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NONLINEAR DIELECTRIC EFFECT IN VERATROLE SOLUTIONS

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Results are presented of NDE measurements in solutions of veratrole in carbon tetrachloride and in heptane close to the temperature of phase transition. Applying the theory of Kielich, the effect associated with statistical-molecular fluctuations was found to take a significant share in the resultant NDE values. For a critical solution the value of the critical index ζ was found to be 0.5.

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1. Introduction

One of the most effective methods of investigating intermolecular correlation in dipolar liquids is the Nonlinear Dielectric Effects (NDE). The measure of this effect is the value $\Delta\varepsilon/E^2$ (where $\Delta\varepsilon = \varepsilon_{\text{high field}} - \varepsilon_{\text{low field}}$, E — strong external electric field).

Owing to the theoretical and experimental work conducted by Piekara, Kielich, Chełkowski and Małecki, for many years now NDE has been used to study intermolecular [1–5, 13] and intramolecular interactions [6–8, 13] in liquid dielectrics.

In 1936 Piekara performed the first NDE measurement for a critical solution of nitrobenzene in hexane [9]. The large fluctuations of concentration occurring in the tested solution caused a change of sign of $\Delta\varepsilon/E^2$ in the vicinity of phase separation temperature.

An important advance in NDE investigations made in recent years was the statistical-molecular theory [10–12] developed by Kielich, which took into account, inter alia, the influence of density fluctuations on NDE values.

Making use of this theory it became possible to elucidate the origin of the positive $\Delta\varepsilon/E^2$ value in the case of nondipolar substances [14]. Lately a revival of interest may be observed in NDE studies in critical solutions [13, 16, 17], associated with the overall development achieved in investigations on phase changes in physics.

From the presented here results of NDE measurements in veratrole (o-dimethoxybenzene) solutions it is possible to trace the course of most of the mechanisms which influence the NDE value.

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Veratrole molecules occur in the form of a few configurations isomers differing in the value of dipole moments [15]. This fact influences the NDE magnitude [6–8, 13].

At small values of veratrole dipole moments the influence of molecular-statistical fluctuation on NDE value may be observed. Since veratrole forms critical solutions with certain substances, this provides an opportunity of studying the influence of critical fluctuations on the value of $\Delta\varepsilon/E^2$.

2. Experimental

NDE measurements were done with an automatic pulse recording device as described in [8]. The thermostated measuring condenser made it possible to measure stability and temperature with an accuracy of ± 0.02 K. Chemical reagents were purified by standard methods, paying particular attention to drying. To facilitate quantitative comparison of experimental and theoretical values the concept of NDE molar constant, S_m, was used [13]. This value is defined by the following equation:

$$S_{\mathrm{m}} = \frac{1}{3\varepsilon_0 F^2}\left[\left(\frac{\partial^{\mathrm{M}}P}{\partial F}\right)_E - \left(\frac{\partial^{\mathrm{M}}P}{\partial F}\right)_{E=0}\right], \tag{1}$$

where: ${}^{M}P = N_{\mathrm{A}}\langle m\rangle_E$ is the molar polarisation, F — local electric field strength, ε_0 — permittivity of free space.

For the local Onsager field the molar constant S_{exp} is determined for an experimental value, i.e.

$$S_{\mathrm{exp}} = \frac{(2\varepsilon^2+n^4)(2\varepsilon+n^2)^2}{\varepsilon^4(n^2+2)^4}\,\frac{M}{\varrho}\,\frac{\Delta\varepsilon}{E^2}, \tag{2}$$

where: ε — permittivity, n — refracting index, M — molecular weight, ϱ — density of the tested substance.

3. Results

Fig. 1 shows the results of measurements of $\Delta\eta/E^2$ against concentrations (x) (in molar fractions) for solutions of veratrole in carbon tetrachloride at temperature 25°C. Three facts are noteworthy here, i.e. the positive sign of value $\Delta\varepsilon/E^2$; the linear form of relation $\Delta\varepsilon/E^2$ against concentration, which in accordance with the theory of Kielich [11, 12] indicates that intermolecular effects may be neglected; the absolute value of $\Delta\varepsilon/E^2$ in veratrole is of the same order as in carbon tetrachloride. This last fact makes it possible to observe the effect of density and translational fluctuations, which in the case of carbon tetrachloride play an important role [10–12].

For pure veratrole the shares of the individual mechanisms in the resultant $\Delta\varepsilon/E^2$ value were calculated.

Making use of the theory of Kielich [10–12] the following effects were taken into account:

$$S_{\mathrm{FL}} = \frac{\beta}{18\varepsilon_0}\langle(\Delta A_{\alpha\alpha}+\beta\Delta M^2)^2\rangle \tag{3}$$

— the influence of fluctuations of statistical polarisabilities and of the square of the total dipole moment,

$$S_A = \frac{\beta}{15\varepsilon_0} \langle 3A_{\alpha\beta}A_{\alpha\beta} - A_{\alpha\alpha}A_{\beta\beta} \rangle \tag{4}$$

— the influence of anisotropic reorientation of induced dipoles,

$$S_{AM} = \frac{2\beta^2}{15\varepsilon_0} \langle 3A_{\alpha\beta}M_\alpha M_\beta - A_{\alpha\alpha}M_\beta M_\beta \rangle \tag{5}$$

— the influence of anisotropic reorientation of induced and permanent dipoles,

$$S_M = -\frac{\beta^3}{45\varepsilon_0} \langle (M \cdot M)^2 \rangle \tag{6}$$

— proportion due to reorientation of permanent dipoles where $\beta = 1/kT$, M_α — component of the vector of dipole moment, $A_{\alpha\beta}$ — linear tensor of electrical polarisability.

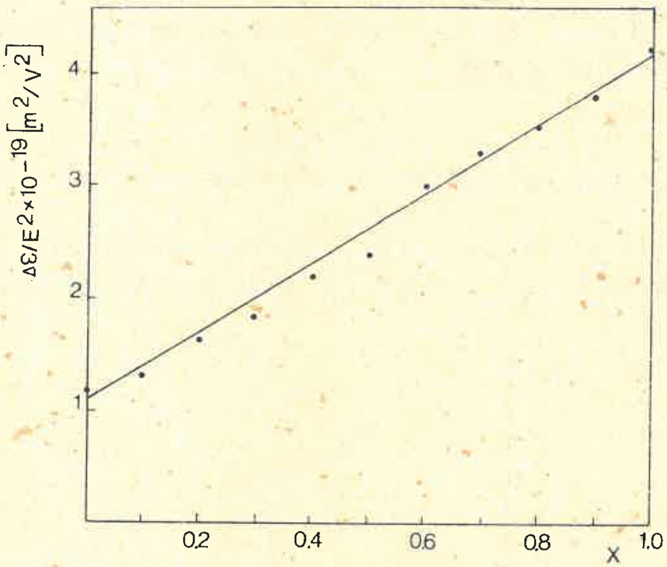

Fig. 1. The dependence of $(\Delta\varepsilon/E^2)$ vs concentrations for solutions of veratrole in CCl_4 at temperature 298 K

The effect due to the existence of configuration isomers was calculated from the formula [8, 13]:

$$S_{CONF} = -\frac{N_A \bar{\mu}^4}{45\varepsilon_0 k^3 T^3} R_S, \tag{7}$$

where

$$R_S = -\tfrac{3}{2} \frac{(\bar{\mu}^2 - \mu_1^2)(\mu_2^2 - \bar{\mu}^2)}{\bar{\mu}^4}.$$

In these calculations the following dipole moments were taken: $\bar{\mu} = 5.7 \times 10^{-30}$ [C.m], $\mu_1 = 5.0 \times 10^{-30}$ [C.m], $\mu_2 = 6.8 \times 10^{-30}$ [C.m]. The less general forms of these equations, as presented in [14] were used for calculations.

Table I shows the values found for the individual effects and experimental values found for NDE molecular constant.

TABLE I

NDE molar constants for pure veratrole at temperature 298 K

	$S \times 10^{25}$ [$C^2m^5J^{-2}$ mol^{-1}]						
T[K]	S_{exp}	S_M	S_A	S_{AM}	S_{FL}*	S_{CONF}	S_{total}
298	19.9	−236.5	1.4	24.3	209.6	34.6	53.3

* An arbitrary value of isothermal coefficient of compressibility $\beta_T = 10 \times 10^{-10}$ [m^2/N] was taken.

A relatively high share of statistical-molecular fluctuations in the resultant value of $\Delta\varepsilon/E^2$ is to be observed. This effect, usually neglected, may play an important role, particularly in the case of substances with small dipole moments.

4. *Critical fluctuations*

In a certain temperature range solutions of veratrole in heptane separate into two phases.

Fig. 2 shows the coexistence curve for a solution of veratrole in heptane. From this figure the critical concentration $x_c = 0.45$ and critical temperature $T_c = 293.6$ K may be determined.

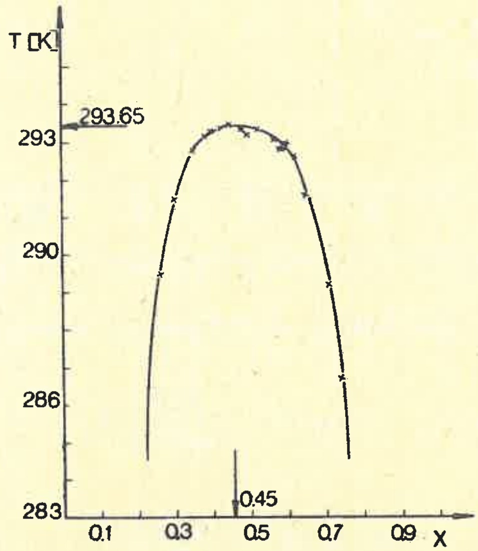

Fig. 2. The coexistence curve for a solution of veratrole in heptane

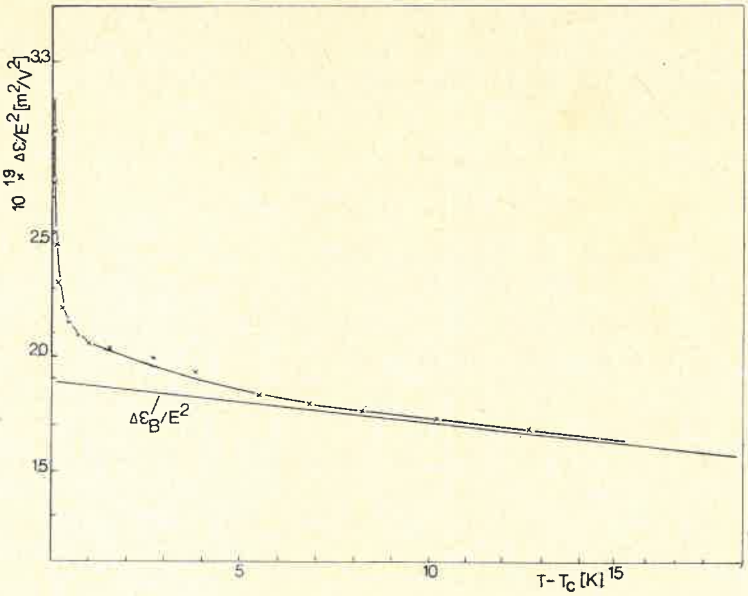

Fig. 3. The dependence of $(\Delta\varepsilon/E^2)$ and $(\Delta\varepsilon_B/E^2)$ vs $T-T_c$ for a critical solution of veratrole in heptane

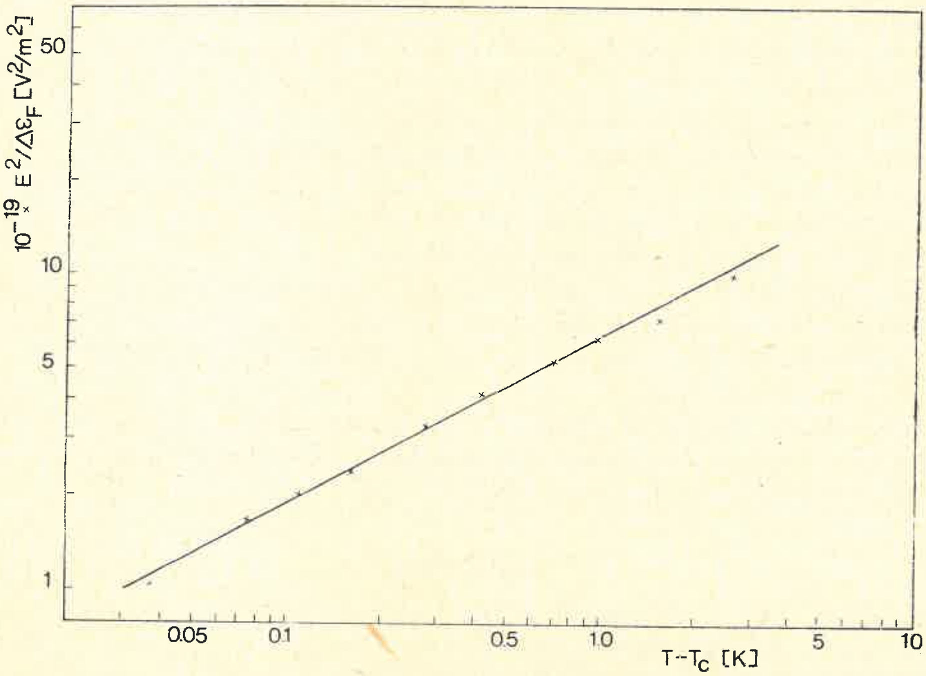

Fig. 4. The dependence of $(\Delta\varepsilon_F/E^2)^{-1}$ vs $T-T_c$ for a critical solution of veratrole in heptane

It is well known that the binary mixture is one of the typical systems of second order phase transition where concentrations are the cause of anomalous behaviour of physical quantities close to T_c. In [16–18] it is shown that for NDE the following condition is satisfied in the critical region:

$$\frac{\Delta\varepsilon}{E^2} \sim \frac{1}{(T-T_c)^{\zeta}}. \tag{8}$$

The curve of $\Delta\varepsilon/E^2$ against $T-T_c$ is shown in Fig. 3.

To take into account the magnitude of the effect due to the critical fluctuations ($\Delta\varepsilon_F/E^2$), all the constituents which are not associated with the critical fluctuations ($\Delta\varepsilon_B/E^2$) must be subtracted from the total value ($\Delta\varepsilon/E^2$) [12].

The assumption of a suitable background effect is of fundamental importance in analysis of the relation (8).

The value of ($\Delta\varepsilon_B/E^2$) was determined for these calculations by fitting measurements done in a temperature range considerably higher than T_c (Fig. 3). Fig. 4 shows the curve of $(\Delta\varepsilon_F/E^2)^{-1}$ against $T-T_c$. From this curve the value of the critical index ζ may be determined, in this case $\zeta = 0.5$.

5. *Discussion*

Test conducted on veratrole in selected solvents gives a useful opportunity for studying in one substance the influence both of statistical-molecular fluctuations and of critical fluctuations on the value ($\Delta\varepsilon/E^2$). From the results obtained it was ascertained that the share of statistical fluctuations S_{FL} in the resultant NDE value outside the critical region is significant (Table I), since due to the small values of veratrole molecules dipole moments the effects associated with intermolecular interactions may be neglected.

For a critical solution of veratrole in heptane the critical fluctuations have a dominant share in the resultant NDE. The obtained value of critical index $\zeta = 0.5$ is in good accordance with the theoretical value for the droplet model [18]. The similar values of critical indices were obtained for other substances [16, 19].

It should be noted, however, that in the critical solution studied here, the background effect ($\Delta\varepsilon_B/E^2$) is large relative to the total ($\Delta\varepsilon/E^2$) value close to T_c (Fig. 3).

For this reason the method of determining ($\Delta\varepsilon/E^2$) will have a considerable influence on the value of index ζ.

With another method of determining background effect, e.g. by measurement of ($\Delta\varepsilon/E^2$) for a veratrole solution in carbon tetrachloride, the value of critical index found may differ by as much as 20% from that given here.

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