

The dielectric constant of the binary liquid system *n*. heptane + methanol near its critical temperature

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Abstract. The electrical capacitance of the binary liquid mixture *n*. heptane + methanol at its critical composition is studied in both one-phase and two-phase regions. The two-phase capacitance data are used with the known functional forms for the order parameter and the diameter to obtain T_c and c_c with greater precision. This helps in reducing the number of unknown parameters in the functional form for the one-phase capacitance. The data show consistency with an alpha (α) exponent for dc/dt in the one phase region.

Keywords. Critical phenomena; binary liquids; critical exponents; critical temperature; critical capacitance.

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1. Introduction

The dielectric constant of binary liquid mixtures is expected to show a singular behaviour near the critical solution temperature of phase separation (Mistura 1973; Stell and Hove 1974; Goulian *et al* 1979; Sengers *et al* 1980). The dielectric constant behaviour at the critical point is expected to behave as

$$\rho^{-1}\varepsilon = \rho_c^{-1}\varepsilon_c(1 + \varepsilon_1 t^{(1-\alpha)} + \varepsilon_2 t + \varepsilon_3 t^{(1-\alpha+\Delta)} + \dots), \quad (1)$$

where ε = dielectric constant of the mixture, ε_c = dielectric constant at the critical temperature T_c , $t = (T - T_c)/T_c$, ρ = density of the system, ρ_c = density of the system at the critical temperature, α = specific heat exponent = 0·11 and Δ = Wegner correction term = 0·5. This implies a density anomaly always hidden along with the intrinsic ε anomaly. However the study of the density of a few systems has shown that the density anomaly contribution is small compared to the intrinsic dielectric constant anomaly (Greer and Jacobs 1980; Theon *et al* 1981). In the absence of a density anomaly the functional form is

$$\varepsilon = \varepsilon_c + A(1)t^{(1-\alpha)} + A(2)t + A(3)t^{(1-\alpha+\Delta)}, \quad (2)$$

where $A(1) = \varepsilon_c \varepsilon_1$ and so on.

Experimental studies on the dielectric constant in binary liquids have indeed shown an anomalous behaviour above the background at the critical temperature. The early literature is reviewed by Arkhangelskii and Semencheko (1967). Jacobs and Greer (1981) report a decrease in ε as $t \rightarrow 0$ in the system polystyrene + cyclohexane. Theon

et al (1981) report a similar behaviour in nitroethane + cyclohexane. They found their data to be consistent with a $(1 - \alpha)$ exponent as per the theoretical model. The study of ϵ on cyclohexane + methanol (Shetty *et al* 1983), carbon disulphide + acetonitrile (Gunasekaran *et al* 1985) and *n*. heptane + methanol (Jyothi *et al* 1984) shows an increase in ϵ as $t \rightarrow 0$. Similar increase in ϵ is seen by Cohn and Greer (1986) in the system perfluromethyl cyclohexane + carbon tetrachloride. They report a $(1 - \alpha)$ exponent for ϵ .

The increase or decrease of ϵ as $t \rightarrow 0$ depends on the sign of the coefficient of the singular term in the functional form for ϵ . This coefficient is proportional to $-dT_c/dE^2$ where E is the electric field (Sengers *et al* 1980). As $t \rightarrow 0$, since $t^{(1-\alpha)} \rightarrow 0$, a negative (positive) coefficient implies an increase (decrease) in ϵ as $t \rightarrow 0$. So systems with positive (negative) dT_c/dE^2 will show increasing (decreasing) ϵ as $t \rightarrow 0$. This is consistent with the ϵ behaviour seen in the systems so far studied (Cohn and Greer 1986).

We have measured the capacitance c of the system *n*. heptane + methanol at its critical composition X_c . In our earlier study of c on the same system, c was studied only in the one-phase region and the data were fitted into a functional form of the type

$$(c - c_c)/c_c = At + B_1 t^\theta + B_2 t^{(\theta+\Delta)} + B_3 t^{(\theta+2\Delta)},$$

(c_c is the critical capacitance) where except for T_c all other parameters were unknown and were expected to come out from the numerical analysis. A large number of unknowns in the numerical analysis cause correlations among the parameters and thus give a large uncertainty in θ . So the θ value obtained showed a range dependence.

In the present study, we attempted to fix as many parameters as possible in the functional form for c . For this we measured capacitance in the two-phase region. T_c and c_c are obtained in two independent ways (Ranjan *et al* 1986): (i) As the system studied are the mixtures of polar and nonpolar liquids, if capacitance is measured in two pairs of electrodes placed on either sides of the centre of the cell, the behaviour seen in the two pairs of plates will be of opposite trend when the liquid mixture phase separates. The temperature and the corresponding value of capacitance at which two pairs of electrodes show opposite trend gives the experimental values of T_c and c_c respectively. (ii) The known functional form for the order parameter and the diameter within a small ($T_c - T$) in the two-phase region are used to locate T_c and c_c respectively. This is discussed again later. The analysis of the resistance data in one phase shows a $(1 - \alpha)$ exponent. From Kumar and Jayannavar (1981) we expect a similar behaviour in capacitance c too.

2. Experiments and observations

The capacitance of *n*. heptane + methanol is studied at 20 kHz. The cell used for the study has two pairs of electrodes to facilitate the two-phase study (Gopal *et al* 1976). The capacitance is measured using a double ratio transformer bridge with a lock-in amplifier as the detector. The bridge is able to detect changes in capacitance ≈ 0.005 pF in 20 pF. The details of the bridge and its importance are discussed by Gunasekaran *et al* (1981). The temperature stability is ± 0.001 K. The temperature controller and experimental set-up are discussed in an earlier work (Gunasekaran 1983).

Though the capacitance is measured in both the electrode pairs, when the data were plotted, the data from the lower electrode pair show large scatter compared

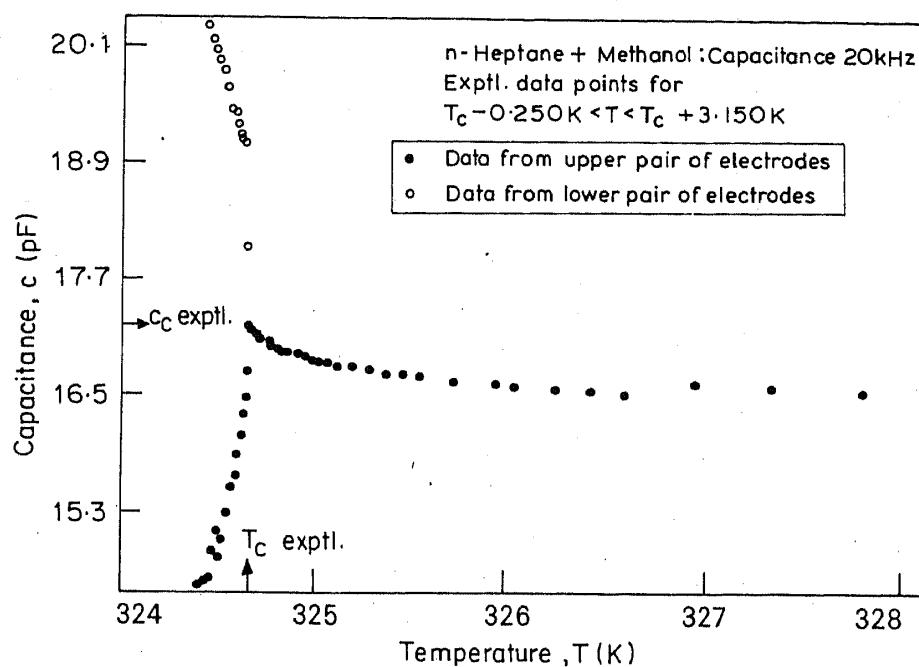


Figure 1. Experimental data points in the temperature range ($T_c - 0.250$) K $< T <$ ($T_c + 3.150$) K for the system *n*.heptane + methanol.

to that from the upper electrode pair. This is suspected to be due to some error in cell connections and is discussed later. In this system the lower electrode pair is dipped in the heavier methanol-rich phase and hence shows higher capacitance than the upper electrode pair values. Our analysis is restricted to the temperature range ($T_c - 0.200$) K $< T <$ ($T_c - 0.009$) K in the two-phase region and ($T_c + 0.009$) K $< T <$ ($T_c + 0.200$) K in the one-phase region. Within this close to T_c region the functional forms are well known (Ranjan *et al* 1986). The region within ± 9 mK around T_c is excluded, since the perturbations due to gravity are serious in this region.

The reported values of T_c and X_c for this sample are $T_c = 324.9 \pm 0.1$ K, $X_c = 61.9$ mole % ± 0.1 % of methanol by Chernova (1965) and $T_c = 324.871$ K, $X_c = 61.35$ mole % of methanol by Viswanathan *et al* (1973). Figure 1 is the values of capacitances as a function of temperature and figure 2 is the experimental data set used for analysis in the one-phase and the two-phase regions.

3. Data analysis

3.1 Analysis of the two-phase data

In the two-phase region, the capacitance difference as measured by the two pairs of electrodes $|c_u - c_L|$ (where $c_u = c$ from the upper pair, $c_L = c$ from the lower electrode pair) is approximated to be proportional to the concentration difference of any one of the components $|X_u - X_L|$ for $|T - T_c|$ small. Since the critical exponent for $|X_u - X_L|$ is β ($\beta = 0.325$) in the two-phase region, $|c_u - c_L|$ can be written as

$$|c_u - c_L| = B(1) (T_c - T)^{0.325}, \quad T < T_c, \quad (3)$$

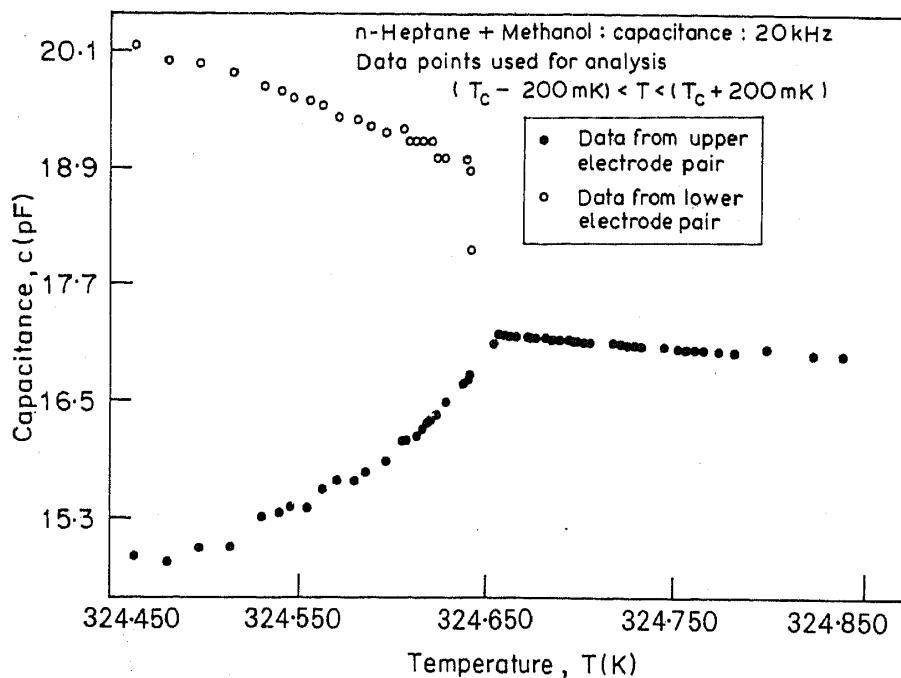


Figure 2. Experimental data points used in analysis in the temperature range ($T_c - 0.200$) K $< T < (T_c + 0.200)$ K close to T_c .

where $B(1)$ and T_c are unknowns. We have varied T_c around the experimental value of T_c ($T_{c\text{exp}} = 324.648$ K) in steps of 0.0002 K each time fixing it in equation (3). We have used Bevington's (1969) nonlinear least square CURFIT program for data analysis. χ^2_v is calculated and that value of T_c for which χ^2_v is the minimum is taken as the critical temperature T_c . This gives for (3),

$$B(1) = 8.902 \pm 0.022, \quad T_c = 324.6472 \pm 0.0007 \quad \text{and} \quad \chi^2_v = 1.72.$$

When all the parameters are floated, the convergence is hard and so we had to fix one of the parameters. Also χ^2_v is obtained by allowing 0.002 K uncertainty in temperature and 0.02 pF uncertainty in $|c_u - c_L|$. Figure 3 gives the fitted curve according to equation (3) and the experimental points. The computed best fit $T_c = 324.647$ K agrees with the directly measured value within the experimental error.

We have used the value of T_c obtained from the order parameter analysis in the diameter analysis in the two-phase region:

$$|c_u + c_L|/2 = D(1) + D(2)|T_c - T| + D(3)|T_c - T|^{1-\alpha} + D(4)|T_c - T|^{2\beta} \quad (4)$$

$$T < T_c.$$

When (4) is analyzed without the linear term, the value of $D(1)$ which is c_c , the critical capacitance, is found to be lower than the capacitance values even at 100 mK above T_c which is meaningless. We have traced the problem to the scatter and errors in the c_L values as mentioned earlier. So we eliminated c_L using equations (3) and (4) so that

$$c_u = D(1) + D(2)(T_c - T) + D(3)(T_c - T)^{1-\alpha} + D(4)(T_c - T)^{2\beta} + D(5)(T_c - T)^\beta. \quad (5)$$

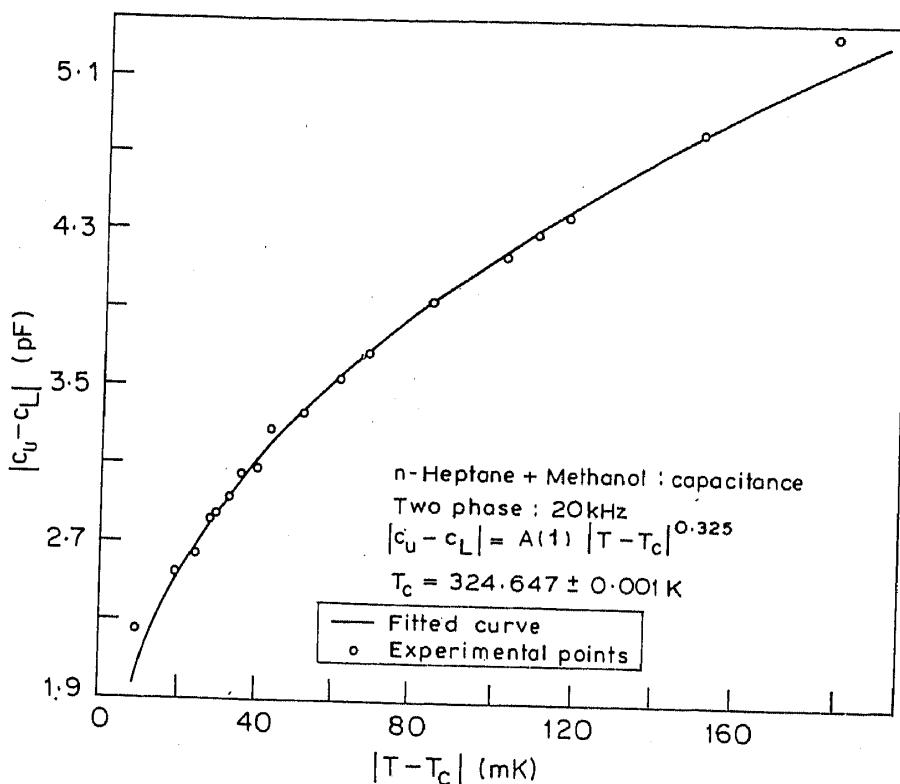


Figure 3. Order parameter $|c_u - c_L|$ as a function of $|T - T_c|$ in the two-phase region with $T_c = 324.647 \text{ K}$ for $(T_c - 0.200) \text{ K} < T < (T_c - 0.008) \text{ K}$. c_u : capacitance from the upper electrode pair. For this system this is the *n*. heptane rich phase in the two-phase region. c_L : capacitance from the lower electrode pair, here methanol-rich phase. Solid line gives the fitted curve calculated from equation (3) and circles are the experimental points.

The number of unknowns is still too many in (5) to give reasonable parameter values and standard deviations. We first set $D(2) = 0$ being the background term valid far away from T_c . Next we studied the effect of dropping one term at a time on the values of χ^2_v and the standard deviations. The $t^{2\beta}$ term is found to give standard deviations $\approx 50\%$ of the parameters. So this term is not justifiable. Thus we are left with

$$c_u = D(1) + D(3) |T - T_c|^{(1-\alpha)} + D(5) |T - T_c|^\beta. \quad (6)$$

$D(1)$ is varied in steps of 0.01 pF around the experimentally observed value 17.2398 pF ($= 17.24 \text{ pF}$). Goodness of fit is closest to 1 when $D(1) = c_c = 17.24$; the fitted parameters are $D(3) = -5.23 + 0.27$, $D(5) = -2.40 \pm 0.07$ and $\chi^2_v = 0.98$. The χ^2_v is not significantly different for $D(1) = c_c = 17.23 \text{ pF}$ and 17.25 pF and so we take $c_c = 17.24 \pm 0.01$. Figure 4 gives the fitted curve and experimental points.

3.2 Analysis of the one-phase data

In the one-phase region we have used the data set in the temperature range 9 mK to 200 mK above T_c . Here an uncertainty of 0.007 pF in c and 0.001 K in temperature is allowed. The exponent $(1 - \alpha)$ in equation (2) is floated in our analysis. That is, the capacitance is fitted to the functional form

$$c_u = c_c + C(1) (T - T_c)^{C(2)} + C(3) (T - T_c)^{(C(2)+0.5)}, \quad T > T_c. \quad (7)$$

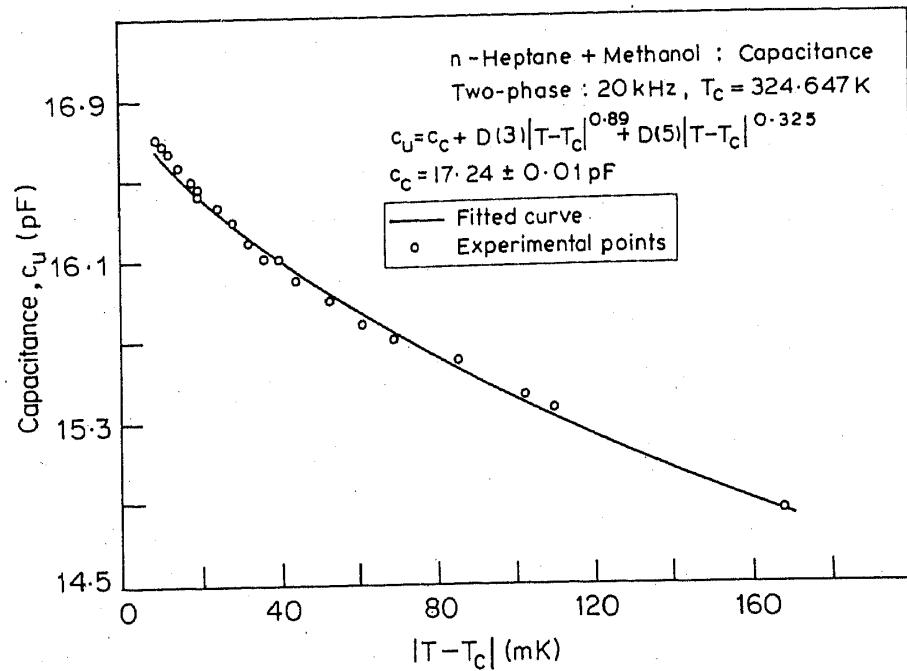


Figure 4. To get c_c , critical capacitance from the two-phase diameter. (See text). c_u as a function of $|T - T_c|$ in the two-phase for $T_c = 324.647$ K in the temperature range ($T_c - 0.200$ K $< T < (T_c + 0.008)$ K). Solid line is the fitted curve calculated from equation (6) and circles are the experimental points. c_c obtained is 17.24 ± 0.01 pF.

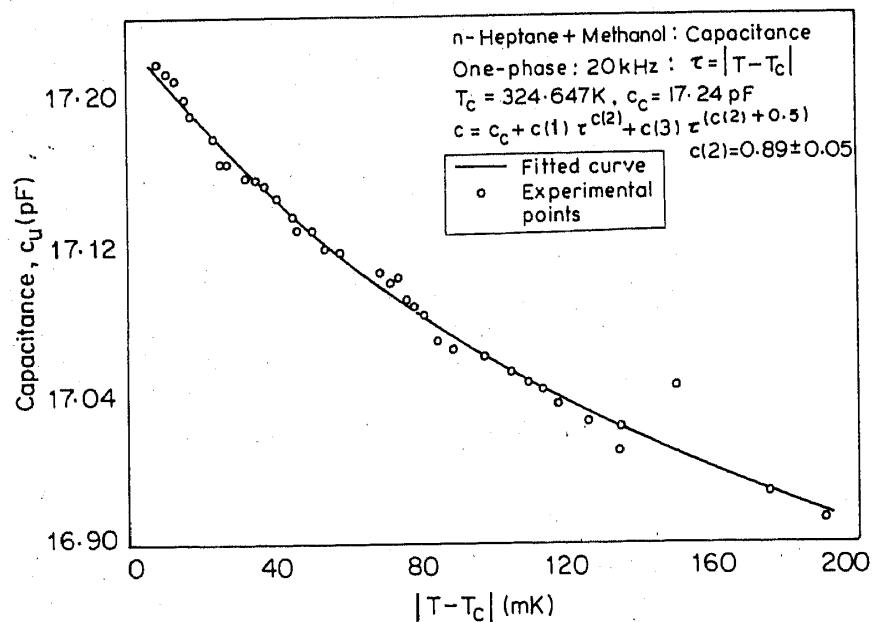


Figure 5. c_u as a function of $|T - T_c|$ in the one-phase region for $T_c = 324.647$ K and $c_c = 17.24$ pF (obtained from two-phase analysis) in the temperature range ($T_c + 0.008$ K $< T < (T_c + 0.200)$ K). Solid line is the theoretical curve calculated from equation (5) and circles are experimental points. Exponent value obtained is $C(2) = 0.89 \pm 0.05$.

Since the data cover only 200 mK above T_c the linear term in equation (2) is not used. For $T_c = 324.647$ K and $c_c = 17.24$ pF the best fit parameters are $C(1) = -2.18 \pm 0.41$, $C(2) = 0.89 \pm 0.05$, $C(3) = 2.36 \pm 0.76$ and $\chi^2_v = 1.17$. The value $C(2) = 0.89 \pm 0.05$ corresponds to the exponent value. This supports the theoretically predicted $(1 - \alpha) = 0.89$ exponent for the dielectric constant of binary liquid system. The two-phase analysis gives c_c values ranging from 17.23 pF to 17.25 pF. The corresponding exponent values range from 1.01 ± 0.05 to 0.80 ± 0.05 . One thus finds that the exponent value is fairly sensitive to the precise knowledge of c_c . The elimination of the data within ± 9 mK around T_c as the gravity affected region makes the c_c determination uncertain from mere data analysis—it is however interesting that the experimental T_c and c_c are recovered in the data analysis which is indicative of self-consistency of the various equations used in the critical region. Therefore measurements of higher accuracy in a system with a small gravity-affected region would be quite interesting. Such measurements are planned in the binary liquid system acetonitrile + cyclohexane which has a low gravity affected region.

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