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CORRELATIONS BETWEEN THE COHESIVE ENERGY DENSITY AND THE ACTIVATION ENERGY OF CONDUCTIVITY IN ORGANIC SOLIDS AND LIQUIDS

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Abstract

Cohesive energy density values for 11 organic liquids are shown to correlate well with their thermal activation energies of dark conductivity, E_a. The same correlation holds also for the monomers of polyvinylchloride and of polyacrylonitrile, while no such correlation is found for other, non-polymeric, solids.

No correlation was found between E_a and several other physico-chemical parameters such as bond energies and heat of formation of organic liquids or solids, correlations which were reported to hold for inorganic substances.

The results are discussed in terms of the different modes of charge transfer dominant in the materials studied.

Several attempts have been made[1] to correlate the activation energy E_a of electrical conduction of solid organic compounds with other, chemically significant, parameters. E_a is obtained from the slope of Arrhenius type plots of log (conductance or resistance) *vs.* inverse absolute temperature.

The chemical approach to the problem of relating E_a to other parameters is mainly due to Vijh,[2] who has established correlations between E_a and the heat of formation, the bond energies and the electronegativities of binary inorganic compounds like CdTe, ZnS, LiF, LiI and the like; though the first attempt of a chemical interpretation of energy levels in inorganic elemental and binary solids is due to Ruppel, Rose and Gerritsen.[3] The correlations obtained are, indeed, convincing though semi-quantitative only and limited to certain restricted classes of solids; their theoretical interpretation is still in its infancy.

It was considered worth while to see whether a similar chemical approach

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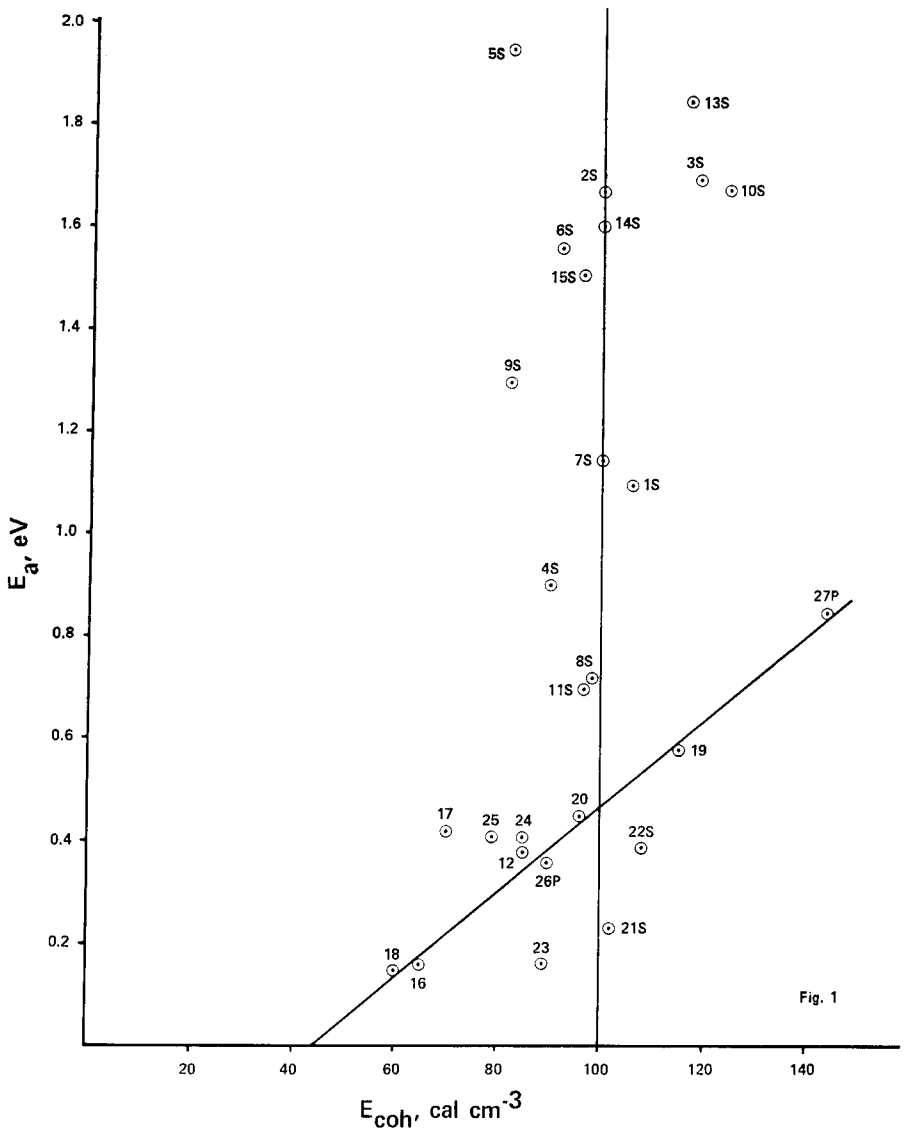

Fig. 1. Correlation between cohesive energy density and thermal activation energy of dark conductivity for organic materials.

Key: Liquids:
12 Benzene; 16 Cyclohexane; 17 Cyclohexene; 18 Heptane; 19 Molten anthracene; 20 Molten naphthalene; 21 Naphthylamine; 22 Naphthoquinoline; 23 Hexane; 24 Carbontetrachloride; 25 Toluene

could yield additional insight in the conduction mechanism of molecular organic solids. However, plotting the experimental value of E_a against the heat of formation, or the average bond energy, showed no trace of any correlation in a plot involving 38 homogeneous organic solid and liquids. For charge transfer complexes, though, correlations between the degree of charge transfer and their bond energies have recently been reported.[4]

The absence of any such correlations in the case of molecular organic crystals and liquids between quantities which correlate very well for inorganic compounds, is further evidence for the general inapplicability of the "classical" energy band model to such systems. Charge transport in molecular solids and liquids usually occurs mainly by nearest neighbour or by variable range hopping, plus contributions from other mechanisms such as tunnelling and, in several cases, also from coherent motion of carriers in very narrow energy bands. However, as a general conclusion, it appears that none of those are rate determining[5]. Moreover, the heat of formation as well as the average bond energy of an organic solid is dominated by the carbon-carbon and carbon-hydrogen bonds and thus does not exhibit any large variations from compound to compound, while E_a values vary from about 0.1 to about 2 eV.

Little correlation has been found to exist between E_a and the heat of fusion or with the heat of vaporization. Some evidence of a correlation might be claimed for E_a and the heat of sublimation, though values for this quantity are not readily available for most of the compounds for which E_a values are listed.[5]

However, from Fig. 1 it is seen that the cohesive energy density E_{coh}, defined[6] as

$$E_{coh} = \frac{H_v - RT}{v} \qquad (1)$$

or, alternatively, as

Solids:

1 Phenanthrene; 2 Benzophenone; 3 Resorcinol; 4 Stilbene; 5 Acridine; 6 Benzanthrone; 7 Benzimidazole; 8 Biphenyl; 9 Imidazole; 10 β-Naphthol; 11 Naphthalene; 13 Anthracene; 14 α-Alanine; 15 Glycine; 26 Vinylchloride monomer; 27 Acrylonitrile monomer.

S means solid; P means polymer;

The abscissae, E_{coh} refer to the cohesive energy densities in cal. cm^{-3} while the ordinates refer to the thermal activation energy of dark conductivity ,in electron volt, E_a. E_a values are from ref. 5 while E_{coh} values were obtained from tables in ref. 7 and/or calculated from Eqs. 1 and 2, using data from the Handbook of Chemistry and Physics Tables.

$$E_{coh} = C\frac{n^2-1}{n^2+2} \qquad (2)$$

does correlate well with values for E_a in the case of the 11 organic liquid semiconductors for which reliable data allowing such comparisons are readily available. In the above H_v stands for the heat of vaporization, R for the gas constant, v for the molar volume, T for the absolute temperature, and n for the refractive index. C is a constant different for each chemical type of compound; its values have been tabulated. The topic of cohesive energy density and of the closely related solubility parameter has been reviewed.[7]

It is of interest to note that the same correlations are also seen to hold for the monomers of polyvinylchloride and of polyacrylonitrile; E_{coh} values for non-polymeric, homogeneous solids however are seen to cluster around the 100 cal cm^{-3} mark while the corresponding E_a values are spread over about an order of magnitude. Thus no correlations appear to hold for these solids.

Thus, the mechanism of charge transfer in organic solids and liquids appears to be basically different; in liquids it appears that transfer between adjacent molecular aggregates rather than within the aggregates is dominant. Such transfer is well known to be of the hopping type rather than *via* a coherent carrier drift in an energy band model[8]. In polymers, the data for which are seen to exhibit the same linear correlation as do the liquids studied, charge transfer is known[5] to be determined by inter-strand or inter-region barriers. Fluorescence phenomena in doped polymers have indeed been related to the solubility parameters of host matrix and guest sensitizer.[9]

The failure of attempts to obtain correlations shown to hold for inorganic solids, also in organic solids, supports the notion of the basic inapplicability of an energy band model to low conductivity materials in which the band width becomes so narrow that, again, carrier transfer is governed by mechanisms other than coherent motion in an energy band.

Applying an electrochemical approach, Lyons[10] has obtained excellent correlations between the potential energy gap—which is related to, but by no means identical with the thermal activation energy of dark conductivity — of organic solids: the energy gap, viz. the energy difference between the ground state of a molecular crystal and an excited state in which an electron-hole pair is separated to a distance sufficient to avoid geminate, coulombic, recombination (a distance of the order of about 15 nm) is derived from Redox potentials and permittivity values of the solid.*)

*) A linear correlation between the polarization energy of aromatic hydrocarbons, such as anthracene and their boiling points has been shown to exist.

Thus, some interesting correlations between observable energy parameters governing the electrical conductivity of organic materials do exist and should provide a fertile field for further studies.

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