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Investigation of the temperature dependence of the dielectric relaxation of chlorobenzene, bromobenzene and iodobenzene

This paper deals with the investigation results of temperature dependence of complex permittivity's$\varepsilon^* = \varepsilon' - i\varepsilon''$ of chloro, bromo and iodo- benzene at wavelength 11,50 cm and 12,80 cm within the temperature range 20 ÷ -80˚. It is established that dielectric properties of given liquids are characteristic of one relaxation time. The dielectric spectra were studied taking into account other frequencies given in the literature. In all investigated liquids, a jump appears in the real and imaginary parts of the complex permittivity at the point of the phase transition. The temperature dependence of the dielectric relaxation time of molecules in the liquid state has been determined. It was found that with an increase in the amount of the halogen substituent, an increase in the relaxation time occurs. Macroscopic and molecular relaxation times were calculated from the experimental values. The thermodynamic quantities characterizing the process of dielectric relaxation are calculated. The activation enthalpy of dielectric relaxation processes is compared. The studies were carried out using the dielectric spectroscopy method. This method allows a more detailed study of the dielectric properties of the objects of study due to the large equilibrium ("static") dielectric constant of the object. It has been determined that the height of the potential barrier separating the two equilibrium positions of a polar molecule is greatest in the state of a pure polar liquid and decreases with dilution in a non-polar solvent.

Keywords: dielectric spectroscopy, complex dielectric constant, dielectric properties, benzene, bromobenzene, chlorobenzene, iodo-benzene.

Introduction

The study of the dielectric properties of polar liquids is one of the most fundamental and complex problems of science, which is of great theoretical and practical importance. Interpretation of experimental data on dielectric relaxation presents difficulties for substances that are characterized by the presence of intramolecular interactions, hydrogen bonds and other complicating factors. Therefore it is advantageous to investigate rather elementary molecules. At the moment, the central place in the works involved in the study of intermolecular interactions in liquids is occupied by studies of the molecular structure of a liquid and the dynamics of its transformation during thermal motion. 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 [2-3]. Studies of the dielectric properties of polar liquids make it possible to obtain extensive information about their molecular structure, intermolecular interactions, information about thermodynamic parameters, mechanisms of molecular processes, as well as the process of absorption of electromagnetic radiation. According to the available literature the investigation results of relaxation phenomena observed in microwave range are rather limited and often-contradicted. In particular by data [4–7] in benzene halogen derivatives the distribution of relaxation time is taken place. Yet the results [8–11] are indicative of presence of one relaxation time. On the base of experimental data analysis the conclusion has been confirmed by probable presence of additional dispersion region at millimetric waves in benzene halogen derivatives.

Various molecular associations are determined in terms of relaxation time τ and dipole moment μ to estimate different molecular interactions among polar molecules or polar-non-polar molecules. Thermodynamic energy parameters are also calculated using Eyring's rate theory to predict molecular dynamics or nature of molecular environment surrounding the polar molecules DMF, DMA or phenol (p-cresol, p-chlorophenol, 2,4dichlorophenol and p-nitrophenol). The existence of the Debye relaxation mechanism in all the systems under observation is validated by the estimated Debye factor from both of the measurement methods [15].

Various molecular associations are determined in terms of relaxation time s and dipole moment l in polar-non-polar liquid mixture. Thermodynamic energy parameters are also calculated from Eyring rate theory to predict molecular dynamics or nature of molecular environment surrounding the polar molecule TBP. Debye relaxation mechanism in all the systems under observation is validated by the estimated Debye factor from both the measurement methods. A new simple microwave sensor is proposed to design for determination of TBP concentration from measured penetration depth at different temperatures under microwave field [16].

The study of the anomalous dispersion of the permittivity of liquids and the strong absorption of electromagnetic energy associated with it makes it possible to judge the nature of intermolecular forces and the molecular structure of polar liquids [12–14].

The anomalous dispersion of polar liquids is determined by the relaxation time τ, which characterizes the process of polarization in a dielectric when an external field is applied. The relaxation time is related to the frequency of the maximum absorbed wave ωm by the condition.

Exsperimental

The polar liquids chlorobenzene, bromobenzene, and iodobenzene (United States, Keysight Technologies) were chosen as the objects of study. Measurements are carried out by method suggested and on assembled installation [3–5] which allows the complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ of highly absorbed substances to be determined.

The short-circuited line method [3–6] uses the relationship between the input impedance Z_0 and the complex propagation constant γ of a line filled with a dielectric. Since the value of γ, in turn, is related to the complex permittivity ε*, by measuring the value of Z_0, one can find the value of the complex permittivity ε*.

$$\gamma = \alpha + i\beta = i\omega(\varepsilon * \mu *)^{\frac{1}{2}}, \tag{3}$$

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, $\mu*$ is the complex magnetic permeability. Taking $\mu* = 1$, we get:

$$\varepsilon* = \varepsilon' - i\varepsilon'' = \frac{\gamma\lambda_1}{2\pi}. \tag{4}$$

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

$$\frac{\mathrm{th}\gamma d}{\gamma d} = -i\frac{\lambda_1}{2\pi d}\frac{Z_0}{Z_1}, \tag{5}$$

where d is the thickness of the dielectric, Z_1 is the wave impedance 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 displacement of the node y1 of the standing wave, due to the introduction of a dielectric into the line before the short circuit:

$$Z_0 = Z_1\frac{q - i\,tg\beta_0 y_1}{1 - iq\,tg\beta_0 y_1}, \tag{6}$$

here $\beta_0 = \frac{2\pi}{\lambda_1}$.

It should be noted that in the case of small and medium losses (tgδ< 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 (tgδ> 0,l), the sample thickness has to be taken so small that it itself becomes a source of noticeable errors. Another disadvantage is the extreme sensitivity of the detector part of the equipment to temperature fluctuations, which seriously complicates temperature measurements. Both of these shortcomings can be eliminated in a new modification of the method [5]. The essence of this modification is that the input impedance of a short-circuited line filled with a dielectric is transformed into a measuring line in such a way that optimal conditions for measurements are created. By measuring the transformed impedance, by the known transformation coefficient, the required input impedance of the line filled with a dielectric is found [3, 4, 6]. Measurements are made out over a wide temperature range. Mean deviation for values ε' does not exceed 1%, for values ε'' is 3%. It should be noted that dielectric properties of abovementioned liquids at low temperatures are not clearly investigated.

The essence of the novelty of the proposed method is that the input impedance of a short-circuited line filled with a dielectric is transformed into a measuring line in such a way that optimal conditions for measurements are created. By measuring the transformed impedance, using a known transformation coefficient, the desired input impedance of the line filled with a dielectric is found.

The method proposed in the article can be used in the microwave range and in the temperature range corresponding to the condition of phase transition from the liquid state of the solutions under study to the solidification phase of the solutions under study.

Result and Discussion

In present paper there have been given investigation results of dielectric relaxation of three benzene halogen derivatives (C_6H_5C1, C_6H_5Br, C_6H_5J) at wave length 11,50 cm and 12,80 cm within the temperature range 20 ÷ -80˚C. Temperature range is effective in liquid phase as well as in solid one of liquids under investigation.

In Figure 1 and 2 there have been shown the data of temperature dependence of real ε' and imaginary ε'' parts of complex dielectric constant ε^* for chlorobenzene, bromobenzene and iodo-benzene. Curve graphs for chlorobenzene and iodo-benzene have been obtained at wavelength 12,80 cm. Curve diagrams for bromobenzene have been obtained at wavelength 11,50 cm.

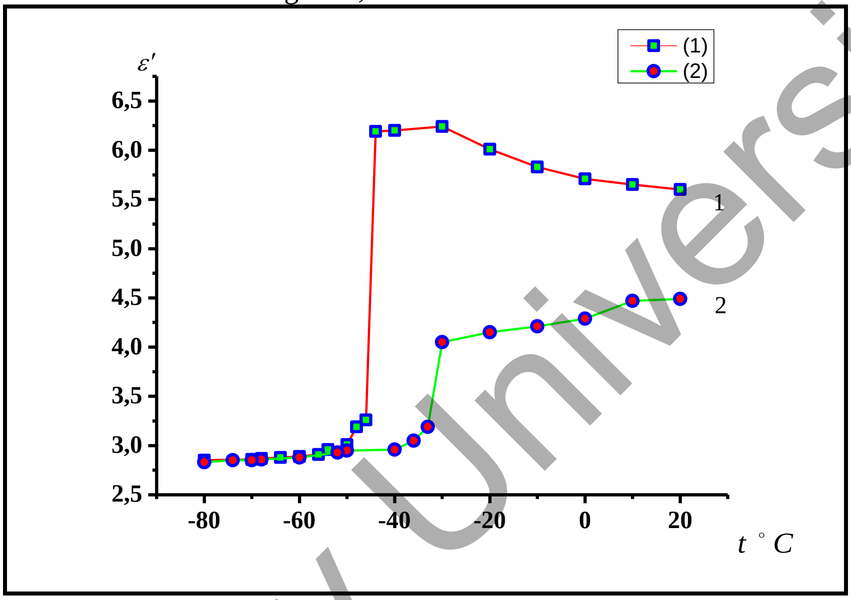

Figure 1. Temperature dependence of dielectric constant ε', 1 is the chlorobenzene; 2 is the iodo-benzene

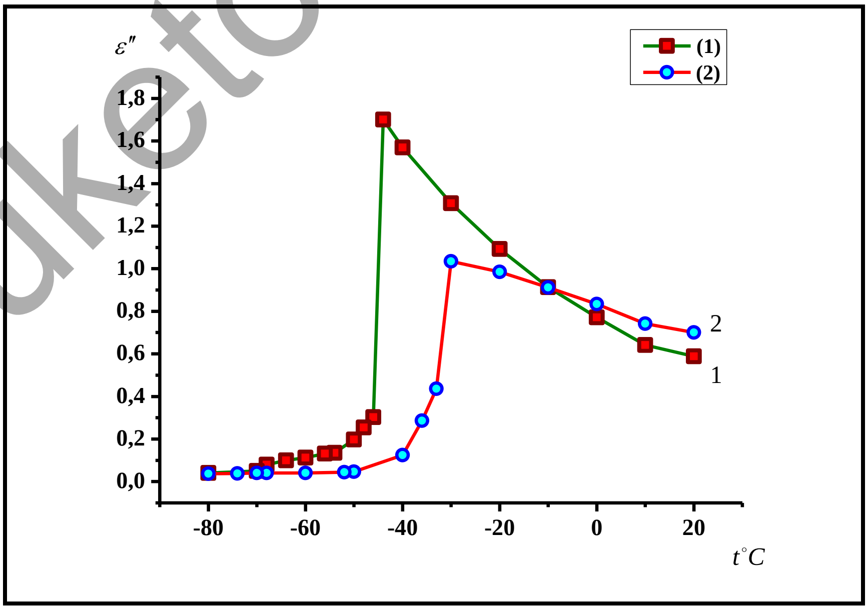

Figure 2. Temperature dependence of absorption coefficient ε'', 1 is the chlorobenzene; 2 is the iodo-benzene

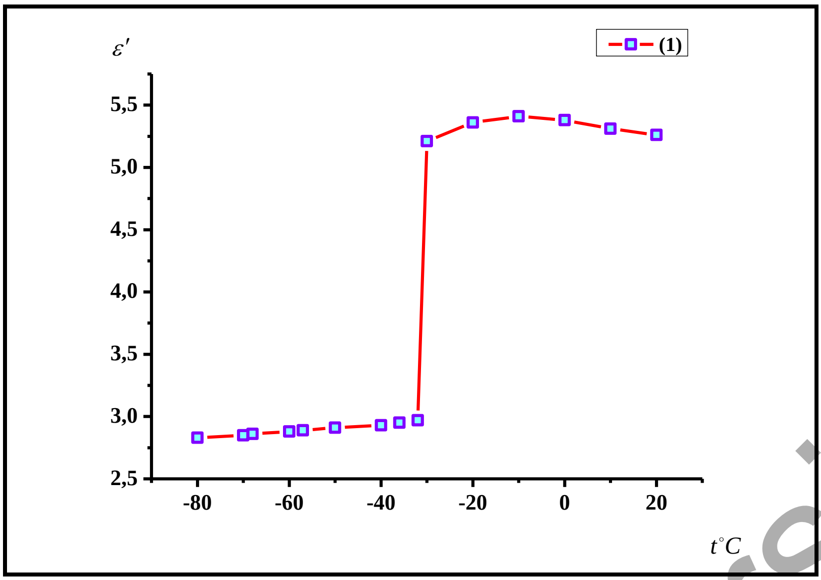

Figure 3. Temperature dependence of dielectric constant ε' is the bromobenzene

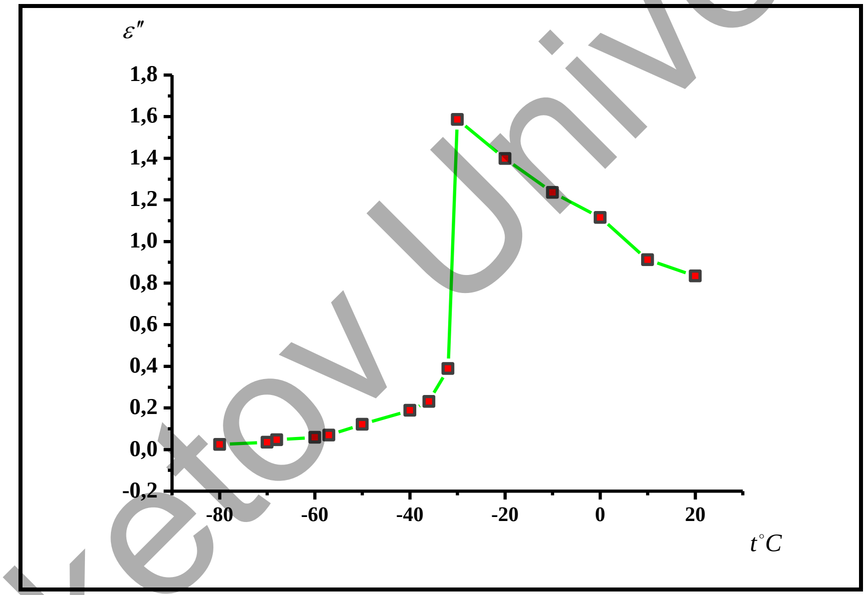

Figure 4. Temperature dependence of absorption coefficient ε'' is the bromobenzene

For all substances under examination the phase transition agrees with the complex dielectric constant jump ε^*. In this case the constant value ε' settles at several degrees after transition (Fig. 3). Dielectric loss is retained at the same range which is observed both by cooling and by heating objects under study. Mentioned pecularities of temperature change of complex dielectric constant values ε^* may be attributed to the liquid structure. According to them close to the hardening temperature the clusters of molecule groups have been occurred (Fig. 4). It is evident that after hardening the dielectric properties over a given temperature ranges are determined by isolated molecules not included in these clusters. While attaching to the clusters the orientation part of polarization is avoided.

Figure 5 illustrates reducible iodo-benzene diagram. In case of chlorobenzene and bromobenzene the diagrams have a similar type. Values ε_0 and ε_∞ have been taken from literature and extrapolated [5].

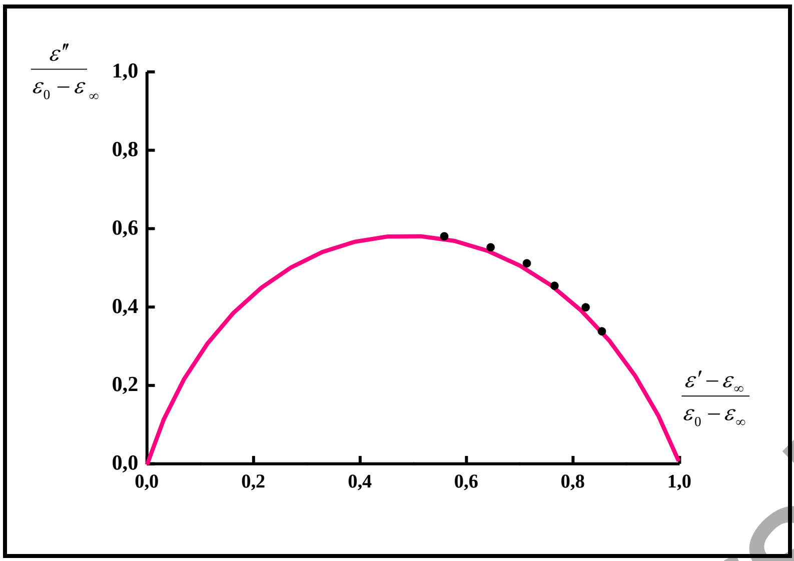

Figure 5. Reducible iodo-benzene diagram

It is seen from the diagram that dielectric properties up to the transition temperature is characteristic of one relaxation time. Therefore relaxation time values have been calculated by the familiar Debye formula. It should be noted that the factor providing for the presence of internal field is taken to be equal a unit. In this case this factor is practically independent of the temperature. Consequently obtained values can be used for interpretation of dielectric relaxation temperature change.

If we suppose that dipole molecule orientation is carried out by its transition through potential barrier separating two equilibrium position of molecules the relaxation time is defined as follows [6]:

$$\tau = exp\frac{U}{RT}(1),$$

where U is the activation energy, R is the Boltzmann constant, T is the temperature. We note that activation energy can be evaluated from slope of the dependence $ln\tau$ on $\frac{1}{T}$.

Table lists the appropriate values of activation energy. There have been presented energy magnitudes established by scattering line width growth values for comparison [7].

Table

Substance	Activation energy kcal /mol	
	Dielectric measurements	Measurements of scattering line width growth values
Chlorobenzene	1,9	2,1
Bromobenzene	2,1	2,3
Iodo- benzene	2,3	2,4

Conclusions

The paper presents a new modification of the short-circuited line method, with the help of which it is possible to study the temperature dependence of the complex permittivity of polar liquids in the microwave range. This method is based on the transformation of the input resistance of a short-circuited line filled with the liquid under study. Data on the temperature dependence of the complex permittivity ε* of chlorobenzene, bromobenzene and iodo-benzene in the range of –80°C ÷ +20°C at a wavelength of 11.5 cm are presented. When passing through the solidification point of these liquids, a sharp change in the value of the complex permittivity ε* was found. The value of the relaxation time over the entire temperature range and the activation energy for the molecules of liquid chlorobenzene, bromobenzene, and iodo-benzene are found. As a result of pursuance of research we can state that in all cases the activation energy for dielectric relaxation have the values rather close to the values established by scattering line width growth.

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С. Азизов

Хлорбензол, бромбензол және йодбензолдың диэлектрлік релаксациясының температураға тәуелділігін зерттеу

Жұмыста 20÷-80 температура аралығындағы 11,50 және 12,80 см толқын ұзындығындағы хлор, бром және йодбензолдың ε^*=ε^́-iε^″ күрделі диэлектрлік өткізгіштіктерінің температураға тәуелділігін зерттеу нәтижелері келтірілген. Бұл сұйықтықтардың диэлектрлік қасиеттері бір релаксация уақытына тән екендігі белгілі болды. Диэлектрлік спектрлер әдебиетте келтірілген басқа жиіліктерді ескере отырып зерттелді. Зерттелген барлық сұйықтықтардың фазалық ауысу нүктесінде күрделі диэлектрлік өткізгіштіктің нақты және болжалды бөліктерінің секірісі пайда болады. Сұйық күйдегі молекулалардың диэлектрлік релаксация уақытында температураға тәуелділігі анықталды. Галоген алмастырғыш мөлшерінің жоғарылауымен релаксация уақытының ұзақтығы арта түсетіні айқындалды. Тәжірибелік мәндерден макроскопиялық және молекулалық релаксация уақыттары табылды. Диэлектриктердің релаксациялану процесін сипаттайтын термодинамикалық шамалар есептелген. Диэлектриктердің релаксация процестерінің активтену энтальпиясы салыстырылды. Зерттеулер диэлектрлік спектроскопия көмегімен жүргізілді. Бұл әдіс объектінің үлкен тепе-теңдік («статикалық») диэлектрлік өтімділігіне байланысты зерттеу объектілерінің диэлектрлік қасиеттерін егжей-тегжейлі зерттеуге мүмкіндік береді. Полярлы молекуланың екі тепе-теңдік жағдайын бөлетін потенциалдық тосқауылдың биіктігі таза полярлы сұйықтық күйінде ең үлкен және полярсыз еріткішпен сұйылтылғанда ең төмен болатыны нақтыланды.

Кілт сөздер: диэлектрлік спектроскопия, күрделі диэлектрлік өтімділік, диэлектрлік қасиеттер, бензол, бромбензол, хлорбензол, йодбензол.

С. Азизов

Исследование температурной зависимости диэлектрической релаксации хлорбензола, бромбензола и йодбензола

В работе представлены результаты исследования температурной зависимости комплексных диэлектрических проницаемостей ε^*=ε^́-iε^″ хлора, брома и йодбензола на длинах волн 11,50 и 12,80 см в интервале температур 20÷–80˚. Установлено, что диэлектрические свойства данных жидкостей характерны для одного времени релаксации. Диэлектрические спектры изучались с учетом других частот, приведенных в литературе. Во всех исследованных жидкостях возникает скачок действительной и мнимой частей комплексной диэлектрической проницаемости в точке фазового перехода. Определена температурная зависимость времени диэлектрической релаксации молекул в жидком состоянии. Установлено, что с увеличением количества галогенового заместителя возрастает продолжительность времени релаксации. Время макроскопической и молекулярной релаксации определяли по экспериментальным значениям. Рассчитаны термодинамические величины, характеризующие процесс диэлектрической релаксации. Сравнивалась энтальпия активации процессов диэлектрической релаксации. Исследования проводились методом диэлектрической спектроскопии. Данный метод позволяет детально изучить диэлектрические свойства объектов исследования благодаря большой равновесной («статической») диэлектрической проницаемости объекта. Установлено, что высота потенциального барьера, разделяющего два положения равновесия полярной молекулы, наибольшая в состоянии чистой полярной жидкости и наименьшая при разбавлении неполярным растворителем.

Ключевые слова: диэлектрическая спектроскопия, комплексная диэлектрическая проницаемость, диэлектрические свойства, бензол, бромбензол, хлорбензол, йодбензол.

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