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Critical-point universality in adsorption: The effect of charcoal on a mixture of isobutyric acid and water near the consolute point

Timothy J. Giesy,[1] Alan S. Chou,[2] Robert L. McFeeters,[2] James K. Baird,[2,3,*] and Douglas A. Barlow[4]
[1]*Department of Chemical Engineering, University of Alabama in Huntsville Huntsville, Alabama 35899, USA*
[2]*Department of Chemistry, University of Alabama in Huntsville Huntsville, Alabama 35899, USA*
[3]*Department of Physics, University of Alabama in Huntsville Huntsville, Alabama 35899, USA*
[4]*Department of Natural Sciences Santa Fe College, Gainesville, Florida 32606, USA*

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The mixture of isobutyric acid and water has a consolute point at a temperature of 25.75 °C and mole fraction 0.1148 isobutyric acid. When charcoal is added to this mixture, the concentration of isobutyric acid is reduced by adsorption. We have measured the action of charcoal on solutions of isobutyric acid and water as a function of isobutyric acid mole fraction at temperatures of 25.85 and 32.50 °C. At the higher temperature, the specific adsorption density (y_2^α/m) satisfies the Freundlich equation $(y_2^\alpha/m) = KX_2^{1/n}$, where y_2^α is the mass of isobutyric acid adsorbed, m is the mass of charcoal, X_2 is the equilibrium mole fraction of isobutyric acid, n is the Freundlich index, and $K = K(T)$ is an amplitude that depends upon the temperature T. At 25.85 °C, a critical endpoint is located at an isobutyric acid mole fraction $X_2^{ce} = 0.09$. When compared with the Freundlich equation at this temperature, a plot of the specific adsorption density as a function of X_2 in the vicinity of the critical-endpoint composition assumes a shape which is reminiscent of the derivative of a Dirac delta function. Using critical-point scaling theory, we show that this divergent pattern is consistent with the principle of critical point universality.

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I. INTRODUCTION

Solutes in a liquid solution in contact with an insoluble solid phase tend to concentrate at the interface separating the two phases. This phenomenon is called adsorption. The theory of adsorption, which was originally proposed by van der Waals [1,2], and then rediscovered and extended by Cahn and Hilliard [3], predicts that the solute concentration should be a function of the spatial coordinate which has its origin on the solid surface and extends into the bulk liquid in a normal direction. In this theory, the free-energy density of the solute in the liquid is assumed to be a functional of the gradient of the concentration. Minimization of this functional with respect to an arbitrary concentration profile leads to an Euler differential equation, whose solution permits the calculation of the spatial dependence of the concentration [1–3].

In the case of a liquid mixture consisting of chemical components, "1" and "2," both of which are to a certain extent adsorbed at the interface, the molar adsorption densities Γ_j $(j = 1,2)$, reckoned in the units of moles per unit area, can be calculated by evaluating the integral

$$\Gamma_j = \int_0^\infty \left[c_j(z) - c_j^o\right] dz, \qquad (1)$$

where $c_j(z)$ is the molar concentration as a function of the coordinate z measured in a direction normal to the interface, and c_j^o is the molar concentration in the bulk of the solution [4].

Critical adsorption becomes possible when an insoluble phase comes into contact with a fluid phase near its critical point. Fisher and de Gennes [5] and subsequently others [6–8] have shown that in critical adsorption, $c_j(z)$ can be represented by a universal function of z. The conditions determining the form of this function have been described by Liu and Fisher [9] and by Zinn and Fisher [10].

A binary liquid mixture with a miscibility gap, such as that illustrated in Fig. 1, is capable of supporting critical adsorption. The boundary separating the two immiscible liquid phases is the curve of temperature T versus mole fraction X_2. The two chemical components 1 and 2 exist as a single liquid phase on the convex side of the phase boundary and as two liquids on the concave side. The maximum with coordinates (X_2^c, T_c) is called the consolute point, or the critical point of solution. Because the phase boundary is concave down, T_c is referred to as an upper critical solution temperature (UCST).

Cahn and Hilliard [3] suggested that the shape of $c_j(z)$ could be probed by using electromagnetic radiation. This idea, extended to include penetrating particle radiation, has been extensively pursued. The experimental methods have included ellipsometry, refractometry, x-ray scattering, and neutron scattering [11–29]. In the majority of cases, the experiments were not directly sensitive to $c_j(z)$ but rather to one of its integrals. Equation (1) is an example. The data obtained in integral form were fitted to parametrized representations of $c_j(z)$ [9,30,31]. Our references [11–29] describe some of these experiments involving, with the exception of Ref. [17], various critical fluids in contact with solids or immiscible liquids. For ease in comparing these references amongst themselves and with subsequent references, we list in parentheses next to each a summary of the experimental conditions arranged in the format (the experimental method, the critical fluid, the adsorbent phase, and the thermodynamic path of approach to the coexistence curve). Reference [28] includes in its Table I a summary of experiments involving the liquid-vapor interface. The results obtained prior to 2001 for a wide variety of interfaces have been authoritatively reviewed by Law [32].

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[*] Author to whom correspondence should be addressed: jkbaird@matsci.uah.edu

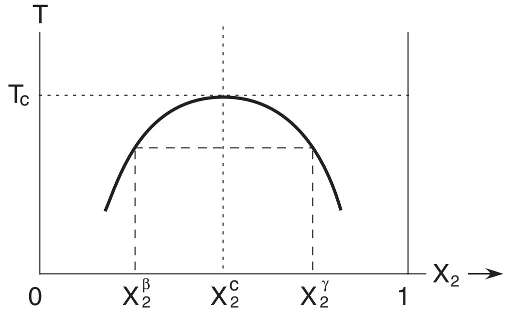

FIG. 1. Phase diagram for a binary liquid mixture with an upper critical solution temperature. The liquid-liquid coexistence curve is the solid curve of temperature T vs mole fraction X_2 of the second component in the mixture. The mixture forms two phases on the concave side of this curve and a single phase on the convex side. The maximum along the curve, which occurs at critical temperature T_c and critical composition X_2^c, locates the consolute point. At a temperature $T < T_c$, the mixture splits into two immiscible liquid phases having compositions X_2^β and X_2^γ, respectively. The horizontal dashed line at $T = T_c$ marks the critical isotherm, while the vertical dashed line at $X_2 = X_2^c$ marks the critical isopleth.

Recently, Law and collaborators [28,31,33] have concluded that for critical adsorption at the liquid-vapor interface, the experimental data for a number of liquids and liquid mixtures are consistent with a single representation of $c_j(z)$.

We have selected the mixture, isobutyric acid and water [34], for investigation because the critical point of solution is located conveniently at isobutyric acid mole fraction $X_2^c = 0.1148$ and temperature T_c, which is near 26 °C (UCST). Charcoal was chosen as the insoluble solid, because it readily adsorbs carboxylic acids [35,36]. With water denoted as component 1 and isobutyric acid as component 2, we have measured the composition dependence of a quantity (the specific adsorption) which is proportional to the integral in Eq. (1) evaluated with $j = 2$. The measurements were made along two different isotherms, one of which was near critical.

Our motivation finds its basis in the thermodynamic theory of critical adsorption [37], which can be summarized as follows: Because the molar adsorptions calculated using Eq. (1) satisfy the Gibbs-Duhem equation [4,38], the number of independent adsorptions can be reduced to one by placing the origin of spatial coordinates on the Gibbs'dividing surface where $\Gamma_1 = 0$ [39]. With this choice of dividing surface, Γ_2 can be identified with the relative adsorption $\Gamma_{2(1)}$ of component 2 with respect to component 1 [38,39]. To specify this interface in the case of a mixture of charcoal, water, and isobutyric acid, we follow Rowlinson and Widom [37] and denote charcoal as phase α and the two immiscible liquid phases on the concave side of the phase boundary in Fig. 1 as phases β and γ, respectively. The uniform liquid phase on the convex side of the phase boundary is referred to as $\beta\gamma$. In this notation, the relative adsorption of isobutyric acid from the $\beta\gamma$ liquid phase onto the solid α charcoal phase is denoted by $\Gamma_{2(1)}^{\alpha,\beta\gamma}$. The composition dependence of this relative adsorption can be calculated using the Gibbs equation

$$\Gamma_{2(1)}^{\alpha,\beta\gamma} = -\left(\frac{\partial \sigma^{\alpha,\beta\gamma}}{\partial \mu_2}\right)_T, \tag{2}$$

where $\sigma^{\alpha,\beta\gamma}$ is the surface tension that acts at the interface where the charcoal α and the $\beta\gamma$ liquid meet [37]. In Eq. (2), μ_2 is the chemical potential of isobutyric acid in the $\beta\gamma$ phase. When the two immiscible liquid phases β and γ merge to form the $\beta\gamma$ phase in the presence of the noncritical α phase, the system is said to reach a *critical endpoint* [40]. By invoking critical-point scaling theory, we can combine the dependence of $\sigma^{\alpha,\beta\gamma}$ on $(T - T_c)/T_c$ with the dependence of μ_2 on $(X_2 - X_2^c)$, and use Eq. (2) to predict how $\Gamma_{2(1)}^{\alpha,\beta\gamma}$ depends upon X_2 as the critical endpoint is approached along an isotherm. The comparison between the theory and experiment serves as a test of the principle of critical-point universality.

Among the authors listed in Refs. [11–29], the closest to us in their choice of materials are Smith and Law [17], who studied the adsorption at the *liquid-vapor* interface of isobutyric acid and water along the critical *isopleth.* Although several authors before us have also studied adsorption along *isotherms* [12,15,16,20,25,26,29], we test the scaling law for μ_2 as $X_2 \to X_2^c$ in the case of *liquid-solid* adsorption. The agreement, which we find between our experimental data and the scaling law, confirms the principle of critical-point universality.

II. THEORY

A. Specific adsorption density

Near a critical endpoint, the molar adsorption $\Gamma_{2(1)}^{\alpha,\beta\gamma}$ can be divided into two parts:

$$\Gamma_{2(1)}^{\alpha,\beta\gamma} = \Gamma_{2(1)}^{\alpha} + \Delta\Gamma_{2(1)}^{\alpha,\beta\gamma}. \tag{3}$$

In Eq. (3), the leading term, $\Gamma_{2(1)}^{\alpha}$, is called the "background" and represents the molar adsorption at the solid α phase that is to be expected in the *absence* of the β-to-γ phase transition. This term is evaluated by extrapolating into the critical region adsorption measurements made outside the critical region. The second term, $\Delta\Gamma_{2(1)}^{\alpha,\beta\gamma}$, is called the "enhancement" and represents the *change* in adsorption associated with the approach to the critical endpoint [37].

The quantity traditionally determined in the laboratory is not $\Gamma_{2(1)}^{\alpha}$ but rather the specific adsorption density y_2^α/m, where y_2^α is the mass of isobutyric acid adsorbed and m is the mass of the charcoal [41]. The two measures of adsorption are related by

$$y_2^\alpha/m = SM_2\Gamma_{2(1)}^{\alpha}, \tag{4}$$

where S is the specific surface area of the charcoal measured in the units of m^2/g, and $M_2 = 88.11$ g/mol is the molar mass of isobutyric acid.

Near the critical endpoint, Eq. (4) becomes

$$y_2^{\alpha,\beta\gamma}/m = y_2^\alpha/m + \Delta y_2^{\alpha,\beta\gamma}/m, \tag{5}$$

where $y_2^\alpha/m = SM_2\Gamma_{2(1)}^{\alpha}$ is the background term, and

$$\Delta y_2^{\alpha,\beta\gamma}/m = SM_2\Delta\Gamma_{2(1)}^{\alpha,\beta\gamma} \tag{6}$$

is the enhancement term.

B. Adsorption at compositions outside the critical region

The *net* lateral movement of isobutyric acid molecules across the surface of the charcoal ceases when the spreading pressure π^{α} is balanced by the surface tension $\sigma^{\alpha,\beta\gamma}$; that is, when $\pi^{\alpha} + \sigma^{\alpha,\beta\gamma} = 0$ [42]. In terms of the spreading pressure, Eq. (2) can be written as

$$\Gamma^{\alpha}_{2(1)} = \left(\frac{\partial \pi^{\alpha}}{\partial \mu_2}\right)_{T,P}. \tag{7}$$

In the Rideal model of adsorption [42], the dependence of the spreading pressure on the molar adsorption $\Gamma^{\alpha}_{2(1)}$ is given by

$$\pi^{\alpha} = nRT\Gamma^{\alpha}_{2(1)}, \tag{8}$$

where R is the gas law constant, T is the Kelvin temperature, and n is an empirically determined parameter called the Freundlich index. In the solution phase, the activity a_2 of component 2 is related to its chemical potential by

$$\mu_2 = \mu_2^{o} + RT \ln a_2, \tag{9}$$

where μ_2^{o} is the chemical potential referred to pure liquid isobutyric acid as the standard state [43].

Upon combining Eqs. (7)–(9), we find

$$d \ln \left(\Gamma^{\alpha}_{2(1)}\right) = \frac{1}{n} d \ln a_2. \tag{10}$$

On the basis of Eq. (4), Eq. (10) can be rewritten as

$$d \ln \left(y_2^{\alpha}/m\right) = \frac{1}{n} d \ln a_2. \tag{11}$$

The integral of Eq. (11) is

$$y_2^{\alpha}/m = K a_2^{1/n}, \tag{12}$$

where K is a "constant" that depends upon the temperature but is independent of X_2. In the solution phase, the activity of isobutyric acid is

$$a_2 = \gamma_2 X_2, \tag{13}$$

where γ_2 is the activity coefficient [43]. At sufficiently low mole fraction, isobutyric acid will behave ideally in aqueous solution, and the value of γ_2 will be unity. In this dilute solution limit, Eq. (12) becomes

$$y_2^{\alpha}/m = K X_2^{1/n}, \tag{14}$$

which is known as the Freundlich isotherm [42,44–46]. For values of X_2 where Eq. (14) applies, a plot of experimental data in the form $y_2^{\alpha,\beta\gamma}/m$ vs X_2 is ordinarily concave down; so the value of the index n is greater than unity. We have chosen Eq. (14) to serve as the background, because, absent critical effects, it is capable of representing the composition dependence of the adsorption of carboxylic acids onto charcoal over a wide range of values of X_2.

C. Adsorption at compositions inside the critical region

Inside the critical region, the surface tension becomes a strong function of composition. The critical enhancement of the molar adsorption can be calculated by writing Eq. (2) in the form

$$\Delta\Gamma^{\alpha,\beta\gamma}_{2(1)} = -\left(\frac{\partial \sigma^{\alpha,\beta\gamma}}{\partial X_2}\right)_T \left(\frac{\partial X_2}{\partial \Delta\mu_2}\right)_T, \tag{15}$$

where $\Delta\mu_2$ is the critical enhancement of the chemical potential [37].

In the vicinity of the consolute point of the two components 1 and 2, the liquid-liquid phase boundary assumes the form [37]

$$\frac{T_c - T}{T_c} = B\left|X_2 - X_2^c\right|^{1/\beta}, \tag{16}$$

where $B > 0$ is a constant, and $\beta = 0.326$ is the universal coexistence curve critical exponent [47], whose standard greek letter designation should not be confused with the Rowlinson and Widom β phase notation. Ramos-Gomez and Widom [48] represent the temperature dependence of $\sigma^{\alpha,\beta\gamma}$ in the critical region by

$$\sigma^{\alpha,\beta\gamma} = \sigma_o \left|\frac{T_c - T}{T_c}\right|^{\mu}, \tag{17}$$

where $\sigma_o > 0$ is a constant, and $\mu = 1.26$ is the standard designation of the surface tension critical exponent [37], which should not to be confused with the chemical potential μ_2. We can make Eqs. (16) and (17) consistent by adopting Eq. (1.12) of Ref. [48]; this renders the composition dependence $\sigma^{\alpha,\beta\gamma}$ in the form

$$\sigma^{\alpha,\beta\gamma} = \sigma_o B^{\mu}\left|X_2 - X_2^c\right|^{\mu/\beta}. \tag{18}$$

Note that $\sigma^{\alpha,\beta\gamma}$ is an even function of its argument. By contrast, its derivative,

$$\frac{\partial \sigma^{\alpha,\beta\gamma}}{\partial X_2} = (\mu/\beta)\sigma_o B^{\mu}\left(X_2 - X_2^c\right)\left|X_2 - X_2^c\right|^{(\mu/\beta)-2}, \tag{19}$$

is an odd function.

Along the isotherm $T = T_c$ of the $\beta\gamma$-to-β-plus-γ transition, the critical enhancement $\Delta\mu_2(X_2)$ of the chemical potential assumes the form [37,49]

$$\Delta\mu_2(X_2) = \bar{\mu}_2\left(X_2 - X_2^c\right)\left|X_2 - X_2^c\right|^{\delta-1}, \tag{20}$$

Where $\bar{\mu}_2 > 0$ is a system-dependent constant, and the critical exponent $\delta = 4.80$ [47]. According to Eq. (20) the enhancement $\Delta\mu_2(X_2)$ is an odd function of X_2. This form, plus the additional restriction $\bar{\mu}_2 > 0$, are a consequence of the condition for phase stability, which requires the derivative

$$\frac{\partial \Delta\mu_2(X_2)}{\partial X_2} = \delta\bar{\mu}_2\left|X_2 - X_2^c\right|^{\delta-1} \tag{21}$$

to be positive definite [50].

Upon substitution of Eqs. (6), (19), and (21) into Eq. (15), we obtain

$$\Delta y_2^{\alpha,\beta\gamma}/m = -\frac{\sigma_o}{\bar{\mu}_2}\frac{\mu}{\beta\delta} S M_2 B^{\mu}\left(X_2 - X_2^c\right)\left|X_2 - X_2^c\right|^{(\mu/\beta)-\delta-1}. \tag{22}$$

The right-hand side of Eq. (22) is an odd function, which is positive for $X_2 < X_2^c$ and negative for $X_2 > X_2^c$. The critical exponent that governs the composition dependence of $\Delta y_2^{\alpha,\beta\gamma}/m$ is the composite $(\mu/\beta) - \delta = -0.93$. Since this exponent is negative, Eq. (22) predicts that along the critical isotherm, $\Delta y_2^{\alpha,\beta\gamma}/m \rightarrow +\infty$ when X_2 approaches X_2^c from *below*, while $\Delta y_2^{\alpha,\beta\gamma}/m \rightarrow -\infty$ when X_2 approaches X_2^c from *above*.

III. EXPERIMENTAL METHODS

Our reaction vessel was a 31-mm–i.d., flat bottom Pyrex test tube. The temperature of this test tube and its contents was maintained using a water bath with a thermostat [51,52]. A long mercury-in-glass thermometer was used to determine the rough value of the temperature, and a Beckmann differential thermometer was used to measure differences in temperature with a precision of ±0.005 °C.

Activated charcoal was obtained from Fisher (50-200 mesh, lot No. P-21553), and isobutyric acid was obtained from Aldrich (lot No. 07710PB). Both were used without further purification. Water was distilled once from a glass system. The binary solvent mixture was prepared by weighing. Visual observation of critical opalescence in a sample of isobutyric acid and water prepared at the critical mole fraction $X_2^c = 0.1148$ (38.8 mass % isobutyric acid [34]) served to identify the critical temperature as 25.75 °C.

To begin an adsorption experiment, a weighed sample of charcoal (mass m equal to ∼1.5 g) was added to the reaction vessel. Fifty grams of the binary solvent mixture were transferred to the reaction vessel containing the carbon. A magnetic stirring bar was introduced, and the reaction vessel was closed with a stopper and suspended in the water bath. The contents of the reaction vessel were stirred continuously for the first 5 min and thereafter stirred intermittently so as to avoid breaking up the charcoal granules by mechanical agitation.

After 1 h, stirring was stopped, and any suspended graphite was allowed to settle by gravitational sedimentation. The concentration of isobutyric acid in the supernatant liquid was measured using a volumetric method for the determination of carboxylic acids [41], which was as follows: A 10-ml sample of the liquid was removed with a serological pipette and drained through filter paper (5.5-cm circle, Whatman No. 1) suspended in a glass funnel. The filtrate was collected in a 125-ml Erlenmeyer flask. As the sole purpose of this filtration was to saturate the filter paper with the solution, the filtrate was discarded. A 14-ml sample of the supernatant liquid was then removed from the reaction vessel and passed through the saturated filter paper into the same flask. When necessary, the flask was warmed in a shallow water bath to merge the phases. Using a volumetric pipette, a 10-ml aliquot of the filtrate was extracted from the flask and diluted with distilled water. Several drops of phenolphthalein indicator were added, and the aliquot was titrated with sodium hydroxide that had been standardized against Mallinckrodt potassium hydrogen phthalate. The mass of isobutyric acid in the 10-ml aliquot was calculated, and scaled for volume using the density of isobutyric acid and water [53]. The scaled mass was subtracted from the mass of isobutyric acid in the original 50-g binary solvent mixture and set equal to $y_2^{\alpha,\beta\gamma}$. Using the weighed charcoal mass m, the specific adsorption density was calculated as the ratio $y_2^{\alpha,\beta\gamma}/m$. The mass of isobutyric acid found from titration of the aliquot was combined with the original mass of water and the molar masses of isobutyric

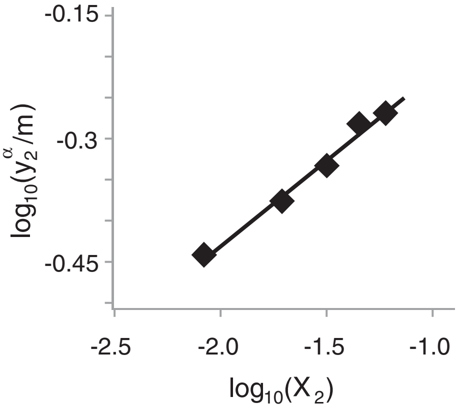

FIG. 2. Specific adsorption density y_2^{α}/m as a function of isobutyric acid equilibrium mole fraction X_2 at 25.85 °C plotted according to Eq. (23). The points correspond to the first five entries in Table I.

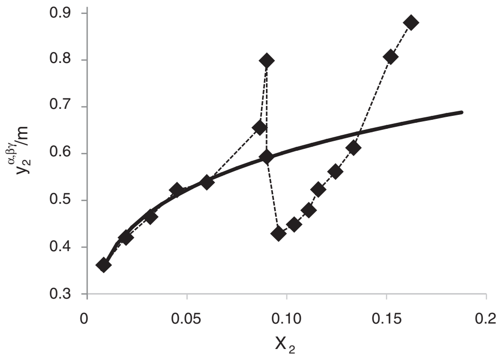

FIG. 3. Specific adsorption density $y_2^{\alpha,\beta\gamma}/m$ as a function of isobutyric acid equilibrium mole fraction X_2 at 25.85 °C. The points correspond to entries in Table I.

TABLE I. Specific adsorption density $y_2^{\alpha,\beta\gamma}/m$, where $y_2^{\alpha,\beta\gamma}$ is the mass isobutyric acid adsorbed onto the surface of a mass m of charcoal as a function of the equilibrium isobutyric acid mole fraction X_2 at 25.85 °C.

X_2	$y_2^{\alpha,\beta\gamma}/m$
0.00836	0.362
0.0195	0.421
0.0317	0.465
0.0450	0.523
0.0599	0.538
0.0865	0.656
0.0899	0.799
0.0900	0.594
0.0959	0.429
0.104	0.449
0.111	0.479
0.115	0.523
0.124	0.561
0.133	0.613
0.152	0.807
0.162	0.880

TABLE II. Specific adsorption density $y_2^{\alpha,\beta\gamma}/m$, where $y_2^{\alpha,\beta\gamma}$ is the mass isobutyric acid adsorbed onto the surface of a mass m of charcoal as a function of the equilibrium isobutyric acid mole fraction X_2 at 32.50 °C.

X_2	$y_2^{\alpha,\beta\gamma}/m$
0.0002	0.148
0.0009	0.223
0.0027	0.309
0.0072	0.347
0.0083	0.375
0.0192	0.467
0.0312	0.535
0.0445	0.597
0.0560	0.652
0.0688	0.668
0.0789	0.706
0.0859	0.737
0.0932	0.774
0.0993	0.758
0.1027	0.840
0.1083	0.823
0.1124	0.951
0.1206	1.038
0.1273	1.356

acid and water to compute the value of X_2. By following this method, we determined the adsorption densities $y_2^{\alpha,\beta\gamma}/m$ as a function of X_2 at temperatures of 25.85 and 32.50 °C. These data are listed in Tables I and II, respectively. The errors in the values of X_2 and $y_2^{\alpha,\beta\gamma}$, respectively, are estimated to be less than ±3%, while the error in the value of m is estimated to be less than ±0.1%.

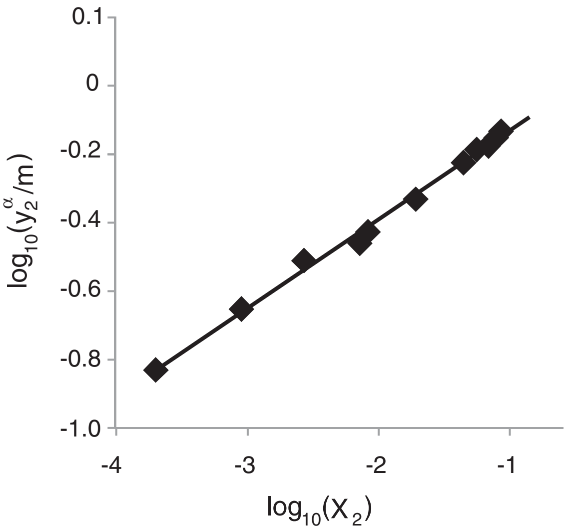

FIG. 4. Specific adsorption density y_2^{α}/m as a function of isobutyric acid equilibrium mole fraction X_2 at 32.50 °C plotted according to Eq. (23). The points correspond to the first 12 entries in Table II.

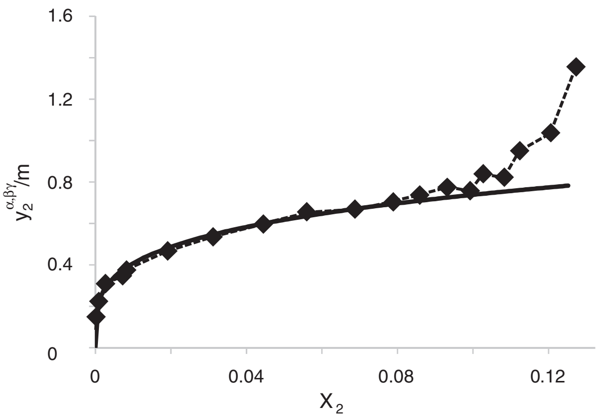

FIG. 5. Specific adsorption density $y_2^{\alpha,\beta\gamma}/m$ as a function of isobutyric acid equilibrium mole fraction X_2 at 32.50 °C. The points correspond to entries in Table II.

IV. DATA ANALYSIS AND RESULTS

The validity of the Freundlich isotherm *outside* the critical region was established by fitting the low concentration data in Tables I and II to the logarithmic form of Eq. (14),

$$\log_{10}\left(y_2^{\alpha}/m\right) = \log_{10} K + (1/n)\log_{10}(1/X_2), \qquad (23)$$

where $\log_{10} K$ and $1/n$ were treated as free parameters.

At 25.85 °C, which is just 0.1 °C above the critical temperature, the five smallest values of X_2 in Table I were considered to define the low-concentration region. The corresponding measurements of $y_2^{\alpha,\beta\gamma}$ were identified with y_2^{α}. The straight line fit of Eq. (23) to these five points is shown in Fig. 2. The linear correlation coefficient [54] for this fit was $R^2 = 0.9871$. The values of the least-squares parameters were $\log_{10} K = -0.011$ and $n = 4.81$. Figure 3 shows a comparison between the complete data set collected at 25.85 °C and Eq. (14) with this parametrization. The critical enhancement is represented by the delta function derivative pattern which appears to be centered on mole fraction $X_2^{ce} = 0.09$, which we identify with the critical endpoint composition.

By contrast, at 32.50 °C, which is 6.75 °C above the critical temperature, the 12 smallest values of X_2 in Table II were considered to define the low-concentration region. The straight line fit of Eq. (23) to these 12 points is shown in Fig. 4. The linear correlation coefficient for this fit was $R^2 = 0.9942$. The values of the least-squares parameters were $\log_{10} K = 0.126$ and $n = 3.88$, respectively. Figure 5 shows a comparison between the complete data set collected at 32.50 °C and Eq. (14) with this parametrization.

V. DISCUSSION AND CONCLUSIONS

At least ten empirical, or semiempirical, equations are in common use to represent the concentration dependence of the specific adsorption density along isotherms [44–46]. A few of these can be derived from simple analytical equations of state linking the spreading pressure π^{α} to the molar adsorption density $\Gamma_{2(1)}^{\alpha}$ [55]. For example, the Freundlich isotherm, represented by Eq. (14), is based upon the equation of state represented by Eq. (8). Equation (8) asserts that the molar adsorption density is directly proportional to the spreading pressure; as such, it is the analog of Henry's law, which states that the solubility of a noncondensable gas in a bulk liquid is proportional to the partial pressure of the gas [55].

Both values of the Fruendlich index, $n = 4.81$ at 25.85 °C and $n = 3.88$ at 32.50 °C, which we found by fitting Eq. (14) at the low values of X_2, lie within the range 2–10. This range is typical for the adsorption of organic substances onto charcoal [56]; moreover, a comparison of our results at these two temperatures confirms previous experimental observations that n decreases with increasing temperature [56].

In Fig. 5, we see that Eq. (14) faithfully represents the noncritical, 32.50 °C adsorption data up to an isobutyric mole fraction of $X_2 = 0.09$ and a bit beyond. A perfect fit extending across the entire range of experimental mole fraction values is thwarted by the last few data points. Similar deviations from the Freundlich equation have been reported in the case of the adsorption of *n*-valeric acid onto charcoal [35]. These deviations were identified with the transition from Freundlich monolayer adsorption to Brunauer, Emmett, Teller (BET) multilayer adsorption [35].

Figure 3 shows specific adsorption data collected at 25.85 °C. These data begin to deviate from the Freundlich equation at mole fraction $X_2 = 0.06$. Similar large changes in adsorption density near a critical endpoint have been reported previously. The collaborators, Findenegg and Loring [12] and Grull and Woermann [20], who studied the adsorption of fluids onto *solids*, both reported a maximum in adsorption along the critical isotherm. As for adsorption at the *liquid-vapor* interface, both Rusanov [57], who studied nitrobenzene and hexane, and Beaglehole [38], who studied aniline and cyclohexane, reported an extremum in the coefficient of ellipticity along the critical isotherm. Although Rusanov suggested that the extremum in the ellipticity represented a maximum in the adsorption, Beaglehole interpreted his extremum as being due to desorption (i.e., negative specific adsorption) of aniline, a behavior which might be consistent with a minimum in the overall adsorption. Both Rusanov and Beaglehole constructed their isotherms from data that had been collected along different isopleths. If these isopleths were sufficiently widely spaced, it was possible that a part of the delta function derivative pattern, which we report, could have gone unnoticed. By contrast, Rother and collaborators [29], who studied the adsorption of *d*-propane onto silica aerogel (a solid), reported in their Fig. 6 a strong delta function derivative pattern similar to our Fig. 3.

According to the principle of critical-point universality, critical phenomena in a binary liquid mixture should find their analogs in critical phenomena in a pure fluid [58]. In the case of a pure fluid, the pressure P has a value which is *uniform* across the liquid-vapor phase boundary. By contrast, the molar volume $\bar{V}$ is *discontinuous* across the liquid-vapor phase boundary. Along the critical isotherm $T = T_c$ of the pure fluid, the pressure difference, $P - P_c = \Delta P(\bar{V},T_c)$ is an odd function of $(\bar{V} - \bar{V}_c)$, where P_c is the critical value of the pressure, and $\bar{V}_c$ is the critical value of $\bar{V}$ [59]. In the case of a binary liquid mixture, the chemical potential μ_2 has a uniform value across the boundary separating the coexisting liquid phases, while the mole fraction X_2 is discontinuous across this boundary. According to the principle of critical-point universality, P and μ_2 form a class of variables called *fields*, whereas $\bar{V}$ and X_2 form a second class of variables called *densities* [58]. With this division of the thermodynamic variables into classes, the principle of critical-point universality suggests that if $P - P_c = \Delta P(\bar{V},T_c)$ is an odd function of $(\bar{V} - \bar{V}_c)$, so also should $\Delta\mu_2 = \Delta\mu_2(X_2,T_c)$ be an odd function of $(X_2 - X_2^c)$ [37,49]. This is the basis for our selection of Eq. (20) to calculate the composition dependence of $\Delta y_2^{\alpha,\beta\gamma}/m$ as shown in Eq. (22).

By identifying $\Delta y_2^{\alpha,\beta\gamma}/m$ with the deviation of the measured isotherm from the Freundlich background in Fig. 3, we can conclude that $\Delta y_2^{\alpha,\beta\gamma}/m$ diverges in a positive sense as X_2 approaches X_2^{ce} from below, and it diverges in a negative sense as X_2 approaches X_2^{ce} from above. This behavior is in satisfactory agreement with our Eq. (22).

Neither the temperature ($T_{ce} = 25.85\,^\circ\mathrm{C}$) nor the composition ($X_2^{ce} = 0.09$) of the critical endpoint corresponds exactly with the temperature ($T_c = 25.75\,^\circ\mathrm{C}$) and composition ($X_2^c = 0.1148$) of the consolute point of isobutyric acid and water. Because of our estimated error in the value of X_2^{ce} is ±3%, the difference between X_2^{ce} and X_2^c cannot be established with complete certainty; nevertheless, the addition of a third component to a binary liquid mixture is ordinarily expected to shift not only the critical temperature, but also the critical composition [60]. In Fig. 3 the data can be seen to exceed background for $X_2 > 0.13$, which may constitute the "crossover" from critical behavior to BET multilayer adsorption, which has been predicted by Kiselev and collaborators [61,62].

Our investigation of adsorption in the system isobutyric acid, water, and charcoal is part of a general search for the existence of couplings between physicochemical phenomena [41] and the critical point of solution of a binary liquid mixture [63,64]. Theoretical considerations have identified a number of possibilities involving chemical equilibrium [63,65–67] and chemical kinetics [64,66–72]. Of these, only the solubility equilibria [63,65], and the rates of various solvolysis, decomposition, and addition reactions [64] have been examined experimentally. As in the case of the adsorption experiment described above, the results obtained so far in all of these experiments seem to confirm the principle of critical point universality.

When considering liquid mixtures, the basis for the concept of critical-point universality can be found in the method of inductive reasoning applied to the macroscopic observations [58]. Despite the success of the method of induction, it is legitimate to inquire into the molecular behavior that necessarily lies beneath the concept of universality. For the moment, all we can say is that as the critical point is approached, a liquid mixture develops fluctuations in the intermolecular correlation length which exceed the range of the intermolecular forces. Under these conditions, the details of the intermolecular forces are suppressed, and all liquid mixtures exhibit the same values of the critical exponents. Beyond this, little more can be said [73].

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