

DIELECTRIC RELAXATION OF HALOGENATED BENZENES IN MICRO-WAVE RANGE

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The complex dielectric constants of chlorbenzene, bromobenzene and iodobenzene at wave lengths 11,5cm and 12,8cm at temperatures from 20 up to - 80 ° C are measured. The jump appears in real and imaginary parts of complex dielectric constant in the point of phase transition in all investigated liquids. The temperature dependence of time of molecule dielectric relaxation in liquid state is found. It is revealed that increase of relaxation time takes place with increase of size halogen substituent. The thermodynamic values characterizing the dielectric relaxation process are calculated. The comparison of enthalpy of activation of dielectric relaxation processes is carried out.

Keywords: molecular spectroscopy, water dielectric properties, dielectric relaxation, benzene, chlorbenzene, bromobenzene, iodobenzene.

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INTRODUCTION

The dielectric relaxation is observed in micro-wave range covering the part of electromagnetic wave spectrum by the length from 30cm up to 1mm in many polar liquids. The successful development of this range gives the premises for intensive investigation of relaxation properties. The interest to these liquids is explained by their comparative simple construction that allows us to use the existing theories for the analysis of experimental data. By data of works [1,2] there is some distribution of relaxation time decreasing with temperature increase in chlorbenzene and bromobenzene.

Later the presence of unique relaxation time is marked for the same compounds [3]. However, the high-frequency limit of ϵ_{∞} Cole-Cole diagram is bigger than square of n^2 refraction index measured in infra-red range [4]. This fact is connected with probable existing of additional absorption region of resonance character in submillimeter range. Indeed, the explicit deviations from Debye properties of fluouro-, chlor-, bromo- and iodobenzene are found at wave lengths from 7 up to 3mm that is explained by the influence of rotational spectrum and it is noted that measurement accuracy is limited [5,6]. The overshoot of index absorption experimental value ϵ'' in comparison with its calculated value by low-frequency data in the case of chlorbenzene at wave length 3mm is explained as partial conferment of Poli's hypothesis. However, it is noted in work that chlorbenzene dielectric properties at $\lambda=4,3\text{mm}$ can be calculated on the base of data obtained at longer waves [7]. These disagreements are explained by big experimental difficulties at work with very small wave lengths. In this connection the low-temperature measurement on longer waves is of a big interest.

Taking into consideration the strong dependence of second dispersion on temperature one can expect that such measurements give the some information on this phenomenon [8]. Besides, the low-temperature measurements allow us to reveal the some peculiarities of dielectric relaxation mechanism at the transition from liquid into solid state. Considering the halogenated

benzenes the all works known from reference are carried out at temperatures higher than solidification point.

The temperature dependence of complex dielectric constant of chlorbenzene, bromobenzene and iodobenzene are studied by us. The temperature interval from 20 up to - 80°C is covered.

EXPERIMENTAL PART

The measurements are carried out in assembled installation working by principle of input resistance transformation of coaxial line filled by the investigated liquid in input of measuring line [9]. The shift of voltage node in measuring line significantly increases in comparison with usual method of short-circuit line in this method because of transformation that allows us to increase the measuring accuracy of ϵ^* strongly absorbing substances [10]. The cell with the sample is thermostated and cooling rate is $\sim 0,1$ grad/min.

The inclination from average values for ϵ' don't exceed 1% and for ϵ'' don't exceed 3%. The initial liquids are treated by drying under calcined chlorbenzene, bromobenzene and iodobenzene. After drying the liquids are rectified in rectifying column. The rectification is carried out three times.

The data of temperature dependence of complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$ of chlorbenzene, bromobenzene and iodobenzene are given in table 1. The data for chlorbenzene and iodobenzene are obtained at wave length 12,80cm and data for bromobenzene are obtained at wave length 11,50cm. The phase transition of all investigated substances coincides with jump of complex dielectric constant. Further the gradual increase of ϵ' real part up to value significantly exceeding the refraction index square and decrease of ϵ'' imaginary part up to zero take place in small temperature interval after jump.

The analogous jump of dielectric constant is observed at acoustic frequencies, in particular, in bromobenzene at frequency 400Hz whereas the losses are absent in whole temperature interval [11].

Table 1

Complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$

t, °C	Chlorbenzene		Bromobenzene		Iodobenzene		t, °C	Chlorbenzene		Bromobenzene		Iodobenzene	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''		ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
Liquid state							Solid state						
20	5,60	0,54	5,17	0,82	4,38	0,67	- 31	-	-	3,05	0,38	-	-
10	5,72	0,65	5,22	0,93	4,35	0,75	- 32	-	-	3,03	0,22	3,06	0,42
0	5,83	0,78	5,31	1,09	4,27	0,84	- 35	-	-	2,93	0,16	2,98	0,22
-10	5,95	0,90	5,40	1,25	4,18	0,91	- 40	-	-	2,83	0,05	2,87	0,10
-20	6,07	1,09	5,31	1,41	4,08	0,97	- 46	3,18	0,30	2,82	-	2,85	0,03
-30	6,15	1,31	5,05	1,57	3,97	1,04	- 48	3,04	0,21	2,82	-	2,85	-
-40	6,16	1,51	-	-	-	-	- 50	2,96	0,17	2,82	-	2,85	-
-45	6,12	1,70	-	-	-	-	- 60	2,81	0,02	2,82	-	2,86	-
							- 70	2,80	-	2,83	-	2,85	-
							- 80	2,81	-	2,83	-	2,85	-

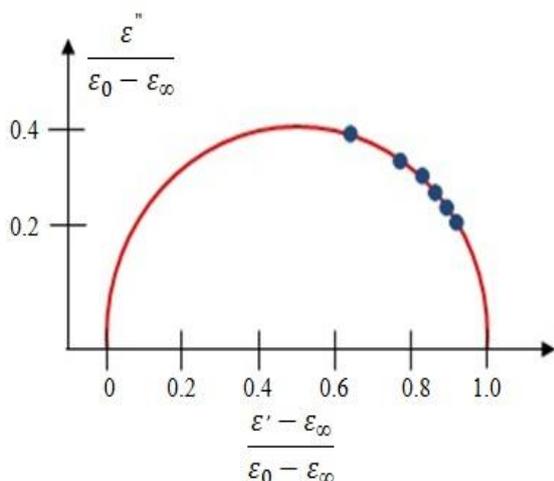


Fig. 1. The reduced diagram for bromobenzene ($\lambda=11,50$ cm).

From the table data it is seen that the peculiarities in temperature motion of complex dielectric constant

Taking into consideration data from table and notion about water structure one can conclude: the peculiarities in temperature dependence of complex dielectric constant connect with the presence of short-range order for water near solidification temperature that reveals itself in microformation form.

One can propose that molecules including in these microformations at temperature of solidification lose the freedom of rotating orientation whereas the rest molecules save it in some temperature interval below solidification point. It would be interesting to carry out the measurements in considered temperature region at more high frequencies where this transition probably reveals more clear.

The reduced diagram for bromobenzene is shown in fig.1. In the case of two other compounds the points are well marked in semicircle in abscissa axis.

This allows us to confirm that dielectric properties of all three liquids are totally successfully can be described with the help of one relaxation time up to the temperature of solidification. That's why the calculation of τ relaxation time is carried out by the formula:

$$\tau = \frac{1}{\omega} \frac{\epsilon''}{\epsilon' - \epsilon_\infty} \quad (1)$$

where ω is circular frequency of applied field. The relaxation time defined by formula (1) is the macroscopic one in the comparison from microscopic and molecular τ_u relaxation times. The connection between them has the form $\tau = \gamma\tau_u$ where γ characterizes the inner field influence and depends on expression choice for the last one. Considering the inner field by Onsager we obtain the expression for γ :

$$\gamma = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \quad (2)$$

γ values calculated by formula (2) are given in first column of table 2. It is seen that practical γ value doesn't change with temperature and consequently, macroscopic and molecular relaxation times differ only by multiplicative constant. The knowing of temperature dependence of relaxation time gives the possibility to define the thermodynamic value characterizing the mechanism of dielectric relaxation process.

The consideration of polar molecular relaxation process as its transition from one equilibrium position into another one by the way of overcoming of energy barrier in theory of absolute velocities leads to the following expression:

$$\Delta F = 2,303 RT \lg (2,08 \cdot 10^{10} \tau T), \quad (3)$$

where ΔF is free activation energy.

Using the known thermodynamic ratio $\Delta F = \Delta H - T\Delta S$ and accepting ΔH activation enthalpy as constant one in considered temperature interval, its value can be defined from line inclination $\lg(\tau T) = \Phi(1/T)$ (fig. 2) by formula

$$\Delta H = 2,303 R \frac{d(\lg \tau T)}{d(1/T)} \quad (4)$$

The transition of activated molecule through energy barrier is accompanied by its bond breakage with neighbor molecules that is characterized by ΔH activation enthalpy value. As it is seen ΔF and ΔH increase with

increase of molecule size, moreover ΔH in all three cases is less than ΔF that leads to negative sign of ΔS activation entropy.

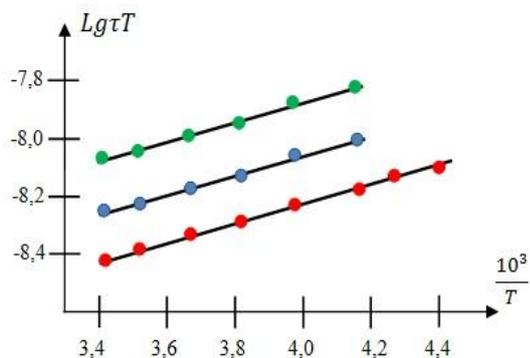


Fig. 2. Temperature dependence τT : 1(red) is chlorobenzene, 2(blue) is bromobenzene, 3(green) is iodobenzene.

One can conclude that the phenomenon of dielectric polarization in studied liquids increases the degree of order in molecule disposition.

The additional information on dielectric relaxation can be obtained by the way of comparison of activation enthalpy value with corresponding data for viscous flow. From table 4 it is followed that ΔH_B activation enthalpy values defined from viscous measurements, exceed ΔH_D values for dielectric relaxation.

This can be quantitatively explained because of the fact that molecule makes the translation and rotational movements whereas it only rotates in dielectric relaxation process. However, as it is seen from table 4, the tendency to $\Delta H_B - \Delta H_D$ difference decrease is observed because of size increase of exchanging halogen. This probably shows the fact that the molecule rotational movement is also accompanied by translational movement with increase of its asymmetry.

Table 2

γ multiplier taking under consideration the inner field;
 τ macroscopic and τ_μ molecular relaxation times ($\tau \cdot 10^{11}$ сек.)

$\tau, ^\circ\text{C}$	Chlorobenzene			Bromobenzene			Iodobenzene		
	γ	τ	τ_μ	γ	τ	τ_μ	γ	τ	τ_μ
20	1,23	1,20	0,98	1,21	1,95	1,61	1,16	2,81	2,43
10	1,23	1,43	1,17	1,21	2,27	1,88	1,16	3,23	2,80
0	1,23	1,67	1,36	1,21	2,58	2,13	1,16	3,83	3,31
-10	1,24	1,86	1,50	1,22	2,85	2,35	1,16	4,45	3,85
-20	1,24	2,20	1,77	1,22	3,38	2,77	1,16	5,15	4,44
-30	1,25	2,61	2,10	1,22	4,22	3,45	1,17	6,05	5,20
-40	1,25	3,02	2,41	—	—	—	—	—	—
-45	1,25	3,44	2,75	—	—	—	—	—	—

Table 3

Activation enthalpy for ΔH_B viscous flow and dielectric relaxation ΔH_D (kcal/mol)

Substance	ΔH_B	ΔH_D	$\Delta H_B - \Delta H_D$
Chlorobenzene	1,61	1,49	0,12
Bromobenzene	1,72	1,65	0,07
Iodobenzene	1,82	1,79	0,03

ΔH values are given in table 3, values are given in table 3 and ΔF values are given in table 4.

Table 4

Free activation energy ΔF (kcal/mol)

$\tau, ^\circ\text{C}$	ΔF		
	Chlorobenzene	Bromobenzene	Iodobenzene
20	2,50	2,79	3,00
10	2,49	2,74	2,95
0	2,47	2,71	2,93
-10	2,42	2,64	2,88
-20	2,39	2,61	2,82
-30	2,37	2,60	2,77
-40	2,31	—	—
-45	2,32	—	—

CONCLUSION

The complex dielectric constant of chlorbenzene, bromobenzene and iodobenzene at wave lengths 11,50 and 12,80cv in interval from 20 up to 80°C is measured.

The jump of real and imaginary parts of complex dielectric constant is observed for all investigated liquids in phase transition point. ϵ' decrease up to value significantly exceeding the refraction index square and ϵ'' decrease up to zero take place after jump in small

temperature interval.

The temperature dependence of dielectric relaxation time for molecules in liquid state is defined.

The thermodynamic values characterizing the dielectric relaxation process are calculated. The comparison of activation enthalpy for processes of dielectric relaxation and viscous flow is carried out. The tendency to decrease of enthalpy difference for both processes is revealed with asymmetry increase.

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