DIELECTRIC RELAXATION AND MOLECULAR MOBILITY IN SOLID CHLOROBENZENE

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The molecular mobility and dielectric relaxation of solid chlorobenzene were investigated to clarify the nature of residual molecular motion below the melting point and its relationship to the structural state of the molecular crystal. Dielectric spectroscopy was employed to measure the real and imaginary components of the complex dielectric permittivity, ε′ and ε″, over the frequency range of 5.5×10^4–5.0×10^6 Hz and the temperature interval from −80 to −40 °C. The measurements revealed two distinct relaxation-dispersion regions in the solid phase, characterized by different relaxation times and activation parameters. The high-frequency (HF) process exhibited relaxation times of approximately 10^{-7}–10^{-8} s and an activation energy of 3.0 kcal mol^{-1}, whereas the low-frequency (LF) process was characterized by relaxation times of about 10^{-6} s and a higher activation energy of 4.62 kcal mol^{-1}. The temperature dependence of the relaxation times followed an Arrhenius relationship. The HF relaxation is attributed to localized rotational motions of chlorobenzene molecules in structurally defective regions, whose contribution increases upon approaching the melting point. The LF process is associated with more hindered molecular rotations within crystallites, where stronger orientational interactions impose a higher potential barrier. The experimentally observed relaxation cannot be explained by Maxwell–Wagner interfacial polarization because the conductivity required for such a mechanism is several orders of magnitude higher than the measured conductivity of chlorobenzene. These results provide quantitative evidence for residual, thermally activated molecular mobility in solid chlorobenzene and demonstrate that dielectric relaxation can distinguish localized defect-assisted motion from more strongly constrained molecular dynamics within crystallites.

Keywords: dielectric spectroscopy, dielectric relaxation, complex dielectric permittivity, solid state, chlorobenzene.
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1. INTRODUCTION

Dielectric relaxation in molecular crystals provides important information about molecular mobility, local structural disorder, and the strength of intermolecular constraints in the solid state. Unlike translational motion, which is strongly suppressed by the crystal lattice, rotational and orientational motions of molecules may remain possible below the melting point. Such residual molecular mobility is particularly important because it reflects the dynamic response of a molecular crystal to its local potential environment and may reveal structural changes that are not directly evident from the macroscopic phase state. Dielectric spectroscopy is therefore a sensitive method for detecting thermally activated molecular motions through their characteristic frequency and temperature dependences.

Chlorobenzene is a suitable molecular system for investigating these phenomena because it is an asymmetric polar aromatic molecule with a non-zero dipole moment. In the solid state, the ordering of molecular dipoles leads to a pronounced decrease in both the dielectric permittivity and dielectric losses upon crystallization [1-7]. Previous microwave measurements have shown, however, that the dielectric permittivity of chlorobenzene does not reach its temperature-independent value immediately below the melting transition. Instead, appreciable changes persist at temperatures approximately 10–15 °C below the phase transition, while the dielectric losses decrease more gradually [8-11]. These observations indicate that molecular motion is not completely suppressed in the solid phase and suggest the presence of residual orientational dynamics below the melting point.

The practical significance of studying residual molecular mobility in solid dielectrics is associated with the possibility of using dielectric relaxation as a non-destructive approach for assessing their structural state, local disorder, and temperature stability. Quantitative characterization of relaxation processes may be useful for the diagnostics and characterization of molecular dielectric materials in which changes in molecular mobility and structural defects affect their electrical properties.

The existence of residual molecular mobility raises an important question concerning the microscopic origin of the dielectric absorption observed in solid chlorobenzene. In molecular crystals, dielectric relaxation can be associated with restricted rotational motion of molecules or molecular fragments, involving thermally activated transitions between energetically favorable orientations imposed by the crystal lattice. In chlorobenzene, the relatively compact chlorine substituent and planar aromatic ring may permit limited rotational or reorientational motions despite the low molecular symmetry. Such motions are expected to be strongly influenced by the local structural environment and by defects in the

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crystal lattice.

Nevertheless, the available information is insufficient to establish a quantitative description of the relaxation spectrum of solid chlorobenzene. In particular, the relationship between the observed dielectric dispersion, the characteristic relaxation times, and the corresponding activation barriers has not been adequately resolved over a broad radio-frequency range. It also remains necessary to distinguish relaxation associated with localized molecular motion in structurally disordered regions from slower motion occurring within more strongly constrained crystalline domains. This distinction is especially relevant near the melting point, where increasing structural disorder may facilitate molecular reorientation before the macroscopic phase transition takes place.

A further issue concerns the possible contribution of interfacial polarization in a polycrystalline solid. Such a mechanism could, in principle, produce a low-frequency dielectric response; however, its applicability to solid chlorobenzene must be tested against the experimentally measured electrical conductivity. The conductivity required for a significant Maxwell–Wagner contribution is several orders of magnitude higher than the experimentally observed conductivity of chlorobenzene, making an interfacial-polarization interpretation physically unlikely. This indicates that the observed dielectric response should instead be considered primarily in terms of molecular, bulk orientational relaxation.

The scientific gap addressed in the present study is therefore the lack of a quantitative separation and physical interpretation of the distinct relaxation processes responsible for the dielectric response of solid chlorobenzene below its melting point. In particular, it is necessary to determine whether the observed dispersion represents a single molecular relaxation process or contains dynamically different contributions associated with different structural environments in the crystal.

To address this problem, the present work investigates the real and imaginary components of the complex dielectric permittivity of solid chlorobenzene over the frequency range of 5.5×10^4–5.0×10^6 Hz and at temperatures from −80 to −40 °C. The temperature and frequency dependences of ε′ and ε″ are analyzed to identify the characteristic relaxation processes, determine their relaxation times and activation parameters, and establish their molecular origin. Particular attention is given to the distinction between high-frequency and low-frequency relaxation, their relation to structural disorder and molecular confinement, and the evolution of molecular mobility on approaching the melting temperature. The resulting analysis provides a quantitative description of residual molecular mobility in solid chlorobenzene and clarifies the role of lattice defects and crystalline constraints in its dielectric relaxation.

2. MATERIALS AND METHODS

2.1. Materials and sample preparation

Chlorobenzene (C_6H_5Cl, CAS 108-90-7) of analytical grade was used as the dielectric material. The compound was dried and subsequently purified by fractional distillation. The purified sample was stored in a tightly closed container to minimize moisture uptake and evaporation losses. Prior to measurements, the sample was transferred into the measuring cell and cooled to the required initial temperature to obtain the crystalline state. The melting point of chlorobenzene is approximately −45.7 °C.

2.2. Experimental setup and measuring equipment

The dielectric properties of chlorobenzene were determined using a state-of-the-art automated resonance measurement system based on a highly stable Keysight/Agilent analyzer, equipped with a resonance measurement unit for studying dielectric materials. The measurements were based on recording changes in the resonance frequency f_r and the quality factor Q of the resonance system upon introduction of the test sample. The real and imaginary components of the complex dielectric permittivity, ε' and ε", respectively, were determined from the changes in the resonance parameters.

The measurements were conducted in the frequency range of 5.5×10^4–5.0×10^6 Hz at temperatures ranging from −80 to −40 °C. The sample temperature was controlled using an automated cooling and heating system, with temperature recorded in the immediate vicinity of the measurement cell. Before starting the measurements, the measurement system was calibrated and the parameters of the empty resonator were checked. The relative errors in determining ε' and ε" were approximately 1% and 5%, respectively.

2.3. Measurement procedure

The sample was initially cooled to the selected temperature and then heated at a controlled rate of approximately 0.2 °C min^{-1}. At each temperature, ε′ and ε″ were measured over the selected frequency range. The frequency dependences of ε″ were used to identify the relaxation-loss maxima and determine the characteristic relaxation time, τ\tau. The temperature dependence of τ was subsequently analyzed using the Arrhenius equation to determine the corresponding activation parameters. The estimated relative uncertainties of the dielectric measurements were approximately 1% for ε′ and 5% for ε″.

3. RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of the dielectric permittivity ε′, measured at different frequencies. It can be seen that both above the melting point and at temperatures below –75 °C, the ε′(T) curves recorded at different frequencies practically coincide. In the intermediate temperature range, there is a pronounced dispersion accompanied by relaxation absorption (Fig. 2).

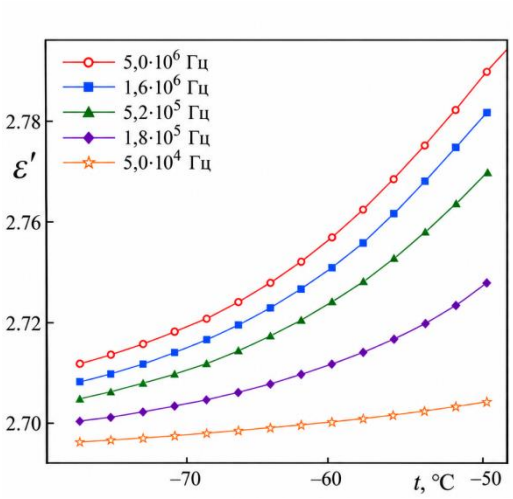


Fig. 1. Temperature dependences of the permittivity ε':

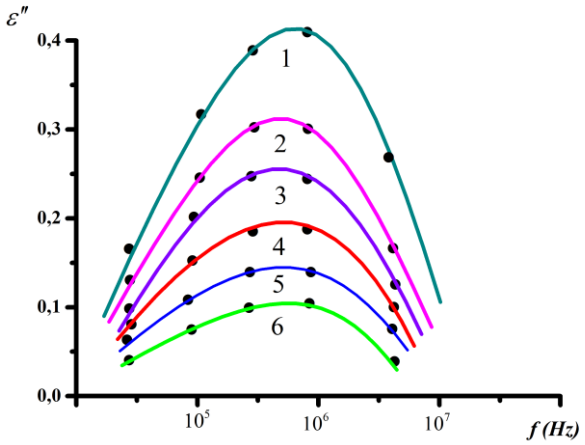


Fig. 2. Frequency dependences of the dielectric loss index ε"
1 – t = -48°C; 2 – t = -52°C; 3 – t = -56°C; 4 – t = -60°C; 5 – t = -64°C; 6 – t = -70°C;

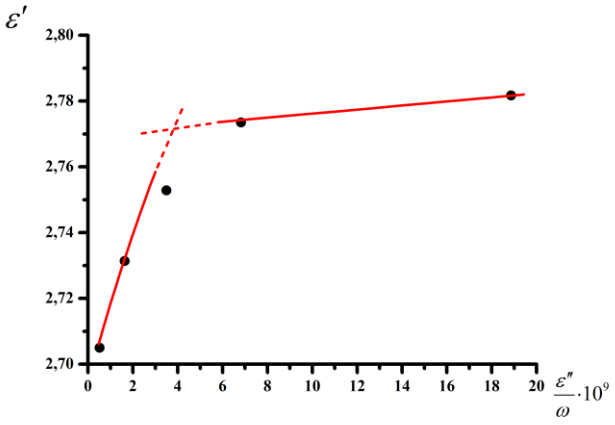


Fig. 3. Linear diagram at temperature t = –48ºC

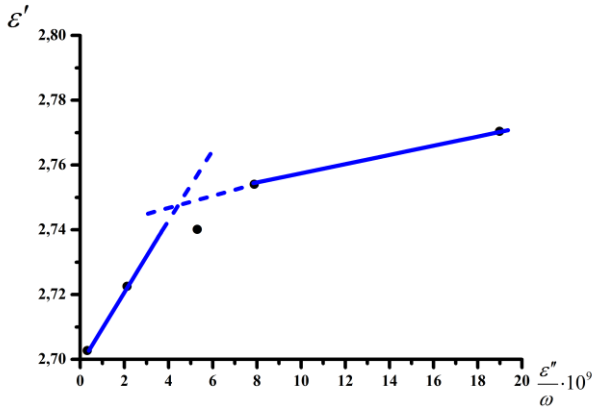


Fig. 4. Linear diagram at temperature t = –52ºC

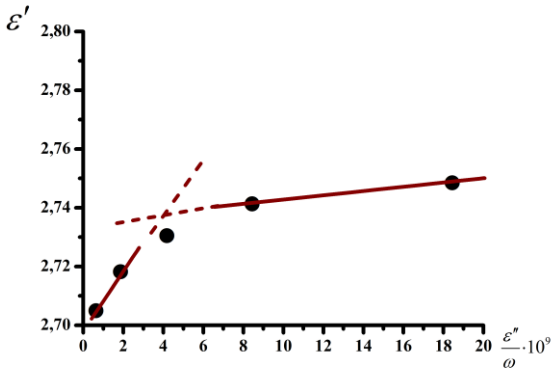


Fig. 5. Linear diagram at temperature t = –56ºC

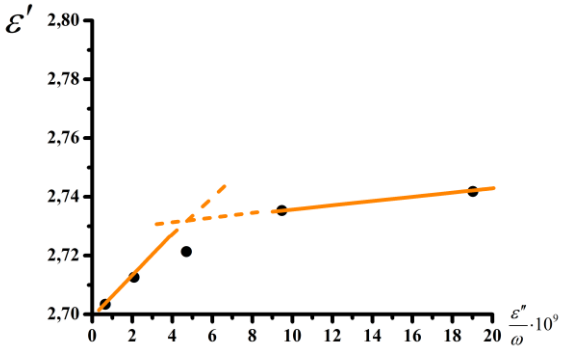


Fig. 6. Linear diagram at temperature t = –60ºC

The frequency dependence of the dielectric loss factor, ε″, exhibits pronounced maxima characteristic of relaxation processes. Analysis of the linear plots (Figs. 3-6) reveals two distinct dispersion regions: a high-frequency (HF) region and a low-frequency (LF) region.

The high-frequency range is characterized by relaxation times on the order of 10^{-7}–10^{-8}s, whereas in the low-frequency range they are approximately 10^{-6}s – that is, an order of magnitude larger. The temperature dependence of the relaxation times is well described by the Arrhenius equation

$$\tau = \tau_0 exp\left(\frac{U}{RT}\right)$$

which allowed us to determine the values of the potential barrier heights U and the pre-exponential coefficients τ_0.

The table 1 shows the energy parameters of relaxation, as well as the thermodynamic characteristics of activation calculated within the framework of the Eyring–Kausman theory. For comparison, the corresponding parameters of liquid chlorobenzene are also given [12-15].

Table 1.

Energy and thermodynamic parameters of relaxation

Parameters	LF – regions:	HF – regions	Liquid phase
U, *kcal·mol* $^{-1}$	4,62	3,0	2,0
τ_0, *sec*	$3{,}75 \cdot 10^{-11}$	$9{,}6 \cdot 10^{-11}$	$4 \cdot 10^{-13}$
ΔF, *kcal·mol* $^{-1}$	6,97	6,70	2,3
ΔH, *kcal·mol* $^{-1}$	4,12	2,50	1,5
ΔS, *kcal·mol* $^{-1}$ *degree* $^{-1}$	– 12,3	– 19,0	– 3,5

The results obtained suggest that the observed spectrum is three-dimensional in nature and is mainly caused by the rotational motion of molecules. Partial disorder of the crystal lattice associated with the formation of defects in the region below the melting point leads to the appearance of a high-frequency relaxation region, whose contribution increases as the temperature approaches the melting point.

The low-frequency region appears to be associated with more difficult movement of molecules in crystallites. This is confirmed by an increase in relaxation times and a growth in the potential barrier compared to the high-frequency process. In this context, it is interesting to compare with NMR data for polycrystalline benzene, where the barrier to molecular rotation around an axis perpendicular to the ring plane is about 3.7 kcal/mol^{-1} [16, 17].

It should be noted that in solid pentasubstituted benzenes with more cumbersome molecules, two Debye dispersion regions are also observed with relaxation times of 10^{-3} – 10^{-5} s and a barrier for the low-frequency region of about 9.5 kcal/mol^{-1} [18], which indicates the universality of the mechanisms under consideration.

4. CONCLUSION

Dielectric spectroscopy has revealed a previously unresolved dual relaxation pattern in solid chlorobenzene below its melting point, providing quantitative evidence for residual thermally activated molecular mobility in the crystalline state. Two dynamically distinct relaxation processes were identified. The high-frequency (HF) process is characterized by relaxation times of 10^{-7}–10^{-8} s and an activation energy of 3.0 kcal mol^{-1}, whereas the low-frequency (LF) process exhibits relaxation times of approximately 10^{-8} s and a higher activation energy of 4.62 kcal mol^{-1}. The Arrhenius temperature dependence of both processes confirms their thermally activated character.

The results establish a direct relationship between the observed dielectric response and the heterogeneous molecular dynamics of the crystal. The HF relaxation is attributed to localized rotational motions in structurally disordered regions and near lattice defects, whose contribution increases toward the melting temperature. In contrast, the LF process reflects more strongly hindered molecular reorientation within crystallites, where stronger orientational interactions impose a higher energetic barrier. The substantially different activation parameters therefore provide a quantitative criterion for distinguishing defect-associated and bulk crystalline molecular motions.

Importantly, the measured electrical conductivity excludes a significant Maxwell–Wagner interfacial polarization contribution. Thus, the observed dielectric dispersion primarily represents bulk orientational relaxation. Overall, the results demonstrate that dielectric spectroscopy can resolve and quantitatively characterize residual molecular mobility and structural heterogeneity in solid chlorobenzene.

From a practical perspective, the results obtained demonstrate that dielectric spectroscopy can be used as a sensitive non-destructive tool for assessing the structural state of solid chlorobenzene and other molecular dielectrics. The separation of relaxation processes according to their characteristic relaxation times and activation energy barriers makes it possible to identify differences in molecular mobility associated with local defects and constraints imposed by the crystal structure, which may be useful for diagnosing structural heterogeneity and evaluating the temperature-dependent behavior of dielectric materials.

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