Bioenergetics (1972) 3, 245-248

Apparent Compensation in the Electrical Conductivity of Polycrystalline Isocytosine

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Received 2 September 1971

Abstract

Values for the activation energy and pre-exponential factor from electrical conductivity measurements on polycrystalline isocytosine were found to be reproducible when evaporated electrodes were used. With pressure contacts a linear relationship exists between activation energy and the logarithm of the pre-exponential factor. This is shown to be an apparent and not a true compensation effect.

From conductivity (σ) measurements on compressed polycrystalline discs of the pyrimidine base isocytosine it was found that values obtained for the activation energy (E_{ACT}), using the equation

$$\sigma = \sigma_0 \exp -\frac{E_{ACT}}{kT} \qquad (1)$$

were extremely reproducible when evaporated gold electrodes were employed, but varied widely from sample to sample and for successive experiments on the same sample with pressure contacts, these being a palladium anode and a platinum cathode.

Conductivity measurements were carried out using a d.c. virtual-earth amplifier [1]. The samples were mounted in a cell through which dry nitrogen was passed and were held in a constant temperature bath. Before each experiment the sample was dried by heating to about 440 K. The sample temperature was monitored by means of a copper/constantan thermocouple mounted inside the cell.

Figure 1 shows two typical Arrhenius plots obtained using evaporated gold electrodes. Values for E_{ACT} and the pre-exponential factor, σ_0, from such plots were 134 ± 3 kJmol^{-1} and $8 \pm 6 \times 10^6$ ohm^{-1} cm^{-1}. Corresponding values, when using pressure contacts, varied greatly

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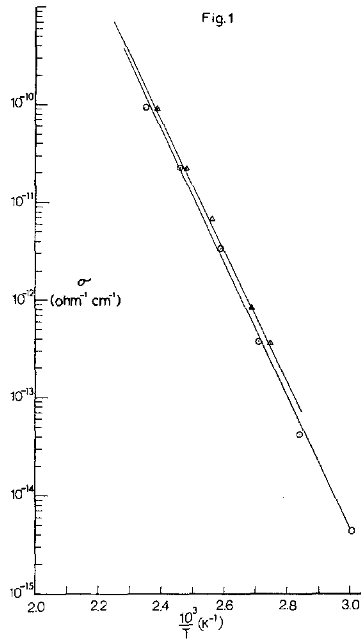

Figure 1. Typical activation energy plots for samples with evaporated electrodes.

(Fig. 2). It can be seen that four of the five lines (A, B, C and E) intersect at $1/T \simeq 2 \times 10^{-3}$ K^{-1}. Similar behaviour has been observed and discussed by Rosenberg *et al.* [2]. When the activation energy obtained from each of the five plots in Fig. 2 is plotted against the logarithm of the corresponding σ_0 value then a very good straight line, with correlation coefficient 0.99, is obtained (Fig. 3). The equation of this line takes the form

$$\log \sigma_0 = \alpha E_{ACT} + \beta \qquad (2)$$

where α and β are constants. Similar "compensation effects" have been observed for large numbers of different organic materials [3, 4], and also for different experiments on the same substance [2, 5], as with isocytosine. The plot in Fig. 3 therefore appears to be a good example of compensation.

However, it has been pointed out [6] that deviations in E_{ACT} are reflected and magnified in the corresponding value of log σ_0. Such a correlation could therefore arise out of error in measurement. This is unlikely to be so here because the differences involved greatly exceed the possible error. Exner [7] has shown that if the temperature range covered in the experiment is limited, with the ratio of the two extreme temperatures close to unity, then a correlation between E_{ACT} and log σ_0

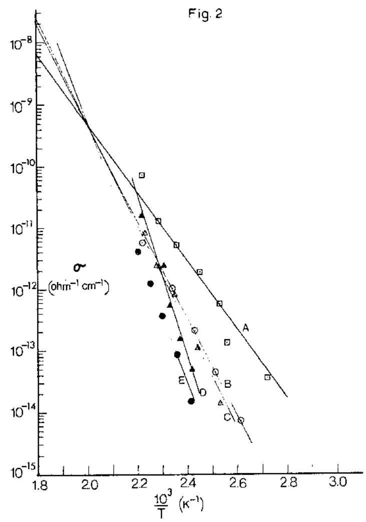

Figure 2. Activation energy plots for samples with pressure contacts.

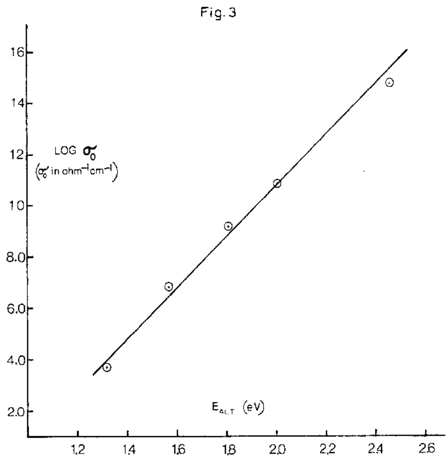

Figure 3. Compensation plot from data in Fig. 2.

will always be found. Here the temperature ratio is approximately 0.8. A more reliable indication of true compensation [6] is gauged from a plot of log $\sigma(T_1)$ against E_{ACT}, where T_1 is a fixed temperature within the range studied. The five points obtained for this plot are widely scattered, and the correlation coefficient now drops to 0.59. It therefore appears that the results in Fig. 3 indicate an apparent and not a true compensation.

That variation in E_{ACT} (and consequently σ_0) is observed when using pressure electrodes but not with evaporated electrodes indicates that variation in the nature of the electrode-semiconductor interface is the cause of the irreproducibility. The suggestion that surface states are the varying factor [5] appears to be confirmed by the present data. When evaporated electrodes are used the metal covers the surface homogeneously and surface vacancies would be difficult to form by, say, evaporation. Reproducible values for E_{ACT} are therefore obtained. However, when pressure electrodes are used the contact between electrode and semiconductor is "rough" and gaps are no doubt present in this interface region. Thus surface vacancy creation is more facile so that variation of temperature may alter the nature and concentration of surface states and give rise to variations in E_{ACT} [5]. These variations in E_{ACT} are reflected in the corresponding values of log σ_0 and, as in the present case, a fortuitous relationship between these two quantities—apparent compensation—may arise.

Acknowledgement

Financial support by the Science Research Council is gratefully acknowledged.

References

1. J. R. N. Evans, Ph.D. thesis (University of Wales, Aberystwyth, 1970).
2. B. Rosenberg, B. B. Bhowmik, H. C. Harder and E. Postow, *J. Chem. Phys.*, 49 (1968) 4108.
3. F. Guttman and L. E. Lyons, *Organic Semiconductors,* Wiley, New York (1967).
4. D. D. Eley, *J. Polymer Sci.*, Part C, 17 (1967) 73.
5. D. D. Eley, A. S. Fawcett and M. R. Willis, *Trans. Faraday Soc.*, 64 (1968) 1513.
6. G. R. Johnston and L. E. Lyons, *Aust. J. Chem.*, 23 (1970) 2187.
7. O. Exner, *Coll. Czech. Chem. Comm.*, 29 (1964) 1094.