

Low Frequency Dielectric Dispersion in 1,4-Butanediol

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The earlier reported dielectric properties of solid 1,4-Butanediol are critically examined in terms of conventional dipolar orientational theory. An explanation of the low frequency dielectric dispersion that involves molecular orientational effects associated with lattice deformations appears to require a value of the order 0.53 to 0.58 for the so-called Kirkwood dipole moment reduction factor. A model involving the hopping of charge carriers between localized energy states is offered as an alternative mechanism for the dielectric dispersion.

The dielectric properties of 1,4-Butanediol have recently been described by Hinopoulos and Sakellariadis [1]. This material was observed to solidify at about 278 K and the relative permittivity at 100 kHz was found to fall from a value of the order 33.5 to around 3.5 on solidifying. At temperatures around 263 to 273 K a dielectric dispersion was observed in the kHz range which the authors suggested arose from the dipolar butanediol molecules having some orientational freedom as a consequence of lattice deformations in the solid structure. The observed dielectric loss was found to increase with the rate of solidification of the material and hence could be considered to be proportional to the number of structural faults in the solid. The purpose of this note is to examine the dielectric data for butanediol more closely, and to indicate that apart from a molecular dipolar orientational mechanism the dielectric results can also be interpreted in terms of an activated charge carrier hopping mechanism. Such charge hopping effects have in the past been considered responsible for the dielectric properties of other molecular solids.

For a dielectric dispersion arising solely from dipolar orientational effects, then from the theories of Debye and Onsager it can be shown [2] that (in S.I. units)

$$\frac{(\epsilon_l - \epsilon_h)(2\epsilon_l + \epsilon_h)}{\epsilon_l(\epsilon_h + 2)^2} = \frac{N\mu^2}{9\epsilon_0 kT} \quad (1)$$

where ϵ_l and ϵ_h define the limiting low and high frequency relative permittivity values of the dielectric dispersion at temperature T , ϵ_0 is the permittivity of free space, N is the density of dipoles of mean dipole moment μ and k is the Boltzmann constant. At 278 K where 1,4-Butanediol solidifies, then from the results of Hinopoulos and Sakellariadis we can take $\epsilon_h \cong 33.5$ and $\epsilon_l \cong 3.5$, which from Eq. (1) gives $N\mu^2 = 3.66 \times 10^{-31} \text{C}^2 \text{m}^{-1}$. The specific density of 1,4-Butanediol can be taken as $1.017 \times 10^3 \text{Kg m}^{-3}$ (Ref. [3]) to give the value for N as $6.8 \times 10^{27} \text{m}^{-3}$ and the corresponding value for the mean dipole moment as $\mu = 7.34 \times 10^{-30} \text{Cm}$ (2.2 Debye units). 1,4-Butanediol is a linear molecule of chemical structure $\text{HO}(\text{CH}_2)_4\text{OH}$. Assuming bond moment values [4] of 0.74 and 1.51 Debye units for the C—O and H—O bonds respectively, then using the formula derived by Eyring [5] the effective dipole moment value for 1,4-Butanediol assuming free rotation about each chemical bond can be calculated to be $7.0 \times 10^{-30} \text{Cm}$ (2.1 Debye units). This theoretical value is in very good agreement with the value derived above using the experimental results of Hinopoulos and Sakellariadis, and confirms their conclusion that 1,4-Butanediol is a polar molecule which acquires freedom of rotation on melting.

Assuming that on solidifying the molecules of 1,4-Butanediol retain a certain degree of rotational freedom, then to a first approximation the dielectric properties can be described using Eq. (1) where the dipole moment factor μ^2 is replaced by the factor $g\mu^2$, with g being the so-called Kirkwood dipole moment reduction factor to take into account steric hindrances and dipole-dipole correlation effects occurring in the solid structure. At 273 K the dielectric dispersion observed for solid 1,4-Butanediol was characterised by the permittivity values $\epsilon_h \cong 3$ and $\epsilon_l > 10$. Using the modification of Eq. (1) just described, then these permittivity values give $g\mu^2 = 2.85 \times 10^{-59} \text{C}^2 \text{m}^2$. Using the theoretical dipole moment value of $\mu = 7.0 \times 10^{-30} \text{Cm}$ then this gives $g = 0.58$, and with the experimentally derived dipole moment value $\mu = 7.34 \times 10^{-30} \text{Cm}$ the corresponding value for the Kirkwood reduction factor is $g = 0.53$. These g values are typical of those found for polymer molecules in dilute solution [6] and as such may perhaps be considered to be too high for a molecular solid whose dielectric loss is considered to arise

from molecular motions associated with lattice deformations.

In describing the dielectric properties of such molecular solids as anthracene and β -carotene, the analogy was made [7, 8] that a solid containing a system of non-interacting electrons hopping over potential barriers will, at a constant temperature, be dielectrically indistinguishable from a solid containing a sparsely distributed set of dipolar entities. For anthracene, the dielectric loss was found to be proportional to the number of crystal lattice defects and as such can be compared with the dielectric properties exhibited by 1,4-Butanediol, although unlike this material anthracene is not a polar molecule. The dielectric loss in anthracene was considered to arise from extrinsically generated charge carriers hopping between localised energy states (traps) associated with lattice defects. This could also be the case for solid 1,4-Butanediol. For example, consider a uniform set of electron trapping sites N_t situated at the Fermi level in the solid material. Electrons in thermodynamic equilibrium with the material will on average occupy just one-half of these available trap sites N_t and the average distance involved in an electron hopping from an occupied to an empty site will be $2s$, where $N_t = 3/4 \pi s^3$. The effective dipole moment of an electron hopping between two such trapping sites will be given by $\mu = 2qs$, where q is the electronic charge. In this way the product $N\mu^2$ in Eq. (1) will be given by

$$N\mu^2 = 2q^2(3/4\pi)^{2/3} N_t^{1/3}. \quad (2)$$

The dielectric dispersion ($\epsilon_1 > 10$, $\epsilon_h \cong 3$) observed by Hinopoulos and Sakellaridis for solid 1,4-Butanediol corresponds to the product $N\mu^2$ in Eq. (1) having the value $N\mu^2 \cong 1.9 \times 10^{-31} \text{ C}^2 \text{ m}^{-1}$, which from Eq. (2) would require an electron trap concentration $N_t \cong 9 \times 10^{20} \text{ m}^{-3}$. Assuming that the presence of one lattice defect is sufficient to produce one electron trap, then this is equivalent to a defect

concentration of 0.13 ppm. Such a defect concentration will exist in even the most carefully crystallised and purified molecular solid. In reality the dominant electronic mechanism will be unlikely to involve the simple model used to derive Eq. (2). For example, the effective hopping electron density will be determined by Fermi-Dirac distribution functions, and not all electron accepting energy states will contribute to a dielectric dispersion. An analysis of the dielectric properties associated with hopping electron phenomena has recently been given by Lewis [9], and apart from anthracene and β -carotene the dielectric properties of polyethylene terephthalate [10] and the perylene-chloranil charge transfer complex [11] have also been interpreted in terms of hopping electron effects.

It will be of interest to investigate the dielectric properties of solid 1,4-Butanediol in more detail. An interpretation of the observed dielectric dispersion in terms of dipole relaxations requires a Kirkwood reduction factor of the order $g = 0.53 - 0.58$. This value is typical of that found for polymer solutions, and it is not clear that such a high value is to be expected for relaxations of molecules in the deformed crystal lattice structure of solid butanediol. Also, in contrast with ionic crystals, the formation of dipolar entities associated with lattice defect pairs will be an unlikely occurrence in the molecular butanediol crystal. It has been shown here that a mechanism involving freely hopping charges may be considered as an alternative to a conventional dipolar relaxation process. Finally, it should also be added that in deriving an estimate of 0.36 eV for the activation energy of the polarization mechanism, the authors of this earlier work [1] used the value of 6 kHz for the frequency of maximum loss. This procedure will have given an underestimate of the activation energy since the results indicate that maximum dispersion in ϵ' (and hence $\max \tan \delta$ value) occurs at a frequency at least as low as 1 kHz.

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