

signal-to-noise ratio. The unbroadened linewidths were obtained by extrapolating the observed power dependence to zero power input. This never caused a change of more than 20% from the last measured value. The extrapolation was assumed to double the measured uncertainties in linewidth.

⁸If the collision frequency ν is not independent of velocity, converting cyclotron-resonance linewidths to mobilities requires numerical integration [see F. Fehsenfeld, *J. Chem. Phys.* **39**, 1653 (1963)]. In 2D, ν is independent of v ; in 3D $\nu = n\sigma v$. We find $\mu_{2D} = e\tau/m$ and $\mu_{3D} = 0.9e\tau/m$, where $\tau = 2Q/\omega$, ω being the experimental frequency, and Q has its usual meaning. The 2D relation was used to convert our data.

⁹W. T. Sommer (private communication) estimates that, in addition to 25% random error, there may have been systematic errors of comparable magnitude in his experiment.

¹⁰This calculation has been done previously by Cole (Ref. 2); however, we find our μ_{2D} to be a factor of 4 lower than his, using the same wave functions and electron-helium interaction (chosen to give the measured value of σ). See also R. S. Crandall, *Phys. Lett.* **37A**, 389 (1971).

¹¹ $\sigma = 4.9 \times 10^{-16} \text{ cm}^2$, B. Bederson and L. J. Kieffer, *Rev. Mod. Phys.* **43**, 601 (1971).

¹²The same behavior was observed whether the discharge point was inside the cavity or in the wave guide although the decay rates were slower with the point in the wave guide. When the point was inside the cavity, the time constant was a few seconds at a discharge current of a few microamperes.

¹³Since μ_{2D} depends on $\int \varphi^4 dz$, it is sensitive only to the spatial extent of φ . A confining electric field of 50 V/cm would give approximately the same value for the integral as does the image potential.

Temperature Dependence of the Electrical Resistance for Isobutyric Acid–Water near the Critical Point

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The electrical resistance of two sealed samples of critical mixtures of isobutyric acid–water have been measured in the reduced temperature ranges $[\epsilon = (T - T_c)/T_c]$ $6.7 \times 10^{-7} < \epsilon < 3.2 \times 10^{-2}$ and $3.3 \times 10^{-7} < \epsilon < 6.6 \times 10^{-2}$. Data analyses indicate that the temperature derivative of the resistance is strongly divergent as $\epsilon \rightarrow 0$.

Friedländer,¹ in his pioneering work, recognized a possible connection between the electrical resistance and the anomalously high shear viscosity for the electrolyte isobutyric acid–water in the critical region. He concluded qualitatively that the resistance was much less affected by critical behavior than was the viscosity. Recently, anomalies in the temperature derivative of the electrical resistance have been observed for ferromagnets near their Curie temperatures,^{2,3} antiferromagnets near their Néel points,⁴ and β brass near the order-disorder transition.⁵ In these materials the charge-carrying species are electrons which are scattered by local magnetic fluctuations that become very large near the second-order phase transition. de Gennes and Friedel⁶ and Fisher and Langer⁷ have presented theories to describe this phenomenon. The Fisher-Langer result that $\partial\rho/\partial T \sim (T - T_c)^{-\alpha}$, where α is the exponent describing the weak specific-heat divergence, seems to be verified for the ferromagnet nickel.² In isobutyric acid–water the charge-carrying species are ions of opposite

sign, and the fluctuations near the critical mixing temperature are in the concentration or density. So far there are no theoretical predictions concerning the temperature dependence of the electrical resistance or its temperature derivative for a binary liquid mixture in the neighborhood of the critical point.

In this Letter we report on an experimental investigation of the electrical resistance and its temperature derivative for critical mixtures of isobutyric acid–water as the critical temperature is approached from the one phase (high-temperature) region.

The isobutyric acid and water used in this study were the same as those described in our earlier report⁸ on the viscosity of this system. The critical composition was 38.0% isobutyric acid by weight, and the critical temperatures were 26.238 and 26.233°C for the two different samples used.⁹

The conductance cells were of a modified Jones-Bollinger¹⁰ design. The resistances of the cells were measured with a Jones¹¹ ac bridge utilizing a lock-in amplifier as a signal generator and

phase-sensitive detector. The measured resistances of the cells were very insensitive to the frequency of the ac signal, so that all measurements were made at 4000 Hz. The precision of the resistance measurements was $\pm 0.001\%$. The temperatures of the cells were controlled to $\pm 0.0001^\circ\text{C}$ in a specially constructed double thermostat. Relative temperatures were precise to $\pm 0.0001^\circ\text{C}$ as determined by a Hewlett-Packard quartz thermometer, while absolute temperatures were measured to $\pm 0.001^\circ\text{C}$ using a platinum resistance thermometer and d.c. bridge.

Two runs were completed in which the resistances of mixtures of critical composition were measured at a series of different temperatures above T_c . In the first run, 124 data points were recorded in the reduced temperature range [$\epsilon \equiv (T - T_c)/T_c$] $6.7 \times 10^{-7} < \epsilon < 3.2 \times 10^{-2}$, while in the second run, 115 points were taken in the range $3.3 \times 10^{-7} < \epsilon < 6.6 \times 10^{-2}$. Measurements were made well away from T_c so that the behavior of the resistance outside the critical region could be ascertained. Thus, we were able to separate the normal variation of resistance with temperature from effects due to the large concentration fluctuations associated with the region near the critical point. Plots of resistance versus reduced temperature showed a very slight excess resistance near the critical point ($\epsilon < 3 \times 10^{-5}$). The effect here is nowhere near as pronounced as the anomalous increase in the shear viscosity for the same system as T_c is approached from the one phase region.^{8,12}

Guided by the behavior of the temperature derivative of the resistivity for metallic systems near a second-order phase transition, we first analyzed the data from both runs according to the model equation

$$dR/dT = A\epsilon^{-d} + B\epsilon^2 + C\epsilon + D. \quad (1)$$

Derivatives were calculated from the experimental data using a five-point sliding-parabola numerical-differentiation computer routine.³ The calculated derivatives were then fitted with Eq. (1) using a weighted nonlinear least-squares procedure. The data analyses yield the following: for run No. 1 with $2.7 \times 10^{-6} < \epsilon < 8.0 \times 10^{-4}$,

$$\begin{aligned} A &= -0.4568 \pm 0.037 \text{ } \Omega/^\circ\text{C}, \\ B &= (-1.554 \pm 0.33) \times 10^8 \text{ } \Omega/^\circ\text{C}, \\ C &= (2.534 \pm 0.33) \times 10^5 \text{ } \Omega/^\circ\text{C}, \\ D &= (-4.775 \pm 0.098) \times 10^2 \text{ } \Omega/^\circ\text{C}, \\ d &= 0.56 \pm 0.10; \end{aligned}$$

for run No. 2 with $6.7 \times 10^{-7} < \epsilon < 4.3 \times 10^{-4}$,

$$\begin{aligned} A &= -0.2308 \pm 0.017 \text{ } \Omega/^\circ\text{C}, \\ B &= (-2.917 \pm 0.97) \times 10^8 \text{ } \Omega/^\circ\text{C}, \\ C &= (3.277 \pm 0.52) \times 10^5 \text{ } \Omega/^\circ\text{C}, \\ D &= (-4.330 \pm 0.082) \times 10^2 \text{ } \Omega/^\circ\text{C}, \\ d &= 0.58 \pm 0.10, \end{aligned}$$

with reduced χ^2 of 0.95 and 1.7, respectively.

In both cases the seventy data points closest to T_c were used for the analysis, and the quality of the fit and optimized parameters were insensitive to variations in the temperature ranges shown. Since Eq. (1) contains a large number of adjustable parameters, T_c was treated as an experimental quantity determined by an abrupt and discontinuous change in the cell resistance as the temperature was lowered in increments of 0.0001°C near T_c . In run No. 1 this abrupt change was a sharp increase in cell resistance, while in run No. 2 the change was an abrupt decrease in resistance. In both cases the value of the measured resistance was no longer reproducible for a given temperature. The difference in behavior in the two runs is attributed to different cell geometries in the two cases. The fact that different cells were used for the two runs also accounts for the differences in the parameters A , B , C , and D for the two fits. Both the quality of the fits and the value of the fitted parameters were not changed appreciably when T_c was incremented in a small range around the observed values. The critical temperatures for both samples were also independently determined to be 26.238 and 26.233°C for samples 1 and 2, respectively, by the visual observation of the appearance of the meniscus as the temperature was lowered. These values are consistent with those values of T_c determined during the resistance runs and are in good agreement with other values reported for the same system.^{8,12-14} Since very long times are required for the appearance of the meniscus when the isobutyric acid-water critical mixtures are only slightly below T_c , we feel that the abrupt change in resistance offers a more reliable method for estimating T_c in this experiment.

In an attempt to avoid possible inaccuracies associated with the numerical differentiation of our experimental data, an alternate method of data analysis was used. Since the direct differentiation method established the existence of an

anomalous increase in dR/dT near T_0 , we then supposed that the data could be represented by the power-law expression

$$d(R - R_{\text{ideal}})/dT = A\epsilon^{-d} + B, \quad (2)$$

where R_{ideal} is the resistance in the absence of critical fluctuations or background resistance. R_{ideal} was estimated from the experimental data for each run away from T_c (32.5–35.7°C for run No. 1 and 36–46°C for run No. 2) and could be well described by the expression

$$R_{\text{ideal}} = a_1\epsilon^3 + a_2\epsilon^2 + a_3\epsilon + a_4, \quad (3)$$

where the least-squares values of a_4 are physically reasonable when compared to the experimental resistance near T_c . Integrating Eq. (2) and combining with Eq. (3) one obtains

$$R - R_c = [A/(1-d)]T_c\epsilon^{1-d} + a_1\epsilon^3 + a_2\epsilon^2 + (BT_c + a_3)\epsilon, \quad (4)$$

where $R_c = a_4 + k$ is the resistance at the critical temperature ($\epsilon = 0$) with k as the integration constant. Dividing by $-\epsilon R_c$ and assigning new symbols to the combined parameters for neatness,

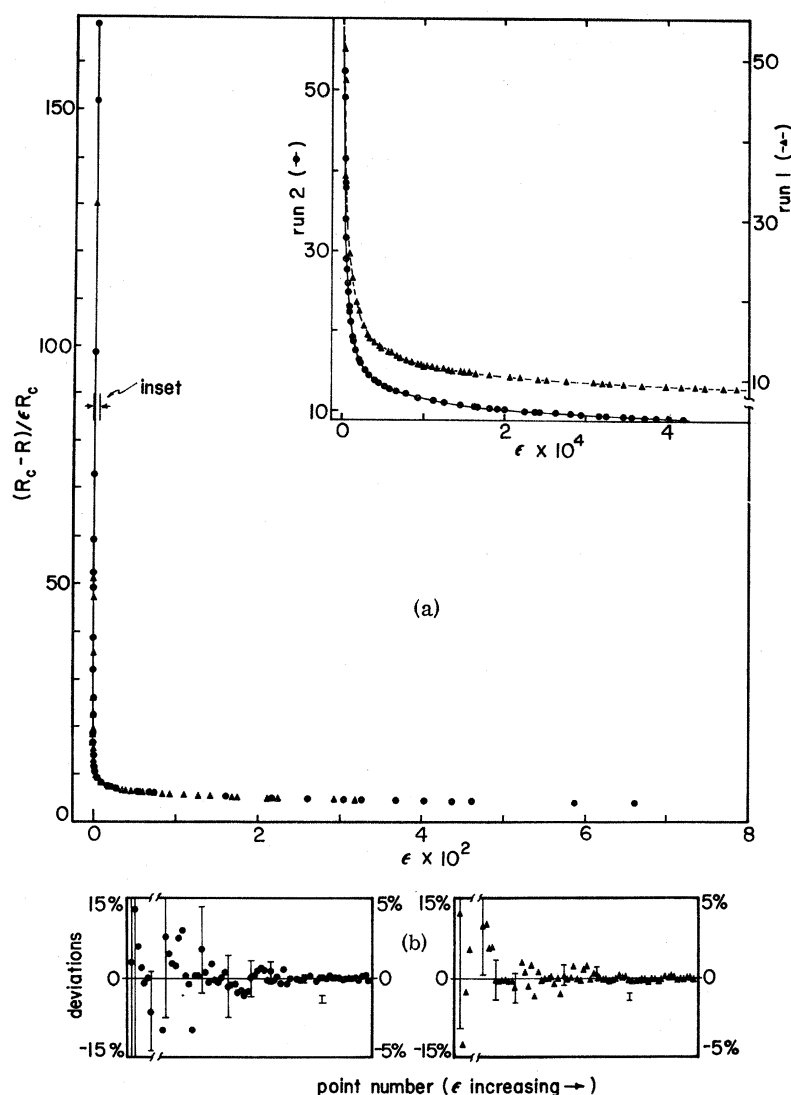


FIG. 1. (a) $(R - R_c)/\epsilon R_c$ versus reduced temperatures ϵ for critical mixtures of isobutyric acid-water. Triangles, run No. 1, circles, run No. 2. For the sake of clarity only a fraction of the data points is shown. The inset shows an expanded plot for the data near T_c . For display purposes, runs No. 1 and No. 2 are displaced as indicated on the ordinate scales. Solid curves represent a least-squares fit with Eq. (5). (b) Deviation plots, $[(R - R_c)/\epsilon R_c]_{\text{expt}} - [(R - R_c)/\epsilon R_c]_{\text{calc}}$ for runs No. 1 and No. 2.

we get

$$(R_c - R)/\epsilon R_c = [A'/(1-d)]\epsilon^{-d} + B'\epsilon^2 + C'\epsilon + D', \quad (5)$$

which close to T_c has the same form as the power-law expression of Eq. (1).

The data from both runs were fitted by Eq. (5) using the weighted nonlinear least-squares method of Deming.¹⁵ The temperature range was systematically narrowed by leaving out high-temperature points on successive calculations. The range reported below was determined when further range narrowing produced no further change in the parameters and the reduced χ^2 . Since the values of the parameters, d in particular, were very sensitive to the value chosen for R_c , we have treated R_c as a parameter rather than attempting to estimate values from extrapolation of the experimental resistance data. The optimized values reported are in excellent agreement with the actual data in each case.¹⁶ Again the value of T_c in each case was that observed experimentally as explained above. The optimized value of the parameters are as follows: for run No. 1 with $6.7 \times 10^{-7} < \epsilon < 9.3 \times 10^{-4}$,

$$A' = (1.3232 \pm 0.34) \times 10^{-3},$$

$$B' = (1.0093 \pm 0.096) \times 10^6,$$

$$C' = (-2.5939 \pm 0.16) \times 10^3,$$

$$D' = 9.0185 \pm 0.12,$$

$$d = 0.71 \pm 0.10,$$

$$R_c = 16845.54 \pm 0.65 \Omega;$$

for run No. 2,

$$A' = (7.5201 \pm 1.8) \times 10^{-4},$$

$$B' = (4.6835 \pm 0.52) \times 10^6,$$

$$C' = (-5.5540 \pm 0.42) \times 10^3,$$

$$D' = 9.8198 \pm 0.14,$$

$$d = 0.72 \pm 0.11,$$

$$R_c = 14374.60 \pm 0.35 \Omega,$$

The seventy points nearest T_c were included in the fit for run No. 1 with the reduced χ^2 of 0.85, with 71 points for run No. 2 in the range $3.3 \times 10^{-7} < \epsilon < 4.2 \times 10^{-4}$ yielding a reduced χ^2 of 0.48. In Fig. 1(a) the calculated values of $(R_c - R)/\epsilon R_c$ versus ϵ are compared with the experimental points from both runs. Deviation plots are presented in Fig. 1(b).

Both methods of data analysis of our results indicate that dR/dT is approached from the one phase region. Even with data of this high quality it is difficult to suggest a numerical value for the critical exponent since it is the derivative of the measured quantity which diverges. This strong divergence is perhaps surprising in light of the weak divergence in dR/dT found in the ferromagnetic nickel system.² Schürmann and Parks¹⁷ have observed a strong divergence in dR/dT for the liquid-metal system gallium-mercury near the critical point. In this system however the specific heat also appears strongly divergent,¹⁸ so that liquid metals as well as ferromagnets may be amenable to the application of the Fisher-Langer theory.⁷ The limited data¹⁹ available on the specific heat of binary organic liquid systems suggest that the heat capacity is not strongly divergent in the critical region. This suggests that the Fisher-Langer treatment may not apply to the divergence of dR/dT for these binary electrolytes.

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directly rather than resistivity, careful determinations of the cell constants were not necessary. We estimate the cell's constants to be $10 \pm 2 \text{ cm}^{-1}$ for both cells.

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Pretransitional Optical Rotation in the Isotropic Phase of Cholesteric Liquid Crystals*

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A sharp increase of the rotatory power in the isotropic phase of cholesteric liquid crystals is observed near the isotropic-cholesteric liquid transition. This is interpreted as a manifestation of short-range chiral orientational order in the isotropic liquid. An application of the Landau-de Gennes theory predicts a $(T - T^*)^{-1/2}$ temperature dependence, in agreement with measured data in the immediate pretransition region.

The existence of short-range orientational order in the isotropic liquid phase of nematic liquid crystals is firmly established,^{1,2} and the experimental observations are well explained by a phenomenological mean-field theory for nearly second-order phase transitions.^{3,4} de Gennes's extension of this theory to cholesteric liquid crystals⁴ was recently tested by Rayleigh-light-scattering experiments in the isotropic phase of a cholesteric system,⁵ which showed that chirality plays a negligible role in Rayleigh scattering except for a narrow temperature range 0.68°C above T^* , the second-order transition temperature. In this region, the experimental data could not be explained by the de Gennes theory. In this Letter, we report the first experimental evidence for the existence of chiral short-range order in the liquid phase: the critical enhancement of optical rotatory power in the isotropic phase of cholesteric liquid crystals.

It is well known that the long-range spiral molecular orientational order of the cholesteric phase gives rise to optical rotatory powers as high as 10^4 deg/mm .⁶ Substances possessing a cholesteric mesophase are also known to exhibit molecular optical activity. The chiral ordering dominates the optical activity of the ordered phase. In the absence of any orientational order, the isotropic liquid would exhibit only the molecular optical activity, which is very weakly depen-

dent on temperature. If chiral short-range order exists in the isotropic phase, then the orientations of different molecules may be coupled in a manner preserving a local spiral conformation over a small correlation distance, which should strongly enhance the optical rotatory power of the liquid. This enhancement is a direct measure of the degree of chiral short-range order.

Experimental analysis is complicated by the fact that the rotatory power of the helical conformation, φ_C (φ_{chiral}), and the molecular optical activity φ_O both depend on the local molecular environment and may become temperature dependent as the local order builds up near the phase transition. Since both contribute to the observed rotations, any scheme for extracting the temperature dependence of φ_C from the data requires justification. This can be circumvented if φ_C predominates. Since this effect should vary quadratically with dielectric anisotropy $\Delta\epsilon$, we chose to study materials for which $\Delta\epsilon$ is large and whose molecular optical activity is small. Esters of cholesterol were found to be unsuitable, since they give rise to $\varphi_C < 1^\circ/\text{cm}$ at 6328 \AA , while φ_O is 2.5 to $4.0^\circ/\text{cm}$. Thus we turned to chiral molecules with a structure similar to that of typical nematics ($\Delta\epsilon = 0.7$ or more), for which φ_C should be more than 2 orders of magnitude larger than for the cholesterol esters, while φ_O should remain small.