Gas-Liquid Critical Properties of Methylamine + Nitrous Oxide and Methylamine + Ethylene Binary Mixtures

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Gas-liquid critical properties of methylamine + nitrous oxide and methylamine + ethylene binary mixtures have been experimentally determined by using a high-pressure view cell. Critical lines in both systems have been found to be continuous between the critical points of the pure components.

Introduction

Experimental data on critical properties of mixtures are needed for many industrial operations. A particular area of application is in separation processes involving supercritical fluids. In supercritical processing, the use of binary or multicomponent extraction fluids permits the adjustment of the operational conditions (such as temperature and pressure) or the solvent characteristics (such as selectivity or reactivity) toward a particular component in the material.

In our laboratories, we are investigating the interactions of supercritical fluids with lignocellulosic materials. We are particularly interested in binary mixtures in which one of the components has reactive capabilities toward various lignocellulosic compounds, especially toward lignin in wood. In this respect, among the various fluids methylamine and its mixtures are especially important. We are interested in the mixtures of methylamine with nitrous oxide, ethylene, and water. Even though some fragmentary data on the critical properties of methylamine and water mixtures at high methylamine concentrations have been reported in the literature (*1*), there is no experimental critical property data available for the methylamine + nitrous oxide and methylamine + ethylene mixtures. Such data are needed for establishing the supercritical one-phase regions and utilizing these mixtures as supercritical processing solvents. This paper reports the critical properties of these mixtures.

Experimental Procedures

***A*. *Experimental Setup*.** The critical point measurements were conducted using a view cell designed for high-pressure phase equilibrium studies in simple mixtures as well as mixtures involving polymeric components (*2*). A schematic diagram of the cell and the solvent delivery system is shown in Figure 1. The cell can be operated at temperatures up to 220 °C and pressures up to 100 MPa. It is made from 316 stainless steel block with a 1.27-cm-diameter chamber hole in the longitudinal direction. Two sapphire windows (1.27 cm thick and 2.54 cm in diameter) at each end of the hole permit the visual observation of the cell content. The sapphire windows are sealed with gold foil on the inside (wetted side) and copper washers on the outside. A sample loading channel (with a diameter 1.27 cm) is located perpendicularly at the center of the chamber hole. This channel is extended further down across the bottom of the chamber hole to house a magnetic stirring bar. Solvent inlet and outlet ports are located at the top and the bottom of the cell. Solvent delivery is achieved by using high-pressure liquid pumps (LDC/Milton Roy Model 2396-89). The cell pressure is measured with an accuracy of ±0.03 MPa by a Dynisco flush mount transducer (Model TPT 432A-10A). [The readings are frequently checked against a calibrated Heise gauge with subdivisions of 0.06 MPa (Model CC-90037).] The temperature is measured with an Omega J-type thermocouple (Model JQSS-116G) with an accuracy of ±0.5 °C. Both temperature and pressure sensors are in direct contact with the fluids. The cell can be operated in a variable or fixed volume mode by using a movable piston or dead plug attachment to close the sample port. In the fixed volume mode, the internal volume of the cell is 16.5 cm^3 with the magnetic stirring bar in place. In the present work, the cell was used in the fixed volume mode. Its use with the variable volume attachment has been described elsewhere (*2*).

***B*. *Operational Procedure*.** The gas-liquid critical point for pure substances and mixtures is determined by a procedure based on visual observations. The fluid to be tested is first introduced into the cell at room temperature. A Sartorius balance with an accuracy of ±0.1 g is used to measure the weight of the cell before and after introducing the fluid. The amount of the fluid in the cell is controlled in such a way that the density of the fluid will be close to (or slightly higher than) its critical density. At room temperature, this amount usually corresponds with the liquid level in the cell being at or slightly above the center line of the chamber hole. After filling, the cell is heated until one-phase regions are achieved, and in the process the position of the meniscus is observed. If the cell is loaded with the correct amount of fluid (corresponding to the critical density), the location of the meniscus remains unchanged until it disappears at the critical point (*3*). After one-phase region is achieved, the system is cooled by natural convection. The cooling rate is estimated to be less than 0.3 °C/min when the temperature difference between the cell and the environment is about 30 °C. If indeed the density is near the critical, in the cooling process, before two-phase regions are encountered the color of the fluid undergoes from clear to yellow, to red glow, and then black. These color changes are not observed if the cell loading does not correspond with the critical density. In such a case, some amount of the fluid is released by opening the outlet valve, and the procedure is repeated until the color changes are observed. Heating and cooling processes are repeated several times in the color change region before a reading (temperature and pressure) is made at the moment when the complete darkness occurs.

The critical points for pure substances measured by this procedure are in excellent agreement with the literature values. Thus, the assessment of the critical condition is made by ensuring that the meniscus position does not change during heating and there are distinct color changes during cooling as well as during heating provided heating is carried out very slowly near the critical point and the meniscus reappears again at the center line across the chamber hole after the complete darkness in the cooling process.

In the determination of the critical condition for binary fluid mixtures, a certain amount of the component with lower vapor pressure (in this work methylamine) is first introduced into the cell at room temperature. Then the second component (nitrous oxide or ethylene) is added. The cell is weighed before and after each filling so that a desired mixture composition can be

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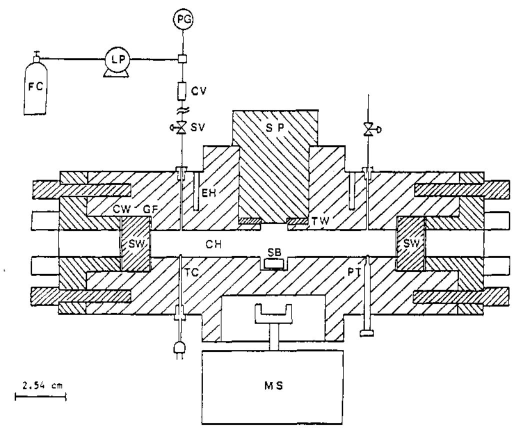

Figure 1. Schematic diagram of the experimental system: FC, fluid cylinder; LP, liquid pump; PG, pressure gauge; CV, check valve; SV, shut-off valve; CW, copper washer; SW, sapphire window; GF, gold foil; EH, electrical heater; CH, chamber hole; TW, Teflon washer; SB, stirring bar; SP, sample port plug; MS, magnetic stirrer; TC, thermocouple; PT, pressure transducer.

Table I. Comparison of the Critical Constants from This Work with Those from Literature (*5*)

	T_c, °C		P_c, MPa		V_c, cm^3 mol^{-1}	
substance	this work	lit.	this work	lit.	this work	lit.
CO_2	31.2	31.0	7.34	7.38	91.9	93.9
N_2O	36.5	36.5	7.27	7.24	95.5	97.4
n-C_4H_{10}	151.5	152.1	3.80	3.80	263.0	255.0
CH_3NH_2	157.7	156.9	7.65	7.43	138.5	140.0

obtained. These additions are achievable directly from the fluid cylinders if the solvent with the lower vapor pressure is introduced first. The fluids could equally be introduced by using the liquid pumps. When the critical densities are a priori unknown, the cell is initially filled to a level above the center line. Then the same operational procedure established for pure fluids is followed. However, if the color changes are not observed at first attempt, the system is reheated so that the one-phase condition is once again achieved, and only then the outlet valve is slightly opened to release some amount of the one-phase mixture without changing the composition. The cooling process is repeated, and the critical condition is established when the color changes are encountered.

C. Materials. The methylamine used was obtained from Linde with 98.0 wt % purity. The nitrous oxide was from Airco with 99.9 wt % purity and the ethylene was from MG Scientific Gases with 99.5 wt % purity. The *n*-butane was from Matheson with 99.5 wt % purity and carbon dioxide was from Airco with 99.8 wt % purity. They were used without further purification.

Results and Discussion

The reliability of the experimental procedure was first tested by measuring the critical points of several pure substances such as carbon dioxide, nitrous oxide, *n*-butane and methylamine. Table I shows the results of these experiments. The critical temperatures and pressures are in excellent agreement with the literature values. Small differences in the case of methylamine may be attributed to the impurities. For all substances the experimentally determined critical volumes show some differences from the literature values. This is, however, understandable since there are inherent difficulties in direct experimental determination of critical volumes. The critical isotherm is very flat at the critical pressure, introducing experimental uncertainties on critical volumes. In the literature, critical volume is often established by extrapolation of values to the critical point (*3*, *4*).

Table II. Critical Properties of Methylamine + Nitrous Oxide

mole fraction of CH_3NH_2	T_c, °C	P_c, MPa	V_c, cm^3 mol^{-1}
0.0	36.5	7.27	95.5
0.195	60.9	8.23	95.1
0.277	69.0	8.53	88.8
0.347	78.3	8.76	89.4
0.368	81.0	8.88	92.6
0.479	96.9	9.21	94.5
0.499	100.5	9.23	101.6
0.571	107.3	9.25	94.4
0.647	119.2	9.16	96.3
0.734	131.6	8.84	101.7
0.904	147.6	8.22	115.8
1.0	157.7	7.65	138.5

Table III. Critical Properties of Methylamine + Ethylene

mole fraction of CH_3NH_2	T_c, °C	P_c, MPa	V_c, cm^3 mol^{-1}
0.0^a	9.3	5.04	130.4
0.141	31.6	6.14	120.7
0.237	50.2	7.08	116.0
0.271	54.5	7.25	105.7
0.339	63.3	7.61	102.0
0.424	77.5	8.09	100.8
0.484	93.6	8.40	108.1
0.510	92.5	8.38	101.7
0.609	106.2	8.56	100.6
0.687	121.3	8.57	107.9
0.811	134.3	8.40	109.3
0.923	151.2	7.89	118.1
1.0	157.7	7.65	138.5

^{a}Data from literature (*5*).

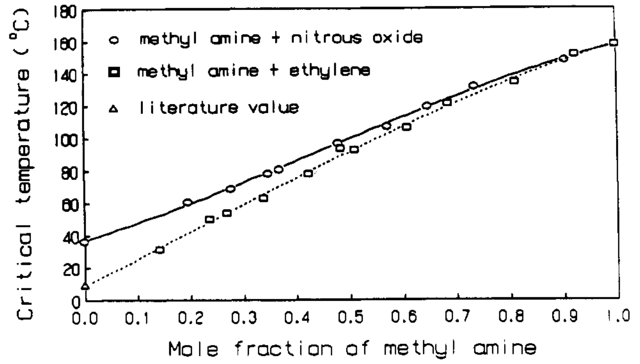

Figure 2. Critical temperature as a function of methylamine mole fraction in the systems methylamine + nitrous oxide and methylamine + ethylene.

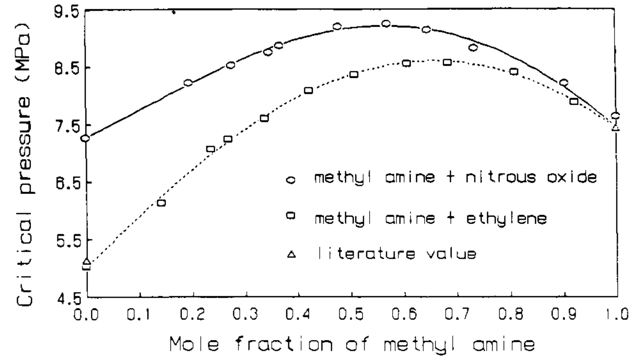

Figure 3. Critical pressure as a function of methylamine mole fraction in the systems methylamine + nitrous oxide and methylamine + ethylene.

Tables II and III show the critical data for the mixtures of methylamine with nitrous oxide and ethylene. The data are presented in graphical form in Figures 2–4. As seen from the

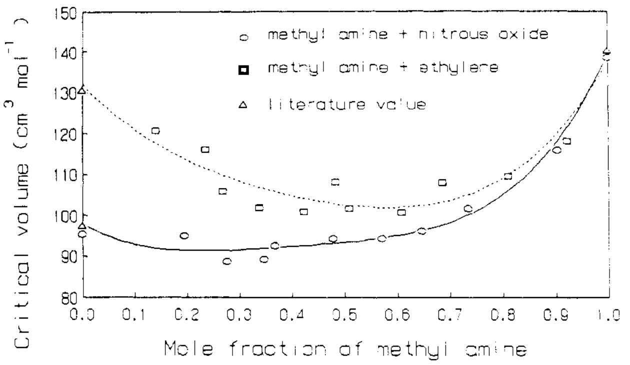

Figure 4. Critical volume as a function of methylamine mole fraction in the systems methylamine + nitrous oxide and methylamine + ethylene.

figures, for both systems the critical lines are continuous over the whole composition range between the critical points of the pure components. The critical pressure passes through a maximum at about 55 and 65 mol % methylamine in its binary mixtures with nitrous oxide and ethylene, respectively. Critical volumes pass through a minimum. The scattering in the critical volume data stems from the difficulty in direct experimental measurement of critical volumes as mentioned above.

Registry No. N_2O, 10024-97-2; CH_3NH_2, 74-89-5; ethylene, 74-85-1.

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High-Temperature Diffusion, Viscosity, and Density Measurements in *n*-Eicosane

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Taylor dispersion technique is used to measure the infinite dilution diffusion coefficients of eight solutes (H_2, CO, CO_2, *n*-C_8H_{18}, *n*-$C_{10}H_{22}$, *n*-$C_{12}H_{26}$, *n*-$C_{14}H_{30}$, *n*-$C_{16}H_{34}$) in *n*-eicosane over the temperature range 100–260 °C at 1.38 MPa pressure. The density and viscosity of *n*-eicosane were measured at the same conditions as well. It is shown that the rough hard-sphere theory can correctly represent the data.

Introduction

Mutual diffusion coefficients, viscosity, and density are the thermophysical properties needed in evaluation of mass-transfer phenomena and in design of equipment for mass-transfer operations. Diffusion data at high temperatures are very scarce and are nonexistent for high-boiling substances. Our objective is to measure these three thermophysical properties in a homologous series of alkanes. We have reported our measurements of diffusion, viscosity, and density in heptane, dodecane, and hexadecane over a wide temperature range previously (*1*, *2*). This work extends the previous study to *n*-eicosane.

Experimental Techniques

Infinite dilution diffusion coefficients of three gaseous (hydrogen, carbon monoxide, and carbon dioxide) and five alkane (octane, decane, dodecane, tetradecane, and hexadecane) solutes in *n*-eicosane were measured by using the Taylor dispersion technique (*3*). In this method, a narrow pulse of solute (A) diluted in the solvent (B) is injected into a tube in which the solvent is moving in slow laminar flow. The pulse ultimately assumes a Gaussian distribution whose temporal variance σ^2 is dependent on the average velocity $\bar{u}$ and molecular diffusivity D_{AB}. At the end of the diffusion tube the concentration $C(t)$ is recorded as a function of time data as the peak elutes through a detector. The normalized first and second temporal moments ($\bar{t}$ and σ^2) are calculated by finite summation. The following equations result in the direct calculation of the diffusion coefficient.

$$D_{12} = \frac{1}{2}\left[\bar{u}L\zeta_0 - \left[(\bar{u}L\zeta_0)^2 - \left(\frac{\bar{u}^2R^2}{12}\right)\right]^{1/2}\right] \quad (1)$$

where

$$\bar{u} = (L/\bar{t})(1 + 2\zeta_0) \quad (2)$$

$$\zeta_0 = \frac{2\sigma^2 - \bar{t}^2 + [\bar{t}^4 + 4\bar{t}^2\sigma^2]^{1/2}}{(8\bar{t}^2 - 4\sigma^2)} \quad (3)$$

Equation 1 accounts for molecular diffusion in both axial and radial directions within the dispersion tube. The tube length L and the radius R are corrected for thermal expansion effects which are significant at temperatures above 100 °C.

Viscosity is measured with the standard capillary viscometer technique, which is based on the Hagen–Poiseuille equation. Density is measured by a new technique we developed which is based on the retention time of the solute peak (*4*, *5*). The retention time is just the first temporal moment $\bar{t}$ calculated from the Taylor dispersion experiment and it depends on the solvent density, dispersion tube volume V_t, and mass flow rate. The tube volume is calibrated by using a fluid of known density such as water. Thus the density of *n*-eicosane can be calculated from

$$\rho_2 = \rho_1 \frac{\dot{m}^{(2)}\bar{t}^{(2)}V_t^{(1)}}{\dot{m}^{(1)}\bar{t}^{(1)}V_t^{(2)}} \quad (4)$$

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