# Isobaric Vapor–Liquid Equilibrium Data for the System: Heptaldehyde–Methyl Undecenoate

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**ABSTRACT:** Isobaric-bubble temperature data at 50 mmHg were collected for the system heptaldehyde–methyl undecenoate over the entire composition range by the indirect method with a standard Swietoslawski-type ebulliometer. The vapor compositions were computed by means of the nonrandom two-liquid equation. The average absolute error in temperature was 0.4°K.
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**KEY WORDS:** Heptaldehyde, methyl undecenoate, NRTL model, VLE.

Separation of mixtures into useful components or fractions is one of the most important activities of any chemical process industry. Distillation is the most important and energy-consuming operation among the separation processes. Hence, accurate knowledge of vapor–liquid equilibrium (VLE) data of any system is of utmost importance for optimum design and efficient operation of distillation columns. Heptaldehyde and methyl undecenoate are the major compounds formed during pyrolysis of castor oil methyl esters (1). Heptaldehyde is widely used as an intermediate for perfumery chemicals while methyl undecenoate is the key intermediate in the preparation of Nylon-11, a widely used industrial polymer (2). These two compounds can be separated in an easy and economical way by distillation under reduced pressure. A literature survey revealed that the VLE data for heptaldehyde–methyl undecenoate system are not available. Isobaric data, as compared to isothermal data, are of more practical value in process engineering calculations. Hence, experiments were carried out under constant pressure of 50 mmHg to study the VLE data.

## EXPERIMENTAL PROCEDURES

The VLE measurements were conducted in a Swietoslawski ebulliometer (3). The ebulliometer was connected to a vacuum system. The pressures were measured by a mercury manometer with an accuracy of 1 mmHg. The temperature was measured with a PT100 thermometer with a precision of 0.1°C.

Bubble points of the system heptaldehyde–methyl undecenoate were determined over the entire composition range at 50 mmHg. For a known composition ($x$) of the liquid mixture

charged in the ebulliometer, the equilibrium temperature ($t$) was recorded when it remained constant for about half an hour. The procedure was repeated for various compositions of the mixture. The mixtures of known compositions were prepared by taking pure components by weight. The compositions are expected to be accurate up to 0.1 mole%.

*Purity of the materials.* Heptaldehyde and methyl undecenoate used were obtained by distillation of the pyrolysis product of castor oil methyl esters. These chemicals were further purified by distillation, and middle cuts were taken for the present study. The purity of these chemicals was checked by means of gas–liquid chromatographic (GLC) analysis and found to be more than 99% for both.

## RESULTS AND DISCUSSION

The bubble temperature data are presented in Table 1. These data are correlated for activity coefficients ($\gamma$) by means of the widely used nonrandom two-liquid (NRTL) model (4,5). The gas phase is assumed to be ideal, and hence the fugacity coefficient is taken as unity. The model parameters are ob-

**TABLE 1**
**Vapor–Liquid Equilibrium Data for the Heptaldehyde–Methyl Undecenoate System[a]**

| $x_1$ | $t_{exp}$(°C) | $t_{calc}$(°C) | $y_{1,calc}$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|
| 0.0000 | 159.6 | 159.7 | 0.0000 | 0.6922 | 1.0000 |
| 0.0539 | 146.1 | 146.1 | 0.4840 | 0.7122 | 0.9989 |
| 0.1162 | 133.2 | 133.3 | 0.7466 | 0.7373 | 0.9946 |
| 0.2066 | 119.7 | 119.3 | 0.8992 | 0.7761 | 0.9826 |
| 0.2958 | 109.1 | 109.1 | 0.9548 | 0.8153 | 0.9638 |
| 0.3985 | 99.7 | 100.1 | 0.9804 | 0.8592 | 0.9340 |
| 0.4980 | 92.8 | 93.3 | 0.9908 | 0.8984 | 0.8975 |
| 0.5924 | 88.8 | 88.2 | 0.9954 | 0.9312 | 0.8568 |
| 0.6533 | 84.9 | 85.3 | 0.9970 | 0.9495 | 0.8279 |
| 0.7207 | 83.0 | 82.6 | 0.9982 | 0.9668 | 0.7939 |
| 0.7877 | 81.1 | 80.1 | 0.9990 | 0.9806 | 0.7583 |
| 0.8293 | 79.0 | 78.8 | 0.9993 | 0.9874 | 0.7356 |
| 0.8933 | 77.5 | 76.9 | 0.9997 | 0.9951 | 0.6997 |
| 0.9375 | 76.2 | 75.7 | 0.9998 | 0.9983 | 0.6746 |
| 1.0000 | 74.2 | 74.2 | 1.0000 | 1.0000 | 0.6387 |

[a]In the table, subscript 1 refers to heptaldehyde and 2 refers to methyl undecenoate. Model parameters used to fit the nonrandom two-liquid equation are $\Delta G_{12}/R = -118.7$, $\Delta G_{21}/R = -36.5544$ and $\alpha = 0.12$. Average absolute error in temperature, $\overline{\Delta t} = 0.4$°K.
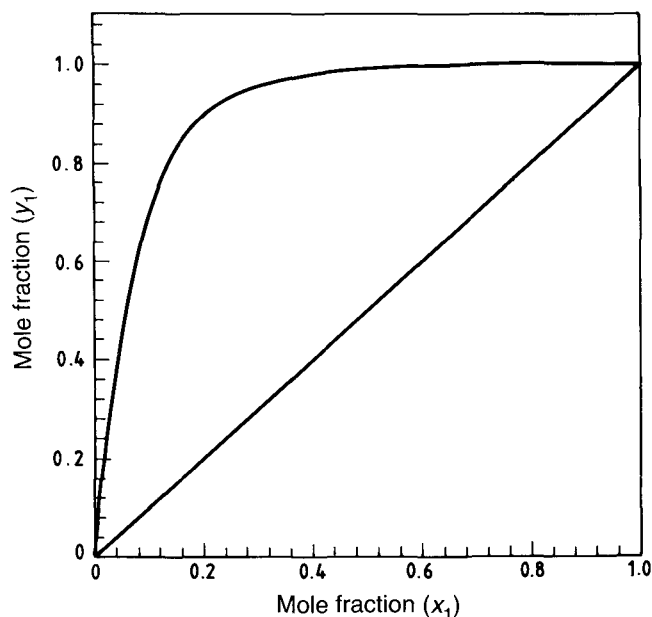
**FIG. 1.** Vapor-phase mole fraction ($y_1$) vs. liquid-phase mole fraction ($x_1$) of heptaldehyde.
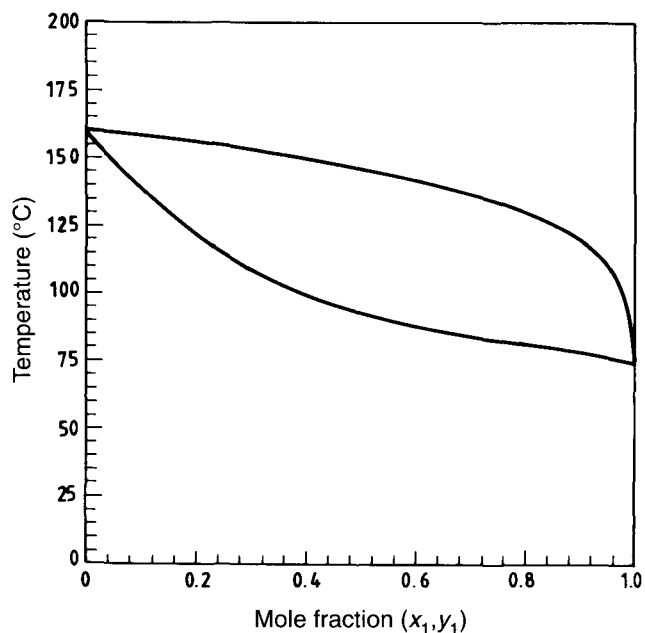


**FIG. 2.** Temperature vs. mole fraction ($x_1$, $y_1$) of heptaldehyde.

tained by minimizing the objective function ($\phi$):

$$\phi = \frac{P_{calc} - P_{exp}}{P_{exp}} \qquad [1]$$

by means of the Nelder Mead optimization techniques (6). The terms $P_{exp}$ and $P_{calc}$ used in Equation 1 denote the experimental and calculated pressures. The computed vapor compositions ($Y$) and the activity coefficients ($\gamma$) are also included in the table. The model parameters, along with the average absolute error in temperature ($\overline{\Delta t}$), are also reported. The data show that the model fits the data reasonably well. The assumption of ideal vapor phase behavior is justified because the pressure used here is low.

The graphs $x_1 - y_1$ and $t - (x_1 y_1)$ are shown in Figures 1 and 2.

## ACKNOWLEDGMENT

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