

The dc Volume Resistivity of Plasticized PVC

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Synopsis

A study has been made of the dc volume resistivity of plasticized PVC using a guarded-electrode system in a sensitive vibrating capacitor–electrometer circuit. Transient effects were found to be pronounced in all but the least plasticized compositions, and the behavior in general was non-Ohmic. The resistivity decreases with plasticizer concentration and with temperature; an Arrhenius-type relationship is observed and resistivity undergoes an inflection at the glass transition temperature. The mechanism of conduction appears to be electrolytic rather than charge injection or semiconduction.

INTRODUCTION

Despite interest in the synthesis of semiconducting polymers,¹ the main activity in the field of the electrical conduction of polymers has been in the actual measurement and understanding the basic mechanism of the conduction process. In general, the better known materials, i.e., those having a commercial basis, are characterized by low conductivity complicated by transient absorption effects, the latter having an origin in dipolar, interfacial, and space-charge polarization response to an applied field. The non-Ohmic, time-dependent behavior at low absolute values of conductivity, together with a sensitivity to the presence of small amounts of impurities and compounding additives, combine to obscure an appreciation of the intrinsic mechanism of the conduction process itself. Thus, although one should in principle be able to distinguish between ionic and electronic mechanisms from, say, the nature of the Hall effect, the liberation (or otherwise) of matter at the electrodes and dependence of current upon certain structural parameters has meant that only in a few cases has such identification been achieved with any degree of confidence.²

Plasticized PVC is an important commercial polymeric material finding use in a wide range of applications. A number of studies of the electrical properties has been made,^{3–11} but these suffer from the fact that they are relevant to only a short time interval, disagreement exists between results of different workers, and, possibly of greatest importance, comparison of data is often hampered by lack of detailed experimental information. For example, Fuoss et al.,³ who consider that the basis of conduction is electrolytic, found considerable difficulty in obtaining reproducible results for samples containing artificially added electrolyte unless special conditioning procedures were carried out. Davies et al.⁵ describe results obtained on a three-electrode system having a surprisingly small guard gap but do not discuss the significance of this in terms of possible surface conduction. There is apparent conflict in the results of Goto⁶ and Würstlin,⁴ the latter finding that the purity of plasticizer is relatively unimportant in determining the resistivity of the compounded material. Conger et al.,¹¹ using a microwave technique, compared their results with those obtained

by conventional dc methods but do not describe the latter so that it is not clear to what extent polarization effects influence the analysis. Where nominally similar systems have been examined at equivalent temperatures, the results of Reddish⁸ and Kallweit⁷ differ by a factor of 10^3 . In view of the general uncertainties, a program of work was initiated in these laboratories trying to establish a reliable measurement technique and leading to a fairly comprehensive investigation of the effect of test parameters on the observed volume resistivities of a series of samples of plasticizer PVC and a single unplasticized sample, although special attention was paid to one composition being typical of that used in electrical application of PVC.

EXPERIMENTAL

Materials

Samples were prepared and supplied by B.P. Chemicals (U.K.) Ltd. in the form of discs 22.6 cm in diameter and nominal thickness 0.165 cm. Compound ingredients of Corvic D 65/8 PVC resin (100 parts by weight), plasticizer (nature and concentration as indicated in the text), white lead stabilizer (5 parts by weight), and calcium stearate (0.05 parts by weight) were thoroughly mixed in a stainless steel beaker and milled at 150°C for 15 min to form a 0.3-cm hide. This was then cut and molded between polished steel platens at 165°C under 4 tons for 4 min and then 50 tons pressure for 2 min before being cooled to 75°C for removal and trimming.

Equipment

A three-electrode system of circular brass backing and guard electrodes was used (Fig. 1). The geometry was such that the criteria for guard-electrode spacing ensured minimum deformation of flux¹² (electrode 1, max. radius 7.6 cm; electrode 3, radius 11.0 cm; and gap between electrodes 1 and 2, 0.35 cm). Location of electrodes was achieved by the use of spacers. Electrode 3 was mounted on 10-cm-long polystyrene feet. The apparatus was mounted in a

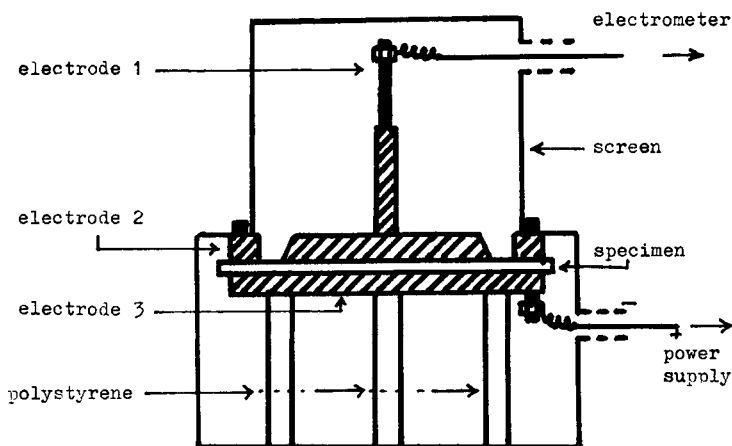


Fig. 1. Electrode system.

tinned steel screen box which was installed in an air-circulating oven. Cooling coils external to the screen were also included for near-ambient temperatures studies. Control of humidity which was generally of 50% R.H. was obtained through the use of standard humidifying systems. The circuit for current measurement is shown schematically in Figure 2 and involved the use of a Vibron electrometer (Electronic Instruments Ltd.) consisting of a converter unit incorporating a vibrator capacitor modulator, ac preamplifier, and standard 10^9 , 10^{10} , 10^{11} , and 10^{12} ohm input resistors with provision for introduction of other resistors if required, together with the electrometer unit proper containing the main amplifier, phase discriminating rectifier, and main indicating meter and controls. The voltage was applied via a regulator (A.P.T. Electronic Industries Ltd., Model 513) and was monitored by means of a digital voltmeter (Digital Measurements Ltd., Model DM 2025).

Procedure

An analysis of possible sources of error has been discussed elsewhere and will not be elaborated here except to say that these were kept to a minimum.¹³ The separate influences of certain parameters the actual magnitudes of which are not a priori readily appreciated were examined, and the results of these studies are reported and discussed first.

It was recognized that mold defects coupled with local stress relaxation effects might give rise to slight surface irregularity which might in turn have a bearing on the current measurements. One hundred random thickness measurements on a typical sample were made using a Mercer dial gauge showing that the average thickness was within 0.3% of the nominal (mold) thickness and the spread was within 6% of this value. The influence of this irregularity presumably accounts for the difference in the results on the effect of pressure using brass and carbon electrodes, the latter being applied from a colloidal graphite dispersion (Acheson Colloids Ltd.) on to a test specimen before mounting under the brass electrodes (see Fig. 3). The slight decrease of current with pressure with the carbon electrodes is presumably a sample bulk compression effect. All subsequent studies were made with carbon electrodes. The effect of time to thermal equilibrium was investigated by taking one specimen of plasticized PVC (containing 50 parts

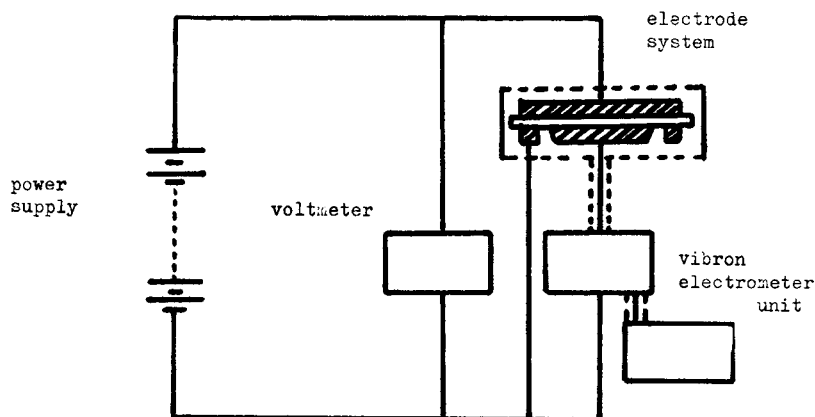


Fig. 2. Circuit diagram.

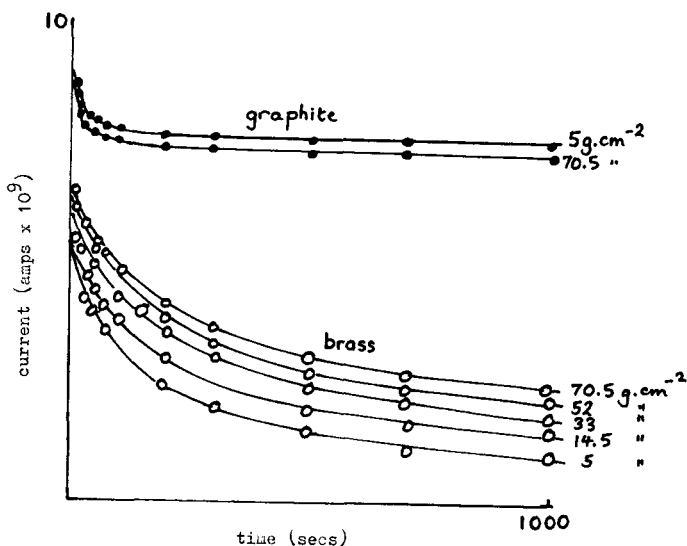


Fig. 3. Influence of electrode pressure (26°C).

diisooctyl phthalate) at room temperature and then following the current-time response under an applied voltage of 500 volts after conditioning at 29°C for the various times indicated in Figure 4. Following each run for steps of increasing time, the sample was discharged, removed from the electrode assembly, and left to stand for a period no less than four times that of the previous equilibration period and duration of test, this interval being found to be sufficient for reproducibility of results. It is clear from Figure 4 that a period of about 3 hr is sufficient for temperature equilibrium, which on the basis of thermal conductivity data of related systems¹⁴ but ignoring environmental constraints is well outside the calculated minimum time.

The results presented so far reflect the time-dependent nature of resistivity, emphasizing the doubtful significance of single-point measurements of electrical conductivity on polymers. They do not show, however, the reproducibility of results on the same or replicate sample. To investigate the former, a sample as above was examined at 26°C (R.H. 50%) over a period of about 100 hr using an applied potential of 500 V, this particular value promoting a reasonable approach to equilibrium in the not-too-inconvenient time scale (Fig. 5, curve 1). Following

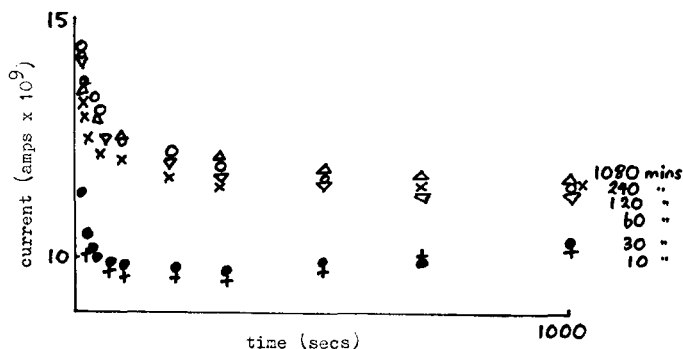


Fig. 4. Influence of equilibration time.

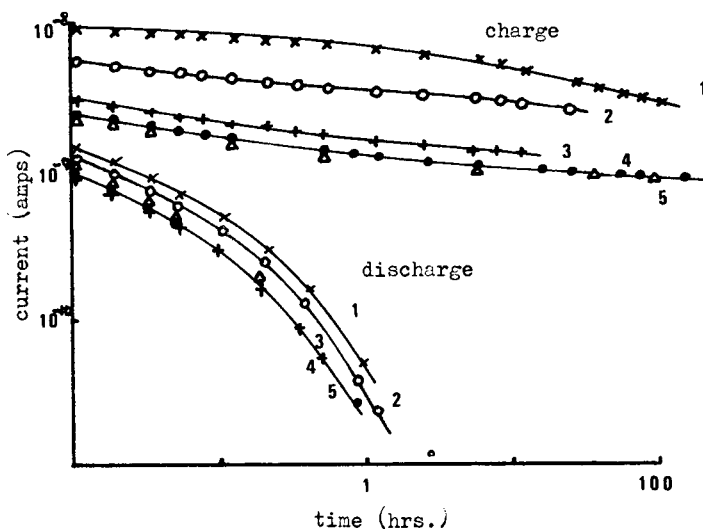


Fig. 5. Variation of current with time for same sample, in sequence (3 and 5 after high-temperature testing).

discharge as before, the measurement was repeated (curve 2) and again after heating, and reheating, to 500°C (curves 3 and 4) and finally after heating at the same temperature for several days (curve 5), discharge procedures being followed after every run as also indicated on Figure 5. The similarity of discharge curves suggests that the charge curves are largely associated with irreversible conduction components, probably loss of traces of moisture. Evidence in support of this proposal was provided by the observation that reproducibility of results from heated sample is good if the sample is stored in a desiccator between runs but that there is a return to preheated levels if the sample is allowed to stand for approximately the same time (two months) in the open laboratory. It is interesting to note that samples originally stored in a desiccator still show higher values of conductivity confirming, as is well known, the difficulty in removing last traces of moisture or solvent from polymers.

Turning to the general case, reproducibility between different samples of nominally the same composition (as above) was examined. The results, which are shown in Figure 6, show the variability which, considering the low absolute levels of conductivity and inherent preparative and experimental conditions, are considered acceptable for going forward to the next series of studies concerned with external variables such as magnitude of applied voltage, temperature, and plasticizer concentration.

The influence of the former was investigated on a sample of composition as before (50 parts by weight, diisooctyl phthalate). Beyond times up to about 20 sec, it was found that Ohm's law is not obeyed, the deviation becoming greater with time. For voltages less than 500 V, the time to equilibrium became excessive (many weeks); so a procedure was adopted of measuring resistivity under decreasing potential conditions, equilibrium now taking only a few days. Corresponding measurements at different temperatures are reported in Figure 7, from which it can be shown as for the results of short-time measurements (Fig. 8) that an Arrhenius relationship of the form

$$\rho = \rho_0 e^{E/RT}$$

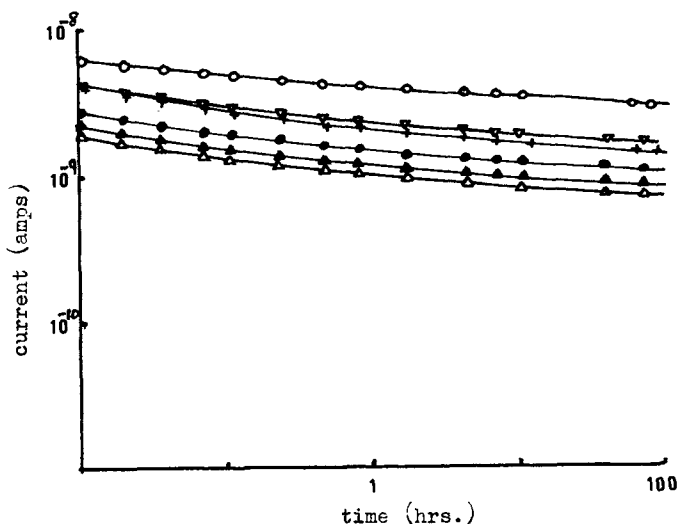


Fig. 6. Variation of current with time for different samples (after 500 V for two days at 50°C).

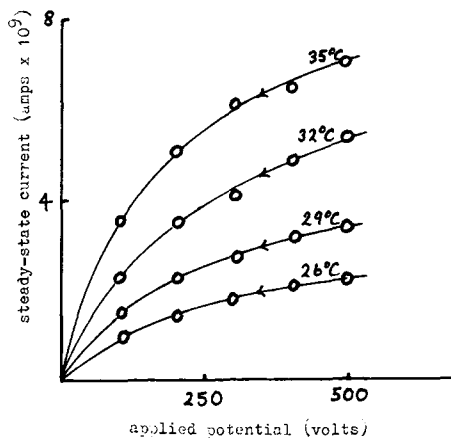


Fig. 7. Variation of current with potential.

exists between resistivity ρ and temperature T , where E is the activation energy for conduction (Fig. 9). The effect of plasticizer concentration was studied using samples containing different amounts of di-2-ethylhexyl phthalate as well as one sample of unplasticized polymer. Equilibrium for the sample of lowest plasticizer concentration (30 parts by weight) was relatively quick (less than 10 hr); but for the other samples, this was much longer, the unplasticized sample, for instance, still not developing on equilibrium current even after two weeks. The results expressed in terms of concentration, and remembering that the resistivity of the unplasticized sample is probably somewhat low, are presented in Figure 10. A separate series of measurements on the sample containing 25 parts by weight of the above plasticizer carried out at different temperatures are shown in Figure 11, where it is seen, as before, that resistivity decreases with increase in temperature but also that an inflection occurs at the glass transition temperature.

Two final series of measurements were made in an attempt to provide some

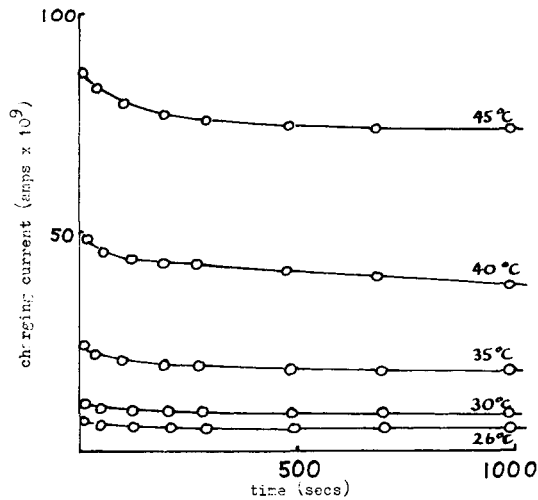


Fig. 8. Variation of current with time and temperature.

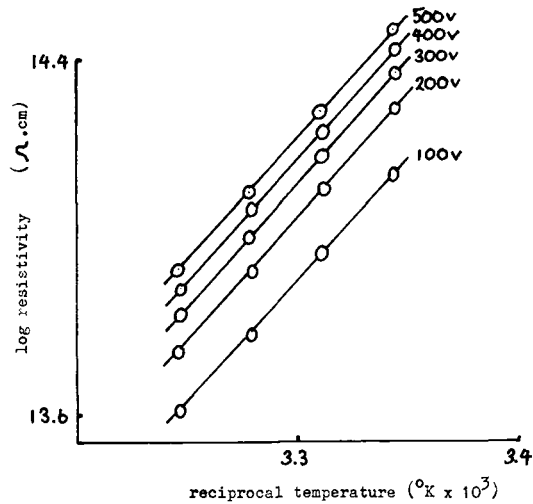


Fig. 9. Variation of resistivity with reciprocal temperature.

insight into the mechanism of conduction. The first involved a proposal to detect gas liberation at the electrodes during electrification (if an electrolytic mechanism exists) by having a test sample mounted in a bulb connected by a capillary to the bulb of a McLeod gauge. It was found, however, that under the applied vacuum, gas pressure was still increasing after 80 days without application of potential indicative of a small, otherwise undetected, leak or gas evolution by the sample. In a second investigation, the possibility of the existence of an electrode charge-injection process was explored using electrodes of different materials. After a number of failures, a satisfactory electrode was deposited on one side of a test sample (containing 50 parts by weight of di-*n*-octyl phthalate) by means of vacuum deposition. It was found that, using this and a carbon counter electrode, the current characteristics were roughly the same irrespective of electrode polarity. This is seen in Figure 12, where equilibrium current results obtained

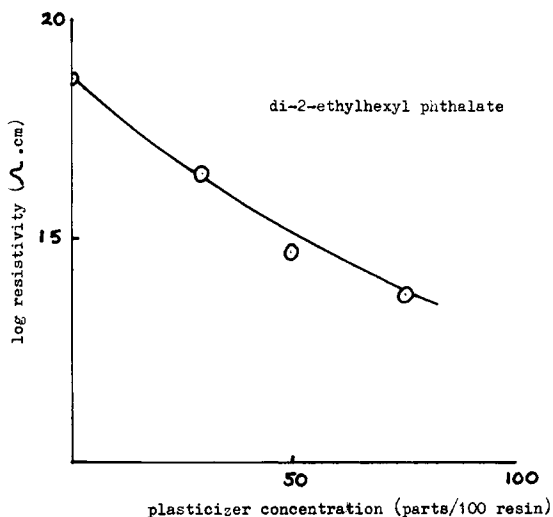


Fig. 10. Influence of plasticizer concentration on resistivity.

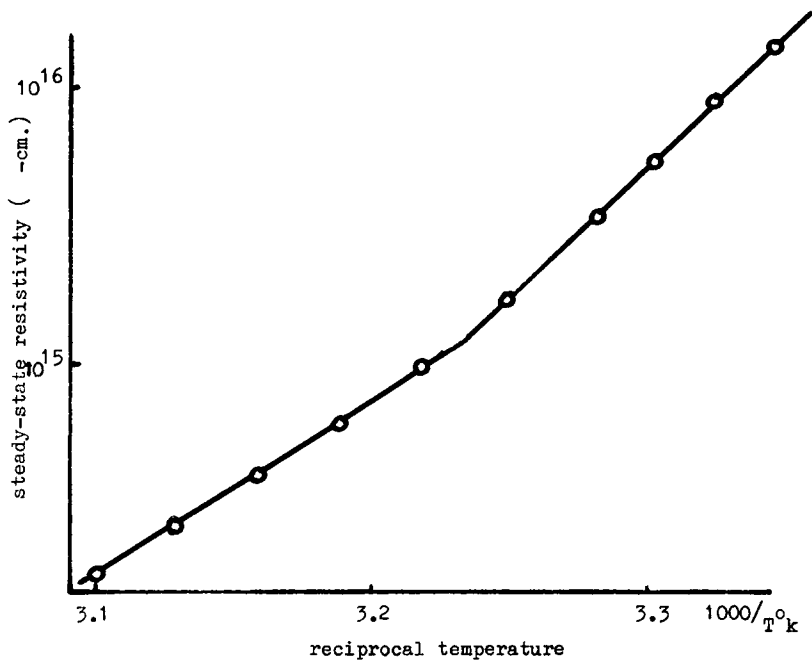


Fig. 11. Steady-state resistivity vs reciprocal temperature (25 parts di-2-ethylhexyl phthalate).

at different decreasing temperatures are plotted against reciprocal temperature.

DISCUSSION

It is clear from this study that considerable care must be taken to obtain reasonably meaningful results for the resistivity of plasticized and unplasticized PVC in that the values vary for nominally the same material both with sample

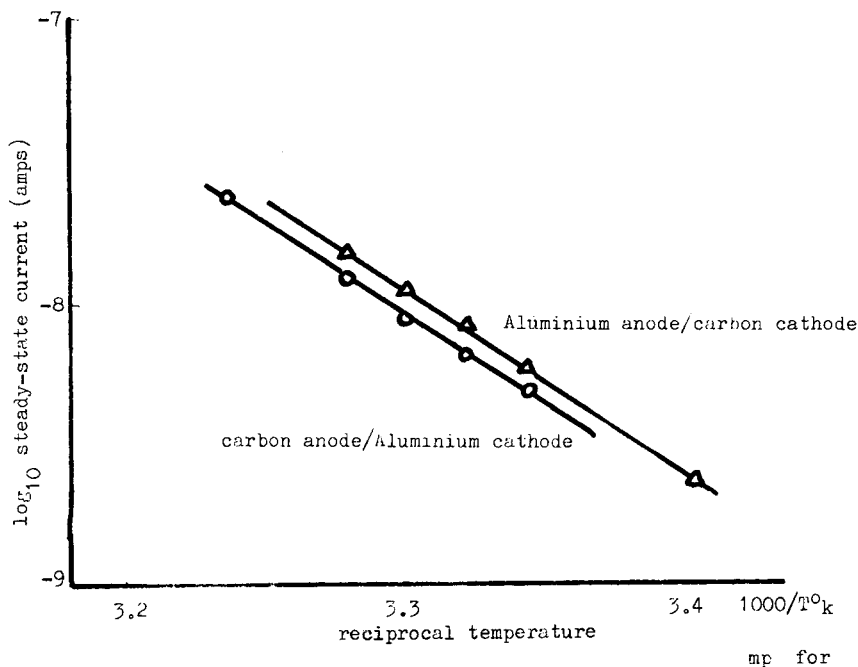


Fig. 12. Steady-state current vs reciprocal temperature for different electrode systems.

and with time. Preconditioning of samples by heating while under high potential leading to a lowering of conductivity is attributed to loss of moisture although this has not been directly detected. Reproducibility of results on samples which have been stored under dry conditions following preconditioning supports this view, however. Standing of samples in a dry atmosphere without preconditioning is not sufficient to achieve reproducibility, indicating the low diffusion characteristics of the material. It is interesting to speculate whether, if the prime interest in these studies had not been with the resistivity of plasticized PVC under typical humidity conditions and one had carried out the conductivity measurements in dry conditions, the same time dependence would have occurred.

From the study of the effect of applied voltage on conductivity it has been seen that at lower potentials a longer equilibration time is required consistent with the above hypothesis as indeed is the fact that heating a sample while under a high potential shortens the time. Deviation from Ohm's law increases with increasing plasticizer concentration and with time of electrification. The effect of decreasing concentration or raising the temperature is to decrease the resistivity of plasticized PVC. A typical value of activation energy independent of applied potential derived from Figure 8 is 10.6×10^4 joules/mole. This is suggestive of a diffusion-based process for conduction in that this is of the order one might expect for the activation energy of diffusion for molecular or ionic species somewhat larger than lower molecular weight gases.¹² The nature of the species is not clear; the studies with different electrodes and the fact that the behavior is non-Ohmic and varies over a period of time is not expected for a charge-injection process; Again, if one considers the influence of the typical values of activation energy on the number of charge carriers produced, say, in an intrinsic semiconduction process¹³ and then relates this number to their mobilities in the overall conduction behavior, then quite impossibly high values of mobility would

be predicted. Similarly, the relative insensitivity of resistivity to chance fabrication variables appears to preclude extrinsic semiconduction. One is therefore tempted to adopt the suggestion of Fuoss that the origin of current is basically ionic; and although Seebeck measurements indicate a predominantly negative conductor, the nature of the species is not easy to identify in the light of the composite nature of the system.

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References

1. J. E. Katon, Ed., *Organic Semiconducting Polymers*, Marcel Dekker, New York, 1968.
2. D. Klemptner and F. E. Karasz, *J. Elastoplast.*, **4**, 181 (1972).
3. R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 2329 (1939).
4. F. Würstlin, *Kunst. Tech.*, **11**, 269 (1941).
5. J. M. Davis et al., *J. Am. Chem. Soc.*, **63**, 361 (1941).
6. K. Goto, *Chem. High Polym. (Jpn.)*, **9**, 411 (1952).
7. J. Kallweit, *Kunststoffe*, **47**, 651 (1957); *Kolloid-Z.*, **188**, 97 (1963); *J. Polym. Sci.*, **4**, 337 (1966).
8. W. Reddish, Symposium on the Electrical Properties of Polymers S.C.I. Monograph 5, Macmillan, New York, 1959.
9. L. H. Wartman, *J. Soc. Plast. Eng.*, **20**, 254 (1964).
10. A. Oster, *Z. Angew. Phys.*, **20**, 355 (1966).
11. N. L. Conger et al., *J. Soc. Plast. Eng.*, **23**, 82 (1967).
12. R. M. Barrer et al., *Polymer (London)*, **8**, 321 (1967).
13. N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals*, O.U.P., Oxford, 1948.
14. R. P. Sheldon and K. Lane, *Polymer (London)*, **6**, 77 (1965).

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