Calculation of the activation volume in semi-conducting polypyrrole

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ABSTRACT

We show that the recent experimentally derived value of the activation volume in semi-conducting polypyrrole is comparable to the value predicted from a thermodynamical model (Varotsos, 1976 [7]; Varotsos et al., 1978 [5]), which interconnects the activation Gibbs energy with the bulk elastic and expansivity data.

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Recently the effect of aging of semi-conducting polypyrrole at ambient temperature for two years duration on the dielectric loss at various pressures was investigated [1]. The negative activation volume of polaron was interpreted as an inwards relaxation of the specimen while polaron passes through the void space separating two polymer chains. Two dielectric loss peaks were measured, a low and a high frequency mechanism which, in earlier papers, were attributed to intra-chain (or intra-grain) and inter-chain (or inter-grain) transport, respectively. Both (with distinct differences) showed a gradual shift of the peak towards higher values while pressure was increased. More specifically, for the high frequency mechanism to which we shall focus, the activation volume $v^{\mathrm{act}} \equiv (\partial g^{\mathrm{act}}/\partial P)_T$ was calculated about $-3.7 \pm 0.3\,\text{Å}^3$.

Revisiting the experimental findings two unusual results occur which we shall attempt to investigate: (i) the activation volume v^{act} is negative, a fact already confirmed and from previous experiments in polypyrrole [2,3] and (ii) v^{act} becomes more negative as the temperature is increased.

Negative activation volume has the meaning that conductivity increases on compression or from another viewpoint that the application of pressure enhances the reorientation of dipoles or quasi-dipoles. Activation volume is a measure so much of the "atomic" as the collective nature of a thermally activated

transition. In this case, this apparent negative volume, most likely does not correspond to an atomic volume but rather to the mean spatial extent of a distortion, such as a polaron or a bipolaron. According to the previous interpretation of the activation volume, the volume or the distribution of volumes (with the resultant energy distribution), primarily depends on the density, orientation and the distances of the polymeric chains, at least as far as interchain/intergrain transport is concerned.

The second finding implies that the thermal variation of the activation volume is large or at least much larger than the bulk one. Notice that the aforementioned remarks are in effect for the activation volume of both the high frequency and low frequency observed mechanisms. Aging induces additional disorder and since polaron activation volume mainly depends on the surrounding environment, the increased temperature dependence seems quite expected, although in the usual theoretical calculations the thermal expansion coefficient of the activation volume β^{act}, is arbitrarily assumed to be zero or equal to the bulk coefficient β [4].

It is useful to investigate whether the previous experimental results find a plausible explanation within the framework of a macroscopic elastic thermodynamic model ($cB\Omega$) [5–9], since, on the one hand actually $cB\Omega$ indicates $\beta^{\mathrm{act}} \gg \beta$ (for polymers β is usually of the order of $10^{-6}\,\text{grad}^{-1}$), and on the other hand, that the application of this model to a variety of other solids led to activation volume values which were in excellent agreement with the experimental values [6,10,11]. According to this model, the Gibbs free energy for defect activation (formation and migration)

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is related dominantly to the elastic work required for the particular process and is proportional to the isothermal bulk modulus, i.e., $g^{act} = c^{act}B\Omega$, where g^{act} denotes the Gibbs free energy for activation ($g^{act} = h^{act} - Ts^{act}$, where h^{act} and s^{act} are the activation enthalpy and the activation entropy, respectively, their temperature (T) dependencies of which, if any, are interconnected [12]), B is the isothermal bulk modulus, c is practically constant and Ω is a volume related with the mean atomic volume. $cB\Omega$ model emphasizes the dominant role of anharmonicity and furthermore that of the elasticity of a solid as the main control parameter of any dynamic process taking place within. Alternatively, within the frame of the $cB\Omega$ model, the elastic work accompanying any process to deform either outward (positive activation volume) or inwards (negative activation volume) an elastic medium, is proportional to $B\Omega$.

Differentiating with respect to pressure, we get

$$v^{act} = B^{-1}\left[\left(\frac{\partial B}{\partial P}\right)_T - 1\right]g^{act} \tag{1}$$

From Eq. (1) comes apparent that the ratio v^{act}/g^{act} is characteristic of the bulk solid and it is independent of the defect mechanism. Eq. (1) was checked at ambient pressure in a wide range of solids [13–16]. The entropic term Ts^{act} is usually much smaller than h^{act}, thus, it is not far wrong to consider $g^{act} \cong h^{act}$ thus we get, $v^{act} = B^{-1}\left[(\partial B/\partial P)_T - 1\right]h^{act}$. The absolute value of the partial pressure derivative of this formula gives the size of the activation volume $|v^{act}| \equiv |(\partial g^{act}/\partial P)_T|$, while its sign, determined from the experiment, implies the correlation between the dynamic processes with the relaxation of the environment; that is, the dynamic rearrangement of the structural units when the relaxing carrier is in its excited state in relation to the structural configuration in the ground state.

We now apply Eq. (1) (absolute values) for $P = 0.1$ MPa and $P = 300$ MPa. Using the values $h^{act} = 0.09 \pm 0.02$ eV (calculated from our experiment), $1/B = 0.061$ GPa^{-1} [17] and $(dB/dP - 1) = 3.6$ [17] gives

$$v^{act} = 3.2^{+0.7}_{-0.7} \text{ Å}^3$$

and for $h^{act} = 0.09 \pm 0.02$ eV, $1/B = 0.05$ GPa^{-1} [17] and $(dB/dP - 1) = 4.4$ [17] we get

$$v^{act} = 3.7^{+0.7}_{-0.7} \text{ Å}^3,$$

respectively. The agreement with the experimental result -3.7 ± 0.3 Å^3 is noteworthy if one also considers the uncertainties involved.

Now we shall focus our attention to the negative sign, which is of prominent importance in view of the fact that negative activation volumes play a key role in the generation mechanism of electric signals detected before earthquakes [18–20], as we discussed elsewhere [21]. For a simple mono-atomic solid, and within the Debye approximation (assuming [22] $\gamma = (dB/dP - 1)/2$), the latter equation can take the form $v^{act} = 2\gamma_I g^{act}/B$, while for ionic crystals (with the assumption [23] that $\gamma = (dB/dP - 1/3)/2$), can reduce to [24] $v^{act} = 2(\gamma - (1/3))g^{act}/B$.

Thus, $cB\Omega$ under these conditions (certain $\gamma = f(dB/dP)$), predicts negative values for values of γ less than 0.33 (or $dB/dP < 1$). However two points must be underlined: (a) the determination of an exact relation between the Grüneisen parameter and the pressure derivative of the isothermal bulk modulus for many different classes of solids (e.g. disordered solids) is an open fundamental question in solid state, and (b) it is crucial to clarify which vibrational mode and thus which γ should someone use. Different experimental methods evaluate different types of γ, as each one excites certain modes. Furthermore, in polymers there are more than one, conduction modes (for example inter-chain, intra-chain), current carrier species (e.g. polarons, bipolarons) and transport mechanisms (e.g. hopping). It is very complicated, in general, to address to the above γ a certain vibrational mode. Each mode, contributes to the anharmonic properties of a solid with a weight which is proportional to the corresponding Grüneisen parameter and most important, its contribution is enhanced or limited, depending on the temperature. Soft modes for instance, that is, one or more branches of excitations with energy vanishing in the low frequency limit, usually correspond to negative γ. Additionally it must be kept in mind that the two previous assumptions for $\gamma = f(dB/dP)$, work for simple solids with much less internal degrees of freedom. Measurements on polymers [25–27] show that certain modes (inter-chain for instance) correspond to γ values less than 1/3 or even negative, while for polyethylene the Grüneisen function at room temperature is less than 0.33. Unfortunately, to the best of our knowledge there no available corresponding data for the Grüneisen function for semi-conducting polypyrrole.

Hence, it is remarkable that the above used macroscopic model predicts so well the experimental calculated value of the activation volume for a complex system and needs further examination of the underlying physical implication that the ratio of v^{act} and the corresponding Gibbs energy does not depend on the defect mechanism while it is only determined from the bulk material.

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