CHAPTER VIII

ELECTRICAL CONDUCTIVITY ANOMALY IN BINARY LIQUID MIXTURES NEAR THE CRITICAL POINT.

Introduction:

A number of publications have appeared concerning the temperature dependence of the electrical resistance R(T) of some selected binary liquid mixture near the critical points has attracted considerable attention recently. The behaviour of the transport properties for a binary liquid mixture was first reported by Friedlander (1901). Later on, it was observed by number of authors (Stein et al, 1972) that the viscosity of binary liquid at critical system shows a anomaly as T_c is approached from single phase region. Stein and Allen (1973) established the existance of strong divergence in the temperature dependence of resistivity for isobutyric acid + water very close to critical temperature T_c. Gammell and Angell (1974) studied the temperature dependence of the electrical resistance for the above mention system, but could not detect any anomaly at all due to critical fluctuation. Stein and Allen (1973) further analysed their data by the help of four methods at very close to T_c($\epsilon \approx 10^{-7}$) and found the critical exponent 'd' in the range $0.50 < d < 0.77$ and concluded that the derivative ($\frac{dR}{dT}$) is strongly divergent near T_c. Jasnow, Goldburg and Semura (1974) reanalysed the data of Stein and Allen and showed that over a limited range of reduced temperature $2 \times 10^{-5} < \epsilon < 10^{-2}$, their data could be fitted to the functional form

$$\frac{R_c - R}{R_c} = a\epsilon^{1-\alpha} - b\epsilon \qquad \ldots 8.1$$

where a = 4.1, b = 1.6 and $\alpha = 0.12$. Jasnow et al. (1974) discarded those data which were very close to the critical point ($3.3 \times 10^{-7} \leqslant \epsilon \leqslant 10^{-5}$) on the ground that they might be subjected to gravitational effects. Shaw and Goldburg (1976) have repeated the Isobutyric acid + water experiment of Stein and Allen and also have carried out similar studies in a critical mixture of pure phenol + water and KCl - doped phenol - water mixture. They observed that their experimental data as well as the data given by Stein and Allen were nicely fitted to the equation

$$\sigma_R = \left(\frac{\sigma - \sigma_c}{\sigma_c}\right) = A\epsilon^{\theta} + B_1\epsilon + B_2\epsilon^2 \qquad \ldots 8.2$$

in the reduced temperature range $10^{-5} \leqslant \epsilon \leqslant 10^{-2}$ and noticed that their results were consistent with the existence of a conductivity singularity of the form

$$\sigma_{sing} = A\,\epsilon^{\theta} \qquad \text{where} \qquad \theta = 0.70^{+.15}_{-.10}$$

Gopal et al (1976, 1977) and Ramkrishna (1978) have studied the temperature dependence of electrical resistivity of several polar, nonpolar critical mixture system near critical point and found the critical coefficient β = b = 0.35, which is becoming the accepted value for giving singularity in derivative $\left(\frac{dR}{dT}\right)$.

The purpose of the present experiment is to measure the electrical conductivity of the three binary liquid systems such as (Methyl alcohol + carbondisulphide), (Nitrobenzene + n Hexane) and (Aniline + Cyclohexane), in the critical temperature region at a frequency of 400 KHz in order to study whether our conductivity data also exhibit a singularity of the form $\sigma_{sing} = A\,\epsilon^{\theta = 2\beta}$ or not.

Experimental Arrangement:

The schematic diagram of the experimental arrangement and the method of determining the r.f. conductivity of the mixture has been described in detail in the chapter II section 2.1.

The oscillator frequency for measurement of r.f. conductivity was fixed at 400 KHz. A dielectric cell was made up of pyrex glass tube of diameter of 2.5 cms., fitted with a pair of stainless steel circular electrodes of diameter 1.5 cms. and 5 mm apart.

Analar grade sample supplied by BDH (London) were used without further purification. The cell was filled with the liquids in proper proportion to the critical mixture was then flamed sealed at the top. To avoid the self-heating of a sample only a low voltage given to the electrodes of the cell by making the very loose coupling. All the measurements were made while looking the liquid from the one phase to two phase region. A thermostat having millidegree temperature stability was used for this study. The detection of T_c was supplemented by a visual observation.

Results and Discussion:

The self diffusion coefficient of organic polar liquid, which is usually closely associated with ionic mobility do not show any unusual behaviour near the critical temperature T_c. But it has been possible to detect (Dutta, Thesis, 1983) a suitable change in ionic mobility by the help of resistance measurement of mixture at critical solution temperature. On this basis it has been thought that the electrical resistance of binary liquid mixture should show some anomaly due to the critical fluctuation near T_c.

In order to show the existence of a singular contribution to the electrical resistance of the several binary liquid system near the critical solution temperature and to determine the critical exponent 'b', number of authors (Jasnow et al, 1974), choose various functional forms to fit the data of temperature dependence resistance R(T) of the systems. The singularity in ($\frac{dR}{dT}$) of binary liquid arises from the critical concentration fluctuation which grow in range and magnitude in the critical region. In the one phase region the functional form of the resistance is given (Gopal, et al, 1976) by

$$R = R_c - A\left(T - T_c\right)^b \qquad \ldots 8.3$$

where b = 0.3 is the critical exponent and Rc is the electrical resistance at critical temperature Tc. Also in the one phase region Show and Goldburg (1976) showed that the conductivity of the binary critical mixture must contain a term of the form $\sigma_{sing} = A\epsilon^{\theta = 2\beta}$ where the reduced temperature $\epsilon = \left(\frac{T - T_c}{T_c}\right)$ and the critical exponent $\theta = 2\beta$ where β is an exponent which characterise the shape of the coexistence curve. They further outline a percolation model of the electrical conduction process in the effective medium approximation and showed the critical exponent $\Theta = 2\beta$.

A Simple Expression for Conductivity $\sigma(T)$ From Percolation Theory:

The percolation theory is more directly applicable to σ (T) rather than R (T). At a particular instant of time there exists a spatial variation of composition in the mixture of polar, nonpolar liquid i.e. $C_{12} = (C_c + \delta C_o)$ and this variation gives rise to a spatial variation of the local conductivity $\sigma(r,t)$ of correlation length ξ . But if the life time of the concentration fluctuation is sufficiently long and the composition of the mixture of spatially inhomogeneous medium considered as static then only the percolation theory is applicable. Approximating the distribution function of composition, the conductivity as a bimodel one reduced temperature $\epsilon << 1$ and latter on averaging the fluctuation over a correlation volume (ξ^3) we get a relation

$$\sigma_{sing} \propto \epsilon^{2\beta} \qquad \text{... (8.4 a)}$$

or

$$\sigma_{sing} = M \epsilon^{2\beta} \qquad \text{... 8.4 b}$$

where M is the parameter $\epsilon = \left(\frac{T - T_c}{T_c}\right)$ is the reduced temperature and β is the critical coefficient which characterises the shape of the coexistence curve.

Further considering effective medium approximation and taking equation (12) of Reference (Landaner, 1952) the conductivity σ can be written as

$$\sigma = \sigma_0 + \sigma_0 B \langle (\delta c)^2 \rangle_{\xi^3} \quad \ldots 8.5 \text{ a}$$

or

$$\sigma = \sigma_0 \left[1 + B \langle (\delta c)^2 \rangle_{\xi^3} \right] \quad \ldots 8.5 \text{ b}$$

where

$$B = \frac{1}{3} \left\{ 2 \left(\frac{\left(\frac{\delta \eta}{\delta c}\right)_0}{\eta_0} \right)^2 - \left(\frac{\left(\frac{\delta n}{\delta c}\right)_0}{n_0} \right)^2 - \frac{\left(\frac{\delta \eta}{\delta c}\right)_0 \left(\frac{\delta n}{\delta c}\right)_0}{n_0 \eta_0} \right\} \quad \ldots 8.6$$

where η is the viscosity, and n is the ion density of system and n_0 , η_0 and σ_0 denotes the value of mean ion density, viscosity and conductivity at C = Cc (critical concentration). Using scaling theory and standard statistical arguments, one find (Jasnow, 1975)

$$C_c^{-2} \langle (\delta c)^2 \rangle_{\xi^3} = d \epsilon^{2\beta} \quad \ldots 8.7$$

where d is of order unity.

On combining equations (8.6) and (8.7), we get the desired relation

$$\sigma = \sigma_0 + \sigma_0 B d \epsilon^{2\beta} \qquad \ldots 8.8\ a$$

or,

$$\sigma = \sigma_0 + M \epsilon^{2\beta} \qquad \ldots 8.8\ b$$

or,

$$\sigma = \sigma_0 + \sigma_{sing} \qquad \ldots 8.8\ c$$

where M = (σ_0 Bd) and actually σ_0 has been regarded here as analytic in ϵ .

All the experimental binary liquid systems were brought into one phase region about 5°C above T_c. The liquids were allowed for few minutes to attain thermal equilibrium. Then the system were slowly cooled with millidegree steps till the mixture comes down to the critical or opalescence region. The r.f. conductivity (K') of the binary liquid mixtures, such as (a) methyl alcohol + carbon disulphide ($CH_3OH + CS_2$) (b) Nitrobenzene + n - hexane ($C_6H_5NO_2 + C_6H_{14}$) and (c) Aniline + cyclohexane ($C_6H_5NH_2 + C_6H_{12}$) have been measured at 400 KHz and at various temperature starting from one phase region to down to T_c. Much care has been taken on measurement of K'_c , the critical temperature r.f.

conductivity. The values of the r.f. conductivity of the three systems at various temperatures above T_c and at T_c are placed in Table (8.1a- 3a). As it is the temperature derivative of electrical resistance is strongly divergent near T_c. So an attempt has been taken to study the r.f. conductivity anomaly near critical temperature of the three polar - nonpolar liquid mixtures at critical concentrations. The r.f. conductivity data are plotted against the reduced temperatures for the three systems shown in Fig. (8.1, 8.2, 8.3). It is observed that the temperature variation conductivity closer to T_c is quite large but when it is away from T_c the variation is small. This clearly indicate the asymtotic behaviour of derivative of conductivity and strongly suggest the existance of r.f. conductivity anomaly near T_c.

Stein and Allen chose to fit the resistance versus temperature data to various functional forms

(a) $$\frac{dR}{dT} = A\epsilon^{-d} + B\epsilon^{2} + C\epsilon + D \quad \text{... 8.9a}$$

(b) $$\frac{R_c - R}{\epsilon . R_c} = \left(\frac{A'}{1-d}\right)\epsilon^{-d} + B'\epsilon^{2} + C'\epsilon + D' \quad \text{... 8.9b}$$

(c) $$R - R_{ideal} = A''\epsilon^{1-d} + B''\epsilon + C'' \quad \text{... 8.9c}$$

(d) $$\left(\Delta R_j - \Delta R_i\right) = A'''\left(\epsilon_i^{1-d} - \epsilon_j^{1-d}\right) + B'''\left(\epsilon_i - \epsilon_j\right) \quad \text{... 8.9 d}$$

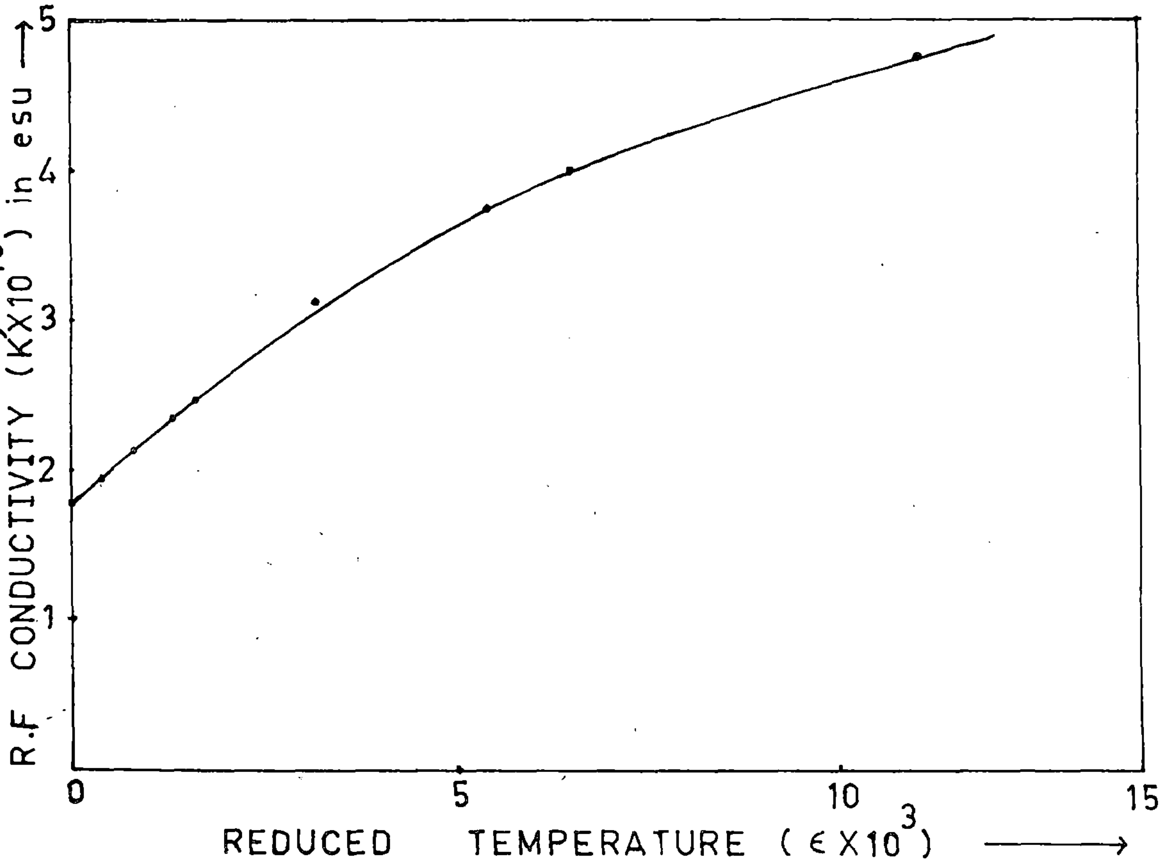

Fig - 8.1 Plot of R.F Conductivity K′ against Reduced temperature ϵ for $CH_3OH + CS_2$.

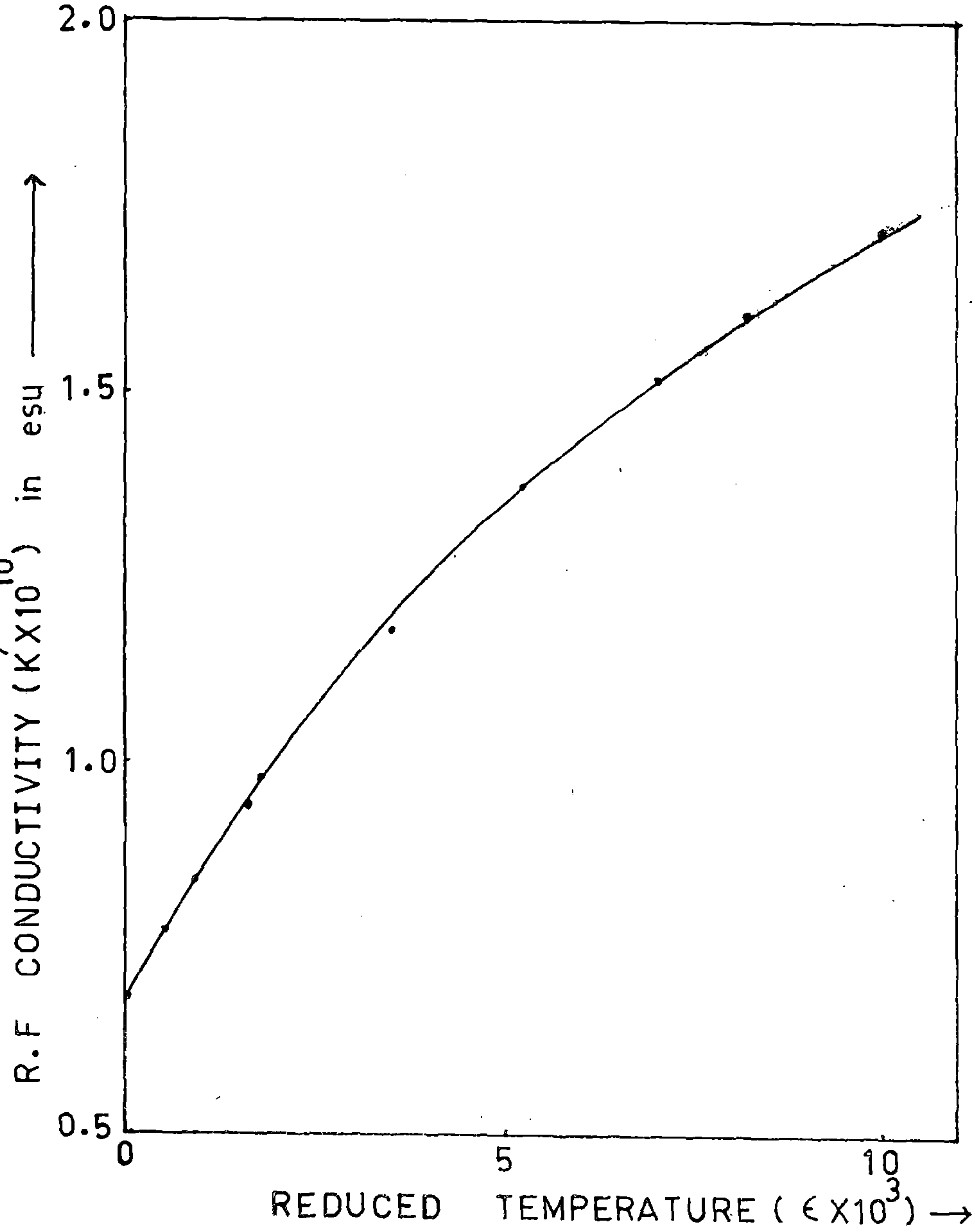

Fig - 8.2 Plot of R.F Conductivity K′ against Reduced temperature ϵ for $C_6H_5NO_2 + C_6H_{14}$.

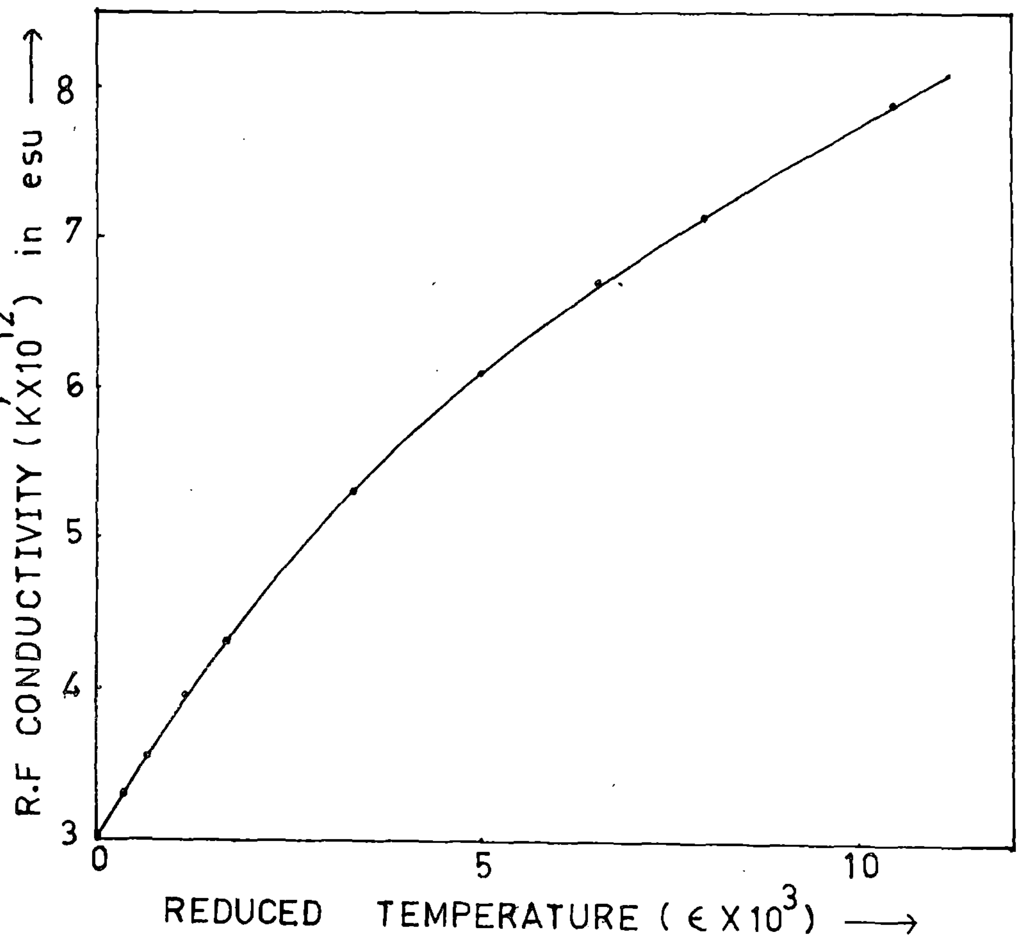

Fig- 8.3 Plot of R.F Conductivity K' against Reduced temperature ϵ for $C_6H_5NH_2 + C_6H_{12}$.

where R_{ideal} is the back ground resistance and

$$\Delta R = (R - R_{ideal}) \qquad \text{and parameter} \quad A''' = \left(\frac{A}{1-d}\right),$$

$$B''' = -B''$$

As the percolation theory is applicable only to temperature variation of conductivity rather than R (T). So we tried to analyse and least squares fits our r.f. conductivity data K' (T) to the Shaw and Goldburg empirical equation of conductivity,

$$\sigma = A' \epsilon^{\theta} + \sigma_c + B_1' \epsilon + B_2' \epsilon^2 \qquad \text{... 8.10}$$

Therefore we can write the equation (8.10) of form

$$K' = A' \epsilon^{\theta} + K_c' + B_1' \epsilon + B_2' \epsilon^2 \qquad \text{... 8.11 a}$$

or

$$K' - K_c' = K'_{singular} + K'_{bkg} \qquad \text{... 8.11 b}$$

where A', B'_1, and B'_2 and θ are the least squares fit values or parameter, singular conductivity $K'_{singular} = A' \epsilon^{\theta}$ and background conductivity $K'_{bkg} = B_1' \epsilon + B_2' \epsilon^2$

Writting the above equation (8.11 a) for conductivity in dimension less unit, we have reduced conductivity

$$K'_R = \frac{K' - K'_c}{K'_c} = \frac{A}{K'_c}\epsilon^{\theta} + \frac{B'_1 \epsilon}{K'_c} + \frac{B'_2 \epsilon^2}{K'_c} \quad \ldots\ 8.12$$

or

$$K'_R = A\epsilon^{\theta} + B_1\epsilon + B_2\epsilon^2 \quad \ldots\ 8.13$$

where the least squares parameters $A = \frac{A'}{K'_c}$, $B_1 = \frac{B'_1}{K'_c}$ and $B_2 = \frac{B'_2}{K'_c}$.

In our present analysis we did not use the higher power of ϵ , so we have eliminated the term $B_2\epsilon^2$. Therefore, the equation (8.13) becomes,

$$K'_R = A\epsilon^{\theta} + B_1\epsilon \quad \ldots\ 8.14$$

In order to get the best least squares fits parameters, we have varied the range of reduced temperature of the order $10^{-4} \leqslant \epsilon \leqslant 10^{-2}$ and determined least squares fit parameters for three sets of ϵ , using the equation (8.14) for each systems. The values of the fits parameters are placed in the Table (8.1 a, 2a, 3a).

It is further observed that all our measured data for three different systems are fits well in equation (8.14) if we consider the critical exponent value $\theta = 0.71$, which is the slope of plot $\log_{10} K'_R$ against $\log_{10} \epsilon$. Figures (8.4, 5 and 6) shows the results of second set ($10^{-4} \leqslant \epsilon \leqslant 10^{-2}$) of all the systems ($CH_3OH + CS_2$), ($C_6H_5NO_2 + C_6H_{14}$) and ($C_6H_5NH_2 + C_6H_{12}$) respectively. In the graph of $\log_{10} K'_R$ plotted against $\log_{10} \epsilon$ the upper dashed line running through the experimental data points which are the least square fits data obtained from equation (8.14). The lower dashed line is the same as upper one but with background conductivity K'_{bkg} subtracted. In the data analysis, only linear background terms ($B_1 \epsilon$) was considered. The values of $\log K'(\epsilon)$, $\log(K'_R - K'_{bkg})$ and $\log \epsilon$ of the three systems are tabulated in table (8.2 a, 2b, and 2c) respectively.

So we find that our data are best fitted to the equation (8.14) in the reduced temperature range $10^{-4} \leqslant \epsilon \leqslant 10^{-2}$ and the amplitude ratio of singular to background $A/B_1 < 1$, provides strong evidence that the conductivity singularities which we have observed, is an experimental fact.

The striking observation made in this studies is that apart from the shape of the conductivity curves Fig. (8.1, 8.2, 8.3) the critical exponent θ for the

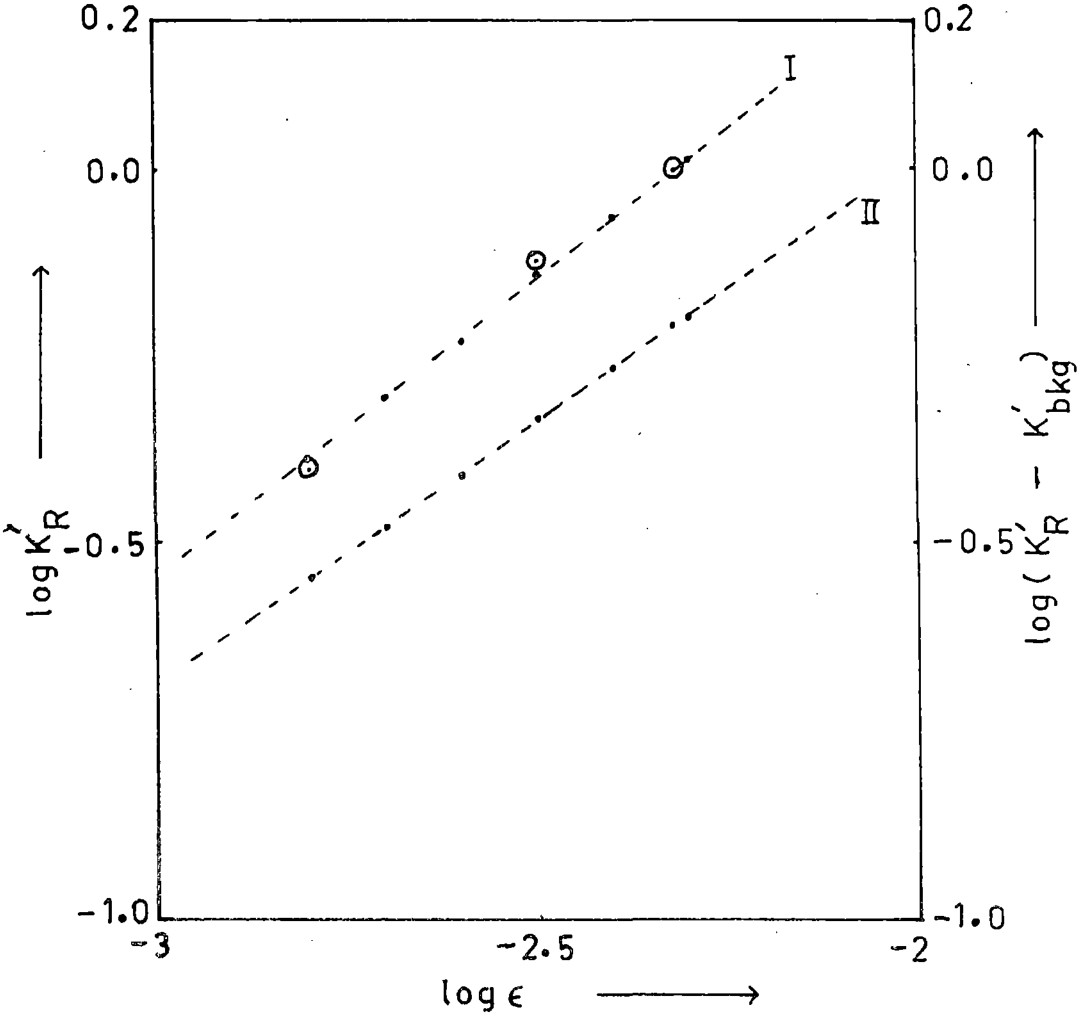

Fig - 8.4 Log-Log plot of reduced conductivity K'_R versus reduced temperature ϵ (I) and also background term K'_{bkg} subtracted (II) for $CH_3OH + CS_2$.

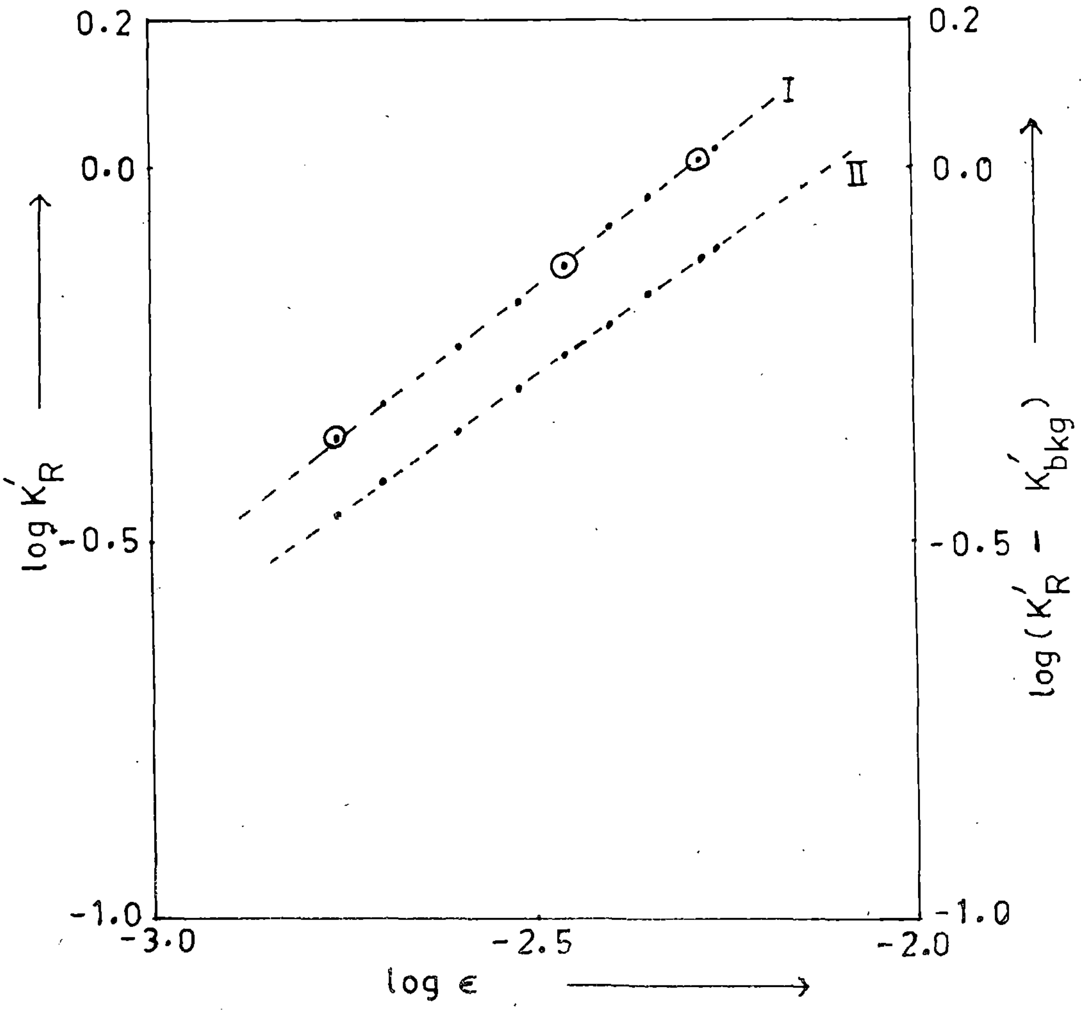

Fig-8.5 Log-Log plot of reduced conductivity K'_R versus reduced temperature ϵ (I) and also background term K'_{bkg} subtracted (II) for $C_6H_5NO_2 + C_6H_{14}$.

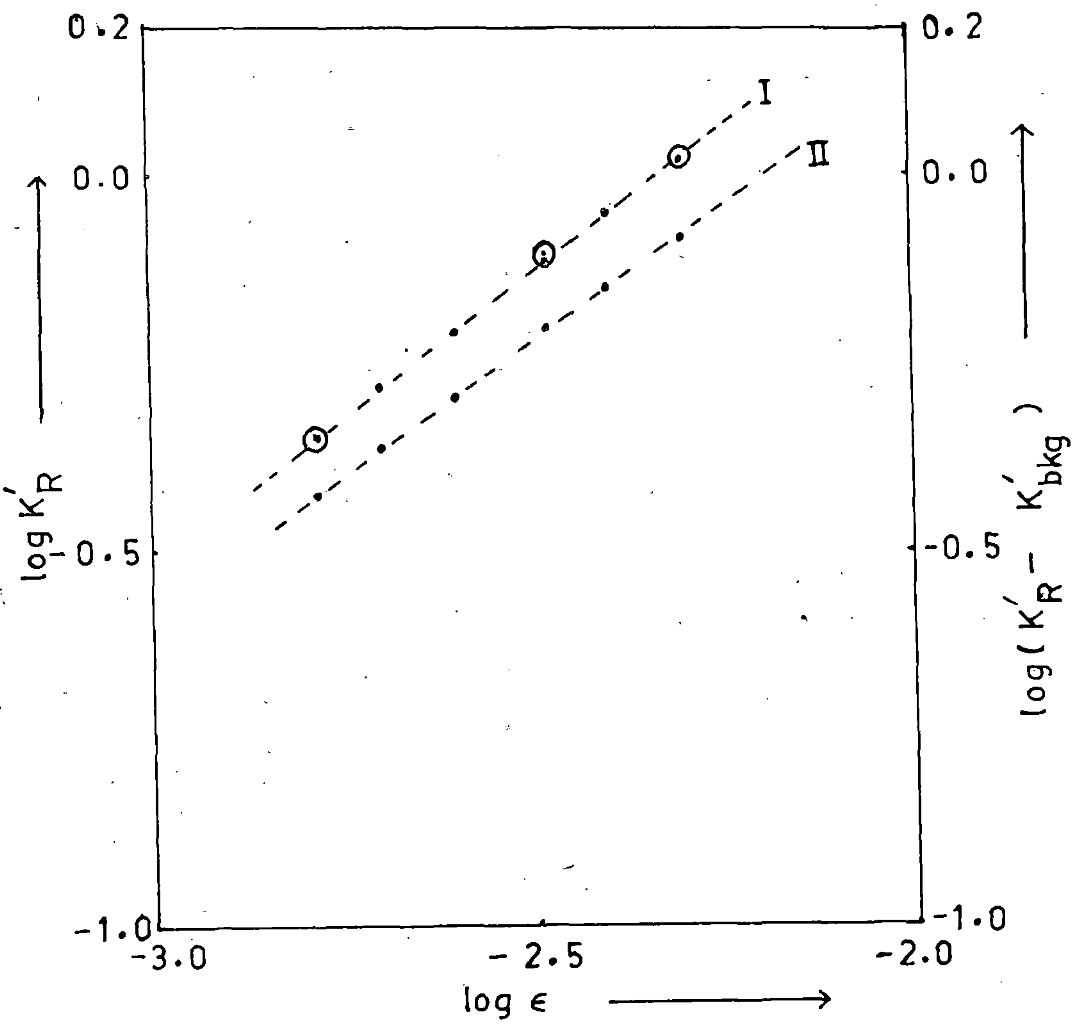

Fig-8.6 Log-Log plot of reduced conductivity K'_R versus reduced temperature ϵ (I) and also background term K'_{bkg} subtracted (II) for $C_6H_5NH_2 + C_6H_{12}$.

three different systems almost have the same value $\Theta =$ 0.71 which agree excellently with the value reported by previous workers (Gopal, 1976).

It has been reported that very near to T_c there is every possibility to expect frequency dependent conductivity anomaly (i.e. of the inverse of the applied frequency) being of the same order of magnitude as the fluctuation life time. But the frequency dependent relaxation effect occurs in the 10^{10} to 10^{12} Hz region in the pure and dilute solution of polar liquid in nonpolar solvent and little high value may be expected at critical opalescence temperature T_c.

But in our present experiment we have taken the frequency 400 KHz, which is quite low compare to the time constant for decay of composition fluctuation at critical temperature. So we can consider that there is no noticeable effect of frequency on critical exponent Θ has taken place at that frequency.

Thus we can conclude that in the one phase region, the conductivity of the binary liquid mixture near critical temperature T_c must contain the term of the form, $K'_{sing} = A\,\epsilon^{\Theta=2\beta}$ with $\Theta = 0.71$ and $\beta \simeq 0.35$, which is an universal value for the temperature variation of the order parameter in critical phenomena.

<u>Table 8.1a</u>

Values of r.f. conductivity (K'), reduced r.f. conductivity (K'_R) at different reduced temperatures (ϵ), fitting equation parameters (θ , A, B_1) and the amplitude ratio A/B_1, R.F. conductivity at critical temperature (T_c = 40.5°C) K'_c = 1.792 x 10^{-10} esu.

System	No. of sets	$\epsilon \times 10^3$	$K' \times 10^{10}$ esu	K'_R	θ	A	B_1	A/B_1
Methyl		1.3	2.35	0.3114				
alcohol	1	0.8	2.15	0.1998	0.12	-0.017	248.23	-6.8×10^{-5}
(15 per-		0.4	1.95	0.088				
cent by		0	1.792					
weight)								
+		4.78	3.568	0.99				
Carbon	2	3.19	3.138	0.75	0.71	27.42	80.59	0.34
disulphide		1.59	2.496	0.393				
(85 percent		0	1.792					
by weight)								
		11.10	4.75	1.651				
Solution	3	6.5	4.0	1.232	0.50	13.26	23.22	0.57
		5.4	3.75	1.093				
		0	1.792					

Table 8.1b

Fitted values of reduced temperature (ϵ), reduced conductivity (K'_R) and reduced conductivity with background term subtracted ($K'_R - K'_{bkg}$) . Fitted equation is $K'_R = 27.42\,\epsilon^{.71} + 80.59\,\epsilon$.

System	$\epsilon \times 10^3$	K'_R	$K'_R - K'_{bkg}$	$\log \epsilon$	$\log K'_R$	$\log(K'_R - K'_{bkg})$
Methyl	1.00	0.2839	0.2033	-3.00	-0.5468	-0.692
alcohol	1.59	0.4107	0.2825	-2.799	-0.3865	-0.549
+						
carbon	2.00	0.4937	0.3325	-2.699	-0.3065	-0.478
disul-	2.5	0.5911	0.3896	-2.602	-0.2283	-0.409
phide	3.19	0.7203	0.4632	-2.496	-0.1425	-0.339
	4.00	0.8663	0.5439	-2.398	-0.0623	-0.264
	4.78	1.002	0.6173	-2.321	+0.00087	-0.2095
	5.00	1.040	0.6373	-2.301	+0.017	-0.196

Table 8.2a

Values of r.f. conductivity (K'), reduced r.f. conductivity (K'_R) at different reduced temperature (ϵ), fitting equation parameters (θ , A, B_1) and the amplitude ratio A/B_1. Taking r.f. conductivity at critical temperature ($T_c = 14^oC$) $K'_c = 0.678 \times 10^{-10}$ esu.

System	No. of sets	$\epsilon \times 10^3$	$K' \times 10^{10}$ esu	K'_R	θ	A	B_1	A/B_1
		1.6	0.94	0.386				
Nitroben-	1	0.9	0.84	0.239	0.85	59.0	89.58	0.66
zene(50		0.5	0.77	0.136				
percent by		0.0	0.678					
weight)								
+		5.226	1.378	1.032				
n-hexane	2	3.484	1.178	0.737	0.71	31.36	52.69	0.60
(50 per-		1.742	0.978	0.442				
cent by		0.0	0.678					
weight)								
Solution		10.0	1.72	1.537				
	3	8.2	1.62	1.375	0 .70	52.34	-56.32	-0.94
		7.0	1.52	1.242				
		0.0	0.678					

Table 8.2b

Fitted values of reduced temperature (ϵ), reduced conductivity (K'_R) and reduced conductivity with back ground term subtracted ($K'_R - K'_{bkg}$).

Fitted equation is $K'_R = 31.36 \ \epsilon^{0.71} + 52.69\epsilon$.

System	ϵ x10^3	K'_R	$K'_R - K'_{bkg}$	Log ϵ	Log K'_R	log ($K'_R - K'_{bkg}$)
	1.00	0.2852	0.2325	-3.00	-0.545	-0.634
	1.742	0.4365	0.3448	-2.759	-0.360	-0.462
Nitro-benzene	2.0	0.4857	0.3803	-2.699	-0.314	-0.420
+	2.5	0.5773	0.4456	-2.602	-0.239	-0.351
	3.0	0.6652	0.5071	-2.523	-0.177	-0.295
n-hexane	3.484	0.7475	0.5639	-2.458	-0.126	-0.249
	4.0	0.8328	0.6221	-2.398	-0.079	-0.206
	4.5	0.9134	0.6763	-2.347	-0.039	-0.170
	5.226	1.0274	0.7521	-2.282	+0.012	-0.124
	5.5	1.0697	0.780	-2.260	+0.029	-0.108

Table 8.3a

Values of r.f. conductivity (K'), reduced r.f. conductivity (K'_R) at different reduced temperature (ϵ), fitting equation parameters (θ , A, B_1) and the amplitude ratio A/B_1. Taking r.f. conductivity at critical temperature (T_c = 31°C) K'_c = 3.0 x 10^{-12} esu.

System	No. of sets.	$\epsilon \times 10^3$	$K' \times 10^{12}$ esu	K'_R	θ	A	B_1	A/B_1
		1.1	3.95	0.317				
Aniline	1	0.6	3.55	0.183	0.87	490.28	-950.1	-0.52
(46 percent		0.3	3.30	0.10				
by weight)		0.0	3.0					
+		4.93	6.11	1.037				
Cyclohe-	2	3.29	5.33	0.777	0.71	35.60	45.53	0.78
xane(54 per-		1.64	4.333	0.444				
cent by weight)		0.0	3.0					
Solution		10.4	7.895	1.632				
	3	7.9	7.15	1.383	0.67	50.07	-71.23	-0.70
		6.5	6.70	1.233				
		0.0	3.0					

Table 8.3b

Fitted values of reduced temperature (ϵ), reduced conductivity (K'_R) and reduced conductivity with background term subtracted ($K'_R-K'_{bkg}$). Fitted equation is $K'_R = 35.6\,\epsilon^{.71} + 45.53\,\epsilon$.

System	$\epsilon \times 10^3$	K'_R	$K'_R-K'_{bkg}$	$\log \epsilon$	$\log K'_R$	$\log(K'_R-K'_{bkg})$
	1.0	0.3094	0.2639	-3.0	-0.509	-0.579
	1.64	0.4496	0.3749	-2.785	-0.347	-0.426
Aniline + cyclo-hexane	2.0	0.5228	0.4317	-2.699	-0.282	-0.365
	2.5	0.6196	0.5058	-2.602	-0.208	-0.296
	3.29	0.7645	0.6147	-2.483	-0.117	-0.211
	4.0	0.8883	0.7062	-2.398	-0.051	-0.151
	4.93	1.0436	0.8192	-2.307	+0.0185	-0.087

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