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Abstract
A critical binary mixture with a low concentration of ions (tetramethylamonium chloride) was investigated by the non-linear dielectric method. It was observed that the addition of ions increases the critical anomaly of the non-linear dielectric effect. The increase was only observable at low frequencies of the measuring field. Possible explanations are presented and discussed. In spite of the very low concentration of ions, some evidence of crossover from Ising-like to the mean field behaviour was found.

1. Introduction

The critical mixing point in binary liquid mixtures belongs to the (3,1) universality class of continuous phase transitions. In the vicinity of the critical point many macroscopic properties have critical divergences manifesting as a strong increase, or decrease, when temperature and concentration approach the critical values. One of the most spectacular critical divergences is the increase in the non-linear dielectric effect (NDE). The NDE is defined as a difference between electric permittivity measured in strong and in weak electric fields: $\Delta\varepsilon = \varepsilon_E - \varepsilon_0$. In dipolar liquids, the increment is negative and proportional to the square of the electric field strength [1]. Fluctuations yield an increase of the NDE increment, and close to the critical point the $\Delta\varepsilon$ increment is always positive, independent of its sign in the non-critical region [2–9].

The NDE increment (usually expressed as Piekara's coefficient $\Delta\varepsilon/E^2$) in critical mixtures can be approximated by the following expression:

$$\Delta\varepsilon/E^2 = A + Bt + Ct^{-\psi} \tag{1}$$

where A, B, C are constants, $t = (T - T_c/T_c)$ is the reduced temperature and ψ is the critical exponent. Most theories [10–13] predict $\psi = \gamma - 2\beta = 0.59$ ($\gamma = 1.234$ in a 3D-Ising model, $\beta = 0.322$—the most frequently obtainable exponent in critical binary mixtures). Zioło and Rzoska pointed out, however, that a strong electric field gives a large anisotropy of

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fluctuations and the exponent ψ should have a semi-classical value of 0.37 [14]. Our previous measurements confirm rather $\psi \cong 0.59$ exponent [5, 9].

Most papers dealing with critical phenomena in binary critical mixtures describe liquids of high purity; however, in common laboratory practice and for commercial applications it is interesting to study the influence of impurities on the critical and pre-critical properties. The effect of ions on dielectric permittivity and conductivity (measured at low field intensity) of critical binary mixtures have been described in several papers [15–18]. It was found that even a small addition of ions considerably increases the low-frequency permittivity. This was explained in terms of the Maxwell–Wagner effect caused by large and long-living concentration fluctuations. When the system is inhomogeneous and contains ions capable of moving in an external electric field, they are located close to the interfacial surfaces, resulting in an increase of macroscopic polarization and, as a consequence, of dielectric permittivity.

Ionic additivities could be particularly interesting because of possible crossover from asymptotic to mean field behaviour [19]. The approach to the critical behaviour of fluids, including one-component fluids as well as complex systems (for example binary mixtures with a critical mixing point), is affected by competition between the correlation length of critical fluctuations and the length characteristic of the investigated system, related to supramolecular structure and/or long-range intermolecular interactions. The theoretical description based on the Landau–Ginzburg–Wilson Hamiltonian [20–24] and analysis of singularities of free energy allow us to predict the transformation from asymptotic (Ising-like) to mean-field behaviour. In binary critical mixtures there are two crossover parameters [23, 24]: the coupling constant (u) and the cutoff Λ:

$$\Lambda^{-1} = \xi_D \upsilon_0^{-1/3} \tag{2}$$

where ξ_D is the characteristic length reflecting a discrete structure and/or interaction and υ_0 is the average volume per molecule. Transformation from mean-field to Ising-like behaviour is controlled by the ratio Λ/κ, where κ is a measure of the distance from the critical point, and for the critical isochore κ becomes asymptotically proportional to the inverse of correlation length; consequently, $\Lambda/\kappa \approx \xi/\xi_D$. For very large Λ (when the cutoff effects are negligibly small) two crossover parameters collapse into a single one which is related to the Ginzburg number [20]. In systems containing ions ξ_D is related to the long-range Coulombic interactions. Such systems could be an interesting candidate for observing the crossover from asymptotic to mean field behaviours [25–29]. For example, in 3-methylpyridine + water + NaCl there was found a tendency for change of the critical exponents from 3D-Ising to mean-field values [30]. For an anomalous NDE increment, asymptotic behaviour and the exponent $\psi = 0.59$ are expected for $t/Gi \ll 1$, where Gi is the Ginzburg number and t the reduced temperature [30]. In simple fluids, the Ginzburg number is close to 0.01 and, assuming that $T_c \approx 300$ K, asymptotic behaviour should be observed when $T - T_c < 3$ K. In the mean-field region a decrease in exponent is expected (in mean-field condition $\gamma = 1$, $\beta = 0.5$, which gives $\psi = \gamma - 2\beta = 0$). However, the main difficulties in experimental observation of the crossover consist in the requirement to observe a critical anomaly far from the critical point. Only those experimental techniques sufficiently sensitive to the critical and pre-critical fluctuations are applicable for detecting crossover-related phenomena. The influence of critical and pre-critical fluctuations on the NDE increment can be observed many degrees before the critical temperature, and hence the NDE experiments should be useful for detecting the mentioned crossover.

To the best knowledge of the authors, the influence of ions on the NDE increment in critical mixtures is presented for the first time. The measurements were performed in an ethanol + dodecane mixture doped with tetramethylammonium chloride (TMAC).
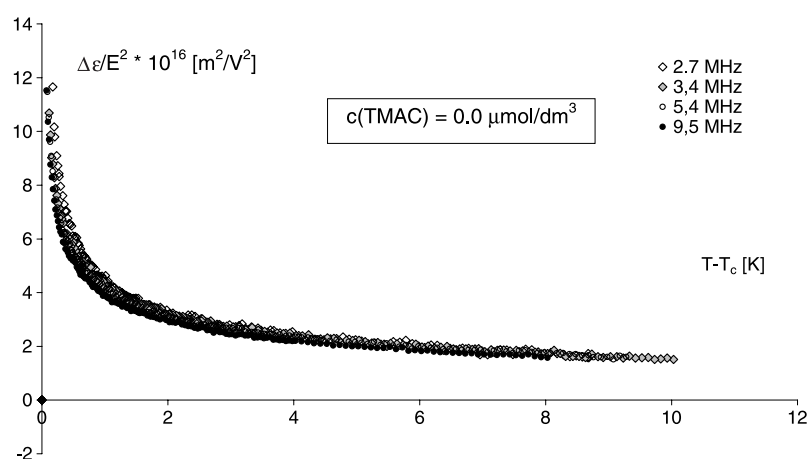
Figure 1. The dependence of $\Delta\varepsilon/E^2$ versus distance from the critical temperature for a pure ethanol + dodecane mixture obtained for four frequencies of the measuring field.

2. Experimental details

The non-linear dielectric effect involves the application of two parallel fields to the investigated material: high-intensity DC pulses (polarizing field), and a low-intensity high-frequency measuring field. A capacitor containing the investigated material is a component of the LC circuit. Comparison of the resonance frequencies observed in the presence and in the absence of the DC field allows calculation of the difference between electric permittivity measured at high and in low electric field strengths. Measurements were performed using the direct answer method. Details of the experimental setup have been described previously [31].

Because the application of a strong electric field to a system containing ions leads to considerable Joule heating (already explored by us to estimate the DC conductivity in a strong electric field [32]), the high voltage (HV) pulses were applied as single, short rectangular pulse of 0.2 ms duration. The largest HV field intensity was between 10^6 and 5×10^6 V m^{-1} and depended on the break-down level. Resolution of NDE experiment was of order of 2% with an absolute accuracy of 10%. The temperature was stabilized with a precision of 0.005 K. In all the experiments, the data were collected at a slowly decreasing temperature (1–0.05 K h^{-1}). The frequency of the measuring field was changed by replacing an inductance coil in the LC circuit. Experiments were done at 2.7, 3.5, 5.5 and 9.5 MHz. The intensity of the high-frequency field was less then 1000 V m^{-1}.

3. Results

NDE experiments were performed in an ethanol + dodecane critical mixture ($x_{c(EtOH)} = 0.68$ [33]) doped by TMAC. Figure 1 presents the temperature dependence of the NDE effect measured at four frequencies in a pure critical mixture. Close to the critical point, a strong increase in the effect is observed. The dependence is almost the same for all frequencies. The results of NDE experiments in mixtures containing ions are presented in figures 2–5. The concentration of the salts was varied between 6.3 and 31.6 μmol dm^{-3}. The most spectacular property is the decrease in the NDE increment in the non-critical region after the addition of salt. For lower frequencies, the decrease is much more pronounced. A similar effect has already been observed in ethanol doped by TMAC as well as in ethanol + p-xylene mixtures doped
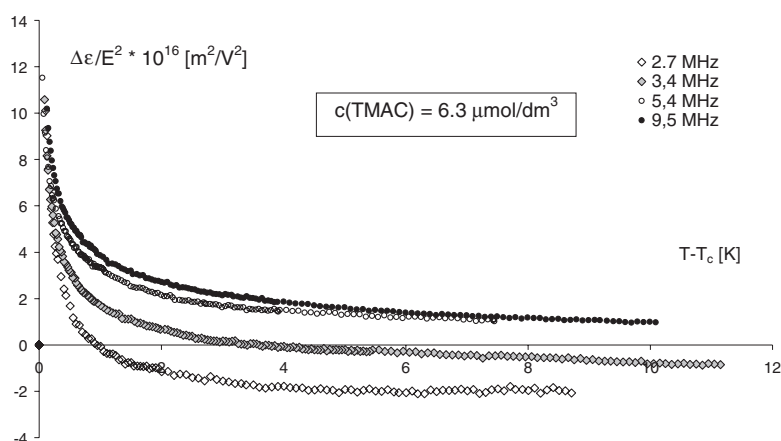
Figure 2. The dependence of $\Delta\varepsilon/E^2$ versus distance from the critical temperature for an ethanol + dodecane mixture with 6.3 μmol dm^{-3} of TMAC.
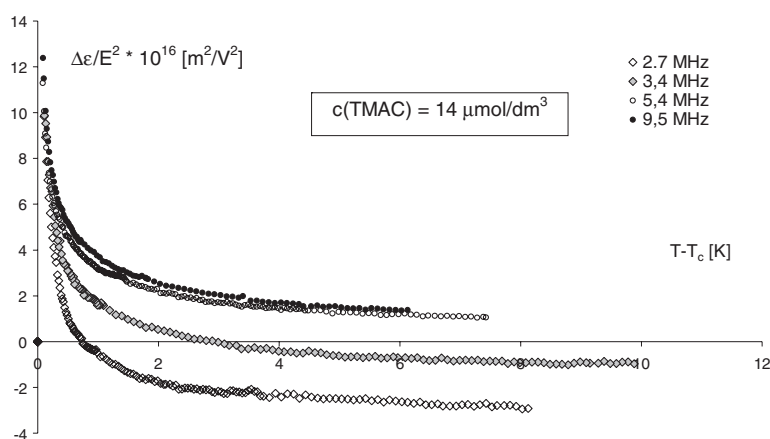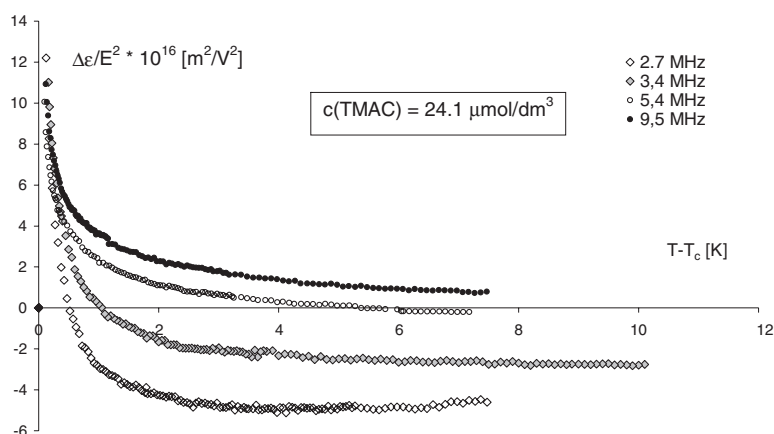

Figure 3. The dependence of $\Delta\varepsilon/E^2$ versus distance from the critical temperature for an ethanol + dodecane mixture with 14.0 μmol dm^{-3} of TMAC.

by TMAC [31]. It was concluded that decrease in the NDE after the addition of ions is related to the electrode polarization effect. A similar decrease is expected in an ethanol + dodecane mixture in the pre-critical region. Independent of the sign of the NDE effect in the pre-critical region, this effect is positive in the vicinity of T_c.

The main question which we would like to answer concerns the effect of ions on the critical properties of the NDE increment. First of all it is necessary to study the critical properties of a pure system under investigation. The ethanol + dodecane mixture has already been investigated [5]. However, previous experiments were performed for just one frequency of measuring field ($f = 4.5$ MHz). As was pointed out by Zioło and Rzoska [8], the NDE critical anomaly could be a function of the frequency of the measuring field, and hence a re-examination of the critical properties of an ethanol + dodecane mixture seems to be necessary.

Figure 1 proves that $\Delta\varepsilon/E^2$ versus temperature in a pure ethanol + dodecane mixture is almost independent of frequency. However, to resolve detailed critical behaviours, a fitting of theoretically predicted equation is needed. According to equation (1), the function describing

Figure 4. The dependence of $\Delta\varepsilon/E^2$ versus distance from the critical temperature for an ethanol + dodecane mixture with 24.1 μmol dm^{-3} of TMAC.
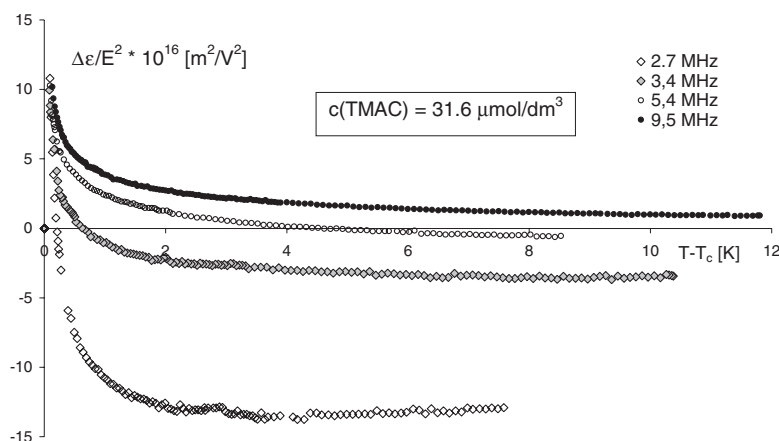
Figure 5. The dependence of $\Delta\varepsilon/E^2$ versus distance from the critical temperature for an ethanol + dodecane mixture with 31.6 μmol dm^{-3} of TMAC.

the critical divergence of the NDE effect (given by Piekara's coefficient) contains five adjustable parameters (A, B, C, ψ, T_c). In spite of a very strong anomaly in the vicinity of T_c, proper estimation of the parameters is very difficult. Not only is there a large number of parameters, but also strong correlation among them considerably impede the calculations. An acceptable description of the experimental data can be obtained for both the exponent $\psi = 0.37$ and for $\psi = 0.59$ after only a small shift of the remaining parameters. It would be very helpful to have an independent estimation of critical temperature, for example that observed by turbidity. However, the phase transition temperature obtained in this way is not necessarily the same as that required in equation (1). Only when the system has a precisely critical concentration is the phase transition temperature equal to the critical one. However, if it is not, T_c in equation (1) will have the meaning of the spinodal temperature. The spinodal temperature is located in the two-phase region and is not available from direct experiment. Only fitting of theoretically predicted curve allows one to calculate it [34]. To improve the reliability of fitting, we try to confine a number of adjusted parameters. Equation (1) is applicable in the close vicinity of

the critical point where asymptotic behaviours are expected. Consequently, if the temperature interval is small (say 1 K), the parameter B describing the non-critical divergence of the NDE increment can be omitted. Another assumption concerns the value of the critical exponent. There are some limiting values of the ψ exponent. There are: the most frequently predicted $\psi = 0.59$ in the asymptotic region [10–13], the semi-classical $\psi = 0.37$ proposed by Zioło and Rzoska [14], and the mean field $\psi \cong 0$. In the restricted temperature interval ($T - T_c < 1$ K) the cross-over from asymptotic to mean field properties in a mixture containing a very low concentration of ions ($c \leqslant 3.1 \times 10^{-5}$ mol dm^{-3}) raises doubts. The model proposed by Zioło and Rzoska [14] assumes strong elongation of fluctuations in the direction of the external field which should lead to a decrease of the critical exponent in the vicinity of T_c. The effect of ions leads to additional elongation and could enhance the phenomena discussed by Zioło and Rzoska. On the other hand, the intensity of the strong electric field was not very high because of the break-down level and it is not clear if the effect discussed by Zioło and Rzoska has to be considered. Taking into account the above, calculations are performed in a temperature interval ($0.1 \leqslant T - T_c \leqslant 1$ K), with fixed ψ exponent values (0.37 and 0.59), and $B \cong 0$ (see equation (1)). Consequently the fitted equation was as follows:

$$\Delta\varepsilon/E^2 = A + Ct^{-\psi}. \tag{3}$$

Table 1 presents the results of fittings.

It is convenient to start the analysis of the fitting results from the critical temperature values. The first part of the table contains parameters obtained in a pure ethanol + dodecane mixture for different frequencies of measuring field. It is obvious that the critical temperature should not depend on the frequency of the measuring field. In spite of the relatively low error of the fitting (± 0.01 K) we suspect that the uncertainty of the obtained critical temperature is larger and can be estimated as ± 0.1 K. In literature a much higher precision of estimation of the critical temperature is often declared. However, the experimental points were obtained in separate runs, including sample preparation, filling the capacitor, temperature stabilization etc. The relatively large uncertainty of the critical temperature could be also be related to the extreme conditions of the NDE experiment (a very strong electric field applied to the electrodes separated by only 0.3 mm) which result in considerable heating of the sample and may disturb the kinetics of approaching the critical point. Taking into account the above, a repeatability of the critical temperature of 0.1 K is acceptable. Analysing T_c obtained in the doped mixtures it seems that the critical temperature slightly increases (0.3 ± 0.2 K) with salt concentration. The increase is roughly consistent with literature values [35].

Parameter 'A' describes the non-critical background of the NDE effect. Table 1 shows a decrease of this parameter with salt concentration. The decrease is much stronger at low frequencies of the measuring field than at high ones. Taking into account strong similarities with the results already obtained in non-critical systems doped by ions [31] the observed change in A is not astonishing and could be considered as 'normal behaviour' for doped systems.

Two separate sets of fittings compare the exponents $\psi = 0.37$ and 0.59. In all cases $\psi = 0.59$ gives a lower error. A preference for the 0.37 exponent was expected in a doped mixture; however, the fitting error points rather at $\psi = 0.59$. In the succeeding discussion, only this value will be considered.

The parameter C is responsible for description of the critical anomaly of the NDE increment. In a non-doped mixture, the critical amplitude is independent of the frequency of measuring field, except for a slight increase for 2.4 MHz. Doping with TMAC doubles the parameter C at low frequencies, whereas at 9.5 MHz no increase of C was observed.

Table 1. Results of the fittings of equation $\Delta\varepsilon/E^2 = A + Ct^{-0.59}$ (part A) and $\Delta\varepsilon/E^2 = A + Ct^{-0.37}$ (part B) to the experimental points. The quality of the fittings are controlled by the mean square error.

(A)

f (MHz)	2.4	3.5	5.5	9.5
$C_{\text{TMAC}} = 0.0\ \mu\text{mol dm}^{-3}$				
T_{c} (°C)	13.21	13.26	13.32	13.27
$A \times 10^{16}$ (m^2 V^{-2})	0.75	1.65	1.71	1.62
$C \times 10^{16}$	0.15	0.11	0.11	0.10
Error	0.0050	0.0107	0.0041	0.0053
$C_{\text{TMAC}} = 6.3\ \mu\text{mol dm}^{-3}$				
T_{c} (°C)	13.49	13.34	13.32	13.50
$A \times 10^{16}$ (m^2 V^{-2})	−4.31	−1.16	0.80	1.16
$C \times 10^{16}$	0.17	0.12	0.11	0.12
Error	0.0111	0.0037	0.0323	0.0026
$C_{\text{TMAC}} = 14.0\ \mu\text{mol dm}^{-3}$				
T_{c} (°C)	13.46	13.41	13.41	13.67
$A \times 10^{16}$ (m^2 V^{-2})	−5.07	−2.07	0.69	0.89
$C \times 10^{16}$	0.18	0.15	0.11	0.12
Error	0.0313	0.0357	0.0033	0.0021
$C_{\text{TMAC}} = 24.1\ \mu\text{mol dm}^{-3}$				
T_{c} (°C)	13.43	13.30	13.38	13.42
$A \times 10^{16}$ (m^2 V^{-2})	−9.58	−5.91	−0.16	0.54
$C \times 10^{16}$	0.28	0.25	0.11	0.13
Error	0.0104	0.0107	0.0124	0.0027
$C_{\text{TMAC}} = 31.6\ \mu\text{mol dm}^{-3}$				
T_{c} (°C)	13.56	13.55	13.54	13.50
$A \times 10^{16}$ (m^2 V^{-2})	−18.53	−4.37	−0.16	1.11
$C \times 10^{16}$	0.32	0.14	0.11	0.12
Error	0.0203	0.1052	0.0073	0.0025

4. Discussion

Before we propose possible explanations for the observed phenomena, it is necessary to consider ion migration under influence of a strong electric field. The electric field intensity used in our experiments was up to $E = 5 \times 10^6$ V m^{-1}, the distance between electrodes was 0.3 to 0.35 mm and the duration of the HV pulse was 0.2 ms. If one assumes a mobility of ions of the order of 4×10^{-8} (m^2 V^{-1} s^{-1}), the distance covered by the ions during the pulse duration is about 0.04 mm. This is about 10% of the distance between the electrodes. Migration of ions produces a concentration gradient inside the capacitor and can give some screening of electrode charges and, as a consequence, a decrease in the effective electric field strength. In constant charge conditions (in the sense of Onuki's explanation [13]), to neglect the screening effect the concentration of ions should be much lower than that used in our experiments. However, our measurements were done in constant potential conditions and, in spite of ion migration, the electric field strength estimated from the pulse amplitude and the distance between electrodes is acceptable. The estimation given above does not take into account self-diffusion which counteracts the non-uniform distribution of ions.

Table 1. (Continued.)

(B)

f (MHz)	2.40	3.50	5.50	9.50
$C_{TMAC} = 0.0\ \mu mol\ dm^{-3}$				
T_c (°C)	13.21	13.26	13.32	13.27
$A \times 10^{16}$ (m^2 V^{-2})	−2.15	−0.83	−0.87	−0.77
$C \times 10^{16}$	0.800	0.618	0.607	0.566
Error	0.0078	0.0161	0.0156	0.0175
$C_{TMAC} = 6.3\ \mu mol\ dm^{-3}$				
T_c (°C)	13.52	13.37	13.35	13.54
$A \times 10^{16}$ (m^2 V^{-2})	−6.84	−3.13	−0.90	−0.51
$C \times 10^{16}$	0.80	0.59	0.52	0.54
Error	0.0208	0.0034	0.0033	0.0023
$C_{TMAC} = 14.0\ \mu mol\ dm^{-3}$				
T_c (°C)	13.49	13.44	13.44	13.70
$A \times 10^{16}$ (m^2 V^{-2})	−7.81	−4.28	−1.03	−1.07
$C \times 10^{16}$	0.848	0.702	0.520	0.582
Error	0.0466	0.0472	0.0032	0.0025
$C_{TMAC} = 24.1\ \mu mol\ dm^{-3}$				
T_c (°C)	13.45	13.34	13.41	13.46
$A \times 10^{16}$ (m^2 V^{-2})	−14.24	−9.20	−2.00	−1.29
$C \times 10^{16}$	1.36	1.12	0.54	0.59
Error	0.0216	0.0146	0.0102	0.0033
$C_{TMAC} = 31.6\ \mu mol\ dm^{-3}$				
T_c (°C)	13.47	13.50	13.40	13.46
$A \times 10^{16}$ (m^2 V^{-2})	−36.19	−10.76	−7.16	−2.20
$C \times 10^{16}$	2.91	1.12	1.15	0.74
Error	1.1917	0.2765	0.1478	0.0433

The increase of the NDE increment in the vicinity of the critical point is usually interpreted on the basis of the droplet model [10]. Polar-component-rich fluctuations are stretched in the direction of the strong electric field, which results in an increase of permittivity (measured parallel to the strong field). If ions exist, they migrate to the boundaries of fluctuations which should lead to additional stretching and can result in an increase of the critical part of the NDE. However, the effect should be observable both at low and at high frequencies of the measuring field, which seems to be inconsistent with our results (the increase of critical amplitude was found for low frequencies only).

To interpret the low-frequency permittivity anomaly it is convenient to consider the existence of a Maxwell–Wagner (MW) effect caused by large and long-lived concentration fluctuations. The MW effect consists of an accumulation of ions at the borders of inhomogeneities (fluctuations in the case of critical systems) which leads to a strong increase in the low-frequency electric permittivity. This effect increases after doping with ions [15, 17]. The MW effect was observed at relatively low frequencies, but the increase in concentration of ions shifts the MW dispersion to higher frequencies [15, 36]. Consequently, in doped critical mixtures the NDE increment may increase, especially when the frequency of the measuring field in an NDE experiment is relatively low and covers, partly at least, the MW dispersion.
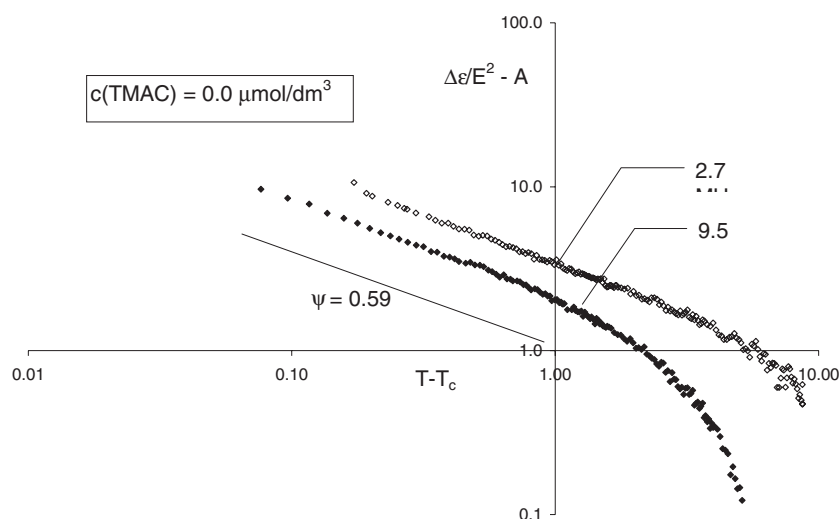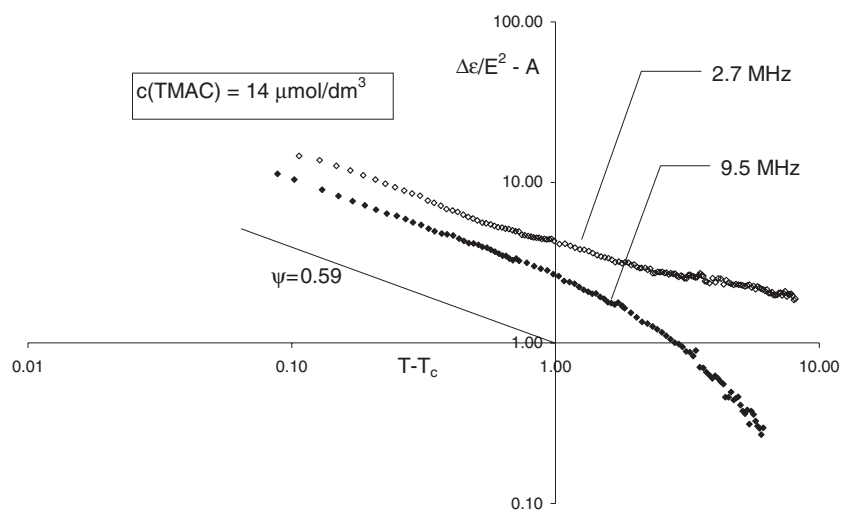
Figure 6. The dependence of $\Delta\varepsilon/E^2 - A$ versus the distance from the critical temperature in a double logarithmic scale for a pure ethanol + dodecane mixture. 'A' is the fitted non-critical term (in see equation (1)).

Consequently, the MW effect could be responsible for the increase in NDE critical anomaly at low frequencies. This seems to be consistent with our observations.

Unfortunately, there are also some possible effects suppressing the critical anomaly of the NDE in ion-doped mixtures. Ions at the boundaries of fluctuations are subjected to the influence of two parallel fields: high-intensity rectangular pulses and low-intensity high-frequency measuring field. The strong field 'freezes' ions at the boundaries and the low-intensity measuring field could not influence the polarization as efficiently as in absence of the strong field.

The proposed mechanism for the increase in the NDE anomaly in doped systems assumes that ions are trapped inside fluctuations. However, the 'border' of a fluctuation is only an area where the chemical potential is changing because of small differences in concentration of a polar component. Interaction between the external field and ions is probably sufficiently strong to remove ions from droplets (fluctuations).

The experimental data were collected over a broad temperature interval (see figures 1–5), but only the close vicinity of T_c has been explored already. It is interesting if, in spite of the extremely low ion concentration, any crossover from asymptotic to mean-field behaviour could be observed. An attempt to detect crossover requires observation of the anomaly at a temperature distant from the critical temperature ($t > 0.01$). Unfortunately, far from T_c the effect of fluctuations on the measured quantity is usually negligible. In this context, the NDE could be a suitable technique for observation of such phenomena. NDE is extraordinarily sensitive to fluctuations [1]. Figures 6–8 presents $\Delta\varepsilon/E^2 - A$ (where A is a non-critical background obtained in the fitting) versus ($T - T_c$) in a double logarithmic scale. In all the presented dependences, close to T_c the slope is close to 0.59. In a pure mixture (figure 6) for temperatures further from T_c there is a 'downturn' in the dependence, which proves leaving of the critical region. In mixtures doped by ions a decrease in the negative slope of this dependence is observed. For the largest concentration for 2.5 MHz, when $T - T_c > 5$ K ($t > 0.017$) the slope seems to tend to 0. Formally, this could be interpreted as a crossover from

Figure 7. The dependence of $\Delta\varepsilon/E^2 - A$ versus the distance from the critical temperature in a double logarithmic scale for an ethanol + dodecane mixture doped by 14 μmol dm^{-3} of TMAC. 'A' is the fitted non-critical term.
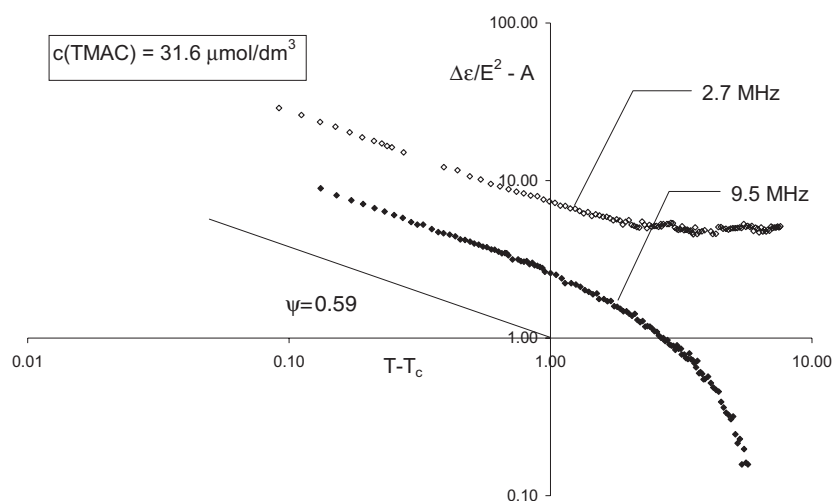
Figure 8. The dependence of $\Delta\varepsilon/E^2 - A$ versus the distance from the critical temperature in a double logarithmic scale for an ethanol + dodecane mixture doped by 31.6 μmol dm^{-3} of TMAC. 'A' is the fitted non-critical term.

asymptotic to mean field behaviour. Unfortunately, this is not a very rigorous conclusion. In correlations, it was assumed that the background is temperature independent (the background was approximated by the A parameter only). This assumption is acceptable when a small temperature interval is analysed. For larger temperature intervals neglecting the temperature dependence of the background could produce an apparent change of the slopes of the analysed dependences. It is also not clear why the mentioned property is only observable at low frequencies of the measuring field.

It is worth mentioning that the dependence of a crossover on measuring frequency is somewhat similar to that presented by Zioło and Rzoska in a nitrobenzene–dodecane critical mixture [8]. When measurements were performed at low frequencies the mean field exponent was observed, while at high frequencies the universal ones were seen. The authors linked this observation to competition between the lifetime of fluctuations (τ) and the inverse of measuring frequency (f_m). When $1/f_m > \tau$ the asymptotic exponent was observed and when $1/f_m < \tau$ the mean field one was.

5. Conclusions

The effect of ions on the critical divergence of the NDE increment in binary mixtures could be observed at low frequencies of the measuring field. The critical amplitude increases after doping of the system by ions. Many mechanisms could be responsible for this: accumulation of ions at the boundary of fluctuations, stretching of fluctuations, low-frequency relaxation related to the Maxwell–Wagner effect. However, the influence of ions on the NDE critical anomaly is relatively small and is only observable at low frequencies.

In spite of the very low concentration of ions, some evidence of crossover from asymptotic to mean field behaviour was observed.

Acknowledgment

References

[1] Chełkowski A 1980 *Dielectric Physics* (Amsterdam: Elsevier Scientific Publishing Company)
[2] Pyżuk W and Zboiński K 1977 *Chem. Phys. Lett.* **52** 577
[3] Chrapeć J, Rzoska S J and Zioło J 1988 *Chem. Phys.* **122** 471
[4] Chrapeć J and Rzoska S J 1989 *Phys. Lett.* A **139** 343
[5] Orzechowski K 1991 *Physica* B **172** 339
[6] Rzoska S J and Zioło J 1993 *Phys. Rev.* E **47** 1445
[7] Rzoska S J 1993 *Phys. Rev.* E **48** 1136
[8] Zioło J and Rzoska S J 1999 *Phys. Rev.* E **60** 4983
[9] Orzechowski K 1999 *Chem. Phys.* **204** 275
[10] Goulon J, Greffe J-L and Oxtoby D W 1979 *J. Chem. Phys.* **70** 4742
[11] Hole J S and Stell G 1984 *J. Chem. Phys.* **81** 3200
[12] Onuki A and Doi M 1992 *Europhys. Lett.* **17** 339
[13] Onuki A 2004 *Nonlinear Dielectric Phenomena in Complex Liquids* ed S J Rzoska and V P Zhelezny (Dordrecht: Kluwer Academic) p 113
[14] Rzoska S J 1993 *Phys. Rev.* E **48** 1136
[15] Thoen J, Kindt R and Van Dael W 1980 *Phys. Lett.* A **76** 445
[16] Thoen J, Kindt R, Van Dael W, Merabet W and Bose T K 1989 *Physica* A **156** 92
[17] Orzechowski K 1997 *J. Mol. Liquids* **73/74** 291
[18] Orzechowski K and Kosmowska M 2004 *Nonlinear Dielectric Phenomena in Complex Liquids* ed S J Rzoska and V P Zhelezny (Dordrecht: Kluwer Academic) pp 89–100
[19] Gutkowski K I, Anisimov M A and Sengers J V 2001 *J. Chem. Phys.* **114** 3133
[20] Anisimov M A, Kiselev S B, Sengers J V and Tang S 1992 *Physica* A **188** 487
[21] Chen Z Y, Abbaci A, Tang S and Sengers J V 1990 *Phys. Rev.* A **42** 4470
[22] Chen Z Y, Albright P C and Sengers J V 1990 *Phys. Rev.* A **41** 3161
[23] Anisimov M A, Povodyrev A A, Kulikov V D and Sengers J V 1995 *Phys. Rev. Lett.* **75** 3146
[24] Anisimov M A, Povodyrev A A and Sengers J V 1999 *Fluid Phase Equilib.* **158–160** 537
[25] Narayanan T and Pitzer K S 1995 *J. Chem. Phys.* **102** 8118

[26] Jacob J, Anisimov M A, Kumar A, Agayan V A and Sengers J V 2000 *Int. J. Thermophys.* **21** 1321
[27] Wagner M, Stanga O and Shoer 2002 *Phys. Chem. Chem. Phys.* **4** 5300
[28] Oleinikova A and Bonetti M 1996 *J. Chem. Phys.* **104** 3111
[29] Gutkowski K I, Bianchi H L and Japas M L 2003 *J. Chem. Phys.* **118** 2808
[30] Hermandez M P, Ortega F and Rubio R G 2003 *J. Chem. Phys.* **119** 4428
[31] Kosmowska M and Orzechowski K 2004 *Chem. Phys. Lett.* **393** 290
[32] Kosmowska M and Orzechowski K 2003 *Polish J. Chem.* **77** 1513
[33] Orzechowski K 1994 *J. Chem. Soc. Faraday Trans.* **90** 2757
[34] Chrapeć J, Rzoska S J and Zioło J 1987 *Chem. Phys.* **111** 155
[35] Eckfeld E L and Luesse W W 1943 *J. Phys. Chem.* **47** 164
[36] Orzechowski K 1990 *Proc. Ist Symp. on Low Frequency Dielectric Spectroscopy and Related Problems (Poland, Krynica)* p 79