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Electric birefringence of a binary liquid mixture near the critical consolute point

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Transient electric birefringence measurements are performed in a critical binary mixture, water and butoxyethanol. The Kerr constant near the critical temperature is described rather accurately by a power law with a critical exponent $\psi = 0.85 \pm 0.05$. The transient electric birefringence is found to exhibit stretched-exponential relaxation of the form $\exp[-(t/\tau)^x]$, with $x = 0.4 \pm 0.05$ and τ diverging as a power law in reduced temperature.

INTRODUCTION

It is well known that a liquid may become birefringent under the application of an electric field if its molecules possess an electric dipole moment or a nonspherical shape. This is the so-called Kerr effect. Recent experiments have demonstrated that binary liquid mixtures showing negligible Kerr effect in normal conditions may present a large Kerr coefficient B near a critical consolute point.[1-3] As the critical point is approached at fixed composition, B grows following a power-law behavior as a function of the reduced temperature $\epsilon = (T_c - T)/T_c$, $B = B_0 \epsilon^{-\psi}$. Theory[4,5] predicts $\psi \approx 0.6$. However, the available experimental data[1-3] seem to indicate that ψ is larger than the theoretical prediction. It has been found experimentally that the relaxation of the electric birefringence in a critical binary mixture not only shows the expected critical slowing down, but also takes a nonexponential form.[6] Successive measurements performed with the critical mixture water-lutidine[7] have found that the relaxation exhibits a stretched-exponential form $\exp[-(t/\tau)^x]$, where $x = 0.4$ and τ diverges as $\tau = \tau_0 \epsilon^{-y}$, where $y = 1.8 \pm 0.2$.[7] The model discussed in Ref. 7 predicts that such a behavior is universal for critical mixtures.

In order to obtain further information on both the static and dynamic Kerr effect, we have performed an investigation with another critical mixture, water and butoxyethanol. This mixture was chosen because, besides having a convenient critical temperature, it presents a large mismatch between the dielectric constants and the indices of refraction of the two components, thus ensuring a large value of the constant B.[6]

EXPERIMENTAL RESULTS

The experiment consists of applying an electric-field rectangular pulse and measuring the transient as well as the steady-state electric birefringence of the solution. A detailed description of the apparatus can be found in Ref. 2. Here, we simply recall that the setup includes a quarter-wave plate inserted between the Kerr cell and the analyzer to increase the sensitivity and reduce parasitic effects due to stress birefringence of the cell windows.[2] The cell itself is made in Teflon and Macor and has platinum electrodes. The optical pathlength is 60 mm, and the electrodes have a separation of 2.5 mm. Temperature control within the thermostatted cell is maintained to ±0.01 °C. Voltage pulses with heights of 0.3–1 kV and durations of 10–300 μs were used. The samples consisted of high purity 2-butoxyethanol ($C_4H_9OCH_2CH_2OH$), purchased from BDH, and deionized, filtered water. The electrical resistivity of the samples was about 200 kΩ cm at 20 °C.

The output of the photodetector, which is linearly related to the difference Δn between the index of refraction $n_\parallel$ (polarization parallel to the applied electric field) and $n_\perp$ (polarization perpendicular to the applied field) is sent to a transient digitizer (Data 6000, Data Precision) which performs the averaging over a prescribed number of runs (typically 50). The duty cycle was extremely low to avoid cumulative heating effects.

The mixture water-butoxyethanol was found to have a lower consolute boundary with a critical point at 49.8 °C and 26% by weight of butoxyethanol. These values are very close to those reported in the literature.[8] By fixing the butoxyethanol concentration at the critical value, we have studied the temperature dependence of the electric birefringence transients. In the investigated range of conditions we have verified that the shape of the birefringence transient does not depend on the applied electric field E, and that the steady-state value Δn is proportional to the

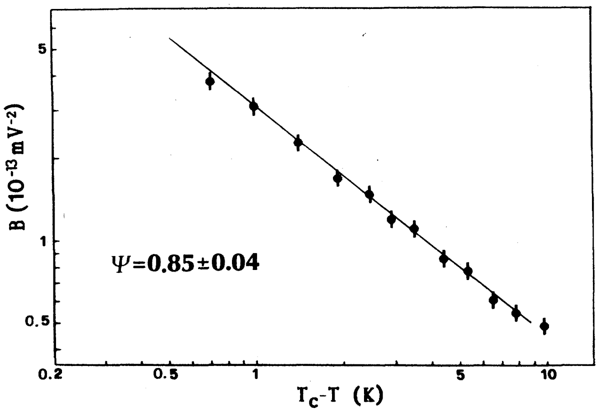

FIG. 1. Kerr constant B vs the temperature distance from the critical point for the mixture water-butoxyethanol at the critical concentration.

TABLE I. The Kerr constant B as a function of the temperature distance from the critical point for the mixture water-butoxyethanol at the critical concentration. The experimental uncertainty on the measured B is ±7%.

$T_c - T$ (K)	B (10^{-13} mV^{-2})
9.77	0.49
7.87	0.54
6.48	0.61
5.40	0.78
4.42	0.86
3.54	1.10
2.95	1.17
2.46	1.46
1.92	1.66
1.43	2.27
1.02	3.03
0.69	3.72

square of the field. The obtained Kerr constant B, defined as $B = \Delta n / \lambda E^2$, with λ the wavelength of probing light, is reported in Fig. 1 (see also Table I) as a function of the temperature distance from the critical point. B can be fitted to a power law of the form $B = B_0 \epsilon^{-\psi}$, with $B_0 = (1.14 \pm 0.1) \times 10^{-14}$ mV^{-2}, and $\psi = 0.85 \pm 0.04$. The uncertainties represent 1 standard deviation.

If a square pulse of a duration t_D is applied at time $t = 0$ and if we call $B(t)$ the birefringence observed at time t, we can define the normalized decay relaxation function as $R(t) = B(t + t_D)/B(t_D)$. A typical shape of $R(t)$ is shown in the semilogarithmic plot of Fig. 2. We see that $R(t)$ is not exponential. However, if we make a log-log plot of $\ln R(t)$ as a function of t, we find that the plot is linear with a slope independent from the temperature, as shown in Fig. 3. This indicates that $R(t)$ obeys a stretched-exponential law, $R(t) \approx \exp[-(t/\tau)^x]$. The exponent x may be derived as the slope of the log-log plot, and τ is determined from the intercept with the horizontal axis.[7]

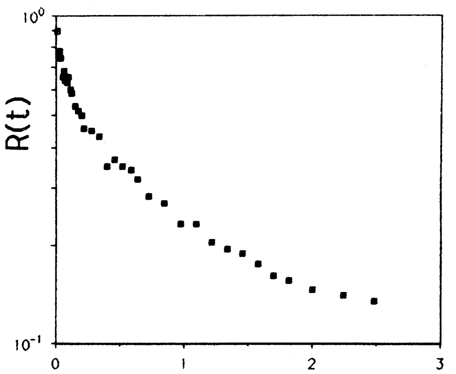

FIG. 2. Normalized decay function $R(t)$ of electric birefringence for the mixture water-butoxyethanol at the critical concentration and at $T_c - T = 1.16$ K, demonstrating nonexponential relaxation.

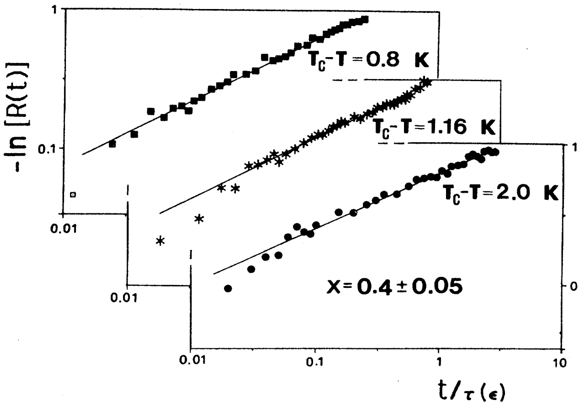

FIG. 3. Logarithmic plot of $\ln R(t)$ vs t at three distinct temperatures, demonstrating stretched-exponential relaxation. The solid line corresponds to a stretch exponent $x = 0.4$.

We find $x = 0.40 \pm 0.05$. The power-law divergence of the relaxation time is shown in Fig. 4 (see also Table II). A linear fit with the law $\tau = \tau_0 \epsilon^{-y}$ yields $y = 1.78 \pm 0.05$.

DISCUSSION

Previously reported measurements of the critical exponent ψ by Pyzuk and co-workers[1] yielded values scattered in the range 0.7–1. Our data on water-lutidine give $\psi = 0.88 \pm 0.03$.[2] Various nonionic micellar solutions have also been studied, obtaining values of ψ in the range 0.08–0.9.[3] It should be noted that the first measurements on two nonionic micellar solutions ($C_{12}He_6$-H_2O and $C_{12}He_8$-H_2O) gave $\psi \approx 0.5$,[6] but in that experiment the

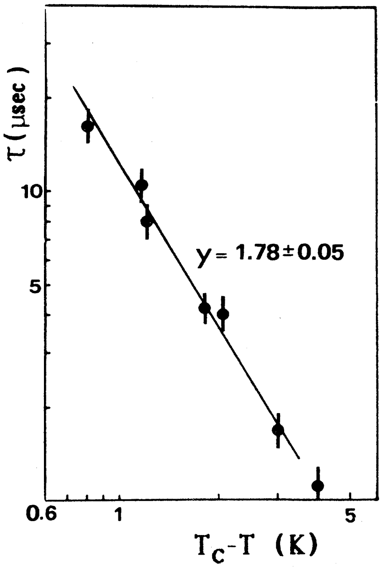

FIG. 4. Power-law divergence of the decay time τ with the reduced temperature ϵ. The slope of the fitted line is 1.78 ±0.05.

TABLE II. The relaxation time τ as function of the temperature distance from the critical point for the mixture water-butoxyethanol at the critical concentration. The uncertainty on the measured τ is ± 12%.

$T_c - T$ (K)	τ (μs)
4.05	1.1
3.05	1.7
2.05	4.0
1.80	4.3
1.20	8.2
1.15	10.1
0.80	16.7

data were not taken sufficiently close to the critical point, as it was shown in a subsequent work.[3]

The calculations by Goulon, Greffe, and Oxtoby[4] and by Hoye and Stell[5] find $\psi = 2\gamma - 3\nu \approx 0.6$, where γ and ν are the critical exponents for the compressibility and the correlation range. The results reported in this work confirm that a discrepancy exists between theory and experiment. At present, we have no explanation for the discrepancy. An aspect of the theories of Refs. 4 and 5 which might perhaps be questioned is that only the effects due to the second-order correlation function are taken into account. Other approaches, which are however not directly applicable to critical systems, indicate that a significant role can be played also by third- and fourth-order correlations in the position of the molecules.[9]

Concerning the dynamic behavior of the Kerr effect, we recall that the model of Ref. 7 predicts a stretch exponent $x = (2-\eta)/(5-\eta)$, where $\eta \ll 1$ is the critical exponent introduced by Fisher,[10] and a divergence of relaxation time with the exponent $y = 3\nu$. Our results are in rather good agreement with those predictions.

We note as a concluding comment that the nonexponential relaxation is a direct consequence of the fact that critical fluctuations involve broadly distributed length scales. The polydispersity effect is much larger in the electric birefringence relaxation than it was found in dynamic light-scattering studies of the decay of concentration fluctuations.[11] This is simply because in the latter case the decay time is a linear function of size whereas in the former case the decay time is proportional to the cube of the size.[7]

ACKNOWLEDGMENTS

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