Critical Properties of Thermally Unstable Substances from Mixture Data

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Smith et al. (1987) have recently proposed a modified sealed tube method for the measurement of the critical temperatures of thermally unstable fluids. They also proposed a new method of analysis of the apparent critical temperature vs. time data obtained in their experiments. Their analysis employed reaction kinetics based on an irreversible first-order reaction and was used to linearize the data and to perform an unambiguous extrapolation to the critical temperature of the undecomposed substance. The method cannot be used for substances that decompose very rapidly well before reaching their critical points, since the reaction rate constant approximately doubles for every 10° increase in temperature. One possibility of reducing the reaction rate is by the addition of a second component with a lower critical temperature. The critical temperature vs. time behavior of the binary system can then be measured and the data extrapolated to the (undecomposed) pure components along the critical locus of the binary system. This idea is examined further below and new data are presented for two *n*-pentadecane/*n*-decane mixtures.

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Development of the Method

To explore the idea further, literature values of the critical properties of binary mixtures of stable substances were examined. The compilation of Hicks and Young (1975) was used for this purpose. Figure 1 shows the critical temperature vs. composition behavior of a homologous series of *n*-alkanes with benzene as the common component. It can be seen that the critical locus

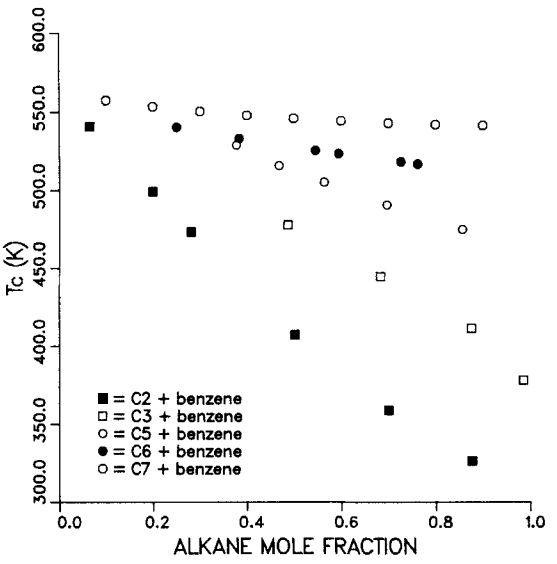

Figure 1. Critical loci of several *n*-alkane/benzene mixtures.

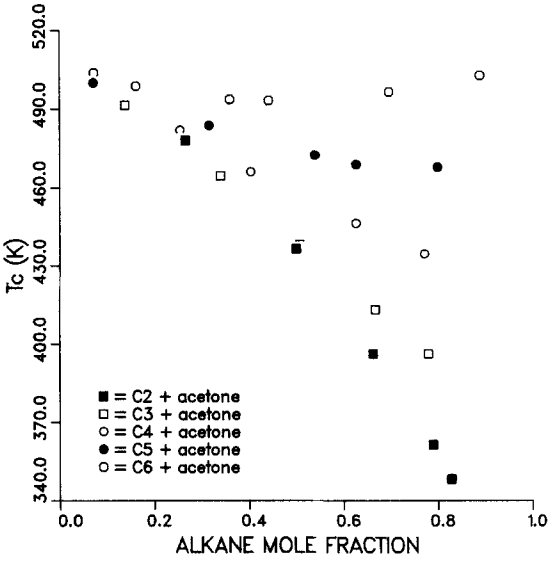

Figure 2. Critical loci of several *n*-alkane/acetone mixtures.

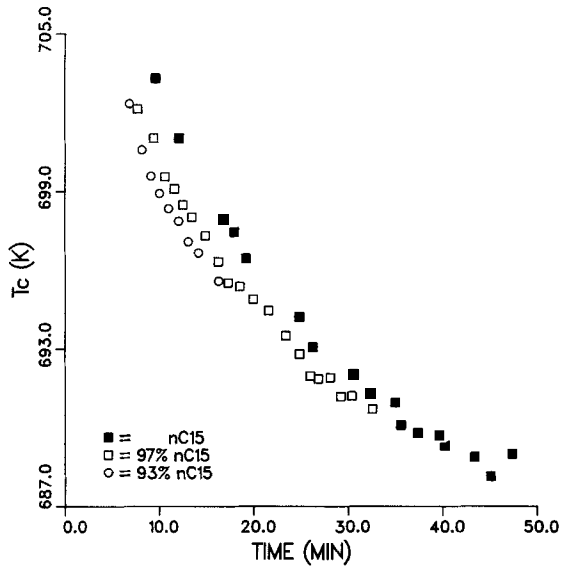

Figure 3. Critical temperature vs. time behavior of *n*-pentadecane/*n*-decane mixtures.

of each binary system can be extrapolated to give the critical temperature of the higher boiling component (benzene, in this case). The extrapolation is accurate when the ratio of critical temperatures of the two components is close to unity and the critical locus of the binary system is approximately linear. When the ratio of critical temperatures of the pure components is much greater than unity, as in the case of the ethane/benzene system, the extrapolation to the pure-component critical point is less accurate due to the curvature of the critical locus. As expected, it is best to extrapolate data close to the critical point of the pure component. It should also be noted that the addition of the second (low-boiling) component causes a lowering of the critical temperature of the binary system, and hence lower reaction rates if the higher boiling component decomposes. The same type of behavior is obtained when the common component

Table 1. Critical Temperatures of two *n*-Pentadecane/*n*-Decane Mixtures

x_1	T^c / K
0.97	705.7
0.93	704.9

is very different from the members of the homologous series, as shown in Figure 2.

In the case of thermally unstable substances, the critical temperature vs. time behavior must also be considered in addition to the critical temperature vs. composition behavior. The critical temperature vs. time behavior must first be analyzed to obtain the critical locus of the binary system consisting of the (undecomposed) high-boiling component and the added low-boiling component. The critical locus may then be extrapolated to the pure (undecomposed) component, as shown in Figures 1 and 2.

New Data and Analysis

Figure 3 shows the critical temperature vs. time behavior of two mixtures, one initially containing 97 mol % *n*-pentadecane and 3 mol % *n*-decane, and the other initially containing 93 mol % *n*-pentadecane and 7 mol % *n*-decane. The measurements were made using the apparatus described in our earlier work (Smith et al., 1987). The extrapolation of the initial few points of the critical temperature-time curve to zero time (as described in Smith et al., 1987) is shown in Figure 4, and the critical points of the mixtures are reported in Table 1. The extrapolation of the critical locus is shown in Figure 5. This gives a critical temperature of 706.3 K for the undecomposed *n*-pentadecane, which agrees with our previously reported value of 706.4 K, within experimental error.

Discussion and Conclusions

The method described above can, in principle, be used to obtain the critical properties of any thermally unstable fluid. It

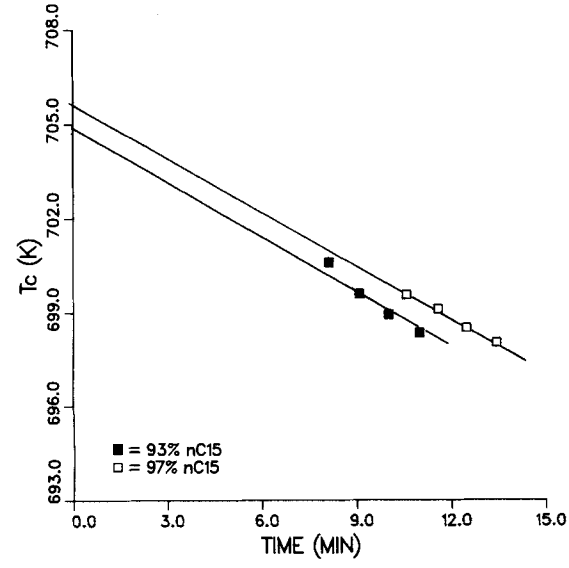

Figure 4. Linear part of critical temperature vs. time behavior of *n*-pentadecane/*n*-decane mixtures.

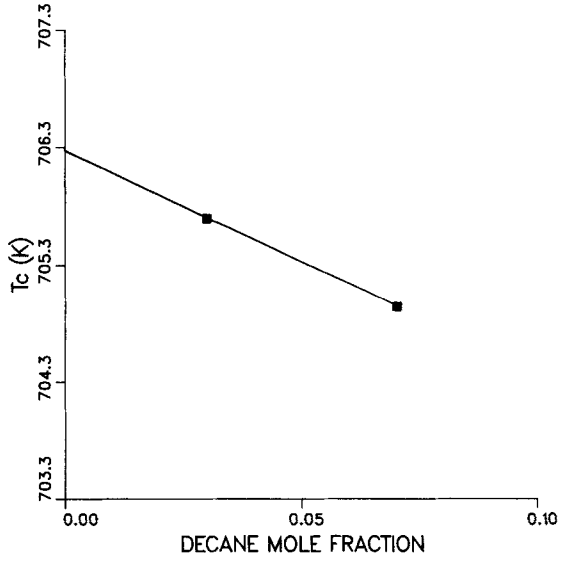

Figure 5. Extrapolation of critical locus of *n*-pentadecane/*n*-decane mixtures.

has the advantage that a knowledge of the decomposition or association kinetics is not required. However, it is assumed that the critical locus is linear. In practice, this is true at high concentrations of the high-boiling component, which in turn implies high reaction rates. The addition of significant amounts of the low-boiling component obviously causes a decrease in reaction rates because of the lowering of the critical temperature. However, as the amount of low-boiling component increases, the critical temperature vs. time curves become steeper, as can be seen in Figure 3, and therefore more difficult to extrapolate to zero time. Therefore, there is obviously a maximum amount of low-boiling component that can be used in this type of experiment.

The analysis described above has obvious implications in the study of the effect of impurities on the physical properties of stable and unstable fluids. Such a study for stable fluids has been attempted by Morrison and Kincaid (1984). Our work represents an initial step in extending the work of Morrison and Kincaid to thermally unstable fluids.

Acknowledgment

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