frequencies, but could be understood in terms of an interionic 'drag effect' which gradually relaxes with increase in frequency. (It is tempting to relate this approach to a previous treatment of dielectric loss in vitreous materials which invoked the Debye–Falkenhagen effect[11].)

It is difficult to say that either of these explanations is 'right' and the other 'wrong'. Thus, according to the Jonscher model, highly 'lossy' electrolytes, such as β-alumina, need a high concentration of mobile ions to give effective charge-screening, but these are precisely the electrolytes which have a strong tendency to cation disorder and hence are likely to exhibit a wide spread in ionic jump frequencies[12]. The main point which emerges from the above discussion is a need for further detailed comparisons of structural, spectroscopic and electrical data, and hence the need for work with crystalline rather than vitreous systems. β-alumina is in many ways a model system, since measurements can be made over a wide range of d.c. conductivities, and extensive cation substitution is possible[13,14].

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[1] Hodge, I. M., Ingram, M. D. & West, A. R. *J. Am. ceram. Soc.* 59, 360–366 (1976).
[2] Grant, R. J., Ingram, M. D. & West, A. R. *J. electroanal. Chem.* 72, 397–401 (1976).
[3] Isard, J. O. *Proc. Inst. Electr. Enginrs*, Suppl. 22, 440–447 (1962).
[4] Macedo, P. B., Moynihan, C. T. & Bose, R. *Phys. chem. Glass.* 13, 171–179 (1972).
[5] Peters, C. R., Bettman, M., Moore, J. W. & Glick, M. D. *Acta crystallogr.* B. 27, 1286 (1971).
[6] Roth, W. L. *Trans. Am. Cryst. Ass.* 11, 51–55 (1975).
[7] Bailey, W., Glownikowsky, S., Story, H. & Roth, W. L. *J. chem. Phys.* 64, 4126–4130 (1976).
[8] Jonscher, A. K. *Nature* 250, 191–193 (1974).
[9] Jonscher, A. K. *Nature* 253, 717–719 (1975).
[10] Jonscher, A. K. *Nature* 256, 566–568 (1975).
[11] Owen, A. E. in *Progress in Ceramic Science*, (ed. Burke, J. E.), 3, (Pergamon, Oxford, 1963).
[12] Grant, R. J., Hodge, I. M., Ingram, M. D. & West, A. R. *J. Am. ceram. Soc.* (in the press).
[13] Yao, Y. F. Y. & Kummer, J. T. *J. inorg. nucl. Chem.* 29, 2453–2475 (1967).
[14] Farrington, G. C. *Electrochim. Acta* (in the press).

The behaviour of long molecules diffusing in solid polyethylene

SEMI-CRYSTALLINE polymers, according to the current two-phase model, consist of an impermeable, denser crystalline phase (the lamellae) and a permeable, less dense amorphous phase (the interlamellar regions)[1]. All permeation and transport properties occur predominantly in the latter, and are a function of the overall amorphous fraction within the bulk and the geometry of the crystallites embedded in the amorphous phase. For linear polyethylene cooled at various rates from the melt, the diffusion coefficient D of gaseous diffusants varies[2,3] according to

$$D \quad x(1-x), \qquad (1)$$

where x is the corresponding crystalline volume fraction, and $(1-x)$ the amorphicity. The diffusional behaviour of long chain diffusants, however, may be very different. For example, it has been suggested[1] that the transport of long chain molecules through the disordered interlamellar regions of polythene will be greatly influenced by the presence of interlamellar tie-molecules and entanglements. These are relatively immobile features in the disordered region which can obstruct the movement of long chain molecules, but not that of smaller (for example, gaseous) diffusants if their size is less than the separation between these features. An extension of de Gennes' ideas on reptation[5] gives a semiquantitative relation for the diffusion coefficient of long molecules in polyethylene: long molecules should diffuse faster in slowly cooled than in quenched polyethylene, in spite of the higher disordered fraction in the latter and in marked contrast to the behaviour of gaseous or light vapour diffusants, because rapid cooling results in a greater profusion of fixed tie-molecules[6], which constrain long diffusants but have little effect on small ones. We report here results which support this model.

We measured D for two linear diffusants of the form n $(CH_2)_NX$, X being a suitable label and $N \simeq 25$ or 45. The matrix was linear polyethylene cooled at two widely differing rates from the melt. The measuring technique was one we have recently developed, based on infrared microdensitometry[7], and involves setting up a known concentration distribution of diffusant within the host matrix, allowing it to broaden for a known time t at the required temperature, then measuring the resulting diffusion-broadened concentration profile. D can be evaluated knowing the shapes of the two profiles as well as t; Fig. 1 shows experimental profiles at the beginning and end of a typical diffusion run: the calculated curves (with the appropriate value of D) when superimposed on the experimental ones, show a good fit.

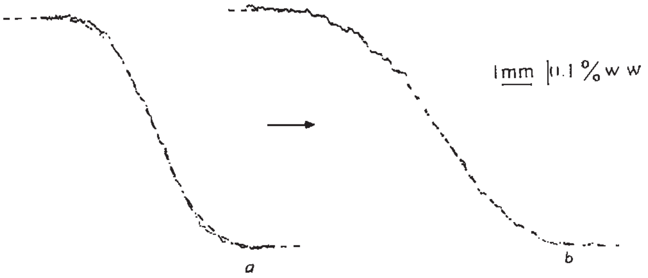

Fig. 1 Concentration–distance profiles as measured ( ) at the beginning (a) and end (b) of a typical diffusion measurement. ----, calculated shapes as evaluated with the appropriate value of D. (t 1.29 · 10^6 s at 91 C; the diffusant is a linear molecule of form n $(CH_2)_{25}X$, X being an ester group; the matrix is linear polyethylene cooled rapidly from the melt, and the scanning frequency corresponds to the ester group absorption peak at 1729 cm^{-1}. D evaluated as 1.3 10^{-8} $cm^2 s^{-1}$.)

Table 1 summarises some of the results, giving D for the two diffusants in both rapidly and slowly cooled polyethylene matrix, and the corresponding values of the crystallinity x as derived from density measurements. In Table 2 we compare the prediction of the model (outlined above), which takes into account the topological constraints on the diffusants, with the experimental results (details of the calculations are given elsewhere[8]). The predictions of the simple two-phase relation, equation (1), are also shown.

Table 2 shows that agreement between observed and predicted ratios is fair to good. In particular, the model predicts correctly that D for the long diffusants used increases in the slowly cooled, more crystalline matrix in contrast to equation (1).

The results provide support for the concept that long diffusants in semi-crystalline polymers may be constrained in a way which small diffusants are not; they suggest that studies involving such diffusants could yield information on the nature of the disordered phase in these polymers not otherwise available.

Table 1 D (in units of 10^{-9} $cm^2 s^{-1}$) for diffusants of form n $(CH_2)_NX$* in linear polyethylene, at 84.8 C

No. of backbone units N	Rapidly cooled matrix	Slowly cooled matrix
$N \simeq 45$	3.3 ± 0.4	6.5 ± 0.7
$N \simeq 25$	9 ± 1.8	11 ± 1.8
Crystalline volume fraction, x	0.751	0.855

*X is an ester group.

Table 2 Calculated and observed values of *D* for diffusants of form *n* $(CH_2)_NX$ in linear polyethylene matrix at 84.8 C

(a) Variation of *D* with cooling rate of matrix

No. of backbone units *N*:	*D* (slowly cooled matrix)/*D* (rapidly cooled matrix) Calculated	Observed	'2-phase', $D \propto (1-x)$
$N \simeq 25$	1.26	1.2±0.3	0.58
$N \simeq 45$	1.52	2.0±0.3	0.58

(b) Variation of *D* with diffusant length

	Rapidly cooled matrix		Slowly cooled matrix	
	Calculated	Observed	Calculated	Observed
$\frac{D_{N=25}}{D_{N=15}}$:	2.18	2.7±0.5	1.80	1.7±0.3

Detailed accounts of both theory[4] and experiment[8] are in press.

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1 Crank, J. & Park G. S., eds *Diffusion in Polymers* (Academic, New York, 1968)
2 Michaels, A. S., Bixler, H. J. & Fein, H. L. *J. appl. Phys.* 35, 3165 (1964).
3 Eby, R. K. *J. appl. Phys.* 35, 2720 (1964).
4 Klein, J. *J. Polym. Sci. Polym. Phys. Edn* (in the press).
5 de Gennes, P. G. *J. chem. Phys.* 55, 572 (1971).
6 Peterlin, A. *Proc. IUPAC Symp. Macromolecules*, Aberdeen 1973, 239–264, (Butterworths, London, 1974).
7 Klein, J. & Briscoe, B. J. *Nature* 257, 386 (1975). Klein, J. & Briscoe, B. J. *Polymer* 17, 481 (1976).
8 Klein, J. & Briscoe, B. J. *J. Polym. Sci. Polym. Phys. Edn* (in the press).

New transient effect observed in rock samples subjected to simulated upper crustal conditions

WHILE making laboratory measurements of the electrical conductivity (σ) of rock samples subjected to temperatures, confining pressures, and pore fluid pressures thought to be appropriate to depths up to 15 km within the Earth, we have observed a hitherto unreported transient behaviour which is only revealed by the simultaneous application of pressure and temperature, and leads to an irreversible decrease in σ with time which could be due to compaction of the rock samples. We suggest that only after such a change has occurred is the condition of rocks collected near the Earth's surface more representative of those at depth in the crust.

Most of the rock samples used in this study are high-grade metamorphics from the Lewisian of NW Scotland, which have a very low porosity (< 1%). These were cored, cut and ground into cylinders of diameter 24.5 mm and length 10–20 mm, and saturated with a 0.5 or 0.05 M sodium chloride solution. Two stainless steel electrodes allowed the a.c. conductance (normally at a frequency of 1.5 kHz) between the sample faces to be measured using a Wayne Kerr B224 transformer bridge. Confining pressure acting on a rock within the Earth (due to the column of rocks above it) was simulated by hydrostatically pressurising the sample (up to 0.4 GPa (4 kbar)) in a pressure vessel. To prevent contamination from the oil pressure-medium the sample and electrodes were sheathed with a Teflon tube. It is believed that most rocks have sufficient strength to prevent their pores shutting completely under such pressure[1], and it is possible therefore for the pore fluid pressure to differ from the confining pressure. To allow for this, a hole passing through one electrode to the surface of the rock sample was connected to a pipe which passed out of the vessel, enabling the pore fluid pressure to be varied independently of the confining pressure. A furnace around the sample allowed temperatures up to 275 C to be reached.

Because the bulk of the measured conductance in saturated rocks occurs through the solutions within the fine pore network, small changes in pore structure have a considerable effect on σ (refs 1, 2), and as σ can be measured accurately, it is probably the most sensitive property to use to investigate such small structural changes. Increasing the confining pressure closes up this pore structure, while increasing the pore fluid pressure has the opposite effect. It is reasonable therefore to assume a model in which the parameter that determines the overall pore structure, and therefore σ, is the pressure differential (known as the effective pressure) between confining and pore fluid pressure[3,4]. Most of our results at room temperature conformed to this model, with σ showing a steady decrease as the effective pressure was increased.

Figure 1 shows the typical behaviour observed when a sample at a fixed effective pressure was heated. From its room temperature value (*a*), σ increased along the path *a–b* as the temperature was increased. We found, however, that if the temperature was held steady at a high enough temperature (*b*), σ fell over a period of time to a lower value (*c*). This drop *b* *c* did not occur suddenly at any specific temperature, and a slight drop has even been observed at temperatures as low as 130 C, although at a very slow rate. Increasing the temperature has the effect of accelerating the rate, and samples were normally heated to around 200 C or above, to enable us to observe a drop in a reasonable period of time. Figure 2*a* shows the time dependence

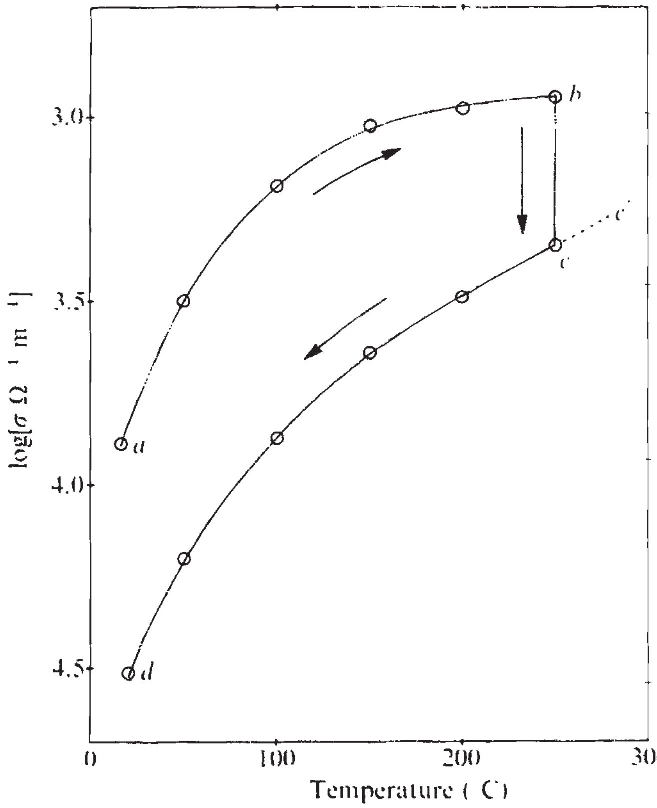

Fig. 1 Irreversible change in conductivity during the initial temperature cycle of a sample of gneiss saturated with 0.5 M NaCl solution and subjected to an effective pressure of 0.2 GPa (2 kbar).