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# Liquid−Liquid Equilibria, Density, Viscosity, and Surface and Interfacial Tension of the System Water + *n*-Butyl Acetate + 1-Propanol at 323.15 K and Atmospheric Pressure

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Liquid−liquid equilibrium (LLE) data are reported for the system water + *n*-butyl acetate + 1-propanol at 323.15 K and atmospheric pressure. The densities, viscosities, and surface tensions have been measured in the homogeneous liquid range for the binary and ternary liquid mixtures, and the liquid interfacial tensions of the conjugate phases located in the isothermal binodal curve have been determined at the same temperature and pressure. The experimental tie-line data were predicted by the UNIFAC method with good results. The empirical method of Othmer and Tobias was used for tie-line correlation, and the method of Pick et al. was applied for binodal data correlation. The molar volumes, $V_m$, the dynamic viscosity, $\eta$, and the surface tension, $\gamma$, of the binary systems were correlated in terms of composition using rational functions. The dilute regions of these systems deserved particular attention due to the physicochemical effects taking place in these regions. To describe the ternary system, binary pair additivity and a rational function were considered for the ternary contributions. The surface tension data of binary mixtures were correlated with the models of Fu et al. and Li et al., and the same models were applied for the prediction of ternary data. The liquid interfacial tension measured for the tie-lines was correlated using the relation proposed by Li and Fu.

## Introduction

Extensive information on the thermodynamic and transport properties of water + alkanol + ester liquid mixtures and their binary subsystems is needed in multiple industrial process areas such as fluid flow, heat and mass transfer, and also for the development of theoretical research on molecular interactions in solutions. The knowledge of density, viscosity, and surface and interfacial tensions of aqueous systems containing aliphatic esters is essential in many fields, such as food, flavor, and fragrance industries. The systems alkanol + alkanoate are also of great interest from a theoretical point of view since in the mixing process the breaking of H-bonded structures of the alcohol occurs and the formation of new H-bonded molecular species between the alcohol and the ester takes place.[1] Ternary mixtures, especially those exhibiting liquid−liquid immiscibility, represent an appropriate testing ground for the application of correlation and prediction models. The importance of liquid−liquid extraction in separation technology has increased over the last 30 years, and it is now usually used in pharmaceutical and food industries for recovering valuable organic materials, for example, the alcohols from aqueous solutions. The present work is part of a research program which has been developed in our laboratory that aims to provide density, viscosity, surface tension, and interfacial tension for water + ester + alcohol.[2−6] These systems show a large liquid−liquid immiscibility area, the water + alkanoate being practically immiscible in all the composition ranges. The measurements of densities of the pure esters in a wide range of temperature and pressure are another task taking part of our recent work.[7,8] In the present work, we report on the density, $\rho$, on the dynamic viscosity, $\eta$, and on the surface tension, $\gamma$, measured in the miscible range of the water + *n*-butyl acetate + 1-propanol liquid system at 323.15 K and atmospheric pressure. From the density data, the excess molar volume, $V^E$, was determined. The rational functions of Myers and Scott[9] and Pando et al.[10] have been used to correlate the above-mentioned properties. The surface tension data of binary mixtures were correlated with the models of Fu et al.[11] and Li et al.[12] The same models were applied for the prediction of this property for the ternary homogeneous liquid mixtures.

On the other hand, the published studies on liquid−liquid equilibrium and on interfacial property data of ternary systems of practical interest are scarce when compared with the wide variety of binary systems which have been investigated. The surface and interfacial tensions of solutions have a great effect on the efficiency of the extraction. Since the aqueous solutions of alkanols can be efficiently extracted with esters, accurate thermodynamic properties and LLE data are needed for extraction processes. Some LLE measurements on ternary systems of the type water + aliphatic ester + alkanol can be found in the literature at temperatures below 323 K.[13−16] Therefore, we decided to determine the liquid−liquid equilibria for the water + *n*-butyl acetate + 1-propanol system at that temperature and to study the interfacial tension between equilibrated liquid phases at the same temperature. The binodal curve was found by the cloud-point method, using a solubility cell assembled for this purpose. The tie-lines were determined by sampling the liquid phases from a cell carefully designed for LLE, and the composition was determined by gas chromatographic techniques. The experimental tie-line data were compared with the predic-

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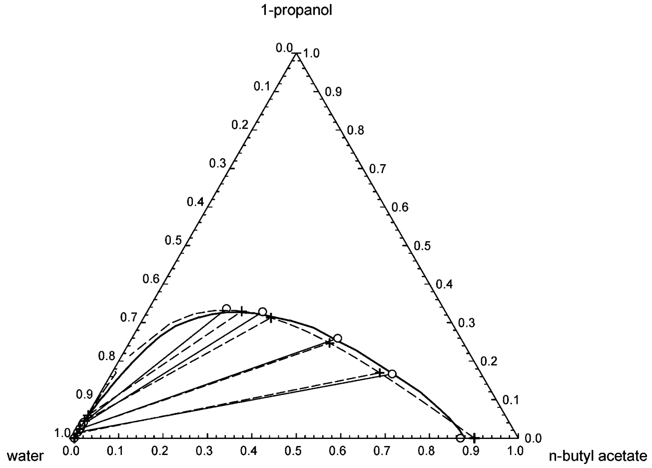

**Figure 1.** LLE data for water + *n*-butyl acetate + 1-propanol at 323.15 K. Experimental: −, binodal curve; -○-, tie-lines. UNIFAC predictions: +, tie-line data; and - - - -, binodal curve.

tions by means of the UNIFAC group contribution method[17] using the LLE interaction parameters reported by Magnussen et al.[18] The tie-line data were also correlated by the simple method of Othmer and Tobias,[19] and the binodal curve was represented following a method proposed by Pick et al.[20] For the ternary system studied, the interfacial tension was determined in the immiscible range at 323.15 K, and the experimental data were correlated with the Li and Fu model.[21] A general behavior is proposed for the correlation of the interfacial tension of the systems water + aliphatic ester + alkanol investigated up to now by our group.

## Experimental Section

***Materials.*** Tridistilled water was used. 1-Propanol (Riedel de Häen) was supplied with a weight fraction purity better than 0.995. *n*-Butyl acetate was supplied by Sigma-Aldrich with a stated purity better than 0.995. The components were used without further purification. The purity of the chemicals was evaluated from measurements of their liquid density, viscosity, and surface tension. The measured values of these properties are compared with those available in the literature in Table 1.

***Experimental Procedure. Measurements.*** The liquid mixtures were prepared by mass using a Mettler AT 200 balance with a precision of $\pm 1 \cdot 10^{-5}$ g. The uncertainty of the mole fraction is estimated to be of the order $\pm 1 \cdot 10^{-4}$. Experimental densities were measured using an Anton Paar DMA 60 digital vibrating tube densimeter, with a DMA 512P measuring cell. The installation for the measurement of density and the peripheral equipment used was already described before.[8] The vibrating tube cell was thermostatted externally by a Julabo P-5 thermostat providing bath temperature stability of (323.15 ± 0.02) K. Pressures were measured with a maximum uncertainty of 0.03 MPa. The calibration equation proposed by Niesen and previously obtained[7] with *n*-heptane and water as calibrating fluids was used. Densities were determined with an uncertainty of the order of $\pm 1 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$. Taking into consideration that the error in the excess molar volume, $V^E$, is determined by the uncertainties in mole fraction and density, the maximum error in $V^E$ resulting from the propagation of errors is $\pm 1 \cdot 10^{-3}\ \mathrm{cm^3 \cdot mol^{-1}}$.

Kinematic viscosities, $\nu$, were determined by using an Ubbelohde viscometer with a Schott-Geräte automatic measuring unit (model AVS-470), for which the uncertainty in the flow time of measurement is ± 0.01 s. The viscosystem AVS-470 was coupled to an optical viscoPump II and a heater controller bath CT52, all from Schott instruments. The temperature was monitored by a digital thermometer with an uncertainty of ± 0.01 K. The viscometer calibration was validated and checked with pure compound (methanol and 1-propanol) viscosity measurements from (298.15 to 323.15) K. Furthermore, kinetic energy corrections were applied to the experimental kinematic viscosity data. For each sample, at least five individual measurements were made, allowing the calculation of the average viscosity as well as the associated precision which was of the order $\pm 0.01\ \mathrm{mm^2 \cdot s^{-1}}$. Considering the uncertainties in the measured time and in the density, the experimental uncertainty in the dynamic viscosity, $\eta$, was about $\pm 0.001$ mPa·s.

Surface and equilibrium liquid−liquid interfacial tensions were measured using a PC controlled KSV Sigma 70 tension balance which employs the Du Noüy ring-detachment method. The platinum ring was thoroughly cleaned by immersion in a concentrated solution of nitric acid during several hours. Then it was rinsed with acetone, carefully flamed in a Bunsen burner, washed again with acetone, and dried. The measurements were automatically corrected to the actual values by means of the Huh and Mason compensation for interface distortion. The temperature inside the surface tension measurement vessel was maintained and controlled at (323.15 ± 0.10) K using an UltraTerm bath. The measurement of density, viscosity, and surface tension in the homogeneous range of liquid was accomplished using the following methodology. A binary mixture was used as a starting point of measurements in the water (1) + 1-propanol (3) system, and the ternary data were obtained following lines of constant molar fraction ratio $x_1/x_3$.

For the surface tension, each experimental point results from a set of about 20 measurements. After the first few measurements, there is a tendency for the repeatability of the measurements, and a practically constant value is obtained. The precision is of the order of $\pm 0.01\ \mathrm{mN \cdot m^{-1}}$.

For the liquid interfacial tension measurements, the liquid mixtures with a known global composition were prepared and kept at 323.15 K in a thermosttated cell and shaken several times during a period of at least 24 h to reach the equilibrium.

***Binodal Curve.*** The binodal curve was determined by the cloud-point method. Water + 1-propanol or *n*-butyl acetate + 1-propanol binaries of known compositions were shaken in an equilibrium cell equipped with a magnetic stirrer and a jacket for circulating water from a Haake D8-G circulator. The temperature was controlled up to about ± 0.01 K using an Alpha Technics digital thermometer, model 4400, with a platinum resistance probe. The third component (the ester or the water) was added until the transition point was reached. Next, some alcohol was added until the disappearance of the cloud point. The liquids were added with weighted syringes. The return to the transition point was next made by adding a small volume of the third component used for a particular binary initial mixture. Repeating this procedure, it was possible to determine some points on the binodal curve over a small ternary composition range. However the previous method was not used extensively to avoid the errors due to the loss of mass by evaporation and successive detection of transition points which was made by observation. The evaporation was controlled by weighting the syringes before and after addition of the liquid components. Therefore, the uncertainty in the values of composition over the binodal curve was determined mainly by the observation of the transition point since the quantities of the titrating compo-

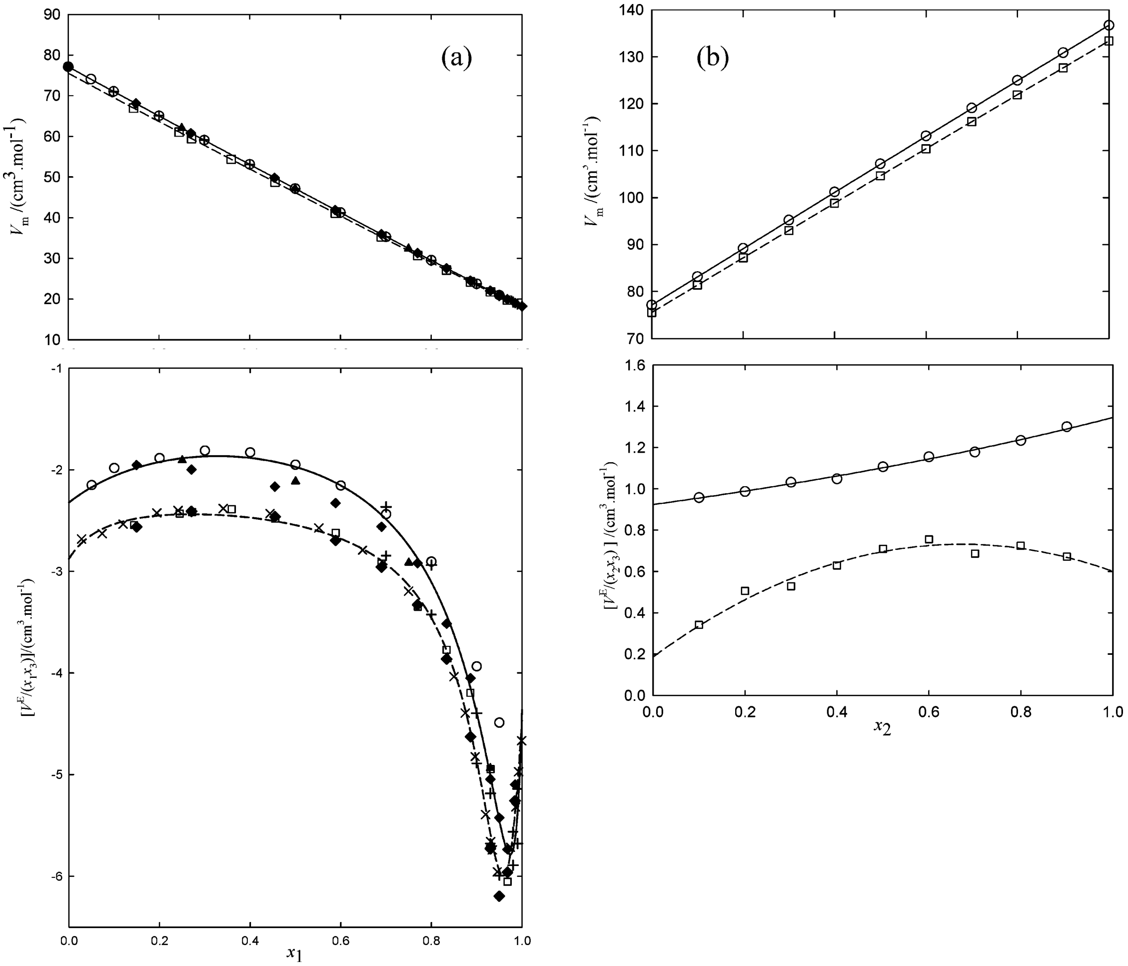

**Figure 2.** Molar volume, $V_m$, and modified excess molar volume function, $V_{ij}^E/x_ix_j$, of the binary systems at (303.15 and 323.15) K as a function of the mole fractions: (a) water (1) + 1-propanol (3); (b) *n*-butyl acetate (2) + 1-propanol (3). The symbols refer to experimental data: □, Johnson et al.;[6] ○, this work; ◆, Mikhail and Kimel;[34] ▲, Kubota et al.;[35] +, Pang et al.;[24] ×, Benson and Kiyoara.[36] The curves were calculated at 303.15 K (----) and at 323.15 K (−). The values of $V_{ij}^E/x_ix_j$ were calculated with eq 5 and those for $V_m$ from the relationship between this property and $V_{ij}^E$, eq 2.

**Table 1. Densities ($\rho$), Viscosities ($\eta$), and Surface Tensions ($\gamma$), of the Pure Substances at 323.15 K**

| | $\rho$/g·cm$^{-3}$ | | $\eta$/mPa·s | | $\gamma$/mN·m$^{-1}$ | |
|---|---|---|---|---|---|---|
| substance | exptl | lit. | exptl | lit. | exptl | lit. |
| water | | 0.98803[22] | | 0.5471[26] | 68.38 | 68.45[30]<br>67.92[31] |
| *n*-butyl acetate | 0.84975 | 0.8497[7]<br>0.85011[23] | 0.502 | 0.500[27]<br>0.481[28] | 22.12 | 22.21[30] |
| 1-propanol | 0.77930 | 0.78102[24]<br>0.7789[25] | 1.115 | 1.107[27]<br>1.1208[29] | 21.36 | 21.37[30]<br>21.31[31] |

**Table 2. Values of the Parameters for the Chromatographic Calibration Curve, Equation 1 of the System Water + *n*-Butyl Acetate + 1-Propanol[a]**

| component | $m$ | $b$ | $R$ | $\sigma$ |
|---|---|---|---|---|
| 1-propanol | 0.8663 | −0.0036 | 0.9991 | 0.0020 |
| *n*-butyl acetate | 0.8298 | −0.0007 | 0.9990 | 0.0030 |

[a] $m$ is the slope; $b$ is the ordinate; $R$ is the correlation coefficient of the fit; and $\sigma$ is the standard deviation of the fit.

nents were determined with good accuracy by mass. Starting with different binaries (water + 1-propanol or *n*-butyl acetate + 1-propanol), the binodal curve was drawn over all the composition range.

***Chromatographic Calibration Curve.*** The analysis of the conjugate phases was carried out by gas chromatography in a TRE METRICS 9001 gas chromatograph equipped with a capillary column (J & W Scientific DB1: 25m × 0.2 mm; film thickness, 0.3 $\mu$m). The internal standard method was used for the calibration of the detector (FID) response to achieve high reproducibility on the concentration of each compound in the conjugate phases on the binodal curves. 1-Butanol was the internal standard in the studied systems and was chosen because it has chromatographic properties close to those of the compounds in the considered multicomponent systems. It is important to underline that each point on the calibration curve for each compound was obtained from multicomponent systems of different known concentrations prepared in the completely miscible region. All the mixtures of known concentration used for the calibration curves of the ternary system studied in this work were prepared by mass.

A straight line, eq 1, was fitted to the FID's response (i.e., chromatographic areas) as a function of mass of each compound, the so-called response factor, by the least-squares method

$$w_i = \left(\frac{A_i}{A_s} - b\right)\left(\frac{w_s}{m}\right) \tag{1}$$

where $w_i$ is the mass of the $i$th component of the system; $A_i$ is the chromatographic area of the component $i$; $A_s$ is the chromatographic area of the internal standard (1-butanol); $w_s$ is the constant mass of the internal standard; and $m$ and $b$ are the slope and the ordinate of the fitted straight line, respectively.

**Table 3. Densities ($\rho$), Viscosities ($\eta$), and Surface Tension ($\gamma$) for the System Water (1) + *n*-Butyl Acetate (2) + 1-Propanol (3) and Its Binary Constituents at 323.15 K and Atmospheric Pressure**

| $x_1$ | $x_2$ | $\rho$ / $g \cdot cm^{-3}$ | $\eta$ / mPa·s | $\gamma$ / $mN \cdot m^{-1}$ | $x_1$ | $x_2$ | $\rho$ / $g \cdot cm^{-3}$ | $\eta$ / mPa·s | $\gamma$ / $mN \cdot m^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.0800 | 0.9200 | 0.85157 | 0.507 | 22.25 | 0.0600 | 0.4000 | 0.81988 | 0.617 | 21.97 |
| 0.0600 | 0.9400 | 0.85107 | 0.506 | 22.20 | 0.0400 | 0.6000 | 0.83140 | 0.545 | 22.11 |
| 0.0400 | 0.9600 | 0.85062 | 0.504 | 22.17 | 0.0200 | 0.8000 | 0.84105 | 0.511 | 22.12 |
| 0.0200 | 0.9800 | 0.85018 | 0.503 | 22.14 | 0.0100 | 0.9000 | 0.84552 | 0.503 | 22.13 |
| 0.9800 | 0 | – | – | 44.44 | 0.1800 | 0.1000 | 0.80403 | 0.927 | 22.09 |
| 0.9500 | 0 | 0.95971 | 0.827 | 29.58 | 0.1400 | 0.3000 | 0.81869 | 0.693 | 22.16 |
| 0.9200 | 0 | – | – | 26.37 | 0.1000 | 0.5000 | 0.82979 | 0.582 | 22.19 |
| 0.9000 | 0 | 0.93504 | 1.036 | 25.27 | 0.0600 | 0.7000 | 0.83857 | 0.522 | 22.18 |
| 0.8000 | 0 | 0.89461 | 1.256 | 24.12 | 0.2400 | 0.2000 | 0.81898 | 0.806 | 22.36 |
| 0.7000 | 0 | 0.86587 | 1.305 | 23.65 | 0.1800 | 0.4000 | 0.82964 | 0.641 | 22.36 |
| 0.6000 | 0 | 0.84441 | 1.291 | 23.42 | 0.1200 | 0.6000 | 0.83750 | 0.557 | 22.34 |
| 0.5000 | 0 | 0.82768 | 1.260 | 23.06 | 0.0600 | 0.8000 | 0.84396 | 0.514 | 22.31 |
| 0.4000 | 0 | 0.81440 | 1.219 | 22.68 | 0.0300 | 0.9000 | 0.84696 | 0.505 | 22.26 |
| 0.3000 | 0 | 0.80364 | 1.180 | 22.29 | 0.3600 | 0.1000 | 0.82179 | 0.980 | 22.68 |
| 0.2000 | 0 | 0.79462 | 1.150 | 21.93 | 0.2800 | 0.3000 | 0.83154 | 0.724 | 22.63 |
| 0.1000 | 0 | 0.78661 | 1.127 | 21.68 | 0.2000 | 0.5000 | 0.83812 | 0.600 | 22.55 |
| 0.0500 | 0 | 0.78294 | 1.121 | 21.55 | 0.1200 | 0.7000 | 0.84322 | 0.536 | 22.41 |
| 0 | 0.1000 | 0.79007 | 0.879 | 21.56 | 0.4500 | 0.1000 | 0.83258 | 1.009 | 22.96 |
| 0 | 0.2000 | 0.79951 | 0.747 | 21.72 | 0.4000 | 0.2000 | 0.83612 | 0.848 | 22.84 |
| 0 | 0.3000 | 0.80787 | 0.662 | 21.84 | 0.3000 | 0.4000 | 0.84095 | 0.665 | 22.69 |
| 0 | 0.4000 | 0.81542 | 0.604 | 21.97 | 0.2000 | 0.6000 | 0.84423 | 0.569 | 22.54 |
| 0 | 0.5000 | 0.82221 | 0.566 | 22.05 | 0.1000 | 0.8000 | 0.84701 | 0.519 | 22.45 |
| 0 | 0.6000 | 0.82846 | 0.538 | 22.12 | 0.0500 | 0.9000 | 0.84839 | 0.507 | 22.36 |
| 0 | 0.7000 | 0.83430 | 0.521 | 22.17 | 0.5700 | 0.0500 | 0.84507 | 1.158 | 23.09 |
| 0 | 0.8000 | 0.83971 | 0.508 | 22.20 | 0.5100 | 0.1500 | 0.84585 | 0.949 | 23.00 |
| 0 | 0.9000 | 0.84484 | 0.502 | 22.18 | 0.6650 | 0.0500 | 0.86301 | 1.194 | 23.13 |
| 0.0900 | 0.1000 | 0.79669 | 0.906 | 21.80 | 0.7800 | 0.0250 | 0.88999 | 1.254 | 23.50 |
| 0.0800 | 0.2000 | 0.80543 | 0.767 | 21.87 | – | – | – | – | – |

The values for the fitted parameters of the calibration curve, eq 1, for 1-propanol and *n*-butyl acetate are given in Table 2, together with the values of the correlation coefficient and standard deviation of the fittings. Each calibration curve contains five experimental points, and each of these points is the result of at least five injections into the chromatograph.

***Liquid–Liquid Phase Behavior.*** The experimental investigation on the liquid–liquid equilibrium of the ternary system water + *n*-butyl acetate + 1-propanol was made in an equilibrium cell built of Pyrex glass with a total volume of 25 $cm^3$, which was enough to take samples from the two equilibrium liquid phases to perform the quantification of their concentration and interfacial tension. This cell is similar to that used by Garcia-Flores et al.[32] The temperature control in the equilibrium cell (up to ± 0.02 K) was achieved by means of a constant-temperature bath-circulator, Haake D8-G, which uses water as thermal fluid in the thermal jacket of the cell. The temperature was measured in the cell thermowell with a digital thermometer (Alpha Technics, model 4400) with a platinum resistance probe, whose readings have an accuracy of 0.01 K. This thermometer was certified (and calibrated in the ITS-90) by the US National Institute of Standards and Technology (NIST) following the Technology Special Publication 250-35.

Five tie-lines of known global concentration were prepared by weighting. The heterogeneous liquid mixtures were transferred into the equilibrium cell, and stirring was carried out with magnetic bars during a period of at least 4 h, then allowed to settle for a 10 h period to obtain two liquid phases in equilibrium at 323.15 K. The samples of both phases were obtained simultaneously with hypodermic syringes with a capacity of 5 $cm^3$ through the sampling glass capillaries in the equilibrium cell, to ensure the right amount of sample for measuring the LLE.

**Table 4. Binodal Data Determined by the Cloud Point Method for the System Water (1) + *n*-Butyl Acetate (2) + 1-Propanol (3) at 323.15 K and Atmospheric Pressure**

| $x_1$ | $x_2$ | $x_1$ | $x_2$ | $x_1$ | $x_2$ |
|---|---|---|---|---|---|
| 0.9899 | 0.0008 | 0.7981 | 0.0266 | 0.3626 | 0.3321 |
| 0.9811 | 0.0008 | 0.7630 | 0.0346 | 0.3601 | 0.3349 |
| 0.9568 | 0.0012 | 0.7211 | 0.0460 | 0.3178 | 0.3956 |
| 0.9402 | 0.0029 | 0.6743 | 0.0611 | 0.2797 | 0.4687 |
| 0.9396 | 0.0029 | 0.6266 | 0.0824 | 0.2515 | 0.5197 |
| 0.9256 | 0.0044 | 0.5911 | 0.1048 | 0.2052 | 0.6204 |
| 0.9111 | 0.0064 | 0.5671 | 0.1208 | 0.1919 | 0.6499 |
| 0.8965 | 0.0079 | 0.5626 | 0.1234 | 0.1613 | 0.7187 |
| 0.8855 | 0.0097 | 0.5623 | 0.1244 | 0.1464 | 0.7636 |
| 0.8775 | 0.0118 | 0.5300 | 0.1485 | 0.1366 | 0.7938 |
| 0.8768 | 0.0120 | 0.4946 | 0.1786 | 0.1204 | 0.8155 |
| 0.8605 | 0.0150 | 0.4621 | 0.2110 | 0.1289 | 0.8207 |
| 0.8544 | 0.0152 | 0.4322 | 0.2434 | 0.1220 | 0.8555 |
| 0.8310 | 0.0197 | 0.4086 | 0.2728 | 0.1210 | 0.8790 |

For the LLE measurements, a constant mass of the internal standard, 1-butanol, was added to all the samples of the equilibrium phases, which were injected with a precision syringe for analysis into the chromatograph, connected to a personal computer which uses commercial software to integrate the signals from the FID, and converted into values of area.

## Results and Discussion

In Table 3, we show the values of density, viscosity, and surface tension for the homogeneous liquid range of the ternary system and for the constituent binaries at 323.15 K as a function of the composition. The experimental values of the binodal curve for water + *n*-butyl acetate + 1-propanol are given in Table 4.

In Table 5, the experimental equilibrium concentration results of the conjugate phases are presented. Each result is the average of at least four injections of the same equilibrium sample into the chromatograph. The binodal curve and the tie-lines are represented in Figure 1. An excellent agreement between the two is observed because the points corresponding to the conjugate phases stay on the binodal curve which stresses the consistency of experimental data.

**Table 5. Experimental Values of the Mole Fraction ($x$), for the Liquid−Liquid Equilibrium and Liquid Interfacial Tension ($\gamma'$), for the Ternary System Water (1) + *n*-Butyl acetate (2) + 1-Propanol (3) at 323.15 K**[a]

| overall composition | | water layer | | organic layer | | | |
|---|---|---|---|---|---|---|---|
| $z_1$ | $z_3$ | $x_1$ | $x_3$ | $x_1$ | $x_3$ | $\gamma$ (mN·m$^{-1}$) | $\gamma'$ (mN·m$^{-1}$) |
| 0.8599 | 0 | 0.9998 | 0 | 0.1305 | 0 | 21.74 | 14.2 |
| 0.8487 | 0.0407 | 0.9842 | 0.0154 | 0.2009 | 0.1664 | 22.40 | 7.3 |
| 0.8400 | 0.0686 | 0.9757 | 0.0238 | 0.2769 | 0.2593 | 22.21 | 5.4 |
| 0.8175 | 0.1109 | 0.9643 | 0.0349 | 0.4117 | 0.3279 | 22.43 | 2.8 |
| 0.8159 | 0.1284 | 0.9580 | 0.0410 | 0.4889 | 0.3363 | 22.56 | 0.0 |

[a] The surface tension ($\gamma$) of the organic layer at equilibrium is also listed.

The excess molar volumes, $V^{\mathrm{E}}$, were obtained from the measured density by the expression

$$V^{\mathrm{E}} = \rho^{-1}\left(\sum_{i=1}^{c} x_i M_i\right) - \sum_{i=1}^{c} x_i M_i \rho_i^{-1} \tag{2}$$

where $x_i$, $M_i$, and $\rho_i$ are the mole fraction, the molecular weight, and the measured density of the pure component $i$, respectively, and $c$ is the number of species.

The viscosity, $\eta$, and the surface tension, $\gamma$, of the binary systems were correlated using the equations

$$\eta = x_i\eta_i + x_j\eta_j + \eta_{ij} \tag{3}$$

and

$$\gamma = x_i\gamma_i + x_j\gamma_j + \gamma_{ij} \tag{4}$$

where $\eta_i$ and $\gamma_i$ are the measured viscosity and surface tension of the pure component $i$, and $\eta_{ij}$ and $\gamma_{ij}$ are the viscosity and surface tension of mixing functions. The dependence of binary properties $X_{ij}$ ($\equiv V_{ij}^{\mathrm{E}}$, $\eta_{ij}$, and $\gamma_{ij}$) on composition has been described by the equation proposed by Myers and Scott,[9] written as

$$\frac{X_{ij}}{x_i x_j} = \frac{\sum_{k=0}^{p} B_k z_{ij}^{k}}{1 + \sum_{l=1}^{m} C_l z_{ij}^{l}} \tag{5}$$

where $z_{ij} = x_i - x_j$. $B_k$ and $C_l$ are adjustable coefficients obtained from the fitting of eq 5 to $V_{ij}^{\mathrm{E}}/x_ix_j$, $\eta_{ij}/x_ix_j$, and $\gamma_{ij}/x_ix_j$ being the experimental $V_{ij}^{\mathrm{E}}$, $\eta_{ij}$, and $\gamma_{ij}$ obtained from eqs 2, 3, and 4, respectively. The function $X_{ij}/x_ix_j$ was suggested by the work of Desnoyers and Perron[33] and shows important physical advantages when compared with other analytical representations: the extrapolation of $X_{ij}/x_ix_j$ to $x_i = 0$ and to $x_j = 0$ gives the differences ($X_i^\infty - X_i$) and ($X_j^\infty - X_j$) between the partial molar property of the components at infitine dilution, $X_i^\infty$ or $X_j^\infty$, and the corresponding global property of pure liquids, $X_i$ or $X_j$.

The viscosity and the surface tension of the ternary mixtures have been calculated using the equations

$$\eta = \sum_{i=1}^{c=3} x_i\eta_i + \eta_{\mathrm{T}} \tag{6}$$

and

$$\gamma = \sum_{i=1}^{c=3} x_i\gamma_i + \gamma_{\mathrm{T}} \tag{7}$$

where the ternary terms $\eta_{\mathrm{T}}$ and $\gamma_{\mathrm{T}}$ are the viscosity and the surface tension of mixing and were found from the expression

$$X_{\mathrm{T}} = \sum_{i<j} X_{ij} + X_{123} \tag{8}$$

where $X_{ij}$ are the viscosity and surface tension obtained by fitting eq 5 to binary data and $X_{123}$ is a ternary contribution expressed by the Pando et al. expression[10]

$$X_{123} = x_1x_2x_3\left(\frac{B_0 + B_1 z_{13} + B_2 z_{23}}{1 + C_1 z_{13} + C_2 z_{23}}\right) \tag{9}$$

This equation was also used to correlate the excess molar volume for the ternary mixtures, $V^{\mathrm{E}}$ ($\equiv V_{\mathrm{T}}$).

The surface tension, $\gamma$, of the binary and multicomponent systems was described by the model proposed by Fu et al.[11]

$$\gamma = \sum_{i=1}^{c} \frac{x_i\gamma_i}{\sum_{j=1}^{c} x_j f_{ij}} - \sum_{i=1}^{c}\sum_{j=1}^{c} \frac{x_i x_j |\gamma_i - \gamma_j|}{\sum_{q=1}^{c} x_q f_{iq} \sum_{r=1}^{c} x_r f_{jr}} \tag{10}$$

where the $f_{ij}$ are adjustable parameters for the binary systems and by the model derived by Li et al.,[12] where

$$\gamma = \sum_{i=1}^{c} x_i\gamma_i - RT\sum_{i=1}^{c}\left[\frac{x_i}{\sum_{j=1}^{c} x_j\Lambda_{ij}} \sum_{j}^{c} x_j\left(\frac{\partial \Lambda_{ij}}{\partial A}\right)_{T,P,x}\right] \tag{11}$$

where

$$\Lambda_{ij} = \exp\left(-\frac{U_{ij} - U_{ii}}{RT}\right), \quad \left(\frac{\partial \Lambda_{ij}}{\partial A}\right)_{T,P,\mathrm{x}} = -\frac{\Lambda_{ij}}{RT}\left[\frac{\partial (U_{ij} - U_{ii})}{\partial A}\right]_{T,P,x}$$

In the preceding relations, $U_{ij} - U_{ii}$ is the difference in the interaction energy between the molecular pair $ij$ and the derivative $[\partial(U_{ij} - U_{ii})/\partial A]_{T,P,x}$ reflects the energy change with the increase in surface area. In a binary system, the adjustable parameters are four, i.e., $(U_{12} - U_{11})$, $(U_{21} - U_{22})$, $[\partial(U_{12} - U_{11})/\partial A]_{T,P,x}$, and $[\partial(U_{21} - U_{22})/\partial A]_{T,P,x}$. Li et al. made the assumption $U_{ij} = (U_{ii} + U_{jj})/2$, reducing the number of parameters to two, i.e., $(U_{12} - U_{11})$ and $[\partial(U_{12} - U_{11})/\partial A]_{T,P,x}$. With the parameters in eqs 10 and 11 obtained from regression of binary surface tension data, the prediction of this property in multicomponent systems was obtained.

In the fitting of eq 5, we have used our data with the experimental information from other authors with the purpose of covering the whole range of composition including the interesting dilute regions. In Table 6, the coefficients, $B_k$ and $C_l$ of eq 5 are presented, and the sources of data are also given. The standard deviations, $\sigma$, of the corresponding fittings

$$\sigma = \left[\sum_{i=1}^{N} \frac{[(X_{ij}/x_ix_j)_{\mathrm{calc}} - (X_{ij}/x_ix_j)_{\mathrm{exp}}]_i^2}{N - n}\right]^{1/2} \tag{12}$$

and the average absolute deviation, AAD, on the global property $X$,

$$\mathrm{AAD} = \frac{100}{N}\left[\sum_{i=1}^{N} |(X_{\mathrm{calc}} - X_{\mathrm{exp}})/X_{\mathrm{exp}}|_i\right] \tag{13}$$

are also tabulated. In eqs 12 and 13, $X(\equiv V_{\mathrm{m}}, \eta, \gamma)$ and the subscripts calc and exp refer to calculated and experimental values. $N$ and $n$ represent the number of experimental points and parameters, respectively. In Table 6, the coefficients corresponding to eq 9 for the ternary data are also listed. They

**Table 6. Coefficients of Equation 5 Fitted to the Excess Molar Volumes, the Viscosity of Mixing, and Surface Tension of Mixing for the Binary and Ternary Systems**

| system | | $B_0$ | $B_1$ | $B_2$ | $C_1$ | $C_2$ | $C_3$ | $\sigma^a$ | AAD$^b$ % | refs |
|---|---|---|---|---|---|---|---|---|---|---|
| water + *n*-butyl acetate | $[V_{12}^E/x_1x_2]/(\mathrm{cm^3{\cdot}mol^{-1}})$ | −0.654 | −0.240 | – | – | – | – | 0.030 | 0.0 | this work |
| | $[\eta_{12}/x_1x_2]/(\mathrm{mPa{\cdot}s})$ | 0.147 | 0.149 | – | – | – | – | 0.006 | 0.0 | this work |
| | $[\gamma_{12}/x_1x_2]/(\mathrm{mN{\cdot}m^{-1}})$ | −65.135 | −19.767 | – | – | – | – | 0.06 | 0.0 | this work |
| water + 1-propanol | $[V_{13}^E/x_1x_3]/(\mathrm{cm^3{\cdot}mol^{-1}})$ | −1.972 | 1.913 | – | −1.300 | −0.157 | 0.470 | 0.21 | 0.1 | this work, Mikhail and Kimel,[34] Pang et al.,[24] Kubota et al.[35] |
| | $[\eta_{13}/x_1x_3]/(\mathrm{mPa{\cdot}s})$ | 1.719 | −0.975 | – | −1.638 | 0.790 | – | 0.12 | 0.7 | this work, Mikhail and Kimel,[34] Pang et al.,[24] Akhtar et al.[29] |
| | $[\gamma_{13}/x_1x_3]/(\mathrm{mN{\cdot}m^{-1}})$ | −88.425 | – | – | −1.041 | 0.069 | – | 68.60 | 3.7 | this work, Vázquez et al.[31] |
| *n*-butyl acetate + 1-propanol | $[V_{23}^E/x_2x_3]/(\mathrm{cm^3{\cdot}mol^{-1}})$ | 1.100 | – | – | −0.187 | 0.003 | – | 0.010 | 0.0 | this work |
| | $[\eta_{23}/x_2x_3]/(\mathrm{mPa{\cdot}s})$ | −0.972 | – | – | 0.584 | −0.049 | | 0.005 | 0.1 | this work |
| | $[\gamma_{23}/x_2x_3]/(\mathrm{mN{\cdot}m^{-1}})$ | 1.241 | 0.102 | 0.328 | – | – | – | 0.03 | 0.0 | this work |
| water + *n*-butyl acetate + 1- propanol | $V_{123}^E/(\mathrm{cm^3{\cdot}mol^{-1}})$ | −1.010 | −2.628 | – | −0.692 | – | – | 0.008 | 0.0 | this work |
| | $\eta_{123}/(\mathrm{mPa{\cdot}s})$ | −2.845 | −1.751 | – | – | 0.873 | – | 0.012 | 0.5 | this work |
| | $\gamma_{123}/(\mathrm{mN{\cdot}m^{-1}})$ | 63.472 | 79.903 | – | 1.003 | – | – | 0.19 | 0.5 | this work |

[a] Standard deviation, eq 12, in the units of respective property. [b] Average absolute deviation, eq 13, of the properties ($V_m$, $\eta$, and $\gamma$).

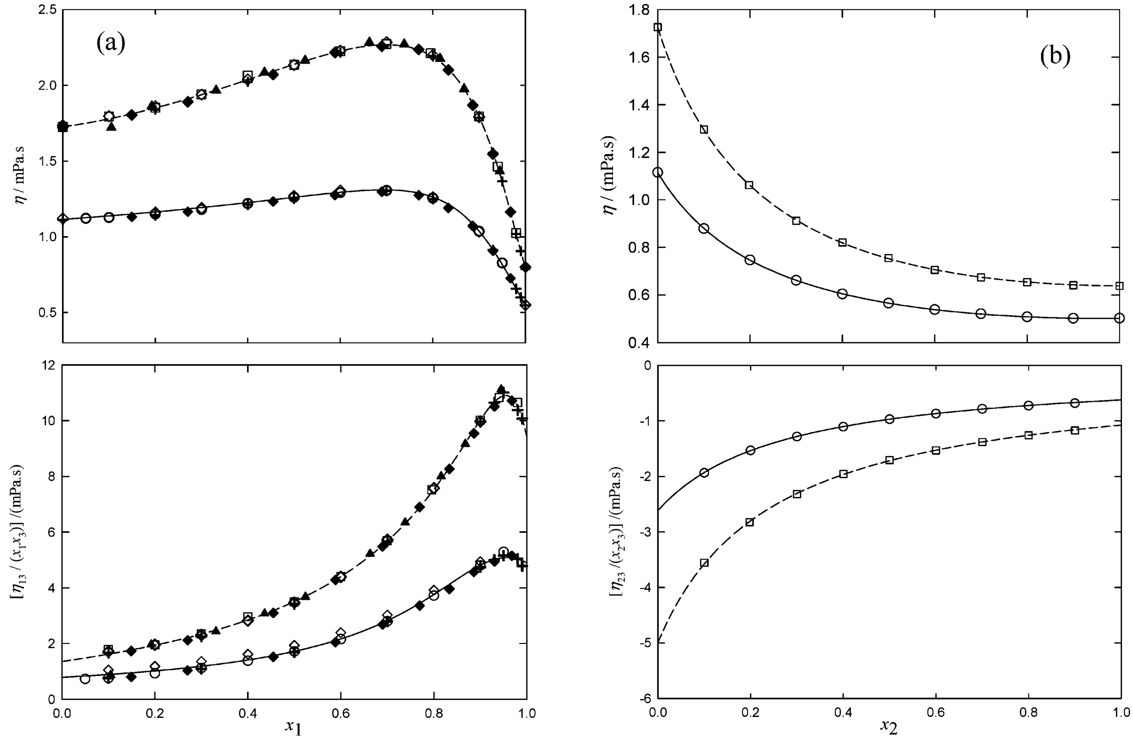

**Figure 3.** Viscosity, $\eta$, and modified viscosity change of mixing, $\eta_{ij}/x_ix_j$, of the binary systems at (303.15 and 323.15) K as a function of the mole fractions: (a) water (1) + 1-propanol (3); (b) *n*-butyl acetate (2) + 1-propanol (3). The symbols refer to experimental data: □, Johnson et al.;[6] ○, this work; ◆, Mikhail and Kimel;[34] ▲, Dizechi and Marschall;[37] +, Pang et al.;[24] ◇, Akhtar et al.[29] The curves were calculated at 303.15 K (----) and at 323.15 K (−). Equation 5 describes $\eta_{ij}/x_ix_j$, and this function was included in eq 3 for the calculation of $\eta$.

were found by fitting eq 8 to experimental properties. From Table 6 we conclude that the standard deviation is low enough to represent adequately the thermodynamic properties of binary systems with eq 5 and of the ternary systems with eq 9 using only three or four terms.

Although the experimental property data presented in this work refer to 323.15 K, we can compare the behavior of the binary systems at different temperatures. The experimental data and his treatment at 303.15 K have been reported in a previous work.[6] It can be seen from Figure 2(a) that the change of 20 °C on the temperature has a little effect on the molar volume as expected. On the other hand, the function $V_{13}^E/x_1x_3$ is negative throughout the whole composition range at both temperatures with a sharp minimum at $x_1 \approx 0.97$. At 303.15 K, the partial molar volume differences at infinite dilution are $(V_1^\infty - V_1) = -2.9\ \mathrm{cm^3{\cdot}mol^{-1}}$ and $(V_2^\infty - V_2) = -4.5\ \mathrm{cm^3{\cdot}mol^{-1}}$, while the corresponding values at 323.15 K are $-2.3\ \mathrm{cm^3{\cdot}mol^{-1}}$ and $-4.5\ \mathrm{cm^3{\cdot}mol^{-1}}$. These values can be compared with those taken from the work by Benson and Kiyhoara[36] at 298.15 K: $(V_1^\infty - V_1) = -2.8\ \mathrm{cm^3{\cdot}mol^{-1}}$ and $(V_2^\infty - V_2) = -4.3\ \mathrm{cm^3{\cdot}mol^{-1}}$. The function $V_{23}^E/x_2x_3$ corresponding to the *n*-butyl acetate + 1-propanol system is represented in Figure 2(b). A marked change on the curvature of this function with the change of temperature is observed.

The experimental and fitted values of $\eta_{ij}/x_ix_j$ and the corresponding viscosity $\eta$ for the binary systems water + 1-propanol and *n*-butyl acetate + 1-propanol as a function of the compositions of water and ester are presented in Figure 3 at (303.15 and 323.15) K. The values taken from the literature are in excellent agreement with our data. For the system water + 1-propanol, a maximum in $\eta_{13}/x_1x_3$ occurs at nearly $x_1 = 0.96$ for both temperatures which is interesting because this value in the molar fraction is practically the same at which the minimum of $V_{13}^E/x_1x_3$ is observed. For the liquid mixtures of *n*-butyl acetate + 1-propanol, the trend of both functions on composition indicates that any of the before mentioned effects are (probably)

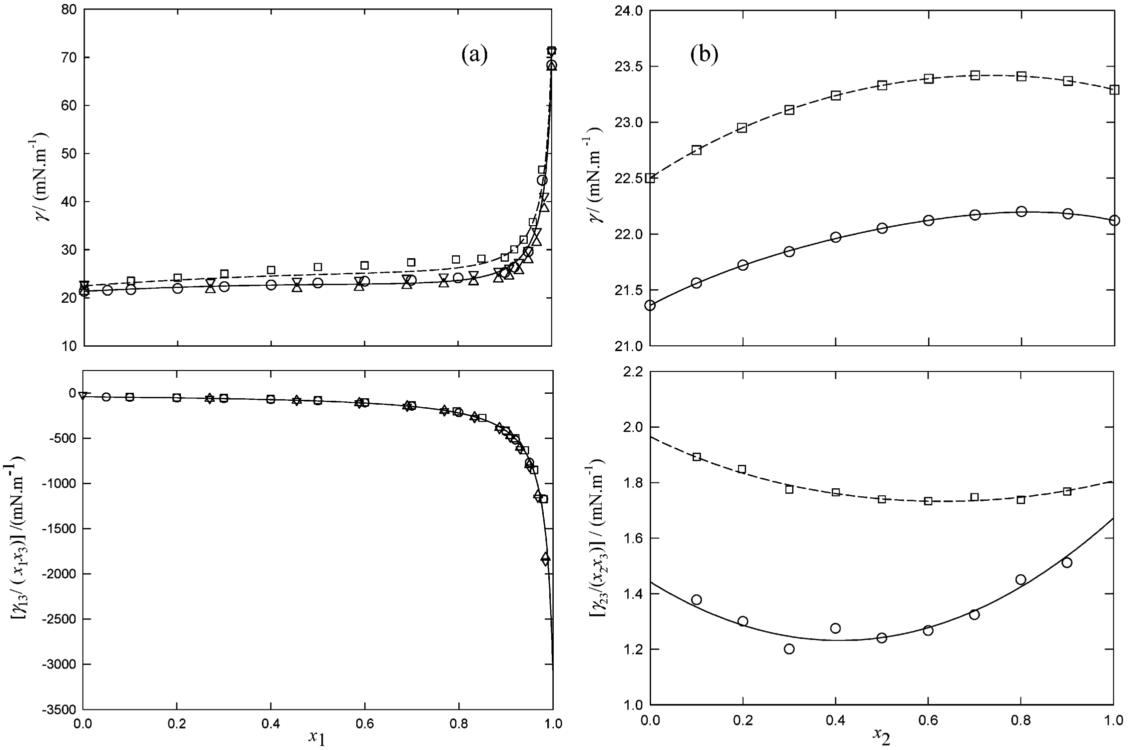

**Figure 4.** Surface tension function, $\gamma$, and modified surface tension change of mixing, $\gamma_{ij}/x_ix_j$, for the binary systems at 303.15 K and 323.15 K as a function of the mole fractions: (a) water (1) + 1-propanol (3) and (b) *n*-butyl acetate (2) + 1-propanol (3). The symbols refer to experimental data: □, Johnson et al.;[6] ○, this work; ▽, Vázquez et al.[31] at 303.15 K; △, Vázquez et al.[31] at 323.15 K. The curves were calculated at 303.15 K (----) and at 323.15 K (—). Equation 5 describes $\gamma_{ij}/x_ix_j$, and this function was used in eq 4 for the calculation of $\gamma$.

**Table 7. Coefficients of Fu et al. and Li et al. Models Applied to the Surface Tension of the Binary Systems**

| system | | Fu et al. | Li et al. |
|---|---|---|---|
| water + *n*-butyl acetate | $\sigma$/(mN·m$^{-1}$) | 0.00 | 0.00 |
| | AAD (%) | 0.0 | 0.0 |
| | parameters | $f_{12} = 2.158$ | $\Lambda_{21} = 2.102\cdot10^{-1}$ |
| | | $f_{21} = 0.0427$ | $(\partial\Lambda_{21}/\partial A)_{T,P,x} = -4.503\cdot10^{-6}$ |
| water + 1-propanol | $\sigma$/(mN·m$^{-1}$) | 1.23 | 1.51 |
| | AAD (%) | 3.9 | 4.2 |
| | parameters | $f_{13} = 22.028$ | $\Lambda_{31} = 1.561\cdot10^{-2}$ |
| | | $f_{31} = 0.032$ | $(\partial\Lambda_{31}/\partial A)_{T,P,x} = -2.753\cdot10^{-7}$ |
| *n*-butyl acetate + 1- propanol | $\sigma$/(mN·m$^{-1}$) | 0.01 | 0.01 |
| | AAD (%) | 0.1 | 0.1 |
| | parameters | $f_{23} = 1.042$ | $\Lambda_{32} = 8.279\cdot10^{-1}$ |
| | | $f_{32} = 0.869$ | $(\partial\Lambda_{32}/\partial A)_{T,P,x} = 2.103\cdot10^{-6}$ |
| water + *n*-butyl acetate + 1-propanol | $\sigma$/(mN·m$^{-1}$)[a] | 1.02 | 0.40 |
| | AAD (%) | 3.6 | 1.4 |

[a] Standard deviation ($\sigma$) and AAD for the prediction for ternary data.

off. The change of the viscosity with temperature is clearly seen. At the maximum value in this property for water + 1-propanol, the change is 1 mPa·s, while for *n*-butyl acetate + 1-propanol it is more than 0.2 mPa·s (about 20 %) in the whole range of composition.

In Figure 4, we have plotted the experimental and the fitted values of $\gamma_{ij}/x_ix_j$ and $\gamma$ as a function of the composition. For the water + 1-propanol system, we conclude that the surface tension increases suddenly for values of $x_1$ larger than 0.95 which corresponds to a marked decrease in the function $\gamma_{13}/x_1x_3$ in this region. To represent the experimental data of this function, a single analytical equation is necessary at (303.15 and 323.15) K. This expected behavior is resulting from the slow change of surface tension with temperature in the range considered. The function $\gamma$ calculated with eq 4 using the analytical form found to express $\gamma_{13}/x_1x_3$ is compatible with our data and those due to Vásquez et al.[31] at 323.15 K. However, at 303.15 K the resulting curve for $\gamma$ describes an intermediate behavior between the two sets of data. For the *n*-butyl acetate + 1-propanol, maxima in $\gamma$ are observed for the solutions with appreciable quantity of ester. From Table 6, we can see that an apparently high standard deviation in $\gamma_{13}/x_1x_3$ is obtained, but as Figure 4(a) shows, this value must be judged taking into account the very large values assumed by that function.

In Figure 5, the ability of eq 8, which includes the rational model eq 9, to represent the behavior of the different properties change of mixing studied on the ternary homogeneous range of composition is shown. This study was made following paths of constant $x_1/x_3$ as represented in the ternary diagram. We conclude that the use of the rational model of Pando et al., eq 9, allows very suitable fittings for all the properties considered. The mixing of the three pure liquids gives either positive or negative values of $V^E$ and $\eta_T$ depending on the path $x_1/x_3$ which is considered, but for the $\gamma_T$ function, high negative values are always observed. It is interesting to follow the path for which $x_1/x_3 = 1$. In approximating the binodal curve starting from the

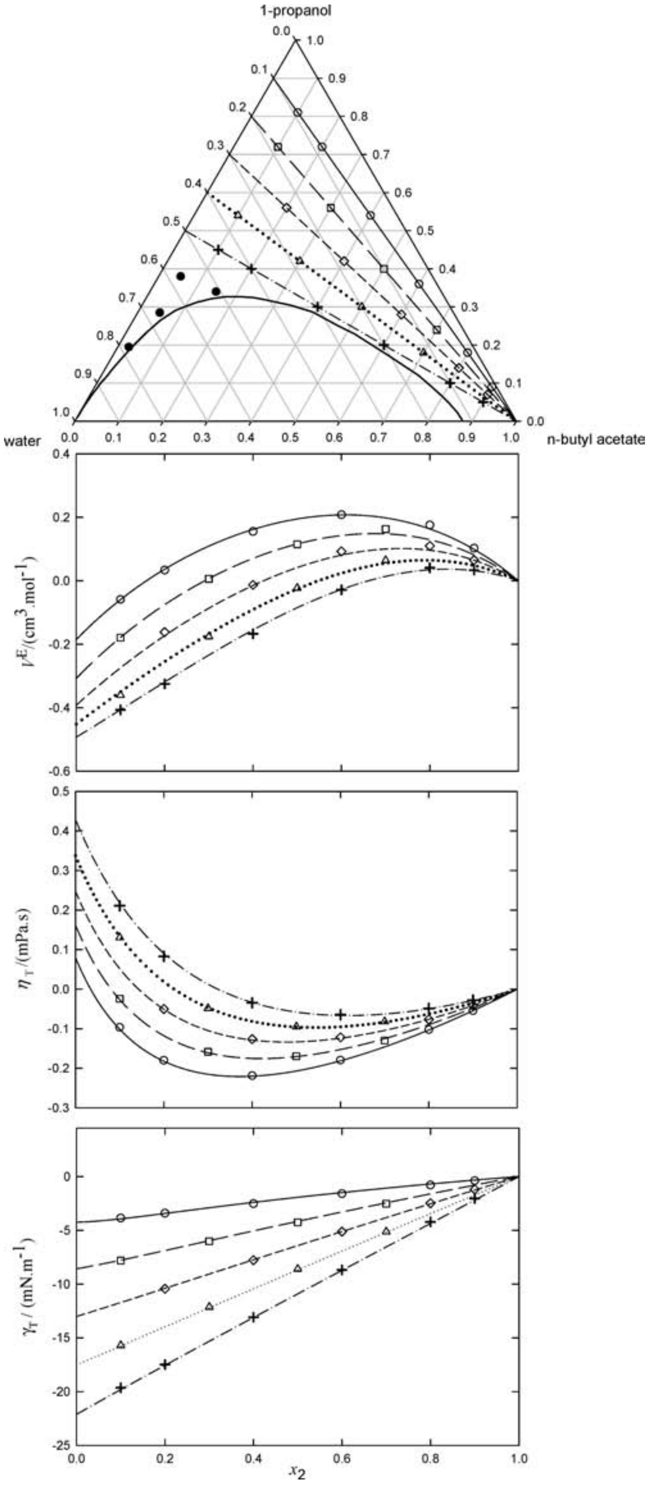

**Figure 5.** Property changes of mixing $V^E$, $\eta_T$, and $\gamma_T$, for the ternary system water + *n*-butyl acetate + 1-propanol, at 323.15 K, along the diagonals of constant ratio $z = x_1/x_3$ as a function of the ester composition, $x_2$: ○, $z = 0.111$; □, $z = 0.250$; ◇, $z = 0.429$; Δ, $z = 0.667$; and +, $z = 1.000$. The curves represent the correlation equation (combined eqs 8 and 9).

water + 1-propanol system, the negative values of $V^E$ and positive values of $\eta_T$ changes to small figures, but $\gamma_T$ is highly negative in this region [(−15 to −10) mN·m$^{-1}$].

The ability of the methods of Fu et al.[11] and of Li et al.[12] to correlate the binary surface tension data and the prediction of the ternary system can be judged from Table 7. The surface tension of the ternary systems can be satisfactorily predicted using these models with corresponding low values of the AAD.

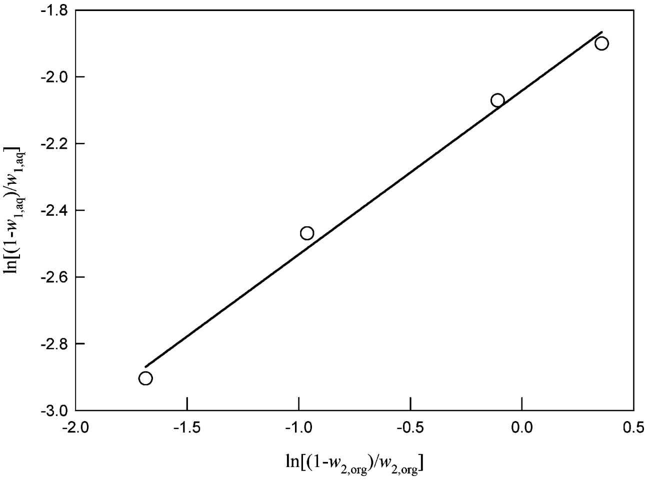

**Figure 6.** Othmer-Tobias correlation for water (1) + *n*-butyl acetate (2) + 1-propanol (3) at 323.15 K. The symbols refer to the experimental tie-line data and the line to the correlation eq 15.

The experimental LLE data of the ternary mixtures were predicted using UNIFAC. The group-interaction parameters used for estimating the activity coefficients in the liquid phases were those given by Magnussen et al.[18] obtained from experimental LLE. Figure 1 shows the experimental LLE diagram and the predictions from UNIFAC. The UNIFAC model predicts a two-phase region in good agreement with that observed experimentally. The slopes of the predicted tie-lines are similar to those measured. The uncertainty of the estimation is defined by the standard deviation

$$\sigma = 100\{\sum_{k}^{n}[\sum_{i}^{3}\sum_{j}^{2}(x_{i,\mathrm{exp}} - x_{i,\mathrm{calc}})_j^2/6n]\}^{1/2} \qquad (14)$$

where $n$ is the number of tie lines ($n = 5$); $x_{\mathrm{exp}}$ indicates the experimental mole fraction; $x_{\mathrm{calc}}$ is the calculated one; the subscript $i$ indexes components; $j$ is the phase; and $k = 1,2, ..., n$ are the tie-lines. For UNIFAC, $\sigma = 0.04$.

The reliability of experimentally measured tie-lines was determined by the application of the Othmer-Tobias correlation,[19] one of the most used for this purpose. This method employs the linear relationship

$$\ln[(1 - w_{1,\mathrm{aq}})/w_{1,\mathrm{aq}}] = m + k\ln[(1 - w_{2,\mathrm{org}})/w_{2,\mathrm{org}}] \qquad (15)$$

where $w_{1,\mathrm{aq}}$ and $w_{2,\mathrm{org}}$ are, respectively, the mass fraction of water (component 1) in the aqueous phase and ester (component 2) in the organic phase. The linearity of the plot in Figure 6 indicates a good consistency of the measured data. The values of parameters are $m = -2.0413$ and $k = 0.4911$, and the standard deviation is $\sigma = 0.050$. Following the method devised by Novák et al.,[20] the correlation of the binodal curve was made using the equation

$$\ln[(x_1/x_2)]/(x_1 - x_2) = \sum_{i=0}^{m} a_i(x_1 - x_2)^i \qquad (16)$$

where $m$ represents the number of data points ($m = 42$). This equation has been used successfully for correlation of binodal curves where the number of terms on the right-hand side varied from 3 to 5.

In this work, we have fitted eq 16 to the binodal data listed in Table 4 obtaining

$$\ln[(x_1/x_2)]/(x_1 - x_2) = 2.8536 + 0.9218(x_1 - x_2) + 1.0762(x_1 - x_2)^2 + 3.004(x_1 - x_2)^{10} \quad (17)$$

The standard deviation of the fit is $\sigma = 0.1$. In Figure 7, the experimental data and the results of correlation from eq 17 are compared. We conclude that the model of Novák et al. describes very well the binodal curve data.

To correlate the liquid interfacial tension, the Li and Fu model[21] was used. The equation of the model is

$$\gamma' = \gamma'_0 \left(\frac{X}{X_0}\right)^k \quad (18)$$

where $X = -\ln[x_1^{\alpha} + x_2^{\beta} + x_{3p}]$; $\gamma'$ is the interfacial tension between the two immiscible liquid phases α and $\beta$ in the ternary system; and $\gamma'_0$ is the interfacial tension of the partially miscible binary pair which corresponds $x_3 = 0$ and $X = X_0$ in eq 18. $x_1^{\alpha}$ is the mole fraction of component 1 in the liquid phase α richer in component 2; $x_2^{\beta}$ is the mole fraction of component 2 in the phase richer in component 1; and $x_{3p}$ is the mole fraction of component 3 in the phase poor in it. In eq 18, the parameter $k$ can be described by the general form $k = \sum_{i=0} k_i X^i$.[21] A satisfactory representation of $\gamma'$ as a function of $X$ is obtained taking into account the dependence of $k$ on the composition ($k = -6.1638 - 8.1540X + 3.7210X^2$). The same conclusion was already taken from past studies on the same type of systems.[4,5]

The interfacial tension data of the present ternary system and of other ternary systems of the type water + aliphatic ester + alkanol at different temperatures were represented as a function of $X$ in Figure 8. As can be seen, most of the data of the ternary systems measured so far can be represented with reasonable approximation by the simple equation $\gamma' = -1.679 + 6.214X$. Most (65 %) of the $\gamma'$ data lie in the corridor corresponding to deviations of ± 1 mN·m$^{-1}$ from the equation given.

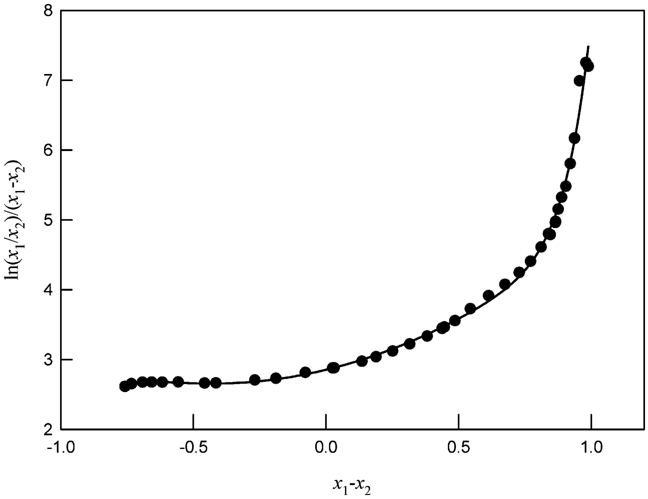

**Figure 7.** Dependence of $[\ln(x_1/x_2)]/(x_1 - x_2)$ on $(x_1 - x_2)$ for the binodal curve. The symbols refer to the experimental data and the line to the correlation with eq 17.

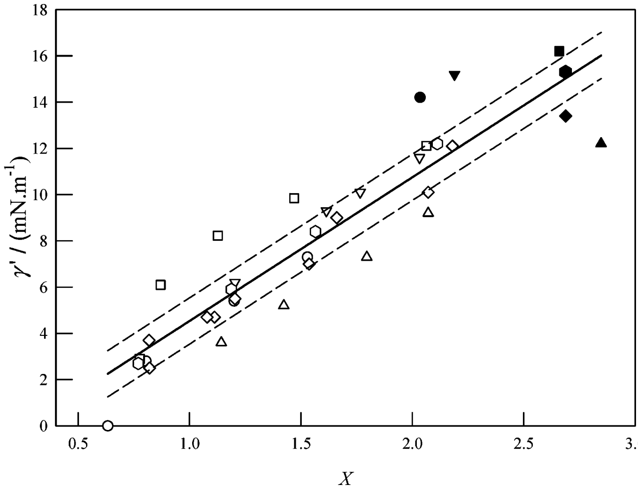

**Figure 8.** Liquid interfacial tension, $\gamma'$, as a function of $X$ for several ternary systems water + ester + alcohol. —, $\gamma' = -1.679 + 6.214X$; - - -, deviations of ± 1 mN·m$^{-1}$ from the line (—). Experimental data: ●, ○, water + *n*-butyl acetate + 1-propanol at 323.15 K, present study; ■, □, water + *n*-butyl acetate + 1-propanol at 303.15 K;[6] ♦, ◇, water + *n*-butyl acetate + methanol at 303.15 K;[4] ▼,▽, water + *n*-pentyl acetate + methanol at 303.15 K;[4] ▲, Δ, water + ethyl propionate + methanol at 303.15 K;[5] ⬢, ⬡, water + ethyl butyrate + methanol at 303.15 K;[2] full symbols correspond to the binary immiscible pair water + ester.

## Conclusions

The densities, viscosities, and surface and interfacial tensions of the system water + *n*-butyl acetate + 1-propanol have been determined experimentally at 323.15 K and atmospheric pressure. The rational functions allow a good representation of the binary property data. Combining our data with other collected from the literature, we have found interesting property behavior using the functions $V_{ij}^{E}/x_i x_j$, $\eta_{ij}/x_i x_j$, and $\gamma_{ij}/x_i x_j$ which were suggested by Desnoyers and Perron. The rational model of Pando et al. allows a very good description of all the properties studied in the homogeneous region of the ternary system.

The methods of Fu et al. and of Li et al. successfully correlate the binary surface tension data. When applied to the prediction of the ternary system, low values of the AAD were obtained.

Experimental liquid–liquid equilibrium and interfacial tension data for the system water + *n*-butyl acetate + 1-propanol at 323.15 K and atmospheric pressure are presented. Tie-line data are accurately predicted from the UNIFAC method. The application of the Othmer-Tobias method indicates the reliability of the experimentally measured tie-lines. The experimental binodal data are successfully correlated with the model of Novák et al. The Li and Fu model can be applied to correlation of interfacial data provided that the parameter $k$ is a polynomial function of $X$, a conclusion which was already established in past studies on the same type of systems. An important conclusion is that most of the data on the interfacial tension for water + aliphatic ester + alkanol systems measured so far can be represented (and predicted up to ± 1 mN·m$^{-1}$) by a simple linear equation on parameter $X$.

### Acknowledgment

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## Literature Cited

(1) Oswal, S. L.; Putta, S. S. R. Excess Molar Volumes of Binary Mixtures of Alkanols with Ethyl Acetate from 298.15 to 323.15 K. *Thermochim. Acta* **2001**, *373*, 141–152.

(2) Kijevcanin, M. L.; Ribeiro, I. S. A.; Ferreira, A. G. M.; Fonseca, I. M. A. Densities, Viscosities and surface and interfacial tensions of the ternary mixture water + ethyl butyrate + methanol at 303.15 K. *J. Chem. Eng. Data* **2003**, *48*, 1266–1270.

(3) Giro, F.; Gonçalves, M. F.; Ferreira, A. G. M.; Fonseca, I. M. A. Viscosity and Density Data of the System Water + *n*-Pentyl Acetate + Methanol. Calculations with a Modified Redlich-Kwong-Soave Equation of State. *Fluid Phase Equilib.* **2003**, *204*, 217–232.

(4) Santos, B. M. S.; Ferreira, A. G. M.; Fonseca, I. M. A. Surface and interfacial tensions of the systems water + n-butyl acetate + methanol and water + n-pentyl acetate + methanol at 303.15 K. *Fluid Phase Equilib.* **2003**, *208*, 1–21.

(5) Kijevcanin, M. L.; Ribeiro, I. S. A.; Ferreira, A. G. M.; Fonseca, I. M. A. Water+esters+methanol: experimental data, correlation and

prediction of surface and interfacial tensions at 303.15 K and atmospheric pressure. *Fluid Phase Equilib.* **2004**, *218*, 141–148.

(6) Johnson, I.; Costa, H. F.; Ferreira, A. G. M.; Fonseca, I. M. A. Density, Viscosity, and Surface and Interfacial Tensions of Mixtures of Water + N-butyl Acetate+1-Propanol at 303.15 K and Atmospheric Pressure. *Int. J. Thermophys.* **2008**, *29*, 619–633.

(7) Gardas, R. L.; Johnson, I.; Vaz, D. M. D.; Fonseca, I. M. A.; Ferreira, A. G. M. PVT Property Measurements for Some Aliphatic Esters from (298 to 393) K and up to 35 MPa. *J. Chem. Eng. Data* **2007**, *52*, 735–751.

(8) Henrique, F. C.; Gardas, R. L.; Johnson, I.; Fonseca, I. M. A.; Ferreira, A. G. M. PVT Property Measurements for Ethyl Propionate, Ethyl Butyrate, and Ethyl Pentanoate Esters from (298 to 393) K and up to 35 MPa. *J. Chem. Eng. Data* **2009**, *54*, 256–262 (festschrift for the 90th birthday of Robin H. Stokes).

(9) Myers, D. B.; Scott, R. L. Thermodynamic Functions For Nonelectrolyte Solutions. *Ind. Eng. Chem.* **1963**, *55*, 43–46.

(10) Pando, C.; Renuncio, J. A. R.; Calzon, J. A. G.; Christensen, J. J.; Izatt, R. M. Correlation and Prediction of Ternary Excess Enthalpy Data. *J. Solution Chem.* **1987**, *16*, 503–527.

(11) J. Fu, J.; Li, B.; Wang, Z. Estimation of fluid-fluid interfacial tensions of multicomponent mixtures. *Chem. Eng. Sci.* **1986**, *41*, 2673–2679.

(12) Li, C.; Wang, W.; Wang, Z. A Surface Tension Model for Liquid Mixtures Based on the Wilson Equation. *Fluid Phase Equilib.* **2000**, *175*, 185–196.

(13) Rao, R. J.; Rao, C. V. Ternary liquid equilibria: methanol-water-esters. *J. Appl. Chem.* **1957**, *7*, 435–439.

(14) Rao, R. J.; Rao, C. V. Ternary liquid equilibria systems: n-propanol-water-esters. *J. Appl. Chem.* **1959**, *9*, 69–73.

(15) Arce, A.; Alonso, L.; Vidal, I. Liquid-Liquid Equilibria of the Systems Ethyl Acetate+Ethanol+Water, Butyl Acetate+Etanol+Water, and Ethyl Acetate+Butyl Acetate+ Water. *J. Chem. Eng. Jpn.* **1999**, *32*, 440–444.

(16) Arce, A.; Blanco, A.; Martínez-Alonso, J.; Vidal, I. LLE data for the systems water+(methanol or etanol) + n-amyl acetate. *Fluid Phase Equilib.* **1995**, *109*, 291–297.

(17) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*, Elsevier: Amsterdam, 1977.

(18) Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. UNIFAC Parameter Table for Prediction of Liquid-Liquid Equilibria. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331–339.

(19) Othmer, D. F.; Tobias, P. E. Tie-Line Correlation. *Ind. Eng. Chem.* **1942**, *34*, 690–693.

(20) Novák, J. P.; Matouš, J.; Pick, J. *Studies in Modern Thermodynamics 7: Liquid-Liquid Equilibria*; Elsevier: New York, 1987.

(21) B. Li, B.; Fu, J. Interfacial Tensions of Two-Liquid-Phase Ternary Systems. *J. Chem. Eng. Data* **1992**, *37*, 172–174.

(22) Sato, H.; Vematsu, M.; Watanabe, K.; Saul, A.; Wagner, W. New International Skeleton Tables for the Thermodynamic Properties of Ordinary Water Substance. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1439–1540.

(23) Malhotra, R.; Woolf, L. A. PVT Property Measurements for the Liquids Propyl Acetate, Butyl Acetate, and 1-Methylethyl Acetate from (278 to 338) K and (0.1 to 380) MPa. *J. Chem. Eng. Data* **1996**, *41*, 1366–1370.

(24) Pang, F. M.; Seng, C. E.; Teng, T. T.; Ibrahim, M. H. Densities and viscosities of aqueous solutions of 1-propanol and 2-propanol at temperatures from 293. 15 to 333.15 K. *J. Mol. Liq.* **2007**, *136*, 71–78.

(25) Garcia, B.; Herrera, C.; Leal, J. M. Shear Viscosities of Binary Liquid Mixtures: 2-Pyrrolidone with 1-Alkanols. *J. Chem. Eng. Data* **1991**, *36*, 269–274.

(26) Kestin, J.; Sokolov, M.; Wakeham, A. Viscosity of Liquid Water in the Range−8 to 150 °C. *J. Phys. Chem. Ref. Data* **1978**, *7*, 941–948.

(27) Lide, D. R. *Handbook of Chemistry & Physics*, 76th ed.; CRC Press: Boca Raton, FL, 1995.

(28) Djojoputro, H.; Ismadji, S. Density and Viscosity Correlation for Several Common Fragrance and Flavor Esters. *J. Chem. Eng. Data* **2005**, *50*, 727–731.

(29) Akhtar, S.; Bhuiyan, M. M. H.; Uddin, M. S.; Sultana, B.; Nessa, M.; Saleh, M. A. Viscosity of Aqueous Solutions of Some Alcohols. *Phys. Chem. Liq.* **1999**, *37*, 215–227.

(30) Jasper, J. J. Surface Tension of Pure Liquid Compounds. *J. Phys. Chem. Ref. Data* **1972**, *1*, 841–1009.

(31) Vázquez, G.; Alvarez, E.; Navaza, J. M. Surface Tension of Alcohol + Water from 20 to 50 °C. *J. Chem. Eng. Data* **1995**, *40*, 611–614.

(32) Garcia-Flores, B. E.; Trejo, A.; Águila-Hernández, J. Liquid-Liquid phase behaviour, liquid-liquid density, and interfacial tension of multicomponent systems at 298 K. *Fluid Phase Equilib.* **2007**, *255*, 147–159.

(33) Desnoyers, J. E.; Perron, G. Treatment of Excess Thermodynamic Quantities for Liquid Mixtures. *J. Solution Chem.* **1997**, *26*, 749–755.

(34) Mikhail, S. Z.; Kimel, W. R. Densities and Viscosities of 1 -Propanol-Water Mixtures. *J. Chem. Eng. Data* **1963**, *8*, 323–328.

(35) Kubota, H.; Tanaka, Y.; Makita, T. Volumetric Behavior of Pure Alcohols and Their Water Mixtures Under High Pressure. *Int. J. Thermophys.* **1987**, *8*, 47–70.

(36) Benson, G. C.; Kiyohara, O. Thermodynamics of Aqueous Mixtures of Nonelectrolytes. I. Excess Volumes of Water-n-Alcohol Mixtures at Several temperatures. *J. Solution Chem.* **1980**, *9*, 791–804.

(37) Dizechi, M.; Marschall, E. Viscosity of Some Binary and Ternary Liquid Mixtures. *J. Chem. Eng. Data* **1982**, *27*, 358–363.

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