The Electrical Resistance of the Lower Consolute System 2,6-Lutidine–Water

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Abstract
The one-phase electrical resistance of the lower consolute system 2,6-lutidine–water has been measured in the reduced temperature range $2 \times 10^{-6} < \varepsilon < 0.11$. Particular attention has been given to the drift in resistance and separation temperature caused by the leaching of ions during long contact with glass surfaces. When correction is made for this effect, no contribution to the electrical resistance due to critical fluctuations is observed. The effect of the leaching of ions has not been taken into account in previously published studies which have observed, and attempted to characterize, a weak divergence in the electrical resistance of critical binary mixtures.

1. Introduction

It is well known that anomalies occur in a variety of both equilibrium and non-equilibrium properties of a system close to a critical point (Sengers 1982). The static scaling hypothesis has proved successful in providing a unified approach to the behaviour of thermodynamic properties in the critical region (Stanley 1971). For small values of the reduced temperature, defined by $\varepsilon = |(T - T_c)/T_c|$, it is postulated that for a generalized homogeneous function $f(\varepsilon)$ there exists the limit

$$
\lambda = \lim_{\varepsilon \to 0} \frac{\ln f(\varepsilon)}{\ln \varepsilon}. \tag{1}
$$

Here $\lambda$ is the critical exponent or index associated with the function $f(\varepsilon)$ and $T_c$ is the critical temperature. Furthermore, $\xi$, the correlation length of the order-parameter fluctuations is envisaged as diverging according to the power law

$$
\xi \propto \varepsilon^{-\nu}. \tag{2}
$$

A similar approach to critical transport properties is based on the dynamic scaling model, where the correlation length

$$
\xi = f(\varepsilon, k) \tag{3}
$$

depends on both the reduced temperature (or equivalent field variable) and the wave vector $k$. The theory of dynamic critical phenomena was recently reviewed by Hohenberg and Halperin (1977). They concluded that the theory has been tested.
successfully to the 10–15% level in pure fluids and binary fluid mixtures, but that there are important quantitative discrepancies between theory and experiment in superfluid helium. Considerable theoretical and experimental interest has been displayed in the temperature dependence of the electrical conductivity at solid state critical points (ferromagnetic, antiferromagnetic or order–disorder transitions). However, it is only in the last 15 years that any attention has been given to the ionic conductivity of binary fluid mixtures near their consolute points.

Gammell and Angell (1972, 1974) made the first study of electrical conductivity in a critical binary fluid mixture. They found no anomalous changes in the isobutyric acid–water system at 0·047 K above the separation temperature. However, precise work on the same system by Stein and Allen (1972) indicated that the temperature derivative of the resistance was strongly divergent. This anomaly was interpreted in terms of a proton hopping model which yielded

\[
\frac{R_c - R}{R_c} \approx A \varepsilon^{1-\alpha} + B \varepsilon,
\]

where \( R_c \) is the experimentally determined critical resistance, \( \alpha \) is the specific heat critical exponent, and \( A \) and \( B \) are constants (Jasnow et al. 1974). Critical transport coefficients are frequently described by expressions such as equation (4), the first term on the RHS representing the contribution from critical fluctuations and the second term the ideal or background contribution (Sengers 1972). Close to the critical point, \( \varepsilon < 2 \times 10^{-5} \), the proton hopping model proved inadequate, and this was attributed to the onset of gravitational effects (Jasnow et al. 1974).

The resistance of isobutyric acid–water, phenol–water and phenol–water doped with KCl has been studied in the reduced temperature range \( 10^{-5} < \varepsilon < 10^{-2} \) by Shaw and Goldburg (1976). These data for the reduced conductivity, defined by \( \sigma_r = (\sigma - \sigma_c)/\sigma_c \), were fitted to an equation of the form

\[
\sigma_r = A_1 \varepsilon^\theta + B_1 \varepsilon + B_2 \varepsilon^2.
\]

Since \( \sigma = 1/R \), when \( \varepsilon \) is small equation (5) differs from (4) only in that a term in \( \varepsilon^2 \) is added to the background contribution and the constants \( A_1, B_1, \) and \( B_2 \) are modified by a factor \( R_c/R \). The value obtained for the exponent \( \theta \) was 0·70 \( \pm \) 0·05, closely approximating \( 2\beta \), where \( \beta \) is the exponent that characterizes the shape of the coexistence curve. Shaw and Goldburg (1976) derived an exponent of \( 2\beta \) from percolation theory, an effective medium approximation, which had previously been applied to metal–semiconductor transitions (Kirkpatrick 1973).

The electrical resistivity of six nonaqueous binary liquid systems in the critical region was reported in a series of papers by Gopal and coworkers (Gopal et al. 1977; Ramakrishnan et al. 1978; Kumar et al. 1979). They interpreted their results in terms of the scattering of conduction ions by concentration fluctuations, denoting the exponent in equation (4) by \( 1 - b \) as distinct from \( 1 - \alpha \) which would imply dependence on the critical heat exponent. Values of \( b \) reported by these workers ranged from 0·32 to 0·50. Their initial conclusion that \( dR/dT \) diverged with \( \varepsilon^{-b} \), where \( b \approx \beta \) (Gopal et al. 1977), was subsequently modified to the suggestion that the anomaly in \( dR/dT \) was not universal in character in binary liquid systems (Kumar et al. 1979).

We report here measurements of electrical resistance of a critical composition of 2,6-lutidine (i.e. 2,6-dimethyl pyridine)–water in the single-phase region from
33 K below the lower consolute point up to $T_c$. This work, which was carried out in conjunction with a study of shear viscosity (Collings and Bajenov, to be published), examines the proposal that electrical resistance measurements provide an effective estimate of the background or ideal viscous behaviour of a critical fluid (Gammell and Angell 1972). We discuss the advantages of the experimental method we have used, the consequences of leaching of ions and examine the difficulties of deriving critical exponents from resistance measurements in fluids.

2. Experimental Details

The conductivity cell was located in the bottom reservoir of a sealable suspended-level viscometer, which has been described elsewhere (Collings and Bajenov 1983). Platinum electrodes, 10 mm square and 0.7 mm thick, were welded to 0.7 mm diameter platinum wire and spaced 12 mm apart. As the resistances being studied were larger than $10^4 \Omega$, the electrodes were not blackened. A cell constant of 0.6323 cm$^{-1}$ was determined with 0.01 demal (0.7453 g L$^{-1}$) potassium chloride solution (Robinson and Stokes 1959).

The apparatus is represented schematically in Fig. 1, where the cell is shown connected as the unknown arm of a GR 1615 capacitance bridge. Measurement of the equivalent parallel resistance of the cell was made using a Gertsch FT-19 ratio transformer and a precision 10 k$\Omega$ resistor. The ratio transformer was connected externally across the 'standard' ratio arm of the bridge and used to supply the conductance balance current through the precision resistor. The value of the resistor was known to better than 5 parts in $10^5$, and its temperature coefficient was about 1 in $10^8$ per K. Capacitance balance was made using the internal bridge controls and balance conditions were monitored on a GR 1232A tuned amplifier–null detector. The discrimination in resistance obtained using this bridge system was 2 in $10^6$, and the uncertainty in measured values of resistance is believed to be less than 4 in $10^4$. A frequency of 1030 Hz was employed in this work to avoid any possibility of a 50 Hz beat from mains frequency. At temperatures close to the separation temperature, the resistance of lutidine–water at the critical concentration varies only slightly with frequency at 1 kHz.
All liquids employed in this work were freshly distilled from the highest purity commercial sources. The purity of the distilled 2,6-lutidine was checked by gas–liquid chromatography and was better than 99·9%. Solutions were made up by weighing degassed components, the lutidine–water compositions having an estimated precision of 1 in $10^4$ in mole fraction. The conductivity of the distilled water used in making up these solutions was less than $2 \times 10^{-5} \ \Omega^{-1} \ \text{cm}^{-1}$. The KCl standard solution was made up from Merck Suprapur salt and Bahnstead Nanopure deionized water. The pH measurements were made on a Corning-EEL Model 12 meter.

A detailed description of the temperature control of the system has been given elsewhere (Collings and Bajenov 1983). The cell was thermostated in a 200 L water bath. Bath temperature fluctuations near the critical point were about 0·2 mK; those within the cell were presumed to be smaller. The relative accuracy of the temperature measurements was estimated to be 0·1 mK.

3. Results

**Drift Rates for Lutidine–Water Mixtures**

A steady drift with time was observed in the resistance of lutidine–water mixtures. For example, over a period of 46 days at 33·38°C (within a few mK of the critical temperature), the resistance of a 6·738 mol% lutidine–water mixture decreased by 36·9%, or 0·033% per hour. The temperature at which phase separation occurred fell progressively by 9·1 mK over the same period. The resistance of the 6·738 mol% lutidine–water mixture at a frequency of 1·03 kHz is shown in Fig. 2 as a function of temperature between 1 and 33·4°C. Shear viscosity measurements (A. F. Collings and N. Bajenov, unpublished) were made in conjunction with these resistance measurements, and are plotted by the solid curve in Fig. 2 for comparison. Resistance data close to the critical point, $0·001 < T_c - T < 1·4 \ \text{K}$, are plotted as a function of $\log(T_c - T)$ in Fig. 3.

The resistances plotted in Figs 2 and 3, and $T_c - T$ values in Fig. 3, are not raw data but have been corrected for the drift with time, described as follows.

The decrease in resistance with time at constant temperature indicates an increase in charge carrier concentration. A plot was made of the change in conductance with time, extending over the 46 days of measurement of the 6·738 mol%
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lutidine–water mixture. A polynomial fit of these conductance–time data was used to correct all resistance values in Figs 2 and 3 to a zero-time value.

The critical temperature was observed by two methods. The onset of phase separation was indicated by a sharp increase in resistance. This increase in resistance continued for several hours without meniscus formation becoming apparent, if the temperature exceeded $T_c$ by only a few mK. When separation was complete—for which the time increased greatly as $T \rightarrow T_c^+$—the measured resistance of the two-phase mixture steadied at a few per cent higher than the sub-critical value and with a similar temperature dependence and drift rate. The construction of the viscometer–resistance cell was such that, after phase separation had occurred, the two-phase boundary bisected the platinum electrodes. The measured resistance above $T_c$ was the sum of contributions from each of the two phases and their interface. Individual measurements in each phase were not possible.

![Figure 3. Resistance of 6.738 mol% lutidine–water as a function of log(Tc - T).](image)

The apparent viscosity of the unseparated two-phase mixture fell sharply from the peak value at the critical point. The agreement between the two observations of the critical temperature, namely the increase in resistance and the peak viscosity, was within 1 mK. A linear correction of 0.2 mK per day to allow for the drift in $T_c$ was made to the values of the temperature difference $T_c - T$ in Fig. 3.

Equations (4) and (5) were proposed for the single-phase resistance of upper consolute systems where $R_c > R$ (Jasnow et al. 1974; Shaw and Goldburg 1976). For lutidine–water, a lower consolute system, we have used a form of equation (4):

$$R = R_c(1 + X\epsilon + Y\epsilon^0).$$

In fitting the experimental data to equation (6), the parameters $X$, $Y$ and $\theta$ were strongly correlated. The inclusion of a term in $\epsilon^2$ made a negligible improvement in the quality of fit and virtually no change to the background and exponential contributions. The parameters $X$ and $Y$ were constrained to be positive in a non-linear least-squares fit to equation (6) of the data for $T_c - T < 1.4$ K, which is
shown in Fig. 3 (dashed curve). The r.m.s. deviation of the data from this curve was 0·095% with

\[ R_c = 40·758 \pm 0·012 \text{k}\Omega, \quad \theta = 0·875 \pm 0·687, \]
\[ X = 4·081, \quad Y = 0·237. \]

An equally acceptable fit (solid curve in Fig. 3) was obtained from a third-order polynomial of \( R \) in \( T_c - T \) with \( R_c = 40·760 \text{k}\Omega \) and an r.m.s. deviation of data of 0·10%. Higher order polynomial fits reduced the deviation minimally but were no longer monotonic.

![Fig. 4. Conductivity change against time in aqueous solutions:](image)

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**Table 1. Initial resistance and pH for a series of aqueous solutions (see Fig. 4)**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>Initial resistance (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6·738 mol% lutidine</td>
<td>33·35</td>
<td>9·10·6A</td>
<td>40·76</td>
</tr>
<tr>
<td>6·767 mol% lutidine</td>
<td>28·50</td>
<td>7·2</td>
<td>72·72</td>
</tr>
<tr>
<td>6·769 mol% lutidine</td>
<td>32·50</td>
<td>6·5</td>
<td>19·22</td>
</tr>
<tr>
<td>6·778 mol% lutidine</td>
<td>33·30</td>
<td>6·7</td>
<td>50·21</td>
</tr>
<tr>
<td>Distilled water</td>
<td>30·00</td>
<td>7·0</td>
<td>371·82</td>
</tr>
<tr>
<td>Distilled water</td>
<td>30·00</td>
<td>8·0</td>
<td>275·18</td>
</tr>
<tr>
<td>0·0014 wt% borax</td>
<td>30·00</td>
<td>6·5</td>
<td>60·91</td>
</tr>
<tr>
<td>6·76 wt% phenol</td>
<td>30·00</td>
<td>2·2</td>
<td>78·46</td>
</tr>
<tr>
<td>38·07 wt% isobutyric acid</td>
<td>30·00</td>
<td>6·7</td>
<td>1·066</td>
</tr>
<tr>
<td>38·07 wt% isobutyric acid</td>
<td>30·00</td>
<td>6·7</td>
<td>34·09A</td>
</tr>
<tr>
<td>37·2 wt% isobutyric acid</td>
<td>30·00</td>
<td>6·7</td>
<td>47·19B</td>
</tr>
</tbody>
</table>

\(^{A}\) The pH of this solution was initially 9·0 but rose slowly to 10·6.
\(^{B}\) Resistances measured in a small cell with a constant of 21·37 cm\(^{-1}\).
Drift Rates for other Aqueous Solutions

To confirm that the drift rates we obtained were not peculiar to the lutidine–water system, we studied conductance drift rates for several aqueous solutions. These results are plotted in Fig. 4. The initial resistances and other pertinent data for these solutions are given in Table 1. To obtain an aqueous solution of comparable pH and resistance to critical lutidine–water mixtures, we studied a 0·0014 wt% borax solution. The rate of increase in the conductivity was approximately five times larger in this solution at 30°C than in lutidine–water. A similar rate of increase was found to occur in distilled water at 30°C. The upper consolute point for phenol–water occurs at 65·5°C at a critical concentration of 35 wt% phenol (Shaw and Goldburg 1976). To obtain a one-phase phenol solution at 30°C, it was necessary to reduce the phenol concentration to less than 8 wt% (Washburn 1928). The pH of a 6·76 wt% phenol–water mixture was found to be 6·5 and, as shown in Fig. 4, its rate of increase in conductivity was similar to that observed in lutidine–water mixtures.

An isobutyric acid–water mixture containing 38·1 wt% acid was prepared. The critical concentration and upper consolute point for this system were reported to be 38·0% and 26·2°C respectively (Stein and Allen 1972). The isobutyric acid dissociates strongly, the pH of the mixture being 2·2 and the initial resistance in the viscometer–conductivity cell 1·066 kΩ. The resistance increased by 6·8% in 6 days. There appeared to be an exponential decay of conductivity, consistent with electrode saturation, as might be expected with the much greater conductivity of the isobutyric acid solution. A smaller volume cell, with a much reduced electrode area and greater separation between the electrodes, was constructed. This had a cell constant of 21·37 cm⁻¹. The 38·1 wt% isobutyric acid solution was transferred to this cell, in which its resistance was 34·09 kΩ. The conductivity showed a very slight increase during the first 30 h after transfer and then a steady decrease was observed as shown in Fig. 4. A 37·1 wt% acid solution was made up, and had an initial resistance of 47·19 kΩ at 30°C. The conductivity of this solution showed an increase in the first two days comparable with that of the lutidine solutions. The conductivity then decreased at a similar rate to that of the 38·1 wt% acid solution.

4. Discussion

The value observed initially for the critical temperature of the 6·738 mol% lutidine–water mixture (at its saturated vapour pressure) was 306·548 K, to which an absolute uncertainty of 3 mK is assigned. This agrees well with recently published values at atmospheric pressure of 306·522 K (Gulari et al. 1972), 306·723 K (Gutschick and Pings 1971) and 307·013 K (Stein et al. 1972). Earlier values reported range from 307·08 to 307·21 K (Loven and Rice 1963; Pancirov and Brumberger 1964; Cox and Herington 1956). In Fig. 2, a close parallel between the shear viscosity and the corrected electrical resistance of the critical lutidine–water composition holds to within 5 K of the critical temperature. In the single-phase critical region, the proportionality between resistance and viscosity suggested by the empirical Walden rule breaks down. Since little or no anomaly is observed in the electrical resistance of the critical fluid, its measurement appears to provide a good means of estimating the ideal viscosity.
It is quite clear from our results that, when corrections are applied for the drift in resistance and critical temperature, a third-order polynomial of $R$ in terms of $\varepsilon$ provides as reasonable a fit of the experimental data as a critical exponent representation.

Changes in Conductance

Variation in the conductance drift rates in aqueous solutions is seen in Fig. 4. We interpret these data as follows. While distilled water and borax solution displayed steady monotonic drifts in conductance, complicated adsorption processes undoubtedly occurred for several hours after the other solutions were transferred to the cell. The scale of Fig. 4 does not permit us to show the variability in the conductance change which was most noticeable in the phenol solution where it took 36 h for the eventual pattern to be established. Adamson (1967) and Kipling (1965) have described adsorption and chemisorption processes for phenol, pyridine and isobutyric acid on various substrates, including glass; the behaviour shown in Fig. 4 is consistent with their findings. The length of time required to obtain an equilibrium pH reading in the lutidine and isobutyric acid solutions was further evidence of adsorption processes. That log $\Delta \sigma$ proved linear with respect to $t^1$ in all cases after the first few days suggests that the change in conductance is diffusion controlled. Hunter (1981) has discussed behaviour analogous to this for the zeta potential in various solutions in contact with glass and quartz surfaces. The change in conductance is apparently due to slow transfer of ions from glass to the liquid. In the case of the isobutyric acid solutions, oxonium ions are replaced by less mobile sodium ions from the glass, causing an increase in resistance with time. The other solutions had comparatively few charge carriers, either because of low ion concentration or weak dissociation, and the influx of sodium ions leads to a decrease in resistance.

Changes in Critical Temperature and Resistance

Changes in $T_c$ and $R$ with time have been observed in previous studies; whether adequate allowance was made for these effects in the analyses is unknown. In their investigation of the coexistence curve of the 2,6-lutidine–water system, Loven and Rice (1963) observed changes in the critical temperature of 3–6 mK during the first day of sample preparation, and 1–2 mK thereafter. This effect was attributed to interaction of the solution with the glass tube and magnetic stirrer casing. Stein and Allen (1972) attributed the drift in resistance in the isobutyric acid–water system to the presence of microorganisms in the sample. Following their example, Shaw and Goldburg (1976) elevated the temperature of their resistance cells and components for several days before commencing a run. They reported that this reduced the drift in resistance from 0·03 to 0·003% per hour. We have found that the percentage change in resistance depends on the initial value of the resistance and on the temperature. It is for this reason that the change in conductance rather than a percentage change in resistance is plotted in Fig. 4. We believe that autoclaving a cell and sample reduces the percentage change in resistance because the leaching process has been accelerated and the initial value of the resistance decreased. In their recent study of low frequency conductivity fluctuations in a consolute system, Kim et al. (1980) noted a drift in the critical temperature of 1 mK per day and attributed an effect on the power spectrum of the current flow to leaching from the capillary surface.
It should be recognized that the drift in resistance implies a shift in the separation temperature. The connection has been overlooked in earlier studies, although marked changes in the separation temperature were observed by ‘doping’ critical systems (Gammell and Angell 1972, 1974; Shaw and Goldburg 1976). Shaw and Goldburg (1976) found that ‘doping’ a critical phenol–water mixture with KCl decreased the resistance by a factor of 30 but increased the separation temperature by 1°C. Gammell and Angell (1972, 1974) added 1·16 wt% (0·1 mol L⁻¹) potassium isobutyrate to a critical isobutyric acid–water mixture, decreasing the resistance by an order of magnitude and lowering the separation temperature by approximately 8°C.

Since our results suggest that the leaching phenomenon occurs widely, the question arises of how this effect was overlooked in earlier studies and to what extent is the analysis of the data affected. In their investigations of upper consolute systems, Stein and Allen (1972) and Shaw and Goldburg (1976) reported that their measurements commenced in the one-phase region at large $T - T_c$ and continued with decreasing $T - T_c$ until the critical point and the onset of phase separation were observed. In these circumstances, the drift in resistance would be readily masked by the change in resistance corresponding to the temperature drop, this resistance change being of opposite sign and for most temperature increments much larger.

The effect of leaching was obvious in our lower consolute study because we made repeated runs at decreasing $T_c - T$.

To illustrate the effect of leaching on the data analysis, we consider the data shown in Fig. 3 by solid circles. These 21 resistance measurements were made over a period of 5 days while decreasing $T_c - T$. During this 5 day period, the change in $T_c$ and decrease in resistance due to the increase in charge carrier concentration were estimated to be 0·7 mK and 2·40%, respectively. A fit of these 21 data points to equation (6) produced an r.m.s. deviation of 0·050% with $R_c = 40·759±0·011$ kΩ and $\theta = 0·997±0·437$. A third-order polynomial fit of $R$ in $\varepsilon$ yielded $R_c = 40·760$ kΩ with an r.m.s. deviation of 0·050%. The reduction in the r.m.s. deviation, compared with those reported in the previous section for the full data set, is to be expected, and reflects the self-consistency of corrections to $T_c$ and $R$ made for a relatively short period of time. For $T_c - T < 1·4$ K, not only is an exponential representation of the corrected resistance data unnecessary, but a linear fit more than suffices. When the same 21 points, without correction of the resistances for the drift with time, were fitted to equation (6), the r.m.s. deviation of the data was 0·15% with the exponent $\theta = 0·201±0·101$. Comparison on the basis of the fitted $R_c$ is meaningless. When the appropriate correction is made to the one-phase resistance of the lutidine–water consolute system for the effect of leaching, the value of the exponent derived from fitting of equation (6) changes from 0·2 to 1·0.

If indeed the leaching of ions is responsible for the drift in resistance and critical temperature, the effect will not be unique to water. Rather it will be related to the dielectric constant of the system being studied. The majority of the consolute binary systems that have been investigated have contained at least one component with a relatively high dielectric constant. Alkane–haloalkane systems are an exception. In most of these studies, glass or glass-windowed cells have been employed and presumably a drift in critical temperature has occurred. The worst case would be the study of an aqueous system in a glass cell with a large surface-to-volume ratio, especially where long equilibration times were employed conscientiously. Since
analyses of critical data have invariably been made in terms of $\log|T - T_c|$, where $T_c$ has been assumed constant, the effect of leaching on critical exponent values may be of considerable consequence. This is particularly true where the critical electrical resistance is concerned, since both $R$ and $T_c$ are affected by the diffusion of ions from glass to fluid.

5. Conclusions

Accurate measurements have been made of the electrical resistance in the one-phase region of the lower consolute system 2,6-lutidine–water. The uncertainty in the measured values of resistance is thought to be less than $4 \times 10^{-4}$. It has been shown that the drift in resistance and critical temperature with time is probably caused by the leaching of ions from the surface of the glass conductivity cell. When correction is made for this effect, no contribution to the electrical resistance from critical concentration fluctuations is observed. Previous studies in which a weak divergence in the critical electrical resistance was observed (Stein and Allen 1972; Jasnow et al. 1974; Shaw and Goldburg 1976; Gopal et al. 1977; Ramakrishnan et al. 1978; Kumar et al. 1979) were not corrected for the effect of leaching. The suggestion that electrical resistance measurements provide an effective estimate of the non-critical viscous behaviour of a critical fluid (Gammell and Angell 1972) is supported.

Acknowledgments

The authors thank R. J. Hunter of Sydney University, and colleagues, J. S. Cook and H. K. Welsh, for discussions of this work.

References


Manuscript received 30 May 1983, accepted 31 July 1984