Critical temperatures and pressures of caprolactam, dimethyl sulfoxide, 1,4-dimethylpiperazine, and 2,6-dimethylpiperazine

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ABSTRACT

The critical temperatures and pressures of caprolactam (CASRN 105-60-2), dimethyl sulfoxide (CASRN 67-68-5), 1,4-dimethylpiperazine (CASRN 106-58-1), and 2,6-dimethylpiperazine (CASRN 108-49-6) have been measured by the pulse-heating technique applicable to thermally unstable compounds. Experimental critical constants have been compared with those calculated using the group contribution methods of Wilson and Jasperson, Marrero and Gani, Hukkerikar and co-workers. The critical properties of dimethyl sulfoxide measured in this work have also been compared with the results of computer simulation by Vahid and Maginn.

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1. Introduction

This paper presents the critical temperatures and pressures of four compounds of industrial importance: caprolactam (the Chemical Abstracts Registry Number is 105—60-2), dimethyl sulfoxide (DMSO, CASRN 67-68-5), 1,4-dimethylpiperazine (CASRN 106-58-1), and 2,6-dimethylpiperazine (CASRN 108-49-6). Caprolactam is an intermediate primarily used in the production of Nylon 6 fibers and resins. About 6.5 billion kilograms of caprolactam are produced annually [1]. Dimethyl sulfoxide (DMSO) is widely employed as a solvent and reaction medium. Piperazine and many of its derivatives have important pharmacological properties. Piperazines are also used in manufacture of resins, plastics, pesticides and other materials.

All the compounds studied in this work decompose at their critical points. Extensive decomposition of caprolactam above 550 K during the vapor pressure measurements was observed by Steele et al. [2] while the critical temperature of caprolactam is about 800 K according to our experiments. DMSO is not a very stable compound as well; it decomposes at about its normal boiling point ($T_{nb} = 462.5$ K). The onset temperature of the decomposition of pure DMSO was 468 K in the experiments of Lam et al. [3]. Using an accelerating rate calorimeter, Yang et al. [4] found that the onset temperature was 472.55 K. The critical temperature of DMSO can be roughly estimated using the Guldberg rule: $T_c = 1.5T_{nb} = 693$ K, so that one may expect that DMSO will be very unstable at the critical point. Piperazine decomposes at the critical point; nevertheless, Steele et al. [5] and VonNiederhausern et al. [6] could measure the critical properties of this compound using special methods. It is reasonable to suggest that dimethylpiperazines are unstable at the critical points too.

The critical properties are equilibrium ones, and, strictly speaking, the critical point of an unstable compound is the critical point of a mixture of its decomposition products at the condition of chemical equilibrium. However, instead of using the critical point of this mixture, most investigators require the point which this compound would have if it were stable and no decomposition occurred. It is the definition that we shall use further. Such a critical point is not attainable in the course of a quasi-static process and in this meaning it is hypothetical. So we want to emphasize once more: by the critical point of an unstable compound, we shall mean a hypothetical critical point which the compound would have if no decomposition occurred.

In practice, the critical properties of an unstable compound can be measured directly because chemical decomposition occurs with a finite rate. To do this, one can quickly heat a sample of the compound under study up to the critical temperature and perform all

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the necessary measurements before considerable decomposition of the material occurs. Several methods applicable to the measurement of the critical properties of thermally unstable compounds have been developed [7–18]. These methods limit decomposition in the course of measuring the critical properties. In reality, the critical properties of a system (the compound under study + a small amount of decomposition products) are measured using these techniques. Some of these methods rely on ascertaining the dependence of the apparent critical properties on residence time. This dependence arises due to the decomposition of a compound under study. The longer the residence time, the larger the molar fraction of decomposition products grows. The critical properties of a pure, non-decomposed compound are determined by the extrapolation of the apparent critical property vs residence time curve to zero residence time.

A knowledge of the critical properties of a compound, even if it is unstable at the critical point, enables estimation of its thermodynamic and transport properties because the critical constants are used as inputs in many correlations based on the law of corresponding states. It is clear, of course, that these correlations work only in the region of stability of an unstable compound.

To reduce the decomposition of the compounds studied in this work in the course of measuring the critical properties, the measurements have been performed by the pulse-heating method with ultralow residence times [14–18].
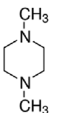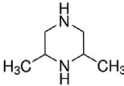
2. Experimental

2.1. Material

Samples of the compounds investigated in this work were purchased from Sigma-Aldrich and used without any additional purification. The purities and Chemical Abstract Service Registry Numbers (CASRN) of the samples are listed in Table 1. Before and after measuring the critical properties of DMSO, IR spectra of the sample were obtained using a Nicolet 6700 FT-IR spectrometer. Both spectra were completely identical.

2.2. Method

The pulse-heating method used for the measurement of the critical temperatures and pressures of the compounds studied was developed by us in the early nineties, and by now the critical properties of about 250 compounds, most of which are thermally unstable, have been measured. Most of these data have been collected in a recent review (Part 12 [19]) and the previous parts of this series of publications. The pulse-heating technique has been described in detail in previous papers [14–18]. The method is based on the phenomenon of the superheat of liquids [20,21] and consists in measuring the pressure dependence of the temperature of the attainable superheat (the line of the attainable superheat) with the help of a thin wire probe heated by electric current pulses. The critical point is the end point on both the vapor-liquid equilibrium line and the line of the attainable superheat. The duration of the heating pulses is short enough - from 0.03 to 1.0 ms — to limit decomposition of thermally unstable compounds in order to measure the critical properties. The line of the attainable superheat of DMSO at a duration of the heating pulse of 0.06 ms is shown in Fig. 1. The last point on this kind of a line corresponds to the apparent values of the critical pressure and temperature.

If a compound under study is thermally unstable at the critical point, the apparent critical pressure and temperature of it may depend on the duration of a heating pulse. In this situation, the measured values of the critical pressure p_c^m and critical temperature T_c^m are determined by the extrapolation of the apparent critical property vs the duration of a heating pulse curve to a zero heating time. In this work, the durations of heating pulses were 0.035, 0.06, 0.11, 0.22, 0.46, and 0.85 ms; the probe lengths were 1, 2, and 3 cm; and three or four samples of each compound were employed. Although each of the compounds studied decompose at their critical points, no obvious dependence of the apparent critical temperature and pressure on the durations of the heating pulses was observed. It is likely that the molar fractions of decomposition products formed during a heating pulse were so small that they did not significantly affect the critical properties. Thus, the measured values of the critical temperature T_c^m and pressure p_c^m were determined by averaging the apparent critical parameters over all the heating times, probe lengths, and samples.

It has been found that for both stable and unstable compounds these measured values of the critical properties p_c^m and T_c^m are a bit smaller than the true critical values. The true critical pressure p_c and temperature T_c are calculated by the following equations:

$$p_c = p_c^m/\pi_o, \quad T_c = T_c^m/\tau_0, \tag{1}$$

Table 1
Purities of compounds used in critical point measurement (Sigma-Aldrich, GC, supplier's certificates of analysis).

Compound	Structural formula	CASRN[a]	Purity (mol. fraction)
Caprolactam		105-60-2	0.9999
Dimethyl sulfoxide		67-68-5	0.999
1,4-Dimethylpiperazine		106-58-1	0.999
2,6-Dimethylpiperazine		108-49-6	0.998

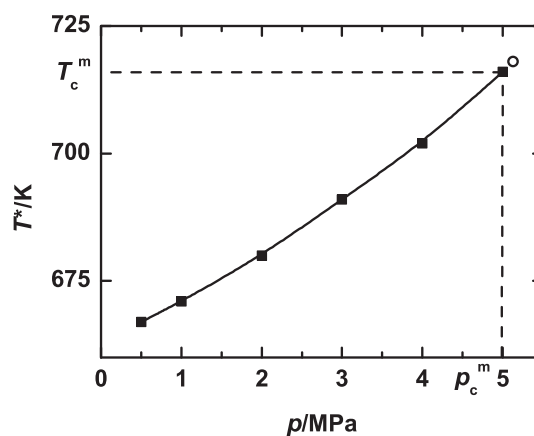[a] Chemical abstracts service registry number.

Fig. 1. Temperature of the attainable superheat of DMSO (■) against the pressure; ○, critical point; p_c^m and T_c^m are the measured values of the critical pressure and temperature. The time from the beginning of a heating pulse to the moment of boiling-up is 0.06 ms.