

Dielectric Relaxation in Clathrates of Dianin's Compound

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Dielectric relaxation has been studied in the clathrates formed by Dianin's compound with ethanol, chloroform and n-heptanol. Recently published crystallographic data have provided the basis for analysis of the complex absorptions found. In the ethanol and heptanol clathrates relaxation is achieved by a combination of rigid body and internal rotations. Evidence is obtained for strong interaction between chloroform molecules in the same cage.

Dianin's compound,¹ 4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman forms clathrates with molecules having a great variety of shapes and sizes.² Preliminary dielectric measurements from this Laboratory³ suggested that guest molecules may have considerable freedom of rotational movement. Other studies⁴ showed that the rotation frequencies were in the microwave region at room temperature and discussed the dielectric properties in relation to the general features⁵ of the crystal structure. Proton magnetic resonance studies of several of the clathrates have also been reported.⁶

Crystallographic studies of the clathrates with chloroform,⁷ ethanol⁷ and n-heptanol⁸ have provided details of the packing of the host molecules and descriptions of the disorder of the guest molecules in the lattice cavities. We present here a study of the dielectric properties of these clathrates and of several others with non-polar guest molecules.

EXPERIMENTAL

Dianin's compound was prepared as described in the literature¹ and purified by recrystallization from ethanol. The clathrates were obtained by recrystallization of the ethanol adduct from the appropriate solvent. Experience with non-polar solvents, especially benzene, showed it was necessary to distil a quantity of the solvent from the solution in order to free it from ethanol, which appeared to be a preferred guest.

Dielectric measurements were made in a three-terminal low-temperature cell, using bridges described by Thompson⁹ (1.6 Hz to 150 kHz) and Weir and Dryden¹⁰ (100 kHz to 10 MHz).

Dianin's compound is very difficult to compress into samples for measurement. Measurement at low temperature in the audio and radio frequency region rather than at microwave frequencies at a higher temperature had the advantage that only one specimen, a 25 mm diameter disk, was needed. In addition, multiple absorption peaks were better resolved at lower temperatures.

The disks were made by compressing the material in a hardened steel die at a pressure of about 150 MPa. The poor quality of the resulting disks made it difficult to compare the magnitude of the dielectric absorption in different specimens.

RESULTS

CLATHRATES OF NON-POLAR MOLECULES

Provided that sufficient care in preparation was taken, clathrates of benzene, n-heptane and n-octane had dielectric absorption (ϵ'') which was less than 0.0005 over

the whole frequency range from room temperature to 90 K. Some early samples of the benzene clathrate showed absorption which proved to have peaks at the same frequencies as those observed in the ethanol compound. This absorption was eliminated by careful attention to the removal of ethanol. Less difficulty was encountered with the *n*-alkane clathrates.

THE CHLOROFORM CLATHRATE

The absorption consists of two components (fig. 1), neither of which appears to be affected by recrystallization. The major absorption, first observed at about 120 K, widens considerably as the temperature is decreased. Over most of the temperature range, the frequency of maximum absorption may be fitted to the Arrhenius equation $f = A \exp(-E/RT)$ to give an activation energy (E) of 12 kJ mol⁻¹ and frequency factor (A) of 10¹³ s⁻¹. Departures at the lowest temperatures indicate an increase in the effective activation energy. The minor absorption is seen only at the lowest temperature and we have not been able to estimate energy parameters.

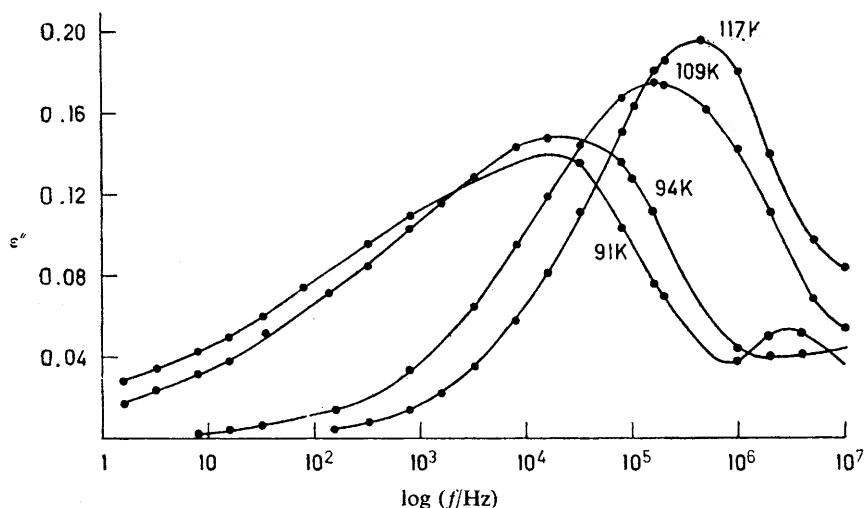


FIG. 1.—Dielectric absorption in Dianin-chloroform clathrate, as a function of temperature.

Over the temperature range 150 to 300 K the low frequency relative permittivity varies as the reciprocal of $(T - T_0)$, where T_0 is about 100 K. Between 150 and 90 K the permittivity deviates from this behaviour, tending to become independent of temperature.

THE ETHANOL CLATHRATE

Absorption peaks are observed at temperatures below 120 K. At the lowest temperatures, there are three distinct absorptions (fig. 2). The absorption curve is fitted well by the sum of three Debye curves, and the change in permittivity across each absorption is twice the maximum absorption. The low frequency relative permittivity is linearly related to the inverse of the absolute temperature, over the temperature range 100 to 300 K, deviating a little at the lowest temperatures.

In the limited temperature range 90 to 120 K in which absorption is observed, the frequencies of maximum absorption may be fitted to the Arrhenius equation to give activation energies of 20.0, 16.5 and 10.3 kJ mol⁻¹ and frequency factors of 8.0×10^{13} ,

1.0×10^{14} and $4.0 \times 10^{12} \text{ s}^{-1}$ for the lowest to highest frequency absorptions respectively.

THE n-HEPTANOL CLATHRATE

Four absorptions are observed. Two move into our measurement range from higher frequencies at about 220 K and pass below our measurement range at about 120 K (fig. 3). They are followed by two smaller absorptions which appear at about 140 K and are the only features remaining at the lowest temperature. None of the

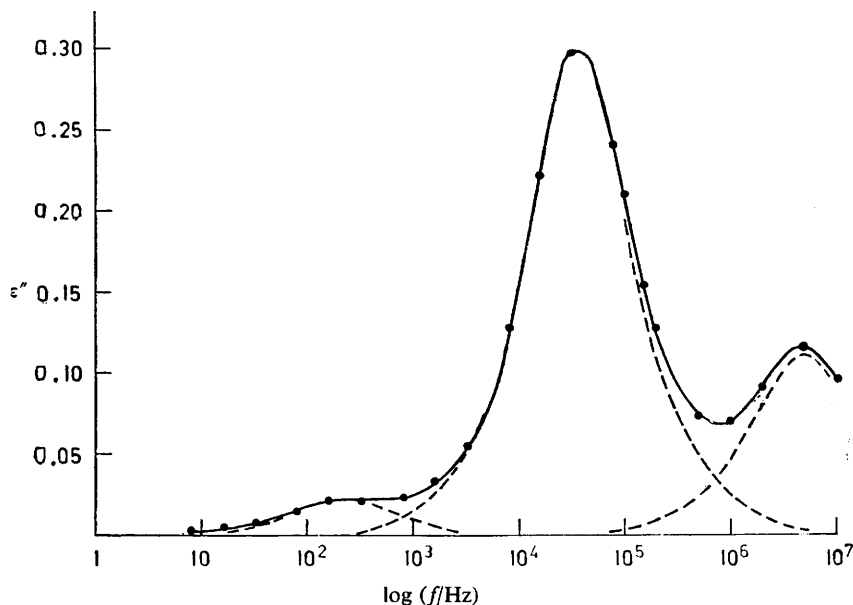


FIG. 2.—Dielectric absorption in Dianin-ethanol clathrate at 92 K. The full curve is the sum of three Debye curves, shown by dotted lines where they do not coincide.

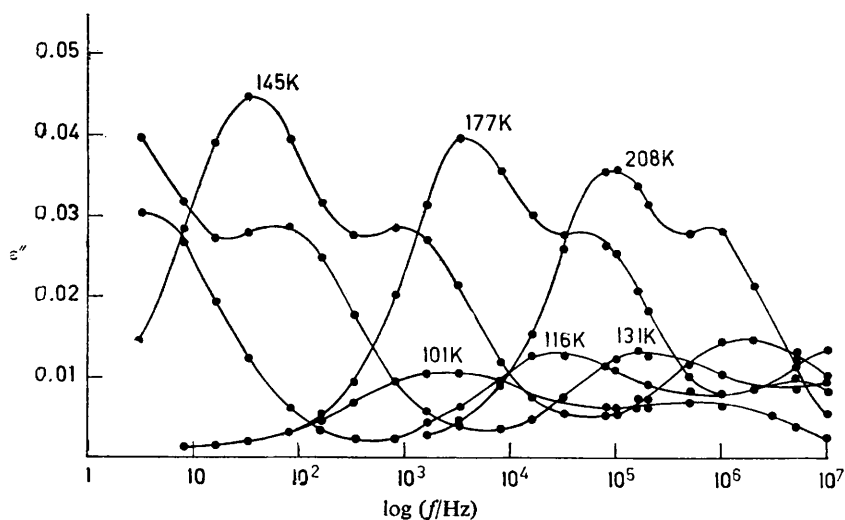


FIG. 3.—Dielectric absorption in Dianin-heptanol clathrate, as a function of temperature.

absorptions may be fitted by a Debye curve. The lowest frequency absorption increases inversely to the absolute temperature while its companion appears to be independent of temperature. The highest frequency absorption is reduced by recrystallization but we have not been able to eliminate it completely. The other high frequency absorption appears to decrease slightly with decreasing temperature.

The activation energies for the absorptions are 32.6, 26.8, 17.2 and 14.2 kJ mol⁻¹ and frequency factors 1.4×10^{14} , 4.0×10^{12} , 1.8×10^{12} and 1.2×10^{13} s⁻¹ respectively.

DISCUSSION

THE CAVITIES IN DIANIN CLATHRATES

The structures of the Dianin clathrates reported by Karle and co-workers^{7,8} belong to space groups $R\bar{3}$. The cavities form columns in the *c* direction, enclosing the threefold symmetry axes. The ends of each cavity are formed by a group of six oxygens, linked by hydrogen bonds to form a hexagon. The walls are formed by six molecules, three attached to alternate oxygens in the bottom hexagon, three to the top, each group resembling a three-pointed crown. The cavity is formed by inverting one crown over another, points interleaved, the whole unit having point symmetry $\bar{3}$.

The space available for guest molecules is simply described by neglecting the threefold symmetry and determining the largest figure of revolution which can be inscribed in the volume bounded by the van der Waals surfaces of the cage molecules. The figure so determined has the shape of an hour glass (fig. 4), 1.1 nm in height. The greatest diameter 0.63 nm is at *Z* = 0.3, repeated at *Z* = 0.7. The ends have a diameter of 0.28 nm and the waist a diameter of 0.4 nm. Small molecules may be fitted in each subcavity giving a molecular ratio, host : guest, of 3 : 1; large molecules may require the whole cavity giving a molecular ratio 6 : 1. In either case, unless guest molecules have the same rotational symmetry as the cavity, they will be distributed randomly over a set of equivalent orientations determined by the cavity symmetry.

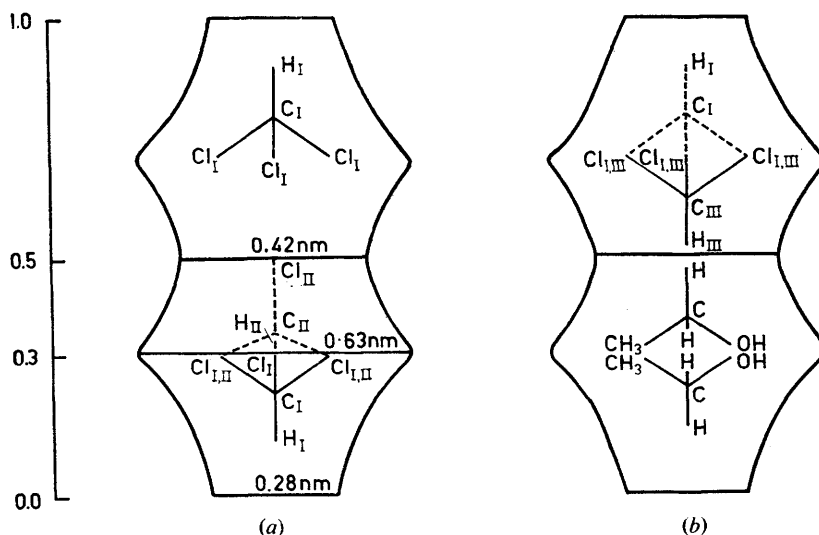


FIG. 4.—Schematic drawing of the cavity in Dianin clathrates showing: (a) chloroform molecules in orientations of type I and II; (b, upper) chloroform molecules in orientations I and III; (b, lower) orientations proposed for ethanol.

CLATHRATES OF NON-POLAR MOLECULES

The measurements have served two purposes. One is to demonstrate that unwanted guests, particularly ethanol, are all too readily accommodated and the other is to show that there is no absorption which arises directly from the cages.

THE CHLOROFORM CLATHRATE

The atomic distribution of chloroform within the cavities of its clathrate has been interpreted ⁷ as a random distribution of chloroform molecules over two types of orientation. Molecules of type I [fig. 4(a)] have all three chlorine atoms in the widest part of the cavity. The C—H bond lies along the symmetry axis, pointing towards the end of the cavity. Full use is made of the molecular symmetry to match the cage symmetry. From published cross-sections ⁷ it is clear that the chlorines fit into lobes extending beyond the inscribed hourglass. Molecules of type II [fig. 4(a), lower part] have chlorines in two of the sites used for type I, the C—H points towards the third site and the third chlorine is at the centre of the cavity with the C—Cl bond lying on the symmetry axis. Because the molecular symmetry is not matched to the cavity, there are three equivalent orientations for type II molecules, obtained from one another by rotation about the axial C—Cl bond. We suggest that a third orientation, type III, is compatible with the atomic distribution described. In type III (fig. 4(b), upper part) all the chlorines are in type I sites, but the carbon is in a type II site, with the C—H bond along the symmetry axis, pointing towards the cavity centre. Type III is related to type I by a reflection in the plane of the chlorine atoms, and consequently its presence allows complete reversal of the dipole moment. The reversal may be effected by first changing a molecule of type I into type II by rotation about the axis joining the chlorines which occupy sites common to both, then obtaining type III by rotation about one of the C—Cl bonds inclined to the crystal axis. If there are two molecules per cavity, such movements must be correlated because it is not possible for both molecules simultaneously to have orientations of type II, which would require two chlorines at the centre of the cavity.

The stoichiometry of the clathrate is not well established, mole ratios of 4 : 1 ² and 6 : 1 ⁷ having been reported. Elemental analysis of our preparation agrees better with the former, indicating an average of 1.5 molecules per cavity. This requires that, if there are no empty cavities, there will be approximately equal numbers of cavities containing one and two molecules of chloroform. Empty cavities require an increase in the number containing two molecules.

Using our observed stoichiometry, an effective dipole moment can be calculated by application of Onsager's equation.¹¹ We find a temperature dependent moment; for example 3.99×10^{-30} C m (1.21 D) at 293 K and 5.48×10^{-30} C m (1.66 D) at 151 K. Replacing the temperature T in the Onsager equation by $(T - 100)$, we obtain 3.20×10^{-30} C m (0.97 D) at both temperatures, in remarkable agreement with the gas phase value of 3.37×10^{-30} C m (1.02 D)¹².

In clathrates of quinol, containing only one guest per cavity, it has been shown ¹³ for the hydrogen cyanide clathrate that the low frequency permittivity varies inversely with the absolute temperature. A replot of data reported ¹⁴ for the methanol-quinol clathrate shows the same temperature dependence. In neither of these is there interference between guest molecules. It seems reasonable to assume that the contribution from molecules in singly occupied cavities of the Dianin chloroform clathrate will have a similar temperature dependence.

The observed temperature dependence of the permittivity in the chloroform

clathrate is strongly indicative of intermolecular interaction. We suggest therefore that the permittivity is dominated by the contribution from cavities containing two molecules of chloroform.

THE ETHANOL CLATHRATE

The structural detail available for the ethanol clathrate is less specific than that for chloroform. Two ethanol molecules are found in each cage, lying essentially perpendicular to the *c* axis in the widest parts of the cage. There is no evidence for atoms at the centre of the cage. Each ethanol molecule has three equivalent orientations with site symmetry C_3 which, for a rigid molecule, would yield one relaxation time.

Interaction of the ethanol molecules by hydrogen bonding through the cavity waist is precluded by their arrangement perpendicular to the *c* axis. Confirmation of the freedom from interaction is provided first by the temperature dependence of the low frequency permittivity, and secondly by the absorption found in samples crystallized from benzene containing a little ethanol. Despite a reduction in intensity of the absorption by a factor of eight, indicating an equivalent reduction in the concentration of ethanol molecules, there is no change in frequency or shape of the absorption.

In the absence of intermolecular interaction, the multiple absorption must be due to the molecule not being rigid. For present purposes, an ethanol molecule may be regarded as a rigid $C-CH_2-O$ group to which are attached two internal rotators, the methyl group and the hydroxyl group. Only rotation of the hydroxyl group produces a change of dipole moment and thus can contribute to relaxation absorption. If we identify one absorption with hydroxyl rotation, the remaining two must be due to relaxation of the dipole of the rigid portion about two axes.

The absorption due to rotation of the hydroxyl group about the $C-O$ bond is proportional to the component, μ_P , of its moment perpendicular to the axis of rotation. The parallel component contributes to the moment μ_R , associated with the rigid part of the molecule. The fraction of the total absorption due to the internal rotation is given by $\mu_P^2/(\mu_P^2 + \mu_R^2)$. The moments μ_P and μ_R , estimated using standard bond moments and angles,¹² are $\mu_P = 4.6 \times 10^{-30}$ C m and $\mu_R = 2.6 \times 10^{-30}$ C m, parallel to the $C-O$ bond. Hence the fractional absorption due to hydroxyl rotation should be 0.7, to be compared with our value of 0.7 for the ratio of the absorption in the largest peak to the total absorption. Therefore we identify this peak as being due to the hydroxyl internal rotation.

It is of interest to compare this result with that of Davies and Meakins¹⁶ for solutions of hydroxy compounds, sterically hindered to prevent intermolecular hydrogen bonding. Two absorptions were found, the larger attributable to internal rotation of the hydroxyl group. We note also that the Arrhenius parameters determined for our major peak compare well with those reported by Meakins¹⁷ for hydroxyl rotation in tricyclohexyl methanol in the solid state.

We consider now the motion of the rigid part of the molecule. Symmetry requires that changes of dipole moment must be perpendicular or parallel to the crystallographic threefold axis. To provide these components, μ_R must be inclined to the axis. The perpendicular component can relax by rotation through the equivalent sites required by the threefold symmetry, while relaxation of the parallel component requires a change in the inclination of μ_R . Because the perpendicular component must be the same for both orientations, the two inclinations must be related as θ and $\pi - \theta$.

A model satisfying these conditions can be derived by postulating that the ethanol molecule has orientations related to those taken by chloroform. We note that the absence of evidence for an atom at the centre of the cavity eliminates consideration of

orientations in which the methyl or hydroxyl is at the centre of the cavity. The proposed orientations are shown schematically in the lower part of fig. 4(b). The relationship to the chloroform orientations I and III is obvious, the methyl and hydroxyl groups fitting into the wall lobes previously mentioned. The two orientations may be interchanged by rotation about the axis joining the methyl carbon and oxygen atoms. With this model the C—O bond makes angles of approximately 70° and 110° with the threefold axis, so that the intensity ratio of absorptions due to the perpendicular and parallel components of μ_R will be $\tan^2 70^\circ$ or approximately 7 : 1 to be compared with our ratio of 5 : 1 for the stronger and weaker absorptions. The experimental ratio would be satisfied if μ_R was inclined to the axis at about 66°.

THE n-HEPTANOL CLATHRATE

From the crystallographic evidence,⁸ each cavity contains one heptanol molecule which lies lengthwise along the symmetry axis, the molecules pointing randomly up and down the axis. It is shown that, because the fully extended molecule is too long to fit into the cavity, the molecule adopts a folded *gauche* configuration at each end, which both shortens the molecule and provides more effective space filling of the hour glass. Each molecule has three equivalent orientations, determined by the crystal symmetry, which should give only one relaxation time for a rigid molecule.

As with ethanol, the multiple absorption peaks must mean that the heptanol molecule undergoes internal rotation. By analogy with our analysis of the ethanol clathrate, we might attempt to assign the largest peak as being due to internal rotation of the hydroxyl group, restricted in range to account for the lower relative strength. However, relative to other hydroxyl rotations, this requires a considerable increase in activation energy. Although examination of scale models suggests that a hydroxyl group experiences greater hindrance in the folded *gauche* than in the extended configuration of the ethanol situation, we feel it unlikely that it will have double the barrier height.

On the other hand, tabulated values¹⁸ indicate the barrier is in the range expected for rigid body rotation of a molecules of this size in close contact with its surroundings. Taking into consideration that the temperature dependence of the absorption magnitudes indicates relaxation by jumps between positions of equal energy we suggest the absorption results from rigid body rotation between the three orientations required by the site symmetry.

The highest frequency absorption which is reduced by careful crystallization may be associated with the presence of water or ethanol. We are unable at present to provide an explanation of the temperature independent intensity of the second absorption.

COMMENTS ON PREVIOUS DISCUSSION

In clathrates with one guest per cavity, Davies and Williams⁴ found μ clathrate $\approx \mu_{lit}$, where μ_{lit} is a gas phase or solution value. With two guests per cavity, in most cases they found μ clathrate $\approx 2\mu_{lit}$. This was interpreted as evidence for dipole coupling and a model was described for acetonitrile requiring simultaneous reversal of both dipoles. They suggested this could be a general phenomenon.

We have recalculated the dipole moments from their published permittivities and find that μ clathrate $\approx \mu_{lit}$. The conclusion that in general there is little interaction between molecules in the same cavity requires confirmation by determination of the temperature dependence of the permittivity.

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