

Fisher's renormalization for the nonlinear dielectric effect from isothermal measurements

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In the case of nonlinear dielectric effect (NDE), temperature measurements of doped binary solutions of critical concentration do not enable a definitive determination of the influence of Fisher's renormalization on the form of the critical effect. For this reason it was attempted to achieve this from isothermal studies of changes in value of the NDE as a function of a third constituent added to the critical solution. It was ascertained that its value is largely independent of the direction of approach to the critical point. Results of an initial investigation of this type are presented here.

INTRODUCTION

Nonlinear-dielectric-effect (NDE) investigations based on the difference in permittivity ϵ^E in a strong and ϵ^0 in a weak electric field E for binary solutions of limited miscibility have been conducted for more than 50 years.¹ Progress towards understanding the causes and finding a quantitative description of the observed behavior was made when attempting to describe this effect in the context of the physics of phase transitions.

Studies carried out since the late 1970s have shown that on approaching the critical temperature T_c the variations in NDE values in a solution of critical concentration x_c may approximately be expressed by the relation^{2,3}

$$\frac{\Delta\epsilon}{E^2} = \left[\frac{\Delta\epsilon}{E^2} \right]_B + \left[\frac{\Delta\epsilon}{E^2} \right]_C = \left[\frac{\Delta\epsilon}{E^2} \right]_B + At^{-\psi} + \dots, \quad (1)$$

where subscripts B and C denote the background and critical effect, respectively:

$$\frac{\Delta\epsilon}{E^2} = \frac{\epsilon^E - \epsilon^0}{E^2} \quad (\text{NDE value}),$$

$$t = (T - T_c)/T_c \quad (\text{reduced temperature}).$$

Theoretical predictions give^{4,5}

$$\psi \approx \gamma - 2\beta \approx 0.59. \quad (2)$$

The experimental, universal value of ψ would appear to be somewhat lower, probably about 0.4.⁶

Based on the droplet model, the value of the critical effect amplitude may be estimated as⁷

$$A \propto \frac{(\epsilon_1 - \epsilon_2)^4}{\epsilon_c^2} \quad (3)$$

where ϵ_i is the permittivity of the i th component of the binary solution ($i=1,2$) and ϵ_c is the permittivity of the solution, which is in reasonably good agreement with experiment.^{6,7}

Another method of verifying the theoretical predictions is by studying the influence of the Fisher's renormalization⁸ on the form of the critical effect.

Doping the binary solution of critical concentration with a third constituent causes the appearance in the im-

mediate vicinity of T_c of a zone described by new, renormalized critical exponents:

$$\gamma \rightarrow \frac{\gamma}{1-\alpha}, \quad \beta \rightarrow \frac{\beta}{1-\alpha}, \quad \alpha \rightarrow \frac{-\alpha}{1-\alpha}. \quad (4)$$

The magnitude of the renormalized zone is proportional to the concentration of the additional constituent. Behavior of this type in critical solutions has been supported by good experimental verification.⁹ The critical exponent described by relation (2) should increase due to Fisher's renormalization. It seems that Fisher's renormalization can be used as an additional test of the theoretically predicted definitions of the power (critical) exponent.

NDE TEMPERATURE INVESTIGATIONS IN DOPED SOLUTIONS

The first investigations of this kind were carried out in the critical nitrobenzene-hexane solution doped with carbon tetrachloride.¹⁰ Although these studies were of a qualitative type, a tendency to reduction in the value of the exponent ψ with increase in concentration of the additive was observed.

Recently, the authors of this paper conducted considerably more accurate NDE measurements in a veratrole-heptane solution of critical concentration doped with 2-nitropropane and in the critical nitrobenzene-heptane solution doped with carbon tetrachloride.⁶ Their results are tabulated in Table I. In the veratrole-heptane solutions, doping also causes reduction in the exponent.

For this solution experimental conditions permitted the temperature of phase transition to be determined only with an accuracy of $\pm 0.05^\circ\text{C}$. As was shown in Ref. 11, even a very slight discontinuity of the phase transformation causes a detectable reduction in the value of exponent ψ . The way in which the meniscus formed in the homogeneous, doped solution indicated a possible discontinuity.¹²

For solutions with a concentration of 2-nitropropane $c > 0.06$ weight fraction, it was possible to observe the displacement of the meniscus together with a drop in temperature. The amplitude of the critical effect increases with an increase in concentration of the additive. This indicates the markedly different solubilities of the 2-

TABLE I. Results of an analysis of the NDE versus temperature measurements in solutions of nitrobenzene-heptane plus carbon tetrachloride and veratrole-heptane plus 2-nitropropane. As compared with results quoted in Ref. 6 details associated with the discussion of background effect are omitted, while values of the critical amplitudes are added. Parameters are calculated using a background from the numerical fitting of the total effect to the equation

$$\frac{\Delta\epsilon}{E^2} = \left(\frac{\Delta\epsilon}{E^2} \right)_B + \left(\frac{\Delta\epsilon}{E^2} \right)_C \simeq (B_1 + B_2t + B_3t^2)_B + (At^{-\psi})_C.$$

ΔT^R means the temperature distance in which the critical effect could be well described by the simple power relation.

Nitrobenzene-heptane plus CCl_4			
x	$A \pm 0.1$	$\psi \pm 0.01$	ΔT^R
mass fraction	($10^{-17} \text{ m}^2/\text{V}^2 \text{ deg}$)		
0	7.77	0.39 ₆	15.0
0.01	7.58	0.39 ₁	13.5
0.02	7.77	0.38 ₈	13.9
0.03	7.96	0.38 ₆	12.0

Veratrole-heptane plus 2-nitropropane			
x	$A \pm 0.1$	$\psi \pm 0.01$	ΔT^R
mass fraction	($10^{-20} \text{ m}^2/\text{V}^2 \text{ deg}$)		
0	7.07	0.40 ₅	6.3
0.025	15.05	0.36 ₀	8.5
0.040	24.21	0.29 ₅	12.2

nitropropane in the two constituents of the binary solution [Eq. (3)]. Further evidence of the action of the additive in this case is provided by the change in the nature of the background effect. In the nondoped system this effect is positive, associated with the intermolecular rotation in the veratrole molecules.¹³ Its value decreases with the rise of temperature. In the doped system the background effect is negative and its absolute value decreases with the rise in temperature. This is principally due to the orientation of the dipoles in the 2-nitropropane molecules in the strong electric field.¹⁴

In the nitrobenzene-heptane plus carbon tetrachloride solutions the additive did not influence the parameters of the critical effect. This is presumably due to the very small dimensions of the renormalized zone. An increase in concentration of the additive could give an increase in the size of the zone but could also ultimately lead to a discontinuity of the phase transformation.

It would appear that for the NDE it is difficult to make an exact determination of the influence of Fisher's renormalization on the parameters of the critical effect by means of temperature investigations of doped solutions.

CRITICAL PROPERTIES IN THE VICINITY OF THE PLAIT POINT

The influence of the Fisher's renormalization on the critical effect may, however, be determined in another way. The appearance of renormalization in the doped

solutions is a result of the transition from the normal critical point to the plait point (Fig. 1). In this system the free energy under atmospheric pressure is a function of three variables:

$$G = G(T, \mu, x), \quad (5)$$

where μ is the chemical potential of a constituent of the binary solution and x is the concentration of the additive. Fisher⁸ proposed treating a solution of this type as a quasibinary system in which the free energy is a function of only two variables, i.e.,

$$G \simeq G^*(T^*(T, \mu, x), \mu^*(T, \mu, x)), \quad (6)$$

where T^*, μ^* are the temperature and chemical potential type fields. This assumption makes it possible to express the critical properties of three-constituent solutions of limited miscibility relative to the new variables (T^*, μ^*) in a manner similar to that for the critical binary solutions. Fisher next related these new variables to the experimental values

$$\Delta T^* \simeq f_T |\Delta T|^{1/(1-\alpha)} + f_x |\Delta x|^{1/(1-\alpha)} + \dots, \quad (7)$$

where $\Delta T = T - T_c$ is the temperature relative to the critical temperature T_c in the doped binary solution, e.g., from the plait point; $\Delta x = x - \bar{x}$ is the concentration relative to the dopant's concentration \bar{x} , e.g., from the plait

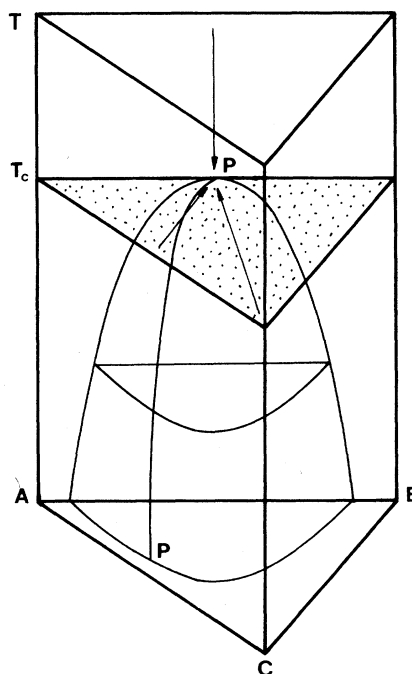


FIG. 1. Critical point and the line of plait points $P-P$ in a ternary solution. Constituents A and B form a solution of limited miscibility. Constituent C is completely miscible with A and B . Its concentration on the $P-P$ line is \bar{x} . Also marked are the directions from which the approach to the critical point was made during the NDE measurements. In our experiment A =hexane, B =nitrobenzene, and C =benzene.

point; f_T, f_x are the normalizing amplitudes; and α is the critical exponent expressing critical changes in specific heat $\alpha \simeq 0.11$.¹⁵

For the previously described temperature studies the following holds well:

$$\Delta T^* \simeq f_T |\Delta T|^{1/(1-\alpha)}, \quad (8)$$

in agreement with relations (4). If a third constituent is added to a solution of critical concentration which is at its critical temperature, then the distance from the critical point (the end of the line of plait points) can be written

$$\Delta T^* \simeq f_x |\Delta x|^{1/(1-\alpha)} = f_x x^{1/(1-\alpha)}. \quad (9)$$

Carrying out Fisher's renormalization investigations in this way considerably reduces the problems associated with possible discontinuity of the phase transformation. Moreover, the critical effect is described at once, mainly by means of one, renormalized exponent. The results obtained from our first, preliminary NDE studies of this type are presented below.

EXPERIMENTAL PROCEDURE

NDE experiments were conducted using an apparatus constructed according to the concept of Małecki.¹⁶ The duration of the impulse from the strong electric field was about 1 ms. The intensity of the electric field was from 4000–35 000 V/cm. The frequency of the measurement field was 2 MHz.

For every value of additive concentration x , measurements of permittivity variations were made for various values of intensity of electric field. Within the limits of error, the observed values of $\Delta\epsilon/E^2$ were always directly proportional to E^2 .

The measurement capacitor had a capacity of 5.5 pF and the distance between the plates was 0.35 mm. The capacitor was placed in the bottom of a glass vessel of 110 ccm capacity, containing about 20 ccm of the critical nitrobenzene-hexane solution of concentration $x_c = 0.43$ mole fraction of nitrobenzene. The vessel was placed in a thermostat which permitted stabilization with an accuracy of ± 0.01 deg/(24 h). The critical temperature of the binary solution, at which the measurements were conducted, was 19.51 °C.

Benzene was added in a continuous process to the sample prepared in this way. After each addition of benzene the solution was mixed. Reagents used in tests were cleaned according to standard procedures¹⁷ and also all the substances were distilled immediately prior to measurements. This ensured a low value of conductivity in the given case, which is of particular significance in NDE investigations. Measurement data were fitted to the given relations by the method of least squares.¹⁸

RESULTS AND DISCUSSION

Test results obtained are presented on Fig. 2. With increasing distance from the critical point the marked positive effect decreases, becoming similar to nitrobenzene

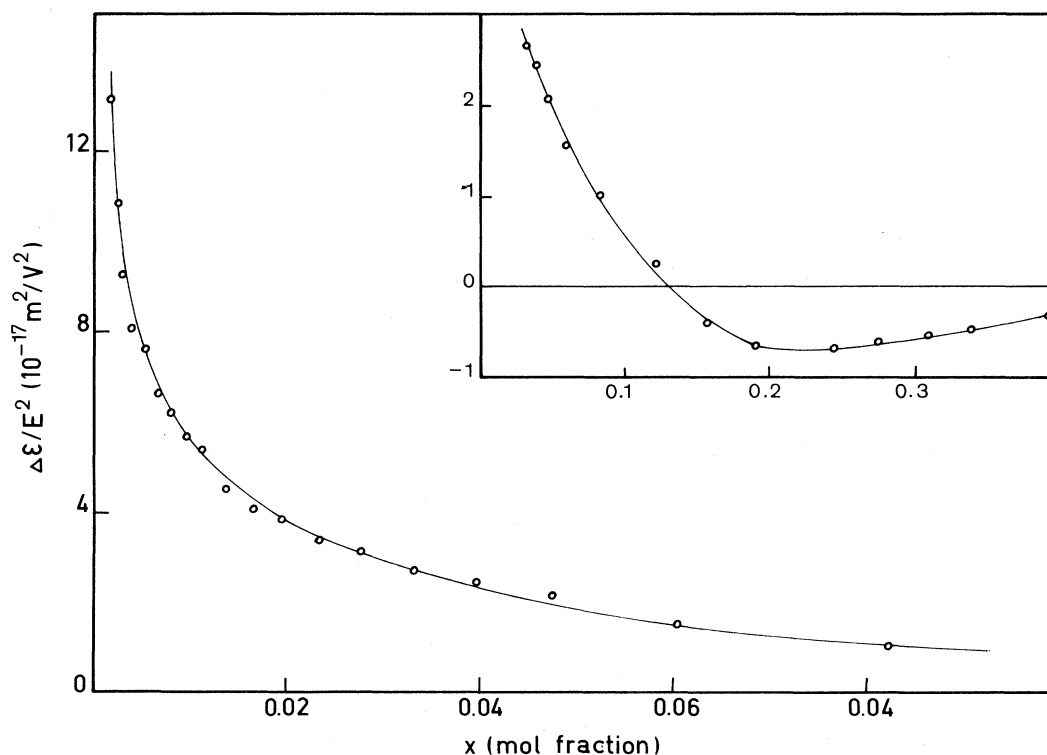


FIG. 2. Isothermal $T = T_c$ curve of $\Delta\epsilon/E^2$ as a function of the concentration of benzene added to a nitrobenzene-hexane solution of critical concentration. Benzene concentration x is shown in mole fraction.

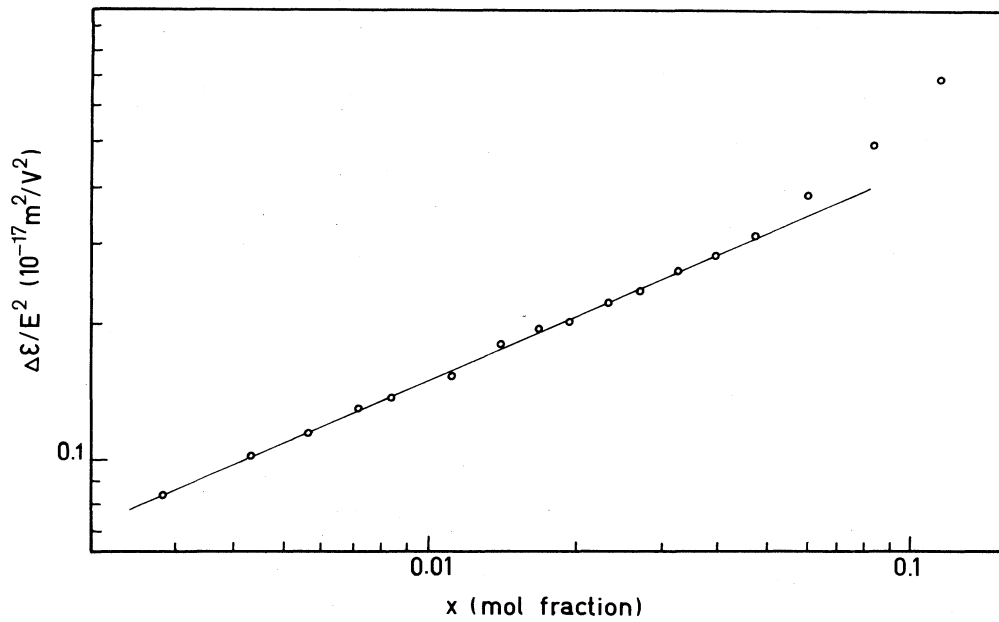


FIG. 3. Log-log curve of $(\Delta\epsilon/E^2)^{-1}$ as a function of benzene concentration x added to a nitrobenzene-hexane solution of critical temperature and concentration.

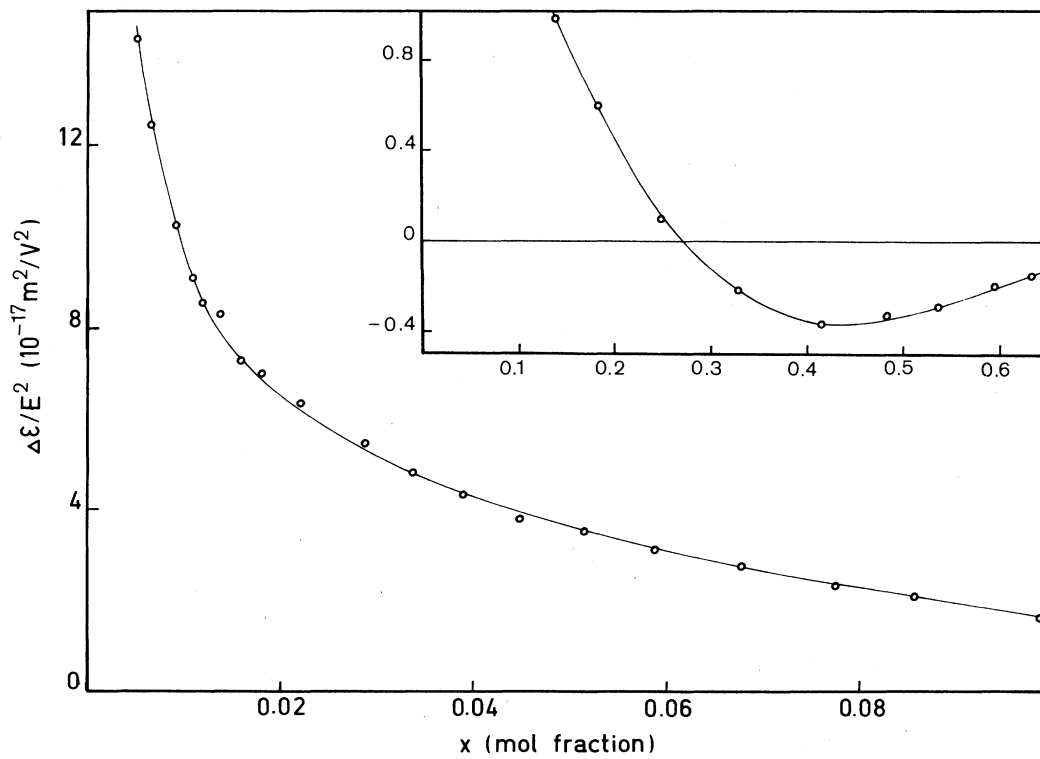


FIG. 4. Isothermal $T = T_c$ curve of $\Delta\epsilon/E^2$ as a function of the concentration of benzene and hexane mixture of mole ratio 1:1x added to a nitrobenzene-hexane solution of critical concentration.

solutions with a nondipole and easy mixing solvent, for small nitrobenzene concentrations.¹⁴ It is noteworthy that in temperature studies it is not until a very large distance from T_c are reached. Even at distances of the order of 80–100°C, the temperature character of the whole effect may be not dominated by the background effect.^{6,19}

In this particular case the noncritical background effect is associated with the orientation of the nitrobenzene dipole in the electric field and is proportional to its concentration. For this reason it was determined by linear extrapolation of the orientational parts of the total obtained effect, giving (Fig. 3)

$$\left[\frac{\Delta\epsilon}{E^2} \right] \simeq \left[\frac{\Delta\epsilon}{E^2} \right]_B + 0.77x^{-0.47_0}$$

(units of $10^{-17} \text{ m}^2/\text{V}^2$), (10)

where

$$\left[\frac{\Delta\epsilon}{E^2} \right]_B = -1.2 + 2.01x, \quad x < 0.055$$

and

$$\chi^2 = 1.76, \quad \psi \pm 0.015, \quad A \pm 0.08.$$

For NDE temperature studies in a nitrobenzene-hexane critical solution⁶ a value $\psi = 0.43_2 \pm 0.01$ was obtained. This, according to the relation (9), gives

$$\frac{\psi}{1-\alpha} \simeq 0.48 \quad \text{for } \alpha = 0.11, \quad (11)$$

which is in good agreement with (10). Thus, a rise in value of ψ was obtained.

NDE measurements were also performed on approaching the critical point from a slightly different direction

(Fig. 1). This was arranged by adding a mixture of benzene and hexane in a mole ratio 1:1 to the binary critical solution.

The results of these studies are shown on Fig. 4. In this case the effect has the form

$$\left[\frac{\Delta\epsilon}{E^2} \right] \simeq \left[\frac{\Delta\epsilon}{E^2} \right]_B + 1.13x^{-0.49_2}$$

(units of $10^{-17} \text{ m}^2/\text{V}^2$), (12)

where

$$\left[\frac{\Delta\epsilon}{E^2} \right]_B = -1.1 + 0.86x, \quad x < 0.065,$$

and

$$\chi^2 = 2.11, \quad \psi \pm 0.015, \quad A \pm 0.1.$$

The concurrence of values of the critical exponent in Eqs. (10) and (12) is noteworthy. This gives evidence that the form of the critical effect is largely independent of the direction of approach to the critical point. Authors Griffiths and Wheeler²⁰ were among the first to point out such a possibility.

The results of the tests conducted in this paper indicate an increase in the critical exponent ψ , which describes the "critical" NDE behavior due to the Fisher renormalization. It would appear that the reduction in ψ observed in the temperature investigations¹⁰ was most probably due to the influence of discontinuity of the phase transformation.

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