DIELECTRIC RELAXATION AND MOLECULAR MOBILITY IN SOLID CHLOROBENZENE

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The dielectric permeability ε′ and dielectric loss factor ε″ of solid chlorobenzene were studied using dielectric spectroscopy in the frequency range $5.5\cdot10^4$-$5.0\cdot10^6$ Hz and in the temperature range –80÷–40°C. Two regions of relaxation dispersion were found in the solid phase, differing in characteristic relaxation times and activation energy parameters. Based on the analysis of the temperature and frequency dependencies of ε′ and ε″, possible mechanisms of molecular mobility associated with the rotational motions of molecules and the structural heterogeneity of the crystal lattice in the region up to the melting point are discussed.

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

The ability of molecules to rotate in the solid state is largely determined by geometric and symmetry factors. As a rule, the so-called “rotational” solid phase is realized in compounds whose molecules have a high degree of symmetry about the axis of rotation. In this case, the minimum free volume required for the molecule to rotate must be significantly less than the volume required for translational motion in the crystal lattice [1-7].

Chlorobenzene is an asymmetric aromatic molecule with a nonzero dipole moment, which makes it a convenient object for studying dielectric properties in the solid phase. It is known that when chlorobenzene solidifies, there is a sharp decrease in dielectric permittivity ε′ and dielectric losses ε″, which indicates the fixation of molecular dipoles in the crystal lattice. At the same time, microwave measurements show that ε′ reaches a constant value only at temperatures 10–15 °C below the phase transition point, while ε″ gradually decreases to negligible values [8–11]. These facts can be interpreted as a manifestation of residual molecular mobility in the solid phase.

In this regard, it seems natural to assume the existence of a radio frequency absorption spectrum in solid chlorobenzene, caused by relaxation processes. The aim of this work is to experimentally study these processes and analyze their energetic nature.

2. EXPERIMENTAL PART

The dielectric permittivity ε′ and dielectric loss factor ε″ of chlorobenzene were measured in the frequency range $5.5\cdot10^4$-$5.0\cdot10^6$ Hz and in the temperature range –80 ÷ –40°C. The measurements were performed using the resonance method. The relative error in determining ε′ was about 1%, and ε″ was about 5%.

The object of study was a carefully dried and distilled sample of CHP (chemically pure) grade chlorobenzene with the following physicochemical characteristics: boiling point 132°C, melting point -45.7°C, refractive index $n_D^2 = 1.5248$.

All experimental data were obtained for samples that, after cooling to the temperature of liquid nitrogen, were heated at a rate of approximately 0.2 °C·min^{-1}, which ensured the reproducibility of the thermodynamic state of the system.

3. RESULTS

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).

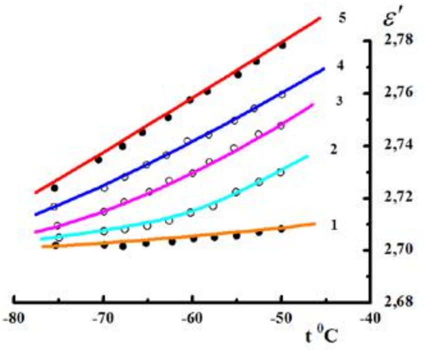

Fig. 1. Temperature dependences of the permittivity ε': 1 – $5,0\cdot10^6$ Hz; 2 – $1,6\cdot10^6$ Hz;3 – $5,2\cdot10^5$ Hz; 4 – $1,8\cdot10^5$ Hz; 5 – $5,5\cdot10^4$ Hz

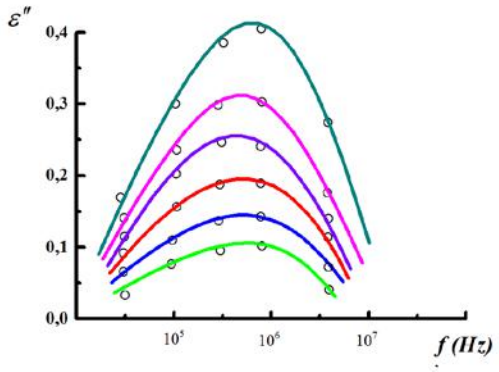

Fig. 2. Frequency dependences of the dielectric loss index ε''

The frequency dependence of the dielectric loss factor ε″ shows maxima characteristic of relaxation processes. Analysis of linear and arc diagrams (Fig. 3-6) reveals the existence of two dispersion regions: high frequency (HF) and low frequency (LF).

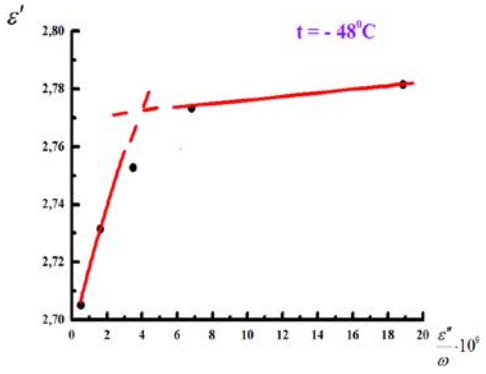

Fig. 3. Linear diagram at temperature t = –48ºC

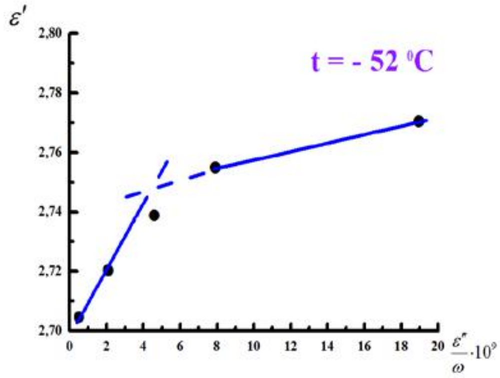

Fig. 4. Linear diagram at temperature t = –52ºC

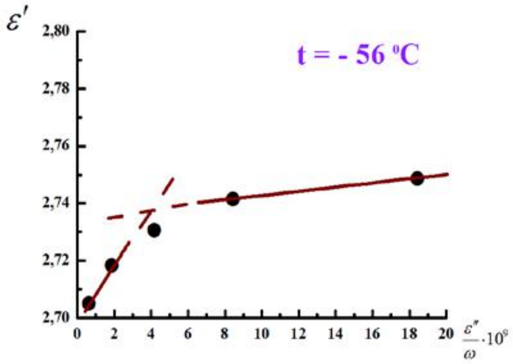

Fig. 5. Linear diagram at temperature t = –56ºC

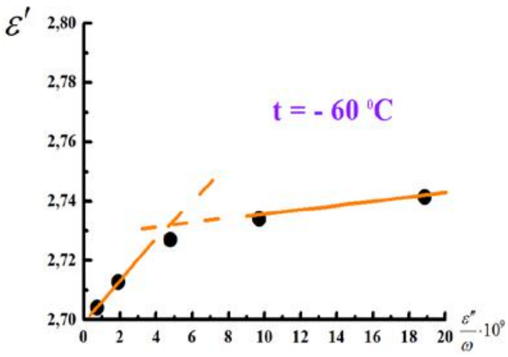

Fig. 6. Linear diagram at temperature t = –60ºC

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

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

which allowed us to determine the heights of the potential barriers U and the pre-exponential factors τ_0.

4. DISCUSSION

The table 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**.**

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.

5. CONCLUSION

The paper shows that in solid chlorobenzene, within the temperature range of –80 to –40°C, two relaxation processes occur, differing in frequency range and energy characteristics. Their occurrence is associated with the rotational mobility of molecules and the structural heterogeneity of the crystal lattice, especially in the region up to the melting point.

The possibility of explaining the observed absorption by interlayer polarization caused by the polycrystalline structure up to the melting point of the samples seems unlikely. Estimates show that for such a mechanism to occur, the conductivity of the interlayers must be on the order of 10–4÷10–5 Ω·cm–1, whereas the experimentally measured conductivity of chlorobenzene does not exceed 10–14 Ω·cm–1.

Thus, the results of dielectric spectroscopy confirm the existence of limited molecular mobility in solid chlorobenzene and provide a quantitative characterization of the corresponding relaxation processes.

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