# THE INVESTIGATION OF EQUILIBRIUM AND DYNAMIC CHARACTERISTICS OF DIELECTRIC POLARIZATION OF CHLOROBENZENE $- n -$ BUTYL ALCOHOL SOLUTION

## S.T. AZIZOV, G.M. ASKEROV

*AZ 1143, H.Javid, ave.,33, ANAS Institute of Physics, Baku, Azerbaijan*
*e – mail: samir_azizov@mail.ru*

The investigation data of equilibrium and dynamic characteristics of dielectric polarizations, the measurement results of dielectric constant ε' and absorption index ε" of chlorobenzene - n – butyl alcohol system, are given in the article. The measurements are carried out on the frequencies 0,008; 0,04; 0,20; 0,50; 1,5; 5,0; 7,5 MHz at temperature from 20 up to -150° C; 25; 50; 500; 1000; 3000; 7500; 14000 MHz at temperature from 20 up to – 40°C at alcohol content in mole percent x = 0,000; 0,270; 0,526; 0,769; 1,000.

## INTRODUCTION

The equilibrium and dynamic characteristics of dielectric polarization of chlorobenzene - n – butyl alcohol system are investigated in the work. The structure of studied solutions higher liquidus line is characterized by strong micro-heterogeneity which is formed in the presence of open hydrogen-bounded chains from alcohol and chlorobenzene molecules. The molecular movement in liquid solutions in interval liquidus-solidus differs by high clusterization. The devitrification phenomenon with following spontaneous crystallization is revealed at temperatures below the solidus line.

## EXPERIMENTAL PART

The dielectric constants ε' and solution absorption coefficient ε" of chlorobenzene - n – butyl alcohol system are measured on frequencies 0,008; 0,04; 0,20; 0,50; 1,5; 5,0; 7,5 MHz in temperature interval from 20 up to –150° C and also on frequencies 25; 50; 500; 1000;3000;7500;14000 MHz in temperature interval from 20 up to – 40°C at content of butyl alcohol in mole percent x = 0,000; 0,270; 0,526; 0,769; 1,000. The equilibrium dielectric constants ε_o are defined at twelve concentrations in temperature interval $20 \div$ – 150°C. The low-frequency measurements are carried out at big

absorption by the method of inductively bounded contours [1]. The short-circuited line method is used in decimeter range, the variable thickness method [2] is used in centimeter range. The error of ε_o, ε' and ε" values is averagely ±1%. The contribution of conduction dielectric loss in total absorption is taken under consideration at low frequencies.

The cooling is carried by liquid nitrogen. The measurements are carried out at continuous heating with velocity less 0,1 grad/min. The temperature is maintained by thermostat on super-high frequencies. The sample temperature is measures by thermocouple. Thermocouple error is less $\pm$ 0,3°.

## RESULT DISCUSSION

The preliminary data and interaction character between system components can be obtained from state diagram. The temperature variation of ε_o is obeyed to linear dependence in liquid state where components are mixed unlimitedly:

$$\varepsilon_0 = A + \frac{B}{T} \qquad (1)$$

The values of A and B constants for some concentrations **x** are given in table 1:

Table 1

| x | 0 | 0,109 | 0,270 | 0,426 | 0,526 | 0,625 | 0,769 | 1,00 |
|---|---|---|---|---|---|---|---|---|
| A | 1,58 | 1,32 | −1,20 | −11,2 | −14,3 | −15,2 | −17,5 | −18,6 |
| $10^{-3} \cdot B°C$ | 1,22 | 1,38 | 2,35 | 5,65 | 7,00 | 7,82 | 9,20 | 10,8 |

At addition of chlorobenzene to alcohol the derivative $\frac{\partial \varepsilon_0}{\partial(1/T)}$ firstly decreases relatively slowly and it strongly decreases below values **x** ~ 0,4. Especially in this concentration region there are the most inclinations ε_0 from additivity. The discussion of inclination reasons from additivity can be considered in terms of equilibrium orientational polarization. According to Kirkwood - Frohlich we have:

$$P = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \qquad V = \frac{4\pi N \mu_0^2}{9kT} g \qquad (2)$$

where $\varepsilon_\infty$ is dielectric constant caused by electronic and atomic contributions in polarization, $\mu_0$ is dipole moment of isolated molecules, V is molar volume, N is Avogadro number, g is correlation parameter taking under consideration the short-range forces. For aliphatic alcohols the model of hydrogen-bounded molecular chains of alternative length with limited

rotation round the bounds of molecular chains [3,4], allows us to describe the observable temperature variation of g parameter. The small g parameter values at high temperatures are caused by decrease of length of molecular chains under influence thermal motion and big g parameter values at low temperatures are caused by increasing rotation slow at which the orientational correlation of neighbor dipoles becomes more effective one.

Within the framework of this model the dilution of $n$ – butyl alcohol in chlorobenzene should be accompanied by redistribution of chains by lengths in favor of shortest lengths and monomers. This leads to the appearance of negative inclinations of $\varepsilon_0$ from additivity because of decrease of hydrogen bond number in volume unit. The character of temperature variation of inclinations is agreed with hypotheses on the bond between thermal motion energy and chain depolymerization process.

The short chains transit into more stable close multimers, often dimers which have the practically zero dipole moment and don't contribute into polarization in chemically inert solvents. That's why the clear minimum [5] appears at small parts of alcohol on $P(x)$ dependence curve. If we take under consideration in first approximation that polarization of $P_1$ chlorobenzene doesn't depend on composition, then $P_2$ alcohol polarization is determined by the expression:

$$P_2 = \frac{P_{12} - (1-x)P_1}{x} \qquad (3)$$

where *12* index is related to solution.

Such interaction is connected with proton-accepter properties of benzene ring. Indeed, according to data of NMR method [6] the open dimers dominate in diluted benzene solutions.

The treatment results in the terms of two independent relaxation processes, each of which has the one relaxation time τ, are calculated by the formula:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{C_1}{(1+i\omega\tau_1)} + \frac{C_2}{(1+i\omega\tau_2)} \qquad (4)$$

where $C_1 + C_2 = 1$, $C_1 = \frac{\varepsilon_0 - \varepsilon_{\infty,1}}{\varepsilon_0 - \varepsilon_{\infty,2}}$; $\varepsilon_{\infty,1}$ is high-frequency limit of low-frequency absorbing region, $\varepsilon_{\infty,2}$ is high-frequency limit of high-frequency absorbing region (table 2). The relaxation parameters of pure component of main dispersions are also given in table 2. The inclinations of dielectric coefficient values calculated by (4) and data of table 2 from experimental ones don't exceed ±2% for ε' and ± (5 – 7) % for ε".

Table 2

| x | t, °C | $\varepsilon_0$ | $\varepsilon_{\infty,1}$ | $\varepsilon_{\infty,2}$ | $10^{12} \cdot \tau_1$, sec | $10^{12} \cdot \tau_2$, sec |
|---|---|---|---|---|---|---|
| 0,000 | 20 | – | 5,72 | 2,58 | – | 12,5 |
|  | 0 | – | 6,08 | 2,62 | – | 16,3 |
|  | – 20 | – | 6,44 | 2,68 | – | 22,0 |
|  | – 40 | – | 6,80 | 2,74 | – | 30,2 |
| 0,270 | 20 | 6,80 | 5,50 | 2,60 | 164 | 12,0 |
|  | 0 | 7,52 | 5,70 | 2,65 | 330 | 15,0 |
|  | – 20 | 8,15 | 5,92 | 2,70 | 790 | 21,0 |
|  | – 40 | 8,95 | 6,18 | 2,77 | 2100 | 29,4 |
| 0,526 | 20 | 9,50 | 5,20 | 2,56 | 360 | 12,5 |
|  | 0 | 11,5 | 5,30 | 2,62 | 750 | 15,0 |
|  | – 20 | 13,4 | 5,44 | 2,72 | 2160 | 21,0 |
|  | – 40 | 15,7 | 5,62 | 2,75 | 6340 | 30,0 |
| 0,769 | 20 | 13,8 | 4,50 | 2,55 | 515 | 12,5 |
|  | 0 | 16,4 | 4,60 | 2,60 | 1200 | 15,6 |
|  | – 20 | 19,0 | 4,68 | 2,65 | 3160 | 21,0 |
|  | – 40 | 22,1 | 4,78 | 2,70 | 9600 | 30,0 |
| 1,000 | 20 | 18,1 | 3,38 | – | 630 | – |
|  | 0 | 21,2 | 3,44 | – | 1400 | – |
|  | – 20 | 24,3 | 3,53 | – | 3700 | – |
|  | – 40 | 27,9 | 3,59 | – | 11000 | – |

From consideration of table 2 it is followed that:

1. The relaxation times of the first region are close to corresponding values for the main absorbing region of $n$ – butyl alcohol. The significant diversions appear only at x ≤ 0,5.

2. The relaxation times and activation energies of the second region don't practically differ from the same ones for the main absorbing region of pure chlorbenzene at all studied concentrations.

3. The extrapolation $\varepsilon_{\infty,1}$ gives values $\varepsilon_0$ of chlorbenzene at $x \to 0$ and at $x \to 1$ it gives the values of high-frequency limit of the main dispersion of $n$ – butyl alcohol.

Thus, the given system in liquid phase is heterogeneous one at molecular level and it consists of clusters. Taking under consideration the investigation results at equilibrium, we can't consider these clusters not depending on each other. The direction in which the relaxation times change in solution will be defined

by interaction nature between molecules of the one and the same cluster, and both of them.

The main dispersion region in $n$ – butyl alcohol is interpreted on the base of cluster decay processes [7] consisting of elongated chains because of breaking of hydrogen bonds under the influence of thermal motion with the following orientation of released molecules. Moreover, the relaxation time is determined by duration of cluster existence. The chain lengths don't practically differ on ones existing in pure state at big concentrations of $n$ – butyl alcohol. The insignificancy of $\tau_1$ change proves this fact. Along with monomer molecules of $n$ – butyl alcohol, the chlorbenzene molecules weakening the hydrogen bond are situated between chains. This leads to more rapid $\tau_1$ decrease.

The strong decrease concentration of free hydroxyls in the system is the evidence of another proton-acceptor behavior of the solvent that is expressed in the apparent absence of additive absorption contribution observed in $n$ – butyl alcohol at micro-waves [8]. One can suppose that complexes of $n$ – butyl alcohol – chlorbenzene will take part in low-frequency absorption. Such possibility is confirmed by the almost threefold decrease of critical frequency corresponding to monomer relaxation of $n$ – butyl alcohol at transition from pure liquid into diluted benzene solution [9].

The absorption below liquidus line is presented by one region which is mainly related to $n$ – butyl alcohol. The relaxation is characterized by asymmetric (x = 0,270 and 0,526) and (x = 0,769) symmetric distributions and is described by equations [2, 10]:

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\omega\tau)^\beta}, \quad 0 < \beta < 1, \qquad (5)$$

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (i\omega\tau)^{1-\alpha}]}, \quad 0 < \alpha < 1, \qquad (6)$$

where $\beta$ and $\alpha$ are distribution parameters.

The change character of relaxation parameters at transition through the liquidus line has many common details with the behavior of bromobenzene – benzene system where the jump of relaxation time $\tau$ and increase of U activation energy value are observed. Considerably, that in both systems the relative increase of relaxing component part in liquid solutions with temperature decrease doesn't correspond to bigger time increase. The high dormancy of relaxation process is caused by the presence of one of the components in solid state. The dispersion asymmetry is the consequence of clusterization processes [11].

In terms of this model the asymmetric distribution should observe in that case if the diffusion time is equal to or bigger than dielectric rotation time. According to this system, this means that the duration of existence of hydrogen-bounded chains is big one and molecules relax without chain dissociation.

**CONCLUSION**

The samples enriched by the alcohol are easily cooled and frozen in the glass form at transition to the temperature regions below solidus. The samples rapidly cooled up to liquid nitrogen temperature ($\sim$ 1 grad/min), the heating leads to the devitrification and reconstruction of supercooled state. The spontaneous crystallization takes place at temperatures $\sim$ – 120°C that is proved by ε' jump decrease up to value which is less than ε' of glass and ε' jump increase in melting point.

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