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# Isobaric Vapor−Liquid Equilibria for the 1-Propanol + Ethylene Glycol Monopropyl Ether and 1-Butanol + Ethylene Glycol Monopropyl Ether Systems

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**ABSTRACT:** Vapor−liquid equilibria (VLE) for 1-propanol + ethylene glycol monopropyl ether and 1-butanol + ethylene glycol monopropyl ether systems were investigated. The systems studied are isobaric VLE of the highly associating fluid mixtures, and the measurements were carried out at several pressures (60 kPa, 80 kPa, and 100 kPa) using Fischer VLE 602 equipment. A consistency test with respect to the experimental data was conducted using Fredenslud and Wisniak methods. Correlations of the experimental data were carried out using a two-term virial equation for vapor-phase fugacity coefficients and the three suffix Margules, Wilson, NRTL, and UNIQUAC models for liquid-phase activity coefficients. The results show good agreements with the experimental data at the C3E1 rich region but not at the alcohol rich region due to the strong and complex association of these systems. Additionally there are no azeotrope points.

## 1. INTRODUCTION

In these days, surfactants are used to improve various value-added industrial processes, including fiber, pharmaceutical, cosmetics, food, agrichemicals, and petrochemical industries. It is therefore important to accurately measure the phase behavior data (i.e., vapor−liquid equilibria (VLE) and liquid−liquid equilibria (LLE)) of surfactants and their mixtures. In particular, ethoxylated alcohol, a nonionic surfactant, and its mixtures with hydrocarbons or alcohols exhibit strong association, due to the participation in both intermolecular and intramolecular associations resulting from the coexistence of ether (O) and hydroxyl (OH) groups in the same molecule. In order to quantify the phase behavior we have performed isothermal VLE[1] and isobaric VLE[2,3] experiments of nonionic surfactants and hydrocarbon mixture systems. However, in contrast to the abundance of phase equilibrium data for water + surfactant[4−7] measured at atmospheric pressure, few data have been collected for nonionic surfactant + hydrocarbon[8,9] and alcohol[10] systems.

Our previous studies have investigated the branch effect of a surfactant (C3E1 and *i*C3E1) mainly in mixtures with linear hydrocarbons, using isothermal VLE of *n*-hexane + C3E1 and *n*-heptane + C3E1,[1] isobaric VLE of *n*-hexane + *i*C3E1 and *n*-heptane + *i*C3E1,[2] and isobaric VLE of *n*-heptane + C3E1 and *n*-octane + C3E1.[3] In this study we measured VLE of both the ethoxylated alcohol and normal alcohol systems, which are 1-propanol + ethylene glycol monopropyl ether (C3E1) and 1-butanol + ethylene glycol monopropyl ether (C3E1), respectively, at several different pressures (60 kPa to 100 kPa). A consistency test of the experimental data was carried out using Fredenslud and Wisniak methods, and correlations were conducted using the two-term virial equation for vapor-phase fugacity coefficients[11] and the three suffix Margules equation,[12] Wilson,[13] NRTL,[14] and UNIQUAC[15] models for liquid-phase activity coefficients.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** 1-Propanol and 1-butanol were supplied by Aldrich (U.S.A.), and the minimum purities are 99.9 % and 99.7 % (GC grade), respectively. Ethylene glycol monopropyl ether (C3E1) was supplied by Aldrich (U.S.A), and the minimum purity is 99.4 % (GC grade). We used these materials without further pre-experimental purification, because there were no other notable peaks detected in the preliminary GC analysis.

**2.2. Apparatus and Procedures.** The apparatus and procedures are exactly the same as described in a previous paper.[2,3] Thus, they are summarized below, and for any detailed description please refer to the original paper.[2,3]

The apparatus used in this work was Labodest VLE 602 (Fischer), which circulates both vapor and liquid phases to achieve fast phase equilibrium.

The pressure and heating rate controller was set at the desirable value which makes about 2 drops per second of vapor circulating speed, and the feed was heated at the isobaric condition. Following that, the feed was boiled in the feed reservoir and transported into the equilibrium cell as an overheated vapor. The feed under the equilibrium condition circulated through both the top- and the bottom-side of the glass tube simultaneously. It is assumed that the composition of the flow circulating through the top-side of the tube is vapor composition and through the bottom-side liquid stream is liquid phase composition. The key point is that the vapor circulating speed should not exceed 2 drops per second to ensure the stable equilibrium state. The system is considered to be under equilibrium conditions, when the temperature in the equilibrium cell remains

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**Table 1. Experimental Vapor−Liquid Equilibrium Data and Activity Coefficients for the Binary System 1-Propanol (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 $T$ | standard deviation of $x_1$ | standard deviation of $y_1$ | $\ln(\gamma_1/\gamma_2)$ |
|---|---|---|---|---|---|---|---|
| 100.0 | 422.75 | 0.00000 | 0.00000 | | | | |
| (0.19)[a] | 420.34 | 0.02056 | 0.08769 | 0.042 | 0.00120 | 0.00045 | −0.10630 |
| | 416.78 | 0.04923 | 0.20814 | 0.042 | 0.00191 | 0.00049 | −0.02026 |
| | 413.60 | 0.07865 | 0.31235 | 0.028 | 0.00062 | 0.00144 | 0.01165 |
| | 410.47 | 0.10999 | 0.40520 | 0.035 | 0.00212 | 0.00219 | 0.03246 |
| | 406.78 | 0.15358 | 0.50186 | 0.042 | 0.00038 | 0.00356 | 0.02315 |
| | 402.13 | 0.21230 | 0.60424 | 0.014 | 0.00163 | 0.00323 | 0.02321 |
| | 397.11 | 0.28264 | 0.69849 | 0.092 | 0.00064 | 0.00197 | 0.03949 |
| | 391.32 | 0.38637 | 0.79505 | 0.090 | 0.00229 | 0.00135 | 0.06224 |
| | 385.77 | 0.51085 | 0.87160 | 0.012 | 0.00354 | 0.00115 | 0.09321 |
| | 379.85 | 0.66334 | 0.93110 | 0.042 | 0.00018 | 0.00086 | 0.12360 |
| | 374.44 | 0.83141 | 0.97112 | 0.057 | 0.00544 | 0.00158 | 0.09672 |
| | 372.20 | 0.90913 | 0.98609 | 0.014 | 0.00013 | 0.00016 | 0.12636 |
| | 370.00 | 1.00000 | 1.00000 | | | | |
| 80.0 | 415.30 | 0.00000 | 0.00000 | | | | |
| (0.16)[a] | 412.82 | 0.01807 | 0.08974 | 0.056 | 0.00061 | 0.00258 | 0.02250 |
| | 410.05 | 0.03939 | 0.18435 | 0.036 | 0.00064 | 0.00307 | 0.03857 |
| | 406.80 | 0.07233 | 0.30538 | 0.059 | 0.00562 | 0.00146 | 0.04619 |
| | 403.81 | 0.10376 | 0.39140 | 0.035 | 0.00300 | 0.00057 | 0.01840 |
| | 399.34 | 0.15837 | 0.51175 | 0.122 | 0.00704 | 0.00322 | 0.00205 |
| | 394.86 | 0.21568 | 0.62045 | 0.064 | 0.00275 | 0.00410 | 0.04826 |
| | 390.96 | 0.27204 | 0.69788 | 0.228 | 0.00446 | 0.00580 | 0.07145 |
| | 385.66 | 0.37833 | 0.78720 | 0.088 | 0.00532 | 0.00043 | 0.03351 |
| | 379.43 | 0.51059 | 0.87831 | 0.042 | 0.00840 | 0.00132 | 0.13798 |
| | 374.01 | 0.66614 | 0.93019 | 0.007 | 0.00045 | 0.00336 | 0.08177 |
| | 369.10 | 0.81573 | 0.96897 | 0.035 | 0.00138 | 0.00050 | 0.11748 |
| | 366.12 | 0.91970 | 0.98793 | 0.023 | 0.00225 | 0.00062 | 0.11891 |
| | 364.20 | 1.00000 | 1.00000 | | | | |
| 60.0 | 406.15 | 0.00000 | 0.00000 | | | | |
| (0.13)[a] | 403.59 | 0.01805 | 0.10223 | 0.014 | 0.00011 | 0.00066 | 0.13414 |
| | 401.09 | 0.03923 | 0.19481 | 0.057 | 0.00020 | 0.00316 | 0.07905 |
| | 397.97 | 0.07247 | 0.29272 | 0.028 | 0.00035 | 0.00215 | −0.04579 |
| | 394.73 | 0.10588 | 0.39100 | 0.000 | 0.00102 | 0.00052 | −0.03578 |
| | 391.12 | 0.14869 | 0.50005 | 0.007 | 0.00279 | 0.00223 | 0.00394 |
| | 386.96 | 0.20718 | 0.61116 | 0.113 | 0.00175 | 0.00559 | 0.03601 |
| | 382.88 | 0.27958 | 0.70070 | 0.035 | 0.00081 | 0.00254 | 0.02273 |
| | 377.49 | 0.38693 | 0.79214 | 0.064 | 0.00632 | 0.00536 | 0.00271 |
| | 371.95 | 0.51977 | 0.87121 | 0.000 | 0.00519 | 0.00202 | 0.01560 |
| | 366.61 | 0.65621 | 0.93091 | 0.379 | 0.00951 | 0.00276 | 0.11652 |
| | 362.02 | 0.79713 | 0.96687 | 0.014 | 0.00130 | 0.00001 | 0.14961 |
| | 358.84 | 0.91872 | 0.98911 | 0.035 | 0.00151 | 0.00004 | 0.21579 |
| | 357.10 | 1.00000 | 1.00000 | | | | |

[a] Standard deviation of P: 99.7 kPa to 100.2 kPa at 100 kPa; 79.8 kPa to 80.2 kPa at 80 kPa; 59.9 kPa to 60.2 kPa at 60 kPa.

constant for at least 30 min. Then, the condensed vapor and liquid composition from the circulating glass tube were sampled by syringe respectively where the samples were analyzed by GC.

## 3. RESULTS AND DISCUSSION

**3.1. Vapor−Liquid Equilibria Measurements.** The isobaric vapor−liquid equilibrium data for the binary systems of 1-propanol (1) + ethylene glycol monopropyl ether (C3E1) (2) and 1-butanol (1) + ethylene glycol monopropyl ether (C3E1) (2) measured at 60 kPa, 80 kPa, and 100 kPa are presented in Tables 1 and 2, respectively. The vapor pressure of each pure component was calculated from the Antoine equation. The constants A, B, and C of the pure components listed in Table 3 were obtained from NIST Web data. Also, the physical properties of the pure components are indicated in Table 3.

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

The fugacity of the vapor, $f_i^V$, and the liquid, $f_i^L$, was calculated by the following equation

$$f_i^V = y_i P \phi_i^V = f_i^L = x_i \gamma_i f_i^O \tag{1}$$

where $x_i$ and $y_i$ are the liquid and vapor phase compositions, respectively, $P$ is the total pressure, $\phi_i^V$ is the fugacity coefficient of the vapor, $\gamma_i$ is the activity coefficient, and $f_i^O$ is the fugacity of the pure $i$ component.

The activity coefficients, $\gamma_i$, in Tables 1 and 2 were calculated from

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

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{3}$$

where the fugacity coefficient, $\phi_i^V$, was calculated from the two-term virial equation of state, and $v_i^L$ is the molar volume of the $i$-component obtained from appendix 1 (1.3) in ref 16. The second virial coefficients $B_{ii}$, $B_{jj}$, and $B_{ij}$ were calculated using a method developed by Hayden and O'Connell's empirical correlation.[11] According to Hayden and O'Connell, the total virial coefficient can be taken as the sum of several contributions represented by the following equation

$$B_{total} = B_{free} + B_{metastable} + B_{bound} + B_{chem} \tag{4}$$

The detailed method and program for the total virial coefficients are explained in appendix 1 (1.1) in ref 16. The constants, i.e. mean radius of gyration (RD), dipole moments (DMU), and association and solvation parameters (ETA), used in this correlation are listed in Table 3. These constants were obtained from ref 16 for 1-propanol and 1-butanol, and those for ethylene glycol monopropyl ether were determined in our previous work.[3]

**3.2. Thermodynamic Consistency Test.** The thermodynamic consistency of the measured data was checked using the methods proposed by Van Ness in ref 16, with the third-order Legendre polynomials,[16] expressed as

$$\begin{aligned} \ln \gamma_1 &= g + x_2 g' \qquad g \equiv G^E/RT \\ \ln \gamma_2 &= g - x_1 g' \qquad g' \equiv (dg/dx_1)_\sigma \end{aligned} \tag{5}$$

$$g = \frac{G^E}{RT} = x_1(1 - x_1) \sum^{k} a_k L_k(x_1) \; k = 0, 1, ..., n \tag{6}$$

$$\begin{aligned} L_k(x_1) &= \{(2k-1)(2x_1 - 1)L_{k-1}(x_1) - (k-1)L_{k-2}(x_1)\}/k \\ L_0(x_1) &= 1 \\ L_1(x_1) &= 2x_1 - 1 \end{aligned} \tag{7}$$

where the subscript $\sigma$ denotes "along the saturation line", $L_k(x_1)$ is the expressions for Legendre polynomials, and $a_k$ is the parameter of Legendre polynomials. The values of $a_k$ presented in Table 4 were obtained by regression.

Although this method is more robust for isothermal data, the isobaric experimental data can be considered as thermodynamically consistent when the average absolute deviation of the vapor phase composition (AAD$y$) is less than 0.01. The AAD$y$ and its pressure (AAD$P$) are included in Table 4. As shown in Table 4, the AAD$y$ values of the 1-propanol + C3E1 systems are 0.0141—0.0161, and for the 1-butanol + C3E1 systems are 0.0115—0.0127. The relatively higher AAD$y$ values are primarily due to the strong association between C3E1 and alcohol. As aforementioned, C3E1 is a self-associating fluid containing both the ether (-O—) and the hydroxyl (—OH—) group in the same molecule. Thus, from such a molecular structure, 5 different types of intermolecular and one intramolecular hydrogen bonding can potentially occur for C3E1 and its alcohol mixture. In addition, we neglect the $dT$ term in the Gibbs—Duhem equation ($dG = -SdT + VdP + \sum x_i d\mu_i$) because of the difficulty in measuring the excess enthalpy, which could possibly lead to a discrepancy in the experiment and calculation. Accordingly, the temperature dependency of the isobaric VLE data, ranging in approximately 50K to 70K in this work, is considered to be the account for the consistency test results, which is intractable without the excess enthalpy in this method.

In order to deal with the temperature dependency, we performed an additional thermodynamic consistency test proposed by Wisniak[17,18] expressed as

$$D_W = 100 \frac{|L - W|}{L + W} \tag{8}$$

where $L$ and $W$ are defined as

$$L = \int_0^1 L_n dx_i = \int_0^1 W_n dx_i = W \tag{9}$$

$$L_n = \frac{T_i^{BP} x_{i,n} \Delta S_{i,n}^0 + T_j^{BP} x_{j,n} \Delta S_{j,n}^0}{x_{i,n} \Delta S_{i,n}^0 + x_{j,n} \Delta S_{j,n}^0} - T_n \tag{10}$$

$$W_n = \frac{RT_n[(x_{i,n} \ln \gamma_{i,n} + x_{j,n} \ln \gamma_{j,n}) - w_n]}{x_{i,n} \Delta S_{i,n}^0 + x_{j,n} \Delta S_{j,n}^0} \tag{11}$$

where $T_n$ is the experimental temperature at each data point, $T_i^{BP}$ and $T_j^{BP}$ are normal boiling points, and $\Delta S_{i,n}^0$ and $\Delta S_{j,n}^0$ are entropy of vaporization of pure components $i$ and $j$, respectively. The $w_n$ and $\Delta S_{i,n}^0$ are defined as

$$w_n = x_{i,n} \ln\left(\frac{y_{i,n} \phi_{i,n}^V}{x_{i,n} \phi_{i,n}^{sat} C_{poyn}}\right) + x_{j,n} \ln\left(\frac{y_{j,n} \phi_{j,n}^V}{x_{j,n} \phi_{j,n}^{sat} C_{poyn}}\right) \tag{12}$$

$$\Delta S_{i,n}^0 = \frac{\Delta H_i^{BP}}{T_i^{BP}} \tag{13}$$

where $\phi_{i,n}^V$ is the vapor fugacity coefficient calculated by the two-term virial equation, $\phi_{i,n}^{sat}$ is the pure component fugacity coefficient, $C_{poyn}$ is the poynting correction factor. In addition $\Delta H_i^{BP}$ is the heat of vaporization, obtained from DIPPR,[19] at the boiling points of components $i$.

According to the Wisniak area test, the data can be considered as thermodynamically consistent when $D_w$ is less than ~3 to 5. The strength of Wisniak test is that it can be performed as an area test and a point test simultaneously by calculating not only $L$ and $W$ but also $L_n$ and $W_n$ at each data point. In this work, $D_w$ is less than 2 and the maximum $D_{wi}$ is less than 2.5 for each experimental system. It suggests, though all AAD$y$ of the measured data are slightly higher than 0.01 by Van Ness test, the experimental data of this work can still be treated as thermodynamically consistent with sufficiently small values of $D_w$ for all systems.

Table 2. Experimental Vapor−Liquid Equilibrium Data and Activity Coefficients for the Binary System 1-Butanol (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 $T$ | standard deviation of $x_1$ | standard deviation of $y_1$ | $\ln(\gamma_1/\gamma_2)$ |
|---|---|---|---|---|---|---|---|
| 100.0 | 422.75 | 0.00000 | 0.00000 | | | | |
| (0.19)[a] | 420.72 | 0.03962 | 0.10713 | 0.014 | 0.00028 | 0.00044 | 0.08375 |
| | 418.46 | 0.08188 | 0.20298 | 0.014 | 0.00010 | 0.00031 | 0.05807 |
| | 415.82 | 0.13267 | 0.30908 | 0.040 | 0.00065 | 0.00139 | 0.07360 |
| | 413.29 | 0.18868 | 0.40387 | 0.000 | 0.00034 | 0.00091 | 0.06213 |
| | 410.76 | 0.24735 | 0.49212 | 0.055 | 0.00331 | 0.00051 | 0.06695 |
| | 408.33 | 0.31407 | 0.57840 | 0.014 | 0.00058 | 0.00137 | 0.07599 |
| | 405.45 | 0.39892 | 0.65736 | 0.006 | 0.00111 | 0.00244 | 0.03320 |
| | 402.24 | 0.49940 | 0.74857 | 0.057 | 0.00065 | 0.00147 | 0.05711 |
| | 399.28 | 0.59756 | 0.82571 | 0.007 | 0.00066 | 0.00222 | 0.11700 |
| | 396.34 | 0.70498 | 0.88626 | 0.007 | 0.00156 | 0.00020 | 0.13290 |
| | 393.88 | 0.80445 | 0.93486 | 0.042 | 0.00116 | 0.00079 | 0.19568 |
| | 392.33 | 0.88513 | 0.96288 | 0.078 | 0.00069 | 0.00184 | 0.15718 |
| | 391.06 | 0.95789 | 0.98874 | 0.093 | 0.00176 | 0.00125 | 0.29155 |
| | 390.28 | 1.00000 | 1.00000 | | | | |
| 80.0 | 415.30 | 0.00000 | 0.00000 | | | | |
| (0.16)[a] | 413.19 | 0.04552 | 0.11257 | 0.042 | 0.00044 | 0.00085 | −0.01724 |
| | 411.12 | 0.08825 | 0.21358 | 0.057 | 0.00044 | 0.00146 | 0.02992 |
| | 408.61 | 0.13887 | 0.31861 | 0.000 | 0.00030 | 0.00007 | 0.05595 |
| | 406.29 | 0.18842 | 0.40795 | 0.007 | 0.00151 | 0.00377 | 0.07336 |
| | 404.10 | 0.24334 | 0.48992 | 0.030 | 0.00171 | 0.00024 | 0.07415 |
| | 401.47 | 0.31307 | 0.58036 | 0.057 | 0.00184 | 0.00211 | 0.08388 |
| | 398.54 | 0.40302 | 0.67335 | 0.064 | 0.00006 | 0.00383 | 0.08358 |
| | 395.79 | 0.49784 | 0.75512 | 0.042 | 0.00049 | 0.00003 | 0.09622 |
| | 392.95 | 0.60674 | 0.82205 | 0.042 | 0.00021 | 0.00163 | 0.05305 |
| | 390.56 | 0.70294 | 0.87709 | 0.007 | 0.00033 | 0.00356 | 0.05599 |
| | 387.91 | 0.80876 | 0.92965 | 0.000 | 0.00849 | 0.00156 | 0.08734 |
| | 385.75 | 0.91768 | 0.97121 | 0.030 | 0.00392 | 0.00327 | 0.05194 |
| | 384.28 | 1.00000 | 1.00000 | | | | |
| 60.0 | 406.15 | 0.00000 | 0.00000 | | | | |
| (0.13)[a] | 404.19 | 0.04614 | 0.11387 | 0.071 | 0.00018 | 0.00020 | −0.02997 |
| | 402.25 | 0.08733 | 0.20964 | 0.042 | 0.00069 | 0.00064 | 0.00791 |
| | 399.78 | 0.13939 | 0.31646 | 0.085 | 0.00054 | 0.00156 | 0.03323 |
| | 397.64 | 0.18846 | 0.40196 | 0.042 | 0.00290 | 0.00426 | 0.04132 |
| | 395.40 | 0.24786 | 0.49402 | 0.028 | 0.00222 | 0.00287 | 0.06002 |
| | 393.05 | 0.31280 | 0.57940 | 0.099 | 0.00349 | 0.00122 | 0.07679 |
| | 390.20 | 0.40741 | 0.67880 | 0.042 | 0.00085 | 0.00437 | 0.08711 |
| | 387.67 | 0.49787 | 0.75345 | 0.014 | 0.00511 | 0.00054 | 0.08570 |
| | 385.05 | 0.59811 | 0.81585 | 0.042 | 0.00212 | 0.00046 | 0.04740 |
| | 382.71 | 0.69388 | 0.87353 | 0.007 | 0.00099 | 0.00112 | 0.06749 |
| | 380.12 | 0.80483 | 0.93120 | 0.028 | 0.00332 | 0.00284 | 0.13849 |
| | 378.14 | 0.91151 | 0.97161 | 0.007 | 0.00104 | 0.00022 | 0.14837 |
| | 376.78 | 1.00000 | 1.00000 | | | | |

[a] Standard deviation of P: 99.7 kPa to 100.2 kPa at 100 kPa; 79.8 kPa to 80.2 kPa at 80 kPa; 59.9 kPa to 60.2 kPa at 60 kPa.

The parameters used in the Wisniak test and subsequently the results obtained from the point and area test are presented in Table 5.

**3.3. Correlations.** The correlation of the data was performed by the two-term virial equation for the fugacity coefficient and four activity models (three suffix Margules, Wilson, NRTL, and UNIQUAC) for the activity coefficients. The parameters (mean radius of gyration (RD), dipole moments (DMU), and association and salvation parameter (ETA)) of the two-term virial equation are shown in Table 3 which were obtained from the ref 16 data for 1-propanol and 1-butanol, and the literature[20−22] for ethylene glycol monopropyl ether. The $\alpha_{12}$ used in NRTL was fixed at 0.47 for all measurements because the systems, including mixtures of a self-associating substance, belong to

**Table 3. Parameters for the Two-Term Virial Equation of State and Antoine Constants**

| | $P_c^a$ | $T_c^a$ | | $10^{10}\ R_D$ | $10^{30}\ \mu$ | | Antoine constants[a] | | |
|---|---|---|---|---|---|---|---|---|---|
| component | (bar) | (K) | $Z_c^b$ | (m) | (Cm) | ETA | A | B | C |
| 1-propanol | 52.00 | 536.9 | 0.254 | 2.736 [c] | 1.68 [c] | 1.40 | 4.87601 | 1441.629 | −74.299 |
| 1-butanol | 45.00 | 562.0 | 0.264 | 3.225 [c] | 1.66 [c] | 2.20 | 4.50393 | 1313.878 | −98.789 |
| C3E1 | 36.50 | 615.2 | 0.248 | 3.871 [d] | 2.00 [e] | 1.20 [f] | 4.37505 | 1504.960 | −78.744 |

[a] NIST Chemistry Webbook.[23] [b] DIPPR.[19] [c] Vapor−liquid equilibria using UNIFAC.[16] [d] Techniques of chemistry.[22] [e] Computer calculations.[21] [f] Group contribution, Joback method.[20]

**Table 4. Legendre Polynomials Parameters[a] and Average Absolute Deviations in Vapor Phase Composition[b] and in Pressure[c] for the Consistency Test of the Studied Systems**

| | P | | | | | AADP [b] | |
|---|---|---|---|---|---|---|---|
| system | (kPa) | $A_0^a$ | $A_1^a$ | $A_2^a$ | $A_3^a$ | (%) | $\mathrm{AAD}y_i^c$ |
| 1-propanol + C3E1 | 100 | −0.09109 | 0.00536 | −0.00160 | 0.08098 | 0.681 | 0.01412 |
| | 80 | −0.11871 | −0.06540 | −0.03309 | 0.06453 | 0.472 | 0.01654 |
| | 60 | −0.10687 | −0.03917 | 0.02767 | 0.08860 | 0.365 | 0.01375 |
| 1-butanol + C3E1 | 100 | 0.03486 | 0.18504 | 0.10461 | 0.14160 | 0.423 | 0.01266 |
| | 80 | −0.02692 | 0.09061 | −0.02321 | 0.08816 | 0.268 | 0.01212 |
| | 60 | −0.02326 | 0.14706 | 0.02269 | 0.11543 | 0.257 | 0.01153 |

[a] Legendre polynomials parameter. [b] Average absolute deviation of pressure. [c] Average absolute deviation of vapor composition.

**Table 5. Heat of Vaporization and the Wisniak Consistency Test Results**

| | $P$ | $\Delta h_k^o$ (kJ/mol)[a] | | Wisniak point test | | Wisniak area test | | |
|---|---|---|---|---|---|---|---|---|
| system | (kPa) | 1-propanol and 1-butanol | C3E1 | min. $D_{wi}$ | max. $D_{wi}$ | $L$ | $D$ | $D_w$ |
| 1-propanol + C3E1 | 100 | 41.690 | 43.052 | 0.879 | 2.484 | 6.244 | 6.474 | 1.811 |
| | 80 | 42.199 | 43.681 | 0.421 | 2.100 | 6.053 | 6.225 | 1.403 |
| | 60 | 42.812 | 44.433 | 0.023 | 1.663 | 5.840 | 5.956 | 0.986 |
| 1-butanol + C3E1 | 100 | 43.152 | 43.052 | 0.041 | 0.940 | 2.696 | 2.710 | 0.264 |
| | 80 | 43.887 | 43.681 | 0.051 | 0.742 | 2.366 | 2.356 | 0.205 |
| | 60 | 44.767 | 44.433 | 0.044 | 1.311 | 2.280 | 2.255 | 0.556 |

[a] DIPPR.[19]

type 4 according to the literature.[14] The pure parameters $q$ (area parameter) and $r$ (volume parameter) were calculated via the method of Abrams and Prausnitz,[15] and the van der Waals area and volume were obtained from the DIPPR Database.[19] The parameters $q$, $r$, and $\alpha_{12}$ are presented in Table 6.

**Table 6. Parameters for the Correlation by NRTL and UNIQUAC**

| component | area parameter ($q$) | volume parameter ($r$) | system | $\alpha_{12}$ in NRTL |
|---|---|---|---|---|
| 1-propanol | 2.512 | 2.7798 | 1-propanol + C3E1 | 0.47 |
| 1-butanol | 3.048 | 3.4542 | 1-butanol + C3E1 | 0.47 |
| C3E1 | 3.832 | 4.3718 | | |

The objective function ($OBJ$) used to quantify the excess Gibbs free energy of the liquid phase is listed as follows

$$OBJ = \sum_{i=1}^{N} \left| \frac{T_i^{\exp} - T_i^{cal}}{T_i^{\exp}} \right| + |y_i^{\exp} - y_i^{cal}| \tag{14}$$

where $T_i^{exp}$, $T_i^{cal}$, $y_i^{exp}$, and $y_i^{cal}$ represent experimental temperature, calculated temperature, experimental vapor phase composition, and calculated vapor phase composition, respectively. Table 7 contains the parameters for each activity model and the average absolute deviations of the temperature (AAD$T$) and AAD$y$. According to Table 7, all AAD$y$ values for each activity model are less than 1 % and AAD$T$ values are within 0.187 % to 0.42 %. Therefore it is illustrated that the experimental vapor phase composition shows reasonably good agreements with calculated values; however, the calculated lines deviate about 0.7K to 1.5K from the measured data. Furthermore, not only dew temperature lines but also bubble temperature lines are shifted as shown in Figures 1 and 2. So, it is reasonable to postulate that the difference between measured data and calculated lines is, in major, caused by $T$, not $y$. The reason is that the binary parameters of the activity models do not consider the temperature dependency explicitly. Also, the systems has strong association because of a variety of inter- and intramolecular hydrogen bonds, which also contributes to the difference between the experimental and the calculated values.

Figures 1 and 2 are the vapor−liquid phase equilibrium diagrams, which compare the experimental data to the calculated lines based

**Table 7. Interaction Parameters for the Activity Models and Absolute Average Deviations for Temperature and Vapor Phase Composition**

| | parameters[a] | | AAD$T$ | |
|---|---|---|---|---|
| model | $A_{12}$ | $A_{21}$ | (%) | AAD$y_i$ |
| 1-Propanol (1) + Ethylene Glycol Monopropyl Ether (2) at 100 kPa | | | | |
| NRTL | 6743.724 | −3766.314 | 0.333 | 0.00350 |
| UNIQUAC | 528.633 | −281.498 | 0.391 | 0.00264 |
| Wilson | −1731.050 | 9173.809 | 0.420 | 0.00245 |
| Margules | −0.020 | 0.213 | 0.299 | 0.00447 |
| 1-Propanol (1) + Ethylene Glycol Monopropyl Ether (2) at 80 kPa | | | | |
| NRTL | 4710.632 | −2997.728 | 0.300 | 0.00484 |
| UNIQUAC | 428.098 | −246.700 | 0.357 | 0.00391 |
| Wilson | −1444.875 | 6032.528 | 0.377 | 0.00395 |
| Margules | 0.041 | 0.178 | 0.326 | 0.00508 |
| 1-Propanol (1) + Ethylene Glycol Monopropyl Ether (2) 60 kPa | | | | |
| NRTL | 4237.967 | −2978.636 | 0.187 | 0.00673 |
| UNIQUAC | 240.972 | −169.709 | 0.207 | 0.00656 |
| Wilson | −915.130 | 2542.123 | 0.207 | 0.00664 |
| Margules | −0.009 | 0.127 | 0.265 | 0.00613 |
| 1-Butanol (1) + Ethylene Glycol Monopropyl Ether (2) at 100 kPa | | | | |
| NRTL | 5761.476 | −3333.462 | 0.216 | 0.00696 |
| UNIQUAC | 369.761 | −232.807 | 0.224 | 0.00641 |
| Wilson | −1849.370 | 5040.444 | 0.237 | 0.00645 |
| Margules | 0.052 | 0.228 | 0.191 | 0.00794 |
| 1-Butanol (1) + Ethylene Glycol Monopropyl Ether (2) at 80 kPa | | | | |
| NRTL | 6977.357 | −3746.208 | 0.295 | 0.00387 |
| UNIQUAC | 456.050 | −265.455 | 0.322 | 0.00373 |
| Wilson | −2118.429 | 6693.267 | 0.332 | 0.00394 |
| Margules | −0.024 | 0.307 | 0.258 | 0.00445 |
| 1-Butanol (1) + Ethylene Glycol Monopropyl Ether (2) at 60 kPa | | | | |
| NRTL | 6734.014 | −3696.594 | 0.251 | 0.00366 |
| UNIQUAC | 446.469 | −263.370 | 0.254 | 0.00408 |
| Wilson | −2221.210 | 7141.162 | 0.277 | 0.00412 |
| Margules | −0.061 | 0.283 | 0.207 | 0.00401 |

[a] NRTL $A_{12} = \Delta g_{12}$; UNIQUAC $A_{12} = \Delta u_{12}$; Wilson $A_{12} = \Delta\lambda_{12}$; Margules $A_{12} = A_{12}$.

on NRTL and UNIQUAC. To enhance the visual readability, calculated lines by Wilson and Margules are omitted. As can be seen in Figures 1 and 2, all calculated lines are shifted downward. Moreover, NRTL exhibits better results than UNIQUAC. These results which are summarized in Table 7 can be explained by the temperature dependency above.

In order to evaluate the performance of each activity model, AAD$y$ and AAD$T$ should be considered simultaneously. However, comparing the AAD$T$ is more effective in our evaluation since the AAD$y$ values are similar for each activity model. According to our correlations, NRTL and Margules tend to have a better agreement than UNIQUAC and Wilson. It reveals that NRTL and Margules models are more suitable for the normal alcohols (i.e., 1-propanol, and 1-butanol) + C3E1 system. Additionally, NRTL performance is better than Margules for 1-propanol + C3E1, with Margules is better for 1-butanol + C3E1 as a comparison. Generally, NRTL tends to show the best agreements between the results than the others including UNIQUAC, Wilson, and Margules.

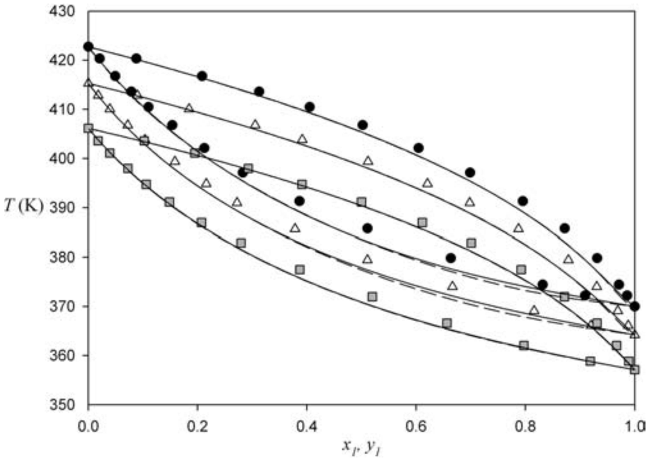

**Figure 1.** Experimental data for the system of 1-propanol (1) + ethylene glycol monopropyl ether (2) at 60 kPa, 80 kPa, and 100 kPa: ●, 100 kPa; Δ, 80 kPa; gray box, 60 kPa; solid curves, NRTL model; medium-dashed curves, UNIQUAC model.

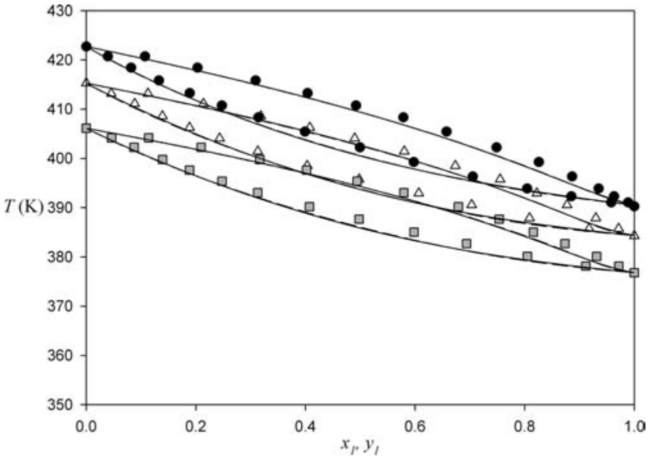

**Figure 2.** Experimental data for the system of 1-butanol (1) + ethylene glycol monopropyl ether (2) at 60 kPa, 80 kPa, and 100 kPa: ●, 100 kPa; Δ, 80 kPa; gray box, 60 kPa; solid curves, NRTL model; medium-dashed curves, UNIQUAC model.

## 4. CONCLUSIONS

The isobaric VLE data for the 1-propanol + ethylene glycol monopropyl ether and 1-butanol + ethylene glycol monopropyl ether systems were measured at 60 kPa, 80 kPa, and 100 kPa. Data correlation was performed by four activity coefficient models: NRTL, UNIQUAC, Wilson, and three suffix Margules.

For the Van Ness consistency test results, AAD$P$ of all the measured systems are less than 1 %, except AAD$y$. Although all AAD$y$ are bigger than 1 %, the experimental data are very comparable, attributed to the lack of the enthalpy term in the Gibbs−Duhem equation and the strong association between alcohol and surfactant molecules. In order to supplement this result, the Wisniak consistency test, which considered the excess enthalpy, was performed. Importantly, the measured data passed the Wisniak consistency test.

The correlation results are in good agreements as all AAD$y$ values are less than 1 %, except the AAD$T$ values are not small, and as a result all calculated lines shifted downward. This illustrated that the activity models cannot predict the binary systems including both alcohol and surfactant well enough. That is because the temperature dependency and the strong association between alcohol and surfactant are not taken into account in the binary parameters. Among the four activity models, NRTL shows the best performance overall.

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## LIST OF SYMBOLS

| | |
|---|---|
| A, B, C | Antoine equation constant, eq 1 |
| $A_i$ | parameters of Legendre polynomial |
| $A_{ij}$ | three suffix Margules model parameter |
| $B_{ii}$, $B_{jj}$ | second virial coefficient of pure components |
| $B_{ij}$ | cross second virial coefficient |
| $D_w$, $L$, $W$ | variables of the Wisniak's consistency test |
| $f_i^L$ | fugacity of component $i$ in the liquid phase |
| $f_i^O$ | fugacity of pure component $i$ |
| $f_i^V$ | fugacity of component $i$ in the vapor phase |
| $\Delta g_{ij}$ | NRTL model parameter |
| $\Delta h_k^o$ | heat of vaporization of pure component $k$ at operating pressure [kJ/mol] |
| $P_c$ | critical pressure [Mpa] |
| $P_i^{sat}$ | vapor pressure of pure component $i$ [bar] |
| $R$ | gas constant |
| $R_D$ | mean radius of gyration [m] |
| $\Delta S_k^o$ | entropy of vaporization of pure component $k$ at operating pressure [kJ/Kmol] |
| $T_c$ | critical temperature [K] |
| $T_k^o$ | boiling point of pure component $k$ at operating pressure [K] |
| $\Delta u_{ij}$ | UNIQUAC model parameter |
| $v_i^l$ | molar volume of the saturated liquid |
| $x_i$, $y_i$ | compositions of the liquid and vapor phases |
| $Z_c$ | critical compressibility factor |

## GREEK LETTERS

| | |
|---|---|
| $\gamma_i$ | activity coefficient of component $i$ |
| $\Delta\lambda_{ij}$ | Wilson model parameter |
| $\mu$ | dipole moment [cm] |
| $\phi_i^V$ | fugacity coefficient of component $i$ |

## SUPERSCRIPT

| | |
|---|---|
| *cal* | calculated value |
| *exp* | experimental value |

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