DIELECTRIC RELAXATION IN BROMOBENZENE-BENZENE AND BROMOBENZENE-HEXANE BINARY SYSTEMS: THERMODYNAMIC ANALYSIS AND SOLVENT INFLUENCE

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This paper presents the results of an experimental study of the complex dielectric permittivity (ε' and ε") of bromobenzene-benzene and bromobenzene-hexane binary systems in the microwave range (λ = 12.8 mm) at temperatures from 293 K to 193 K. The aim of the study is to establish the relationship between molecular dynamics, thermodynamic parameters, and the nature of the solvent in the process of dielectric relaxation. The temperature dependence of the dielectric relaxation time (τ) for each system was determined. It was found that an increase in the size of the halogen substituent leads to an increase in τ. Based on the theory of absolute reaction rates, the thermodynamic parameters of relaxation process activation were calculated: free energy (ΔF), enthalpy (ΔH), and entropy (ΔS). The influence of intermolecular interactions and solvent structure on energy barriers and system order in the process of dipole reorientation is shown.

Keywords: dielectric relaxation, bromobenzene, benzene, hexane, thermodynamics, microwave range, relaxation time, intermolecular interactions.
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1. INTRODUCTION

The study of the dielectric properties of polar liquids and solutions is an important tool for understanding molecular dynamics and intermolecular interactions [1,2]. Dielectric relaxation, caused by the reorientation of molecular dipole moments in an alternating electric field, provides valuable information about the structure and dynamic processes in condensed media [3,4].

The theoretical consideration of dielectric relaxation is traditionally based on two main approaches: Debye theory [5] and the theory of absolute reaction rates [6,7]. Debye theory relates the relaxation time to the size of the molecule and the viscosity of the environment. The theory of absolute reaction rates considers relaxation as a kinetic process, expressing the relaxation time through thermodynamic activation parameters. To apply the latter approach, it is necessary to know the temperature dependence of the relaxation time [8-10].

Despite a large number of studies, the influence of the nature of the solvent on the thermodynamic parameters of dielectric relaxation and the mechanism of intermolecular interactions in binary systems requires further study.

The scientific novelty of this work lies in establishing a correlation between the thermodynamic parameters of bromobenzene dielectric relaxation and the molecular properties of solvents (benzene and hexane). The applied significance lies in obtaining fundamental data for the development of new materials with specified dielectric properties and optimization of technological processes using microwave radiation.

2. MATERIALS AND METHODS

The experimental methodology is described in [11]. Measurements of the dielectric permittivity (ε') and dielectric loss tangent (ε") of the solutions under study were performed using a R2-66 panoramic standing wave ratio meter and a indicator device Ya2R – 67 indicator device in the microwave range at a wavelength λ = 12.8 mm. The temperature of the samples was controlled with an accuracy of ±0.1 K. The objects of study were placed in a specially designed short-circuited measuring waveguide cell at the end. The measuring cell was placed in a thermostat and contained a device for smooth adjustment of the solution layer thickness. The research results were obtained during continuous cooling at a rate of 0.1–0.2 degrees/min. The spread of measurement results for ε' is less than 1%, and for ε" less than 4%.

Bromobenzene, benzene, and hexane were thoroughly purified by rectification to achieve a high degree of purity – chemically pure. Double systems were prepared by mixing the components in specific molar ratios.

The relaxation time was determined using the formula [12-13]:

$$\tau = \frac{1}{\omega}\frac{\varepsilon''}{\varepsilon' - \varepsilon_\infty}$$

3. RESULTS AND DISCUSSION

Tables 1 and 2 present the results of measurements of dielectric permittivity (ε') and dielectric loss tangent (ε") for bromobenzene-benzene and bromobenzene-hexane systems as a function of temperature and concentration. These results were obtained during continuous cooling at a rate of approximately 0.1–0.2 degrees/min. In most cases, a sharp decrease in ε′ and ε″ is observed at the

Table 1

Bromobenzene – benzene								
t, ^{0}C	x_2 = 0,459		x_2 = 0,560		x_2 = 0,718		x_2 = 1,000	
	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
Liquid state								
20	3,98	0,33	4,27	0,40	4,66	0,52	5,25	0,73
10	4,02	0,37	4,32	0,45	4,74	0,58	5,35	0,83
0	4,06	0,43	4,39	0,52	4,82	0,69	5,39	0,97
– 10	4,10	0,51	4,45	0,63	4,90	0,82	5,43	1,12
– 20	4,13	0,60	4,50	0,75	4,94	0,98	5,38	1,31
– 30	4,15	0,70	4,52	0,88	4,93	1,16	5,29	1,49
– 33	4,16	0,74	4,53	0,94	4,92	1,21	–	–
– 40	–	–	4,54	1,04	4,90	1,32	–	–
– 42	–	–	4,54	1,07	4,88	1,35	–	–
– 47	–	–	–	–	4,84	1,43	–	–
Solid state								
–31	–	–	–	–	–	–	3,12	0,31
–34	3,38	0,52	–	–	–	–	2,98	0,16
–38	3,00	0,22	–	–	–	–	2,87	0,08
–43	2,63	0,07	3,25	0,40	–	–	2,84	0,02
–48	2,57	0,02	2,81	0,12	3,17	0,34	2,83	–
–50	2,56	–	2,69	0,06	2,90	0,19	2,83	–
–52	2,55	–	2,64	0,03	2,79	0,15	2,83	–
–58	2,55	–	2,63	0,01	2,74	0,04	2,83	–
–60	2,55	–	2,62	–	2,72	0,02	2,83	–
–70	2,55	–	2,62	–	2,71	–	2,83	–
–80	2,55	–	2,62	–	2,71	–	2,83	–

Table 2

Bromobenzene - hexane								
t, ^{0}C	x_2 = 0,300		x_2 = 0,562		x_2 = 0,794		x_2 = 1,000	
	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
Liquid state								
20	2,80	0,10	3,60	0,23	4,34	0,40	5,25	0,73
10	2,84	0,11	3,65	0,25	4,42	0,45	5,35	0,83
0	2,88	0,13	3,69	0,29	4,49	0,53	5,39	0,97
– 10	2,92	0,15	3,72	0,34	4,53	0,62	5,43	1,12
– 20	2,95	0,17	3,75	0,39	4,52	0,71	5,38	1,31
– 30	2,99	0,20	3,75	0,44	4,49	0,81	5,29	1,49
– 34	3,00	0,21	3,75	0,48	4,46	0,86	–	–
– 40	3,02	0,24	3,75	0,51	–	–	–	–
– 50	3,04	0,29	–	–	–	–	–	–
– 55	3,04	0,32	–	–	–	–	–	–
Solid state								
–31	–	–	–	–	–	–	3,12	0,31
–35	–	–	–	–	3,52	0,57	2,96	0,15
–38	–	–	–	–	3,19	0,32	2,87	0,08
–41	–	–	3,58	0,42	2,96	0,20	2,85	0,06
–45	–	–	3,02	0,21	2,75	0,11	2,84	0,01
–51	–	–	2,79	0,09	2,70	0,04	2,83	–
–53	–	–	2,66	0,05	2,67	0,01	2,83	–
–56	2,92	0,24	2,55	0,03	2,65	–	2,83	–
–58	2,77	0,14	2,52	0,01	2,65	–	2,83	–
–60	2,62	0,11	2,50	–	2,65	–	2,83	–
–65	2,45	0,04	2,50	–	2,65	–	2,83	–
–70	2,33	0,02	2,50	–	2,65	–	2,83	–
–80	2,32	–	2,50	–	2,65	–	2,83	–

solidification point. At the same time, it was noted that at the onset of solidification, the wave number q = Emin/Emax (E – electric field strength) passes through a sharply pronounced maximum. The wave number is not reflected in the values of ε'', since at the same time there is a very rapid and significant shift of the standing wave node. It is possible that in this case, in order to obtain more complete information, it is necessary to take a larger number of experimental points in a very narrow temperature range near the solidification point. After the jump, there is a further decrease in ε' and a drop in ε'' to zero. This behavior has already been noted for pure polar components and attributed to the existence of individual "free" molecules in liquids along with clusters [14-17]. These, in turn, contribute to the orientation polarization in a small temperature range below the solidification point. This point of view is confirmed to a certain extent in the case of hexane solutions, where such a transition is noticeably prolonged compared to a pure polar component (Fig. 1, 2). In benzene solutions, this is less pronounced.

Figures 1 and 2 show the temperature dependences of the dielectric constant for the bromobenzene – hexane system.

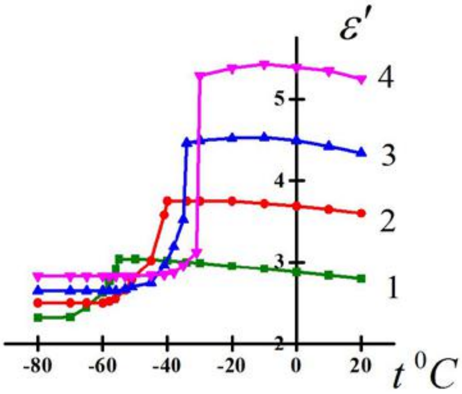

Fig. 1. Temperature dependence of the dielectric constant ε' for the bromobenzene – hexane system, at a bromobenzene concentration in mole fractions: 1 – 0.294; 2 – 0.556; 3 – 0.745; 4 – 1.000

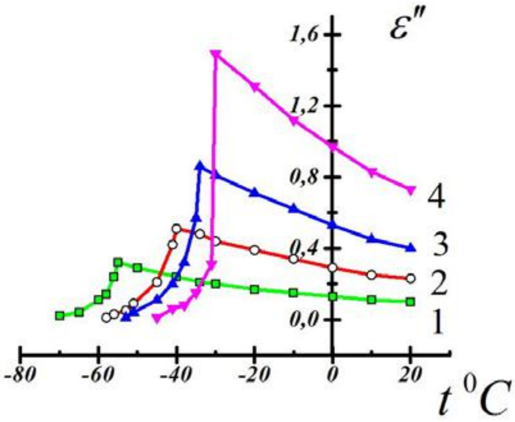

Fig. 2. Temperature dependence of dielectric losses ε'' for the bromobenzene – n-hexane system, at bromobenzene concentration in mole fractions: 1 – 0.294; 2 – 0.556; 3 – 0.745; 4 – 1.000

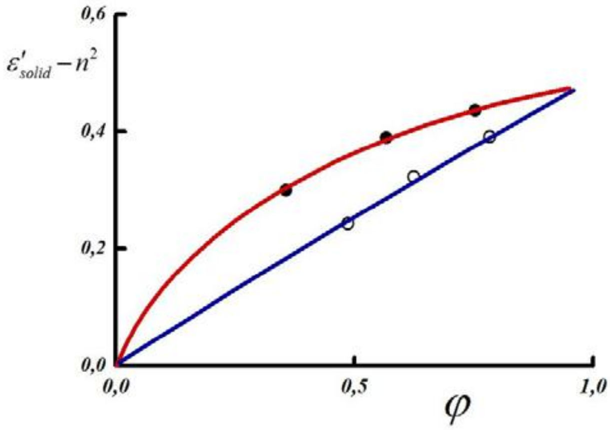

Fig. 3. Dependence of $\varepsilon_{solid}' - n^2$ for the bromobenzene – benzene (1) and bromobenzene – hexane (2) systems on the concentration expressed in mole fractions.

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

When the temperature reaches approximately –60°C, the dielectric permittivity ceases to change in almost all cases, and the contribution of orientation polarization can be considered negligible. However, as can be seen in Fig. 3, the dielectric permittivity ε_{solid}' in the solid state greatly exceeds the corresponding value of the square of the refractive index n^2 at 20°C. Since the change in density with temperature is insignificant, the difference $\varepsilon_{solid}' - n^2$ should be explained by the contribution of infrared polarization.

It is interesting to note that the high-frequency dielectric permittivity ε_∞ at 20°C, obtained from the circular diagram, also exceeds the value n^2 at all concentrations [18-20].

On the other hand, ε_{solid}' is slightly greater than ε_∞. This confirms the assumption made in [21-23] that the difference between ε_∞ and n^2 is mainly due to additional resonance-type dispersion.

Interpreting dielectric relaxation as a kinetic process makes it possible to reveal new details of the mechanism of this phenomenon. The relaxation time is expressed by the Arrhenius equation:

$$\tau = \frac{h}{kT}\, exp\left({}^{\Delta F}/_{RT}\right) \qquad (1)$$

where ΔF is the free activation energy, defined as:

$$\Delta F = \Delta H - T\Delta S \qquad (2)$$

where ΔH is the activation enthalpy, ΔS is the activation entropy, h is Planck's constant, k is Boltzmann's constant, R is the universal gas constant, and T is the absolute temperature. The value of ΔH was calculated from the slope of the dependence of ln(Tτ) on 1/T, and ΔS was calculated using equation (2).

Table 3 shows the results of the corresponding calculations. It was assumed that ε_∞ in solution changes additively.

Table 3

x_2	ΔF				$T\Delta S$				ΔH
	20^0	0^0	-20^0	-40^0	20^0	0^0	-20^0	-40^0	
Bromobenzene – benzene									
0,459	2,61	2,52	2,44	–	1,18	1,09	1,01	–	1,43
0,560	2,64	2,53	2,47	2,38	1,15	1,04	0,98	0,89	1,49
0,718	2,70	2,60	2,52	2,44	1,14	1,04	0,96	0,88	1,56
1,000	2,76	2,70	2,61	–	1,11	1,05	0,96	–	1,65
Bromobenzene - hexane									
0,294	2,36	2,26	2,16	2,08	1,30	1,20	1,10	1,02	1,06
0,556	2,49	2,38	2,31	2,23	1,24	1,13	1,06	0,98	1,25
0,745	2,60	2,50	2,43	–	1,18	1,08	1,01	–	1,42
1,000	2,76	2,70	2,61	–	1,11	1,05	0,96	–	1,65

4. CONCLUSIONS

Measurements of dielectric permittivity ε' and dielectric loss tangent ε'' were performed in bromobenzene-benzene and bromobenzene-hexane double systems at a wavelength λ = 12.8 mm in the temperature range from 293 K to 193 K. It was found that the phase transition is accompanied by a sharp decrease in ε' and ε''. Based on the temperature dependence of the relaxation time, the thermodynamic parameters of the dielectric relaxation process activation were determined: ΔF, ΔH, and ΔS. It has been shown that the nature of the solvent affects the magnitude of the potential barrier separating the two equilibrium positions of the polar bromobenzene molecule and the degree of order in the system.

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