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Heat capacity and thermal expansion anomalies in the nitromethane–1-butanol mixture near its upper critical point

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The heat capacity per unit volume C_p and density ρ of the nitromethane-1-butanol critical mixture near its upper consolute point are determined in this work. C_p data are obtained at atmospheric pressure as a function of temperature in the one-phase and two-phase regions, using a differential scanning calorimeter. The suitability of DSC for recording C_p as a function of T in the critical region is confirmed by measurements of the nitromethane-cyclohexane mixture, the results being quite consistent with reported data. By fitting the C_p data in the one-phase region, the critical exponent α is found to be 0.110 ± 0.014—and hence consistent with the universal accepted value—and the critical amplitude $A^+=0.0606\pm0.0006\ \mathrm{J\,K^{-1}\,cm^{-3}}$. ρ data were only obtained in the one-phase region, using a vibrating tube densimeter. The amplitude of the density anomaly was found to be $C_1^+=-0.017\pm0.003\ \mathrm{g\,cm^{-3}}$, which is moderately low in spite of the large difference between the densities of the pure liquids. The thermodynamic consistency of the A^+ and C_1^+ values was examined in relation to the previously reported value for the slope of the critical line dT_c/dp. The results of this analysis were consistent with previous work on this matter.

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I. INTRODUCTION

The most fascinating feature of critical phenomena is universality since it implies that systems of a different physical nature exhibit similar behavior near the critical point. Liquid mixtures in the vicinity of the liquid-liquid critical point, pure liquids near the gas-liquid critical point, and uniaxial ferromagnetic materials near the Curie point all belong to the universality class of the three-dimensional Ising model [1,2]. This endows the experimental study of systems such as pure liquids or liquid mixtures with considerable interest as it allows theoretical results to be checked and experimentally less readily accessible systems to be addressed. At the microscopic level, universality originates from the long-range nature of the fluctuations of the order parameter associated with the critical-point transition. It is now assumed that the order parameter for the liquid-liquid transition in binary mixtures is concentration [3]. Thus, a mixture in the critical region behaves as a series of clusters of macroscopically fluctuating concentration in such a way that microscopic details of short-range intermolecular interactions lose significance at the expense of universality. The mean size of the clusters is quantified in terms of the correlation length ξ, which diverges to $+\infty$ at the critical point [1,2] and, therefore, is much greater than the range of intermolecular interactions near enough the critical point.

Macroscopic properties reflect these underlying microscopic features and some exhibit anomalous behavior as a result [1,2]. Thus, in the vicinity of the liquid-liquid critical point, the isobaric heat capacity per unit volume C_p exhibits a positive anomaly (it diverges to $+\infty$) along an isobaric path according to

$$C_p=B+Et+\frac{A^\pm}{\alpha}t^{-\alpha}(1+D^\pm t^{\Delta_1}+\cdots), \tag{1}$$

where $t=|T-T_c|/T_c$ denotes the reduced temperature and T_c the critical temperature. The first two terms on the right-hand side of Eq. (1) represent the background contribution, which dominates far away from the critical point, and all others the critical contribution, which becomes important as the critical point is approached. This last encompasses several terms, namely, the power-law divergence term, which is characterized by the critical amplitude $A^\pm$ (where $+$ refers to the one-phase region and $-$ to the two-phase region) and by the critical exponent α. It is well established that critical exponents are universal—they are the same for all systems belonging to the same universality class—as obtained from both experiments and theory. Specifically, the three-dimensional Ising model provides predictions for the critical exponents in the renormalization group (RG) context, which agree closely with experimental results. Thus, the accepted value of α is 0.110 [1,2]; moreover, recent RG calculations [4,5] gave a more precise value (0.1099 ± 0.0007). The other terms in Eq. (1) are corrections for pure power-law behavior called correction-to-scaling terms and are only relevant at temperatures far from T_c. Equation (1) only shows the first correction-to-scaling term, which encompasses the critical amplitude $D^\pm$ and the critical exponent Δ_1 (estimated to be 0.504 ± 0.008 from RG calculations [4,5]).

Although it takes a finite value at the critical point, the temperature dependence of the density ρ—i.e., the thermal expansion—reflects the behavior of the isobaric thermal expansivity α_p, which exhibits an anomaly (positive or negative) with the same critical exponent α as C_p [1,2]. Therefore, ρ is expressed as follows:

$$\rho=\rho_c+Ct+C_1^\pm t^{1-\alpha}(1+C_2^\pm t^{\Delta_1}+\cdots). \tag{2}$$

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Again, the first two terms on the right-hand side of the equation represent the background contribution and the others the critical contribution; also, ρ_c equals ρ at $T=T_c$.

Although available experimental evidence [1,2,6–28] confirms that the behavior predicted by Eqs. (1) and (2) is accurate, there are still some obscure aspects in the relationship between C_p and ρ near the critical point, particularly as regards the thermodynamic consistency of these properties. Let us start from the generalized Mayer relation

$$C_p - C_v = T\alpha_p\left(\frac{\partial p}{\partial T}\right)_v, \tag{3}$$

where C_v denotes the isochoric heat capacity per unit volume. Based on the postulates of Griffiths and Wheeler [29], C_v is negligible relative to C_p in the immediate vicinity of the critical point as it takes a finite value at it. Also, $(\partial p/\partial T)_v \rightarrow (\partial p/\partial T)_c$ as the critical point is approached—the latter quantifying the slope of the critical line, which is usually expressed as dT_c/dp. Under these conditions, Eq. (3) predicts that dT_c/dp will dictate the sign of the α_p anomaly: positive (divergence to $+\infty$) when $dT_c/dp>0$ and negative (divergence to $-\infty$) when $dT_c/dp<0$. Based on these factors, Eq. (3) relates A^+ to C_1^+ as follows:

$$\frac{A^+}{\alpha} = \pm\frac{(1-\alpha)C_1^+}{\rho_c(dT_c/dp)}, \tag{4}$$

where the plus sign is applied to lower consolute points and the minus sign to upper consolute points. Jacobs and Greer [30] checked the quantitative accuracy of Eq. (4) from reported C_p, ρ, and dT_c/dp data for five different critical mixtures and concluded that the equation was rather inaccurate in most cases. The large number of approximations required to derive it precludes identifying the origin of the inaccuracy. Assuming C_v to be negligible relative to C_p can introduce some error as C_v may exhibit a $t^{-\alpha}$ anomaly in the experimentally accessible region [31–33]. Deleting correction-to-scaling terms in Eqs. (1) and (2) can also lead to error. Another potential source of error is the high uncertainty in the experimental determination of C_1^+; in some cases, the density anomaly is so small that it goes unnoticed at the measurement precision level.

In summary, the sources of error affecting the thermodynamic consistency of C_p and ρ, and the extent of their effects, are unclear. Additional information with a view to rigorously establishing the validity range for Eq. (4) is therefore required. In this paper, we report C_p and ρ data for the nitromethane–1-butanol critical mixture at atmospheric pressure as a function of temperature near its upper consolute point. C_p data were obtained in both the one-phase and two-phase regions whereas ρ data could only be measured in the one-phase region. The experimental results were used to calculate the critical amplitudes A^+ and C_1^+ by fitting to Eqs. (1) and (2); also, the reported value of dT_c/dp [34] was used to examine the relationship between both in the light of Eq. (4). The methodology used to obtain A^+ was checked against previously reported results for the nitroethane-cyclohexane system [18].

II. EXPERIMENT

A. Sample preparation and chemicals

Nitromethane (99% pure) and 1-butanol (over 99.5% pure) were obtained from Fluka, while nitroethane and cyclohexane, in purity above 99.5% and 99.9%, respectively, were purchased from Aldrich. Nitromethane, nitroethane, and 1-butanol were dried over Fluka molecular sieves of 4 nm mesh size and degassed prior to use. On the other hand, cyclohexane was used as received. Critical mixtures were studied according to previously reported critical composition x_c values (0.582 for the nitromethane–1-butanol mixture [35] and 0.453 for the nitroethane-cyclohexane mixture [18]). They were prepared under a nitrogen atmosphere, using a Mettler AE-240 balance, and vigorously stirred prior to placement in the measuring cells. We determined T_c in our laboratory from turbidity measurements and obtained a value of 290.90 ± 0.01 K for the nitromethane–1-butanol mixture and 296.62 ± 0.01 K for the nitroethane-cyclohexane mixture, which deviated from the previously reported values [18,35]. These shifts in T_c can be ascribed to the presence of impurities, which are known to affect the critical composition to a much lesser extent [36].

B. Heat capacity per unit volume

Isobaric heat capacities per unit volume were obtained by using a Setaram micro DSC II differential scanning calorimeter. This instrument and the underlying experimental methodology (DSC) are described elsewhere [37]. The two measuring cells of the calorimeter were filled with 1 ml of sample and arranged in such a way that no vapor phase could contact the detection zone of the calorimeter. One of the cells held a reference substance (1-butanol in the present measurements) and the other the critical mixture. Working in a down-scan mode, the calorimetric signal is the differential heat flow associated with a temperature decrease. We used a scanning rate of $0.01\ \mathrm{K\,min^{-1}}$, which afforded a reproducibility of ±0.02 mW in the signal. Under these conditions, the reproducibility in the C_p measurements was estimated to be $\pm0.0002\ \mathrm{J\,K^{-1}\,cm^{-3}}$—somewhat poorer in the immediate vicinity of the critical point owing to the difficulties inherent to the experimentation in the critical region [1,2]. The procedure was less reliable in the two-phase region as the calorimeter design did not allow the mixture to be stirred. The temperature was measured to within ±0.002 K with a platinum resistance thermometer. Signals were calibrated against two substances of known heat capacity (viz. 1-butanol and toluene).

Normally, it is high-resolution adiabatic scanning calorimetry (ASC) that is employed for studying the heat capacity of mixtures near the liquid-liquid critical point. The main advantage of these calorimeters with respect to DSC lies on the possibility of stirring the samples for the former (difficult to implement for the latter), which produces important data in

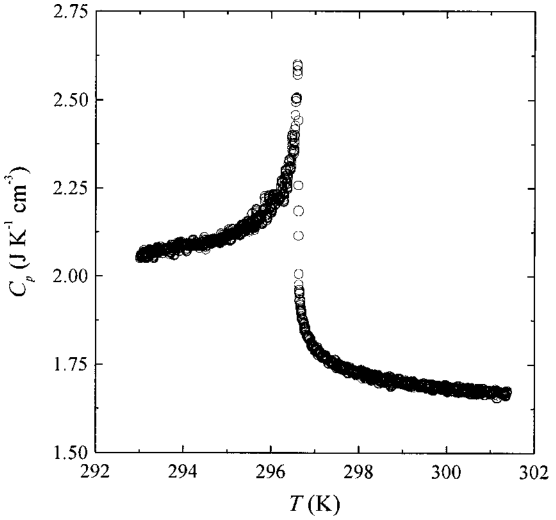

FIG. 1. Heat capacity per unit volume C_p of nitroethane-cyclohexane in the critical region along an isobaric path.

the two-phase region. This factor together with the lower scanning rates provided by ASC with respect to DSC, make the former significantly more effective than the latter for studying C_p near the liquid-liquid critical point. Nevertheless, DSC has been proved to be useful for the measurement of data in the one-phase region [38]—particularly, with a view to determining A^+. In this work, we assessed the suitability of our DSC calorimeter with the nitroethane-cyclohexane mixture, for which previously reported data existed (Thoen, Hamelin, and Bose [18]). The C_p values obtained over the temperature range 293.02–301.39 K are shown in Fig. 1. They were fitted to Eq. (1) using approach (b) as described in Sec. III A; the final results are contained in Table I. The value of $A^+ = 0.0291 \pm 0.0008\ \mathrm{J\,K^{-1}\,cm^{-3}}$ was quite similar to that previously reported by Thoen, Hamelin, and Bose ($0.0282 \pm 0.0004\ \mathrm{J\,K^{-1}\,cm^{-3}}$). This validates our calorimeter and confirms that DSC is, for some purposes, a reliable choice for determining C_p near the liquid-liquid critical point.

C. Density

Density values were obtained by using an Anton-Paar DSA-48 vibrating tube densimeter. The experimental procedure is described elsewhere [39] and has previously been employed to study density near the critical point [24,26]. The densimeter was calibrated with water and *n*-octane as density standards, and the temperature was measured to ±0.002 K with a platinum resistance thermometer. The density measurements thus obtained were reproducible to within about $\pm 0.000\,005\ \mathrm{g\,cm^{-3}}$.

TABLE I. Fitting parameters of Eq. (1) and standard deviation *s* for a nitroethane-cyclohexane critical mixture. *B*, *E*, and A^+ are in $\mathrm{J\,K^{-1}\cdot cm^{-3}}$. The fixed value of α is 0.110.

B	E	A^+	α	D^+	s
1.248	0.30	0.0291	Fixed		0.005
±0.011	±0.14	±0.0008			
$T_c = 296.618 \pm 0.002$ K					

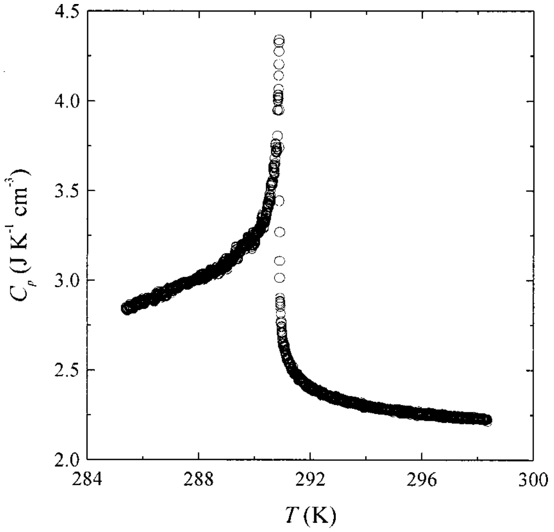

FIG. 2. Heat capacity per unit volume C_p of nitromethane–1-butanol in the critical region along an isobaric path.

III. RESULTS AND DISCUSSION

A. Fitting procedures and results

Figure 2 shows the C_p values obtained over the temperature range 285.40–298.37 K. Although the standard procedure involves simultaneous fitting to data of both the one-phase and two-phase regions [10–13], we have decided to eliminate the latter from the analysis owing to their limited precision (see experimental section). Fitting to Eq. (1) was carried out using three different approaches where *B*, *E*, A^+, and T_c were always used as fitted parameters. In approach (a) no correction-to-scaling terms were used and the critical exponent α was used as a fitted parameter. In approach (b), no correction-to-scaling terms were employed and α was fixed at its accepted value. Finally, in approach (c), the first correction-to-scaling term was used and the critical exponents α and Δ_1 were fixed at their accepted values. The values of the coefficients together with the standard devia-

TABLE II. Fitting parameters of Eq. (1) and standard deviations *s* for nitromethane–1-butanol critical mixture. *B*, *E*, and A^+ are in $\mathrm{J\,K^{-1}\,cm^{-3}}$. The fixed value of α is 0.110.

Fit	B	E	A^+	α	D^+	S
(a)	1.39	0.60	0.061	0.110		0.005
	±0.13	±0.17	±0.005	±0.014		
(b)	1.387	0.60	0.0606	Fixed		0.005
	±0.012	±0.12	±0.0006			
(c)[a]	1.36	0.4	0.062	Fixed	0.1	0.005
	±0.05	±0.4	±0.002		±0.3	
$T_c = 290.898 \pm 0.002$ K						

[a] Δ_1 is fixed at its RG value (0.504).

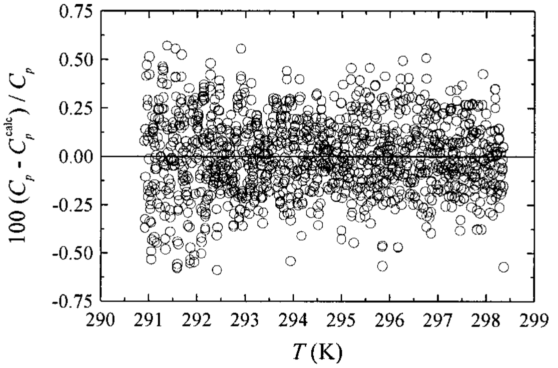

FIG. 3. Residuals for the heat capacity per unit volume C_p of nitromethane–1-butanol in the one-phase critical region calculated from Eq. (1) with fitting approach (b).

tions of the fits were obtained by using the Marquardt's algorithm for nonlinear equations [40] during the optimization process and they are shown in Table II. The attained T_c (the same for all approaches) was identical to that obtained from a preliminary simultaneous fitting to data of the one-phase and two-phase regions. The inclusion of the correction-to-scaling term resulted in no improved description of the experimental results, so it was insubstantial. Approach (a) was useful because it allowed α to be determined; however, the most reliable value for A^+ was obtained by using approach (b), as fixing α at its universal value avoided correlation between parameters [1]. Figure 3 shows the residuals of the fittings obtained using approach (b). As can be seen, there was very strong consistency between experimental data and those calculated both near and away from T_c. This consistency as well as the quality of the data can be checked from a bilogarithmic representation of the critical contribution $C_p - B - Et$ against t in a temperature range covering 1 K above T_c (Fig. 4). A straight line with slope -0.11 represents the power-law behavior predicted by Eq. (1).

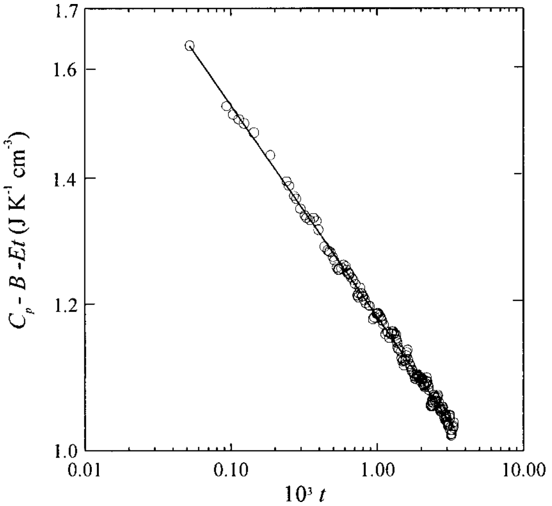

FIG. 4. Bilogarithmic representation of the critical contribution to the heat capacity $C_p - B - Et$ versus the reduced temperature t in a range of 1 K above T_c. The slope of the full curve is -0.11, in accordance with Eq. (1).

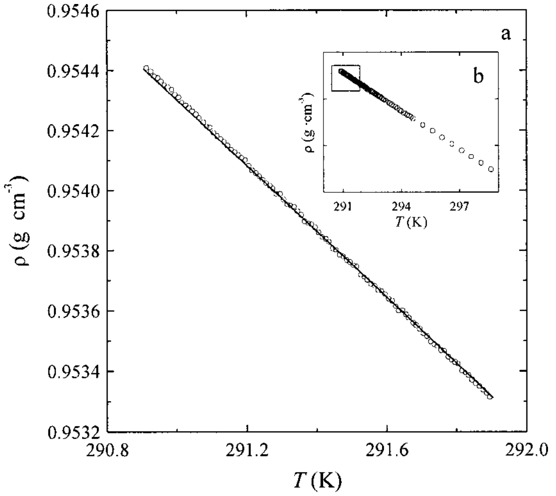

FIG. 5. Density ρ of nitromethane–1-butanol in the one-phase critical region along an isobaric path. (a) Data 1 K above the critical temperature. (b) Data over the whole measuring range. Values calculated from Eq. (2) with fitting approach (b).

Figure 5 shows the ρ data obtained for the nitromethane–1-butanol mixture over the temperature range 290.91–298.64 K. The density anomaly could not be observed on this scale [see Fig. 5(b)]. The results of the fitting to Eq. (2) can help to detect it. Thus, two types of fitting including (a) background and critical terms (with no correction-to-scaling terms) or (b) background terms alone were used. In both cases, T_c was fixed to the value obtained in the fitting of heat capacity data (see Table II). Because of the difficulty inherent in detecting small anomalies, we chose to fix α in (a). The purpose of fitting (b) was to determine the relative significance of the critical term. As can be seen from Table III, fitting approach (a) did not significantly reduce the standard deviation with respect to (b); however, the inclusion of the critical term is justified by the graphs of Figs. 4(a) and 5. Figure 5(a) shows the experimental ρ values obtained 1 K above T_c, as well as those provided by approach (b). The negative deviation in the calculated values from the experimental ones in the immediate vicinity of T_c reveals a positive anomaly in the isobaric thermal expansivity, which was to be expected for this system ($dT_c/dp > 0$ [34]). Figure 6 confirms the inefficiency of approach (b) in the immediate vicinity of T_c in terms of residuals and justifies the inclusion of the critical term (random residuals both near and away from T_c).

TABLE III. Fitting parameters of Eq. (2) and standard deviation s for a nitromethane–1-butanol critical mixture. ρ_c, C_0, and C_1^+ are in g cm^{-3}. The fixed values of α and T_c are 0.110 and 290.898±0.002 K, respectively.

Fit	ρ_c	C_0	C_1^+	α	s
(a)	0.954 428	−0.293	−0.017	Fixed	0.000 010
	±0.000 004	±0.007	±0.003		
(b)	0.954 412	−0.3185			0.000 013
	±0.000 004	±0.0005			

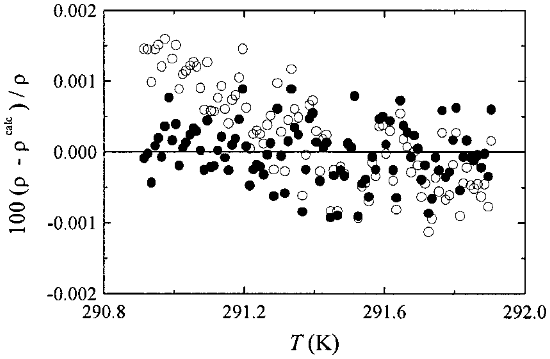

FIG. 6. Residuals for the density ρ of nitromethane–1-butanol in the one-phase critical region calculated from Eq. (2) with (●) fitting approach (a) and (○) fitting approach (b).

B. Analysis and interpretation of the results

The value of the critical exponent α obtained from the C_p data for the nitromethane–1-butanol mixture (0.110 ± 0.014) is consistent with the universal accepted value. The anomaly in C_p ($A^+ = 0.0606 \pm 0.0006\ \mathrm{J\,K^{-1}\,cm^{-3}}$) is relatively large as A^+ typically ranges from 0.001 to 0.1 $\mathrm{J\,K^{-1}\,cm^{-3}}$. Two-scale factor universality [1] relates the behavior of C_p with that of the correlation length. Thus, a dimensionless parameter $X = A^+(\xi_0^+)^3/k_B$ is established where k_B denotes the Boltzmann constant and ξ_0^+ the critical amplitude of the correlation length. The accepted value for X—around 0.019 [13]—has been derived from theoretical calculations and experimental determinations. Accordingly, the predicted value of ξ_0^+ for this system is 1.63 ± 0.06 Å, which should be confirmed from light scattering experiments.

The amplitude of the density anomaly is $C_1^+ = -0.017 \pm 0.003\ \mathrm{g\,cm^{-3}}$, which can be considered to be moderately small taking into account that C_1^+ can be significantly larger ($C_1^+ = -0.06\ \mathrm{g\,cm^{-3}}$ for the methanol-cyclohexane mixture [22]). The consistency of the large value of A^+ with that of C_1^+ in the context of Eq. (4) can only be ascribed to a very small value of dT_c/dp. In fact, dT_c/dp for this system is $4.6 \pm 0.7\ \mathrm{mK\,bar^{-1}}$ [34], which is very small—the typical values for this quantity range from -30 to 30 $\mathrm{mK\,bar^{-1}}$. Using this datum in Eq. (4) yields $C_1^+ = -0.027 \pm 0.008\ \mathrm{g\,cm^{-3}}$, which exceeds, in absolute value, its experimental counterpart. This might be due to the fact of neglecting C_v, which produces enhanced $|C_1^+|$ values in the calculation. In summary, Eq. (4) provides an acceptable qualitative prediction and a modest quantitative prediction. This result is consistent with that found from the analysis of Jacobs and Greer [30]. One other fact to be taken into account concerning the density anomaly is the relationship between its amplitude and the density difference between the two pure liquids $\Delta\rho$. Hamelin *et al.* [41] hypothesized that C_1^+ must be proportional to $\Delta\rho$; however, the existing data showed no evidence of such a correlation [30]. The large value of $\Delta\rho$ for the nitromethane–1-butanol mixture ($\rho_{\mathrm{nitromethane}} = 1.129\,58$ [35] and $\rho_{\mathrm{1\text{-}butanol}} = 0.805\,73$ [35] at 298.15 K) along with the moderately small density anomaly found in this work appear to contradict a proportionality relationship between C_1^+ and $\Delta\rho$.

IV. SUMMARY AND CONCLUSIONS

In this work, the behavior of C_p and ρ for the nitromethane–1-butanol critical mixture was studied with a view to expanding the available knowledge about the critical behavior of liquid mixtures. The anomaly in C_p for this mixture is relatively large and the value of the critical exponent α is quite consistent with the universal accepted value. By contrast, the anomaly in ρ is moderately small. This can be ascribed to a small value of dT_c/dp in accordance with Eq. (4). Although this equation performs well in qualitative terms, quantitative consistency is only modest, as found in previous studies. The large difference between the densities of the pure liquids in this mixture provides additional evidence against the proposed proportionality between $\Delta\rho$ and C_1^+.

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