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Electroactive probe diffusion through DMF/polyacrylonitrile gels: free volume behaviour

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Abstract

Precise diffusion coefficient measurements have been performed using chronoamperometry in highly concentrated ionically conducting polymer solutions made with DMF as the solvant (solid polymer gels). The D variation with the temperature lets appear a transition temperature which is characteristic of the system. Interpretation of the results in terms of a free volume law is proposed and agrees well with the experimental D variation and allows to determine some of the parameters for a given gel.

Keywords *: Polyacrylonitrile, Chronoamperometry, Diffusion, Free volume, Ferrocene*

1. Introduction

The understanding of dynamic properties of polymeric solutions requires investigations into the large relaxation spectrum associated with short range and long range fluctuations which occur within polymer chains. These dynamic properties depend on several variables such as the chain length, the polymer concentration and the temperature. The local friction coefficient governs all dynamic properties of polymers above the glass transition temperature. Consequently, it is of interest to attempt to characterize the local molecular dynamics in polymer systems[1] . Diffusion coefficients in polymer gels have attracted some attention[2,3,4,5,6,7].

Furthermore, the well known electrochemical technique of chronoamperometry is an accurate method to measure the diffusion coefficient of an electroactive molecule in a solution provided the solution is conducting enough. Some of us have shown, in previous works, that it was possible to study the behaviour of some electroactive molecules embedded into concentrated solution of Nafion in strongly resistive solvants[8,9]. Free or bonded electroactive molecules have also been shown to bring valuable information on the formation and subsequent evolution of silica polymer gels[10,11]. The polyacrylonitrile gel is a polyelectrolyte containing ionic sulfonic groups which insure an ionic concentration of about 0.3 M, quite sufficient for performing electrochemistry. When an electroactive probe such as decamethylferrocene (DMFC) is dissolved into a concentrated copolymer solution, its diffusion may be dependent on the polymer motion, and therefore may bring informations on the polymer dynamics. So the diffusion kinetics

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of DMFC have been studied in a variety of concentrated (25% to 33% w/w) solution in pure or in low aqueous dimethylformamide (DMF) as a function of solution temperature.

In this study, experimental results will be shown to fit accurately a free volume law for the polymer motion, which has allowed to extract the corresponding parameters for this system.

2. Experimental

The copolymer, $\{-(CH_2-CH(CN))_n-(CH_2-CH(CH_3)(CH_2SO_3^-))_m-$, (n = 0.9673, m = 0,0327) }, was supplied by RHONE-POULENC (France) with an average molecular weight equal to 250 000 g mol^{-1} (the polydispersity is 1.8).

In a typical run, a concentrated polymer solution (33 %) was prepared in the following way : the copolymer (0,5 g) was mixed in a cylindric electrochemical cell (height : 10 cm, diameter : 2 cm) with 1 g of a 1.5 10^{-2} mol L^{-1} DMFC solution in DMF[12]; after mixing the concentration in the final solution was approximatively 10^{-2} mol L^{-1} with DMFC homogeneously dissolved in the system. Then, a 3 mm diameter glassy carbon electrode was introduced as a working electrode ; in addition, a silver wire quasi-reference electrode and a platinum wire as a counter electrode, wrapped around the working and the réference electrode were also introduced[13]. The electrodes were forced into the polymer solution. The test tube was then sealed and left overnight under dinitrogen atmosphere to obtain a completely homogeneous solution and to have a close contact with all three electrodes.

The three electrodes were then connected to an electrochemical device, and the test tube was placed into a thermostated vessel. The chronoamperometric curves were recorded by applying a anodic potential of 300 mV higher than the peak potential of DMFC (determined by cyclic voltammetry). The electrochemical apparatus was made of a home made potentiostat[14] fitted with an ohmic drop compensation system, a PAR 175 pilot, a Nicolet digital oscilloscope and a Sefram plotter. Measurements were performed while the temperature was lowered ; it was observed that operating the reverse way did not affect the results. Before recording any chronoamperometric curve, the temperature was kept stable at least 10 mn or until observation of identical cyclic voltammogram of DMFC.

3. Results and discussion

3.1. Electrochemical behaviour of concentrated polymer solutions.

Fig. 1 represents the cyclic voltammograms that can be obtained from the glassy carbon electrode dipped into a concentrated 28,6 % polymer solution in DMF at different temperatures. It can be clearly seen that, even at a very low temperature as 223 K, well-behaved cyclic voltammograms are obtained, typical of a semi-infinite diffusive behaviour, similarly to what could have been observed with a classical solution without polymer. As it could be expected, the voltammograms are completely reversible, which shows that both the reduced and the oxidized forms of the ferrocenic electroactive probe are stable in our system, and that no aging of the electrode surface occurs.

When a potential step is applied to the electrode, the currents obtained over a large temperature range have been found to follow the classical Cottrell[15] law i =

$AC^{o}F(D/\pi t)^{1/2}$, (A: electrode area, C^{o}: probe concentration, D: probe diffusion coefficient, F: Faraday constant) with an excellent accuracy, as shows the quality of the linearity of curves plotted in Fig. 2. Such an ideal behaviour is probably due to the total absence of convection in the polymer solution, in the measure time range, at the difference of a classical solution. This has also been observed in polymer gels[10,11].

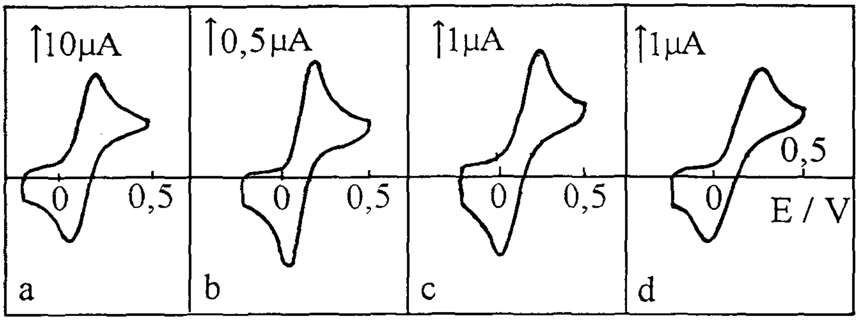

Fig. 1 : Cyclic Voltammograms of a 10^{-2} mol.L^{-1} DMFC solution in polymer / DMF : 0,286 at different temperatures : a : 353 K, b : 263 K, c : 238 K, d = 223 K; scan speed : a, b, c : 100 mVs-1, d : 50 mV s-1.

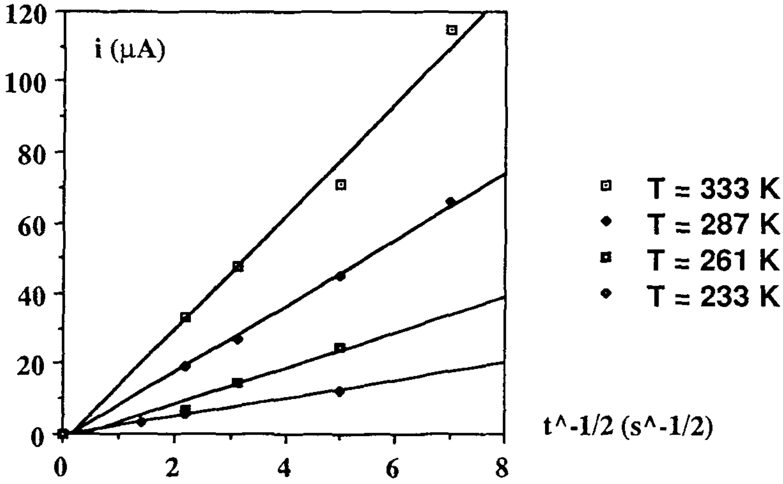

Fig. 2 : Cottrell plots obtained from chronoamperometry performed at 0,5 V vs Ag wire quasi-reference on a 10^{-2} mol.L^{-1} DMFC solution in polymer / DMF : 0,33.

The linearity of the Cottrell plots also indicates that the DMFC molecules exhibit a true isotropic diffusive behaviour in the polymer solution, which is not surprising being given the small size of this molecule, only slightly larger than the solvent. This allows us, not only to extract the absolute value of the diffusion coefficient, but also the relative variation of this diffusion coefficient with the temperature. While the experimental error linked to the probe concentration and the electrode area limit the acuracy of the absolute values determination, the relative variation can be determined with an excellent precision, the variations of the parameters other than D being neglectable.

3.2. Analysis of the data.

Fig. 3 shows the typical $\log(DT^0/D^0T)$ variation with temperature for a 33 % w/w polymer solution which shows an inflection point near 285 K. We have verified that the exchange of the T° does not affect the plots aspects meaning that concentrated solutions of polymer changes really of behaviour beetwen 285 and 300 K We have confirmed using DSC analysis that a transition was observable around the same temperature with a relative error of about 5 K according to the sample, thus showing that the polymer dynamics are closely related to the variations of the probe diffusion coefficient in the polymer solution. Furthermore, some crystallization area have been observed at 120°C[14].

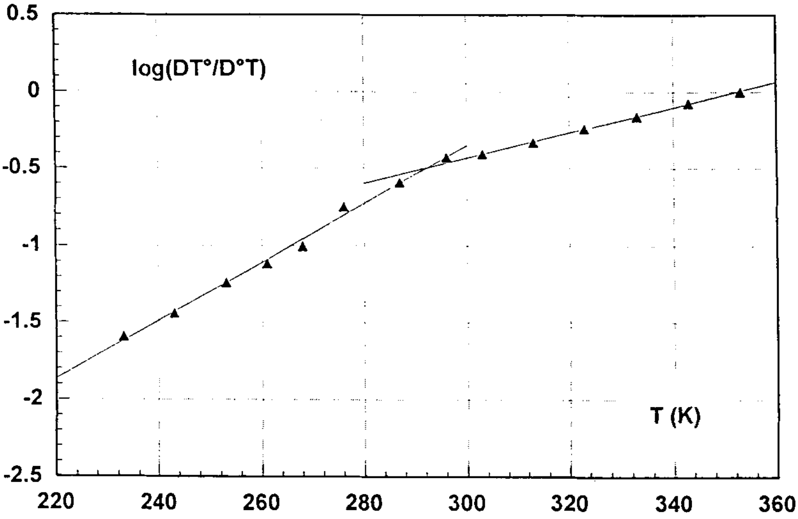

Fig. 3 : Dependence of DT^0 / D^0T for DMFC in polymer / DMF : 0,33 with the temperature.

3.3. Agreement with a free volume law.

The diffusion coefficient, D, is expressed in a usual way as the ratio kT / ζ where ζ is the friction coefficient (k is the Boltzmann constant) ; then, the friction coefficient is supposed to depend on the fractional free volume f of the solution according to the relationship $\zeta \alpha \exp(B/f)$, B is a constant of order unity[15]. The linear dependence of f on the temperature is written as $f = f_0 + \alpha(T-T^0)$ where α is the coefficient of thermal expansion ; f_0 is the fractional free volume corresponding to the reference temperature T°. Let D° denote the diffusion coefficient at T°, then, D and D° obey the following equations

$$1/\ln(DT^0/D^0T) = f_0^2/B\alpha(T-T^0) + f_0/B \qquad [1]$$

and

$$(T\text{-}T^\circ)/\ln(DT^\circ/D^\circ T) = f_0^2/B\alpha + (T\text{-}T^\circ)f_0/B \qquad [2]$$

Consequently, $f_0^2/B\alpha$ and f_0/B are obtained from plots of $1/\ln(DT^0/D^0T)$ and $(T\text{-}T^\circ)/\ln(DT^\circ/D^\circ T)$ using $1/(T\text{-}T^\circ)$ or $T\text{-}T^\circ$, as variables ; T° may be chosen arbitrary in the whole temperature range.

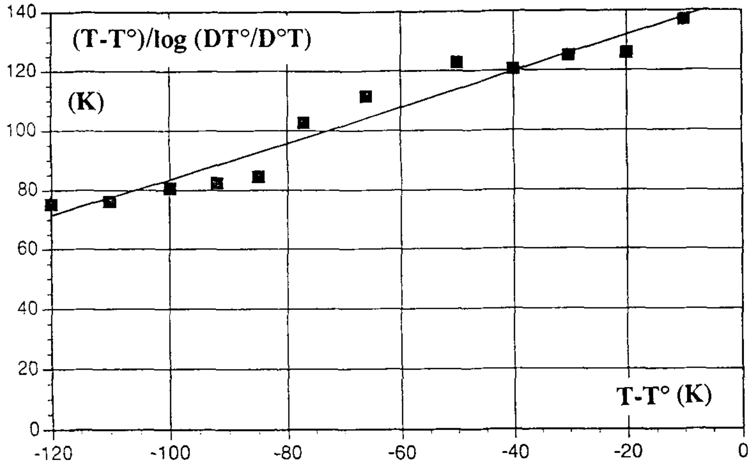

Fig. 4 : Dependence of $(T\text{-}T^\circ)/\ln(DT^\circ/D^\circ T)$ with T-T° for DMFC in polymer / DMF : 0,33 for T° = 353 K.

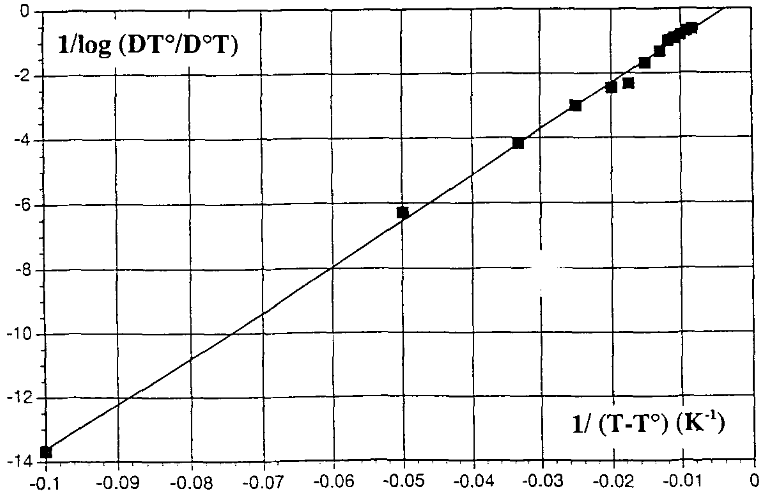

Fig. 5 Dependence of $1/\ln(DT^\circ/D^\circ T)$ with $1/(T\text{-}T^\circ)$ for DMFC in polymer / DMF : 0,33 for T° = 353 K.

Figs. 4 and 5 display both representations for a given value of T° (300°K) and linear representations are obtained. This validates our forecoming analysis in terms of free volume. Similar curves were drawn for a sampling of T° values, and the result are displayed in Table 1. It is clear that two sets of values are obtained, one for high temperatures ($f_0^2/B\alpha \approx 55$ at high temperatures, and 25 at low temperatures). This confirms the existence of a transition temperature between 300 and 273 K, and permits to obtain two equations for the determination of all the polymer parameters (f_0, B and α). It is also clear that the experimental value of the f_0^2/B ratio of the polymer determined after the transition is twice the value determined before the transition, as it could be expected. Similarly the f_0/B values display the same behaviour and go from roughly 0.12 to 0.25 upon crossing the transition temperature.

However, the α/f_0 does not vary that much, and keeps a constant value through the transition temperature crossing. This is probably due to the fact that both f_0 and α rise in a similar proportion in the polymer gel. This parameter is roughly equal to $5\ 10^{-3}$, which shows that the gel free volume does not vary a much with the temperature.

T° (K)	353	333	303	268	261	243
$f_0^2/B\alpha$ (K^{-1})	$6{,}1\ 10^{1}$	$5{,}2\ 10^{1}$	$4{,}8\ 10^{1}$	$2{,}3\ 10^{1}$	$2{,}6\ 10^{1}$	$2{,}5\ 10^{1}$
f_0/B	$2{,}6\ 10^{-1}$	$2{,}4\ 10^{-1}$	$2{,}3\ 10^{-1}$	$1{,}3\ 10^{-1}$	$1{,}3\ 10^{-1}$	$1{,}1\ 10^{-1}$
α/f_0 (K^{-1})	$4{,}3\ 10^{-3}$	$4{,}6\ 10^{-3}$	$4{,}8\ 10^{-3}$	$5{,}5\ 10^{-3}$	$4{,}9\ 10^{-1}$	$4{,}5\ 10^{-3}$

Table I : $f_0^2/B\alpha$, f_0/B and α/f_0 values in function of T° of an polymer DMF solution (the concentration is 0,33 w/w).

4. Conclusion

We have shown that electrochemistry of electroactive molecules embedded into rubbery polymer solutions can bring significant informations on their behaviour. The observed ferrocene diffusion is mainly influenced by local dynamics, on which the polymer dispersity should not have any discernable effect. Transition temperature of the polymer gel (rubbery solution) can be determined by following the variations of the diffusion coefficient of the electroactive species. In the case of concentrated polymer solutions that we examined, the results have been analyzed in the framework of a free volume law and a good fit has been obtained which allowed to determine some parameters of the gels.

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REFERENCES

[1] P. G. de. Gennes (1979) « Scaling concepts in polymers physics », Cornell University Press, Ithaca.

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[2] H. B. Tatistcheff, I Fritsch-Faules and M. S. Wrighton, (1993) *J. Phys. Chem.*, 97, 2732.

[3] S. Sasaki and H. Maeda, (1996) *Bull. Chem. Soc. Jpn*, 69, 2173.

[4] C. V. Nicholas, M. A. Desai, P. M. Vagdama, S. Lucas, M. B. McDonnell, (1991) *J. Chem. Soc. Faraday Trans*, 87, 293.

[5] B. J. Balcom, A. E. Fischer, T. A. Carpenter and L. D. Hall, (1993) *J. Am. Chem. Soc.*, 115, 3300.

[6] A. Aoki, R. Rajagopalan and A. Heller, (1995) J. Phys. Chem, 99, 5102.

[7] H. Yoon, H. Kim and H. Yu, (1989) *Macromol.*, 22, 848.

[8] P. Audebert, P. Aldebert, B. Divisia-Blohorn and J. M. Kern, (1989) *J. Chem. Soc., Chem. Commun.*, 939.

[9] C. P. Andrieux, P. Audebert, B. Divisia-Blohorn, P. Aldebert and F. Michalak, (1990) *J. Electroanal. Chem.* 296, 117.

[10] P. Audebert, P. Griesmar and C. Sanchez, (1991) *J. Mater. Chem.*, 1, 699.

[11] P. Audebert, P. Griesmar, P. Hapiot and C. Sanchez, (1992) *J. Mater. Chem.*, 2, 12.

[12] The sulfonic ions concentration is about 0,3 mol L^{-1} enough to ensure that no migration effect occurs.

[13] This electrode arrangement allows to minimize the ohmic drop as much as possible.

[14] D. Garreau and J. M. Savéant, (1972) *J. Electroanal. Chem.*, 35, 309.

[15] A. J. Bard and L. L. Faulkner (1980) « Electrochemical Principles, Fundamentals and Applications », M. Dekker, New.York.

[16] J. P. Cohen Addad, J. P. Marchand and A. Viallat, (1994) *Polymer*, 35, 1629.

[17] J. D. Ferry, « Viscoelastic properties of polymers », (3rd Edition), J. Wiley, New York, 1980.