Phase Behavior of the Acetonitrile + Butane System at Temperatures from 311.40 K to 436.82 K

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Visual observations of the co-existing phases over the temperature range from 311.40 K to 436.82 K and up to gas−liquid critical pressure for acetonitrile + butane mixtures have been made. Nine gas−liquid critical points, dew and bubble pressures, and densities at 20 K intervals from 333.15 K to 433.15 K and $p-T-\rho-x$ relationships for three-phase liquid−liquid−vapor equilibrium were established. This system forms a minimum boiling azeotrope up to the gas−liquid critical point. On the p,T projection, the three-phase line terminates in a liquid−liquid upper critical end point, from which the liquid−liquid critical curve (of upper critical solution temperatures) starts vertically to high pressures.

Introduction

Phase equilibria for polar + nonpolar mixtures are hard to predict from pure component data. In this respect, basic experimental measurements of such systems still are necessary. These highly nonideal mixtures show interesting phenomena and properties such as an interrupted gas−liquid critical curve, positive azeotropy, a liquid−liquid immiscibility gap, and a large positive excess molar Gibbs energy, and they are sensitive to intermolecular forces, giving a severe test for the theoretical concepts associated with equations of state, mixing rules, etc.

Aliphatic C_4 hydrocarbons in binary mixtures with strongly polar acetonitrile are of special scientific and industrial interest. The value of the dipole moment for the acetonitrile, as an average from available literature data, is 3.95 D (Warowny, 1994). Straight distillation of the C_4 mixtures cannot provide a good separation, but extractive distillation using a polar solvent can readily result in practically complete separation for industrial needs (e.g. synthetic rubber). Acetonitrile is one of the best extractive distillation solvents for the separation of close boiling paraffinic and olefinic hydrocarbons (Black, 1959; Laird and Howat, 1990). The knowledge of critical phenomena, especially in the vicinity of the critical point of the solvent, has recently become an area of increased research activity (Gude and Teja, 1994).

Rodriguez and McLure (1983) established the gas−liquid critical loci for acetonitrile with the C_4−C_{11} *n*-alkanes and presented $p-T$ and $T-x$ projections of the gas-liquid critical loci which indicate the presence of a minimum temperature, except for butane. On the other hand, azeotropes were reported for acetonitrile + propane (Gould, 1973) and for acetonitrile + butane (Gorshkov et al., 1975). In order to resolve the doubt as concerns the existence of the minimum boiling azeotrope up to the gas−liquid critical loci, measurements of the dew and bubble points for 20 isopleths (loci of constant mole fraction) and measurements of the 9 critical points in the vicinity of the critical point of butane have been performed.

For the present system, a limited amount of information is available concerning the behavior of the vapor−liquid equilibrium (Torres et al., 1981; Torres-Robles, 1980; Andreescu et al., 1975; Black, 1959), and the critical data. The gas−liquid critical $p-T-x$ locus for two mixtures was published by Rodriguez and McLure (1983). The bubble point pressure data were reported by Torres-Robles (1980) at three temperatures (322.04 K, 333.15 K, and 344.26 K), and as graphical information given by Black (1959) at two temperatures (324.82 K and 338.71 K). There are no published data for the dew point pressure that we know of. The upper coexistence temperatures (UCXT) were reported by Torres-Robles (1980) at two temperatures (322.04 K and 333.15 K), by Evans and Sarno (1967) at 333.15 K, and by Pavlov et al. (1970) using a graphical form (for an unknown pressure) with temperature−weight fraction axes. The three-phase liquid−liquid−vapor (3F-LLV) equilibrium data of this work extend both the solubility data and the experimental information for the UCST (upper critical solution temperature) data presented by McLure et al. (1982) for the binary mixtures of acetonitrile (C_2H_3N) with C_5 and higher *n*-alkanes.

Experimental Section

Acetonitrile samples were the same as those used in the previous work of Warowny (1994), while butane of research grade (with a stated purity of at least 99.9 mole %) was supplied by Fluka A.G. No attempts were made at further purifying the butane. All samples were, however, degassed and dried over molecular sieves.

The apparatus, filling procedure, and method of the measurements used in this study have been described in detail elsewhere (Warowny, 1994) and for the purpose of this paper are only summarized. The liquid acetonitrile and liquid butane were freed from traces of air and other noncondensable gases by distilling it several times back and forth from one liquid nitrogen trap to another under dynamic high vacuum, and the residual gas was pumped off continuously. The degassed substances were distilled into glass capillary ampules which were flame sealed and weighed. One or two ampules with acetonitrile and butane of known masses were placed into a crusher joined with a high-pressure Pyrex glass tube equipped in a special valve from one side and sealed from the other end. Before the ampules were broken, the system (crusher−glass tube) was evacuated. The sealed end of the glass tube was kept frozen by the liquid nitrogen to transfer the whole amount of the substance(s) from the crusher. Finally, the special valve was closed and the glass tube was inverted and connected to the pressure systems (the other vacuum, generating, and measurement). The top part of the tube was kept frozen until mercury, used as an intermediate fluid, was introduced to the glass tube. The double-wall empty thermostat, equipped with windows on both the front and back, with back lighting was moved down on its rails in order to cover the vertical mounted glass tube. Finally, the thermostat was filled with the silicone oil.

S0021-9568(95)00242-1 CCC: $12.00

Determinations of temperature, pressure, and density were carried out for samples confined by mercury and the formation of a new phase(s) was observed visually in the oil bath. Equilibrium between phases was attained by stirring using a 1.59 mm ($^1/_{16}$ in.) steel ball placed inside the glass tube, moved up and down by means of a magnet. Stirring was stopped when measurements were taken. Near the upper part of the glass tube, where the studied substances rested, the temperature was kept constant to better than 0.005 K. Four to eight levels were measured: reference level, level of mercury, height of mercury meniscus, interface levels and their menisci, and level of the steel ball. Heights were related to the sealed top of the glass tube (reference level). Level readings were made with a Wild KM-305 cathetometer and were precise to within ±0.01 mm. The volumes were calculated from the dimensions of the glass tube. Volume corrections were made for the shape of the meniscus levels, which were assumed to be elliptic. The shape of the meniscus depended on temperature and pressure. Also, corrections for the variation of the internal radius of the tube with pressure (Warowny, 1994) and with temperature were added. The linear thermal expansion coefficient for Pyrex glass 3 × K^{-1} (Touloukian and Ho, 1977) taken as an average at the measured temperature range was used. The volume of the steel ball was subtracted from the total volume or from the volume of the lower phase for the 3F-LLV equilibrium measurement. The results of this experiment are sets of isopleths at constant temperature.

The boundaries of the liquid−vapor, liquid−liquid, and liquid−liquid−vapor regions were determined by straightforward visual observation. The procedure for measuring the dew and bubble points was described earlier by Warowny (1994). The bubble point was found by visual observation of the appearance of the first vapor bubble in the tube; then the volume was increased to the dew point, when the last liquid was visible. Establishing the correct volume for the dew point of the mixture was a difficult task. For a binary system with three phases in equilibrium at a specified temperature, the number of degrees of thermodynamic freedom is zero. Volumes for the three-phase equilibrium (measured only for one mixture $x = 0.06051$ at 333.15 K) were determined by visual inspection of their interface levels, with the inverted meniscus for the gas phase. Liquid−liquid equilibrium below the UCEP point was determined by starting the experiment from the liquid−liquid−vapor equilibrium for a given isopleth. The temperature was increased and the volume was adjusted until the last drop of one of the liquid phases (upper or lower) and the last bubble of the vapor phase were visible. Temperature, pressure, reference level, mercury level, and level of the steel ball were recorded. The measured point was still a three-phase point, so for the recorded temperature, the pressure was cross-checked with the earlier established pressure for 3F-LLV equilibrium. The solubility boundary (from pressure slightly above the 3F-LLV equilibrium to high pressures) was found by observing the appearance of the first traces the second liquid phase as a function of temperature while the pressure was adjusted.

The following procedure was applied to the measurements of the critical locus for mixtures. Starting a few degrees below the critical temperature of butane, a critical region was found by observation of the dew and bubble points with increasing temperature. Temperature, pressure, and volume were adjusted until a flat interface meniscus was approximately in the mid-volume of the fluid. Small changes in temperature and pressure caused the meniscus to change to a brown opalescent fog. The mixture was stirred by moving a steel ball up and down the tube with a magnet, and measurements were taken when the moving opalescence ring was stopped at some level. It was believed that equilibrium near the critical point was reached. Disturbing the temperature and returning to the previous value resulted in reappearance of the meniscus or the opalescence ring at almost the same level. Small variation in temperature and pressure, or even only in pressure, established the critical opalescence at a slightly different level than before. The above procedure was repeated three to four times for the measurement of sets of the temperature, pressure, and volume in order to determine the correct values for the critical point, when the vapor and liquid volumes are equal.

Masses were determined with an accuracy of ±0.000 02 g. In the worst case (3−5 mg of one weighed compound), the mixture was prepared with an accuracy of ±0.0005 in the mole fraction and the accuracy was decreased to ±0.0007 mole fraction by errors in weighing, by correction for weighed air in the empty ampules, and by errors made during fillings of the glass tube. The volume of the tube was calibrated with an uncertainty of ±0.15%. The accuracy decreased to ±0.25% for the levels in the area where the tube changed its inner diameter from 3.27 mm to 8.29 mm (Warowny, 1994). The largest volume uncertainty was for measurements of the three-phase equilibrium, which had several meniscus levels, including inverted and different shapes. Density, as a ratio of mass to volume, was estimated to be within ±0.4%. The worst accuracy of density determination was for the dew point measurements, and as critical point was approached where $d\rho/dT$ increased dramatically. The contributions of all sources of error to the density measurements led to the conclusion that densities were determined with an accuracy of better than ±0.5%.

The temperature was measured with a platinum resistance thermometer calibrated against a primary standard at the NPL, Teddington, England, on the IPTS-68. Near the glass tube at the middle of the measured level, the temperature was continuously monitored using a digital Hewlett-Packard quartz thermometer. The maximum uncertainty in the measured temperature was ±5 mK (Warowny, 1994), but overall the maximum uncertainty was lowered to ±20 mK because of unidentified systematic errors of the instruments. The combined estimated accuracy of ±0.05% was associated with the pressure measurement system (Warowny, 1994). However, considering the systematic errors of the instruments, we claimed the accuracy ±0.06%. The capillary ampules were free of air as a sufficient degassing of the samples is a crucial problem particular to this method, since the presence of residual volatile gases leads to large errors in pressure determination. Unfortunately, some residual air was introduced into the glass tube when the hand-operated mercury pump displaced mercury from the metallic part of the system. Compression of the fluid to the bubble point volume makes a difference between dew and bubble point pressures (for one of the worst cases, as for the butane, even to 5 kPa). The same amount of impurity makes an error in the dew point pressure of butane within the stated accuracy of the measurement. For all mixtures, the boiling pressures were corrected for the compression effect. Experimental accuracies of the dew and bubble point pressures were estimated to be less than ±0.1% and ±0.2%, respectively. Residual air had an insignificant effect on the density measurements.

The experimental accuracy in the determination of the critical temperatures is estimated to be ±0.05 K. Accuracy of the critical pressure is taken as an avarage from accuracies of the dew and bubble pressures. For example, it is claimed to be ±6 kPa for 4000 kPa.

Table 1. Vapor Pressure and Saturated Densities for Butane

	p^s/kPa			ρ^D/kg m^{-3}		ρ^B/kg m^{-3}	
	dew	bubble		dew		bubble	
T/K	this work	this work	lit.[a]	this work	lit.[a]	this work	lit.[a]
313.14	378.3			9.38			
313.15			379.5		9.43		554.7
323.14	495.6	500.9		12.23		540.9	
323.15			497.0		12.26		542.1
333.14	638.2			15.69			
333.14	637.9	641.5		15.80		529.1	
333.15			639.8		15.73		528.9
343.14	809.9			19.94			
343.15			810.9		19.99		
353.14	1013.0	1018.1		25.15		499.7	
353.15			1013.4		25.18		500.1
363.15	1250.2			31.47			
363.15			1250.2		31.52		
373.15	1527.3	1530.6		39.38		466.2	
373.15	1527.2	1531.4		39.35		466.3	
373.15			1526.1		39.35		466.8
383.15			1843.1		49.06		
383.15	1845.4			49.23			
393.15			2208		61.55		425.5
393.15	2210	2215		61.49		425.3	
393.16	2211			61.78			
413.15			3109		103.6		364.5
413.15	3113	3116		103.6		363.7	
413.16	3112	3116		103.8		364.9	

Data of Haynes and Goodwin (1982) were interpolated.

Results and Discussion

Data are presented in the form of tables and in diagrams. Discussion is restricted to outlining the experimentally observed behavior of phase equilibria in the x acetonitrile − x) butane system, where x is the mole fraction. Van Ness et al. (1973) paid attention to the importance of using the same materials and apparatus in measurements of both vapor pressure (p^S) of the pure components and the vapor−liquid equilibrium of their mixtures. They examined all the factors that played a part in the various reduction methods for constant temperature vapor−liquid equilibrium data. The PVT experimental data of this work for butane at the bubble and dew points are given in Table 1, where specific volumes are expressed as densities. Correlations of physical properties reported by Haynes and Goodwin (1982) are the best available published data for butane. Thus, the present results and data already published were compared with the data of Haynes and Goodwin (1982). The deviations between available experimental data for butane (vapor pressures and saturated densities) and the correlations of Haynes and Goodwin (1982) are shown in Figures 1−3. Also, earlier correlations reported by Das et al. (1973) are included in the Figures 3. According to Table 1, the differences between bubble point pressures (p^B) and dew point pressures (p^D) resulting from the compression effect are from 2 to 5 kPa, and they are smaller than literature values having a comparable purity of substances, for example Brewer et al. (1961). Small disagreements between our dew point pressures (p^D) and results given by Haynes and Goodwin (1982) were found. The differences range from 0.14% for the highest pressures to −0.31% for the lowest pressure. As shown in Figure 1, the dew point pressure deviations of the present work are consistent with available literature data. The average absolute fractional deviation of saturated liquid density data of this work is 0.12%, and the maximum absolute deviation is 0.22%. In Figure 2, they bound the correlational results of Haynes and Goodwin (1982). In Figure 3, fractional deviations of the saturated vapor density of this study are shown to agree reasonably well with both correlations. Saturated vapor densities of this work have average fractional deviations of 0.22% and a maximum absolute fractional deviation of 0.53%. Volatile impurities in the system, after compression, result probably in a critical temperature difference of $\Delta T = 0.08$ K as compared with the value given by Haynes and Goodwin, as reported in Table 2. Chang et al. (1984) have shown that small concentrations of impurities in a fluid can have a strong effect on the thermophysical properties of that fluid in the vicinity of the critical region. Recently, a comprehensive review on this subject was presented by Ambrose and Young (1995). Analysis of the measured butane properties against those reported in the literature (Figures 1−3 and critical data reported by Ambrose and Tsonopoulos (1995)) indicated that results of this work are as good as or in some cases better than those available elsewhere in the literature.

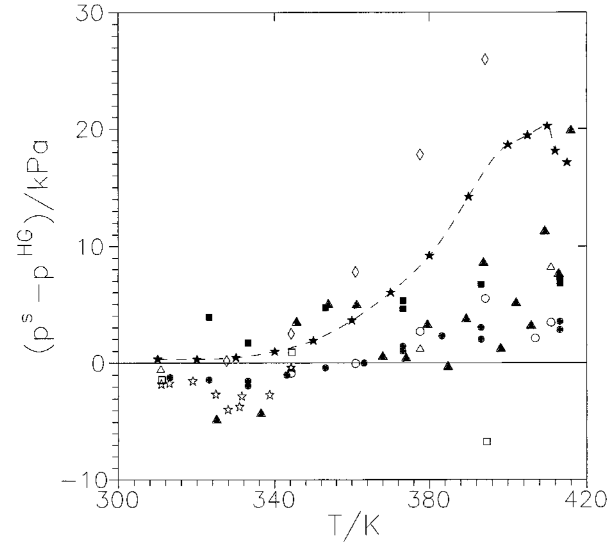

Figure 1. Deviations between experimental vapor pressure of butane and correlated data of Haynes and Goodwin (1982) [($p^s - p^{HG}$)]: (●) dew pressures of this work; (■) bubble pressures of this work; (□) Niesen (1989); (☆) Torres-Robles (1980); (★) Das et al. (1973); (○) Connolly (1962); (△) Olds et al. (1949); (▲) Kay (1940); (◇) Sage et al. (1937).

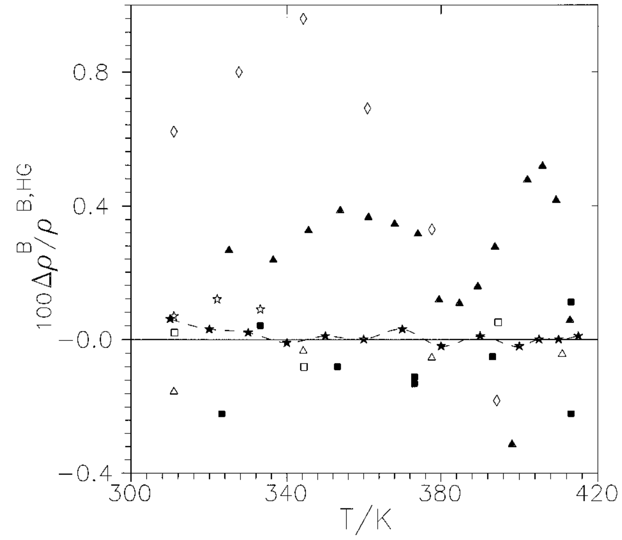

Figure 2. Fractional deviations $\Delta\rho^B/\rho^B = \{\rho^B - \rho^{HG}\}/\rho^{HG}$ of the experimental saturated liquid density of butane from the Haynes and Goodwin correlation: (■) this work; (□) Niesen (1989); (★) Das et al. (1973); (△) Olds et al. (1949); (☆) TC-NGAA (1942); (▲) Kay (1940); (◇) Sage et. al (1937).

Extensive phase diagrams are usually compiled from experimental data measured in different laboratories using different kinds of apparatus. The scale of the $p-T$ diagram in Figure 4 corresponds to the present measurements and

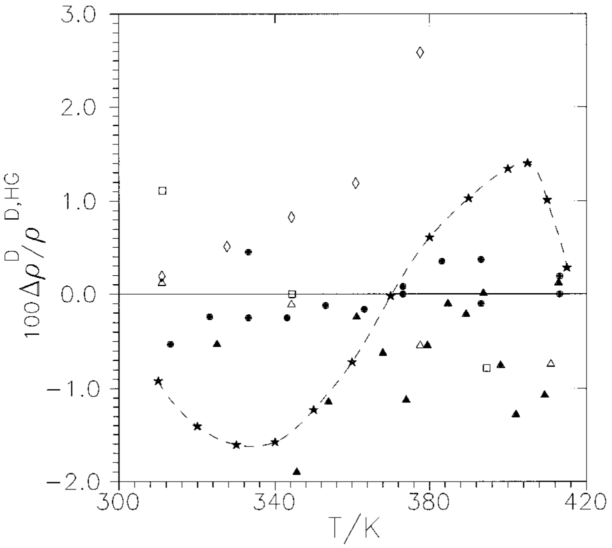

Figure 3. Fractional deviations $\Delta\rho^D/\rho^D = \{\rho^D - \rho^{HG}\}/\rho^{HG}$ of the experimental saturated vapor density of butane from the Haynes and Goodwin correlation: (●) this work; (□) Niesen (1989); (★) Das et al. (1973); (△) Olds et al. (1949); (▲) Kay (1940); (◇) Sage at al. (1937).

Table 2. Critical Data on *x* Acetonitrile + (1 − *x*) Butane Mixtures

x	T^C/K	p^C/kPa	ρ^C/kg m^{-3}	ref
0.0000	425.16	3796	227.85	*a*
0.0000	425.12 ± 0.1	3796 ± 10	228 ± 3	*b*
0.0000	425.08	3794	227.5	this work
0.0197	425.06	3838	228.2	this work
0.0271	425.07	3856	228.4	this work
0.0494	425.28	3891	228.9	this work
0.078	429.3	3890		*c*
0.0935	426.46	3954	230.1	this work
0.093	430.3	3940		*c*
0.1071	427.08	3974	230.6	this work
0.1312	428.20	4014	231.8	this work
0.1998	433.15	4181	237.5	this work[d]
0.2229	435.19	4255	240.4	this work
0.2422	436.82	4315	242.7	this work
1.0000	547.9	4830		*e*
1.0000	545.5 ± 0.3	4830 ± 20		*f*
1.0000	547.9		237.1	*g*

Haynes and Goodwin (1982). [b] Ambrose and Tsonopoulos (1995)—temperature was expressed on ITS-90. [c] Rodriguez and McLure (1983). [d] Values of this work for 433.15 K were extracted from the present experimental data. [e] Ambrose and Townsend (1978). [f] Rodriquez and McLure (1979). [g] Ter-Gazarian (1906).

to the acetonitrile data obtained with the present apparatus and published by Warowny (1994). The experimental points are not shown to allow an easier view. The present measurements are limited to the area bounded by four curves: the homoazeotropic dashed line, dotted gas−liquid critical curve, the vapor pressure line for pure acetonitrile, and the liquid−liquid phase separation line. The azeotropic line persists up to the critical locus. At the lowest temperatures, the liquid−liquid immiscible region is restricted by the UCST locus and by the three-phase equilibrium line AB, where point B is the liquid−liquid upper critical end point (ll-UCEP).

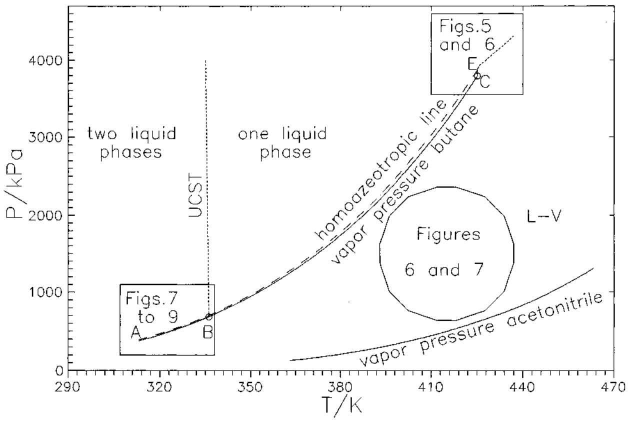

Figure 4. $p-T$ projection of the phase equilibria for the acetonitrile + butane system covering the present measurement range: B, liquid−liquid upper critical end point; C, critical point of butane; E, intersection point of the azeotropic line with gas−liquid critical curve.

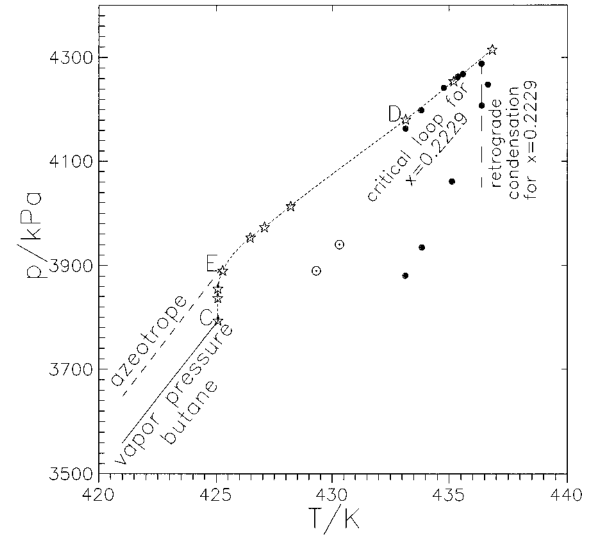

Figure 5. Critical temperature−critical pressure dependence of the *x* acetonitrile + (1 − *x*) butane system: (☆) this work; (●) the critical loop points for $x = 0.2229$; (⊙) Rodriguez and McLure (1983) data; C, critical point of *n*-butane; D, extracted critical point at 433.15 K (explanation in the text); E, intersection of the dashed azeotropic line with the dotted critical curve. The dotted line goes through critical points of this work.

The experimental critical temperature, critical pressure, and critical density for eight mixtures located near the critical point of butane are reported in Table 2. The mercury vapor pressure was subtracted from the total pressure, but the mercury effect on the critical temperature is an open question. Corresponding values from the literature are also given in Table 2 where available. The critical points are plotted as stars in Figures 5 and 6. Special care has been taken for mixtures near the critical point to measure accurately the coexistence surface. Experimental data for $x = 0.2229$ near the critical point are given in Table 3 and are plotted in Figure 5. For this mixture (and probably for the system as well), the liquid and vapor coexist in equilibrium at temperatures and pressures higher than those corresponding to the critical point of the isopleth. Retrograde condensation was observed for this mixture, and for the other mixture ($x = 0.2422$) it was observed but not recorded. The region where the critical opalescence was observed or the curvature of the meniscus was not distinguished was called here critical. Data for the critical region are marked with stars in Table 3. A detailed study of the $p-T-x$ data for the critical points show that the critical temperature exhibits a minimum at $x = 0.023$. The azeotropic line intersects the critical curve at point E (as shown in Figure 5 using a larger scale), where the azeotropic curve is tangent to the gas−liquid critical curve. The critical point D (Figures 5 and 6) for the 433.15 K isotherm was extracted from the liquid and vapor saturation lines which have to merge with the critical curve. As shown in Table 2 and Figure 5, the present critical data are at a substantially lower temperature, by as much as 4 K, than those of Rodriguez and McLure (1983), for a comparable composition of the mixture. Their claim of a lack of the minimum boiling

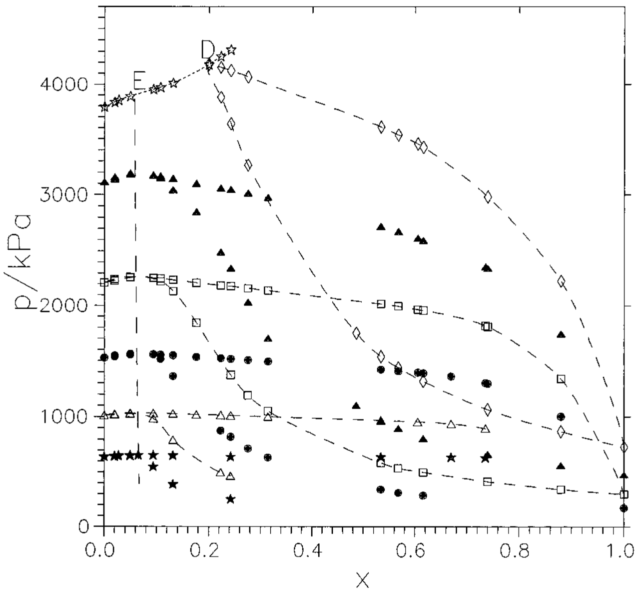

Figure 6. Critical, dew, and bubble pressures for the *x* acetonitrile − *x*) butane system from 333.15 to 436.82 K: (★) 333.15 K;) 353.15 K; (●) 373.15 K; (□) 393.15 K; (▲) 413.15 K; (◇) 433.15 ☆) critical points. Letters D and E are the same as in Figure 5. Short-dashed lines go through experimental dew and bubble pressures at 433.15 K, 393.15 K, and 353.15 K. Long-dashed and dotted curves describe the azeotropic loci and the gas−liquid critical loci, respectively.

Table 3. *x* Acetonitrile + (1− *x*) Butane Experimental Data in the Vicinity of the Gas−Liquid Critical Region *x* = 0.2229

T/K	p/kPa	ρ/kg m^{-3}	remarks^c
433.14	3881	122.3	dew
433.84	3935	126.2	dew
435.11	4061	135.3	dew
436.38	4208	149.4	dew
436.64	4248	165.6	dew^{*a}
436.36	4288	192.3	dew^{*b}
435.58	4268	225.6	dew*
435.37	4263	233.0	dew*
435.19	4255	240.4	**critical point**
435.10	4253	243.9	bubble*
434.77	4242	252.0	bubble*
433.81	4199	280.0	bubble
433.14	4163	295.0	bubble

Maximum temperature region. [b] Maximum pressure region. Stars refer to the critical region.

azeotrope at its critical locus for the acetonitrile + butane system was based on only the behavior of two compositions which were close to each other (Table 2 and Figure 5) and on the behavior of the binary systems of the higher hydrocarbons with acetonitrile. Although in the work of Rodriguez and McLure (1983) the experimental accuracies were lower for the acetonitrile + butane system than for the other systems depicted in the original $p-x$ projection (where also a large scatter in the pressure between two compositions is observed). In this work, the minimum boiling azeotrope was found over the entire measured temperature range including 413.15 K, which is the closest to the critical temperature. As shown in Table 2 and in Figure 5, the critical temperatures for the four compositions, including pure butane, are almost constant while the corresponding pressures increase significantly.

The numerical values of the dew and bubble point measurements of this work in the $\{xC_2H_3N + (1-x)C_4H_{10}\}$ system at temperatures from 333.15 K to 433.15 K are presented in Table 4. Adjustments have been made to the bubble point pressure results for all mixtures in order to eliminate the compression effect arising from volatile impurities. Dew and bubble point pressures as a function of composition for six isotherms at 20 deg temperature intervals are shown in Figure 6. Dew point, bubble point, and three-phase $p-x$ results for the 333.15 K isotherms are shown in Figure 7 using an expanded scale. The only data available for direct comparison were the bubble point pressures at 333.15 K of Torres-Robles (1980). As shown in Figure 7, they are in good agreement with the present data.

The simplest method for determining the azeotrope location is to determine where the dew and bubble points are equal. In this work, there were insufficient experimental data for a number of mixtures near the azeotrope location mainly on its right side ($x > x^{AZ}$). Thus, fitting the dew point pressures to get the azeotrope would not be successful. The azeotropic pressure p^{AZ}, being the maximum as a function of composition, was determined for each isotherm from the experimental bubble point values in the composition range from pure butane ($x = 0$) to the composition $x = 0.1312$, using a cubic regression fit. Repeating the estimation after removing vapor pressure butane yields identical results, except for small differences at the two lowest temperatures (at 333.15 K $x^{AZ} = 0.062$ changes to $x^{AZ} = 0.065$, and at 353.15 K $x^{AZ} = 0.066$ changes to $x^{AZ} = 0.065$). The determination of the azeotropic composition was made by the parabolic regression fit of the differences between bubble and dew point pressures as a function of composition. The zero value was found for the p^B-p^D from three available values of the p^B-p^D at the given isotherm in the composition range from pure butane to $x = 0.0494$, and the corresponding composition could be treated as an azeotrope locus. The temperature−composition relationship for the azeotropic locus was determined from the combined calculational results of both methods by fitting to the parabolic curve T^{AZ} against x^{AZ}. The mixture exhibits positive azeotropy with a small composition change from $x = 0.065$ to 0.055 as temperature increases to its critical value. The critical azeotropic composition $x^{C,AZ} = 0.055$ and the critical azeotropic temperature $T^{C,AZ} = 425.37$ K were found from the intersection of the azeotropic line with the critical $T^C(x)$ curve. The value of the critical azeotrope does not intersect the critical curve at its minimum temperature ($x = 0.023$, $T = 425.06$ K). The inferred azeotropic results for both calculational methods and available literature data are reported in Table 5. The results of this work are in disagreement with only one available result reported by Gorshkov et al. (1975) who claimed a positive azeotrope at 313.15 K with $x = 0.030$. Although the difference in the azeotropic temperatures (Gorshkov et al. (1975) and Horsley et al. (1973)) was as small as 5 K in two different homologous systems of Table 5, the azeotropic compositions are almost identical.

Results of this work are in good agreement with the graphical data (at 338.71 K) published by Black (1959). In his original figure, the azeotrope is located somewhere in the range of 0.06−0.08 mole fraction of the acetonitrile. As shown in Figure 7, at 333.15 K the two bubble pressures of Torres-Robles (1980) being in the vicinity of the azeotrope location agree very well with the data of this work. The results of this study were used to develop an empirical relation for the dependence of azeotropic pressure on temperature.

$$\ln(p^{AZ}/\text{kPa}) = a + b(T^{AZ}/\text{K})^{-1} + c(T^{AZ}/\text{K})^{-2} \qquad (1)$$

The values for the parameters of eq 1, obtained from the least squares of the data in Table 5, are $a = 15.6357$, $b = -3444.70$, and $c = 131853$. Equation 1 predicts a critical azeotropic pressure of 3897 kPa at 425.37 K. Although in this work the change in composition of the azeotrope with pressure is small, it shows good agreement with the qualitative rule credited to Kamienski (1931) that an

Table 4. Dew and Bubble Points[a] of the *x* Acetonitrile + (1 − *x*) Butane Mixtures

x	T/K	p^D/kPa	p^B/kPa	ρ^D/kg m^{-3}	ρ^B/kg m^{-3}
0.0197	333.14	643.1	648.1	15.89	534.0
	353.13	1018.8		25.36	
	353.14		1025.5		504.9
	373.15	1537.8		39.63	
	373.15		1547.2		470.8
	393.15	2230	2244	62.75	428.6
	413.16	3142	3159	105.9	366.6
0.0271	333.14	644.9	651.2	15.91	532.7
0.0494	333.14	648.7	653.4	15.86	532.1
	353.14	1026.6		25.18	
	353.14		1031.2		504.8
	373.14	1552.3		39.39	
	373.15		1560.2		470.5
	393.15	2257	2264	62.34	428.2
	413.16	3182		105.8	
	413.15		3190		367.1
0.0935	333.14	549.8	653.2	12.88	539.8
	353.14	982.4	1030.2	23.27	510.1
	373.15		1556.8		473.7
	393.15		2255		434.0
	413.15		3174		373.5
0.1071	373.15	1515.0			
	373.15		1553.8		
	393.16	2223	2249		
	413.16	3149	3164		
0.1312	333.13	385.3	650.8	8.58	543.2
	353.12	791.1	1026.0	18.02	515.1
	373.15	1360.8		33.08	
	373.15		1547.7		480.5
	393.15	2133		54.16	
	393.15		2236		439.4
	413.16	3044	3143	88.06	381.8
0.1758	353.14		1019.2		
	373.15		1533.4		
	393.15	1843.5	2209		
	413.16	2850			
	413.15		3100		
0.2229	353.14	497.2	1013.7	10.57	523.6
	373.15	876.1	1521.7	18.46	490.9
	393.15		2186		451.2
	413.13	2491	3060	58.65	401.2
	433.14	3881		122.4	
	433.14		4154		297.8
0.2422	333.14	249.0		5.47	
	333.14		639.6		555.1
	353.14	466.7	1010.4	9.82	527.1
	373.14	818.8		17.13	
	373.16		1515.9		495.2
	393.15	1371.4	2177	29.46	454.3
	413.16	2344	3047	53.51	404.9
	433.15	3636	4126	102.3	307.6
0.2755	373.15	714.6	1505.5		
	393.15	1188.0	2158.4		
	413.15	2029			
	413.16		3015		
	433.15	3263	4067		
0.3141	353.14		999.2		
	373.15	634.2			
	373.15		1493.5		
	393.15	1048.9	2137		
	413.16	1703.1			
	413.16		2977		
0.4858	413.15	1101.3		19.71	
	433.18	1749.5		31.89	
0.5338	333.14		636.1		603.9
	353.14		967.0		577.3
	373.15	341.0		5.97	
	373.15		1421.4		551.4
	393.15	585.8	2015	10.00	519.1
	413.16	961.5		16.40	
	413.15		2720		484.0
	433.14	1537.1		26.68	
	433.14		3607		439.1
0.5675	373.15	310.5			
	373.15		1406.5		
	393.15	536.3	1995.0		
	413.16	896.7	2673		
	433.15	1436.1			
	433.15		3534		
0.6051	353.14		953.5		593.9
	373.15		1393.2		567.0
	393.15		1964.2		537.6
	413.16		2614		504.5
	433.15		3453		465.8
0.6158	373.09	285.9		4.84	
	373.15		1388.1		569.1
	393.15	498.1	1956.7	8.14	540.1
	413.15	806.4	2594	13.38	507.8
	433.14	1315.6		21.64	
	433.15		3423		469.7
0.6698	333.14		635.9		
	353.14		936.9		
	373.15		1359.5		
0.7354	333.14		629.5		650.5
	353.14		895.3		626.4
	373.15		1300.8		600.5
	393.15		1817.5		573.9
	413.15		2358		544.8
0.7399	373.15		1294.3		601.9
	393.15	413.5	1808.3	6.55	575.3
	413.15	663.7	2345	10.53	546.4
	433.15	1063.7		16.99	
	433.14		2980		513.9
0.8796	373.15		1003.0		648.3
	393.15	341.2		5.29	
	393.15		1339.1		624.6
	413.16	562.2	1743.1	8.89	597.8
	433.15	867.6		13.72	
	433.14		2227		568.6

Bubble point pressures were corrected for the compression effect.

Table 5. Composition, Temperature, and Pressure of Azeotropes for the *x* Acetonitrile + (1 − *x*) Butane System[a]

system	T^{AZ}/K	x^{AZ}	P^{AZ}/kPa	ref	method
$C_2H_3N + C_3H_8$	328.15	0.0309		Gould (1973)	
$C_2H_3N + n\text{-}C_4H_{10}$	333.15	0.030		Gorshkov et al. (1975)	
	425.37	0.0552	3897	this work[b]	inferred data
	413.15	0.0569	3191	this work	inferred data
		0.0583	3191		bubble fit
		0.0562	3191		$p^B - p^D$ fit
	393.15	0.0595	2265	this work	inferred data
		0.0595	2265		bubble fit
		0.0568	2265		$p^B - p^D$ fit
	373.15	0.0617	1561.4	this work	inferred data
		0.0627	1561.3		bubble fit
		0.0643	1561.6		$p^B - p^D$ fit
	353.15	0.0637	1031.5	this work	inferred data
		0.0646	1031.8		bubble fit
		0.0606	1031.2		$p^B - p^D$ fit
	333.15	0.0653	654.1	this work	inferred data
		0.0650	654.3		bubble fit
		0.0660	654.0		$p^B - p^D$ fit

[a] Data of this work were extracted from experimental bubble and dew point pressures reported in Tables 1 and 4. Calculational methods are explained in the text. [b] Point E in Figures 4−6.

increase of pressure on a binary positive azeotrope produces a concentration increase of a component having the higher dp^s/dT value, here butane.

The circle points of Figure 8 are the loci of the three-phase liquid−liquid−vapor equilibrium (3F-LLV) which ends in the UCEP (point B in Figures 4, 8, and 9), where

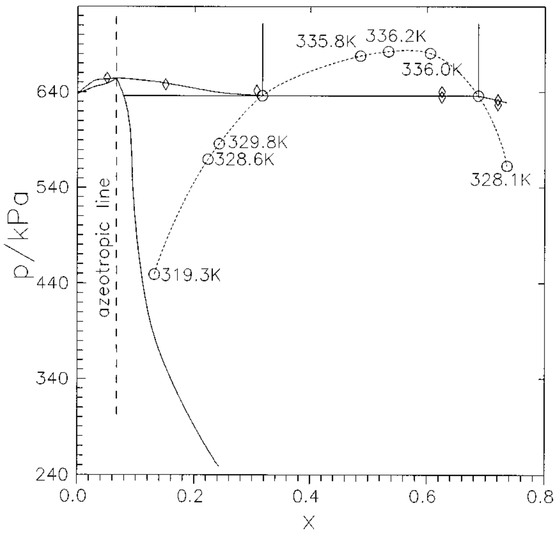

Figure 7. Phase behavior at 333.15 K and the three-phase equilibrium of the x acetonitrile + $(1 - x)$ butane system. Solid lines go through dew, bubble, and three-phase equilibrium data at 333.15 K. The dotted line goes through UCXT points (correspond to the marked temperatures): (◇) Torres-Robles (1980).

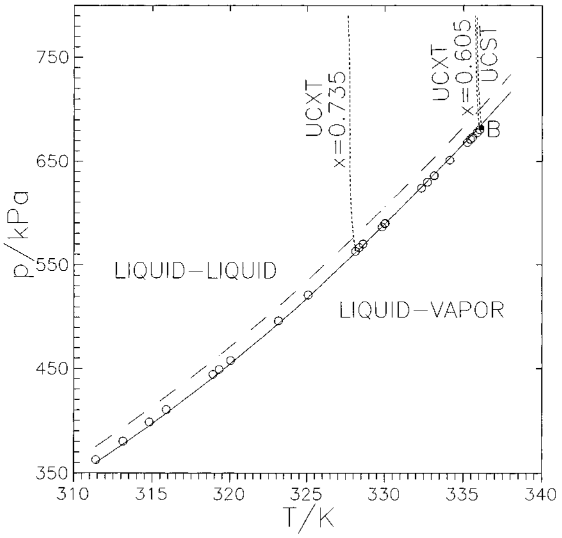

Figure 8. The p–T projection of the three-phase equilibria for x acetonitrile + $(1 - x)$ butane system: (●) upper critical end point; (○) three-phase liquid–liquid–vapor equilibrium; (—) vapor pressure of butane; (— — —), azeotrope; (- - -), upper critical coexistence temperatures, and upper critical solution temperature.

Table 6. Upper Coexistence Temperature as a Function of Pressure for x Acetonitrile + $(1 - x)$ Butane Mixtures

T/K	$x = 0.6051$ p/kPa	$x = 0.7354$ p/kPa
336.02	680.6	
335.98	678.4	
335.92	696.5	
335.81	709.1	
335.68	848.0	
335.63	1142.3	
335.58	1910.1	
335.53	3035	
335.52	3672	
328.11		563.1
327.91		588.5
327.62		790.4
327.58		2820

the gas and one of the liquid phases become identical. The temperature and pressure of the UCXT were determined visually for two compositions ($x = 0.6051$ and $x = 0.7354$), and they are reported in Table 6. The UCXT curves extend steeply to high pressures from three-phase loci, as showed in Figure 8. In the vicinity of the three-phase location, positive slope $(\mathrm{d}p/\mathrm{d}T)_x$ changes to negative slope with a decrease in temperature. Numerical data for $x = 0.6051$ are given in Table 6 as proof of this behavior. The composition of the UCST is approximately $x = 0.6051$ and therefore identical temperature–pressure behavior was assumed for both curves (UCXT and UCST). The dotted curve of the UCST locus shown in Figures 4 and 8 starts from the ll-UCEP and rapidly reaches high pressure with a small decrease in temperature.

If values of the temperature and pressure are perused more closely on the expanded temperature scale of Figure 8, it will be seen that 3F-LLV equilibrium pressures ($p^{\mathrm{3F-LLV}}$) in the vicinity of point B lie below the vapor pressure for butane, and they cross it at $T = 330.63$ K and $p = 598.9$ kPa. The differences between the values of the vapor pressure of butane ($p^{\mathrm{S,Butane}}$) and the values of $p^{\mathrm{3F-LLV}}$ are close to the uncertainty of the pressure measurements, so the value extracted from this intersection is only approximate. Selected experimental pressures for the three-phase equilibrium and their relative deviations from the vapor pressure of butane are summarized in Table 7. From the increase in the negative values of fractional deviations, it is evident that the present system forms a positive heterogeneous azeotrope outside of the measured range. Solubility data in Table 7 were determined visually for a given overall composition as explained earlier in the Experimental Section. In order to show p,T,x relations for the three-phase equilibrium, the p–x diagram (Figure 7) and T–x diagram (Figure 9) were drawn. The liquid–liquid boundary locus was determined experimentally for seven compositions presented in Table 7, where L_1 stands for the n-butane-rich liquid phase (upper phase) and L_2 for acetonitrile-rich liquid phase (lower phase). At 333.15 K the UCXT compositions, and corresponding pressure and densities (Table 7) were inferred by the graphical cubic spline fitting from UCXT experimental data. In Figure 7 at 333.15 K and for 636.2 kPa, two branches of the saturated liquid curve intersect the three-phase horizontal straight line at $x_1 = 0.317$ (L_1 boundary locus) and at $x_1 = 0.687$ (L_2 boundary locus). The solubility data determined by Torres-Robles (1980), by Pavlov et al. (1970), and by Evans and Sarno (1967) are compared with the present measurements in Figure 9. Data for the upper liquid phase are in reasonable agreement but the critical region and lower liquid phase data show a discrepancy. Large scatter between available data is observed at 333.15 K.

Finally, the composition of the gas phase in equilibrium with immiscible liquids at 333.15 K was calculated for the overall mole fraction x_1 from the mass balance equation (2)

$$y_1 = x_1^{\mathrm{V}} = M_2A/\{M_2A + M_1(B - A)\} \qquad (2)$$

where

$$A = m_1 - x_1^{\mathrm{L_1}}M_1\rho^{\mathrm{L_1}}V^{\mathrm{L_1}}/[x_1^{\mathrm{L_1}}M_1 + (1 - x_1^{\mathrm{L_1}})M_2] - x_1^{\mathrm{L_2}}M_1\rho^{\mathrm{L_2}}V^{\mathrm{L_2}}/[x_1^{\mathrm{L_2}}M_1 + (1 - x_1^{\mathrm{L_2}})M_2]$$

$$B = m - \rho^{\mathrm{L_1}}V^{\mathrm{L_1}} - \rho^{\mathrm{L_2}}V^{\mathrm{L_2}}$$

where m is mass, M is molecular weight, and V is volume. The subscript 1 refers to acetonitrile and superscripts V, L_1, and L_2 represent gas phase and liquid phases in equilibrium. The volumes of the gas phase and two liquid phases in equilibrium for three measurement sets were calculated from interface levels (mercury/lower phase, two liquid phases, and gas phase/upper phase) and from the dimensions of the glass tube as described earlier. The

Table 7. Three-Phase Liquid−Liquid−Vapor Equilibrium for the *x* Acetonitrile + (1 − *x*) Butane System

			UCXT; 3F-LLVE			
T/K	p^{3F-LLV}/kPa	RD[a]	phase L$_1$ (upper)	phase L$_2$ (lower)	gas phase	remarks
311.40	362.6	0.73				LLVE
314.82	398.5	0.87				LLVE
315.90	410.4	0.87				LLVE
318.91	444.4	0.73				LLVE
319.30	449.1	0.72	0.1312			x_1
			559.1			ρ/kg m^{-3}
320.04	457.8	0.67				LLVE
323.14	496.5	0.56				LLVE
325.06	521.5	0.44				LLVE
328.11	563.1	0.22		0.7354		x_1
				657.2		ρ/kg m^{-3}
328.36	566.6	0.23				LLVE
328.60	570.0	0.19	0.2229			x_1
			559.9			ρ/kg m^{-3}
329.82	586.3	−0.05	0.2422			x_1
			561.2			ρ/kg m^{-3}
329.98	589.4	0.05				LLVE
330.02	589.9	0.07				LLVE
332.33	623.8	−0.15				LLVE
333.14	635.9	−0.24				LLVE
333.15[b]	636.2	−0.35	568.8	639.8		ρ/kg m^{-3}
			0.3167	0.6868	0.0021	x_1, y_1
			0.3167	0.6868	0.0565	x_1, y_1
			0.3167	0.6868	0.0796	x_1, y_1
334.14	651.0	−0.34				LLVE
335.25	668.3	−0.42				LLVE
335.74	676.2	−0.46				LLVE
335.85	677.8	−0.48	0.4858			x_1
			591.5			ρ/kg m^{-3}
336.02	680.6	−0.53		0.6051		x_1
				615.9		ρ/kg m^{-3}
336.15	682.5	−0.51	0.5338			x_1
			599.9			ρ/kg m^{-3}
336.22[c]	$x_1 = 0.571$ $p = 683.5$ kPa $\rho = 607.3$ kg m^{-3}					

[a] RD = 100($p^{3F-LLV} - p^{S,Butane}$)/$p^{S,Butane}$. [b] The pressure and densities for this temperature were inferred from the experimental data, and the gas phase composition y_1 was calculated from eq 2 for the total mole fraction $x_1 = 0.6051$ of the acetonitrile. [c] Inferred values of the UCEP.

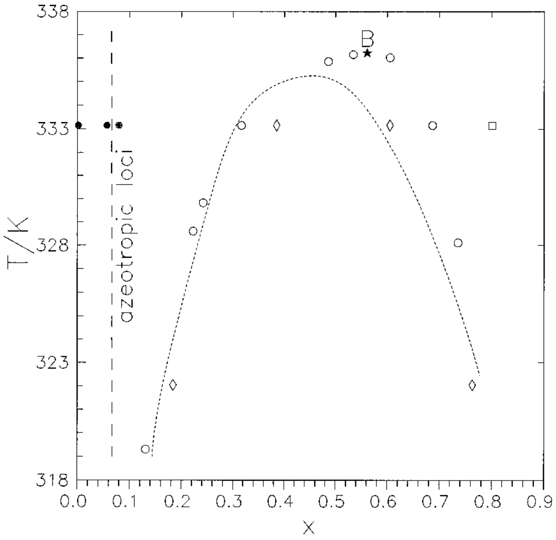

Figure 9. Three-phase coexistence points as a function temperature and mole fraction: (●) scattering of the calculated gas phase composition for the three-phase equilibrium at 333.15 K; (○) an upper critical coexistence location for corresponding pressures of Figure 7 (the lowest values of the UCXT); (★) upper critical end point; (- - -) solubility graph (for unknown pressure) by Pavlov et al. (1970); (◇) Torres-Robles (1980); (□) Evans and Sarno (1967).

numerical results are given in Table 7, and they are plotted in Figure 9. A large scattering of y_1 ranging from 0.0021 to 0.0796 is observed as a consequence of errors in measurements of the coexisting volumes in the three-phase equilibrium. Also indirect determination of the liquid phase compositions and corresponding densities in three-phase equilibrium has a strong influence on the calculated value of y_1.

In conclusion, we can say that the following data are a good approximation for the ll-UCEP: $x = 0.571$, $T = 336.22$ K, and $p = 683.5$ kPa. The inferred UCEP data are included in Table 7.

The influence of intermolecular forces is reflected in the sign and magnitude of the Krichevskii parameter (Krichevskii, 1967) given by

$$(\partial p/\partial x)^{\infty,C}_{T,V} = (\mathrm{d}p^{C}/\mathrm{d}x)^{\infty} - (\mathrm{d}T^{C}/\mathrm{d}x)^{\infty}(\mathrm{d}p/\mathrm{d}T)^{C}_{\sigma} \qquad (3)$$

The derivatives $(\mathrm{d}p^C/\mathrm{d}x)^\infty$ and $(\mathrm{d}T^C/\mathrm{d}x)^\infty$ are the slopes of the critical lines at infinite dilution and $(\mathrm{d}p/\mathrm{d}T)^C_\sigma$ is limiting slope of the vapor pressure curve of the solvent at its critical point (here the solvent is butane). The Krichevskii parameter describes solvent−solute interaction in the vicinity of the critical point of the solvent. For calculation of both auxiliary coefficients in the concentration range from pure *n*-butane to $x = 0.0197$, straight lines were assumed. Values for those coefficients are $\mathrm{d}T^C/\mathrm{d}x|^\infty = -1.02$ K and $\mathrm{d}p^C/\mathrm{d}x|^\infty = 2236$ kPa, and the final result is $(\partial p/\partial x)^{\infty,C}_{T,V} = 2294$ kPa. The addition of acetonitrile to butane at its critical point results in an increase in pressure and a decrease in temperature.

Conclusions

The purpose of this paper is to report new data on phase equilibria for the acetonitrile + butane system. Additionally, the azeotropic loci and the Krichevskii parameter for dilute acetonitrile were obtained.

On the $p-T$ projection, the system reveals the following features: a continuous gas−liquid critical curve with a minimum in temperature, a homoazeotropic line up to the critical curve, a three-phase line (L_1L_2V) ending at the ll-UCEP point, from where a second curve of liquid−liquid nature goes to high pressures with a negative value of d*p*/d*T* (at constant composition). The line of the 3F-LLV equilibrium intersects the vapor pressure curve of *n*-butane and at lowest temperatures approaches the homoazeotropic line. At the intersection of these two lines, the heteroazeotrope is expected to exist.

This system belongs to class IIa, following the classification scheme of van Konynenburg and Scott (van Konynenburg and Scott, 1980; Scott and van Konynenburg, 1970).

Acknowledgment

I am grateful to Dr. A. E. Mather for discussion.

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Received for review September 25, 1995. Accepted March 19, 1996.[⊗]

JE950242S

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1996.