

**DETERMINATION OF DIPOLE MOMENTUM AND RELAXATION
TIME OF MOLECULAR ASSOCIATES OF BENZOLE**

Ch.O.KADJAR, R.M.KASIMOV, M.I.VELIYEV, S.R.KASIMOVA

*Institute of Physics, Azerbaijan National Academy of Sciences,
AZ 1143, Baku, G. Javid av.33*

On the basis of microwave measurements of dielectric losses of benzole at different frequencies the values of its relaxation time and effective dipole momentum per one benzole molecule have been determined.

According to [1], by results of research of a light scattering in fluid and vaporous benzole for the first time there was experimentally demonstrated existence of molecular associates, mostly of dimer type, in fluid benzole. It has allowed to suppose that dimers, arising in fluid benzole, and more complicated associates represent unstable germs of benzole chips [2, 3]. Thus, as in crystalline benzole, the nearest neighbouring molecules are oriented in such a manner that their symmetry axes will form one another angle, close to 90° . Such orientation of molecules in dimer can arise with the help of weak hydrogen bindings C-H ... C, which the enthalpy of formation is about $6\div 8$ kJoule/mol. It is in 3-4 times less on value in comparison with the enthalpy of formation of hydrogen bindings of a type O-H ... O, having a place in water, alcohols and other hardly associate liquids. As the formed dimer is asymmetrical, the reallocating of electronic density in non-polar molecules of benzole will cause to arising of the electrical dipole moment in dimer. Such dimer will represent a polar molecule itself. According to calculations [2] it was proved, that effective dipole moment of one molecule of benzole in dimer, is about 0,1D, and the mean time of such kind of hydrogen bindings' life makes 10-12s.

Availability of electrical dipole moment for, as was considered, non-polar benzole testify to a capability of existence for it of dispersion area arranged in microwaves range. Showed [4, 5] experimental data of measurement of dielectric properties of fluid benzole in a millimeter-wave range indicate that it has absorbing power in this wave band. Thus, describing this capacity the loss angle's tangent $tg\delta$ increases on value with increase of frequency and reach $25\cdot 10^{-3}$ units value at frequency 70GHz [4]. The analysis of mentioned above modern theoretical submissions about a molecular structure of fluid benzole and data of measurements of its microwave dielectric properties allows to make a conclusion that to observed absorption of microwave radiation in benzole there meets a low frequency interval of its dispersion area. Because of a smallness of benzole dipole moment's value the small interval of change of inductivity value ϵ' of benzole with frequency is typical for the found wave dispersion, and this interval is commensurable with a measuring error of the value ϵ' itself. It makes finding of dipole moment μ and relaxation time τ of benzole according to the data of measurements of its dielectric properties outside of and in the field of its dispersion more difficult.

For the solution of a problem of definition μ , τ for weak polar materials, such as benzole, we shall use the way, developed in work [6] during definition τ of polar materials by the data of measurement of dielectric properties in the field of a dispersion of their weak solutions in non-polar solvents. It is possible to consider, that the process of installation of an electric polarization in benzole or other associate liquids flows past is exponential, and therefore, behavior of inductivity ϵ' and dielectric losses ϵ'' with frequency of such liquids should be described by equations of Debye:

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + (\omega\tau)^2}, \quad \varepsilon'' = \frac{\omega\tau(\varepsilon_0 - \varepsilon_\infty)}{1 + (\omega\tau)^2}, \quad (1)$$

where $\varepsilon_0, \varepsilon_\infty$ – out of dispersion static and high frequency values of inductivity of material, τ - macroscopic time of a relaxation, ω - circular frequency [5].

For definition μ of material in fluid phase the equation of Onzager-Kirkwood-Frelikh, injected from the statistical theory of an electric polarization will be used:

$$\mu^2 = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \frac{9kT}{4\pi N_A}, \quad (2)$$

where k – Bailsman's constant, T – the absolute temperature, N_A - Avocados number [7].

The value included in computational equations (1) and (2) of difference $\varepsilon_0 - \varepsilon_\infty$ cannot be determined experimentally, as it is commensurable with existing measurement errors of ε_0 and ε_∞ . It could be determined with usage of the data of measurements ε' and ε'' obtained at different frequencies of measurement. Supposing, that the values $\varepsilon_0, \varepsilon_\infty$ are close to each other enough, the equation (2) can be shown by another way:

$$\mu^2 = \frac{3(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_0 + 2)^2} \frac{9kT}{4\pi N_A} \quad (3)$$

In that case, it's enough to know the values of ε_0 and the difference $\varepsilon_0 - \varepsilon_\infty$ to determine the value μ .

Let's allow that the wave dispersion for benzole is a dispersion of a relaxational type and is described by the theory of Debye, for definition of its relaxation time τ we shall take offered in work [6] simple method of definition τ , which is based on usage of the data of measurements only of dielectric losses ε'' , obtained at two diverse on value frequencies f_1 and f_2 .

At the Debye description of dielectric properties of material their values of dielectric losses $\varepsilon''_1, \varepsilon''_2$ measured accordingly at two frequencies f_1 and f_2 , are equal:

$$\varepsilon''_1 = \frac{\omega_1\tau(\varepsilon_0 - \varepsilon_\infty)}{1 + (\omega_1\tau)^2}, \quad \varepsilon''_2 = \frac{\omega_2\tau(\varepsilon_0 - \varepsilon_\infty)}{1 + (\omega_2\tau)^2}. \quad (4)$$

From the joint solution of equations (4) follows, that

$$\tau = \frac{1}{2\pi f_2} \sqrt{\frac{\alpha - \beta}{1/\beta - \alpha}}, \quad (5)$$

where $\alpha = \varepsilon''_2/\varepsilon''_1$, $\beta = f_2/f_1$, $\varepsilon''_1, \varepsilon''_2$ - the value of dielectric losses of solution, measured accordingly at frequencies f_1 and f_2 .

For determination of a difference $\varepsilon_0 - \varepsilon_\infty$ we shall use the same equations (4) - (5). As a result we shall have:

$$\varepsilon_0 - \varepsilon_\infty = \varepsilon''_2 \frac{1 - \beta^2}{\beta} \cdot \frac{1}{\sqrt{(\alpha - \beta)(1/\beta - \alpha)}} \quad (6)$$

Found from an equation (6) values $\varepsilon_0 - \varepsilon_\infty$ can be used at further calculus μ according to the equation (3).

For determination μ and τ of benzole we use the data of measurement ε' and ε'' , obtained in work [4] and well enough matched with the data of measurements of other writers [5]. According to these data of value of dielectric losses ε'' of benzole are 0,0025, 0,0035 and 0,0059 accordingly at the temperature of 25°C and frequencies of

measurement 24, 35 and 70 GHz. Thus the values of inductivity ε' at these frequencies remained within the limits of 2,278 and close to value ε_0 , measured at low frequencies [5]. Using these values ε'' and f in equations (5) and (6) we shall get, that a relaxation time τ and effective dipole moment μ of one molecula of benzole are accordingly $1,23+0,07 \cdot 10^{-12}$ sec and 0,10D. So they are close to theoretically estimated values, according to the data [2], and proved the legitimacy of the used method of their finding.

1. М.И.Шахпаронов, *Методы исследования теплового движения молекул и строения жидкостей. М.; изд.МГУ, (1963) 335.*
2. М.И.Шахпаронов, *Диэлектрическая радиоспектроскопия.М.; изд.МГУ, (1996) 332.*
3. М.И.Шахпаронов, *Механизмы быстрых процессов в жидкостях. М.; Высшая школа, (1980) 352.*
4. J.Crosseley, S.Walker, *Canad. J. Chem.*, **46** (1968) 847.
5. Я.Ю.Ахадов, *Диэлектрические параметры чистых жидкостей. М.; изд.МАИ, (1999) 854.*
6. Ч.О.Каджар, С.Р.Касимова, *Азерб.хим.журнал*, № 2 (2001) 38.
7. С.Ј.В.Вотчер, *Theory of Electric Polarisation.Vol.1. Dielectric in Static Field. Amsterdam, London, N.Y., (1973) 377.*

**BENZOLUN MOLEKULAR ASSOSIATLARININ DIPOL MOMENTİ VƏ
RELAKSASIYA MÜDDƏTİNİN TƏYİNİ**

Ç.O.QACAR, R.M.QASIMOV, M.İ.VƏLİYEV, S.R.QASIMOV

Mikrodalğa diapazonunda dielektrik ölçmələrdən bir benzol molekuluna düşən dielektrik relaksasiya müddəti və effektiv dipol momentinin qiymətləri təyin olunmuşdur.

**ОПРЕДЕЛЕНИЕ ДИПОЛЬНОГО МОМЕНТА И ВРЕМЕНИ
РЕЛАКСАЦИИ МОЛЕКУЛЯРНЫХ АССОЦИАТОВ БЕНЗОЛА**

Ч.О.КАДЖАР, Р.М.КАСИМОВ, М.И.ВЕЛИЕВ, С.Р.КАСИМОВА

По данным микроволновых измерения диэлектрических потерь бензола при различных частотах определены значения его времени релаксации и эффективного дипольного момента, приходящегося на одну молекулу бензола.

Редактор: А.Гарибов