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# Isobaric vapor–liquid equilibria for the *n*-heptane + ethylene glycol monopropyl ether and *n*-octane + ethylene glycol monopropyl ether systems

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ABSTRACT

Vapor–liquid equilibria (VLE) for the *n*-heptane + ethylene glycol monopropyl ether and *n*-octane + ethylene glycol monopropyl ether systems were measured. Isobaric VLE measurements of the associating fluid mixtures were conducted at several pressures (60 kPa, 80 kPa and 100 kPa) using Fischer VLE 602 equipment. The experimental data were correlated using a two-term virial equation for vapor-phase fugacity coefficients and the three suffix Margules equation, Wilson, NRTL, and UNIQUAC models for liquid-phase activity coefficients. The results show good agreement with the variety of models.

## 1. Introduction

For several decades, surfactants have been attracting considerable attention because they have numerous applications in various industries, including detergent, cosmetic, pharmaceutical, food and petrochemical industries. It is important to accurately assess the phase behavior data (e.g., vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE)) of mixtures containing surfactants. To quantify phase behavior we conducted VLE experiments using nonionic surfactants and hydrocarbon mixture systems under both isothermal [1] and isobaric conditions [2]. Ethoxylated alcohol {H-$(CH_2)_i$-$(OCH_2CH_2)_j$-OH or C*i*E*j*} surfactants can participate in both inter-molecular and intra-molecular associations because they have both ether (O) and hydroxyl (OH) groups in the same molecule. However, in contrast to phase equilibrium data for water + surfactant [3–6] measured at atmospheric pressure, minimal data have been collected for nonionic surfactant + hydrocarbon systems [7,8].

Our previous study investigated the branch effect of a surfactant (C3E1 and *i*C3E1) in a mixture with linear hydrocarbons, using isothermal VLE of *n*-hexane + C3E1 and *n*-heptane + C3E1 [1] and isobaric VLE of *n*-hexane + *i*C3E1 and *n*-heptane + *i*C3E1 [2]. In this study we measured vapor–liquid equilibria for *n*-heptane + ethylene glycol monopropyl ether (C3E1) and *n*-octane + ethylene glycol monopropyl ether (C3E1) systems at three different pressures, ranging from 60 kPa to 100 kPa. The experimental data were correlated with values from the two-term virial equation for vapor-phase fugacity coefficients [9] using the three suffix Margules equation [10], Wilson [11], NRTL [12], UNIQUAC [13] models for liquid-phase activity coefficients.

## 2. Experimental

### 2.1. Materials

*n*-Heptane and *n*-octane with a minimum purity of 99.0% (GC grade) were supplied by TCI (Japan) and Aldrich (U.S.A.), respectively. Ethylene glycol monopropyl ether (C3E1) with a minimum purity of 99.4% (GC grade) was supplied by Aldrich (U.S.A.). There were no other notable peaks detected in preliminary GC analysis; therefore, we used these materials without further pre-experimental purification.

### 2.2. Apparatus and procedures

Experimental details are described in a previous paper [2]. Phase equilibrium data were determined using a Labodest® VLE 602 apparatus (Fischer), which circulates both vapor and liquid phases to quicken the achievement of the phase equilibrium. This apparatus consists of three parts (heating cell, equilibrium cell, circulating glass tube), and all parts are connected to each other. The pressure was measured by a Fischer digital manometer with an accuracy of

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**Table 1**
Experimental vapor–liquid equilibrium data and activities for the binary system *n*-heptane (1) + ethylene glycol monopropyl ether (2) at 60 kPa, 80 kPa, and 100 kPa.

| $P$ (kPa) | $T$ (K) | $x_1$ | $y_1$ | Standard deviation of $x_1$ | Standard deviation of $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|
| 60.0 | 406.15 | 0.000 | 0.000 | | | | 1.000 |
| | 401.80 | 0.009 | 0.137 | 0.00036 | 0.00076 | 4.292 | 1.000 |
| | 397.63 | 0.019 | 0.257 | 0.00288 | 0.00149 | 4.168 | 1.001 |
| | 392.24 | 0.034 | 0.386 | 0.00328 | 0.00648 | 3.986 | 1.002 |
| | 386.09 | 0.058 | 0.521 | 0.00207 | 0.00565 | 3.717 | 1.005 |
| | 376.27 | 0.115 | 0.688 | 0.00538 | 0.00712 | 3.159 | 1.021 |
| | 366.30 | 0.233 | 0.805 | 0.00407 | 0.00401 | 2.340 | 1.087 |
| | 359.59 | 0.486 | 0.880 | 0.00065 | 0.00170 | 1.548 | 1.362 |
| | 355.92 | 0.720 | 0.919 | 0.00805 | 0.00107 | 1.226 | 1.967 |
| | 354.76 | 0.877 | 0.938 | 0.00182 | 0.00173 | 1.061 | 3.608 |
| | 354.61 | 0.930 | 0.961 | 0.00219 | 0.00212 | 1.022 | 5.112 |
| | 354.56 | 0.961 | 0.970 | 0.00286 | 0.00083 | 1.007 | 6.587 |
| | 354.56 | 0.982 | 0.982 | 0.00539 | 0.00071 | 1.002 | 8.045 |
| | 354.70 | 1.000 | 1.000 | | | 1.000 | |
| 80.0 | 415.30 | 0.000 | 0.000 | | | | 1.000 |
| | 410.73 | 0.013 | 0.142 | 0.00115 | 0.00515 | 3.457 | 1.000 |
| | 403.26 | 0.037 | 0.344 | 0.00183 | 0.00055 | 3.368 | 1.001 |
| | 396.96 | 0.060 | 0.487 | 0.00164 | 0.00623 | 3.263 | 1.002 |
| | 388.70 | 0.103 | 0.619 | 0.00190 | 0.00402 | 3.052 | 1.008 |
| | 381.19 | 0.168 | 0.731 | 0.00285 | 0.00115 | 2.714 | 1.027 |
| | 372.39 | 0.309 | 0.837 | 0.00021 | 0.00134 | 2.080 | 1.117 |
| | 368.18 | 0.473 | 0.875 | 0.00256 | 0.00364 | 1.610 | 1.317 |
| | 365.39 | 0.651 | 0.903 | 0.00610 | 0.00209 | 1.304 | 1.731 |
| | 363.79 | 0.917 | 0.957 | 0.00086 | 0.00113 | 1.027 | 4.563 |
| | 363.56 | 0.971 | 0.980 | 0.00505 | 0.00028 | 1.004 | 6.718 |
| | 363.75 | 1.000 | 1.000 | | | 1.000 | |
| 100.0 | 422.75 | 0.000 | 0.000 | | | | 1.000 |
| | 418.39 | 0.018 | 0.136 | 0.00006 | 0.00362 | 2.673 | 1.000 |
| | 413.01 | 0.037 | 0.283 | 0.00303 | 0.00798 | 2.713 | 0.999 |
| | 407.80 | 0.058 | 0.410 | 0.00027 | 0.00448 | 2.733 | 0.999 |
| | 398.34 | 0.107 | 0.582 | 0.00330 | 0.00117 | 2.702 | 1.000 |
| | 388.39 | 0.182 | 0.727 | 0.00106 | 0.00036 | 2.516 | 1.013 |
| | 379.32 | 0.330 | 0.828 | 0.00300 | 0.00138 | 2.010 | 1.097 |
| | 374.64 | 0.528 | 0.880 | 0.00099 | 0.00183 | 1.497 | 1.371 |
| | 372.35 | 0.730 | 0.906 | 0.00404 | 0.00288 | 1.190 | 2.039 |
| | 371.07 | 0.924 | 0.954 | 0.00041 | 0.00040 | 1.021 | 4.462 |
| | 370.83 | 0.973 | 0.980 | 0.00066 | 0.00041 | 1.003 | 6.234 |
| | 371.15 | 1.000 | 1.000 | | | 1.000 | |

±0.01 kPa. The temperature was measured by a temperature sensor located in an equilibrium cell with an accuracy of ±0.01 K. The Cottrell pump mixes vapor and liquid phases by enhancing mass transfer between the two phases.

We set the pressure and heated the feed to adjust the temperature. The pressure and temperature are controlled automatically by a built-in electronic controller. When the pressure and temperature remained constant for at least 30 min, we assumed that the system reached equilibrium conditions. Sampling was conducted using a syringe, and the samples were analyzed by a gas chromatograph equipped with a thermal conductivity detector and a Porapak Q column (length: 1.83 m, diameter: 3.18 mm, mesh range: 80/100). Helium was used as carrier gas.

## 3. Results and discussion

The isobaric vapor–liquid equilibrium data for the binary systems of *n*-heptane (1) + ethylene glycol monopropyl ether (C3E1) (2) and *n*-octane (1) + ethylene glycol monopropyl ether (C3E1) (2) measured at 60 kPa, 80 kPa, and 100 kPa are presented in Tables 1 and 2. Boiling temperatures of each pure component at the designated pressure were calculated from the Antoine equation with constants *A*, *B*, and *C* (Table 3). Also, physical properties of the pure components are shown in Table 3.

$$\frac{\log_{10} P_i^{\text{sat}}}{\text{bar}} = A - \frac{B}{C + T/K} \qquad (1)$$

where $P_i^{\text{sat}}$ is the vapor pressure of the pure *i*th component.

The activity coefficient, $\gamma_i$, was calculated by

$$\gamma_i = \frac{y_i P}{x_i P_i^{\text{sat}}} \exp\left[\frac{(B_{ii} - v_i^L)(P - P_i^{\text{sat}}) + (1 - y_i)^2 P\delta_{ij}}{RT}\right] \qquad (2)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (3)$$

where $x_i$ and $y_i$ are the liquid and vapor phase compositions, respectively, $P$ is the total pressure, and $B_{ij}$, $B_{ii}$ and $B_{jj}$ are the second virial coefficients. The activities in Tables 1 and 2 are calculated by Eq. (2).

The second virial coefficients were calculated by the Hayden and O'Connell's empirical correlation [9]. The constants used in this correlation for *n*-heptane and *n*-octane were obtained from Fredenslund et al. [14], and those for ethylene glycol monopropyl ether were determined in this work.

The thermodynamic consistency of the experimental data was tested using the method of Fredenslund et al. (1977), with the third-order Legendre polynomial. Accordingly, although this method is more robust for isothermal data, the isobaric experimental data can be considered thermodynamically consistent when the average deviation of the vapor-phase composition is less than 0.01. The parameters of the Legendre polynomial and the average absolute deviations of the vapor phase composition (AAD*y*) and the pressure (AAD*P*) are presented in Table 4. As shown in Table 4, *n*-heptane + C3E1 systems are considered thermodynamically consistent, but the AAD*y* values of the *n*-octane + C3E1 systems are slightly higher than 0.01. This result is due primarily to the proximity of the azeotrope point. Thus, we must consider that the rapid composition change on the plateau near the azeotrope point of