

## Electric Birefringence of Critical Micellar Solutions

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(Received 26 November 1984)

Measurements of static and dynamic electric birefringence of nonionic micellar solutions near the critical consolution point show a diverging Kerr coefficient  $B$  and a diverging rise time of the birefringence signal. The static data are consistent with the droplet model which predicts that  $B$  grows as the correlation length  $\xi$ . The transient behavior, observed for the first time in a critical system, shows a strong asymmetry between rise and decay of birefringence. The rise is nonexponential and follows, sufficiently close to the critical point, a universal function of scaled time. The time-scaling factor approximately behaves as  $\xi^{-2}$ .

PACS numbers: 64.70.Ja, 78.20.Jq, 82.70.-y

It is known from the work of Pyzuk and co-workers<sup>1</sup> that some binary liquid mixtures show electric birefringence (Kerr effect) in the critical region. As the critical point is approached the static Kerr coefficient grows following a power-law behavior as a function of the reduced temperature. Such a divergence was predicted by Goulon, Greffe, and Oxtoby<sup>2</sup> through a calculation based on the droplet model.<sup>3</sup> The central idea is that the applied electric field distorts the spontaneous critical fluctuations. These anisotropic fluctuations then play the role of nonspherical molecules in ordinary electric birefringence. This effect is qualitatively similar to flow birefringence in critical fluids which was recently described both experimentally<sup>4</sup> and theoretically.<sup>5</sup>

We report in this paper the observation of critical electric birefringence in nonionic micellar solutions near their critical consolution point. By exploiting the fact that relaxation times in micellar solutions are longer than in mixtures of two small-molecule liquids, we have been able to study for the first time the dynamics of the critical Kerr effect.

Water-amphiphile systems are peculiar critical binary mixtures because one of the components, the amphiphile, spontaneously associates to form a micelle with an aggregation number around 100.<sup>6</sup> Light-scattering experiments have shown that critical micellar solutions behave similarly to ordinary critical binary mixtures.<sup>7</sup> The present experiment suggests that these solutions may permit one to study aspects of the critical behavior which are otherwise difficult to observe.

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. Two nonionic micellar solutions have been investigated, the first consisting of water and *n*-dodecyl hexaoxyethylene glycol monoether ( $C_{12}Et_6$ ) which shows a lower consolution point at the temperature  $T_c = 52^\circ\text{C}$  and at the amphiphile concentration  $c_c = 1.5\%$  by weight, and the second being  $H_2O-C_{12}Et_8$  which presents the critical point at  $T_c = 77^\circ\text{C}$  and  $c_c = 3.2\%$ .<sup>7</sup> The two compounds  $C_{12}Et_6$  and  $C_{12}Et_8$

were synthesized and purified by E. Platone and co-workers (Eni Ricerca, S. Donato, Italy).

Particular care was taken to eliminate all ionic impurities in both amphiphile and water in order to reduce as much as possible Joule heating of the sample during the application of the electric pulse. Typically the resistivity of our samples was  $0.8\text{ M}\Omega\cdot\text{cm}$  at  $20^\circ\text{C}$ . The cell temperature was controlled within  $0.01^\circ\text{C}$ . Voltage pulses with height of  $0.4\text{--}1.2\text{ kV}$  and duration of  $10\text{--}300\ \mu\text{s}$  were applied to two electrodes with a length of  $5\text{ cm}$  and a gap of  $2\text{ mm}$ . The estimated temperature rise after a single pulse was always less than  $0.02^\circ\text{C}$ . The induced birefringence was observed by our putting the sample cell between two crossed polarizers, sending a He-Ne laser beam through the solution, and observing the transmitted light as function of time. The output of the photodetector is sent to a transient digitizer (Data 6000, Data Precision) which performs the average over a prescribed number of runs. The duty cycle was extremely low to avoid cumulative heating effect.

Two typical birefringence signals, referring to the  $H_2O-C_{12}Et_6$  system at the critical concentration and at two distinct temperatures, are shown in Fig. 1.<sup>8</sup> Note that the signal taken closer to  $T_c$  presents a much longer rise time and a much larger steady state. The decay time is, in both cases, considerably faster than the rise time and indistinguishable from our instrumental response time ( $\sim 500\text{ ns}$ ). The birefringence signal is proportional to  $(\Delta n)^2$  where  $\Delta n$  is the difference between the index of refraction  $n_{\parallel}$  (polarization parallel to the applied electric field) and  $n_{\perp}$  (polarization perpendicular to the electric field). The steady-state value  $\Delta n_s$  can be expressed as  $\Delta n_s = \lambda B E^2$ , where  $E$  is the applied electric field,  $\lambda$  the wavelength of the laser beam, and  $B$  the Kerr coefficient. We have verified that both  $B$  and the shape of the birefringence signals do not depend on  $E$  in the investigated range of conditions.

The measured values of  $B$  as function of the temperature distance from the critical point for  $C_{12}Et_6$  and  $C_{12}Et_8$  solutions at the critical concentration are report-

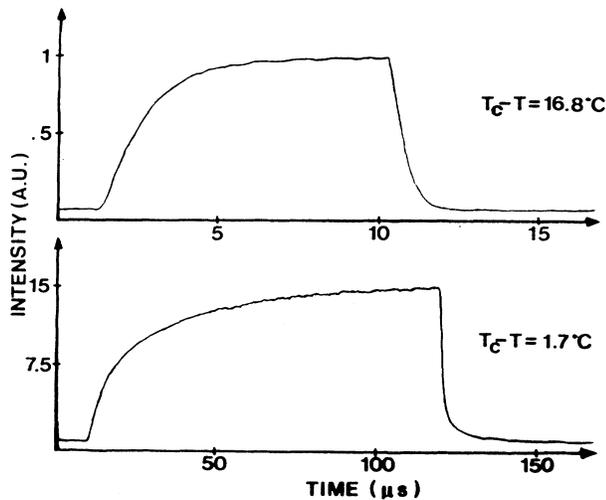


FIG. 1. Two electric birefringence signals observed in  $C_{12}Et_6$ . The signals represent an average over 32 (upper trace) and 16 (lower trace) pulses.

ed in Fig. 2. The data can be described by the power law  $B = B_0(1 - T/T_c)^{-\Psi}$ , with  $B_0 = 1.06 \times 10^{-13} \text{ V}^{-2} \cdot \text{m}$  and  $\Psi = 0.52 \pm 0.05$  for  $C_{12}Et_6$  solutions, and  $B_0 = 0.37 \times 10^{-13} \text{ V}^{-2} \cdot \text{m}$  and  $\Psi = 0.49 \pm 0.05$  for  $C_{12}Et_8$  solutions. Both solutions do not show any appreciable birefringence far away from  $T_c$  (apart from the very weak birefringence due to pure water), so that the analysis of our data does not require any subtraction of a noncritical part, as was necessary for the data of Ref. 1.

Since micelles are spontaneous aggregates, it is possible in principle that the micelle size and shape change with  $T$ . In the case of  $C_{12}Et_8$  micelles, recent NMR self-diffusion<sup>9</sup> and quasielastic neutron-scattering<sup>10</sup> experiments clearly demonstrate that micelles remain small and globular as  $T$  increased toward  $T_c$ . For  $C_{12}Et_6$  micelles the situation is more controversial. The observed fast decay times (see Fig. 1) are not compatible, for both amphiphile solutions, with the hypothesis that large anisotropic micelles are present in the system, because, in such a case, both the rise time and the decay time would be controlled by the rotational diffusion of the micelles, and therefore both would become very long in presence of large micelles.

The calculation of  $B$  by Goulon, Greffe, and Oxtoby<sup>2</sup> is based on the droplet model which describes the critical fluid as a dispersion of droplets with an appropriate composition and size distribution.<sup>3</sup> The droplets become elongated in the direction of the applied electric field, with a shape determined by the balance between surface tension and electrostatic forces.<sup>11</sup> In the case of critical micellar solutions, a single droplet may be viewed as a random cluster of micelles. The temperature dependence of  $B$  along the critical

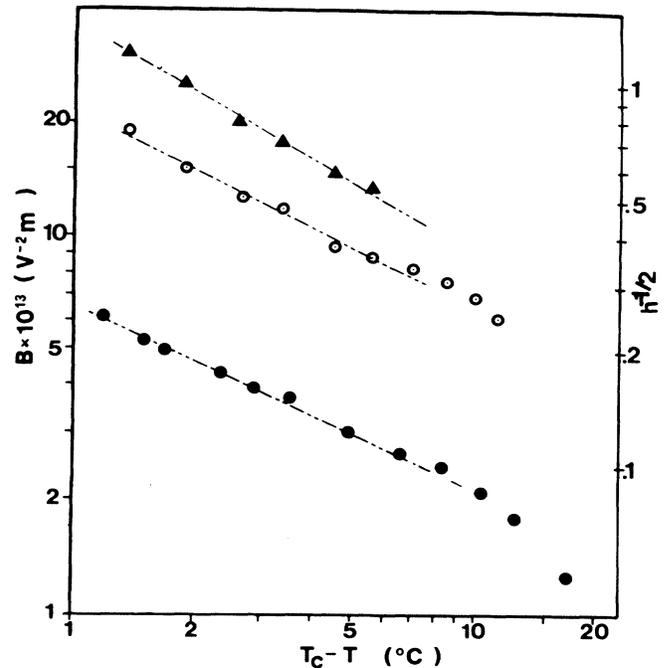


FIG. 2. The Kerr coefficient of  $C_{12}Et_8$  (solid circles) and of  $C_{12}Et_6$  (open circles) solutions at the critical concentration reported as a function of the temperature distance from the critical point. The figure presents also the square root of the time-scaling factor  $h$  (solid triangles) for the  $C_{12}Et_6$ - $H_2O$  system.

isoconcentration line is given as<sup>2</sup>

$$B = A (dn/dc)^2 (d\epsilon/dc)^2 (\xi_0/\Gamma) (1 - T/T_c)^{-\Psi}, \quad (1)$$

where  $A$  is a constant;  $dn/dc$  is the index of refraction increment;  $d\epsilon/dc$  is the static electric permittivity increment;  $\xi_0$  and  $\Gamma$  are defined in terms of the power laws for the correlation length,  $\xi = \xi_0(1 - T/T_c)^{-\nu}$ , and for the surface tension,  $\sigma = \Gamma/\xi^2$ ; and  $\Psi = \nu \times (1 - 2\eta)$ ,  $\eta$  being, as usual, the exponent introduced by Fisher. A very recent rigorous theory<sup>12</sup> of the Kerr effect confirms that, near a critical point, the divergence of  $B$  is correctly expressed by Eq. (1).

Our data are consistent with a power-law dependence of  $B$  on the reduced temperature. In order to compare the measured  $\Psi$  with the theoretical prediction we can use the values of  $\Psi$  measured by light scattering,<sup>6</sup>  $\nu = 0.53 \pm 0.05$  for  $C_{12}Et_6$  and  $\nu = 0.44 \pm 0.04$  for  $C_{12}Et_8$  solutions. We find that the measured  $\Psi$  is roughly in agreement with the theoretical prediction. Since the two systems have similar  $\xi_0$  and  $dn/dc$ ,<sup>6</sup> the fact that  $B_0$  is three times larger for  $C_{12}Et_6$  than for  $C_{12}Et_8$  solutions must be attributed, according to Eq. (1), to differences in  $d\epsilon/dc$  and in  $\Gamma$ . Note that the theoretical treatment predicts also electric-field-induced shifts of both  $T_c$  and  $c_c$ , but we checked

that this effect is too small to influence our data.

The obtained birefringence signals show that the onset time of birefringence becomes longer and longer as  $T$  approaches  $T_c$ . If we represent the signal as  $\Delta n = \Delta n_s \{1 - f(t)\}$ , the experimental  $f(t)$  does not follow a simple exponential law as a function of time (except for the transients observed in  $C_{12}Et_8$  at  $T_c - T > 4^\circ C$ ), and its shape depends on the temperature distance  $T_c - T$ . However, we found that, sufficiently close to  $T_c$  ( $T_c - T < 2^\circ C$  for  $C_{12}Et_8$ , and  $T_c - T < 5^\circ C$  for  $C_{12}Et_6$  solutions) all the transients have the same shape provided that they are reported as function of a scaled time variable  $t^* = ht$ .

We show in Fig. 3 some transients (only three, for clarity of presentation), observed at different temperatures, which are graphically superposed by a simple scaling of time. The scaling factor  $h$  calculated from the  $C_{12}Et_6$  data follows approximately the power law  $h = h_0(1 - T/T_c)^\mu$ , with  $\mu = 1.2 \pm 0.1$ . The limited temperature range over which scaling was verified did not allow us to derive  $\mu$  for  $C_{12}Et_8$  solutions, but we can say that, at fixed temperature distance from  $T_c$ ,  $h$  is about four times larger for  $C_{12}Et_6$  than for  $C_{12}Et_8$  solutions.

Since the droplet model describes correctly the divergence of the static electric birefringence, we decided to extend its application also to the dynamics. The function  $f(t)$  is derived by averaging of the single-droplet transient over the probability density of droplet sizes. By assuming that the single droplet transient is exponential with a time constant  $Cr^\alpha$ ,  $\alpha$  being

a positive number, we obtain  $f(t)$  as

$$f(t) = N \int_{r_c}^{\infty} g(r/\xi) \exp(-t/Cr^\alpha) dr, \quad (2)$$

where  $g(r/\xi)$  is the scaling function introduced in Eq. (1) of Ref. 3, and  $N$  is a constant. The cutoff radius  $r_c$  takes into account the fact that small-size fluctuations have too short a lifetime to be deformed by the electric field. Close to  $T_c$  the effect of the cutoff is negligible, and Eq. (2) defines a universal function of scaled time,  $f(t^*)$ , where  $t^* = ht$  and  $h^{-1} = C\xi^\alpha$ . We have tried to calculate theoretically the time-dependent deformation of the droplet by adapting to critical binary mixtures a theory available for the oscillations of a viscous liquid drop in an immiscible liquid.<sup>3</sup> This approach predicts  $\alpha = 3$ , whereas the obtained value of  $\mu$ , combined with the value of  $\nu$  derived from light scattering, would indicate that  $\alpha$  is close to 2.

We have calculated explicitly the integral of Eq. (2) for  $\alpha = 2$  and  $\alpha = 3$  by making the choice<sup>3</sup>  $g(r/\xi) = \exp(-r^2/2\xi^2)$ . As shown in Fig. 3, the experimental  $f(t^*)$  is better approximated by the curve corresponding to  $\alpha = 2$ . It is interesting to note that the observed strongly nonexponential dynamic behavior comes, according to Eq. (2), from the fact that the electric birefringence experiment probes critical fluctuations of all possible size with a highly nonlinear weight.

We have checked by a double-pulse experiment whether memory effects are present. We found indeed that the rise of the second birefringence pulse

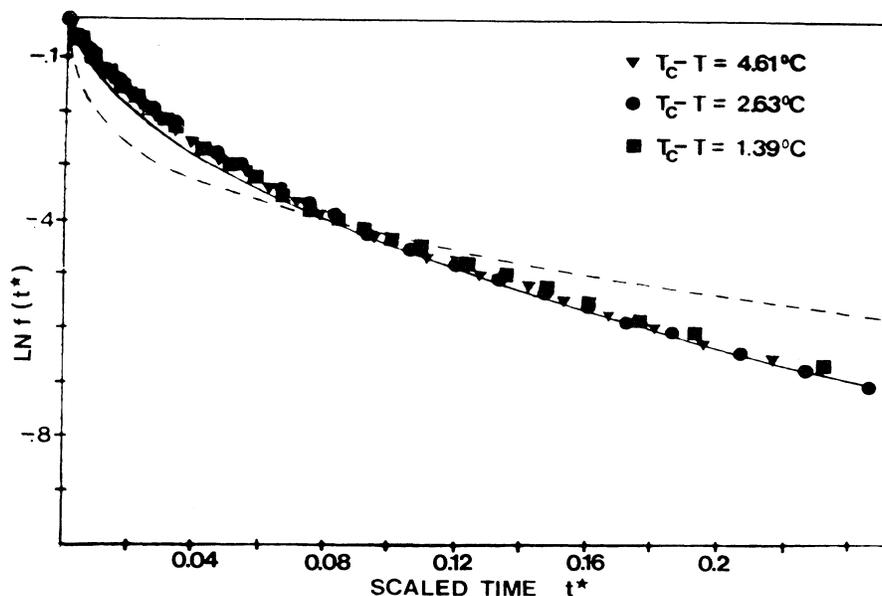


FIG. 3. The function  $f(t^*)$  of scaled time  $t^*$  as observed in  $C_{12}Et_6$  solutions at three distinct temperatures. The full and dashed lines represent the theoretical  $f(t^*)$  calculated with, respectively,  $\alpha = 2$  and  $\alpha = 3$ .

is faster when the second electric pulse immediately follows the first. With progressive increase in the delay of the second pulse, the two birefringence pulses become more and more similar. When the delay is comparable to or larger than the rise time of the first pulse no memory effect exists. As an example, at  $T_c - T \approx 3^\circ\text{C}$  in  $\text{C}_{12}\text{Et}_8\text{-H}_2\text{O}$ , the rise time of the first birefringence pulse (measured between 10% and 90% of the final value) is about  $15\ \mu\text{s}$ , whereas the rise time of the second birefringence pulse is only  $8\ \mu\text{s}$  for a delay of  $3.2\ \mu\text{s}$  between the electric pulses, and becomes approximately  $15\ \mu\text{s}$  for a delay of  $8\ \mu\text{s}$ . This latter experiment shows that, when the electric field is turned off, the critical fluctuation becomes isotropic in a time interval which is shorter than the fluctuation lifetime, and suggests that the rise time of birefringence is controlled by the process of building up, rather than deforming, a fluctuation.

As a conclusion, we have shown that micellar solutions near the critical consolution present electric birefringence with a diverging Kerr coefficient. The critical exponent, measured along the critical isoconcentration line, is  $\Psi \approx 0.5$ . The growth of birefringence after the sudden application of the electric field follows, close to  $T_c$ , a universal function of scaled time. The experimental time-scaling factor follows a power-law behavior as function of the reduced temperature. Some of these aspects may be explained with a dynamic droplet model which fails, however, to describe the asymmetry between rise and decay of the electric birefringence. The double-pulse experiment offers some hint for a more satisfactory dynamic description of the process.

As a final comment, it should be mentioned that some microemulsions are also known to exhibit a large Kerr effect<sup>14,15</sup> near a phase separation point, but a systematic study of the critical behavior has not yet been reported.

We thank M. Corti, P. G. Gobbi, H. Hoffmann, and

M. Angel for many useful suggestions about the experiment, E. Platone for the preparation and gift of the nonionic amphiphiles, and T. Bellini for help in the measurements. This work was supported by Progetto Finalizzato Chimica Fine e Secondaria del Consiglio Nazionale delle Ricerche Contract No. 83.00197.95 and by the European Economic Community and Italian Ministry of Public Education grants.

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