Impurity effects on the critical behaviour of the electrical resistance of binary liquid mixtures

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Abstract. The electrical resistance of the binary liquid system cyclohexane + acetic anhydride is measured, in the critical region, both in the pure mixture and when the mixture is doped with small amounts (≈ 100 ppm) of H_2O/D_2O impurities. T_c was approached to about $t = 3 \times 10^{-6}$ where $t = (T - T_c)/T_c$. The critical exponent $b \approx 0.35$ in the fit of the resistance data to the equation $dR/dT \sim t^{-b}$ does not seem to be affected appreciably by the impurities. There is a sign reversal of dR/dt in the non-critical region. Binary liquid systems seem to violate the universality of the critical resistivity.

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

1. Motivation for the present work

There is a singular contribution to the electrical resistance of the binary liquid systems near the critical solution temperature. The temperature derivative of the electrical resistance (dR/dT) in binary liquids is characterized by the equation $dR/dT \sim t^{-b}$, where the critical exponent b seems to be of the order of 0.35, thus giving a singularity in dR/dT. The singularity in dR/dT of binary liquids arises from the critical concentration fluctuations which grow in range and magnitude in the critical region. One of the theoretical endeavours to explain this anomaly is the percolation model (Shaw and Goldburg 1976), which gives in the mean field approximation $b = (1 - 2\beta)$, where β is the order parameter critical exponent ≈ 0.33. A second model considers the scattering of the conducting ions by the concentration fluctuations (Ramakrishnan et al 1978) and gives the value of b as $1 - \nu$ where ν is the correlation length exponent ≈ 0.66.

The nearest neighbour hopping model for the electrical conduction (Jasnow et al 1974) has also been applied to the problem and gives $b = \alpha$, where α is the specific heat exponent ≈ 0.1. The first careful experiments on the resistivity of binary liquid mixtures by Stein and Allen (1973), approaching T_c as close as $t \approx 10^{-7}$ gave $b \approx 0.55$. Jasnow et al suggested that the data below $t \lesssim 10^{-5}$ could be affected by gravity effects and fitted the remaining data to a $b \approx \alpha \approx 1/8$ exponent. Stein and Allen's data have been again reanalysed by Shaw and Goldburg (1976) to give a $b \approx 0.35 \approx \beta$ exponent. In the isobutyric acid+water system studied by Stein and Allen, Gammell and Angell (1974) did not find any singularity in electrical resistivity! (In a private communication, Professor Angell suggests that the result could have arisen because T_c was not

approached close enough). Subsequently Klyubin *et al* (1975), Shaw and Goldburg (1976), Gopal *et al* (1976a, 1977) and Ramakrishnan *et al* (1978) have studied several polar+nonpolar mixtures and find $b \approx 0.35$, which is becoming the accepted value.

In contrast to binary liquids, the dR/dT anomaly shows a different behaviour in magnetic and allied systems. Nearly all the theoretical calculations, starting with those of Fisher and Langer (1968), suggest that the critical resistivity is proportional to magnetic energy, thus yielding the specific heat critical index α for dR/dT both above and below T_c. These theories consider the scattering of the conduction electrons by spin fluctuations. A few of the earlier calculations (Suezaki and Mori 1969; Takada 1971) suggested a $(2\beta-1)$ exponent for dR/dT. However the recent calculations (Kasuya and Kondo 1974; Richard and Geldart 1975, 1977; Binder *et al* 1976; Balberg *et al* 1976) use a renormalisation group form of the correlation function and the appropriate energy and spin sum rules. These recent theories confirm the earlier result of Fisher and Langer (1968) that the resistivity should follow an energy-like behaviour in the magnetic systems and thus dR/dT should have an α-singularity. The specific heat type behaviour is indeed observed in binary alloys, binary liquid metals, ferromagnets and antiferromagnets, some of the representative experiments being those of Simon and Salamon (1971), Schürmann and Parks (1971, 1972), Parks (1972), Shacklette (1974), Rao *et al* (1975), Singh and Geldart (1976), Balberg *et al* (1978). Though occasional measurements report a non-α behaviour for dR/dT (Craven and Parks 1973; Thomas *et al* 1973) the majority of the recent accurate experimental findings support the belief that there is a near universal behaviour of electrical resistance in ferromagnets, antiferromagnets, metallic binary alloys and binary liquid metals.

Against this background, the critical resistivity in binary liquids seems to be defying the α-singularity behaviour. Since it is only in binary liquids that the near universality seems to be violated, one must check whether there are extraneous factors that might affect the nature of anomaly for dR/dT in binary liquids. Two such possible factors are (i) the dispersion of the resistivity anomalies, and (ii) the effect of small amounts of impurities which cannot be avoided in samples.

For practical considerations only AC (≈ 1 kHz) resistance was measured by all the workers in binary liquids. Due to the critical slowing down, the relaxation frequency of the concentration fluctuations can match the frequency used to measure the electrical resistance. Such a 'matching effect' can lead to a dielectric dispersion/absorption and thus to an anomalous increase in electrical resistance (Gammell and Angell 1974). But if the exponent b really represents such a 'frequency-matching' effect (which is fundamentally non-critical in character), then it must be a strong function of frequency used to measure the resistance. A study (Kumar *et al* 1978) of exponent b as a function of freequency (from 10 Hz to 100 kHz) on two binary liquid systems reveals that there is no noticeable effect of frequency upon b. Thus any contribution from dielectric dispersion is not significant.

However, the question of effect of impurities on the exponent b is not yet clearly settled. Since traces of impurities, especially water, are present in polar+nonpolar binary liquids and contribute to the electrical conduction (Gopal *et al* 1977; Ramakrishnan *et al* 1978), such a study assumes even more importance. Small traces (≈ 100 ppm or so) cannot be avoided in polar liquids even in the purest form available. The simulation of a likely physical picture in the so-called 'pure' binary

liquids (polar+nonpolar and also others) and the checking of the universal behaviour for dR/dT in binary liquids motivated the present study. A short version of the present work is being published elsewhere (Kumar and Gopal 1979).

2. Experimental arrangement

The binary liquid system chosen for the study of impurity effects is $C_6H_{12}+(CH_3CO)_2O$ (which is of the nonpolar+polar type). Its critical composition (x_c) and the critical solution temperature (T_c) are known (Gopal *et al* 1976b). Analar grade samples were used without further purification. Liquids of the same purity were used to study the coexistence curve of these binary liquids. A gas chromatographic analysis revealed H_2O traces ≈ 50 ppm in $(CH_3CO)_2O$. A pyrex glass cell of 10 ml capacity was used with one pair of stainless electrodes. The height of the cell was kept small ≈ 9 mm (to reduce the gravity effects). The H_2O used for doping the pure liquids was distilled and deionised. Spectroscopic grade D_2O was used. Doping was done using a 100 μ ml resolution pippette. Immediately after adding the impurity, the liquids were put in an ice-bath (to suppress the evaporation) and flame-sealed. All the dopings were done in a short time, 1–3 min to avoid moisture absorption.

The experiment was carried out in a multi-stage thermostat with a stability of better than 1 mK. Due care was taken for the thermal equilibrium and other details which are important in critical point phenomena experiments. A typical run took about a week's time to cover a temperature range $(T-T_c) \approx 2°C$. Aged and calibrated thermistors were used both for the temperature control and the temperature measurement. Absolute temperatures, based on a platinum resistance thermometer, are accurate to 50 mK while the temperature resolution is 1 mK. The electrical resistance was measured using an AC resistance measurement method at 1 kHz. A peak-to-peak voltage of ≈ 0.1 V between the electrodes and a lock-in-amplifier system enabled the measurement of resistance to an accuracy of 0·005%. To avoid self-heating of the sample only a small voltage was given to electrodes. The general experimental techniques have been described in Gopal *et al* (1976a). The capacitive part of the impedance (quadrature signal) was balanced but its resolution was not good enough to comment on the dielectric constant anomaly.

All the measurements were made while cooling the liquids from the one-phase to the two-phase region. The pair of electrodes was so placed as to detect heavier polar phase (lesser resistance) as T_c is approached. The detection of T_c was also supplemented by a visual observation.

3. Results

There was a marked decrease in the resistance of the binary liquids by adding water which confirms the earlier speculation that the impurity conduction prevails in polar+nonpolar binary liquids. Adding water forms acetic acid which dissociates, yielding protons for conduction. Table 1 summarises the percentage fall in resistance by adding H_2O. In contrast to H_2O, there is increase in resistance when D_2O is doped (perhaps resulting from exchange of H^+ and D^+ ions). The fall in resistance by adding H_2O is shown in figure 1. An asymptotic decrease seems to set in after ≈ 200

Table 1. Composition (x_c) of the binary liquid system $C_6H_{12}+(CH_3CO)_2O$ filled in the present experiments. The change in resistance resulting from the impurity doping is also noted.

System*	x_c**	Change in electrical resistance
Pure	0·5746	
50 ppm H_2O	0·5745	decrease by 56%
100 ppm H_2O	0·5747	decrease by 66%
200 ppm H_2O	0·5745	decrease by 70%
300 ppm H_2O	0·5745	decrease by 72%
100 ppm D_2O	0·5745	increase by 70%

*Impurity content in terms of volume of $(CH_3CO)_2O$

**In terms of mole fraction of C_6H_{12}. The earlier reported values of x_c and T_c are $0·5745\pm0·001$ mole fraction of C_6H_{12} and $52·568\pm0·05°C$ respectively (Gopal *et al* 1976b). An independent measurement of the T_c by the visual observation technique gives an *increase* of T_c by nearly 40 mK per 100 ppm of impurity.
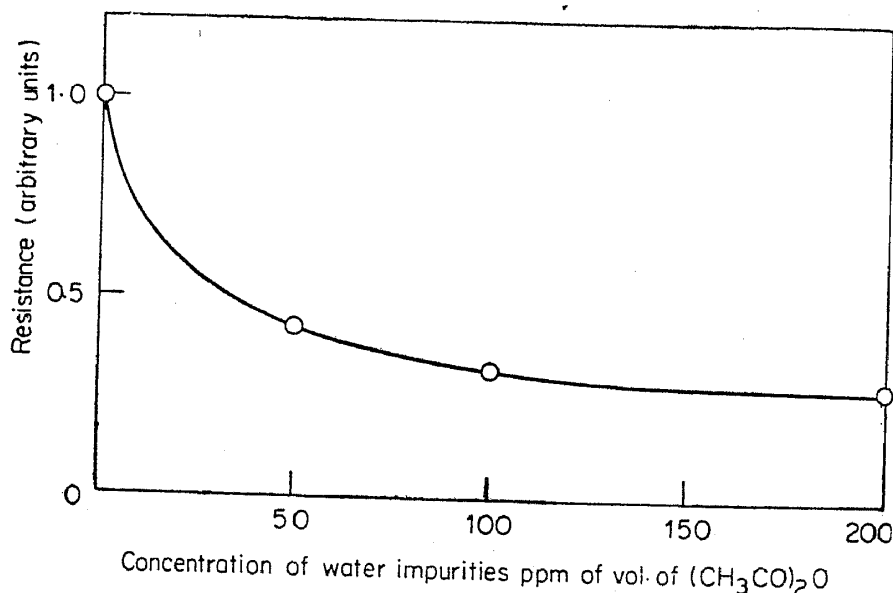

Figure 1. Fall of resistance with the increased doping of water impurity in the binary liquid system cyclohexane + acetic anhydride.

ppm level of impurities. The data shown in figure 1 were taken at approximately 2°C above T_c.

The electrical resistivity data for the pure mixture and for the mixture doped with 50 ppm of H_2O are summarised in figure 2, where a convenient scale of the normalised resistance (R/R_c) and the temperature deviation $(T-T_c)$ has been used. The actual data cover a much wider range. Since a restricted range is shown on an enlarged scale, the scatter in data is visible. There is a decrease of resistance as the temperature is increased. However when the doping level was increased, this fall of resistance near T_c was gradually overtaken by an increase of resistance with temperature further away from T_c. These features are summarised in figure 3. In all the cases the plot of (R_c-R) versus $(T-T_c)$ on a logarithmic scale was linear near T_c, indicating a
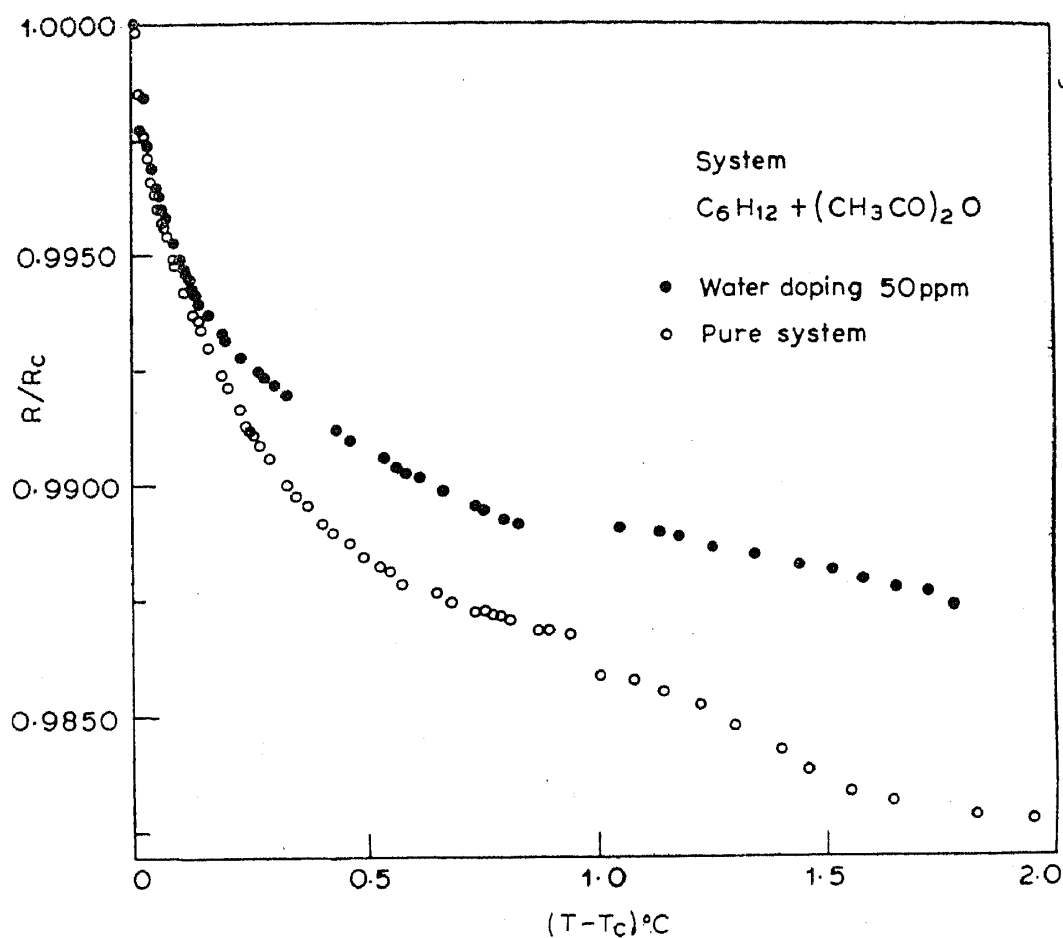
Figure 2. Plot of normalized resistance against temperature deviation for the pure system $C_6H_{12}+(CH_3CO)_2O$ and when the same system $C_6H_{12}+(CH_3CO)_2O$ is doped with 50 ppm of H_2O impurity.

power law behaviour. Such a plot for the simpler cases of the pure mixture and for the 50 ppm doped mixture is shown in figure 4. The plots are more involved at higher levels of doping and are discussed a little later.

In order to analyse the observations, the measured electrical resistance data were fitted to the equation

$$(R-R_c)/t\,R_c \;=\; At^{-b} \,+\, B, \tag{1}$$

where R_c is the electrical resistance as $T \to T_c$ and $t=(T-T_c)/T$. To exclude the gravity affected region, only the data for the temperature range $10^{-5} \lesssim t \lesssim 10^{-2}$ were fitted to the above equation, though T_c was approached to $t=2\times10^{-6}$. R_c, T_c and b were treated as fit parameters. A least square fit using a linear regression was done rather than a non-linear CURFIT programme of analysis. The value of b has an error bar of $\pm\,0\cdot05$. This includes an estimate of systematic error in data. The linear regression coefficient in all the cases is $\approx 0\cdot998$. The T_c obtained from curve fitting was within 3 mK of the observed values, which increases by ≈ 40 mK/100 ppm of H_2O impurities. The results are summarised in table 2.
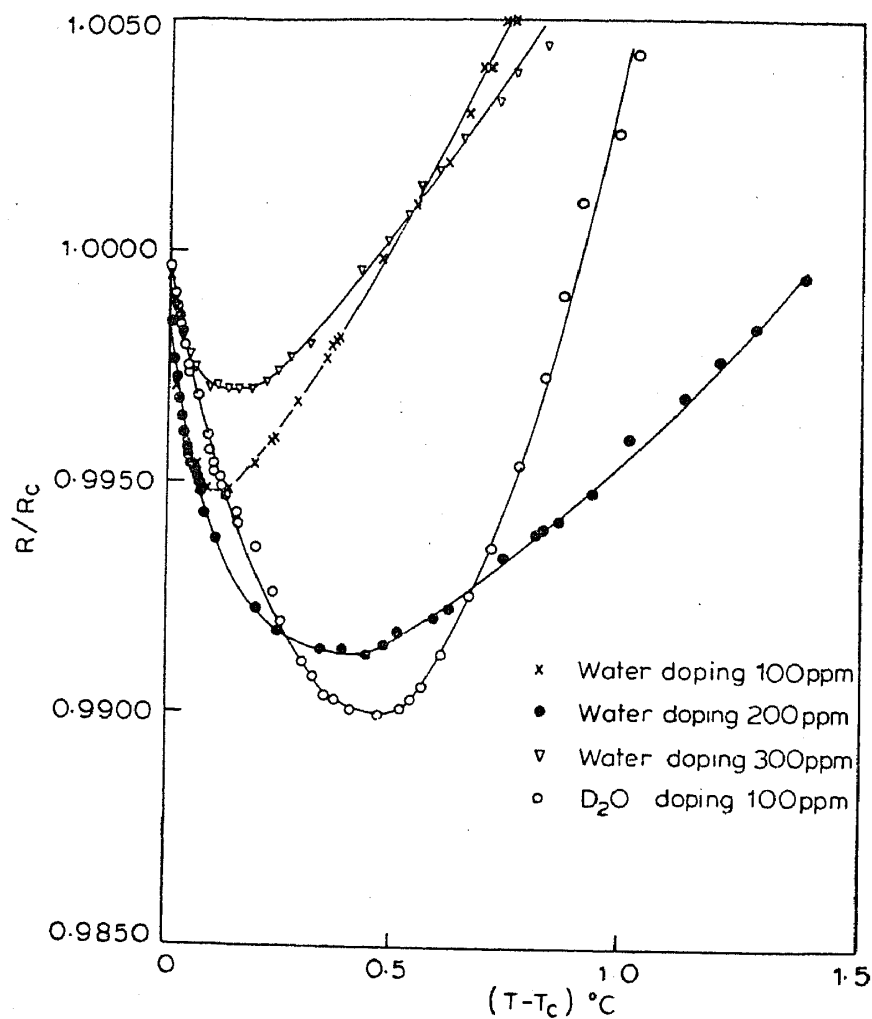
Figure 3. Plot of R/R_c against $(T-T_c)$ exhibiting a sign reversal for dR/dT for $T \gg T_c$ for H_2O doping $\geqslant 100$ ppm. The range of $(T-T_c)$ where the sign reversal occurs is different for the different dopings of the system $C_6H_{12}+(CH_3CO)_2O$. The run for 50 ppm H_2O was partly affected by power failures and is hence less reliable.
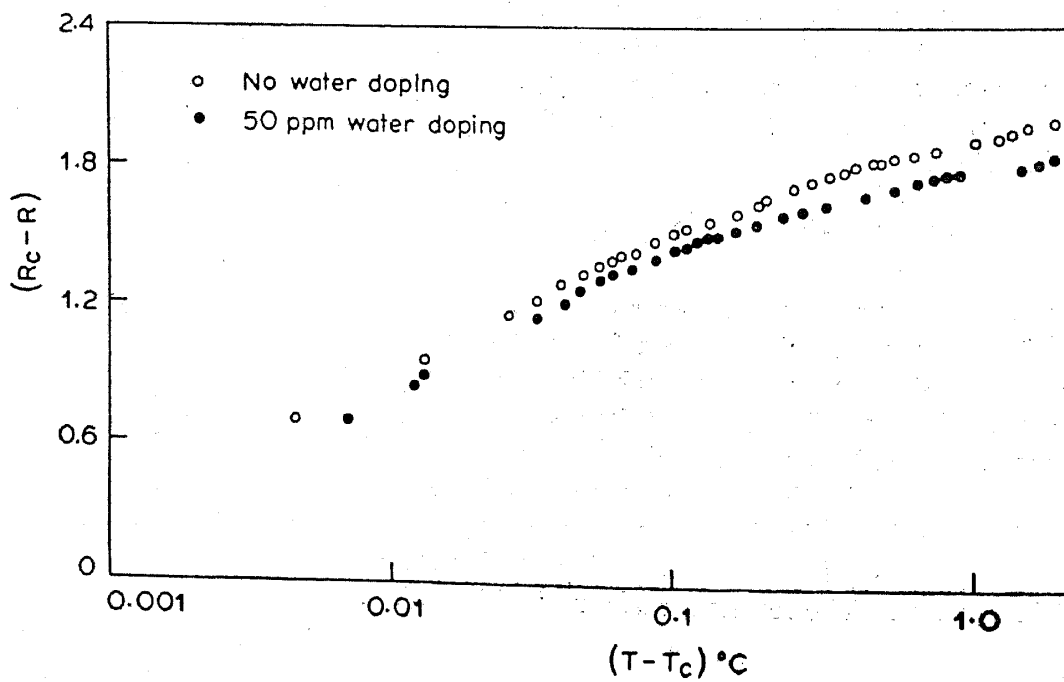

Figure 4. Log-log plot of (R_c-R) and $(T-T_c)$ for the pure system and when the same system $C_6H_{12}+(CH_3CO)_2O$ is doped with 50 ppm H_2O.

Table 2. Value of the critical exponent (b) for dR/dT and the amplitude ratio (A/B) for the entire data; b' and C/D are the corresponding values when the high temperature linear contribution is excluded from the total measured resistance.

System	b (± 0.05)	A/B (± 0.05)	b' (± 0.05)	C/D (± 0.05)
Pure	0·31	0·249	0·31	0·239
50 ppm* H_2O	0·49	0·340	0·50	0·100
100 ppm H_2O	0·40	−0·122	0·40	0·122
200 ppm H_2O	0·31	−0·235	0·31	0·235
300 ppm H_2O	0·40	−0·120	0·40	0·120
100 ppm D_2O	0·26	−0·234	0·26	0·201

*The run for 50 ppm H_2O was partly affected by power failures and is hence less reliable.
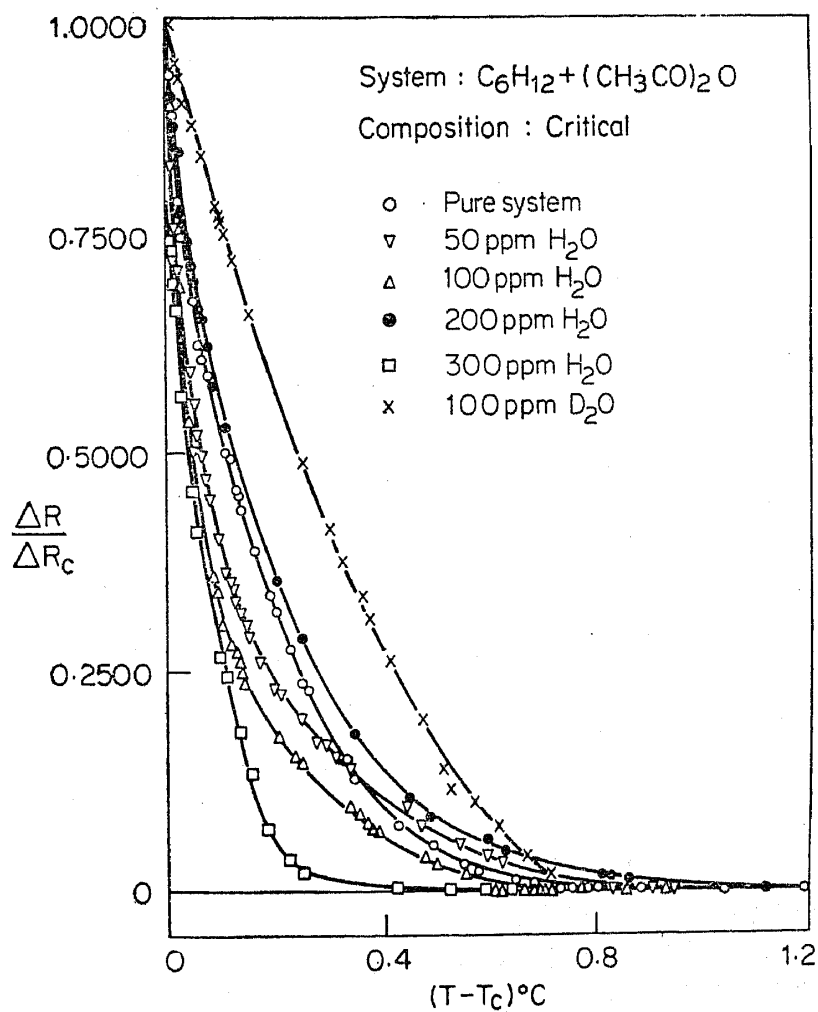

Figure 5. Plot of normalised value of the 'excess resistance' ($\triangle R/\triangle R_c$) against temperature deviation ($T-T_c$) for the system $C_6H_{12}+(CH_3CO)_2O$. It emphasises the equivalence of all the systems when viewed in this manner.

As noted in figure 3, there is a sign reversal of dR/dT for $T \gg T_c$, suggesting a change in the mechanism of the resistivity in the high temperature region. Thus if one subtracts the high temperature resistance from the total resistance, one could get a more realistic estimate of b and also of the amplitude ratio of the singular to analytic contribution. This high temperature resistance is taken as straight line fit and this contribution was subtracted from the total measured resistance. The remaining data ($\triangle R$) for all the systems are shown in figure 5, which stresses the equivalence of all the cases when viewed in this manner. The remaining data ($\triangle R$) were fitted to the equation

$$(\triangle R - \triangle R_c)/t\triangle R_c = C\, t^{-b'} + D. \tag{2}$$

The values of the critical exponents $b \approx b'$, which should be the same except for the deviations caused by curve fitting, and the coefficients (A, B, C and D) of the singular and analytic terms for the best fit are given in table 2.

4. Discussion

Among the factors that cause the critical phenomena experiments to deviate from 'ideality' (Anisimov 1975), the impurity is perhaps the most important since it cannot be avoided at low levels. A study of the effects of such hidden variables on the critical exponents of the equilibrium properties like specific heat, phase diagram, etc. led to the renormalisation of the corresponding critical exponents (Fisher 1968; Fisher and Scesney 1970). However, there is no analysis concerning the effect of impurities on the transport properties in the critical region. The other transport properties such as viscosity, thermal conductivity, thermoelectric power, mutual diffusion coefficient, etc. have no agreed value of the critical exponents (Sengers 1973: Hohenberg and Halperin 1977). In addition, the value of the exponent for viscosity and thermal conductivity (in binary liquids) is very close to 0, thus making it difficult to choose between cusp, logarithmic and power law behaviour in the critical region. In contrast the value of b is quite large (≈ 0.35) in binary liquids. Also the electrical resistivity is easily changed by impurities. Thus the electrical resistance is a favourable case to probe the impurity effects on a transport property in the critical region.

The results given in table 2 show some spread in the values of the exponent $b \approx b'$. A large part of this is due to the scatter in the data. It is also known that the inclusion of higher order correction terms in equation (2) improves the fit and gives better values of the parameters, though the number of such parameters is increased. However considering the difficulties in these experiments and the absence of systematic effects, it is safe to conclude that the exponent b is not affected by the impurities. The same appears to be true of the ratio C/D of the singular to the analytic amplitude of the resistance. Clearly these important points have to be checked by further experiments.

The result that b is not appreciably affected by the impurities is in keeping with an earlier measurement by Shaw and Goldburg (1976), where they studied a fixed amount of impurity KCl added to phenol+water and dioxane+water systems. However, our study differs from that of Shaw and Goldburg in that the scale and the nature of impurity we chose are more likely to be naturally present. In addition, Shaw and

Goldburg did not cover any range of impurities. The other earlier measurements on the impurity effects in the dynamic critical phenomena include light scattering experiments (Bak and Goldburg 1969, 1970; Goldburg and Pusey 1972). There is no effect when the amount of impurity added is small and there is a renormalisation of the critical exponents when the impurity added is quite large ($\approx 50\%$).

The importance of the reported work lies in the scale of impurities added (a few parts in 10^4–10^5) which ensures that the system is still binary. Although, in principle, the impurity added would make the system ternary, it requires really a large amount of impurity to alter the nature of critical phenomena. The above orders of impurities are indeed present in any system (water traces in polar liquids, isotopic compositions in fluids, defects and non-magnetic impurities in ferro- and antiferro- magnets and metallic binary alloys). Thus the levels of impurities added are small enough to simulate a likely physical situation in any given system and the consequent anomaly in dR/dT for the system. This anomaly does not seem to be affected appreciably by the impurities at these levels.

In principle, the imaginary part of the resistivity should have an anomaly similar to that in the real part. Unfortunately, accurate dielectric constant measurements in critical binary liquids are not available, obviously because of the great difficulties in measuring with high resolution small capacitance of the order of 1–10 pF when they are shunted by resistances of the order of about 5–10 kilo-ohms. It is however very interesting that both a and $(1-\nu)$-type singularities have also been theoretically predicted for the temperature derivative of the dielectric constant $d\epsilon/dT$ in the case of fluids (Mistura 1973; Bedeaux and Mazur 1973; Stell and Hoye 1974). The experimental situation is also not clear in the case of fluids. An anomaly in ϵ is observed by Hocken and coworkers (1976) near the gas-liquid critical point of SF_6, though the behaviour of $d\epsilon/dT$ does not seem to follow a simple power law. No evidence for the critical anomaly in $d\epsilon/dT$ is found in ^3He by Doiron and Meyer (1978). In view of the close similarity in the critical behaviour of these many systems, it would be of great interest if high resolution dielectric constant measurements could be performed in critical binary liquid systems.

The sign reversal in dR/dT at $T \gg T_c$ is difficult to explain at present. Although the present study suggests a minima in resistive (R) vs temperature (T) plots, this was not observed for the pure and 50 ppm cases in the present experiments. In the earlier reported work for the so-called ' pure ' binary liquid systems no minima was observed (Ramakrishnan *et al* 1978). The non-observation of the minima in R (or R/R_c) vs T [or $(T-T_c)$] plot requires confirmation in another binary liquid system. It is likely that the level of the doped impurity upto 50 ppm gets neutralised by an unknown impurity which is already present and that the resistivity minimum is noticeable only for the impurity level > 50 ppm. The data do not seem to make any difference to the value of the exponent b for the anomaly in dR/dT.

The insensitivity of the critical exponent b for dR/dT in binary liquids, to the frequency used for measurements and to the level of impurities (both with certain limits at least), places the resistivity anomaly on a firm footing. One is led to conclude that the value $b \approx 0.35$ is genuine in binary liquids. Recent measurements of the specific heat of binary liquids (Anisimov *et al* 1972; Govindarajan *et al* 1973; Klein and Woermann 1975a; Pegler *et al* 1977; Thoen *et al* 1978) give the value of its critical exponent a as nearly 0.1. Thus the specific heat type behaviour is not reflected by dR/dT in binary liquids. There has been a suggesion (Klein and Woermann 1975b)

that the volume thermal expansion anomaly and its consequent change of the ion density should be reflected in the dR/dT anomaly. However the thermal expansion anomaly is also very weak in binary liquids (Ramachandra *et al* 1974; Greer and Hocken 1975; Morrison and Knobler 1976; Scheibmer *et al* 1978) and so it is difficult to expect anything stronger than an α-singularity in dR/dT by this process. There is an argument (M E Fisher, private communication) that if one approaches T_c still closer, then an α-singularity would be revealed in the dR/dT of binary liquids as well. Here again, one knows that the region $t \lesssim 10^{-5}$ is beset with the problems caused by the gravity effects (Dickinson *et al* 1973; Greer *et al* 1975) and at present one does not know how to take care of them. Moreover the temperature range $10^{-5} \lesssim t \lesssim 10^{-2}$ has given accurate values of the critical exponents for a number of other properties. No cross-over phenomenon from one exponent of dR/dT to another exponent has been noticed in this range. The problem assumes significance because one is probably seeing a breakdown of the universal behaviour of a critical property.

In this connection, it is interesting to note the analysis of the stochastic damping of a Brownian particle by Jasnow and Gerjuoy (1975). They conclude that if the averaging of the concentration fluctuations is done over a fixed distance or a temperature independent parameter, dR/dT would follow an α-singularity. However a $(1-\nu)$ singularity for the temperature derivative of the resistance is obtained, if the averaging is done over a temperature-dependent distance like the correlation length ξ. One conjecture for the different behaviour of dR/dT in binary liquids could be that the variable length scattering dominates in these systems (unlike in other solid systems where the nearest-neighbour or fixed distance scattering occurs). The critical exponent b is related to ν, which results from the temperature dependence of the correlation length (Ramakrishnan *et al* 1978).

Two consequences of this conjecture can be tested. Firstly one should have $b \approx 1-\nu$ in the case of liquid-gas systems also, where again the (impurity) conduction should be governed by the temperature dependent scale factor in the form of the correlation length ξ. So far no such measurement has been performed. Secondly an impurity concentration of ≈ 100 ppm implies on an average the presence of an impurity molecule after every 20 molecules of the system or an effective impurity-impurity separation of ≈ 100 Å. The correlation length diverges as $\xi_0 t^{-\nu}$. Though it has not been measured for the present system, typical values are $\xi_0 \approx 2$ Å, $\nu = 0.66$ so that even for $t \approx 10^{-3}$, the correlation length has become of the order of 200 Å. If any fixed distance scattering effect were present, giving a $t^{-\alpha}$ term in dR/dT, it is probably buried in the dominant $t^{\nu-1}$ term. If data of higher accuracy can be obtained, one should try to see the presence of the two terms.

Acknowledgements

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