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An apparatus for measuring the upper critical solution temperature using the effluent from a flow calorimeter: application to mixtures of acetonitrile with cyclohexane, propane and butane ☆

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Abstract

A thermostated sapphire capillary was inserted into the exit line of a flow calorimeter. This capillary is used to visually determine the upper critical solution temperature (UCST) for acetonitrile + cyclohexane, + propane, and + butane at several pressures. The UCST results were combined with liquid + liquid results obtained earlier from breaks in the excess molar enthalpy versus mole fraction curves to obtain the liquid + liquid phase diagrams for acetonitrile + propane, and + butane at 5 and 10 MPa.

Keywords: Apparatus; Binary system; Calorimeter; Flow calorimeter; LLE; UCST; VLE

1. Introduction

In earlier papers [1–7] we reported the measurement of liquid + liquid equilibria from excess enthalpy measurements. The compositions of the phases in equilibrium were obtained from the breaks in the $H_m^E(x)$ curves. $T(x)$ can be obtained with good

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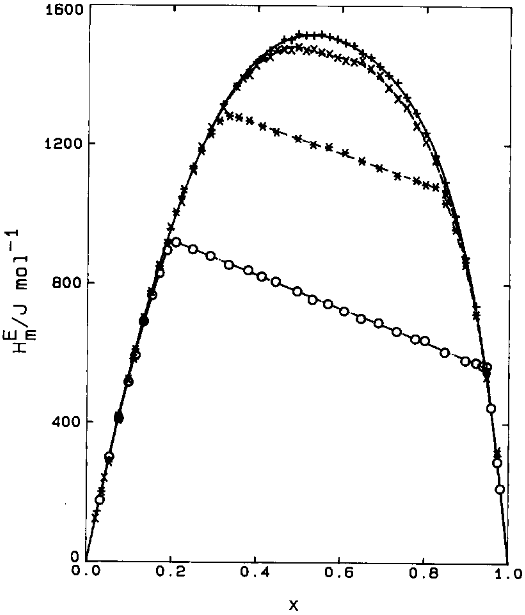

Fig. 1. Excess enthalpies for $(1-x)CN_3CN + xC_3H_8$ [6] at a pressure of 10 MPa and temperatures of ○, 298.15 K; *, 323.15 K; ×, 333.15 K; and +, 338.15 K. The breaks in the $H_m^E(x)$ curves at the three lower temperatures result from liquid + liquid phase separation.

accuracy if the temperature is well below the upper critical solution temperature (UCST).

However, the calorimetric results cannot be used to accurately obtain the equilibrium mole fractions at temperatures near the UCST. This can be seen in Fig. 1 where H_m^E is shown at 10 MPa and 298.15, 323.15, 333.15, and 338.15 K for $(1-x)CH_3CN + xC_3H_8$ [6]. At the two lower temperatures, the breaks in $H_m^E(x)$ can be determined accurately, but at 333.15 K it becomes difficult, because the breaks in $H_m^E(x)$ are hard to find. The H_m^E results at 338.15 K are above the UCST and no breaks are present.

In the procedure we used to estimate the liquid + liquid curves, the equilibrium (x,T) values obtained from the breaks in the H_m^E curves were fitted to the equations

$$T = T_c + k|y - y_c|^{1/\beta} \qquad (1)$$

$$y = \alpha x/(1 + x(\alpha - 1)) \qquad (2)$$

$$y_c = \alpha x_c/(1 + x_c(\alpha - 1)) \qquad (3)$$

where β is the critical exponent, T_c and x_c are the critical temperature and mole fraction, respectively, and k and α are fitting parameters. Liquid + liquid curves can be obtained from these equations from a minimum of two sets of $H_m^E(x)$ measurements (which give four values of x) by setting β at the critical exponent value of 0.318 and fitting the values of (x,T) to Eqs. (1)–(3) to obtain values for the four parameters, but serious questions arose as to the accuracy of x_c and T_c using this procedure, especially when the H_m^E measurements were made far from the critical point.

Accurate liquid + liquid curves could be obtained from $H_m^E(x)$ measurements using Eqs. (1)–(3) if an accurate value of T_c could be obtained from an independent phase measurement, and then combined with the equilibrium mole fractions obtained from $H_m^E(x)$. In this paper we describe a method for obtaining this independent T_c value, along with the equilibrium (x,T) results, from a flow calorimetric apparatus.

2. Experimental

The procedure involves inserting an apparatus to measure T_c in the exit line of the flow calorimeter. The design of the flow calorimeter is given in an earlier paper [8]. The phase apparatus contains a 50 mm long sapphire capillary with a 3.8 mm inside diameter and a 6.35 outside diameter, inserted in the exit line of the calorimeter as shown in Fig. 2. The two fluids are mixed in the flow calorimeter at a temperature above the UCST so that complete mixing occurs. The mixture (with a known composition) exits the calorimeter through a stainless steel capillary line that is heated to keep the temperature above the UCST, and enters the thermostated bath surrounding the sapphire capillary. The mixture passes through coils of stainless steel capillary tubing inside the thermostat to equilibrate the mixture with the bath temperature, flows through the sapphire capillary, and exits the apparatus through the back pressure regulator. A Sodev Model CT-C thermostat circulates fluid through the bath. The temperature of this thermostat, which can be

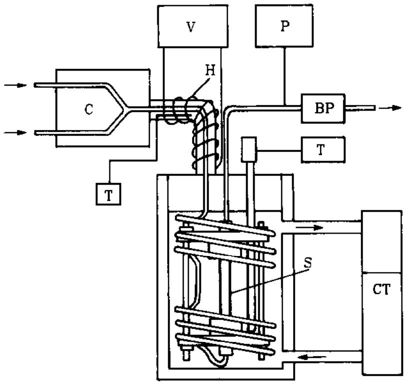

Fig. 2. Apparatus for observing phase separation near the UCST. The components of the apparatus are as follows: C, flow calorimeter where mixing occurs; V, variable transformer; H, heat tape; T, Hart thermometer for measuring the equilibrium temperature; P, pressure transducer for measuring the pressure; BP, back pressure regulator; S, sapphire capillary; CT, circulation thermostat.

programmed to linearly increase or decrease with time, is lowered slowly until the fluid in the sapphire capillary becomes cloudy. The bath temperature where this occurs is read with a Hart Model 1506 resistance thermometer calibrated against a Rosemount thermometer (ITS-90), and is taken as the equilibrium temperature at the mole fraction of the mixture. Pressures were measured with a Sensotec Model 450D transducer, which was checked with a Heise gauge and calibrated against a dead-weight gauge. Temperatures and pressures are considered to be accurate to ±0.02 K and ±0.1 MPa, respectively.

Fisher Scientific HPLC grade 99.9 mass% of acetonitrile, Phillips 99.5 mass% of propane and of butane, and Phillips Research Grade 99.99 mass% of cyclohexane were used without further purification in the measurements of the phase equilibria.

3. Discussion

The apparatus was tested with the $(1-x)CH_3CN + x\text{c-}C_6H_{12}$ system at 0.4 MPa. We have made extensive direct visual measurements of the liquid + liquid equilibria in this system at ambient pressure [1]. The comparison between these earlier measurements and the visual measurements made in the sapphire capillary is shown in Fig. 3. The agreement is excellent near the UCST. The critical temperature we obtained earlier was 347.84 K at ambient pressure (0.1 MPa) and we obtain a value of 347.92 K at 0.4 MPa with this new apparatus.

It is evident from Fig. 3 that our method does not work well at compositions and, hence, temperatures far removed from the UCST. The method works well when the phases in equilibrium have very similar densities, and this occurs near the

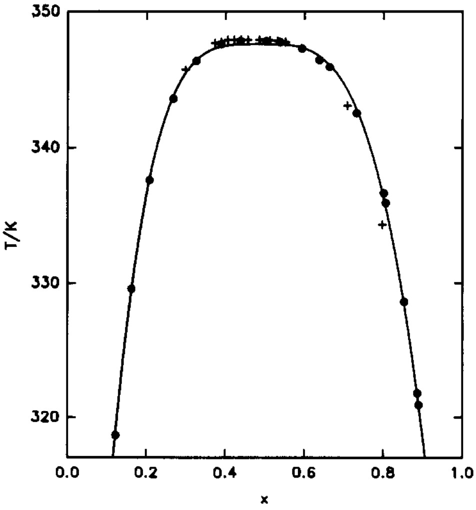

Fig. 3. Comparison of liquid + liquid equilibrium (x,T) values for $(1-x)CH_3CN + x\text{c-}C_6H_{12}$ at 0.4 MPa. ●, visual measurements reported earlier [1]; +, results obtained from this study.

critical point. When the densities of the two phases become quite different, however, the phases separate into globules in the capillary and the contact required to maintain equilibrium does not occur. Thus, the method does not give reliable results at compositions and, hence, equilibrium temperatures significantly below the UCST.

It is pleasing to see how well two different types of equilibrium measurements made with the calorimetric apparatus complement one another. Equilibrium compositions obtained from breaks in the H_m^E curve can be accurately obtained only at compositions well removed from the critical point. In contrast, the visual capillary method works well only near the UCST. Thus, the combination of the two kinds of measurements, fitted to Eqs. (1)–(3), provides a method for the determination of a liquid + liquid diagram over a considerable range of temperature and composition.

We have used calorimetric measurements to study the (liquid + liquid) equilibrium in $(1-x)CH_3CN + xC_nH_{2n+2}$ where n is 3, 4 [6,7]. We reported H_m^E measurements for these systems, some of which show breaks corresponding to phase separation. We used the breaks to establish the compositions of the phases in equilibrium. These compositions were then used with Eqs. (1)–(3) to predict the UCST, but without a separate determination of the critical temperature the extrapolation was a long one and subject to error.

In this present study, we have used the capillary to determine T_c for these systems at 5 and 10 MPa, and combined these results with the equilibrium (x,T) measurements obtained earlier from the $H_m^E(x)$ results, to obtain the liquid + liquid diagram at these two pressures. Measurements with the capillary were not made at 15 MPa even though H_m^E measurements were made at that pressure. We have not used the sapphire capillary at pressures above 10 MPa, even though the manufacturer claims it should hold together at higher pressures.

The visual measurement of T_c at 5 MPa for $(1-x)CH_3CN + xC_3H_8$ is 335.7 K, and this agrees well with the value of 335.5 K predicted earlier [6] using only Eqs. (1)–(3) and the (x,T) results obtained from the breaks in $H_m^E(x)$. The agreement is not as good at 10 MPa where a value for T_c of 332.6 K is obtained visually while 333.0 K is obtained from fitting the $H_m^E(x)$ results to Eqs. (1)–(3). The agreement is worse in $(1-x)CH_3CN + xC_4H_{10}$ where differences between the visual observation of T_c and the extrapolated values of T_c obtained from $H_m^E(x)$ [7] are as much as 5 K. In this system, the $H_m^E(x)$ results were obtained at fewer temperatures, and the liquid + liquid results obtained at these temperatures were further from the UCST, which increased the length of the extrapolation to the critical point. In both sets of measurements it is apparent that the accuracy with which the liquid + liquid diagram can be obtained is improved significantly by including visual results near the UCST in the fitting of (x,T) results to Eqs. (1)–(3).

The UCST results (T_c) at different pressures, obtained from the visual measurements as the highest equilibrium temperature, are given in Table 1. The coefficients given in Table 2 were obtained by setting T_c in Eq. (1) at the value given in Table 1 and fitting Eqs. (1)–(3) using the equilibrium (x,T) values obtained from the $H_m^E(x)$ curves and the visual measurements. The fit was improved by letting β vary, rather than setting it to the value of 0.318. These coefficients should give (x,T) equilibrium isobars of reasonable accuracy.

Table 1
Values for the UCST (T_c) obtained from visual measurements with the capillary

	p/MPa	T_c/K	p/MPa	T_c/K
$(1-x)CH_3CN + xC_3H_8$	5	335.66	7.5	333.81
	6	334.82	10	332.60
$(1-x)CH_3CN + xC_4H_{10}$	5	333.59	7.5	333.58
			10	333.63

Table 2
Coefficients for Eqs. (1)–(3) obtained by setting T_c at the values given in Table 1 and fitting Eqs. (1)–(3) to the (x,T) equilibrium results obtained from breaks in the $H_m^E(x)$ curves

System	p/MPa	T_c/K	x_c	k	α	β	s/K[a]
$(1-x)CH_3CN + xC_3H_8$	5	335.66	0.5724	−793	0.959	0.315	0.235
	10	332.60	0.5874	−975	0.900	0.287	1.059
$(1-x)CH_3CN + xC_4H_{10}$	5	333.59	0.5247	−1289	1.100	0.261	0.003
	10	333.63	0.5339	−1363	1.007	0.254	0.003

[a] s is the standard deviation.

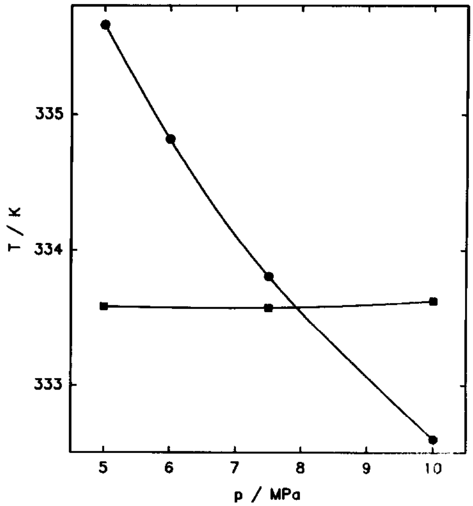

Fig. 4. Comparison of the UCST as a function of pressure obtained in this study for $(1-x)CH_3CN + xC_nH_{2n+2}$: ●, $n=3$; ■, $n=4$.

Fig. 4 compares the UCST as a function of pressure obtained from the visual measurements for $(1-x)CH_3CN + xC_3H_8$ and $(1-x)CH_3CN + xC_4H_{10}$. The pressure coefficient for the propane system is large and negative, but small and positive for the butane system. The effect of pressure on the critical temperature T_c is given to good approximation by

$$\frac{dT_c}{dp} = \frac{T_c V^E_{m,c}}{H^E_{m,c}} \tag{4}$$

For both systems, H^E_m is positive and of moderate value. Thus, the difference in dT_c/dp for the two systems must result from differences in V^E_m. We have not been able to find experimental V^E_m results for these systems reported in the literature, but Eq. (4) predicts that for acetonitrile + propane V^E_m must be large and negative, while for acetonitrile + butane it must be small and positive. The UCST for acetonitrile + propane is not far below the critical temperature of propane (369.85 K). It would not be unexpected to find that V^E_m becomes large and negative as the critical temperature of the alkane is approached.

We also tested the capillary with the $(1-x)C_2H_4 + xC_2H_6$ system to see if the apparatus could be used to investigate vapor + liquid equilibrium. We have just recently completed H^E_m measurements on this system which we will soon be publishing. The $H^E_m(x)$ results suggest that at 5 MPa and 298.15 K, a temperature between the critical points of ethane and ethene, the critical point of the mixture should occur at $x \approx 0.7$. Visual observation through the capillary verified this prediction. In the procedure followed, the temperature and pressure were held at 298.15 K and 5 MPa, respectively, and the mole fraction range was scanned. At $x < 0.7$, the solution was clear and one phase was present in the capillary. Just before reaching $x = 0.7$, the meniscus appeared and bubbles of a second phase were visible. At $x = 0.7$, critical opalescence was present, and at $x > 0.7$, the solution cleared again and the second phase disappeared.

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