

## Heat capacity anomaly near the critical point of aniline-cyclohexane

Paul F. Rebillot and D. T. Jacobs<sup>a)</sup>

*Physics Department, The College of Wooster, Wooster, Ohio 44691*

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The heat capacity of the liquid–liquid mixture aniline-cyclohexane has been measured for the first time near its upper critical consolute point using an adiabatic calorimeter. Two data runs provide heat capacity data that are fitted by equations with background terms and a critical term. The critical exponent  $\alpha$  was determined to be  $0.104 \pm 0.011$ , consistent with theoretical predictions. When  $\alpha$  was fixed at its theoretical value of 0.11 to determine the critical amplitudes  $A^+$  and  $A^-$ , our value for the amplitude ratio  $A^+/A^- = 0.59 \pm 0.03$  was consistent with most experimental determinations in liquid–liquid mixtures, but was slightly larger than either theoretical predictions or recent experimental values in liquid–vapor systems. The two-scale-factor universality ratio  $X$ , now consistent among experiments and theories with a value between 0.019 and 0.020, is consistent in this system using one published value for the correlation length, but not with another. © 1998 American Institute of Physics. [S0021-9606(98)50534-X]

### INTRODUCTION

The study of critical point phenomena has matured so that recent theoretical extensions study complex systems both near a critical point and over an extended region in thermodynamic space. Large density or concentration fluctuations near a system's critical point effectively mask the identity of the system and produce universal phenomena which have been well studied in simple liquid–vapor and liquid–liquid systems.<sup>1–3</sup> Such systems have provided useful model systems to test theoretical predictions which can then be extended to more complicated systems. Along various thermodynamic paths, several quantities exhibit a simple power-law dependence close to the critical point. The critical exponents describing these relationships are universal and should depend only on a universality class determined by the order-parameter and spatial dimensionality of the system. Liquid–liquid mixtures, liquid–vapor systems, and uniaxial ferromagnetic materials are thought<sup>1–3</sup> to belong to the three-dimensional Ising model which, in a renormalization group (RG) context, predicts<sup>4</sup> values for the critical exponents. These values, for the most part, agree very well with experimental results.<sup>1–3</sup> Several universal amplitude ratios have also been predicted and many have been experimentally tested, with mixed results.<sup>5</sup> A particularly powerful observation is that only two critical exponents are linearly independent, and the leading amplitudes can be interrelated using only two-scale factors.<sup>1–3</sup> Thus universality could be used with two experiments to determine all the leading critical behavior of a given system.

The heat capacity provides a delicate probe of the system near a critical point and can determine essential amplitude and exponent values. In particular, a precise measurement of the heat capacity of the liquid–liquid mixture aniline-cyclohexane at its critical composition will determine

the amplitude of the power-law divergence in the one-phase region and its effect on the universal ratio  $X$ , as well as the universal ratio of the amplitudes describing the data above and below the critical temperature.

The heat capacity has a weak divergence near the critical point that is governed by the critical exponent  $\alpha$ , different amplitudes in the one- and two-phase regions, and a critical contribution  $B_c$  due to the background heat capacity.<sup>6</sup> Correction-to-scaling terms extend the theoretical description further from the critical point.<sup>3,6</sup> While a vapor–liquid system measured along the critical isochore would have a weak divergence in the heat capacity at constant volume, a binary fluid mixture near its critical consolute point will have the same type of divergence<sup>3</sup> in its heat capacity at constant pressure when measured along a path of constant, critical composition  $x = x_c$ .

$$C_{px} = (B_{bg} + B_c) + Et + \frac{A^+}{\alpha} |t|^{-\alpha} (1 + D^+ |t|^{\Delta_1} + \dots)$$

one phase, (1a)

$$C_{px} = (B_{bg} + B_c) + Et + \frac{A^-}{\alpha} |t|^{-\alpha} (1 + D^- |t|^{\Delta_1} + \dots)$$

two phase, (1b)

where  $C_{px}$  is the temperature dependent heat capacity at constant pressure and at the critical composition,  $B_{bg}$  is the background heat capacity far from the critical temperature  $T_c$  in the one-phase region,  $t = (T - T_c)/T_c$  is the reduced temperature,  $A^{+/-}$  is the amplitude of the leading divergence,  $D^{+/-}$  is the amplitude of the first correction to scaling term, and  $\Delta_1$  is the universal exponent for the correction term. The one- and two-phase amplitudes are denoted by the + and – superscript, respectively; the background terms and the critical exponents are predicted<sup>6</sup> to be the same above and below the critical point. A linear background term,  $Et$ , arises from the regular part of the free energy and hence should be the

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: djacobs@acs.wooster.edu

TABLE I. Heat capacity data for two runs at the critical composition in aniline-cyclohexane. Temperatures are in °C, and  $\delta C_p$  is the propagated error in  $C_p$ . An\* marks the data points not used in the fit.

Temperature	$C_p$ J/(cm <sup>3</sup> K)	$\delta C_p$ J/(cm <sup>3</sup> K)	Temperature	$C_p$ J/(cm <sup>3</sup> K)	$\delta C_p$ J/(cm <sup>3</sup> K)
run 1					
28.5125	3.653	0.018	31.5246	3.299	0.018
28.5571	3.657	0.019	31.5751	3.297	0.021
28.6019	3.673	0.019	31.6248	3.288	0.028
28.6463	3.672	0.024	31.6746	3.296	0.028
28.6904	3.671	0.024	31.7252	3.288	0.029
28.7352	3.668	0.015	31.7759	3.287	0.028
28.7800	3.684	0.012	31.8258	3.280	0.023
28.8246	3.687	0.014	31.8757	3.286	0.019
28.8698	3.702	0.019	31.9264	3.287	0.015
28.9150	3.700	0.019	run 2		
28.9601	3.708	0.022	27.6290	3.591	0.014
29.0044	3.712	0.023	27.6756	3.598	0.016
29.0483	3.721	0.020	27.6756	3.598	0.016
29.0913	3.741	0.021	27.7221	3.602	0.015
29.1339	3.725	0.020	27.7685	3.608	0.013
29.1771	3.761	0.022	27.8150	3.599	0.012
29.2209	3.744	0.017	27.8607	3.608	0.013
29.2654	3.773	0.017	27.9063	3.611	0.015
29.3097	3.767	0.017	27.9518	3.613	0.023
29.3539	3.789	0.023	27.9974	3.613	0.023
29.3972	3.801	0.027	28.0435	3.613	0.019
29.4390	3.820	0.023	28.0888	3.622	0.017
29.4805	3.826	0.022	28.1342	3.623	0.014
29.5221	3.814	0.021	28.1803	3.625	0.013
29.5643	3.857	0.019	28.2724	3.632	0.014
*29.6078	3.828	0.020	28.3185	3.635	0.015
*29.6516	3.808	0.021	28.3644	3.641	0.017
*29.6959	3.748	0.021	28.4104	3.646	0.017
29.7412	3.646	0.020	28.4562	3.648	0.013
29.7877	3.540	0.021	28.5013	3.649	0.018
29.8347	3.466	0.021	28.5457	3.655	0.027
29.8824	3.433	0.021	28.5900	3.662	0.030
29.9312	3.410	0.023	28.6342	3.659	0.024
29.9804	3.396	0.020	28.6790	3.673	0.018
30.0297	3.386	0.025	28.7244	3.673	0.013
30.0297	3.386	0.025	28.7697	3.683	0.015
30.1288	3.362	0.022	28.8152	3.678	0.027
30.1785	3.367	0.018	28.8598	3.694	0.028
30.2282	3.364	0.020	28.9503	3.724	0.020
30.2780	3.354	0.019	28.9946	3.706	0.021
30.3271	3.352	0.017	29.0389	3.727	0.022
30.3760	3.355	0.020	29.0837	3.728	0.031
30.4258	3.352	0.020	29.1278	3.734	0.027
30.4755	3.347	0.022	29.1710	3.742	0.019
30.5246	3.337	0.019	29.2149	3.757	0.022
30.5735	3.337	0.018	29.2594	3.766	0.020
30.6240	3.328	0.021	29.3038	3.770	0.018
30.6748	3.327	0.021	29.3475	3.765	0.024
30.7249	3.324	0.047	29.3911	3.790	0.021
30.7744	3.316	0.050	29.4349	3.852	0.018
30.8230	3.324	0.026	29.4784	3.813	0.016
30.8721	3.317	0.024	29.5215	3.806	0.013
30.9221	3.312	0.023	29.5645	3.822	0.012
30.9716	3.309	0.035	*29.6083	3.787	0.013
31.0210	3.312	0.033	*29.6526	3.736	0.018
31.0713	3.309	0.019	*29.6972	3.751	0.022
31.1217	3.304	0.020	29.7422	3.665	0.020
31.1722	3.303	0.029	29.7887	3.516	0.025
31.2228	3.315	0.030	29.8364	3.470	0.025
31.2734	3.302	0.024	29.8846	3.428	0.018
31.3231	3.290	0.025	29.9332	3.415	0.021
31.3729	3.296	0.026	29.9821	3.404	0.024
31.4235	3.300	0.074	30.0311	3.398	0.018
31.4740	3.293	0.071	30.0795	3.384	0.017

TABLE I. (Continued.)

Temperature	$C_p$ J/(cm <sup>3</sup> K)	$\delta C_p$ J/(cm <sup>3</sup> K)	Temperature	$C_p$ J/(cm <sup>3</sup> K)	$\delta C_p$ J/(cm <sup>3</sup> K)
30.1278	3.370	0.018	31.1507	3.309	0.017
30.2242	3.370	0.021	31.2003	3.302	0.014
30.2736	3.370	0.022	31.2500	3.304	0.016
30.3232	3.364	0.019	31.3006	3.301	0.015
30.3728	3.360	0.017	31.3509	3.297	0.015
30.4218	3.351	0.020	31.4012	3.310	0.019
30.5186	3.347	0.019	31.4508	3.295	0.019
30.5685	3.351	0.017	31.5006	3.293	0.014
30.6517	3.338	0.019	31.5511	3.297	0.022
30.7009	3.336	0.024	31.6015	3.298	0.028
30.7501	3.333	0.020	31.6521	3.295	0.022
30.8002	3.328	0.016	31.7028	3.301	0.026
30.8504	3.324	0.017	31.7534	3.291	0.025
30.9005	3.320	0.017	31.8032	3.294	0.021
30.9508	3.317	0.020	31.8531	3.288	0.020
31.0003	3.311	0.019	31.9028	3.289	0.019
31.0498	3.309	0.020	31.9525	3.287	0.019
31.1003	3.310	0.023			

same above and below the critical point. The critical exponents  $\alpha$  and  $\Delta_1$  are predicted<sup>7</sup> to be  $0.110 \pm 0.003$  and  $0.51 \pm 0.03$ , respectively.

Some amplitude ratios are predicted to be true universal quantities that should be the same for all systems in a given universality class (three-dimensional Ising for bulk, liquid–liquid mixtures). The ratio of the leading, singular, heat capacity amplitude in the one-phase region to that in the two-phase region is now predicted to be  $A^+/A^- = 0.541 \pm 0.014$  by RG<sup>6</sup> and  $0.523 \pm 0.009$  by series<sup>7</sup> calculation. One can also relate  $A^+$  to the amplitude  $\xi_o$  of the correlation length in the one-phase region defined by  $\xi = \xi_o t^{-\nu}$  using two-scale-factor universality:<sup>7</sup>  $X = A^+ \xi_o^3 / k_B$ , where  $k_B$  is Boltzmann's constant, and  $\nu$  is another universal critical exponent whose value<sup>4</sup> is about 0.63. The value of  $X$  is predicted from RG<sup>8</sup> to be  $X = 0.01966 \pm 0.00017$  and from series<sup>7</sup> to be  $0.0188 \pm 0.00015$ .

These predictions have been tested in other liquid–liquid mixtures with mixed results.<sup>1–3</sup> Recent experiments measuring the heat capacity of liquid–liquid mixtures have given  $A^+/A^-$  in the range 0.52 to 0.71,<sup>9–14</sup> a value typically larger than the 0.52 value determined in liquid–vapor systems.<sup>15</sup> To determine the universal quantity  $X$ , the value of the correlation length amplitude  $\xi_o$  must be determined in a separate experiment. For the system aniline–cyclohexane, turbidity has been used to determine  $\xi_o$  with the reported values of  $\xi_o = 0.210 \pm 0.002$  nm from data<sup>16</sup> which were later reanalyzed<sup>5</sup> to find  $\xi_o = 0.245 \pm 0.005$  nm. Since  $\xi_o$  enters as the cube in  $X$ , the error in  $\xi_o$  usually dominates the error in  $X$ . A number of values of  $X$ , ranging from 0.015 to 0.027, have been determined<sup>5</sup> in a variety of systems. Recent determinations in other liquid–liquid systems have found  $X$  to be  $0.019 \pm 0.003$  in triethylamine and water,<sup>13</sup>  $0.019 \pm 0.004$  in triethylamine and heavy water,<sup>11</sup> and  $0.020 \pm 0.002$  in 3-methylpentane and nitroethane.<sup>12</sup>

The value of  $A^+$  for the aniline–cyclohexane system reported here has also been calculated from measurements of the temperature derivative of the refractive index in the one-

phase region combined with literature values for the derivative's background value, and the pressure derivative of the critical temperature, to obtain<sup>5</sup>  $A^+ = 0.017 \pm 0.004$  J/(cm<sup>3</sup>K). Values of  $A^+$  determined by refractive index tend to be small,<sup>13</sup> possibly due to an intrinsic anomaly in the refractive index, an issue which is not yet resolved.<sup>17,18</sup>

## EXPERIMENT

The heat capacity of a critical mixture of aniline and cyclohexane was measured using an adiabatic calorimeter similar to that used previously<sup>13</sup> for studies in triethylamine and water. Our calorimeter was used in a “step” mode, where a fixed energy was added to the cell and the resulting temperature step was measured. We found this improved the resolution and reproducibility in this system over the scanning mode used before. Most of the details of our calorimeter have been discussed previously and we describe the essential features below and refer the interested reader to our earlier work<sup>13</sup> for details.

A critical composition sample of aniline and cyclohexane was used. The aniline was 99.5% pure from Acros Organics, while the cyclohexane was anhydrous (water <0.005%), 99% pure from Aldrich. The mixture used in this experiment was 53.0% by weight cyclohexane with a total mass of 15.341 grams, which is a volume of 17.47 mL at the critical point. This concentration of aniline and cyclohexane is the most recently determined critical concentration<sup>19</sup> of 53.0% by weight (59.7% by volume) cyclohexane, and is the same composition used by other investigators of this system.<sup>20–22</sup> The sample preparation was done in a dry box under a nitrogen atmosphere and a small nitrogen vapor bubble was left above the fluids to keep the pressure close to one atmosphere. This system exhibits an upper consolute point around 29.73 °C.

The mixture was sealed in a cylindrical, gold-plated, copper cell with a Kalrez (DuPont perfluoroelastomer) o-ring. The cell is surrounded with a nested set of cylindri-

cal, nickel-plated, copper stages forming a thermostat. A passive radiation shield surrounds the cell and is in turn encompassed by a reference stage that is actively temperature controlled so as to be at the same temperature as the cell throughout the experiment. Two additional actively controlled stages are maintained approximately 0.1 K below the next inner stage. All the stages are attached to each other with hollow nylon stand-offs. This assembly is placed in a stage that has an ambient temperature determined by a Lauda RT-7 bath that circulates water through copper tubing soldered to the outside walls and lid. Some stirring mechanism is essential to achieve thermal equilibrium, especially in the two-phase region.<sup>11-13</sup> Our critical mixture was sloshed by rotating the entire thermostat through a 20° arc with a frequency about 0.6 Hz while current was applied to the cell heater (about 2 min) and then the thermostat was held still while waiting for equilibrium (about 7 min).

The temperature of the stages is determined by thermistors embedded through the lids and into the side wall of each stage. The cell and reference stage use matched, "ultra-stable" Thermometrics thermistors while the other stages use Yellow Springs thermistors. All of the thermistors are wired in series with a 100 kΩ Vishay standard resistor and a 1.5 V battery. The resistance of each thermistor is determined by measuring the voltage across the standard resistor and across each thermistor using a 7 1/2 digit Keithley 2001 multimeter. Each thermistor has been calibrated relative to a Guildline platinum resistance thermometer, which provides an accuracy of 10 mK in absolute temperature.

The digital multimeter measures the thermistor and standard resistor voltages and the voltage applied to the cell heater, and reports each to a Macintosh 8600 computer using a GPIB bus. The computer data acquisition and control software is written in the programming language LabVIEW and uses a software proportional integral differential (PID) controlling algorithm to maintain the reference stage temperature within 1 mK root-mean-square (rms) of the cell temperature. The program measures, controls, and records temperatures with a cycle time of 13 s. A temperature step is achieved by applying 8 mW of power to the cell heater for about 2 min, which results in an increase in temperature of the cell and fluids of about 15, with a temperature resolution around 0.1, mK. Three such steps are combined in the data presented.

Two data runs are reported here on a critical composition of aniline and cyclohexane between 27.5 and 32 °C. Each data run takes almost two full days and entails over 10 000 sets of stage temperatures, cell temperature, and cell heater voltage. Taking steps allows an average heat capacity to be determined that rounds the anomaly at the critical point. We also found it difficult to mix these fluids with such different densities when in the two-phase region; this also causes a rounded anomaly and noisy two-phase data, as others<sup>11,12</sup> have reported, when stirring was not effective. The principal raw data are the initial and final cell temperature after a constant power was applied for a measured time. The resulting energy divided by the temperature step gives the heat capacity.

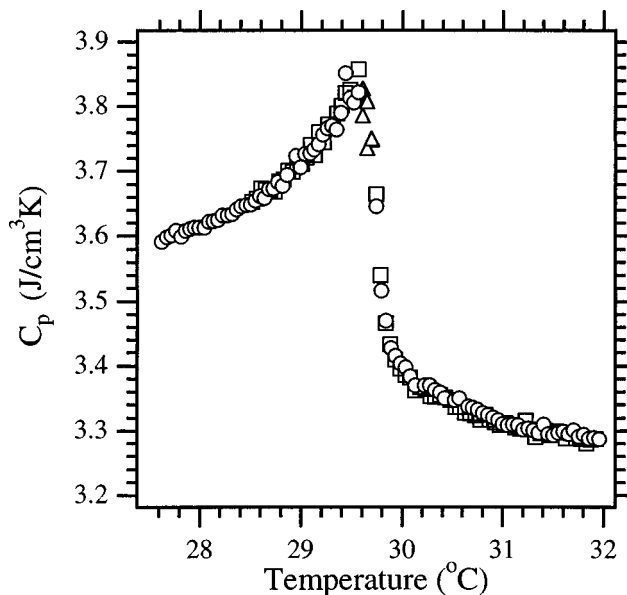


FIG. 1. The heat capacity  $C_p$  of the fluid mixture aniline and cyclohexane as given in Table I. Run 1 (squares) and run 2 (circles) are shown without their errors for clarity. The three points in each run closest to the critical point in the two-phase region are denoted with a triangle and were not used in the weighted, least squares fits.

$$C_p = \frac{\left[ \frac{V^2}{R} \right] \cdot \Delta t}{\Delta T \cdot V_0} - 1.19 \quad (\text{J}/(\text{cm}^3\text{K})), \quad (2)$$

where  $\Delta T$  is the final minus the initial cell temperature after a voltage  $V$  has been applied for a time  $\Delta t$  to the cell heater of constant resistance  $R$ ,  $V_0$  is the fluid volume, and the empty cell heat capacity has been subtracted. The heat capacities so determined from the two runs are listed in Table I and illustrated in Fig. 1. The errors represent the random fluctuations in the raw data and the propagated error from determining the equilibrium cell temperatures.

## ANALYSIS AND INTERPRETATION

A weighted, nonlinear, least squares routine was used to fit the equations to the data by finding the best set of parameters that minimizes<sup>23</sup> the reduced chi-square  $\chi^2/N$ . In the following, our quoted parameter errors are those given by the program and should be considered the  $1\sigma$  error.

In analyzing the heat capacity data shown in Table I, we use the equations

$$C_p = C_{p_0} + Et + A|t|^{-\alpha} \quad (\text{one-phase}), \quad (3a)$$

$$C_p = C_{p_0} + Et + A'|t|^{-\alpha} \quad (\text{two-phase}), \quad (3b)$$

where  $t = (T - T_c)/T_c$ . In particular, we force equal exponent values above and below the critical point as predicted by theory.<sup>6</sup> A smooth, continuous background specific heat near the critical point is expected,<sup>3,6</sup> which means the background amplitudes  $C_{p_0}$  and  $E$  are the same in the one- and two-phase region. Our data are not precise enough to warrant the inclusion of correction to scaling terms. We simultaneously fit these equations to the one- and two-phase data

TABLE II. The heat capacity data from Table I are analyzed using Eq. (3). A nonlinear, weighted least squares fit is simultaneously done in the one- and two-phase region for each run. Units on  $C_{p0}$ ,  $E$ ,  $A$ , and  $A'$ , are  $\text{J}/(\text{cm}^3\text{K})$ . The parameter errors are the one standard deviation uncertainty given by the fitting program. No error on a parameter means it was fixed. An\* marks the best fit in our judgment.

Fit #	$C_{p0}$	$E$	$A$	$A'$	$T_c$	$\alpha$	$\chi^2/N$
*1	$1.63 \pm 0.01$	-0.86	$0.269 \pm 0.009$	$0.457 \pm 0.009$	$29.732 \pm 0.002$	0.11	0.32
2	$1.63 \pm 0.01$	$-1.4 \pm 0.7$	$0.268 \pm 0.009$	$0.459 \pm 0.009$	$29.732 \pm 0.002$	0.11	0.35
3	$1.59 \pm 0.05$	-0.86	$0.30 \pm 0.06$	$0.50 \pm 0.08$	$29.732 \pm 0.002$	$0.104 \pm 0.011$	0.36

except the three, two-phase points in each run closest to  $T_c$ , where obvious rounding occurs. This still leaves 156 data points and six adjustable parameters:  $C_{p0}$ ,  $E$ ,  $A$ ,  $A'$ ,  $T_c$ , and  $\alpha$ . The parameter  $E$  should reflect the noncritical fluid behavior and has<sup>24</sup> a small negative value of  $-0.86 \text{ J}/(\text{cm}^3\text{K})$  for the composition used. Allowing  $E$  to vary does not improve the fits (see Table II) and thus we fix its value for most fits to the data. Allowing the critical exponent  $\alpha$  to vary gives a value of  $0.104 \pm 0.011$ , consistent with the theoretical value of 0.11, but doing so substantially increases the errors in the amplitudes. Because of the interdependence of the fitting parameters, it is important to fix critical exponents at their theoretical values so consistent amplitudes can be intercompared through universal ratios such as  $X$ . Thus, most fits have  $\alpha$  fixed. The critical temperatures were determined by the fits as shown in Table II. The best is fit 1, not only because the reduced chi-square is lowest, but the resulting equation is the simplest that fits the data.

TABLE III. Amplitude ratios determined from this experiment on aniline+cyclohexane [AN-CY] in comparison with other experimental and theoretical values. Five other recently measured binary liquid systems (triethylamine-water [TEA-H<sub>2</sub>O], triethylamine-heavy water [TEA-D<sub>2</sub>O], 3-methylpentane+nitroethane [3MP-NE], 2,6-lutidine+water [2,6 L-H<sub>2</sub>O], and nitroethane+cyclohexane [NE-CY]) are provided for comparison. The most recent liquid-vapor measurements in SF<sub>6</sub> are also given.

System	$A^+/A^-$	$X$
<b>Experiment</b>		
AN-CY	$0.59 \pm 0.03$	$0.0197 \pm 0.0010^a$ $0.032 \pm 0.002^b$
TEA-H <sub>2</sub> O	$0.56 \pm 0.02^c$	$0.019 \pm 0.003^c$
TEA-D <sub>2</sub> O	$0.57 \pm 0.01^d$	$0.019 \pm 0.004^d$
3MP-NE	$0.56 \pm 0.02^e$	$0.020 \pm 0.002^e$
2,6L-H <sub>2</sub> O	$0.57 \pm 0.25^f$	
NE-CY	$0.52 \pm 0.01^g$	
Liquid-vapor	$0.52 \pm 0.02^h$	
<b>Theory</b>		
Series	$0.523 \pm 0.009^i$	$0.0188 \pm 0.0002^i$
RG	$0.541 \pm 0.014^j$	$0.0197 \pm 0.0002^k$

<sup>a</sup>Using  $\xi_o = 0.210 \pm 0.002 \text{ nm}$  from Reference 16.

<sup>b</sup>Using  $\xi_o = 0.245 \pm 0.005 \text{ nm}$  from Reference 5.

<sup>c</sup>Reference 13.

<sup>d</sup>Reference 11.

<sup>e</sup>Reference 12.

<sup>f</sup>Reference 10.

<sup>g</sup>Reference 14.

<sup>h</sup>Reference 15.

<sup>i</sup>Reference 7.

<sup>j</sup>Reference 6.

<sup>k</sup>Reference 8.

The heat capacity fits given in Table II provide a consistent set of amplitude values when  $E = -0.86 \text{ J}/(\text{cm}^3\text{K})$  and  $\alpha = 0.11$ , which can be converted to the amplitudes of Eq. (1) to be:  $B_c = -0.47 \pm 0.05$ ,  $A^+ = 0.0296 \pm 0.001$ ,  $A^- = 0.0503 \pm 0.001 \text{ J}/(\text{cm}^3\text{K})$ , where all the errors are one standard deviation estimates. This value of  $A^+$  is substantially larger than the value calculated from refractive index measurements, which was also the case in triethylamine and water.<sup>13</sup> Our value of the universal ratio  $A^+/A^- = 0.59 \pm 0.03$  is consistent with experimental values determined in several binary-liquid systems recently (see Table III) and slightly larger than theoretical predictions using either renormalization group<sup>6</sup> or series<sup>7</sup> calculations.

The two-scale-factor universality ratio  $X = A^+ \xi_o^3 / k_B$  can be calculated from our value of  $A^+$  and the most recently published<sup>5</sup> value for  $\xi_o = 0.245 \pm 0.005 \text{ nm}$ , which gives  $X = 0.032 \pm 0.002$ . This value disagrees with other recent experimental determinations and with theoretical predictions (see Table III). However, using the value of the correlation length determined in the original<sup>16</sup> paper,  $\xi_o = 0.210 \pm 0.002 \text{ nm}$  when  $\nu = 0.633$  and  $\gamma = 1.22$ , gives  $X = 0.0197 \pm 0.008$ , which agrees closely with the theoretically predicted and experimentally observed values.

## CONCLUSION

The heat capacity of the binary liquid mixture aniline-cyclohexane has been measured near its upper critical consolute point using an adiabatic calorimeter. The critical exponent  $\alpha$  was determined to be  $0.104 \pm 0.011$ , consistent with theoretical predictions. When  $\alpha$  was fixed at its theoretical value of 0.11, our values of  $A^+ = 0.0296 \pm 0.001$  and  $A^- = 0.0503 \pm 0.001 \text{ J}/(\text{cm}^3\text{K})$  gave a ratio of  $A^+/A^-$ , consistent with previous experiments and theory, but the value of  $A^+$  was inconsistent with the value calculated from refractive index measurements<sup>5</sup> in this aniline and cyclohexane system and inconsistent with the reanalyzed value<sup>5</sup> of the correlation length  $\xi_o = 0.245 \pm 0.005 \text{ nm}$ , if  $X$  is a universal ratio. However, our value for  $A^+$  is consistent with the originally published<sup>16</sup> value of  $\xi_o = 0.210 \pm 0.002 \text{ nm}$ .

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