# DIELECTRIC RELAXATIONS OF CHLORBENZENE-BENZENE AND CHLORBENZENE-N-HEXANE SOLUTIONS

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The measurement results of dielectric constant ε' and absorption coefficient ε″ obtained for concentrated solutions chlorbenzene-benzene, chlorbenzene-n-hexane at wave lengths λ = 12,80 and λ = 3,26 *cm* at temperature 20°C are given in the article. The static dielectric constant is obtained at frequency 1MHz. The obtained experimental values ε',ε″ and ε₀ of investigated systems in (ε',ε″) plane locate on the semi-circle the center of which is on ε' axis. In this case the high-frequency limit value of $\varepsilon_\infty$ dielectric coefficient exceeds the corresponding $n^2$ refraction index square. The macroscopic and molecular relaxation times are calculated on the base of experimental data.

## INTRODUCTION

The increased values of dielectric relaxation times in comparison with their values in diluted solutions are usually observed in pure dipole liquids. If in the first case the relaxation process is the cooperative one, then the relaxation time characterizes the separate molecule in diluted solutions. In this connection the investigation of dielectric relaxation dependence on polar molecule concentration is of great interest.

On the example of carried out double system investigations one can confirm that the concentration dependence of $\tau$ relaxation time ratio to $\eta$ viscosity can be used for the evaluation of clusterization degree of polar molecules [1]. As a result, one can define the special relaxation mechanism in the case of concentration solutions of some cyclohexane derivatives in nonpolar solvents [2].

In some works, [3 – 5] the explanation of dielectric properties of some systems in micro-wave range on the base of perception on concentration fluctuation, is given.

In present work the investigation results of dielectric relaxation of chlorbenzene-benzene, chlorbenzene-n-hexane in microwave range are presented. The data of dielectric relaxation is expanded on the region of investigated concentration solutions.

The dielectric constant ε' and absorption coefficient ε″ of double systems chlorbenzene-benzene, chlorbenzene-n-hexane in total concentration interval are measured at wave lengths λ = 12,80 and λ = 3,26 *cm* at temperature 20°C. Besides, the static dielectric constant of these systems in total concentration interval at frequency 1MHz and temperature 20°C is measured.

## EXPERIMENT TECHNIQUE

The data at λ = 12,80 *cm* are obtained by the method described in [6]. In the comparison with the known method Roberts-Hippel [7] consisting in measurement of input impedance of short-circuit transmission line filled by investigated dielectric, in the given method the transformation of this impedance on

measuring line input is carried out in such way that the optimal measurement conditions in the case of strongly absorbing substances are formed. The deviations from average values are 1% for ε' and 3% for ε″.

The method [8] which leads to measurement of standing-wave factor dependence on height of liquid column short-circuit waveguide is applied at wavelength λ =3,26 *cm*. The deviations from average values don't exceed 1% for ε' and 2% for ε″.

The measurements at frequency 1MHz are carried out on Q-meter. The deviations from average values are less than 1%.

## RESULTS AND THEIR DISCUSSION

The measurement results of ε' dielectric constant, $\varepsilon''$ absorption coefficient and static dielectric constant ε₀ for the studied systems are given in tables 1,2. Further, there are values of $\tau_M$ macroscopic and $\tau_\mu$ molecular relaxation times. The polar component concentration in mole percent is designated by x.

$\tau_M$ calculation is carried out on the following formulas:

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

$$\tau_M = \frac{1}{\omega}\ \frac{\varepsilon_0 - \varepsilon'}{\varepsilon''} \tag{2}$$

where ω is circular frequency of applied field.

$\tau_M$ values, obtained by above mentioned two formulas, well agree in 3 – 5% limits and only in several cases at very small difference ε₀ – ε,' the values defined by (2) more deviate from average values. That's why one can suppose that the values of high-frequency dielectric constant $\varepsilon_\infty$ given in tables 1,2 are real ones. Note that $\varepsilon_\infty$ value in all cases for the pure polar component exceeds the corresponding $n^2$ refraction index square. The difference $\varepsilon_\infty - n^2$ monotonously decreases as far as dilution of solution. These results well agree with data of [9] in which the analogous phenomena in solutions of halogenated benzene are observed. The supposition on presence of additional absorbing region of resonance character at

more high frequencies is made on the base of these data. Such proposition is enough proved only in the case of overlapping of bigger frequency interval and first of all of the submillimeter range. The low-temperature measurements can be the additional information source.

Table 1

| | | | chlorbenzene-benzene | | | | | |
|---|---|---|---|---|---|---|---|---|
| x | $\varepsilon_0$ | $\varepsilon_\infty$ | $\lambda$=12,80 cm | | $\lambda$=3,26 cm | | $\tau_M \cdot 10^{11}$sec | $\tau_\mu \cdot 10^{11}$ sec |
| | | | $\varepsilon'$ | $\varepsilon''$ | $\varepsilon'$ | $\varepsilon''$ | | |
| 0,000 | 2,28 | 2,28 | 2,28 | – | 2,28 | – | 0,87 | 0,87 |
| 0,179 | 3,07 | 2,34 | 3,06 | 0,10 | 2,90 | 0,31 | 0,95 | 0,88 |
| 0,368 | 3,84 | 2,40 | 3,81 | 0,22 | 3,45 | 0,64 | 1,05 | 0,92 |
| 0,567 | 4,60 | 2,46 | 4,54 | 0,35 | 3,97 | 0,98 | 1,14 | 0,96 |
| 0,778 | 5,20 | 2,52 | 5,12 | 0,45 | 4,34 | 1,25 | 1,19 | 0,99 |
| 1,000 | 5,70 | 2,58 | 5,60 | 0,54 | 4,63 | 1,47 | 1,25 | 1.02 |

Table 2

| | | | chlorbenzene-n-hexane | | | | | |
|---|---|---|---|---|---|---|---|---|
| x | $\varepsilon_0$ | $\varepsilon_\infty$ | $\lambda$=12,80 cm | | $\lambda$=3,26 cm | | $\tau_M \cdot 10^{11}$sec | $\tau_\mu \cdot 10^{11}$ sec |
| | | | $\varepsilon'$ | $\varepsilon''$ | $\varepsilon'$ | $\varepsilon''$ | | |
| 0,000 | 1,89 | 1,89 | 1,89 | – | 1,89 | – | 0,60 | 0,60 |
| 0,243 | 2,63 | 2,03 | 2,62 | 0,06 | 2,57 | 0,21 | 0,68 | 0,63 |
| 0,461 | 3,40 | 2,16 | 3,38 | 0,14 | 3,20 | 0,46 | 0,77 | 0,68 |
| 0,658 | 4,15 | 2,31 | 4,12 | 0,24 | 3,76 | 0,77 | 0,88 | 0,75 |
| 0,837 | 4,92 | 2,44 | 4,86 | 0,38 | 4,24 | 1,11 | 1,07 | 0,89 |
| 1,000 | 5,70 | 2,58 | 5,60 | 0,54 | 4,63 | 1,47 | 1,25 | 1.02 |

Table 3

| system | $\gamma$ on formula (3) | $\gamma$ on formula (4) | $\gamma$ on formula (5) |
|---|---|---|---|
| chlorbenzene-benzene | 1.17 | 1.17 | 1.17 |
| chlorbenzene-n-hexane | 0,83 | 1,67 | 1,23 |

The molecule orientation is lightened at solution dilution. The transition from $\tau_M$ to $\tau_\mu$ leads to the insignificant quantitative changes. It is known that the difference between $\tau_M$ and $\tau_\mu$ is in the fact that so-called "inner field" existing in pure dipole liquids significantly decreasing as far as dilution in nonpolar solvents, is taken under consideration at $\tau_M$ definition. $\tau_\mu = \tau_M$ can be accepted at infinite dilution.

That's why one can use $\tau_M$ values in pure liquid and extrapolated ones to infinite dilution for finding of $\gamma$ multiplier taking under consideration the inner field in pure polar liquid. We use the relation from [10]:

$$\gamma = \frac{\tau_M}{\tau_\mu} = \frac{\tau_{M_1} \eta_2}{\tau_{M_2} \eta_1} \qquad (3)$$

where $\eta$ is liquid viscosity, index1 corresponds to pure liquid, index 2 corresponds to infinite dilution in nonpolar solvent.

By other side, the theoretical expression for $\gamma$ value has the following form:

$$\gamma = \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2} \qquad (4)$$

$$\gamma = \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty} \qquad (5)$$

The results of corresponding calculations are given in table 3.

From the table, it is followed that Debye expression for $\gamma$ significantly deviates from experimental data. The comparably best agreement takes place at the use of formula (5) by which $\tau_\mu$ values given in table 1,2.

The divergences in n-hexane case are probably connected with the direct proportionality between relaxation time and viscosity. Indeed, if the viscosity of n-hexane in 2,5 times less than chlorbenzene one, then $\tau_\mu$ changes only in 1,7 times. By other side, the benzene viscosity is less in 1,24 times than chlorbenzene one, whereas $\tau_\mu$ decreases in 1,16 times. If we consider that extrapolation is associated with some error, then we should recognize the presence of proportionality between $\tau$ and $\eta$ values in benzene solution. According to solution in n-hexane, then the molecule mobility is less than one can expect proceeding of viscosity changes. This is proved by the fact that double viscosity decrease is accompanied by 30% $\tau_\mu$ decrease for chlorbenzene at transition from benzene to n-hexane. It is significant that the deviations from proportionalities between $\tau$ and $\eta$ values are weak ones at significant concentrations of polar molecules.

**CONCLUSION**

At wave lengths λ = 12,80 and λ = 3,26 *cm* and temperature 20°C the dielectric constant ε' and absorption coefficient *ε″* of double system chlorbenzene-benzene, chlorbenzene-n-hexane are measured.

The values of macroscopic and molecular relaxation times are calculated on the base of experimental data. The possibility of existence of additional absorption region at more high frequencies is noted. The dependence of relaxation process on viscosity and also on sizes and forms of solvent molecules is investigated.

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