

THE LOW-FREQUENCY DIELECTRIC PROPERTIES OF BENZENE-BROMOBENZENE SYSTEM

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The complex dielectric constants of benzene-bromobenzene system at frequency 3 MHz in temperature region from 20°C up to 100°C, which overlap the liquid phase, solid phase and phase between lines of liquidus and solidus, are measured by resonance method. The thermodynamic values characterizing the dielectric relaxation process are calculated.

Keywords: dielectric spectroscopy, dielectric constant, dielectric properties of benzene –bromobenzene solutions.

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1. INTRODUCTION

The investigation of dielectric properties can significantly add the results of physicochemical analysis that allows us to reveal such peculiarities of molecular thermal motion which can't be revealed with the help of usual technique. Thus, the most total state diagram can be constructed on the base of temperature-concentration dependence of ϵ_0 equilibrium dielectric constant of benzene-bromobenzene system than the diagram by data of thermal analysis [1]. The correctness of this diagram is confirmed by data of nuclear-magnetic resonance (NMR) [2].

2. EXPERIMENTAL PART

The dielectric constants of benzene–bromobenzene system in temperature interval from 20°C up to 100°C at frequency 3 MHz and bromobenzene content in mole fractions 0,086; 0,175; 0,267; 0,361; 0,459 and 0,64 are measured. The dielectric constants ϵ' and absorption indexes ϵ'' on

waves of lengths 4.0 and 2,14 cm at bromobenzene content in mole fractions 0,175; 0,267; 0,361 and 0,64 are also measured in the same temperature interval.

The measurements at frequency 3 MHz are carried out by resonance method. The error of values doesn't exceed 1%. ϵ' and ϵ'' values are measured in micro-wave region by Poly method [3] in liquid phase and by method of short-circuit line [4] at more low temperatures. ϵ' error is 1–2%, ϵ'' is not more 3–5%. All measurements are carried out at continuous cooling with velocity 0,1 deg/min. The physical constants of refined compounds are well agreed with data giving in reference [5].

The temperature dependence curves of equilibrium dielectric constant ϵ_0 for six solutions of benzene-bromobenzene system are shown in fig. 1. The jump changes of ϵ_0 are clearly revealed in all curves. The dependence of temperature on concentration corresponding to these jump changes in limits of test accuracy coincides with state diagram (fig. 2) obtained with the help of thermal analysis [6].

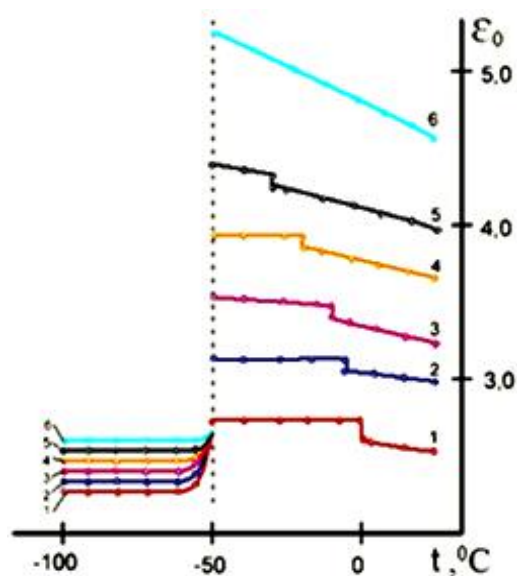


Fig. 1. Temperature dependence of equilibrium dielectric constant ϵ_0 of benzene –bromobenzene solutions at bromobenzene content in mole fractions: 1 – 0,086; 2 – 0,175; 3 – 0,267; 4 – 0,361; 5 – 0,459; 6 – 0,640.

The equilibrium dielectric constant ε_0 increases by jump the value of which increases with the decrease of polar component concentration in points of crystallization beginning. This jump is absent on curve 6 (fig. 1) which corresponds to eutectic concentration. From state diagram it is seen that the jump of equilibrium dielectric constant ε_0 is caused by transition of benzene in solid phase. In this case benzene dielectric constant value is greater than value ε_0 corresponding to liquid phase because of density increase. The benzene crystallization continues with further temperature decrease and composition of liquid phase is added by bromobenzene. The heterogeneities appeared by such way in system bromo-benzene should decrease ε_0 in comparison with values which are expected on the base of data for temperatures higher liquidus line.

The consideration of fig. 1 allows us to emphasize the two temperature region in which molecules of bromo-benzene have definite orientational freedom. In this connection the temperature dependences of dielectric coefficients of investigated solutions on the waves of lengths 4,0 and 2,1 cm are measured, where the main absorption region should be observed [7].

ε' and ε'' values for the solution with content of bromobenzene in molar fractions on the wave of the length 4,0 are shown in fig. 2. From fig. 2 it is seen that the changes in the form of fractures are revealed at the pass through the point of crystallization beginning on the curves. The dispersion below liquidus line significantly shifts to the side of more low frequencies and the small symmetric distribution of relaxation times near the most probable relaxation time τ_0 increasing with temperature decrease.

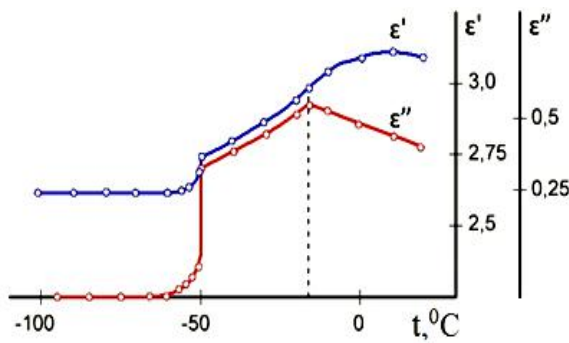


Fig.2. The temperature dependences of dielectric constant ε' and electric absorption index ε'' of benzene - bromobenzene solution in molar fractions 0,267 on the wave length of 4,0 cm.

The frequency dependences in liquidus-solidus interval is found from Cole - Cole equation [8]:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau_0^{1-a}} \quad (1)$$

where ε_∞ is high-frequency dielectric constant, a is parameter of relaxation time distribution, ω is circular

frequency, $i = \sqrt{-1}$.

$a = 0$ higher liquidus line. The times of dielectric relaxation are defined by Cole -Cole graphical method [8].

The activation of dielectric relaxation process can be studied in detail with the help of theory of reaction absolute velocity [9]. In this theory the connection between dielectric relaxation time and activation thermodynamic parameters is established:

$$\tau_0 = \frac{h}{kT} \exp \frac{\Delta F}{RT} = \frac{h}{kT} \exp \frac{\Delta H}{RT} \exp \left(-\frac{\Delta S}{R} \right) \quad (2)$$

where ΔF , ΔH , ΔS are free energy, enthalpy and entropy of activation correspondingly, h is Plank constant, k is Boltzmann constant, R is gas constant, T is absolute temperature.

ΔF value is calculated by the equation:

$$\Delta F = 2,303 RT \lg (2,08 \cdot 10^{10} \tau_0 T) \quad (3)$$

The activation entropy ΔH is found from inclination of $\lg(\tau_0 T)$ dependence on $\frac{1}{T}$ according to equation:

$$\Delta H = 2,303 R \frac{d \lg(\tau_0 T)}{d(1/T)} \quad (4)$$

The activation entropy of ΔS activation is found from the equation:

$$\Delta F = \Delta H - T\Delta S \quad (5)$$

The activation free energy stays the same as in liquid phase because of big growth of ΔH and ΔS .

The observable effects can't be explained by the only one concentration change, i.e. the relaxation times in liquidus-solidus not higher values corresponding electric concentration but they exceed the values for pure bromobenzene (fig. 3). From dielectric measurements it is followed that at temperatures below liquidus line the volume parts taken by liquid phase are characterized by high molecule order the kinetic behavior of which is essentially differ from the one observed in liquid state higher liquidus line.

3. CONCLUSION

The dependence of equilibrium and complex dielectric constants of hypoeutectic solutions of benzene-bromobenzene system on temperature and concentration is studied. The dielectric relaxation times are obtained.

The relaxation of bromobenzene molecules in liquidus - solidus interval where they are in liquid solution is characterized by solid state values.

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