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Electrical resistance and dielectric constant anomaly in the critical liquid mixture methanol + cyclohexane

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Abstract. The electrical resistance R and the dielectric constant ϵ of the critical binary liquid mixture methanol plus cyclohexane has been measured near the critical point at five different spot frequencies from 10—100 kHz. The data are analysed using a nonlinear least squares routine. The fit is equally good for an α (= 0·1) divergence or a $1-\nu$ (= 0·35) divergence of dR/dT and $d\epsilon/dT$. Additional reasons are advanced to indicate that the α divergence is a better description.

Keywords. Electrical resistance; dielectric constant; critical phenomena.

1. Introduction

Many thermodynamic quantities exhibit anomalous behaviour near their second-order phase transition point. The universality and other features of the critical point phenomena are well known (Stanley 1971; Ma 1976; Kumar *et al* 1982). The temperature derivatives of the resistance R and the dielectric constant ϵ are expected to show singular behaviour near the critical point

$$(R - R_c)/R_c = A\,(1)\,t + A\,(2)\,t^{\theta} + A\,(3)\,t^{\theta+\Delta} + \ldots,$$

and

$$(\epsilon - \epsilon_c)/\epsilon_c = B''\,(1)\,t + B''\,(2)\,t^{\theta} + B''\,(3)\,t^{\theta+\Delta} + \ldots, \tag{1}$$

where $t = (T - T_c)/T_c$, T is the temperature, T_c is the critical temperature, R_c is the resistance at $T = T_c$, ϵ_c is the dielectric constant at $t = 0$, θ is an exponent, whose value lies betwen 0 and 1, and $\Delta = 0{\cdot}5$ is the first Wegner correction exponent (Wegner 1972). When $T \to T_c$, dR/dt and $d\epsilon/dt$ both diverge to infinity with the leading singular term being $t^{-(1-\theta)}$.

The theoretical and the experimental situation regarding the exponent $(1 - \theta)$ is inconclusive. As regards the resistance divergence, the theoretical calculations as well as the experimental observations yield both values of the exponent $(1 - \theta)$ as $1 - 2\beta$ or $1 - \nu = 0{\cdot}35$ and as $(1 - \theta) = \alpha = 0{\cdot}1$ (Jasnow *et al* 1974; Shaw and Goldburg 1976; Ramakrishnan *et al* 1978). In the dielectric anomaly, the theoretical predictions favour $1 - \theta = \alpha = 0{\cdot}1$ (Sengers *et al* 1980) while the experimental situation is not clear between the choice of 0·1 or 0·35 (Thoen *et al* 1980, 1981; Balakrishnan *et al* 1982; Gunasekaran and Gopal 1982) for the exponents. On very general theoretical considerations, one should get the same exponent for the dR/dt and dϵ/dt divergences (Kumar and Jayannavar 1981). Thus the situation warrants further investigation.

So far no studies have been undertaken to investigate the resistivity and dielectric constant on the same samples, in spite of the interrelation between the two. The present work seems to be the first such investigation. A preliminary account of this has been briefly reported earlier (Shetty *et al* 1981; 1982).

2. Experimental measurements

A novel double ratio transformer bridge has been developed to measure the dielectric constant of partially conducting liquids (Gunasekaran *et al* 1981). This method uses two ratio transformers for balancing the resistive and capacitive components of an a.c. bridge. Independent estimates of R and C with 10–100 ppm resolutions are possible without interference from ground capacitances and leakage inductances. A fixed standard resistance and capacitance are needed. The error signal from the bridge is detected for its in-phase and quadrature components using a vector lock-in-amplifier built here. The ratio-transformers, wound on supermumetal toroidal cores become ineffective at high frquencies and thus the absolute errors in the R and C values approach 1 % at 100 kHz. The low frequency limit of 10 Hz is set again by the large magnetizing currents of the transformer. At frequencies of 1 kHz the absolute accuracies are in the region of 0·1 to 0·03 %.

The experiment is carried out in a paraffin oil bath of 35 litres capacity, whose temperature is controlled to ± 1 mK using a PID controller. Initially the bath temperature is raised to 5 or 6 ° above the critical temperature and all measurements are made while cooling the bath temperature in steps of a few mK. The experiment is conducted with the liquids filled in a glass cell of height 1 cm into which a pair of platinum electrodes, 1mm apart, are dipped. The liquids used are of Analar grade and are used without further purification. The critical concentration of this liquid mixture is $X_c = 0{\cdot}2903$ mass fraction of methanol with a critical temperature $T_c =$ 319·026 K (Huang and Webb 1969). Since the dielectric constant and the resistivity depend upon a fixed cell constant, measured resistance and capacitance are analysed to preserve the high resolution of the data.

3. Analysis

The data consist of resistance R and capacitance C readings as a function of temperature at different frequencies 10 and 100Hz, 1, 10 and 100 kHz for the resistance, and 5, 10, 50 and 100 kHz for the capacitance. The electrode polarization problem makes the capacitance measurements at lower frequencies difficult.

The data are analysed by fitting them to the equations of the form (1) using a non-linear least squares procedure like the CURFIT program (Bevington 1969). This type of analysis proves to be indecisive. The estimation of R_c and C_c proves to be uncertain and different choices lead to different values of the other parameters. The exponent $(1-\theta)$ has values ranging from 0·05 to 0·5. Also because of the large number of parameters to be estimated, correlations among their values are set up yielding χ^2 which cannot be separated out, for instance the residuals become less than the errors in the measurements for a range of the parameter values. The possibility of leaving R_c or C_c as a free parameter, to be obtained from the least square analysis itself, adds one more parameter to be estimated and makes the correlations even worse.

As a result, a better procedure of data analysis seems to work with the differentiated forms of (1) eliminating the need to know R_c and C_c. The increase of scatter in data during the numerical differentiation is countered by other criteria of judging the goodness of fit, instead of using χ^2 as a test. For instance one has

$$\mathrm{d}R/\mathrm{d}t = L + Mt^{-(1-\theta)} + Nt^{-(1-\theta+\Delta)},$$

$$\mathrm{d}C/\mathrm{d}t = \bar{L} + \bar{M}t^{-(1-\theta)} + \bar{N}t^{-(1-\theta+\Delta)}. \qquad (2)$$

The M or $\bar{M}$ term is the asymptotic singularity and the N or $\bar{N}$ term with Δ taken as 0·5 is the first Wegner correction to scaling. One may use the criterion that the correction to scaling must be smaller than the main singularity in order to choose the preferred values of the parameters.

Consider the resistance data first. To analyse the $\mathrm{d}R/\mathrm{d}T$ data, the $(1 - \theta)$ value was fixed at 0·1 and 0·35, the theoretically predicted exponents. The best fitted data are reproduced in figures 1 and 2. Table 1 gives the values of the best fit parameters.

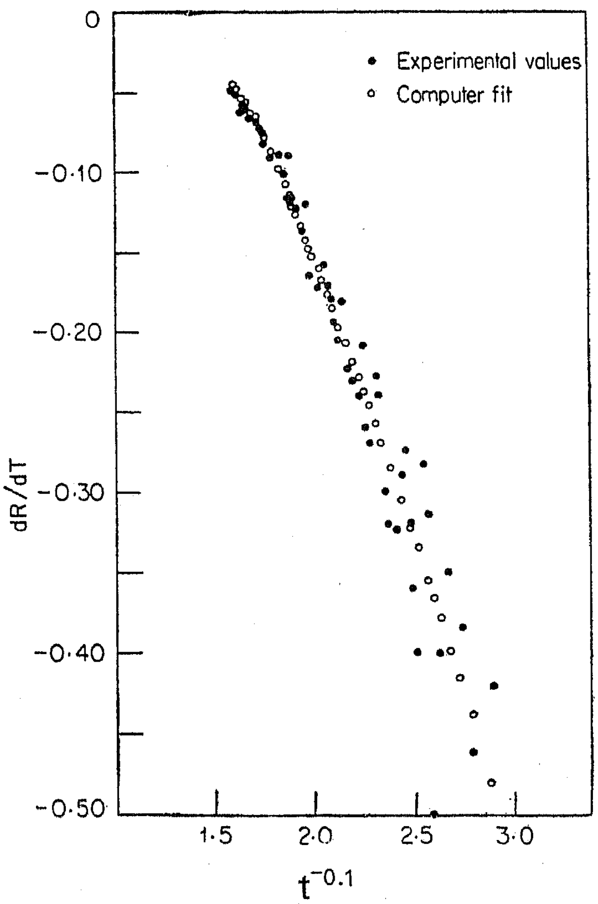

Figure 1. $\mathrm{d}R/\mathrm{d}T$ *vs* $t^{-0.1}$ data for 1 kHz.

From the parameters one can discuss whether the magnitude of the Wegner correction term is smaller than the main singular term in the critical region.

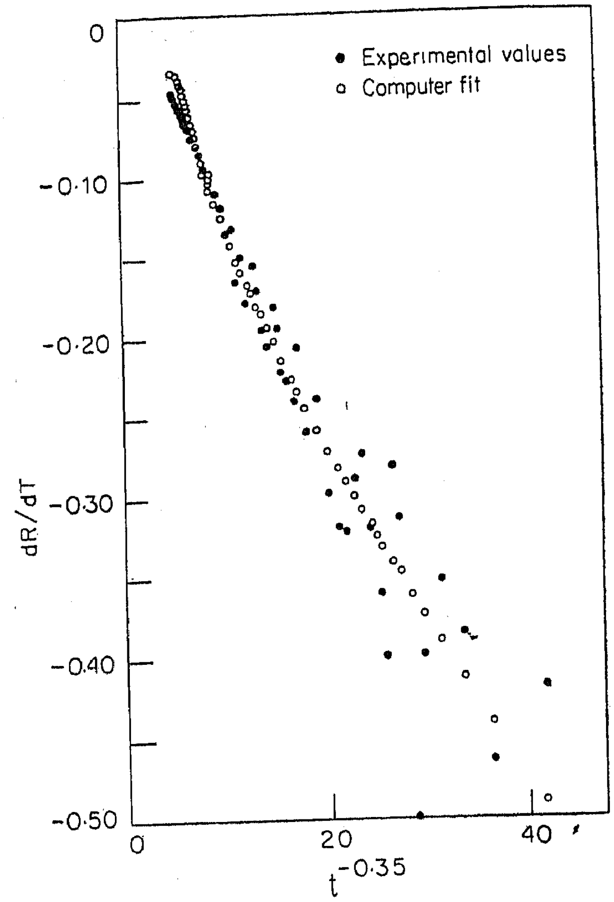

Figure 2. dR/dT *vs* $t^{-0.35}$ data for 1 kHz.

Table 1. Best fit parameters for dR/dT data.

Frequency	$t^{-0.1}$ fit	$t^{-0.35}$ fit
10 Hz	$L=0{\cdot}341$ $M=-\ 0{\cdot}253$ $N=0{\cdot}191$	$L=-\ 0{\cdot}373$ $M=-0{\cdot}004$ $N=0{\cdot}743$
100 Hz	$L=0{\cdot}672$ $M=-0{\cdot}389$ $N=-0{\cdot}641$	$L=-0{\cdot}189$ $M=-0{\cdot}009$ $N=0{\cdot}402$
1 kHz	$L=0{\cdot}669$ $M=-0{\cdot}392$ $N=-0{\cdot}562$	$L=-0{\cdot}250$ $M=-0{\cdot}008$ $N=-0{\cdot}535$
10 kHz	$L=1{\cdot}22$ $M=-0{\cdot}62$ $N=-1{\cdot}74$	$L=0{\cdot}075$ $M=-0{\cdot}018$ $N=-0{\cdot}618$
100 kHz	$L=1{\cdot}05$ $M=-0{\cdot}549$ $N=-1{\cdot}39$	$L=-0{\cdot}058$ $M=-0{\cdot}013$ $N=0{\cdot}776$

Note: The coefficients L, M and N are in general functions of ω and θ where ω is the frequency and θ is the exponent (0·1 or 0·35). The values of the coefficients are given to three significant figures.

Table 2. Coefficients and ratios of singular and correction terms for dR/dT data.

Frequency	0·1 fit			0·35 fit		
	$Mt^{-0.1}$	$Nt^{+0.4}$	X	$Mt^{-0.35}$	$Nt^{+0.15}$	Y
Datum point closest to T_c						
10 Hz	−0·683	0·003	22·7	−0·136	0·163	0·834
100 Hz	−1·05	−0·012	87·5	−0·306	0·088	3·47
1 kHz	−1·05	−0·010	105·0	−0·272	0·117	2·32
10 kHz	−1·68	−0·032	52·5	−0·612	−0·136	4·50
100 kHz	−1·48	−0·026	56·9	−0·442	0·170	2·60
Datum point farthest from T_c						
10 Hz	−0·404	0·029	13·9	−0·020	0·372	0·053
100 Hz	−0·622	−0·097	6·41	−0·045	0·201	0·223
1 kHz	−0·627	−0·085	7·37	−0·040	0·268	0·149
10 kHz	−1·00	−0·265	3·77	−0·090	−0·309	0·291
100 kHz	−0·878	−0·211	4·16	−0·065	0·389	0·167

X represents $\mid M(0{\cdot}1, \omega)t^{-0.5}/N(0{\cdot}1, \omega) \mid$ and Y represents $\mid M(0{\cdot}35, \omega)t^{-0.5}/N(0{\cdot}35, \omega) \mid$

Consider the fit of 1 kHz dR/dT data. In the $t^{-0.1}$ plot, the singular term $M\,t^{-0.1}$ is nearly 100 times larger than the correction to the singular term when $T \simeq T_c$ and nearly 7·34 times larger when T is farthest away from T_c. In the $t^{-0.35}$ fitting the singular term $Mt^{-0.35}$ is nearly 2·31 times the correction to singular term closest to T_c and only 0·149 times the correction to singular term farthest away from T_c. The contributions from the singular and correction terms and their ratios are tabulated for all the different frequencies in table 2. To test the suitability of parameters one can use the X^2 or similar numerical criteria. But, this method has the difficulties of correlations among the parameters and of having to decide among residuals which are all less or comparable to the experimental uncertainties. If one uses a criterion that the contribution from correction-to-singular term should be smaller than the contribution from the singular term, when the $t^{-0.1}$ fit is found to be more acceptable. The correction term becomes important when one is going away from T_c. At the data points farthest away from T_c the correction term is smaller than the main singular term for the 0·1 fit at all frequencies. For the 0·35 fit the correction term becomes larger than the main term.

To analyse the dC/dT data, the $(1-\theta)$ value is once again fixed at 0·1 and 0·35. Figures 3 and 4 show the fits obtained and table 3 gives the values of the test fit parameters for all the different frequencies.

Consider the fit for 50 kHz data. One notices that the fit obtained with one Wegner correction to scaling term for $(1-\theta)=0{\cdot}1$ gives a maximum at small values of dC/dT. Since the estimation of $\overline{L}$, $\overline{M}$ and $\overline{N}$ with the exponent fixed amounts to a linear least square estimation, this implies an inadequacy of the functional form. Therefore, a fit was tried with the next order Wegner term

$$\overline{L} + \overline{M}t^{-(1-\theta)} + \overline{N(1)}t^{-(1-\theta+\Delta)} + \overline{N(2)}t^{-(1-\theta+2\Delta)}. \tag{3}$$

The addition of a second correction term removes the pronounced maximum and gives a good fitting. The values of correction and singular terms, and their ratios for all the frequencies, *i.e.* 5, 10, 50 and 100 kHz are summarised in table 4. Once again,

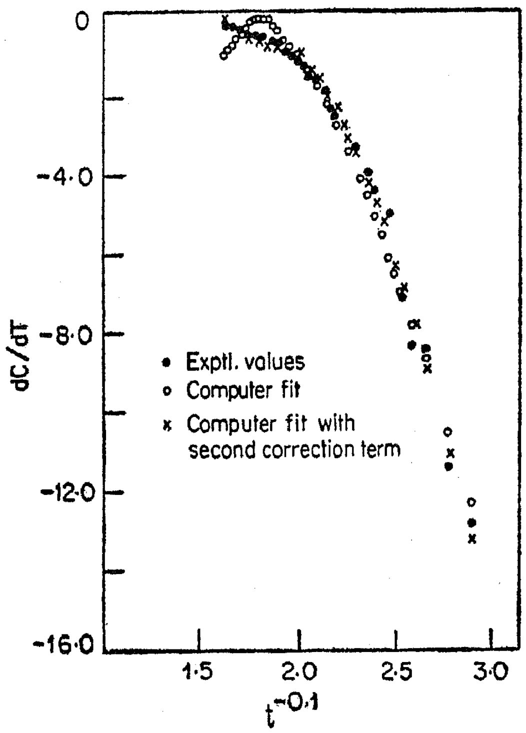

Figure 3. dC/dT *vs* $t^{-0.1}$ data for 50 kHz.

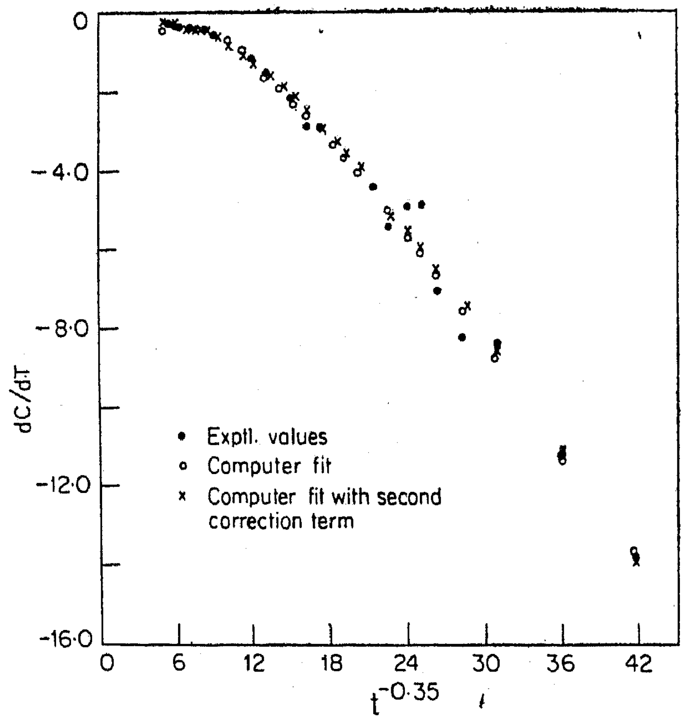

Figure 4. dC/dT *vs* d$t^{-0.35}$ data for 50 kHz.

if the criterion regarding the relative magnitudes of the singular and correction terms is used, the $t^{-0.1}$ fit would be preferred. At the datum point farthest away from T_c where the correction term begins to be important, the main singularity is still larger the 0·1 fit, while it becomes 1/4 to 1/5 of the correction contribution in the 0·35 fit. erefore this criterion indicates an $\alpha(=0{\cdot}1)$ singularity for dC/dT. However two rection terms are needed for the alpha exponent fitting, while the $(1-\nu)=0{\cdot}35$ onent fitting gives a reasonable shape of the curve with one correction term as in ire 4. This point makes it difficult to prefer the exponent categorically. Clearly s question needs to be investigated further.

Table 3. Best fit parameters for dC/dT data.

Frequency	$t^{-0.1}$ fit		$t^{-0.35}$ fit	
5 kHz	$\bar{L}$	68·68	$\bar{L}$	23·22
	$\bar{M}$	27·45	$\bar{M}$	0·6940
	$\bar{N}(1)$	271·5	$\bar{N}(1)$	49·88
	$\bar{N}(2)$	1192	$\bar{N}(2)$	105·7
10 kHz	$\bar{L}$	69·77	$\bar{L}$	22·70
	$\bar{M}$	27·93	$\bar{M}$	0·6970
	$\bar{N}(1)$	274·4	$\bar{N}(1)$	48·20
	$\bar{N}(2)$	1198	$\bar{N}(2)$	97·74
50 kHz	$\bar{L}$	56·77	$\bar{L}$	14·78
	$\bar{M}$	23·11	$\bar{M}$	0·5490
	$\bar{N}(1)$	212·2	$\bar{N}(1)$	28·81
	$\bar{N}(2)$	888·4	$\bar{N}(2)$	43·78
100 kHz	$\bar{L}$	47·04	$\bar{L}$	13·11
	$\bar{M}$	19·15	$\bar{M}$	0·4640
	$\bar{N}(1)$	177·6	$\bar{N}(1)$	26·68
	$\bar{N}(2)$	757·2	$\bar{N}(2)$	49·18

Note. The coefficient $\bar{L}$, $\bar{M}$, $\bar{N}(1)$ and $\bar{N}(2)$ are in general functions of ω and θ where ω is the frequency and θ is the exponent (0·1 or 0·35). The values of the coefficients are given to four significant figures.

Table 4. Coefficients and ratios of singular and correction terms for dC/dT data.

uency	0·1 fit				0·35 fit			
	$\bar{M}t^{-0.1}$	$\bar{N}(1)t^{+0.4}$	$\bar{N}(2)t^{+0.9}$	$\bar{X}$	$\bar{M}t^{-0.35}$	$\bar{N}(1)t^{+0.15}$	$\bar{N}(2)t^{+0.65}$	$\bar{Y}$
um point closest to T_c								
5 kHz	79·60	3·801	0·0715	21·34	28·45	10·12	0·1057	2·840
10 kHz	80·99	3·841	0·0718	21·48	28·57	9·784	0·0977	2·949
50 kHz	67·01	2·970	0·0533	22·97	22·54	5·848	0·0437	3·883
100 kHz	55·53	2·486	0·0454	22·75	19·02	5·416	0·0491	3·543
um point farthest from T_c								
5 kHz	43·92	41·26	16·69	1·787	3·747	24·19	4·652	0·1917
10 kHz	44·68	41·70	16·77	1·792	3·763	23·37	4·300	0·1973
50 kHz	36·97	32·25	12·43	1·865	2·964	13·97	1·926	0·2460
100 kHz	30·64	26·99	10·60	1·869	2·505	12·93	2·163	0·2326

$\bar{X}$ represents $|\bar{M}t^{-0.1}/(\bar{N}(1)t^{+0.4} + \bar{N}(2)t^{+0.9})|$ and $\bar{Y}$ represents $|\bar{M}t^{-0.35}/(\bar{N}(1)t^{+0.15} + \bar{N}(2)t^{+0.65})|$

Finally we note that the standard deviations* obtained for L, M and N of dR/dT data at 1 kHz are 0·0030, 0·0064 and 0·27 for the 0·1 fit and $0{\cdot}47\times10^{-4}$, 0·0130 and 0·11 for 0·35 fit. For dC/dT data at 50 kHz the standard deviations of $\overline{L}$, $\overline{M}$, $\overline{N(1)}$ and $\overline{N(2)}$ are as follows: 0·0044, 0·019, 3·1 and 78 for the 0·1 fit and $0{\cdot}75\times10^{-4}$, 0·0190, 0·140 and 5·1 for the 0·35 fit.

In conclusion, we may say that when the dR/dT and dC/dT data are analysed for their critical divergence, both 0·1 and 0·35 exponents give good fit. As mentioned in §1, the mere experimental data is probably unable to resolve this ambiguity. The 0·1 exponent seems to be preferred if we expect the contribution from the singular term to be the leading contribution in the critical region.

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*There exists a logical complication in the CURFIT program published in Bevington's book, which was pointed out to us by Dr Scott of the University of California (Scott 1982). The parameter FLAMDA becomes very large if the iterations are allowed to continue after the convergence and affects the standard deviation values. The program is to be changed slightly. The unmodified ARRAY matrix must be stored as ARSAV and finally the ARSAV matrix is inverted to get the standard deviations.