Critical point phenomena in the electrical resistivity of binary liquid systems: $CS_2 + CH_3CN$ and $CS_2 + CH_3NO_2$

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Abstract. Electrical resistance measurements are reported on the binary liquid mixtures $CS_2 + CH_3CN$ and $CS_2 + CH_3NO_2$ with special reference to the critical region. Impurity conduction seems to be the dominant mechanism for charge transport. For the liquid mixture filled at the critical composition, the resistance of the system above T_c follows the relation $R = R_c - A(T - T_c)^b$ with $b = 0.6 \pm 0.1$. Below T_c the conductivities of the two phases obey a relation $\sigma_2 - \sigma_1 = B(T_c - T)^\beta$ with $\beta = 0.34 \pm 0.02$, the exponent of the transport coefficient being the same as the exponent of the order parameter, an equilibrium property.

Keywords. Critical phenomena; binary systems; critical indices; transport properties resistivity.

1. Introduction

The behaviour of the electrical resistivity near the critical point of phase transitions has attracted considerable attention recently. In ferromagnetic systems like nickel and other materials the derivative of the resistivity has a divergence of the type

$$dR/dt \sim (T - T_c)^{-\alpha}, \quad \alpha \approx 1/8 \tag{1}$$

when T_c is approached (Craig *et al* 1967, Parks 1972), which has been explained by Fisher and Langer (1968) as the result of the critical scattering of the conduction electrons. A similar α-singularity occurs in the case of alloys like β-brass showing order-disorder transitions (Simons and Salamon 1971). The resistivity of antiferromagnets near their Neel temperature (Craven and Parks 1973, Rao *et al* 1975) shows more complicated features. Anomalies in the electrical resistivity of binary liquid metal systems have also been reported (Adams 1970, Schurmann and Parks 1971 *a, b*).

In contrast to these situations where the charge carriers are due to conduction electrons, the cases where the conduectivity is due to heavier ions have not received attention (Anisimov, 1975). The electrical resistivity of binary polar-nonpolar liquid systems near their critical solution temperature has been studied from the modern point of view of critical phenomena so far is only one system, isobutyric acid + water, by two groups of workers (Stein and Allen 1972, Gammell and Angell 1972). Even here Stein and Allen find a strong anomaly in dR/dT, going to infinity as $(T - T_c)^{-0.4}$ while Gammell and Angell find no anomaly at all.

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Jasnow *et al* (1974) analyse the data of Stein and Allen and suggest an $\alpha \approx 1/8$ anomaly in dR/dT. Moreover these two experiments have been confined to the one-phase region and the behaviour in the two-phase region is not known.

The electrical resistivity near the critical selution temperature of two binary liquid systems, $CS_2 + CH_3CN$ and $CS_2 + CH_3NO_2$, has been investigated, revealing interesting features. The behaviour, while showing the general similarity with other critical point phenomena in universality behaviour, throws up two features whose theoretical significance is not yet clear. Preliminary versions of this study have been reported briefly earlier (Lele *et al* 1974, Ramakrishnan *et al* 1975).

2. Experimental arrangement

In making the resistance measurements, a pyrex cell with two pairs of stainless steel electrodes, as shown in figure 1, was used. The chemical inertness, the ease of fabrication and the need to measure the resistances both in the one-phase and in the two-phase regions were the main considerations in the design of this cell. The cell is of diameter 35 mm and has a capacity 60 cm^3. The electrodes, of 18 mm diameter, were about 1 mm apart, the first pair being 0·5 cm from the bottom of the cell and the second pair being at a height of 4·5 cm from the bottom.

The binary liquid systems chosen needed a knowledge of the critical composition X_o and the critical temperature T_c. The two systems have been earlier studied in the laboratory (Govindarajan *et al* 1972, Gopal *et al* 1973, 1974), giving $X_o = 59·20$ mole % of CS_2 and $t_o = 50·21_0°$ C for the system $CS_2 + CH_3CN$ and $X_c = 57·35$ mole % of CS_2 and $t_c = 62·07_2°$ C for the system $CS_2 + CH_3NO_2$. The same stock of liquids were available, thereby fixing X_c and T_c quite precisely. The cell was filled with the liquids in the proper proportion to form the critical mixture and was then flame sealed at the top. The interface came in between the two pairs of electrodes, enabling the resistivity of each phase to be measured individually, below T_c.

The resistance of the liquids was measured at a frequency of 1000 Hz. In one set of experiments, a transformer ratio arm bridge was used and in another set, a conventional Wheatstone bridge configuration was used, both measurement techniques yielding the same values. Some measurements were also performed
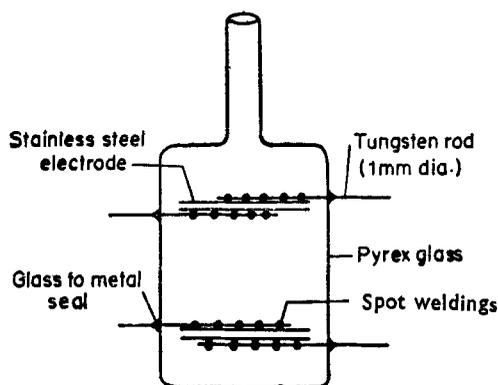
Stainless steel
electrode

Tungsten rod
(1mm dia.)

Glass to metal
seal

Pyrex glass

Spot weldings

Figure 1. Resistance cell.

at 30 Hz, yielding identical resistances. The voltages across the electrodes were ~ 1 V peak-to-peak and a lock-in-amplifier detector system enabled resistances to be measured with a precision of 1 in 20,000. The choice of the frequency and the voltage levels were the result of the need to avoid sample polarization and self-heating and the requirement of adequate sensitivity in the lock-in-amplifier built here.

The experimental conditions are such that what is measured is the low frequency a.c. conductivity. Since the lowest relaxation frequencies are in the tens of Mega-hertz region, this may be taken as the d.c. conductivity for all practical purposes. The high frequency conductivity, planned to be studied, may also be of interest. These liquids being essentially of the insulating type, the conduction process must be largely of the impurity type. The liquids have a purity of $99 \cdot 9\%$ as reported earlier and the dominant impurity responsible for electrical conduction is likely to be water molecules, which are present especially in the polar liquids. Their concentration, of the order of 50–100 ppm, is akin to the case of isolated impurities. While measurements with varying amounts of impurities would be desirable, and are planned, the addition of too much of impurities changes X_e and T_c. Therefore the present measurements were confined to the same samples used for measuring the coexistence curves.

A thermostat having millidegree temperature stability was used for the studies. It consisted of a 10 litre capacity paraffin oil bath, very well stirred and enclosed in a shield connected to a fine temperature controller. The shield itself was thermally insulated and enclosed in a second shield which has a coarse temperature control. The whole assembly was placed in a room with its own temperature control. The temperature sensors for both temperature control and measurement were aged thermistors, operated at microwatt power dissipation levels. They were periodically calibrated against platinum resistance thermometers. The absolute temperatures are correct only to $\pm 0 \cdot 05$ K, whereas temperature differences could be resolved to about 1 millidegree.

3. Observations

The experiments were conducted by taking initially the system to the one phase region about $10°$ above T_e. The liquids were allowed several hours to attain thermal equilibrium, monitored by the absence of changes in the resistance values. Then the system was slowly cooled, with millidegree steps and hours of equilibrium times in the critical region. The resistances in the high temperature one-phase region and in the low temperature two-phase regions were measured as a function of temperature. Very near T_c the resistance measurement became difficult because of the development of " noise " in the system. The onset of fluctuating electrical voltages near the critical temperature is known in the case of ferroelectric materials (Burgess 1965) and superconductors (Glover 1970) and their study in their own right would be interesting. This was not possible with the signal-to-noise ratio in the present lock-in-amplifiers constructed here.

In spite of the care taken to make the two pairs of electrodes identical, the resistances of the homogeneous one phase measured by the two pairs of electrodes differed slightly by a constant factor. This is the result of the $\sim 10\%$ difference in the geometrical factor, especially the spacings between the two electrodes of

a pair. To make the analysis simple, the resistance measured by one of the pairs was multiplied by the normalising constant and these normalised resistances would be quoted below as the measured resistances. Further one could have obtained the specific resistivity in ohm-cm of the liquid system by multiplying the measured resistance R(in ohms) with the factor 103 ± 20 where the uncertainty arises primarily from the lack of information about the correct spacing between the electrodes of a pair after the glass blowing and annealing operations were done. Consequently it is best to discuss the observations in terms of the normalized measured resistances, preserving the full accuracy, rather than in terms of the coefficient of specific resistance or resistivity of the liquids.

As the temperature was lowered, the one-phase resistance which was about 15 k ohms at 70° C in the case of, say, the $CS_2 + CH_3NO_2$ system, increased to about 18 k ohm around 62°C, the critical region. The phase separation was marked by a sudden change in the resistances. In the next 4°C interval, the resistance of the CS_2-rich upper layer increased enormously to several Megaohms, while the resistance of the CH_3NO_2-rich lower phase decreased by about 70%. The measured resistances behaved similarly in the case of the $CS_2 + CH_3CN$ system also. The observations are presented in figure 2, on a semilogarithmic scale to cover the large range of resistances.

There is a superficial resemblance between figure 2 and the coexistence curves of these systems. However, since there is no simple linear relationship between the resistance and the composition, it is not easy to reconstruct the T-X coexistence curves from the observed resistances.

As mentioned in section 1, the only measurements on similar systems available earlier are on the resistivity behaviour of the isobutyric acid + water system in the one-phase region, where the resistance has a strong anomaly in dR/dT according to Stein and Allen (1972) and no anomaly according to Gammell and Angell (1972). The data of Stein and Allen have been reinterpreted by Jasnow *et al* (1974) to fit a weaker α-anomaly suggested by their theory. Therefore the measurements in the one-phase region are analysed first.

The functional form for the resistance in the one-phase region is

$$R = R_o - A(T - T_o)^b \tag{2}$$

and the plot of $R_o - R$ against $T - T_o$ is given in figure 3 for both the systems. While T_o is known quite accurately, there is a little uncertainty in the estimation of R_o because of the very rapid variation of the resistance in the critical region. A least square analysis of the observations in the form of eq. (2) with R_o, A and b as adjustable parameters was used to get the best estimate of the parameters. This analysis gave $R_o = 56$ k ohm, $A = 35$ and $b = 0.55$ for the $CS_2 + CH_3CN$ system and $R_o = 17.5$ k ohm, $A = 16.5$ and $b = 0.56$ for the $CS_2 + CH_3NO_2$ system. However, the fit was such that a slightly different value of R_o, differing by ± 0.02 k ohm, would still give an acceptable fit and therefore the best value of b should be preferably given as 0.56 ± 0.1.

Coming to the low temperature two-phase region, it seems a good first choice to attempt a fit of the form

$$R_1 - R_2 = B (T_c - T)^\beta \tag{3}$$

where R_1 is the resistance of the upper phase and R_2 that of the lower phase at
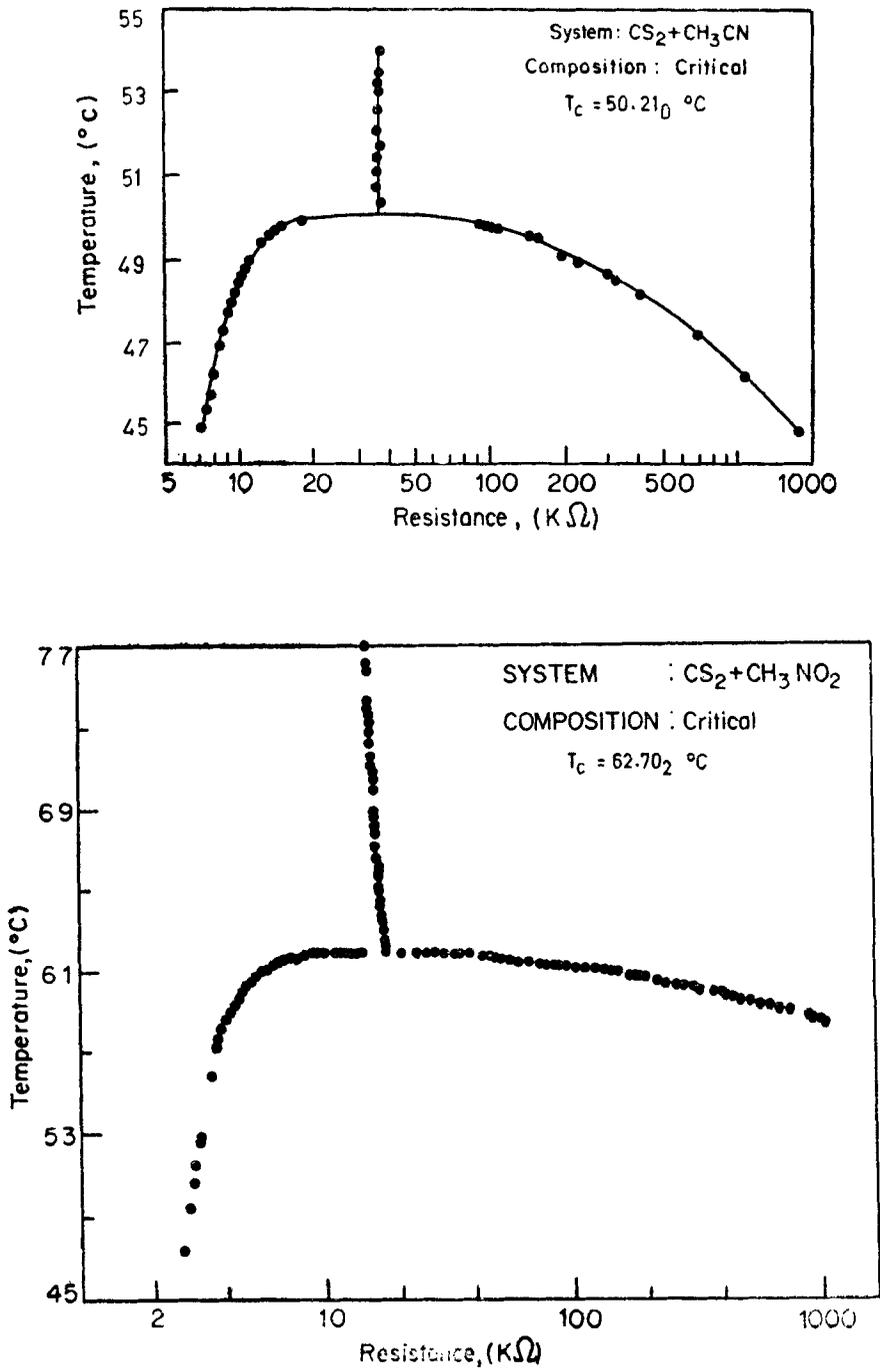
Figure 2. Plot of temperature *vs.* normalised resistance. (*a*) System CS₂ + CH₃CN (*b*) System CS₂ + CH₈NO₂.
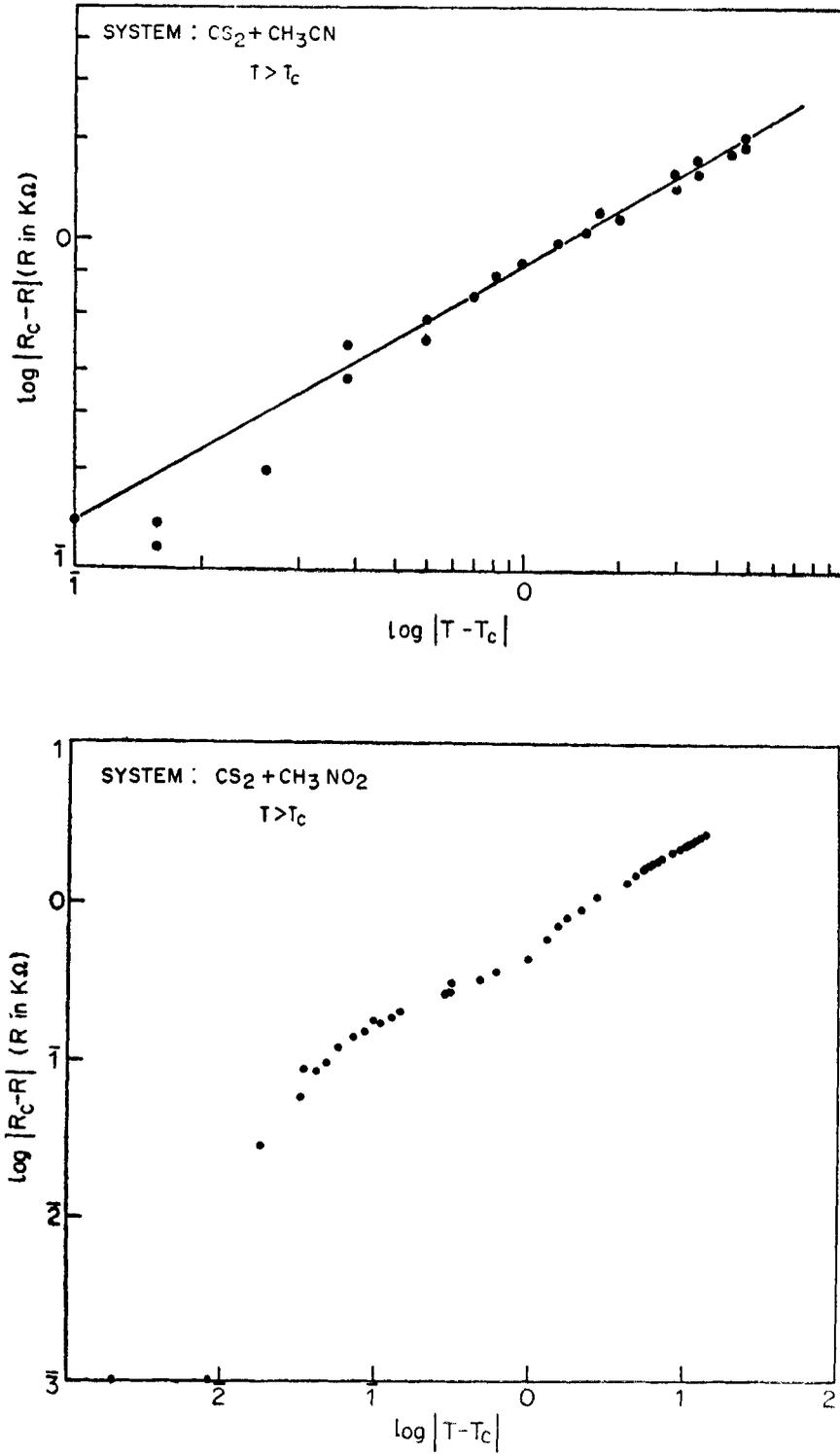
Figure 3. Log-log plot of $|R_c - R|$ *vs.* $(T - T_c)$ (*a*) System $CS_2 + CH_3CN$, (*b*) System $CS_2 + CH_3NO_2$.

a temperature T. Figure 4 shows such an attempt by plotting $(R_1 - R_2)$ against $(T_e - T)$ on logarithmic scales. No linear fit is obtained and if segments of the curve are fitted to straight lines, one would get values of the exponent in eq. (3) ranging from 0.3 to 0.8. In view of this, one attempted a functional form

$$\sigma_2 - \sigma_1 = B(T_e - T)^\beta \tag{4}$$

where $\sigma = 1/R$ is the conductance of the phase. This plot, given in figure 5, gives a much better linear fit suggesting the correctness of eq. (4) and also giving the exponent $\beta = 0.35 \pm 0.01$ for the $CS_2 + CH_3CN$ system and $\beta = 0.34 \pm 0.01$ for the $CS_2 + CH_3NO_2$ system. The value $\beta \sim 0.33$ is in striking agreement with the universal value obtained in critical point phenomena for the temperature variation of the order parameter, as has indeed been observed for the order parameter in these systems in the study of their coexistence curves. It is interesting that the exponent of the transport coefficient is the same as the exponent for an equilibrium property.

4. Discussion

The striking observation made in these studies is the universality in the resistivity behaviour, in complete consonance with the universal behaviour observed in other critical phenomena. As mentioned in the introduction, there have been some conflicting observations on the resistivity of polar + nonpolar binary liquids exhibiting partial miscibility. Apart from the shape of the resistivity curves (figure 2) the exponents also have the same value. This confirmation of the universal resistivity behaviour is reassuring.

The behaviour in the high temperature one-phase region is given by the eq. (2)

$$R = R_e - A(T - T_e)^b$$

with $b = 0.56 \pm 0.1$. The value of b is in excellent agreement with the value reported by Stein and Allen (1972) in their original observations on the isobutyric acid + water system. Schurmann and Parks (1971) also report a value of $b = 0.4$ in their study of the resistivity of the sodium + lithium system in the one-phase region. As contrasted to these reports, Gammell and Angell (1972) report no anomaly in their observations on the same isobutyric acid + water system. Their measurements were done at 1.67 kHz, unlike the observations of Stein and Allen performed at 4 kHz. Jasnow and coworkers (1974) reanalysed the data of Stein and Allen and reported $1 - b \approx 0.12$, the specific heat exponent. They outlined a nearest neighbour hopping model for the conduction process and derived an α-exponent for the singularity in dR/dT, which is the same as the behaviour in a ferromagnet. It should also be mentioned that Klein and Woermann (1975) have reported a study of the thermal expansion of the isobutyric acid + water system and mention in passing that the dissociation of the weak acid and the consequent association phenomena may give a large value ~ 0.5 to the exponent of the resistivity anomaly. Kluybin and coworkers (1975) have measured the 4 kHz a.c. conductivity of the system triethylamine + water and find dR/dT going as $(T - T_e)^{-0.4}$. Very recently Shaw and Goldburg (1976) have measured the 4 kHz conductivity in the phenol + water and the isobutyric acid + water systems and find $dR/dT \sim (T - T_c)^{-0.3}$ in both systems. They also outline a percolation model of the electrical
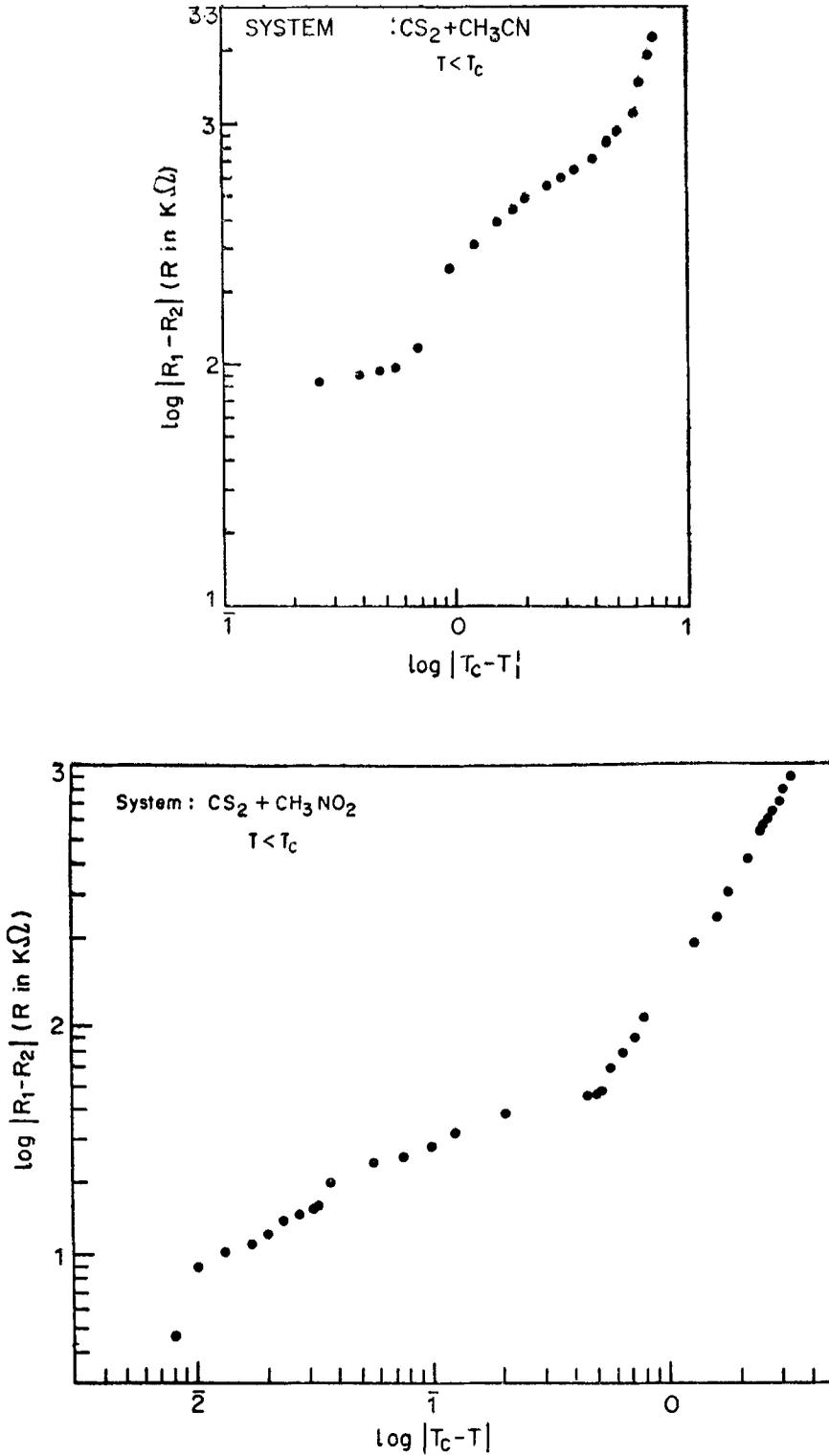
Figure 4. Plot of log | $R_1 - R_2$ | vs. Log ($T_o - T$), (a) System $CS_2 + CH_3CN$, (b) System $CS_2 + CH_3NO_2$.

conduction process, which yields $dR/dT \sim (T-T_e)^{2\beta-1}$. Since $\beta \approx 0 \cdot 33$, this is a strong anomaly similar to the experimental observations. Nityananda (1976) has outlined a slightly different conduction model which yields $dR/dT \sim (T-T_e)^{\nu-1}$ where $\nu \approx 0 \cdot 66$.   In a discussion of this paper Singh has pointed out that a different averaging process in the same model would yield $dR/dT \sim (T-T_e)^{-a}$, ($a = 1/8$), the same weak anomaly suggested by Jasnow and coworkers (1974). The situation is very similar in the model of Brownian motion with stochastic damping, discussed by Jasnow and Gerjoy (1975) and applied to the electrical conduction
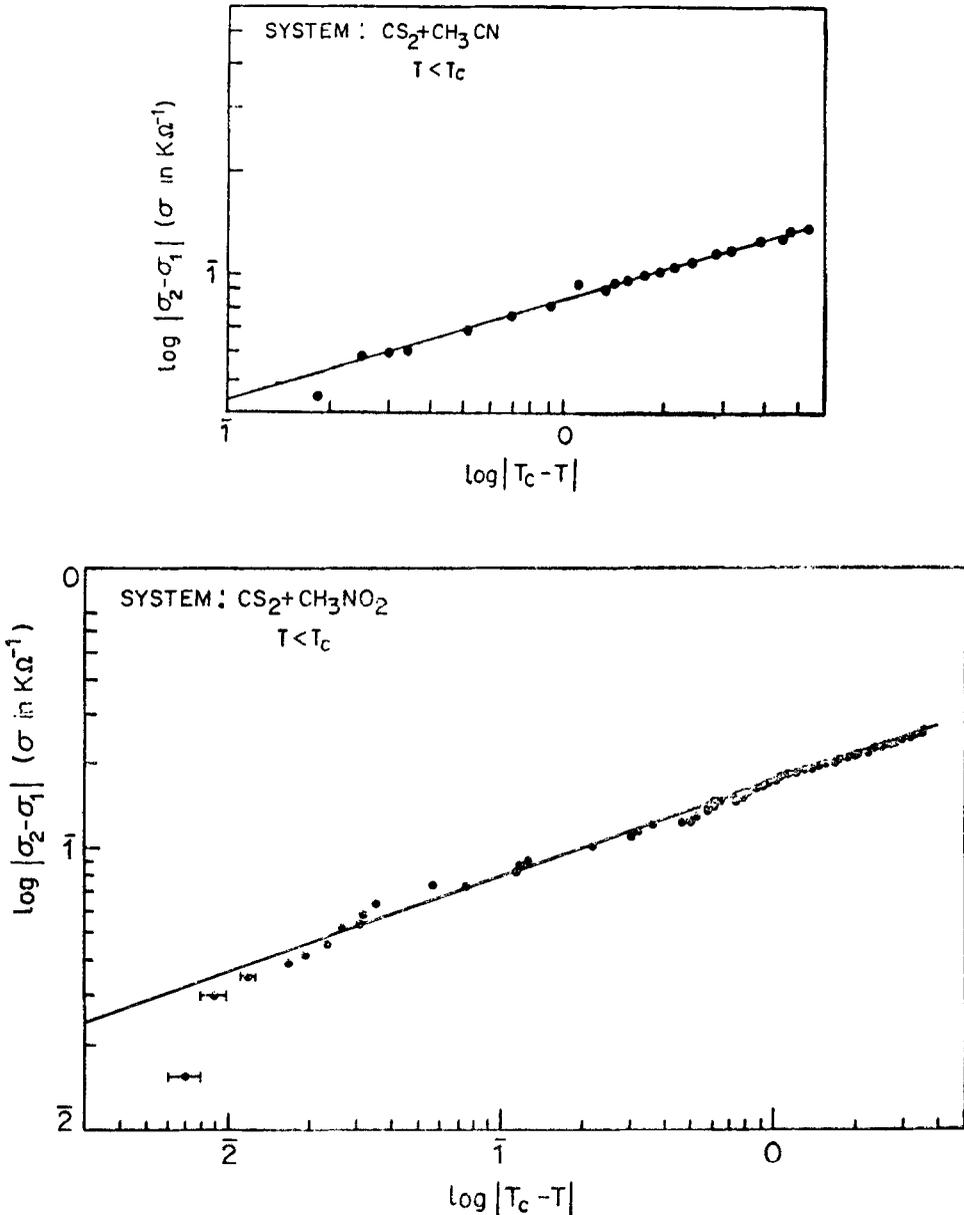

Figure 5. Log-Log plot of $|\sigma_2 - \sigma_1|$ *vs.* $(T_e - T)$ (*a*) System $CS_2 + CH_3CN$, (*b*) System $CS_2 + CH_3NO_2$.

problem in a binary liquid system. It is found that if the averaging is done over a volume element of the order of ξ^3 (ξ = the temperature dependent correlation length), then $dR/dT \sim (T - T_c)^{2\beta-1}$, a strong singularity, whereas if the averaging is done over a temperature independent volume of the order of the size of the Brownian particle then $dR/dT \sim (T - T_c)^{-\alpha}$, a weak singularity. Clearly, further theoretical studies are needed to clarify the situation. It is of historical interest that as early as in 1901, Friedlander (1901) had suggested a study of the electrical conduction of these systems in connection with the anomalous behaviour of viscosity near the critical solution temperature and its possible relationship with electrical drift conduction.

The low temperature two-phase region throws up a problem of a different kind. Here the conductances follow the eq. (4)

$$\sigma_2 - \sigma_1 = B (T_c - T)^\beta$$

with a value $\beta = 0 \cdot 34 \pm 0 \cdot 02$. This value of β is indeed the universal value for the temperature variation of the order parameter in critical phenomena (Stanley 1971). What is surprising is that the resistances do not obey the relation

$$R_1 - R_2 = B' (T_c - T)^\beta. \tag{3}$$

To be strict, asymptotically as $T \rightarrow T_c$, eq. (3) is followed and one can also show that in this limit both $\sigma_2 - \sigma_1$ and $R_1 - R_2$ must have the same exponent. The conductivity difference obeys eq. (4) over an extended range $10^{-5} < (T_c - T)/T_c < 10^{-2}$, while the range of validity of eq. (3) for the resistivity difference is quite limited. One may also point out that Shaw and Goldburg suggest an analysis in terms of the conductivities even in the one-phase region. In the earlier studies in the two-phase region of the binary liquid systems, Schurmann and Parks (1971 *a*) find a similar $\beta \sim 0 \cdot 34$ exponent for $R_2 - R_1$ in the metallic system gallium + mercury, while Pettit and Camp (1974) find the $\beta \sim 0 \cdot 35$ exponent for $\ln \sigma_2 - \ln \sigma_1$ in the semiconducting system selenium + thallium. While the agreement among the various β values is good, one must find out which is the preferred parameter to be used in the analysis.

Finally it remains to discuss the possible frequency dependent effects. The present measurements were made at 32 Hz and 1 kHz, while some of the earlier measurements have been made at even higher frequencies. While the frequency dependent relaxation effects occur in the 10^6–10^{11} Hz region in the pure liquids, the relaxation processes become slower as $T \rightarrow T_c$ and the frequency dependent effects may start possibly in the kHz region, as was indeed suggested as a possibility by Gammell and Angell (1974). The present measurements have not specifically looked for these effects very close to T_c and it would be worthwhile to study the resistivity over a range of frequencies.

These several questions can be answered only by further theoretical and experimental investigations. Some of these studies have been initiated and will be reported in due course.

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