

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Electrical Conductivity in Poly(vinyl Chloride)

R. J. Fleming^a; J. H. Ranicar^a

^a Department of Physics, Monash University Clayton, Victoria, Australia

To cite this Article Fleming, R. J. and Ranicar, J. H. (1970) 'Electrical Conductivity in Poly(vinyl Chloride)', *Journal of Macromolecular Science, Part A*, 4: 5, 1223 – 1237

To link to this Article: DOI: 10.1080/00222337008061015

URL: <http://dx.doi.org/10.1080/00222337008061015>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Electrical Conductivity in Poly(vinyl Chloride)

R. J. FLEMING and J. H. RANICAR

*Department of Physics
Monash University
Clayton, Victoria 3168, Australia*

SUMMARY

Conductivity and Seebeck coefficient measurements have been made on commercially-available molded PVC samples containing a range of impurities and on much purer specimens recast from tetrahydrofuran solution. Activation energies measured in the latter materials were not very reproducible; it seems likely that the evaporation of gold electrodes thermally initiates a dehydrochlorination reaction which renders the samples unstable. A range of activation energies from 1.4 to 1.8 eV was observed in the impure samples. The Seebeck coefficient measurements indicated that the majority carriers were negatively charged; the linearity of the current-voltage relationship up to applied field strengths of 80,000 V/cm then suggested an electronic conduction mechanism, although considerable polarization effects were observed in both pure and impure samples. The Seebeck coefficient results also showed that even the purest PVC obtainable is unlikely to be an intrinsic semiconductor, and that the electron transport mechanism probably corresponds more closely to the small polaron hopping model than to the conventional energy-band formation model commonly applied to inorganics.

INTRODUCTION

During the last decade considerable interest has been taken in the conduction of electricity through organic solids. Polymeric materials in

particular have received much experimental attention in an attempt to synthesize organic alternatives to conventional inorganic semiconductors such as germanium and silicon. Thus the PAQR polymers [1] are examples of materials "tailored" as semiconductors possessing fairly-accurately predictable specific resistivities within the range 10^5 - 10^{10} ohm cm; the xanthene polymers [2], although synthesized in the same way (condensation of an aromatic hydrocarbon with an aromatic acid anhydride in the presence of a catalyst such as zinc chloride), have specific resistivities of the order of 10^3 ohm cm, i.e., approaching that of germanium and silicon. It has even been proposed [3] that it should be possible to synthesize a polymeric organic charge-transfer complex that would be a superconductor at or close to room temperature. At the other end of the resistivity range we find polytetrafluorethylene, polystyrene, polyethylene, and polyvinyl chloride. Although these materials would normally be classified as insulators, possessing specific resistivities of order 10^{15} ohm cm or greater, their resistivities can be considerably reduced by raising the temperature slightly (typically an order of magnitude per 10°C) or by exposing the samples to ionizing radiation. Unlike the case for the semiconducting polymers mentioned above, very little effort has so far been directed towards elucidating the charge transfer mechanism operative in polymeric insulators. Reference to a recently compiled bibliography [4] yielded only two relevant papers on PVC [5, 6], and the samples described therein had undergone pyrolysis treatment at temperatures up to 700°C and extensive dehydrohalogenation by a dispersion of sodium amide in liquid ammonia, respectively. It would therefore appear that, as far as may be judged from the open literature, very little is known about the nature of electrical conductivity in "normal" PVC. Accordingly an investigation, as yet incomplete, was undertaken to attempt to answer the following questions:

1. What are the majority charge carriers?
2. What is the source of these carriers, i.e., is the material an intrinsic semiconductor or are the carriers provided by impurities?
3. What is the concentration of the carriers?
4. What is the charge transport mechanism, i.e., does a hopping process dominate or do the carriers move in energy bands as pictured in conventional band theory?

In the work so far undertaken we have investigated the dependence of bulk current on temperature and applied voltage, thereby obtaining specific conductivity and activation energy values, and have also measured the

Seebeck coefficient, thereby identifying the sign of the majority carriers. Pulsed photoconductivity measurements of the carrier mobilities have recently been initiated, but although the resulting estimates of the order of magnitude of the mobilities are utilized in the discussion to follow, it is considered that the results obtained to date are not sufficiently comprehensive to justify detailed presentation.

MATERIALS

Quantitative physical measurements on polymers are frequently marred by an incomplete knowledge of the nature and concentration of the impurity content of the samples. Accordingly the results of corresponding measurements on "pure" samples and those containing additives were compared. The pure samples were obtained in thin disk form by recasting PVC powder (which was alleged to contain negligible concentrations of additives) from tetrahydrofuran solution. The disks were subsequently placed in a chamber continuously evacuated to a pressure of 10^{-3} torr for 10 days in order to remove as much of the residual solvent as possible. The impure molded samples, which were supplied directly by commercial manufacturers, contained typically 25% w/w diisooctyl phthalate as plasticizer, and 5% w/w barium/cadmium/zinc/stearic acid complex as filler and preservative agents. Figure 1 shows the absorption spectra of pure (a) and impure (b) samples obtained at room temperature using an SP 700 spectrophotometer. The sample thickness was 0.1 mm. The UV cut-off for the impure sample occurs at much longer wavelengths, the absorption peak around 340μ presumably being due to additives.

APPARATUS AND RESULTS

The conductivity measurements were carried out on circular samples approximately 0.1 mm thick in a conventional sandwich-type cell shown in Fig. 2. The cell was continuously evacuated to a pressure of 10^{-6} torr during measurements. Gold electrodes were evaporated onto both faces of the samples; typical diameters of sample, top electrode, and bottom electrode were 4.0, 2.0, and 3.5 cm, respectively. A guard ring consisting of a thin copper annulus approximately 3.5 cm in diameter was attached to the top surface of the samples, outside the gold electrode, by means of silver-loaded Araldite. All measurements were made in the dark, although the cell was

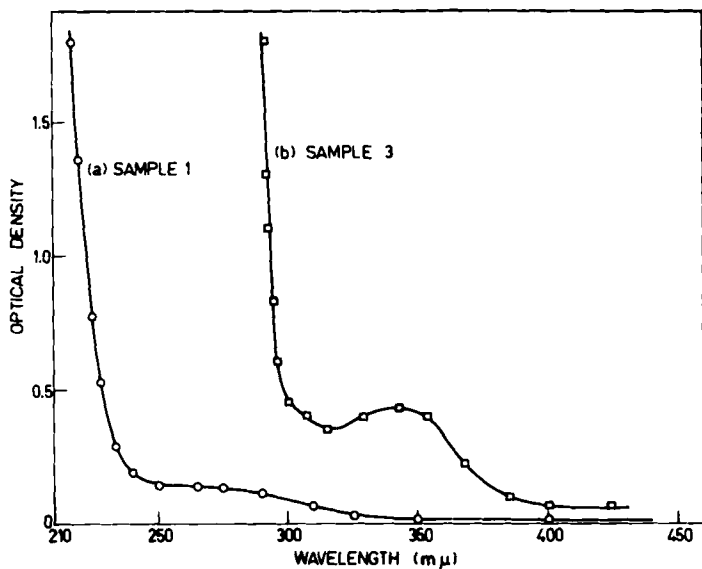


Fig. 1. Absorption spectra of pure (a) and impure (b) PVC samples 0.1 mm thick.

designed to permit irradiation of the samples through a Spectrosil window located in the bottom of the casing. Additional electrostatic shielding was provided by an earthed metallic box enclosing the cell.

On application of a voltage to a thermally-equilibrated sample, or on changing the magnitude of a previously-applied voltage, a time-variation of current such as that shown in Fig. 3 was obtained. A relatively large current flows during the first few seconds in order to establish a potential difference across the sample; the subsequent decay was found to follow the superposition principle [7] closely, and most probably arises from the re-orientation of electric dipoles, associated with chlorine atoms on the polymer chain. For both pure and impure samples the currents continued to decrease slowly for at least 24 hr. The currents recorded 30 min after each voltage change are plotted in Fig. 4 as a function of applied voltage at constant sample temperature. No departure from linearity was observed up to electric field strengths of 80,000 V/cm for impure specimens. On altering the temperature of the sample at constant voltage, dipole reorientation again occurred, the time required to attain equilibrium decreasing with increasing temperature. Plots of the logarithm of the steady current flowing after 2 hr against reciprocal sample temperature appear in Fig. 5. It will be seen that impure PVC (Fig. 5b) obeys the usual semiconductor relationship

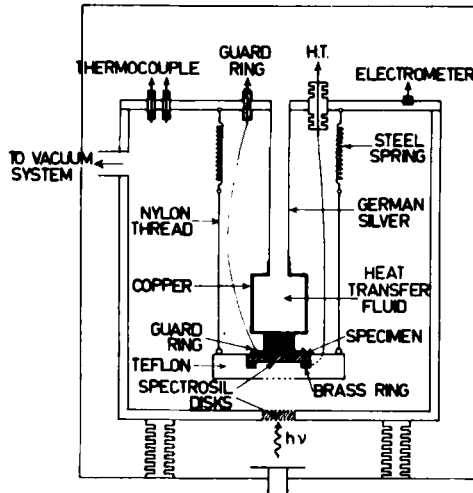


Fig. 2. Conductivity cell used to determine activation energies and specific resistivities.

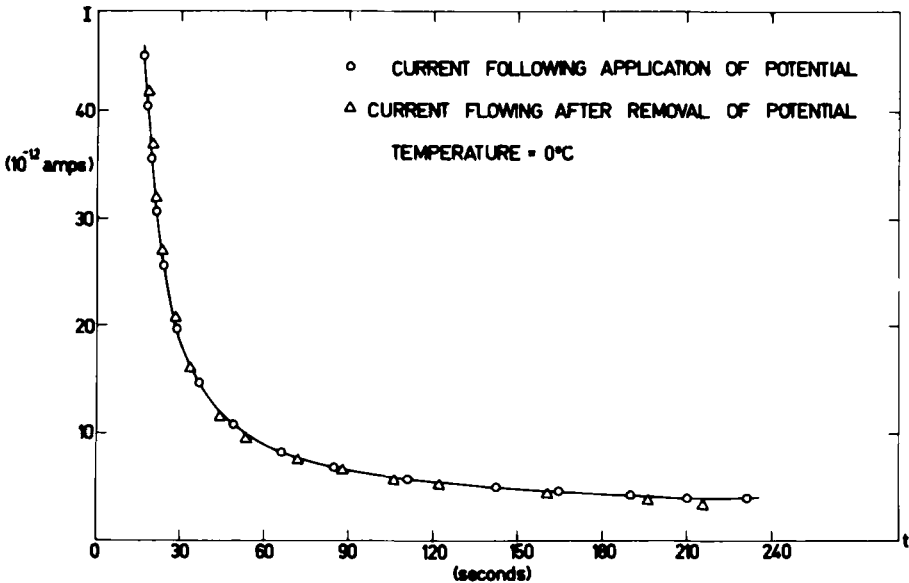


Fig. 3. Time variation of current following change of electric field strength.

$$\rho = \rho_{273} \exp (E_a/kT)$$

over the temperature range shown, where ρ is the specific resistivity, ρ_{273} its value at 273°K, E_a the activation energy, k is Boltzmann's constant, and T is the absolute temperature. Measurements were restricted to the temperature range above 0°C by the requirement that the input impedance of the Carey 401 vibrating reed electrometer be at least an order of magnitude greater than that of the samples. Figure 5a shows two changes of slope for pure PVC, around 30 and 35°C, which are probably associated with the onset of thermal dehydrochlorination [8]. Large changes in the Seebeck coefficient values for the pure material in roughly the same temperature region, also attributed to thermal dehydrochlorination, are discussed later. Table 1 shows ρ_{273} and E_a data for both pure and impure

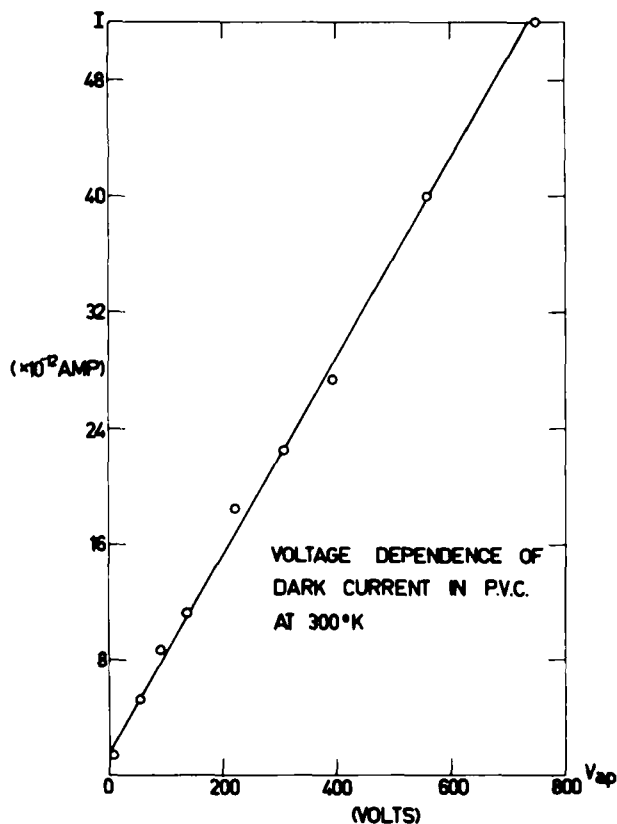


Fig. 4. Current-voltage characteristic at constant temperature.

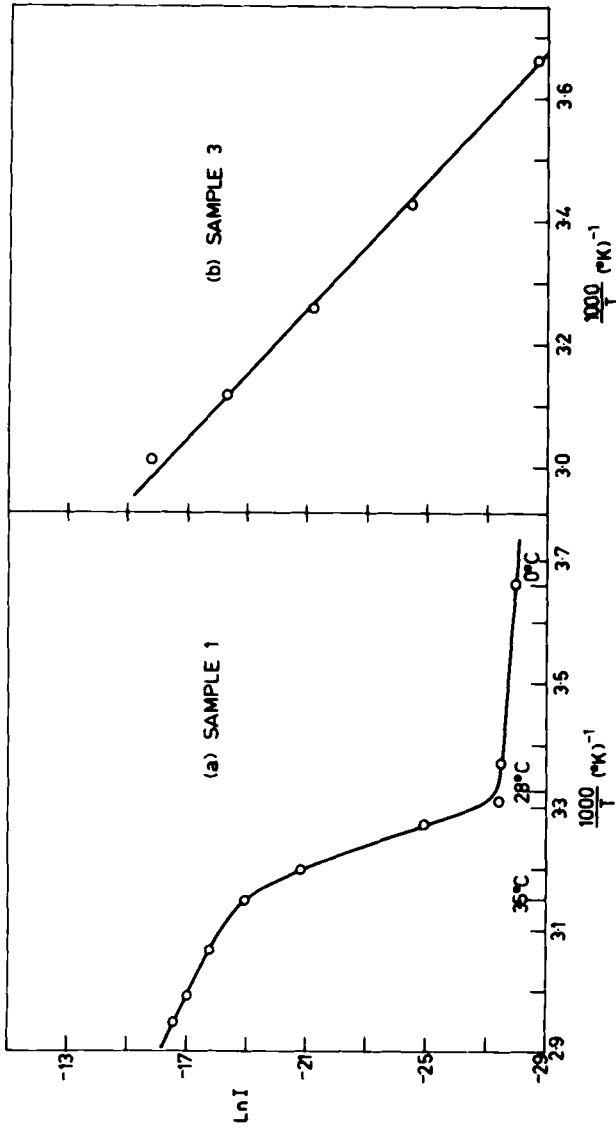


Fig. 5. Dependence of steady current values on sample temperature.

Table 1. Impurity Contents, Activation Energies, and Specific Resistivities for Pure and Impure Samples

Sample	Impurity content (w/w)	Activation energy (eV)	ρ_{273} (ohm cm)
1	nil	0.13 ($0 < T < 30^\circ\text{C}$) 5.68 ($30^\circ\text{C} < T < 35^\circ\text{C}$) 0.85 ($35^\circ\text{C} < T < 66^\circ\text{C}$)	2.4×10^{17}
2	25% (20% DIOP plasticizer)	1.77 (below T_g)	7.2×10^{17}
3	30% (25% DIOP plasticizer)	1.73 (below T_g)	8.8×10^{17}
4	33% (32% DIOP plasticizer)	1.42 (below T_g)	1.0×10^{16}

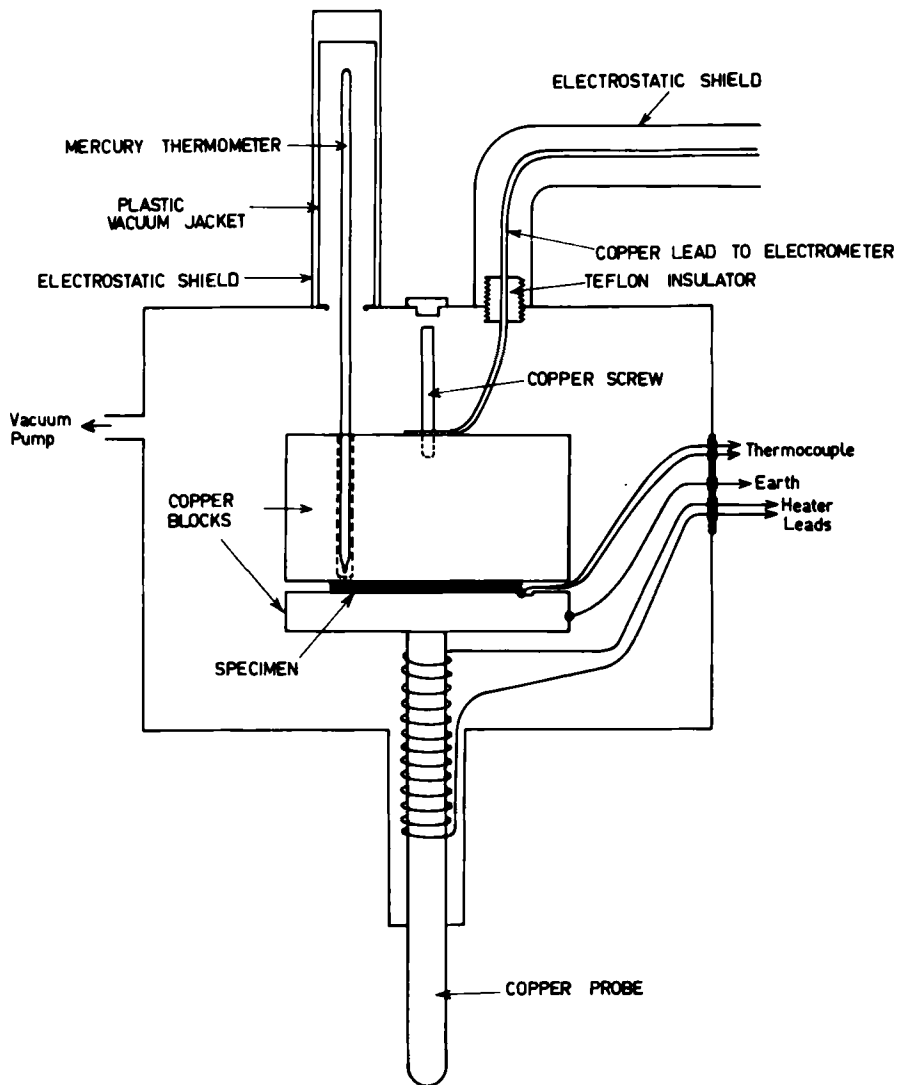


Fig. 6. Seebeck coefficient apparatus.

samples. It would appear that the addition of plasticizer increases the specific resistivity up to a w/w content of about 30%, beyond which it decreases sharply. The influence of impurity concentration on activation energies measured in the impure specimens seems much less. Although the $\ln I$ vs $1/T$ plots for the pure specimens nearly always showed three distinct regions, the activation energy values observed in the region of lowest temperatures, in which the samples were most stable, fluctuated considerably. The values ranged from 0.13 to 0.75 eV.

The Seebeck coefficient apparatus is shown in Fig. 6. Sample thicknesses were chosen in the range 1 to 3 mm in order that a larger temperature difference ΔT and hence a larger voltage difference ΔV might be established. Copper electrodes, leads, and contacts were used throughout the measuring circuitry in order to reduce to a minimum the anomalous voltages frequently observed in these measurements. Voltage and temperature differences were recorded during both heating and cooling cycles, and the resulting Seebeck coefficients $Q = \Delta V/\Delta T$ were in good agreement. The temperature of the top surface of the samples increased typically by 1°C when the bottom surface was heated through 15°C . The differences between the mean temperature of top and bottom surfaces varied between 10 and 30°C . The anomalous voltages ranged from 10 to 50 mV, and are shown in the ΔV vs ΔT plots of Fig. 7. It will be seen that, for the pure samples, Q changes rapidly above about 35°C , presumably due to the onset of thermal dehydrochlorination. Table 2 gives more detailed results. The negative sign of Q indicates the negative polarity of the top (colder) surface of the samples, implying that the majority current carriers possess a negative sign, i.e., they are either electrons or negative ions. The marked increase in Q for the impure material at higher average sample temperature (see Table 2) is attributed to a transition through the glass temperature T_g .

DISCUSSION

We consider first the experimental activation energies. The lowest value of 0.13 eV obtained for pure PVC in the temperature range $0\text{--}30^\circ\text{C}$ would indicate either electron or hole majority carriers, since authors postulating ionic conduction mechanisms in polymers usually report very much larger activation energies [9-11]. The linear current-voltage relationship at high field strengths referred to above also tends to support this conclusion; the negative Seebeck coefficient then indicates electrons, as opposed to

Table 2. Temperature Dependence of Q for Pure and Impure Samples

Pure material					Impure material					
T _{top} (°C)	T _{bottom} (°C)	T _{av} (°C)	Q(mV/°C)	T _{top} (°C)	T _{bottom} (°C)	T _{av} (°C)	Q (mV/°C)	T _{top} (°C)	T _{bottom} (°C)	Q (mV/°C)
23.6	33.0	28.3	-1.45	22.7	37.3	30.0	-1.52			
25.8	38.3	32.0	-1.53	31.4	57.4	44.4	-1.48			
26.9	44.5	35.2	-0.55	34.7	59.3	47.0	-1.50			
36.9	49.7	43.3	+0.36	36.0	71.4	57.7	-1.54			
				49.5	73.0	61.3	-1.62			
				61.5	77.0	69.3	-1.50			
				62.0	90.0	76.0	-2.04			
				62.8	93.2	78.0	-2.10			
				70.0	100.0	85.0	-2.14			

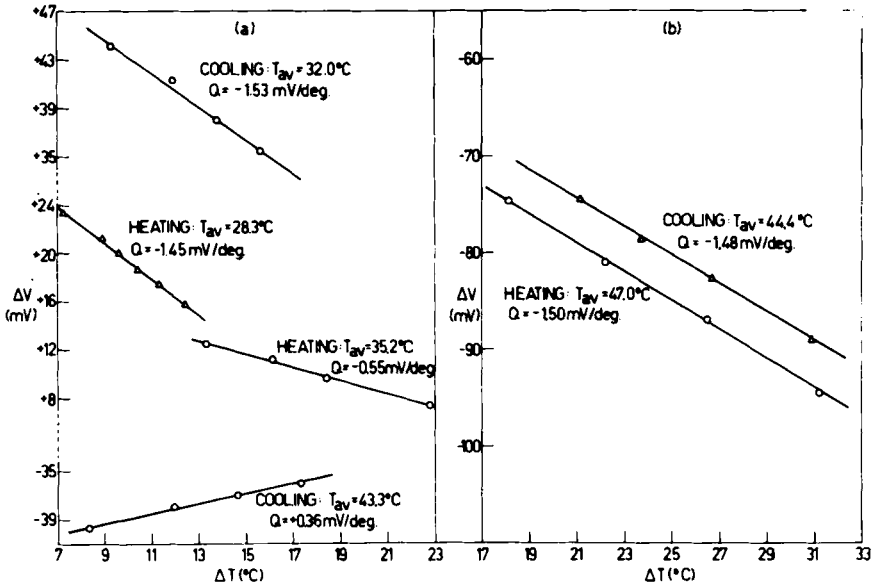


Fig. 7. ΔV vs ΔT plots for pure (a) and impure (b) samples.

holes, as the majority carriers. Substitution of the values $-1.5 \text{ mV/}^{\circ}\text{C}$ and 0.13 eV for Q and E_a , respectively, in the formula [12]

$$Q = \frac{-k(c-1)}{e(c+1)} \left(2 + \frac{E_a}{kT} \right)$$

for an intrinsic semiconductor, where e is the absolute magnitude of the electronic charge and $c = \mu_e/\mu_h$ is the ratio of electron to hole mobility, yields negative c values. Substitution of $E_a = 0.75 \text{ eV}$ yields a value for c around 3.5, which is reasonable [13], but difficulties then arise concerning the concentration of charge carriers. For an intrinsic semiconductor,

$$n = 2 \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} \exp \left(\frac{-E_a}{kT} \right)$$

where n = carrier concentration and m^* = effective mass of the carriers, here assumed equal to the rest mass of the electron. One obtains $n = 10^6\text{-}10^7/\text{cc}$ with $E_a = 0.75 \text{ eV}$ and $T = 300^{\circ}\text{K}$. Since $\mu_e = 3.5\mu_h$, one can calculate the μ_h and μ_e values required to produce the observed specific conductivities σ from the equation

$$\begin{aligned}\sigma &= n_e e \mu_e + n_h e \mu_h \\ &= 4.5 n e \mu_h\end{aligned}$$

Putting $\sigma = 2 \times 10^{-18} \text{ (ohm cm)}^{-1}$, corresponding to $\rho = 5 \times 10^{17} \text{ ohm cm}$, $n = 10^7/\text{cc}$, $e = 1.6 \times 10^{-19} \text{ coulombs}$, one obtains $\mu_h \approx 3 \times 10^{-7} \text{ cm}^2/\text{V-sec}$. This is very much less than values in the range 10^{-2} - $10^{-3} \text{ cm}^2/\text{V-sec}$ obtained from preliminary pulsed photoconductivity mobility measurements. It would therefore seem unlikely that the pure PVC samples are intrinsic semiconductors.

If one asserts that all the samples on which measurements were made are extrinsic semiconductors, it is desirable that some physical significance then be attached to the term "activation energy," and that an explanation be advanced for the dependence of both activation energy and specific resistivity on impurity concentration. Unfortunately the data available at present is too incomplete, i.e., the range of impurity concentration investigated is too narrow and the results for pure PVC are not sufficiently reliable to permit such discussion. It is perhaps worth noting that the activation energies observed in the impure materials lie within the range 1-2 eV which is normally considered characteristic of rigid, noncross-linked, polar materials [14].

One can, however, advance some tentative conclusions on the nature of the charge transport mechanism. There are two possibilities for organic semiconductors:

- 1) Valence and conduction bands are formed in the samples as pictured in Bloch's energy-band scheme for inorganics [15], i.e., the energy levels of the electrons and holes in the parent molecules are broadened into bands by overlap of the molecular orbitals. The behavior of electrons and holes is then described by a wavefunction in the usual quantum-mechanical formulation.
- 2) Electrons and holes move by a series of hops between appropriate sites, i.e., the small polaron hopping mechanism [16]. The carriers interact so strongly with the intermolecular vibrations that the lattice is severely distorted in their neighborhoods. Carrier mobility is then determined by the rate at which the lattice distortion relaxes.

Glarum [17] showed that the band model would be appropriate for drift mobilities considerably greater than $1 \text{ cm}^2/\text{V-sec}$, and the hopping model for drift mobilities much less than $1 \text{ cm}^2/\text{V-sec}$. Accordingly the

preliminary mobility values of 10^{-2} - 10^{-3} $\text{cm}^2/\text{V}\cdot\text{sec}$ quoted above point towards the hopping model. Further, for n-type semiconductors [18], if band formation occurs

$$|S| = \frac{kA}{e} + \frac{E_a}{T}$$

where $|S|$ is the absolute magnitude of the Seebeck coefficient, and A is a scattering parameter whose value, according to scattering theory based on the energy band formation scheme, cannot exceed 4. However, values of A up to 20 have been reported [19-21], and are considered to arise from the existence of discrete conductive states localized at lattice sites which charge carriers can occupy via a hopping process. Substitution of $|S| = 1.5 \text{ mV}/^\circ\text{C}$, $E_a = 1.75 \text{ eV}$, and $T = 300^\circ\text{K}$, yields $A = -50$. Such a result probably supports the hopping model of charge transport, although the physical significance of the activation energy and its energy balance role are not clear.

CONCLUSION

Three conclusions may be drawn from this work: 1) PVC, even in the purest stable form available, is unlikely to be an intrinsic semiconductor, 2) the majority carriers in both pure and impure PVC are negatively charged, most probably electrons, and 3) Charge transport occurs via a hopping mechanism. Further activation energy and specific resistivity measurements on a wide range of plasticized PVC samples and more precise mobility determinations are in hand and will be published later.

REFERENCES

- [1] H. A. Pohl, in *Modern Aspects of the Vitreous State*, Vol. 2 (J. D. MacKenzie, ed.), Butterworths, London, 1962, p. 72.
- [2] R. McNeill and D. E. Weiss, *Aust. J. Chem.*, **12**, 643 (1959).
- [3] W. A. Little, *Phys. Rev.*, **A134**, 1416 (1964).
- [4] F. Gutmann and L. E. Lyons, *Organic Semiconductors*, Wiley, New York, 1967, pp. 736-49.
- [5] A. A. Berlin et al., *Polym. Sci. USSR*, **5**, 378 (1964).
- [6] E. Tsuchida, *J. Polym. Sci., Part A*, **2**, 3347 (1964).
- [7] R. J. Munick, *J. Appl. Phys.*, **27**, 114 (1956).

- [8] V. A. Kargin and M. N. Shteding, *Khim. Prom.*, **3**, 9 (1955).
- [9] A. E. Binks and A. Sharples, *J. Polym. Sci., Part A-2*, **6**, 407 (1968).
- [10] L. E. Amborski, *J. Polym. Sci.*, **62**, 331 (1962).
- [11] D. D. Eley and D. I. Spivey, *Trans. Faraday Soc.*, **57**, 2280 (1961).
- [12] Ref. 1, p. 90.
- [13] H. A. Pohl and J. P. Laherrere, *Proceedings of the Fourth Conference on Carbon*, Pergamon, New York, 1960, p. 261.
- [14] R. W. Warfield and M. C. Petrie, *SPE. Trans.*, **1**, 180 (1961).
- [15] F. Seitz, *Modern Theory of Solids*, McGraw-Hill, New York, 1940, p. 303.
- [16] J. Holstein, *Ann. Phys. (N.Y.)*, **8**, 325, 343 (1959).
- [17] S. H. Glarum, *J. Phys. Chem. Solids*, **24**, 1577 (1963).
- [18] N. B. Hannay, *Semiconductors*, Reinhold, New York, 1959, p. 42.
- [19] F. Gutmann and H. Keyzer, *Nature*, **205**, 1102 (1965).
- [20] M. M. Labes, R. A. Sehr, and M. Bose, "Semiconductor Properties of Organic Molecular Complexes," in *Proceedings of the Princeton University Conference on Semiconduction in Molecular Solids*, Princeton Univ. Press, Princeton, N.J., 1960, p. 47.
- [21] R. Sehr et al., *Electrical Conductivity in Organic Solids* (H. Kallman and M. Silver, eds.), Wiley (Interscience), New York, 1961, p. 322.