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# Chemical reactions near critical points: The dissociation of weak acids

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We have reanalyzed published data on the conductance as a function of temperature near the liquid-liquid critical points of isobutyric acid + water [A. Stein and G. F. Allen, J. Chem. Phys. **59**, 6097 (1973)] and of phenol + water [C.-H. Shaw and W. I. Goldburg, J. Chem. Phys. **65**, 4906 (1976)]. The aim was to test whether the anomalous decrease in the conductance near the critical point could be ascribed to a critical anomaly in the extent of acid dissociation and/or in the rate of proton transfer. In this new analysis, background contributions due to the normal temperature dependence of the dissociation constant and due to confluent critical singularities are given consideration. We find that the leading critical anomaly in the conductance is characterized by a critical exponent $1-\alpha$, where $\alpha$ is the exponent associated with the specific heat at constant pressure and composition. The exponent $1-\alpha$ is expected for an anomaly in the extent of the dissociation reaction and also for an anomaly in the proton-transfer rate.

## I. INTRODUCTION

Knowing that thermodynamic[1,2] and transport properties[3] behave anomalously near fluid critical points, we may ask how these anomalies affect the rates and extents of chemical reactions that occur in fluids near critical points. Recently several different theoretical arguments have been advanced about critical anomalies in reaction rates[4,5] and equilibria.[6–9] While some qualitative experiments suggest that such critical anomalies may exist,[10–14] no quantitative experimental evidence has been previously presented.

We consider here the particular case of the dissociation of a weak acid in water near an acid-water liquid-liquid critical point:

$$\mathrm{H}A+\mathrm{H_2O}\rightleftarrows A^-+\mathrm{H_3O^+}\ .$$

The electrical conductivity of such a system is proportional to the number of ionic species present, which is proportional to the extent of the acid-dissociation reaction. The conductivity is also proportional to the rate at which the ionic species move, which, for aqueous weak acids, is the rate of the proton-transfer reaction. Thus anomalies in the rate or extent of acid dissociation will be reflected in the behavior of the conductivity.

Anomalous decreases in the conductivities as functions of temperature near the acid-water liquid-liquid critical points have been reported for the systems isobutyric acid + water[15,16] and phenol + water[16] and also for one base-water system, triethylamine + water.[17] No such conductivity anomaly was seen in a study of the base-water system 2,6-lutidine + water.[18] The conductivities (presumably due to impurities) in a number of critical liquid systems which are not acid or base systems have also been studied.[19] We will consider here only the acid systems, since no data were published for triethylamine + water and since the mechanism for the conductivity in a system not acidic or basic will be different.

A number of explanations can be offered for the critical anomaly in the conductivity of an acid-water system.

(1) Stein and Allen[15] suggested that the anomaly is due mainly to viscous drag on the acid anion and should therefore have a temperature dependence which is the inverse of that of the viscosity. If we ignore analytic background terms, the leading anomalous term for such a mechanism is expected to be

$$\sigma\sim\frac{1}{\eta}=t^{\nu z_\eta}=t^{0.031}\ , \tag{1}$$

where $\sigma$ is the electrical conductivity, $\eta$ is the viscosity, $t$ is the reduced temperature $(T-T_c)/T_c$, $T_c$ is the critical temperature, $\nu$ (=0.063) is the critical exponent for the correlation length[1,2,20] and $z_\eta$ (=0.05) is a critical exponent for the viscosity.[3]

(2) Jasnow, Goldburg, and Semura[21] attributed the anomaly in the conductivity to an anomaly in the proton-transfer rate. Following Fisher and Langer,[22] they argued that near the critical point the proton-transfer rate should have the temperature dependence of the nearest-neighbor correlation function:

$$\sigma\sim t^{1-\alpha}=t^{0.89}\ , \tag{2}$$

where $\alpha$ (=0.11) is the critical exponent for the heavy capacity at constant pressure and composition.[2,20]

(3) Shaw and Goldburg[16] introduced a percolation model for the conductivity and predicted a critical contribution of the following form:

$$\sigma\sim t^{2\beta}=t^{0.65}\ , \tag{3}$$

where $\beta$ (=0.325) is the critical exponent describing the coexistence curve.[1,2,20]

(4) More recently, Gitterman[7] has suggested that the anomalous conductivity is due to an anomaly in the *extent* of the acid dissociation, from which he predicts a critical contribution:

$$\sigma\sim x\sim t^{1/\delta}=t^{0.207}\ , \tag{4}$$

where $x$ is the concentration of protons and $\delta$ ($=4.82$) is the critical exponent for the critical isotherm.[1,2,20]

(5) Wheeler[9] disputes Gitterman's analysis of the anomaly in the extent of dissociation, asserting that only a weak anomaly can appear:

$$\sigma \sim x \sim t^{1-\alpha} = t^{0.89} . \tag{5}$$

We mention here for completeness the consideration given by Procaccia and Gitterman[4] and Milner and Martin[5] the critical anomalies in the rates of relaxation of reacting systems after they have been perturbed from chemical equilibrium. Since chemical equilibrium is not disturbed in the conductance experiments which we analyze, we do not expect these approaches to be applicable.

The published analyses of the measurements of the conductances of acid-water critical mixtures have been ambiguous because of the extreme sensitivity of the fits[15,16,21] to the fitting procedure. In these previous analyses the critical exponent for $\sigma$ was left free, analytic background terms were added, and all the coefficients were left free. The critical exponent was strongly correlated to all the amplitudes and the choice of background terms was crucial.

We have reexamined the conductance data for isobutyric acid + water[15] and for phenol + water.[16] In our analysis we (1) fix the exponent at the various possible theoretical values given in Eqs. (1)—(5), (2) correct for the normal temperature dependence of the acid dissociation constant, and (3) use the renormalization-group form for corrections to the leading anomalous term.[1,2,23] We find that the evidence overwhelmingly favors the exponent $1-\alpha$ for the conductance. There are then two possible mechanisms for the anomaly. The exponent $1-\alpha$ is predicted both by Jasnow *et al.*[21] for an anomalous proton-transfer rate and by Wheeler[9] for an anomalous extent of dissociation.

## II. DATA ANALYSIS

### A. Computer methods

All least-squares fits were done on a Commodore 8032 microcomputer (8-bit word, 32-kbyte memory, where 1 kbyte$\equiv$1024$\times$8 binary digits) using a weighted, nonlinear least-squares-fitting program written in BASIC. Experimental uncertainties in the conductivity and in the temperature were used to weight the data points by the usual methods for the propagation of errors.[24] Goodness of fit is expressed in terms of the reduced chi squared $\chi_\nu^2$ which should be near unity for a "good" fit to the data.[24]

### B. Background terms

In Eqs. (1)—(5) we have given predictions for that term in $\sigma$ which is most anomalous as the critical point is neared. In order to extract from the experimental data that part of the conductance which constitutes the leading critical anomaly, we must pay careful attention to the background behavior of the conductance. We consider explicitly three background contributions: (1) the background temperature dependence of the acid-dissociation constant, (2) the background temperature dependence of the mass density, and (3) the confluent, less-singular, critical contributions. We also comment on gravity effects.

#### *1. Temperature dependence of the acid-dissociation constant, $K_a$*

The dissociation constant of a weak acid will vary with temperature and, in fact, have a maximum at some temperature.[25] Thus the concentration of conducting species will have a normal, background temperature dependence which can significantly affect our analysis of conductance data.

The dissociation constant $K_a(T)$ for isobutyric acid + water is plotted in Fig. 1(a), from the data of Everett *et al.*[26] The critical temperature $T_c$ for this mixture is about 26°C. Note the change in slope of $K_a(T)$ near $T_c$. We have fitted the following function to these data:

$$\log_{10} K_a = \frac{A_1}{T} + A_2 \log_{10} T + A_3 , \tag{6}$$

where $K_a$ is in moles per l, $T$ is in K, $A_1 = -2106 \pm 42$, $A_2 = -17.6 \pm 0.3$, and $A_3 = 45.8 \pm 0.9$. (Uncertainties are given as one standard deviation.)

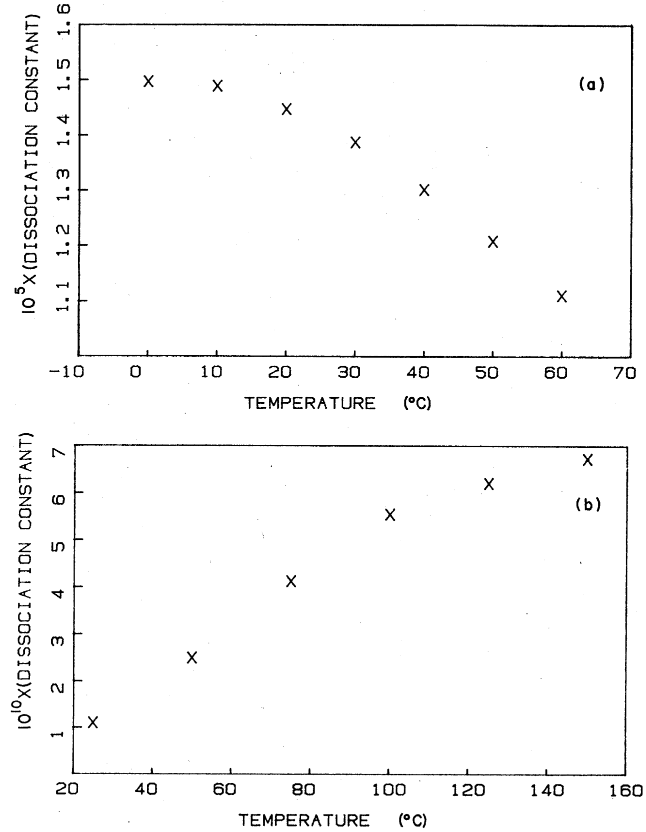

FIG. 1. (a) The dissociation constant $K_a$ as a function of temperature for isobutyric acid in water. The data are taken from Everett *et al.* (Ref. 26). The dissociation constant is in moles per l. (b) The dissociation constant $K_a$ as a function of temperature for phenol in water. The data are taken from Tsonopoulos *et al.* (Ref. 27). The dissociation constant is in moles per l.

For phenol + water, $K_a(T)$ is plotted in Fig. 1(b), from the work of Tsonopoulos *et al.*[27] The critical temperature of the mixture is around 65 °C, in a region of $K_a(T)$ which is nearly linear. Tsonopoulos *et al.*[27] provide a function like Eq. (6) for the system phenol + water.

From these plots, we might expect that the change of $K_a$ with temperature will be more important in analyzing the conductance for isobutyric acid + water than for phenol + water. We find this to be true, as we discuss below.

The dissociation constants $K_a(T)$ shown in Fig. 1 are defined by

$$K_a=\frac{a_{H_3O^+}a_{A^-}}{a_{HA}a_{H_2O}}\ , \tag{7}$$

where $a_i$ is the activity of species $i$. The dissociation constant is related to the concentrations $x_i$ of species $i$ by

$$K_a=\frac{(x_{H_3O^+}\gamma_{H_2O^+})(x_{A^-}\gamma_{A^-})}{(x_{HA}\gamma_{HA})(x_{H_2O}\gamma_{H_2O})}\ , \tag{8}$$

where $\gamma_i$ is the activity coefficient of species $i$. If we take $x_{H_3O^+}$ $(=x_{A^-})$ to be a measure of the extent of reaction, then $K_a^{1/2}(T)$ is proportional to the extent of reaction only when the solution is nearly ideal and the activity coefficients near unity. In using $K_a(T)$ to correct for the background temperature dependence of the extent of reaction, we are assuming that the noncritical temperature dependence is the same for the nonideal solution as for the ideal solution.

How do we correct for $K_a(T)$? For constant mass density, the conductance $\sigma$ will depend on the concentrations $(x_i)$ of charged species and on the mobilities $(u_i)$ of these species:

$$\sigma=\sum_i C_i x_i u_i\ , \tag{9}$$

where $C_i$ are constants. If we assume that the largest term in (9) is that due to the protons, which we designate by subscript $H$, then

$$\sigma\approx C_H x_H u_H\ . \tag{10}$$

Both $x_H$ and $u_H$ could contain critical anomalies, due to anomalies in the extent of reaction and in the proton-transfer rate, respectively. The background contribution due to $K_a(T)$ is expected to be proportional to $K_a^{1/2}(T)$. We have tried fits for $\sigma(T)$ and for $\sigma K_a^{-1/2}$.

### 2. *Temperature dependence of the mass density*

The conductance $\sigma$ depends upon the mass density $\rho$, so any anomaly in $\rho$ will appear in $\sigma$. It is well known[2] that $\rho(T)$ has a critical anomaly characterized by the exponent $1-\alpha$. We must consider this density anomaly in analyzing conductance data.

Morrison and Knobler[28] measured $\rho(T)$ near $T_c$ for isobutyric acid + water. They found an effect of only about $10^{-6}\rho$, whereas the conductivity anomaly is a 0.8% effect and $\sigma$ was measured with a resolution of $10^{-5}\sigma$. Therefore we can ignore the effect of density on conductance for isobutyric acid + water.

Krichevskii *et al.*[29] measured $\rho(T)$ for a nearly critical mixture of phenol + water with a resolution of $10^{-5}\rho$ and saw no evidence of a critical anomaly. The $\sigma$ anomaly is a 0.1% effect, measured with a resolution of $5\times10^{-5}\sigma$. Thus we can ignore the effect of density on conductance for phenol + water.

### 3. *Confluent singularities*

From renormalization-group theory[1,2,23,30] it has been shown that, in addition to the leading anomalous term, there are higher-order critical contributions, characterized by the critical exponent $\Delta$ $(=0.50)$.[20] We expect such contributions to lead to the following functional form for $S$, where $S=\sigma$ or $\sigma K_a^{-1/2}$:

$$S=S_1(1+S_2t^D+S_3t+S_4t^{D+\Delta}+\cdots)\ , \tag{11}$$

where $S_i$ are constants, $D$ is the leading critical exponent, $\Delta$ is the "correction" exponent, and $t$ is the reduced temperature. We will use this function to fit $\sigma$ and $\sigma K_a^{-1/2}$, testing to see how many terms are needed and which of the predicted exponents [Eqs. (1)–(5)] gives the best fit to the data.

### 4. *Gravity effects*

Gravity effects can distort experimental measurements very near critical points.[2] For isobutyric acid + water and for phenol + water, gravity effects become important for $t<2\times10^{-5}$, so we will omit data in this region.[16,21]

## C. Analysis of isobutyric acid + water data

The conductance data of Stein and Allen[15] for isobutyric acid + water consist of two runs. For run 1, points 21 and 27 were omitted as outliers, point 124 (as listed in Stein's thesis[15]) contained a typographical error which was easily corrected, and points 1 through 8 were omitted because of gravity effects; 114 points remained for $2.1\times10^{-5}<t<3.2\times10^{-2}$. For run 2, points 1 through 33 were omitted because of gravity effects and points 47 and 101 were corrected for typographical errors. Further-

TABLE I. Values of $\chi_\nu^2$ for fits of the conductance of isobutyric acid + water (Ref. 15) to the function $S=S_1(1+S_2t^D+S_3t+S_4t^{D+\Delta})$, where $S$ is either $\sigma$, the conductance, or $\sigma K_a^{1/2}$, where $K_a$ is the dissociation constant, and where $t=(T-T_c)/T_c$. $T_c$ and $\Delta$ were held fixed at the experimental (Ref. 15) and theoretical (Ref. 20) values, respectively. The exponent $D$ was fixed at the values in this table. Only the amplitudes $S_1$, $S_2$, $S_3$, and $S_4$ were allowed to vary. The underlined values indicate the best fits.

| | Run 1 | | Run 2 | |
|---|---|---|---|---|
| $D$ | $\sigma$ | $\sigma K_a^{-1/2}$ | $\sigma$ | $\sigma K_a^{-1/2}$ |
| $\nu z_\eta=0.031$ | 129.0 | 16.0 | 82.0 | 11.0 |
| $1-\alpha=0.89$ | 7.6 | $\underline{1.0}$ | 7.0 | $\underline{0.84}$ |
| $2\beta=0.65$ | 11.0 | 49.0 | 8.2 | 34.0 |
| $1/\delta=0.207$ | 8.9 | 53.0 | 7.3 | 20.0 |

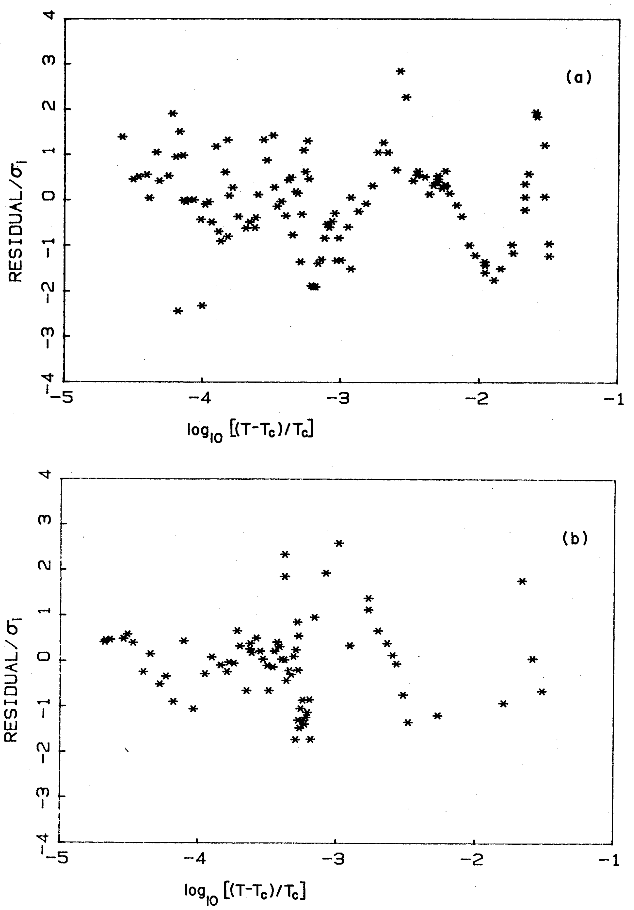

FIG. 2. Residual plots for fits of the equation $\sigma K_a^{-1/2}=S_1(1+S_2t^{1-\alpha}+S_3t+S_4t^{1-\alpha+\Delta})$ to the measurements of Stein and Allen (Ref. 15) of the conductance of a critical mixture of isobutyric acid + water. Here $\sigma$ is the conductivity, $K_a$ is the dissociation constant, and $t$ is the reduced temperature $(T-T_c)/T_c$. (a) is for run 1 ($\chi_\nu^2=1.0$) and (b) is for run 2 ($\chi_\nu^2=0.84$). The residual is the deviation of the experimental point from the fitted line and $\sigma_i$ is the estimated standard deviation for that point.

more, for run 2 we found that only by limiting the data to the same reduced temperature range as that of run 1 could we fit the data with only four terms in Eq. (11); thus we excluded data points 108 through 115. We therefore used 74 points in the range $2.1\times10^{-5}<t<3.1\times10^{-2}$ for run 2.

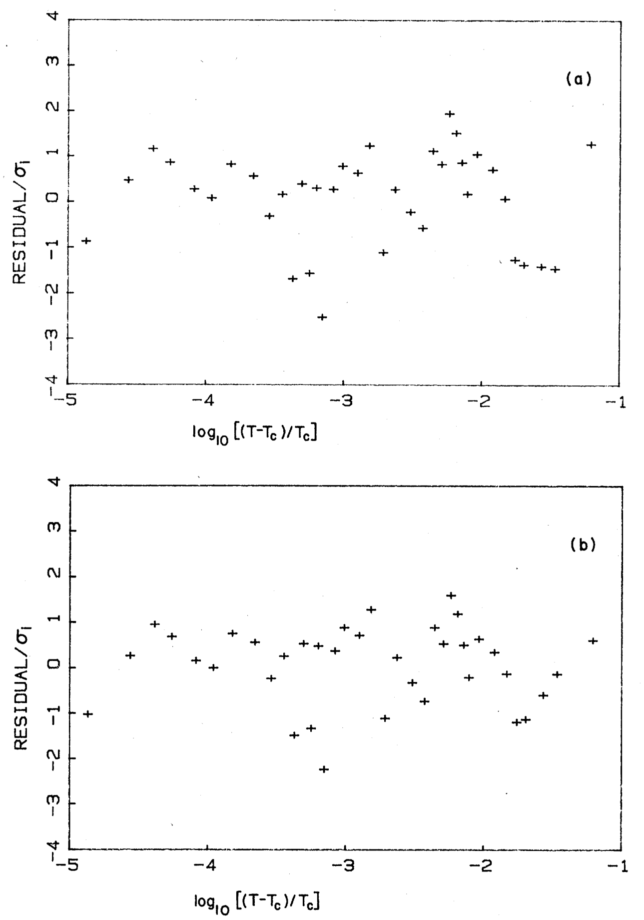

FIG. 3. Residual plots for fits of the equation $S=S_1(1+S_2t^{1-\alpha}+S_3t+S_4t^{1-\alpha+\Delta})$, where $t=(T-T_c)/T_c$, to run 13 of the measurements of Shaw and Goldburg (Ref. 16) of the conductance of a critical mixture of phenol + water. For (a), $S=\sigma$, the conductivity, and $\chi_\nu^2=0.83$. For (b), $S=\sigma K_a^{-1/2}$, where $K_a$ is the dissociation constant and $\chi_\nu^2=1.2$. The residual is the deviation of the experimental point from the fitted line and $\sigma_i$ is the estimated standard deviation for that point.

For both runs, we assumed the uncertainty in the temperature $\sigma_T$ to be 0.0001 K for $t<3\times10^{-3}$ and 0.001 K for $t>3\times10^{-3}$. We took the uncertainty in the resistance to be 0.0005%. We fixed $T_c$ at the experimental values. The value of $\Delta$ was fixed at 0.50.[20] We found that Eq. (11) with three terms did not provide a good fit

TABLE II. Values of $\chi_\nu^2$ for fits of the conductance of phenol + water (Ref. 16) to the function $S=S_1(1+S_2t^D+S_3t+S_4t^{D+\Delta})$, where $S$ is either $\sigma$, the conductance, or $\sigma K_a^{1/2}$, where $K_a$ is the dissociation constant, and where $t=(T-T_c)/T_c$. $T_c$ and $\Delta$ were held fixed at the experimental (Ref. 16) and theoretical (Ref. 20) values, respectively. The exponent $D$ was fixed at the values in this table. Only the amplitudes $S_1$, $S_2$, $S_3$, and $S_4$ were allowed to vary. The underlined values indicate the best fits.

| | Run 11 | | Run 12 | | Run 13 | |
|---|---|---|---|---|---|---|
| $D$ | $\sigma$ | $\sigma K_a^{-1/2}$ | $\sigma$ | $\sigma K_a^{-1/2}$ | $\sigma$ | $\sigma K_a^{-1/2}$ |
| $\nu z_\eta=0.031$ | 3.3 | 2.0 | 1.6 | 0.84 | 3.3 | 2.9 |
| $1-\alpha=0.89$ | 1.8 | 1.7 | 1.7 | 1.4 | 0.83 | 1.2 |
| $2\beta=0.65$ | 2.6 | 2.4 | 2.0 | 1.9 | 3.2 | 3.9 |
| $1/\delta=0.207$ | 3.8 | 2.7 | 2.3 | 1.6 | 4.9 | 3.5 |

TABLE III. Values of $\chi_\nu^2$ for fits of the conductance of phenol + water + KCl (Ref. 16) to the function $S=S_1(1+S_2t^D+S_3t+S_4t^{D+\Delta})$, where $S$ is either $\sigma$, the conductance, or $\sigma K_a^{1/2}$, where $K_a$ is the dissociation constant, and where $t=(T-T_c)/T_c$. $T_c$ and $\Delta$ were held fixed at the experimental (Ref. 16) and theoretical (Ref. 20) values, respectively. The exponent $D$ was fixed at the values in this table. Only the amplitudes $S_1$, $S_2$, $S_3$, and $S_4$ were allowed to vary. The underlined values indicate the best fits.

| | Run 21 | | Run 22 | | Run 23 | |
|---|---|---|---|---|---|---|
| $D$ | $\sigma$ | $\sigma K_a^{-1/2}$ | $\sigma$ | $\sigma K_a^{-1/2}$ | $\sigma$ | $\sigma K_a^{-1/2}$ |
| $\nu z_\eta=0.031$ | 24.0 | 81.0 | 3.5 | 33.0 | 5.7 | 28.0 |
| $1-\alpha=0.89$ | 8.4 | 13.0 | 1.7 | 3.1 | 0.98 | 3.8 |
| $2\beta=0.65$ | 25.0 | 46.0 | 6.2 | 24.0 | 9.7 | 25.0 |
| $1/\delta=0.207$ | 36.0 | 95.0 | 8.7 | 45.0 | 11.0 | 41.0 |

to the data for any $D$ value chosen [Eqs. (1)–(5)], for either $S$ or for either run.

The goodness of fit $\chi_\nu^2$ for Eq. (11) with four terms and for various values of $D$ is given in Table I. Only $\sigma K_a^{-1/2}$ (not $\sigma$) provided a satisfactory fit to the data. The importance of $K_a(T)$ for this system is not surprising, as discussed above. For $\sigma K_a^{-1/2}$, the only good fit was for $D=1-\alpha$. The residual plots for the two good fits are shown in Fig. 2.

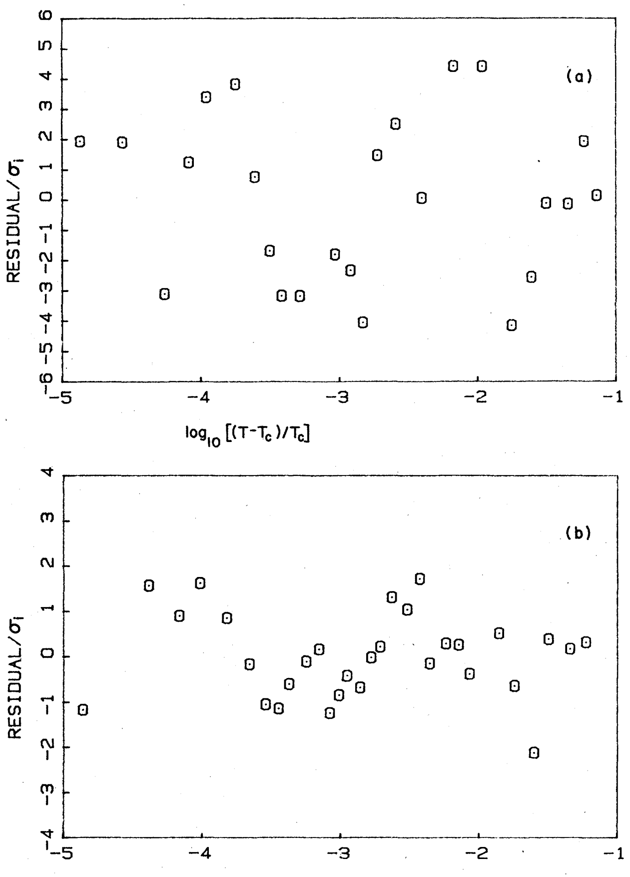

FIG. 4. Residual plots for fits of the equation $\sigma=S_1(1+S_2t^{1-\alpha}+S_3t+S_4t^{1-\alpha+\Delta})$ for the measurements of Shaw and Goldburg (Ref. 16) of the conductance of a critical mixture of phenol + water + KCl. Here $\sigma$ is the conductivity and $t=(T-T_c)/T_c$. (a) is for run 21 ($\chi_\nu^2=8.4$) and (b) is for run 23 ($\chi_\nu^2=0.98$). The residual is the deviation of the experimental point from the fitted line and $\sigma_i$ is the estimated standard deviation for that point.

We conclude that the leading critical anomaly in the conductance $\sigma$ of isobutyric acid + water is well characterized by an exponent $1-\alpha$ when $\sigma$ is divided by $K_a^{1/2}$ to correct for the background temperature dependence of the extent of dissociation.

### D. Analysis of phenol + water data

The measurements[16] of the conductance near the critical point of phenol + water consist of three runs, labeled, 11, 12, and 13. For run 11, we omitted point 1 due to gravity effects and points 36 and 38 as outliers. There remained 35 points in run 11 and $t$ ranged from $2\times10^{-3}$ to $7\times10^{-2}$. For run 12, point 32 was removed as an outlier, leaving 32 points in the $t$ range $2\times10^{-5}$–$8\times10^{-2}$. For run 13 (the run with the smallest errors in $\sigma$) all points were retained and $2\times10^{-3}<t<8\times10^{-2}$.

In the paper of Shaw and Goldburg[16] the precision in the temperature $\sigma_T$ was given as 0.5 mK. In his thesis, Shaw[16] gives the temperature stability as 0.2 mK. We have used $\sigma_T=0.2$ mK. That we obtain $\chi_\nu^2\approx1.0$ in our fits supports this choice. The uncertainties in the resistance measurements were obtained from the Appendix of Shaw's thesis. $T_c$ was held at the experimental values and $\Delta$ at 0.50.[20]

Equation (11) with only three terms could not be satisfactorily fitted to the data for any $D$ or either $S$. The goodness of fit for Eq. (11) with four terms and for various values of $D$ is given in Table II.

Examining Table II, we find, as we did for isobutyric acid + water, that the data support the exponent $1-\alpha$. The difference between fits to $\sigma$ and to $\sigma K_a^{-1/2}$ is not very important for phenol + water, as we might expect due to the nearly linear behavior of $K_a(T)$ near $T_c$. Run 12 narrowly favors an exponent $\nu z_\eta$; we are inclined to discount this result, since the other two runs agree with one another and contradict run 12. The residual plots for the best run, run 13, are given in Fig. 3.

We conclude that the weight of the experimental evidence favors an exponent $1-\alpha$ for the leading critical anomaly in the conductance in phenol + water. The fit for phenol + water is not sensitive to the background temperature dependence of $K_a$.

TABLE IV. Coefficients for fits of the conductance of critical liquid mixtures to the function $S = S_1(1+S_2 t^{(1-\alpha)}+S_3 t + S_4 t^{(1-\alpha)+\Delta})$, where $t=(T-T_c)/T_c$, $\alpha=0.11$ (Ref. 20), $\Delta=0.50$ (Ref. 20), $S=\sigma$ or $\sigma K_a^{-1/2}$, $\sigma$ is the conductivity, and $K_a$ is the dissociation constant. The units are $\sigma$ in $\Omega^{-1}$, $T$ in K, and $K_a$ in moles per 1. Uncertainties ($\sigma_{S_i}$) are given as one standard deviation.

| System | Run | $S$ | $S_1 \pm \sigma_{S_1}$ | $S_2 \pm \sigma_{S_2}$ | $S_3 \pm \sigma_{S_3}$ | $S_4 \pm \sigma_{S_4}$ |
|---|---|---|---|---|---|---|
| Isobutyric | 1 | $\sigma K_a^{-1/2}$ | $0.015\,805\,91 \pm 2\times10^{-8}$ | $5.30 \pm 8\times10^{-3}$ | $-2.94 \pm 0.02$ | $5.04 \pm 0.02$ |
| acid + water | 2 | $\sigma K_a^{-1/2}$ | $0.018\,522\,32 \pm 3\times10^{-8}$ | $5.16 \pm 1\times10^{-2}$ | $-2.70 \pm 0.03$ | $4.83 \pm 0.04$ |
| Phenol | 11 | $\sigma$ | $2.283\,04\times10^{-5} \pm 6\times10^{-10}$ | $2.0 \pm 0.1$ | $2.4 \pm 0.2$ | $2.6 \pm 0.2$ |
| + water | | $\sigma K_a^{-1/2}$ | $1.254\,27 \pm 3\times10^{-5}$ | $2.0 \pm 0.1$ | $-0.8 \pm 0.2$ | $1.9 \pm 0.2$ |
| | 12 | $\sigma$ | $2.288\,19\times10^{-5} \pm 7\times10^{-10}$ | $1.7 \pm 0.1$ | $3.1 \pm 0.3$ | $1.6 \pm 0.3$ |
| | | $\sigma K_a^{-1/2}$ | $1.256\,94 \pm 4\times10^{-5}$ | $2.2 \pm 0.1$ | $-0.3 \pm 0.2$ | $1.4 \pm 0.2$ |
| | 13 | $\sigma$ | $2.479\,39\times10^{-5} \pm 1\times10^{-10}$ | $1.83 \pm 0.03$ | $2.86 \pm 0.06$ | $1.94 \pm 0.07$ |
| | | $\sigma K_a^{-1/2}$ | $1.359\,847 \pm 9\times10^{-6}$ | $1.83 \pm 0.04$ | $-0.47 \pm 0.07$ | $1.47 \pm 0.07$ |
| Phenol | 21 | $\sigma$ | $1.139\,53\times10^{-4} \pm 3\times10^{-9}$ | $3.2 \pm 0.1$ | $-0.4 \pm 0.2$ | $2.9 \pm 0.2$ |
| + water + KCl | 22 | $\sigma$ | $1.171\,26\times10^{-4} \pm 1\times10^{-9}$ | $2.56 \pm 0.03$ | $0.79 \pm 0.07$ | $2.09 \pm 0.06$ |
| | 23 | $\sigma$ | $1.171\,33\times10^{-4} \pm 7\times10^{-10}$ | $2.59 \pm 0.03$ | $0.74 \pm 0.05$ | $2.10 \pm 0.05$ |

### E. Analysis of phenol + water + KCl data

Shaw and Goldburg[16] also made measurements of the conductance of a critical mixture of phenol + water to which KCl had been added. Their intention was to see if the conductance anomaly changed when the main charge carriers were the salt ions.

The measurements consist of three runs, labeled 21, 22, and 23. For run 21, we omitted points 11 and 12 as outliers; 24 points remained. For run 22, we used all 30 points. For run 23, we omitted points 25 and 32 as outliers, leaving 30 points. For all three runs, $t$ was in the range $1\times10^{-5}$–$9\times10^{-2}$. We set the uncertainty in temperature at 0.2 mK. The uncertainties in the resistance were taken from the Appendix of Shaw's thesis. $T_c$ was held at the experimental values and $\Delta$ at 0.50.[20]

Four terms were required in Eq. (11) to fit the data. The goodness of fit for Eq. (11) with four terms is shown in Table III. The best fits for all three runs are fits of $\sigma$ with an exponent of $1-\alpha$. For run 21, $\chi_\nu^2$ is large for the best fit, but the residuals [Fig. 4(a)] are randomly scattered, suggesting that the random error was simply underestimated for that run. The good fit to $\sigma$ is lost if $\sigma$ is divided by $K_a^{1/2}$. We find, therefore, that the leading critical anomaly in the conductance of phenol + water + KCl is characterized by the exponent $1-\alpha$.

## III. SUMMARY AND DISCUSSION

For all three systems, the critical anomaly in the conductance is best characterized by an exponent $1-\alpha$. The coefficients for all fits with exponent $1-\alpha$ are given in Table IV.

For isobutyric acid + water, consistency with a $1-\alpha$ anomaly is obtained after dividing the conductance by the square root of the dissociation constant to correct for the normal temperature dependence of the dissociation constant. For phenol + water, the correction for $K_a(T)$ is not important; this result is not surprising, since $K_a(T)$ for phenol + water is nearly linear near $T_c$. The addition of KCl to the phenol + water system does not change the exponent of the critical anomaly. The KCl adds a large background conductance due to the salt; this can be seen from the $S=\sigma$ fits in Table IV, which show that $S_1$ is ten times larger for phenol + water + KCl than for phenol + water. The total amplitude $S_1S_2$ of the leading anomaly is about $5\times10^{-5}$ for phenol + water and about $3\times10^{-4}$ when KCl is added. The total amplitude of the confluent singularity $S_1S_4$ is likewise increased. The total amplitude of the third term $S_1S_3$ is about the same, with or without the KCl. Thus the presence of the KCl seems to increase the amplitudes of the critical terms in the conductance. This change could be caused by the expected increase in acid dissociation due to the presence of the salt.[31]

In summary, our analysis shows that the anomaly in the conductance near liquid-liquid critical points of mixtures of weak acids in water has a leading critical exponent of $1-\alpha$, where $\alpha$ ($=0.11$) is the exponent which characterizes the specific heat at constant pressure and temperature. Such a critical exponent is expected from either an anomalous extent of reaction[9] or from an anomalous proton-transfer rate.[21]

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