

DIELECTRIC RELAXATION OF THE ABSORPTION SPECTRUM IN CHLOROBENZENE – BENZENE AND CHLOROBENZENE – HEXANE SOLUTIONS

SAMIR AZIZOV

*Ministry of Science and Education Republic of Azerbaijan, Institute of Physics,
H.Javid ave131., AZ-1073 Baku, Azerbaijan,
email: samir_azizov@mail.ru*

The article presents the results of a study of the dielectric constant of solutions of a polar liquid in a non-polar solvent: chlorobenzene - benzene, chlorobenzene - hexane. The measurements were carried out at a wavelength $\lambda = 12.80$ cm in the temperature range from -80°C to 20°C . The temperature dependence of the dielectric relaxation time of molecules in the liquid and solid states of the studied solutions is determined. The thermodynamic quantities characterizing the process of dielectric relaxation are calculated for solutions of chlorobenzene - benzene, chlorobenzene - hexane.

Keywords: Dielectric spectroscopy, dielectric relaxation, chlorobenzene, benzene, hexane.

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1. INTRODUCTION

The study of the dielectric properties of polar liquids and their solutions in nonpolar solvents is one of the most fundamental and complex problems of science, which is of great theoretical and practical importance. At present, studies of the molecular structure of a liquid and the dynamics of its rearrangement in the course of thermal motion occupy a central place in works devoted to the study of intermolecular interactions in liquids. To solve these problems, modern physical and physico-chemical research methods are used, such as diffraction and thermodynamic methods, dielectric, acoustic spectroscopy, etc. [1]. Among these methods, an important place belongs to dielectric spectroscopy. Studies of the dielectric properties of solutions of polar liquids in nonpolar solvents make it possible to obtain extensive information about their molecular structure, intermolecular interactions, information about thermodynamic parameters and mechanisms of molecular processes.

The relaxation properties of polar molecules are mainly studied either using the Debye theory [1, 2] or using the theory of absolute reaction rates [3 – 5]. In the first case, the relaxation time of a polar molecule is interpreted in connection with its magnitude and the viscosity of the environment. And in the second case, the rate of change of the relaxation process is taken into account, where the relaxation time is expressed in terms of thermodynamic activation quantities.

This paper presents studies of the dielectric relaxation of chlorobenzene in nonpolar solvents benzene and hexane.

2. MATERIALS AND RESEARCH METHODS

Solutions of the polar liquid chlorobenzene in nonpolar solvents benzene and hexane (United States, Keysight Technologies) were chosen for research.

Measurements of permittivity ε' and dielectric loss

ε'' of binary systems chlorobenzene – benzene ($x_2 = 0.179$; $x_2 = 0.368$; $x_2 = 0.567$; $x_2 = 0.778$; $x_2 = 1.000$), chlorobenzene–hexane ($x_2=0.300$; $x_2=0.562$; $x_2=0.794$; $x_2 = 1.000$) were carried out at a wavelength $\lambda = 12.80$ cm in the temperature range from -80°C to 20°C ,

The temperature dependence of the dielectric coefficients of the studied liquid was studied [5 – 9]. The proposed method uses the relationship between the input impedance Z_0 and the complex propagation constant γ of a line filled with a dielectric.

According to the theory of long lines, we have:

$$\gamma = \alpha + i\beta = i\omega (\varepsilon^* \mu^*)^{1/2} \quad (1)$$

where α is the damping constant characterizing the decrease in the amplitude of the wave propagating along the line, β is the phase constant characterizing the change in the phase of the same wave, μ^* is the complex magnetic permeability.

Taking $\mu^* = 1$, we get:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{\gamma\lambda_1}{2\pi} \quad (2)$$

where λ_1 is the wavelength in the air part of the line.

The value of γ is related to the input impedance Z_0 as follows:

$$\frac{th\gamma d}{\gamma d} = -i \frac{\lambda_1}{2\pi d} \cdot \frac{Z_0}{Z_1} \quad (3)$$

where d is the thickness of the dielectric, Z_1 is the wave resistance of the air part of the line.

The input impedance Z_0 is expressed in terms of the experimentally determined running coefficient $q = E_{\min}/E_{\max}$ (E is the electric field strength) and the node displacement γ_1 of the standing wave:

$$Z_0 = Z_1 \frac{q - i \operatorname{tg} \beta_0 \gamma_1}{1 - iq \operatorname{tg} \beta_0 \gamma_1} \quad (4)$$

here $\beta_0 = \frac{2\pi}{\lambda_1}$. Equation (3) is solved by a graphical

method, in the form:

$$\frac{thT e^{i\tau}}{T e^{i\tau}} = C e^{i\xi} \quad (5)$$

here $T e^{i\tau}$ – polar form of the complex quantity γd . C and ξ are the modulus and argument, respectively, of the right side of equation (5). Substituting the notation $Z_0/Z_1 = R + iX$, then from equation (4) we get:

$$\begin{cases} R = \frac{q(1+tg^2 \beta_0 \gamma_1)}{1+q^2 tg^2 \beta_0 \gamma_1} \\ X = \frac{(q^2-1)tg \beta_0 \gamma_1}{1+q^2 tg^2 \beta_0 \gamma_1} \end{cases} \quad (6)$$

Taking into account (3) and (6) we have:

$$\begin{cases} C = \sqrt{A^2 + B^2} \quad \text{где } A = \frac{\lambda_1}{2\pi d} X \\ tg \xi = \arctg \frac{B}{A} \quad \text{где } B = \frac{\lambda_1}{2\pi d} R \end{cases} \quad (7)$$

Having determined the values C and ξ from expressions (6) and (7), we find T and τ from the graphical solution of equation (5) given in (7).

Since $T e^{i\tau} = \gamma d = d(\alpha + i\beta)$, then

$$\begin{cases} \alpha = \frac{T \cos \tau}{d} \\ \beta = \frac{T \sin \tau}{d} \end{cases} \quad (8)$$

Bearing in mind (2), to determine the real and imaginary parts of the complex permittivity, we obtain the following expressions:

$$\begin{cases} \epsilon' = \left(\frac{\lambda_1}{2\pi}\right)^2 (\beta^2 - \alpha^2) \\ \epsilon'' = \left(\frac{\lambda_1}{2\pi}\right)^2 2\alpha\beta \end{cases} \quad (9)$$

An analysis of the method showed that in the case of small and medium losses $tg\delta < 0.1$, accurate results are achieved at thicknesses that are multiples of an odd number of quarters of the wavelength in the sample. For large losses $tg\delta > 0.1$, the thickness of the sample has to be taken so small that it itself becomes a source of noticeable errors.

3. RESULTS AND DISCUSSION

On fig. 1.2 shows the temperature dependence of the permittivity ϵ' and dielectric losses ϵ'' for the chlorobenzene-hexane system, with the chlorobenzene content in mole fractions being 0.300; 0.562; 0.794 and 1.000.

At the point of solidification of the studied solutions, a sharp decrease in the values of dielectric permittivity ϵ' and dielectric losses ϵ'' is observed.

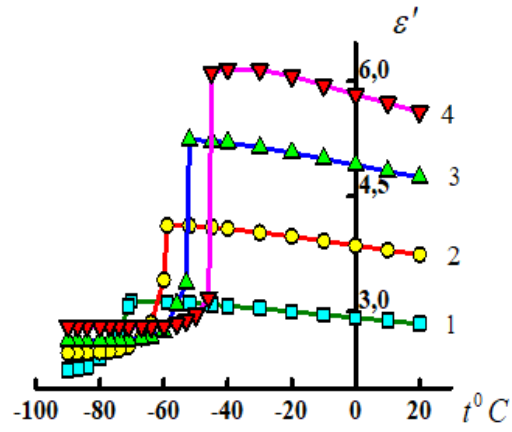


Fig. 1. Temperature dependence of ϵ' for the system chlorobenzene – hexane, 1 - 0.300; 2 - 0.562; 3 - 0.794; 4 - 1,000.

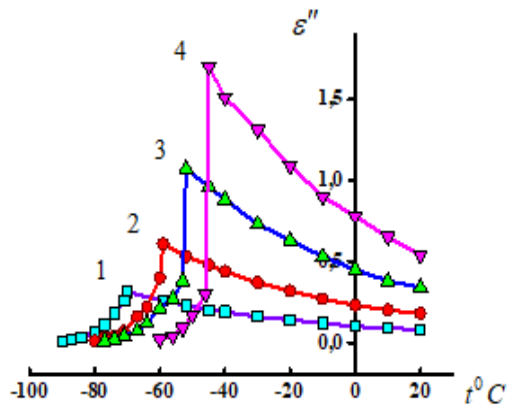


Fig. 2. Temperature dependence of ϵ'' for the system chlorobenzene - hexane, 1 - 0.300; 2 - 0.562; 3 - 0.794; 4 - 1.000.

Another type of complex permeability versus temperature curve $\epsilon^* = f(T)$ was found in the chlorobenzene-benzene system at chlorobenzene concentrations in mole fractions $x_2 = 0.179$ and $x_2 = 0.368$. In both cases, at the solidification point, there is a slight drop in the values of the permittivity ϵ' , while the values of the dielectric loss ϵ'' continue to grow (Fig. 3.4).

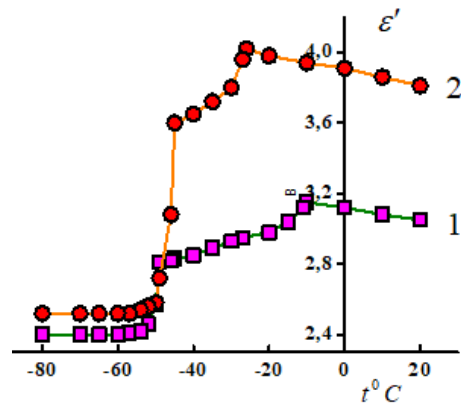


Fig. 3. Temperature dependence of ϵ' for the system chlorobenzene – benzene, 1 - 0.179; 2 - 0.368.

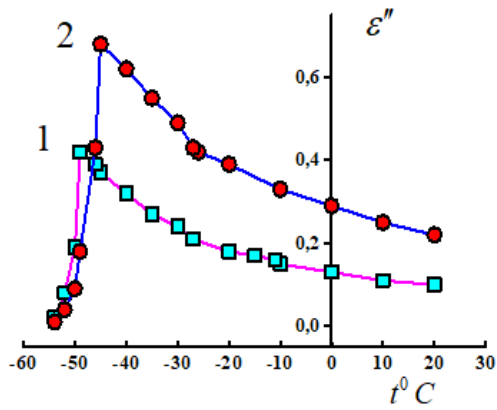


Fig. 4. Temperature dependence of ϵ'' for the system chlorobenzene - benzene, 1 - 0.179; 2 - 0.368.

This is more clearly manifested in the graph of the temperature dependence of the loss angle tangent $\text{tg}\delta = \epsilon''/\epsilon'$ for solutions of chlorobenzene - benzene (Fig. 5). The loss of rotational mobility of molecules occurs only when cooling is 200 below the solidification point $x_2 = 0.368$ and 400 – for $x_2 = 0.179$.

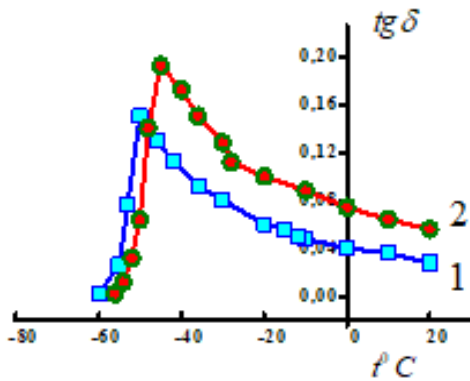


Fig. 5. Temperature dependence of $\text{tg}\delta$ for the system chlorobenzene - benzene, 1 - 0.368; 2 - 0.179.

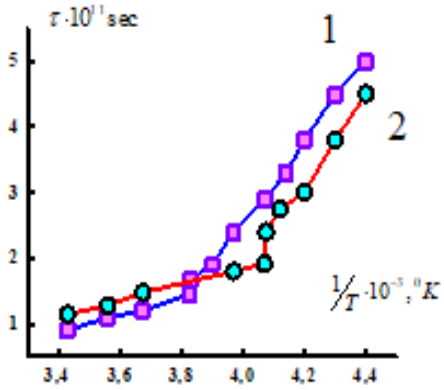


Fig. 6. Temperature dependence of relaxation time τ for the system chlorobenzene - benzene, 1 - 0.179; 2 - 0.368.

On fig. Figure 6 shows the temperature dependence of the relaxation time. As can be seen, at the point of solidification on the straight line of the graph, there is a sharp bend in the curve of the graph. Activation energy U according to the relation

$$r = A \exp(-U/RT) \quad (10)$$

equals 1.77 kcal/mol in liquid and 4.5 kcal/mol below the solidification point for $x_2 = 0.358$ and 1.65 kcal/mol in liquid and 4.7 kcal/mol below the solidification point for $x_2 = 0.179$.

Thus, at given concentrations, the solid state is characterized by the presence of two phases - an intermediate metastable phase, which passes with further cooling into a stable low-temperature phase.

Table 1 gives the results of the corresponding calculations for the studied solutions of chlorobenzene - benzene, chlorobenzene - hexane.

Table 1.

Values ΔF – free energy change, ΔH – enthalpy change, ΔS – activation entropy change for the process of dielectric relaxation in the temperature range $-40^\circ\text{C} \div 20^\circ\text{C}$

x_2	ΔF				$T\Delta S$				ΔH
	20^0	0^0	-20^0	-40^0	20^0	0^0	-20^0	-40^0	
Chlorobenzene – benzene									
0,179	2,37	2,98	–	–	–1,13	–1,04	–	–	1,24
0,368	2,44	2,35	2,27	–	–1,10	–1,01	–0,93	–	1,34
0,567	2,48	2,40	2,32	2,24	–1,06	–0,98	–0,90	–0,82	1,42
0,778	2,50	2,42	2,35	2,27	–1,04	–0,96	–0,89	–0,81	1,46
1,000	2,50	2,47	2,39	2,31	–1,01	–0,99	–0,90	–0,82	1,49
Chlorobenzene – hexane									
0,300	2,20	2,09	2,03	1,95	–1,20	–1,09	–1,03	–0,95	1,00
0,562	2,28	2,19	2,11	2,04	–1,16	–1,07	–0,99	–0,92	1,12
0,794	2,40	2,31	2,25	2,17	–1,07	–0,98	–0,92	–0,84	1,33
1,000	2,50	2,47	2,39	2,31	–1,01	–0,99	–0,90	–0,82	1,49

The results of the corresponding calculations of the values of ΔF , ΔH and ΔS of the studied solutions chlorobenzene - benzene, chlorobenzene - hexane show that the height of the potential barrier separating the two equilibrium positions of the polar molecule is the largest in the state of a pure polar liquid and decreases with dilution in a nonpolar solvent, and this is more pronounced in hexane than in benzene.

CONCLUSION

In almost all cases, the phase transition is accompanied by a sharp drop in the dielectric permittivity ϵ' and dielectric losses ϵ'' temperatures. Based on the temperature dependence of the relaxation time, the values of thermodynamic parameters for the process of dielectric relaxation are determined. The results are discussed in connection with the size and shape of the solvent molecules.

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