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Nonlinear Dielectric Effect of Critical Liquid Mixtures: Propylene Carbonate + Monoalkylbenzene Systems

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The nonlinear dielectric effect (NDE) is measured in the one-phase region of propylene carbonate + monoalkylbenzene systems. The deviations from the regular molecular behavior are determined by the reference solution method at a very wide temperature distance, up to 180 K, from the critical point. The data are analyzed under the assumption of the universality of the precritical NDE by making use of empirical crossover functions. The precritical NDE anomalies are large. The critical exponent $\psi = 0.396 \pm 0.01$ and the correction exponent $\Delta = 1.02 \pm 0.1$ both differ from the theoretical values.

KEY WORDS: binary liquid mixtures; critical phenomena; nonlinear dielectric effect; propylene carbonate solutions.

1. INTRODUCTION

The nonlinear dielectric effect (NDE) consists of the change $\Delta\varepsilon$ of the electric permittivity of a liquid under the action of a strong electric field E. This effect, characterized by the NDE constant, $D = \Delta\varepsilon\, E^{-2}$, is related to the orientation of anisotropic molecules as well as to the changes of molecular conformations and correlations taking place in the field [1]. In binary mixtures a fluctuational effect arises if a system composed of components of different intermolecular interactions has a tendency to separate into two particular liquid phases. The pretransitional contribution, D_C, depending strongly on the reduced temperature distance t from the spinodal curve,

$$D_C = At^{-\psi}g(t), \qquad t = T/T_{sp} - 1 \tag{1}$$

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becomes a dominating factor in the vicinity of the critical solubility point, where it varies according to the simple power law. The deviations from this behavior, which may be of importance at high temperatures, are represented by a weakly temperature dependent function $g(t)$. The main reason for the NDE anomalies in critical binary mixtures is the field-induced deformation of the composition fluctuations resulting in the anisotropy of the internal field and the effective polarizability [2, 3].

According to the theory based on the static droplet model of precritical solutions, we have [2, 3]

$$\psi = 2\gamma - 3\nu \approx 0.59 \tag{2}$$

$$A = A'(dX/d\mu)_0^2 \, \xi_0^{-3} (d\varepsilon/dX)^4 \, \varepsilon^{-2} \tag{3}$$

$$g(t) = 1 \tag{4}$$

where A' is the constant related to the droplet model, ν or γ is the critical exponent of the correlation length $\xi = \xi_0 t^{-\nu}$ or susceptibility $dX/d\mu = (dX/d\mu)_0 \, t^{-\gamma}$, and ξ_0 and $(dX/d\mu)_0$ are the respective amplitudes. X and μ denote the concentration of any component of a binary mixture and its chemical potential, respectively. In contrast to the universal exponent ψ and crossover scaling function $g(t)$, the amplitude A can be controlled experimentally by selecting the components 1, 2 of the mixture. Since the amplitude can be approximated as

$$A \sim (\varepsilon_1 - \varepsilon_2)^4 \, \varepsilon^{-2} \tag{5}$$

the NDE should be a function of the difference between the permittivities of the components.

The application of the NDE method in the study of critical phenomena in two- and one-component systems is briefly reviewed in Ref. 4. In this work we focus attention on the numerical determination of the critical parameters, in order to get information about binary liquid mixtures and to test the relevant theory. In the previous reports some discrepancies were found to occur between the predictions of the droplet model and experiment [5].

To perform this new test, critical binary mixtures with permittivity differences as large as possible were necessary. Such mixtures were found among systems composed of a strongly dipolar compound (sulfolane, butylsultone, propylene carbonate, methylformamide, etc.) and an almost-apolar hydrocarbon. In the present work the NDE is studied in *propylene carbonate + monoalkylbenzene* systems of large but similar electric permittivity differences, $\varepsilon_1 - \varepsilon_2$ being about 70–90 (cf. Ref. 6). Thus the

NDE increments are large and can be accurately measured even far away (100 K) from the critical point.

The aim of the present work is to analyze the experimental results in order to test the universality of the precritical contributions and to propose a reasonable empirical crossover function, as well as to determine the critical exponents and solubility temperatures.

2. EXPERIMENTAL TECHNIQUE

Propylene carbonate, i.e., *dl*-4-methyl-1,3-dioxolan-2-one (99%, Riedel-de Häen), was dried over Sikkon, twice fractionated in the spinning column in a low-pressure dry nitrogen atmosphere, and redistilled under the same conditions immediately before the measurement. Hydrocarbons (min. 99%) were dried over calcium hydride and/or distilled; traces of olefins, if present, were adsorbed on an alumina chromatographic column.

The NDE was measured at 1.5 MHz by means of a single-pulse apparatus [7], adapted, by use of the phase discriminator as the output circuit, to transform the relatively high-capacitance changes, $C_0\,\Delta\varepsilon$ up to 0.3 pF, into proportional voltage signals. The liquids to be examined were subjected to electric field pulses of 1-ms duration and up to 6-$\mathrm{MV \cdot m^{-1}}$ intensity. In some cases simultaneously with the pulse field, an additional dc field of 0.6 $\mathrm{MV \cdot m^{-1}}$ was applied in order to decrease the concentrations of ionic impurities and the electrical conductivity of the sample. The conductivity of the purified propylene carbonate was $1\text{–}5 \times 10^{-7}\,\Omega^{-1} \cdot \mathrm{m}^{-1}$, and that of the solutions was much lower.

The temperature of the sample, varied in a range of 60 K above 280 K, was stabilized within 0.02 K and monitored by means of a thermistor sensor. To check the constancy of $\Delta\varepsilon\, E^{-2}$ the relative electric permittivity changes $\Delta\varepsilon$ were determined at every-temperature from several readings for at least four electric field intensities E. The data for $\Delta\varepsilon\, E^{-2}$ measurements are presented in Table I.

In the *propylene carbonate + s-butylbenzene* system, for which the critical temperature was attainable in our NDE experiments, several phase coexistence temperatures T_{cx} were determined by the visual method to allow construction of the phase diagram. The critical concentration, $\varphi_{\mathrm{c}} = 0.345 \pm 0.005$ volume fraction of propylene carbonate, was assessed by numerical analysis of the $T_{\mathrm{cx}}(\varphi)$ data. Assuming a rectilinear diameter of the coexistence curve we found that

$$\varphi - \varphi_{\mathrm{c}} = 0.735\,|t| \pm 0.694\,|t|^{0.322}, \qquad t = T_{\mathrm{cx}}/283.71 - 1 \tag{6}$$

where all the numerical values are doubtful in the last digits given. For

Table I. The NDE Constant $D = \Delta\varepsilon E^{-2}$ (in $10^{-17}\,\mathrm{V}^{-2} \cdot \mathrm{m}^2$) vs Temperature T (in K) for the Propylene Carbonate + Alkylbenzene Systems of the Near-Critical Concentrations φ (in Volume Fraction of Propylene Carbonate)

(a)

Alkyl	s-Butyl, $\varphi = 0.3473$		t-Butyl, 0.3486		Propyl, 0.3436	
	T	D	T	D	T	D
	287.84	256	285.98	22.0	284.94	11.51
	287.94	249	287.37	19.7	285.61	11.28
	288.04	221	287.75	19.6	286.94	10.15
	288.12	187	290.24	16.7	292.87	6.38
	288.32	153	291.81	14.4	296.00	5.47
	288.54	127	293.81	13.1	298.04	4.30
	288.82	115	296.38	10.87	300.59	3.33
	289.21	106.5	299.97	9.87	305.09	1.81
	289.43	93.5	300.25	8.39	310.92	0.01
	289.62	91.0	303.10	7.63	317.00	−1.80
	290.12	83.8	304.67	5.29	320.22	−2.78
	290.70	74.4	306.46	5.37	323.42	−2.71
	291.03	71.2	309.81	3.74	325.83	−3.35
	291.50	68.4	313.91	2.64	329.26	−3.58
	291.70	67.5	315.68	1.09	334.26	−4.31
	291.84	64.3	323.74	−1.29		
	292.51	57.5	328.44	−2.77		
	292.95	57.2	333.09	−2.81		
	293.82	50.2	333.72	−2.61		
	295.04	44.8				
	295.79	42.6				
	296.66	40.4				
	298.06	34.8				
	300.32	29.7				
	301.63	27.3				
	303.27	24.6				
	305.75	20.8				
	309.75	15.9				
	313.37	11.49				
	316.64	8.67				
	321.33	6.75				
	325.79	4.34				
	329.98	3.63				

Table I. (*Continued*)

(b)

Alkyl	iso-Propyl, $\varphi = 0.3499$		Ethyl, 0.3567		Methyl, 0.3409		(Hydrogen), 0.339	
	T	D	T	D	T	D	T	D
	284.89	5.44	287.22	−8.10	285.10	−12.8	284.93	−15.5
	286.93	4.45	290.50	−8.34	287.91	−12.6	288.65	−14.8
	289.27	3.55	292.53	−8.96	291.29	−12.2	292.00	−14.4
	295.23	1.50	299.08	−8.32	299.36	−11.6	304.49	−12.5
	298.40	0.78	299.41	−8.33	303.54	−11.4	309.51	−12.0
	308.04	−1.99	303.89	−8.46	306.56	−11.3	313.71	−11.6
	311.32	−2.69	305.06	−8.21	310.80	−11.1	317.94	−12.0
	315.04	−3.20	308.36	−8.85	316.10	−11.0	322.07	−11.85
	318.98	−3.66	312.56	−8.50	321.88	−10.96	326.98	−11.11
	323.81	−4.28	312.58	−9.21	328.01	−10.58	332.2	−10.77
	328.99	−4.67	317.97	−8.11	332.83	−10.29		
			329.93	−9.30				
			333.88	−9.61				

binary systems containing propylene carbonate with t-butyl- and propylbenzenes, the critical temperatures were also determined (see Table II) and compared with those resulting from NDE data analysis.

3. DATA ANALYSIS

To analyze the precritical anomalies, we measure NDE in six *propylene carbonate + monoalkylbenzene* systems at the critical concentra-

Table II. Critical Temperatures of the Propylene Carbonate + Alkylbenzene Systems, T_c^{expt}—Observed Visually, and T_c^{extr}—Extrapolated from the NDE Data Fitted as $D_C = At^{-\psi} \exp(-Bt^{\Delta})$, $t = T/T_c - 1$[a]

Alkyl	T_c^{expt} (K)	T_c^{extr} (K)	Range of data
s-Butyl	287.71	287.74 ± 0.02	$6.6 \times 10^{-4} < t < 1.7 \times 10^{-1}$
t-Butyl	271.2	271.4 ± 0.2	$7.3 \times 10^{-3} < t < 3.6 \times 10^{-1}$
Propyl	264	263.3 ± 0.3	$9.6 \times 10^{-3} < t < 4.3 \times 10^{-1}$
iso-Propyl	259	258.2 ± 0.4	$1.6 \times 10^{-2} < t < 4.4 \times 10^{-1}$
Ethyl	<250	235.1 ± 1.5	$3.4 \times 10^{-1} < t < 6.2 \times 10^{-1}$
Methyl	<250	204 ± 12	$6.0 \times 10^{-1} < t < 7.2 \times 10^{-1}$

[a] Fitting parameters: $\psi = 0.35_6$, $\Delta = 1.0_2$, $A = 18_{.3} 10^{-17}\ \text{V}^{-2} \cdot \text{m}^2$, $B = 6_{.1}$.

tions, where $T_{sp} = T_c$. As shown in Fig. 1 the largest critical nonlinear dielectric effects in binary liquids, higher by one order of the magnitude than those in the classical *nitrobenzene + hydrocarbon* systems [8], are observed in the *propylene carbonate + s-butylbenzene* systems. As shown in Fig. 2, in other monoalkylbenzene systems the precritical anomalies are smaller.

The crucial point in data analysis is the exact resolution of the total effect D:

$$D = D_C + D_B \tag{7}$$

into the critical contribution D_C and the noncritical background D_B [3]. As yet this problem has not been resolved beyond any doubt. However, in many cases satisfactory results can be obtained by using the NDE values

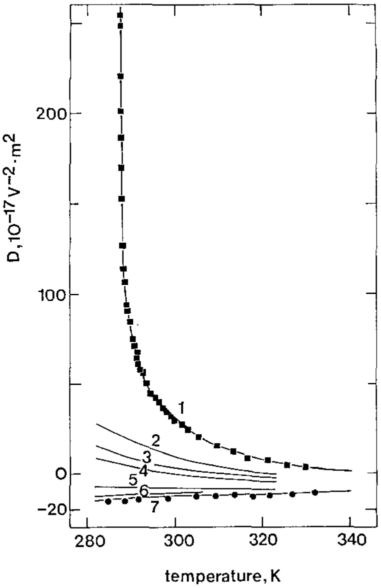

Fig. 1. The NDE constant D of the critical solutions of propylene carbonate in (1) s-butylbenzene, $\varphi = 0.3473$, (2) t-butylbenzene, $\varphi = 0.3486$, (3) *n*-propylbenzene, $\varphi = 0.3436$, (4) iso-propylbenzene, $\varphi = 0.3499$, (5) ethylbenzene, $\varphi = 0.3567$, and (6) toluene, $\varphi = 0.3409$. The data for the noncritical reference solution in benzene (7), $\varphi = 0.339$, are given for comparison. Curves 1–6 are calculated according to Eqs. (1), (7), (8), and (10); curve 7 is plotted from Eq. (8).

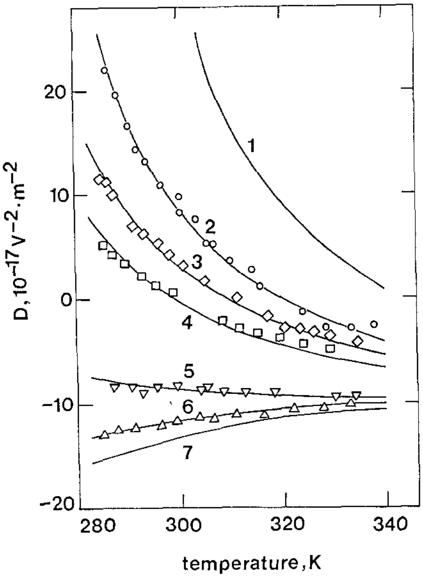

Fig. 2. Enlarged fragment of Fig. 1 with the experimental points shown for solutions 2–6. The precritical increment D_C is found from the difference between the effects measured in the given solution (1–6) and the reference solution (7).

measured in a properly chosen reference solution as the regular molecular component D_B. The reference system is obtained by replacing one of the constituents by another, which is molecularly similar but which gives a much lower critical solution temperature [3, 9].

In the examined systems, the critical temperature is controlled by the alkyl chain at the aromatic component. Since for the systems with the unsubstituted benzene ring, an extremely large temperature depression is expected without any substantial change in molecular NDE contributions, we assumed that the *propylene carbonate + benzene* system is an appropriate noncritical reference. In order to determine the noncritical background precisely, the NDE was measured in the whole range of concentrations, including pure propylene carbonate. By fitting the double polynomial

$$D_B = \sum_{i=1}^{k} \sum_{j=1}^{l} a_{ij} \varphi^i T^{-j} \tag{8}$$

to 116 experimental points, the optimal coefficients a_{ij} were determined for $k=4$, $l=3$. The form of the background $D_B(\varphi, T)$ will be discussed elsewhere, with reference to the molecular NDE contributions in strongly polar systems.

The precritical contributions were extracted from the experimental data with the help of Eqs. (7) and (8). They were analyzed in terms of Eq. (1) for a set of trial crossover functions by the nonlinear least-squares method. In our multiparameter fitting program the modified Gauss–Seidel algorithm combined with the quadratic approximation method [10] was used.

3.1. The Crossover Function

The form of the function for crossover from the singular precritical behavior, $g(t) \rightarrow 1$, to the regular molecular one, $g(t) \rightarrow 0$, is not theoretically known. The commonly used Wegner corrections [11] with linear or quadratic terms in t^{Δ},

$$1 - g(t) = A_1 t^{\Delta} + A_2 t^{2\Delta} + \cdots \tag{9}$$

where $\Delta = 0.5 \pm 0.005$ is the universal correction-to-scaling exponent, do not apply in the case of a wide temperature range [12]. We had to use, therefore, empirical $g(t)$ functions, choosing two-parameter ones in order to limit the number of adjustable constants. For example,

$$g(t) = \exp(-x^C), \qquad x = Bt^{\Delta} \tag{10}$$

where C is imposed.

By definition, the corrections close to the critical point are not very important, but they become significant far away from that point. Therefore the critical exponent ψ and the amplitude, determined in the critical region, are not senstive to the form of $g(t)$, in contrast to the correction exponent Δ, determined from high-temperature data. When analyzing the experimental results with a set of trial functions, we could also observe that (i) parameter C, which controls the ratio A_1/A_2 of the coefficients of the expansions terms, is practically immaterial, and (ii) both even and odd terms in x are necessary to ensure a good fit, and therefore $\exp(x)$ is a better function than $1 - \mathrm{th}(x)$, $(1 + x^2)^{-1}$, etc. Thus, Eq. (10), $C = 1$, was finally accepted for further processing as the crossover function.

3.2. The Critical Exponents

Analysis of the data over the range $7 \times 10^{-4} < t < 1.3 \times 10^{-2}$ for the s-butylbenzene solutions yields the critical parameters:

$$\psi = 0.396 \pm 0.009$$

$$A = (14.6 \pm 0.8) \times 10^{-17}\ \mathrm{V}^{-2} \cdot \mathrm{m}^2$$

the uncertainties being due mainly to the experimental error in T_c. The parameters do not vary markedly with the narrowing of the temperature range. The best fit, requiring T_c by 0.03 K higher than that observed, results in an exponent equal to 0.37_3, so ultimately $\psi = 0.385 \pm 0.025$ can be safely accepted. This value is in disagreement with the theoretical predictions [cf. Eq. (2)] based on the droplet model [2], as well as those based on the statistical microscopic approach [13]. We also obtained this value of the critical exponent for the *adiponitrile + propylbenzene* system (which has large precritical NDE increments [3]), where $\psi = 0.40 \pm 0.02$.

It should be stressed that the experimental NDE exponent determined from careful data analysis should be, in fact, a universal parameter which does not depend on the examined systems, the numerical methods used [5], or the temperature range analyzed [the present work]. The question is, however, whether the NDE exponent determined for solutions of propylene carbonate, which is the equimolar mixture of *d*- and *l*-forms, should be related to the binary-mixture exponent $\psi \approx 0.59$ or to the ternary-mixture exponent $\psi^* = \psi/(1-\alpha) \approx 0.65$. Both these values are evidently higher than the experimental value close to 0.39.

Searching for physical phenomena which may influence the apparent critical NDE parameters, one should consider the precritical slowing down and the frequency dispersion effects. They have not been examined so far in liquid mixtures, but recently they have been shown to be important in pretransitional NDE in the isotropic phase of liquid crystals [14]. In the latter case, if both factors in the data analysis are neglected, a marked overestimation of $T_{I-N} - T^*$ and underestimation of the critical exponent occur.

3.3. The Crossover Parameters

A satisfactory fit of Eqs. (1) and (10) to the data for all six propylene carbonate solutions is easily obtainable by taking the critical temperatures as the only parameters distinguishing the solutions. Since the critical amplitudes and crossover functions for all systems are similar, the common values of the relevant parameters, $A = 18_{.3} \times 10^{-17}\ \mathrm{V}^{-2} \cdot \mathrm{m}^2$ and $B = 6_{.1}$, can be accepted. Thus, the increments D_C instead of $D_C/Ag(t)$ can be plotted vs t to demonstrate the importance of the crossover corrections for temperatures above 2×10^{-2} as well as to illustrate the universal character of the critical NDE, as shown in Fig. 3.

This universality is additionally confirmed by the examination of the critical exponent determined from the whole range of data up to $t = 60 \times 10^{-2}$. Under these conditions, we found that the common value for all the systems is $\psi = 0.35_6$, which is not very much different from that

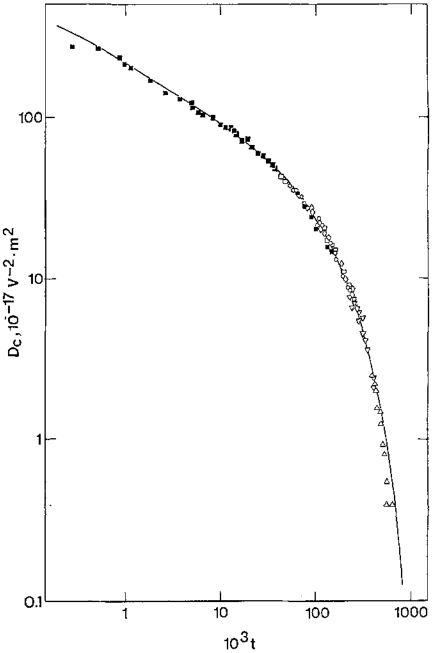

Fig. 3. Results of forcing the precritical NDE increments D_C, shown in Figs. 1 and 2, into a single curve defined by Eqs. (1) and (10). For the numerical values of the critical exponents, amplitudes, and temperatures see Table II; to identify the experimental points consult Figs. 1 and 2.

determined for the *propylene carbonate* + *s-butylbenzene* system alone. Like the critical NDE exponent, also the correction one

$$\Delta = 1.02 \pm 0.1$$

appears to be in disagreement with the theoretical predictions [cf. Eq. (9)]. This is, however, a sensible result because coupling exists between these experimental parameters.

In conclusion, data analysis of the recent NDE experiments in binary liquids [5; the present work] provides reasonably determined critical exponents. However, the meaning of their numerical values is still vague and requires further theoretical elucidation as well as new NDE measurements in the frequency domain.

3.4. The Critical Temperatures

The critical temperatures of the propylene carbonate mixtures, which complete the set of fitting parameters, are collected in Table II. The uncertainties given there result from the sensitivity of T_C to the forms of the crossover functions tested. It is seen that the values covering the 50 K range are determined reasonably well. They appear to be placed in a logical sequence: the longer and less branched the alkyl chain of the hydrocarbon component, the higher is the consolute temperature of the system.

The four highest temperatures have been verified by direct observation of the phase separation above 250 K. The agreement between the numerically estimated and the directly observed critical temperatures supports the assumptions of the numerical analysis, which can be applied, therefore, to determine the experimentally unattainable temperatures of the NDE singularities. This is essential in the study of the spinodal curves of binary liquids, the supercooling limits of the isotropic phase of liquid crystals [3a, 4], and the virtual temperatures of continuous phase transitions masked by crystallization, the presence of other competitive phase transitions, and so on.

The determination of the virtual critical points in liquids or liquid crystals by numerical analysis of the data is not new; e.g., the depolarized light-scattering technique has been previously applied to estimate several $N-I$ transitions [15]. In this view the NDE technique is competitive to light scattering. In spite of the limitations resulting from uncertainties in the background term and usually effects much smaller than those observed in the present work, this method is unique in some special cases, e.g., for examination of isorefractive or strongly nonisodielectric systems.

4. CONCLUSIONS

The NDE method is a good tool for the study of liquid mixtures under precritical conditions, and the precritical NDE increments are observed even far away from the spinodal. The method is particularly suitable for mixtures of components differing markedly in their electric permittivities. The experiment and the up-to-date theory are not in full aggreement because the theory neglects the slowing-down effect near the critical point, as well as the corrections to the asymptotic behavior far from the critical point. However, the precritical NDE may be well described in terms of the droplet model if empirical critical exponents and the crossover function are used. Numerical analysis of the NDE vs temperature provides reasonably determined critical temperatures, as was shown for the propylene carbonate + alkylbenzene systems. This should allow the examination of the systems with experimentally unattainable virtual critical points, e.g., for some binary liquids and monotropic nematogens.

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