form aggregates in our systems.

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