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

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MS received 11 June 1986; revised 8 January 1987

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 $c_e$ 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 ($\alpha$) exponent for $dc/dt$ in the one phase region.

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

PACS No. 64.70

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 Hoye 1974; Goulau et al 1979; Sengers et al 1980). The dielectric constant
behaviour at the critical point is expected to behave as

$$
\rho^{-1} \varepsilon = \rho_e^{-1} \varepsilon_e (1 + \varepsilon_1 t^{(1-\alpha)} + \varepsilon_2 t + \varepsilon_3 t^{(1-\alpha+\Delta)} + \ldots),
$$

(1)

where $\varepsilon$ = the dielectric constant of the mixture, $\varepsilon_e$ = dielectric constant at the critical
temperature $T_c$, $t = (T - T_c)/T_c$, $\rho$ = density of the system, $\rho_e$ = density of the system at
the critical temperature, $\alpha$ = specific heat exponent $= 0.11$ and $\Delta$ = Wegner correction
term $= 0.5$. This implies a density anomaly always hidden along with the intrinsic $\varepsilon$
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

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

(2)

where $A(1) = \varepsilon_e \varepsilon_1$ 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 Arkhangel'skii and Semencheko (1967). Jacobs and Greer
(1981) report a decrease in $\varepsilon$ as $t \to 0$ 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 $\varepsilon$
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 $\varepsilon$ as $t \to 0$. Similar increase in $\varepsilon$ is seen by Cohn and Greer (1986) in the
system perfluoromethyl cyclohexane + carbon tetrachloride. They report a $(1 - \alpha)$
exponent for $\varepsilon$.

The increase or decrease of $\varepsilon$ as $t \to 0$ depends on the sign of the coefficient of the
singular term in the functional form for $\varepsilon$. This coefficient is proportional to $-\frac{dT_c}{dE^2}$
where $E$ is the electric field (Sengers et al 1980). As $t \to 0$, since $t(1-\alpha) \to 0$, a negative
(positive) coefficient implies an increase (decrease) in $\varepsilon$ as $t \to 0$. So systems with positive
(negative) $\frac{dT_c}{dE^2}$ will show increasing (decreasing) $\varepsilon$ as $t \to 0$. This is consistent with
the $\varepsilon$ 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 $\theta$. So the $\theta$ 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 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 $\approx 0.005$ pF
in 20 pF. The details of the bridge and its importance are discussed by Gunasekaran
et al (1981). The temperature stability is $\pm 0.001$ 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
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\% \(\pm 0.1\)\% 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 \(\beta (\beta = 0.325)\) in the two-phase region, \(c_u - c_L\) can be written as

\[
|c_u - c_L| = \beta (1 - T) = -0.325, \quad T < T_c, \tag{3}
\]

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

\[
|c_u - c_L| = -0.325, \quad T < T_c,
\]

\[
|c_u - c_L| = B(1 - T)^{0.325}, \quad T < T_c,
\]
where \( B(1) \) and \( T_c \) are unknowns. We have varied \( T_c \) around the experimental value of \( T_c \) (\( T_{c\text{exp}} = 324.648 \text{ K} \)) 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. \( \chi^2 \) is calculated and that value of \( T_c \) for which \( \chi^2 \) is the minimum is taken as the critical temperature \( T_c \). This gives for (3),

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

When all the parameters are floated, the convergence is hard and so we had to fix one of the parameters. Also \( \chi^2 \) 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 \( T_c = 324.647 \text{ K} \) 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:

\[
|c_u + c_L|/2 = D(1) + D(2)|T_c - T| + D(3)|T_c - T|^{1-z} + D(4)|T_c - T|^{2\beta} \\
T < T_c.
\]

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

\[
c_u = D(1) + D(2)(T_c - T) + D(3)(T_c - T)^{1-z} \\
+ D(4)(T_c - T)^{2\beta} + D(5)(T_c - T)\beta.
\]
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 $\chi_s^2$ 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

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

(6)

$D(1)$ is varied in steps of $0.01 \text{ pF}$ around the experimentally observed value $17.2398 \text{ pF}$ ($=17.24 \text{ pF}$). Goodness of fit is closest to 1 when $D(1) = c_e = 17.24$; the fitted parameters are $D(3) = -5.23 + 0.27$, $D(5) = -2.40 \pm 0.07$ and $\chi_s^2 = 0.98$. The $\chi_s^2$ is not significantly different for $D(1) = c_e = 17.23 \text{ pF}$ and $17.25 \text{ pF}$ and so we take $c_e = 17.24 \pm 0.01$. 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 $0.007 \text{ pF}$ in $c$ and $0.001 \text{ K}$ in temperature is allowed. The exponent $(1-a)$ in equation (2) is floated in our analysis. That is, the capacitance is fitted to the functional form

$$c_u = c_e + C(1) (T - T_o)^{c(2)} + C(3) (T - T_e)^{c(2)+0.5}, \quad T > T_c.$$  

(7)
Figure 4. To get $c_c$, critical capacitance from the two-phase diameter. (See text). $c_c$ 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 $17.24 \pm 0.01$ pF.

Figure 5. $c_c$ 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 $C(2) = 0.89 \pm 0.05$. 
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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 \( \chi^2 = 1.17 \). 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 \pm 0.05 to 0.80 \pm 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 \( \pm 9 \) 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.

Acknowledgements

The authors thank the DST and IISc-ISRO project for financial assistance in carrying out the work. They are grateful to CSIR for providing a fellowship to one of the authors (YJ). Finally the suggestions from the referees are gratefully acknowledged.

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