

TRAPPED ELECTRONS IN AMORPHOUS SOLIDS: A METHOD FOR ESTIMATING THE CONCENTRATION OF MOLECULAR VACANCIES

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The densities for *n*-propanol and *n*-butanol in their glassy and crystalline forms have been measured at 77 K. The density difference of ca. $0.11 \text{ cm}^3 \text{ g}^{-1}$ is comparable with that normally found between liquids and solids at their melting points. The maximum yield of trapped electrons in the γ -irradiated glassy alcohols has been estimated and, if it is assumed that they are exclusively trapped at molecular-sized vacancies present only in the glasses, then such vacancies account for no more than ca. 1.0% of the volume difference between the crystalline and glassy materials. Much of the remaining difference can be accounted for in terms of long and bent hydrogen bonds in the glasses.

1. Introduction

An essential part of some theories of the liquid state is the presence of molecular-sized vacancies giving rise to some free volume in the liquid. However, direct measurements of such free volume have not been made, and it is necessary to rely on indirect measurements which can be interpreted in terms of free volume, an example being that of viscous flow [1–3]. The ability of some solvents to solvate electrons in the liquid or glassy state is now well established [4]. One popular and, in our view [5], reasonable theory for electron trapping is that they are largely confined to molecular-sized, nearly spherical vacancies. This has its roots in the F-centre model, and is supported by the fact that many solvents fail to give trapped electrons (e_t^-) when irradiated in their crystalline forms, but give high yields of e_t^- in their glassy forms. Since glasses can be viewed as infinitely viscous liquids, this observation may prove to be a method for estimating the number of such vacancies in liquids.

The aim of this study was to look for possible links between the glass-crystal density differences Δd and the limiting concentration of trapped electrons. In one limit, Δd might stem entirely from the presence of such vacancies, in which case Δd could be used to estimate their concentration. In the other limit, Δd might be very much greater than that estimated from the (e_t^-), in which case we propose that the latter can be used as an approximate measure of the concentration of molecular vacancies.

2. Experimental

The density measurements were carried out using the apparatus shown in fig. 1. A 5 cm³ flask with a B9 joint (A) was connected to a water reservoir (C). Samples of alcohols in either glassy or crystalline states were ground to a fine powder using a Spex freezer-mill, operating at 77 K. During the grinding process, care was taken that the temperature of the solids did not rise appreciably from mechanical heating, by grinding for periods of <30 s. The sample was then transferred to the pre-cooled flask A containing about 1 ml of liquid nitrogen. Evolution of gaseous nitrogen prevented condensation of water vapour during the transfer operation. The transfer was made through a funnel using liquid nitrogen to carry the solid as a suspension. Enough sample was added to fill the flask after packing with a glass rod. A jointed, narrow-bore tube (B) was then attached to A, and liquid nitrogen was introduced to above a calibration mark on B. During this procedure, A and B were immersed in liquid nitrogen. This was cooled below 77 K by Joule–Thomson cooling, using a medium frit (D) connected to a vacuum pump. The degree of cooling was sufficient to prevent boiling of the liquid nitrogen in the large Dewar flask as well as in the density measuring system. Liquid nitrogen was then connected to the reservoir C via a stopcock linked to a nujol bubbler E. When the level of the liquid nitrogen reached the calibration mark on B, the stopcock was opened to the reservoir C. All the remaining liquid nitrogen was allowed to evaporate and the resultant gas was collected in the gas-measuring system. The amount of gas evolved was measured by weighing the amount of water displaced in the container. The weight of the sample was obtained at room temperature by difference. The amount of water introduced into the system was checked by a blank run using no sample and was found to be negligible. Five separate determinations for each sample gave the results in table 1. The deviations are relatively small for our purposes.

The yield of trapped electrons was determined for methanol, ethanol, *n*-propanol

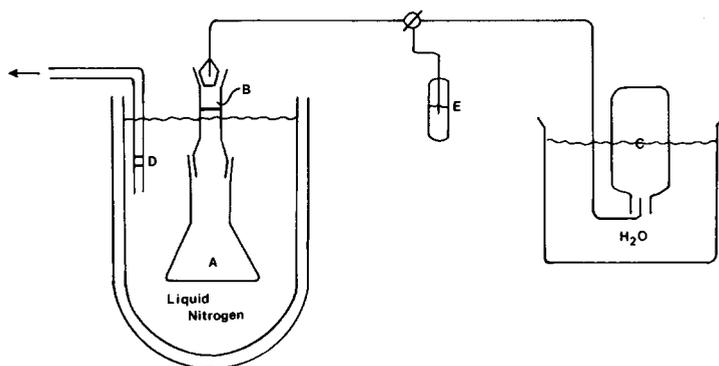


Fig. 1. Apparatus for density measurements at 77 K.

Table 1

Representative relative densities for crystalline and glassy *n*-butanol and *n*-propanol (only the average of five determinations is given for the latter).

Alcohol	Crystalline	Glass	$\Delta d/\text{cm}^3 \text{g}^{-1}$
<i>n</i> -butanol	0.6955	0.6512	
	0.7139	0.6113	
	0.7147	0.6423	
	0.7280	0.6369	
	0.7387	0.6682	
average	0.7182 ± 0.012	0.6420 ± 0.014	0.107
<i>n</i> -propanol, average	0.769 ± 0.010	0.681 ± 0.010	0.110

and *n*-butanol. All solvents were of Analar quality. Methanol and ethanol were distilled from magnesium powder, and *n*-propanol and *n*-butanol were distilled from sodium metal. Samples were prepared for irradiation and esr analysis at 77 K by pipetting the solvents into liquid nitrogen to form frozen spheres of approximately 3 mm diameter. After irradiation at 77 K, the spheres were transferred to a quartz insert Dewar flask and protected from light. The resulting esr spectra were recorded on a Varian E3 spectrometer fitted with a C1024 CAT. The samples were then bleached with visible light, and the resulting spectra digitally subtracted from the originals. By using judicious subtractions and additions, the original spectra of trapped electrons were obtained free from other features. By double-integrating techniques, the relative yields of e_{tr}^- per gram for the various alcohols were obtained. The absolute yield for e_{tr}^- in ethanol was measured using a sample of phosphorus-doped silicon of known spin density (table 2). It was ascertained that samples ground at 77 K gave yields of e_{tr}^- identical with the normal unground samples.

Table 2

Yields of trapped electrons in various glassy alcohols.

Alcohol	Yield of e_{trapped}^- electrons ($\times 10^{18} \text{g}^{-1}$)
MEOH	11
EtOH	6
<i>n</i> -PrOH	4.2
<i>n</i> -BuOH	3.0

3. Results and discussion

3.1. Densities

Despite the inherent errors described above, our results (table 1) show a consistent difference in the densities of glassy and crystalline *n*-propanol and *n*-butanol that is well beyond experimental errors. These results were obtained under identical conditions to those used to study e_t^- . However, they can be compared with other estimates for Δd ($=d_{\text{crystal}} - d_{\text{glass}}$) under different conditions. For example, liquid methanol has a density of $0.9029 \text{ cm}^3 \text{ g}^{-1}$ at its mp of 173.5 K, and the crystalline solid has a density of ca. $1.02 \text{ cm}^3 \text{ g}^{-1}$ just below the mp [6]. Hence $\Delta d \approx 0.117 \text{ cm}^3 \text{ g}^{-1}$, in close agreement with our results for the glasses. Similarly, for a range of liquids which do not necessarily form amorphous solids, it has been found that the difference in density for the liquid and crystalline solid states close to the mp's, gives $\Delta d \approx 0.12$. The results have been discussed empirically [7] and theoretically [8]. The similarity between these results for liquids and ours for glasses supports our contention, given below and elsewhere [9] that results for glasses can often be safely extrapolated to the liquid state.

3.2. Concentrations of e_t^-

A variety of estimates of relative and absolute $[e_t^-]$ trapped in glasses have been made, based upon optical spectra [10] and on esr spectra [11]. It is usually found that the $[e_t^-]$ reaches a maximum as the radiation dose is increased, and we will use these values for the present discussion. Optical studies depend upon an estimate of the total oscillator strength for the characteristic visible and near infrared (IR) bands, which is probably close to unity [12]. They suffer from the difficulty of assessing the total spectral region covered by the absorption band. If some cavities are asymmetric, there may well be broad components spreading over a wider wavelength range than is usually utilized.

Estimates based on esr measurements such as those in this study suffer from the errors involved in subtraction of derivative spectra and double integration of signals, together with the perennial difficulty of translating signal strength into an absolute measure of the number of spins. Also, care has to be taken to avoid microwave saturation effects.

Our results, taken with those of others [10,11], lead to the approximate value of $5 \times 10^{18} \text{ spins g}^{-1}$ for glassy alcohols (table 2).

3.3. Trapped electron volumes

There is no direct method for measuring the effective volume of trapped electrons. However, the free volume available to F-centre electrons in alkali halide crystals is about the volume of the anion since major volume changes are prohibited by

crystal forces. We have shown that there is a close correlation between the optical results for F-centres and those for trapped or solvated electrons [13] and this simple correlation leads to volumes for e_{f}^- in the region of 180 \AA^3 .

Simple theories support this value [13], as do some more sophisticated calculations [14,15], although we stress that not all models for e_{f}^- depend upon the presence of a central vacancy.

We conclude that an effective volume of $100\text{--}300 \text{ \AA}^3$ is reasonable for most trapped electron centres. This is roughly the volume of a molecular vacancy and we consider that such vacancies account for the majority of trapping sites.

3.4. Available volumes

If this volume is taken as a mean value then only ca. 1.0% of the "free" space in these glasses is effective in trapping electrons on the present theory. Alternatively, we can say that only 1.0% of the measured volume differences actually consist of molecular-sized vacancies in the glasses.

Alternatively, it could be argued that many such vacancies remain, but that chemical reactions limit the number of trappable electrons. Our results and those of others [10,11] show that whereas the $[e_{\text{f}}^-]$ reaches a maximum and then slowly falls as the dose increases, the $[R\cdot]$ continues to increase at a slowly falling rate. This falling rate is to be expected since the probability of reaction between e_{f}^- and $R\cdot$ to give diamagnetic species steadily increases. This process, however, must affect $[e_{\text{f}}^-]$ and $[R\cdot]$ equally. An alternative reaction for e_{f}^- is with the cations, ROH_2^+ :



This reaction certainly occurs readily [16], but we have found no sign of $R\cdot$ radicals in this study, nor indeed of any other new radical centre. We therefore suggest that loss of e_{f}^- occurs because of e_2^{2-} formation, which is forced upon the system because most available traps are filled. There is good evidence for this process in alkali hydroxide glasses [17].

3.5. Other forms of free volume

It seems likely that the major volume increment for the glasses is not due to cavities but to weak and bent hydrogen bonds. This can be understood in terms of the structure of the liquid state, as revealed, for example, by IR spectroscopy. Thus, the fundamental O–H stretching absorption is a broad band for liquid or glassy alcohols, which spreads from the low-frequency limit of the crystalline solids through to higher frequencies. These are indicative of O–H groups that are more weakly hydrogen-bonded than those in the ordered crystals. Weaker hydrogen bonds are longer or bent and both factors will lead to a small volume increment. How significant this may be can be gauged by the following simple calculation. We

assume that on average, hydrogen bonds in, say, glassy methanol, are longer than those in the crystal by 0.1 Å. Further, we equate this increase with an increase in the effective molecular diameter, which leads to a volume increment of ca. 0.06 cm³ g⁻¹. Thus, hydrogen-bond loosening may well account for an appreciable proportion of the measured increase, and possibly for all of it.

We conclude that molecular vacancies capable of trapping electrons account for only ca. 1.0% of the excess volume in the glasses, the remainder being due to imperfect hydrogen bonds.

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