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# Binary LLE for Propyl Vinyl Ether (PVE) + Water, Ternary LLE for PVE + Methanol or Ethanol + Water at 298.15 K, and $V^E$ and $\Delta R$ at 293.15 K for the Mixture of PVE + Ethanol + 2,2,4-Trimethylpentane

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Liquid−liquid equilibrium (LLE) data from 288.15 K to 323.15 K are reported for the binary system of propyl vinyl ether (PVE) + water, and tie-lines for the ternary systems of PVE + methanol or ethanol + water at 298.15 K were analytically determined by using a stirred and thermoregulated cell. The experimental data were correlated by using the NRTL equation. Additionally, the deviations in molar refractivity ($\Delta R$) at 293.15 K for the binary systems of PVE + ethanol, ethanol + 2,2,4-trimethylpentane, and PVE + 2,2,4-trimethylpentane were measured, and the excess molar volumes ($V^E$) and $\Delta R$ for the ternary system of PVE + ethanol + 2,2,4-trimethylpentane were determined from the measured densities and refractive indices.

## Introduction

Vinyl ethers (ROCH=CH$_2$, where R is an alkyl group) are used in different industries, particularly as solvents, as motor oil additives, for the manufacturing of coatings, or as intermediates for the synthesis of flavors, fragrances, and pharmaceuticals.[1] For the synthesis and separation of these compounds, reliable data of the physical properties and phase equilibrium behavior are required. However, to date, only a limited number of studies have been performed on these type of compounds. Relatively few investigations have been reported for alkyl vinyl ether compounds, and there are no data for propyl vinyl ether (PVE) as far as we know.[2]

In the present work, we report liquid−liquid equilibrium (LLE) data at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K for the binary system of PVE + water and also for the ternary systems of PVE + methanol or ethanol + water at 298.15 K by an analytical method using tie-line measurement. Additionally, refractive indices ($n_D$) at 293.15 K for the binary systems of PVE + ethanol, ethanol + 2,2,4-trimethylpentane, and PVE + 2,2,4-trimethylpentane and also densities ($\rho$) and $n_D$ for the ternary system of PVE + ethanol + 2,2,4-trimethylpentane were measured by using a digital vibrating-tube density meter and a precision digital refractometer. Then excess molar volumes ($V^E$) and deviations in molar refractivity ($\Delta R$) were derived from the measured densities and refractive indices. The experimental binary and ternary LLE data were correlated using the common NRTL model equation. The experimental binary $\Delta R$ data were correlated with the Redlich−Kister polynomial, and ternary $V^E$ and $n_D$ data were correlated with the Cibulka equation, respectively.

## Experimental Section

***Materials.*** The chemicals used in this investigation were analytical commercial grade purity. All the chemicals were dried using molecular sieves with a pore diameter of 0.4 nm except methanol, which was dried with 0.3 nm molecular sieves. Water was distilled twice with a mass fraction of 99.9 %. The purity of the chemicals was checked by gas chromatography and by comparing the density and refractive index with values reported in the literature.[3,4] The water content of the chemicals, determined by Karl Fischer titration (Metrohm 684 KF-Coulometer), was less than $6 \cdot 10^{-5}$. The density and refractive index of the substances are listed in Table 1.

**Table 1. Densities and Refractive Indices of Pure Components**

| | $\rho$ at 298.15 K | | $n_D$ at 298.15 K | |
|---|---|---|---|---|
| chemicals | present study | lit. value | present study | lit. value |
| PVE | 0.76298 | – | 1.38931 | – |
| ethanol | 0.78532 | 0.78517[b] | 1.35933 | 1.35924[b] |
| methanol | 0.78654 | 0.78663[a] | 1.32670 | 1.3264[a] |
| water | 0.99703 | 0.99704[a] | 1.33252 | 1.33250[a] |
| 2,2,4-trimethylpentane | 0.68818 | 0.68774[b] | 1.38898 | 1.38900[b] |

[a] Ref 3. [b] Ref 4.

***Apparatus and Procedure.*** LLE was measured analytically by measuring the tie-lines for all the binary and ternary systems. The self-designed LLE measuring system was used which consists of three parts: equilibrium glass cell, thermostat (Lauda MD 20 with DLK15 cooler) with a precision temperature measuring system, and Corning PC-320 magnetic stirrer. The accuracy of the temperature measurement was better than ± 0.02 K. When the system temperature was reached, the sample mixture was stirred rigorously in an equilibrium cell for about 8 h and then allowed to settle for about 16 h at constant temperature. After that, an equilibriated sample from both phases was taken and analyzed using gas chromatography (HP 5890N) with an HP-FFAP (Polyethylene Glycol TPA, 25 m × 0.20 mm × 0.30 $\mu$m) capillary column and a thermal conductivity detector. The accuracy for the measured mole fraction was estimated as $\pm 1 \cdot 10^{-4}$. The measuring procedure is described in detail elsewhere.[5] Densities for the determination of $V^E$ were measured using a digital vibrating glass tube densimeter (Anton Paar, model DMA 5000, Graz, Austria). The uncertainty of this densimeter is better than $1 \cdot 10^{-5}$ g·cm$^{-3}$. The detailed operating procedures have been described elsewhere.[6,7] Refractive indices ($n_D$) of the pure components and mixture samples were measured

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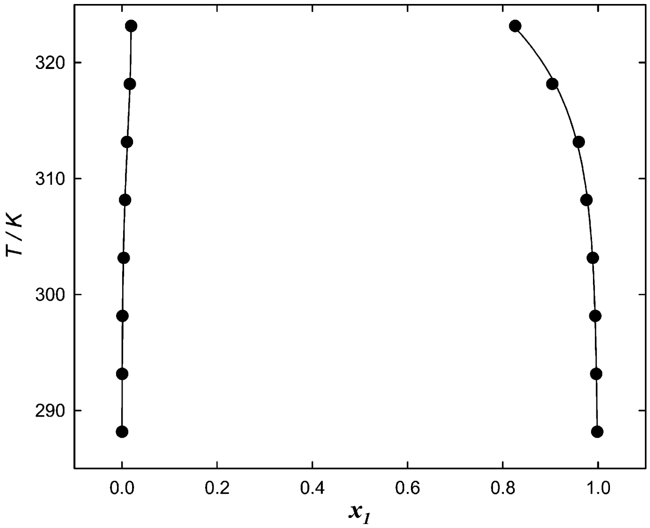

**Figure 1.** LLE for the binary system: ●, PVE (1) + water (2). Solid curves were calculated from the NRTL equation.

**Table 2. Experimental Data for the Binary System of PVE (1) + Water (2)**

| | organic phase | aqueous phase |
|---|---|---|
| $T$ (K) | $x_1$ | $x_1$ |
| 288.15 | 0.9982 | 0.0004 |
| 293.15 | 0.9961 | 0.0007 |
| 298.15 | 0.9941 | 0.0012 |
| 303.15 | 0.9889 | 0.0041 |
| 308.15 | 0.9756 | 0.0067 |
| 313.15 | 0.9595 | 0.0106 |
| 318.15 | 0.9038 | 0.0167 |
| 323.15 | 0.8260 | 0.0193 |

**Table 3. NRTL Model Parameters and Mean Deviation between the Calculated and Experimental Data for the Binary System**

| | NRTL parameters[a] | |
|---|---|---|
| PVE (1) + water (2) | $ij = 12$ | $ij = 21$ |
| $a_{ij}$/K | 253135.099 | −1086969.840 |
| $b_{ij}$/K | −2462.264 | 11013.369 |
| $c_{ij}$/K | 8.109 | −37.030 |
| $d_{ij}$/K | −0.009 | 0.041 |
| $\alpha$ | | 0.200 |
| $\Delta x_1$ | | 0.0024 |

[a] Parameters (K): $A_{ij} = a_{ij} + b_{ij}T + c_{ij}T^2 + d_{ij}T^3$.

with the help of a digital refractometer (KEM, model RA-520N, Kyoto, Japan). The uncertainty of this refractometer is $\pm\, 5 \cdot 10^{-5}$ within a range from 1.32 to 1.40 and $\pm\, 1 \cdot 10^{-4}$ within a range from 1.40 to 1.58. Mixture samples were prepared with the same procedure as the density measurements.

## Results and Discussion

***LLE and Data Correlation.*** The LLE data for the binary system of PVE (1) + water (2) at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K and under atmospheric pressure are listed in Table 2 and plotted in Figure 1. It was supposed to have only an upper critical solution temperature. The measured binary LLE data were correlated only with the NRTL equation because there is no reported physical property for the UNIQUAC equation. The adjustable binary parameters of the NRTL equation are listed in Table 3 along with the mean deviations between experimental and calculated values. The NRTL model gave good correlation results with a 0.24 % mean deviation of the PVE mole fraction. The solid lines in Figure 1 represent the calculated values from the NRTL equation. Because of high volatility of PVE, it was too difficult to measure the LLE at high temperature. The experimental tie-line data for the ternary systems PVE (1) + methanol or ethanol (2) + water (3) at 298.15 K are given in Table 4. Ternary data were also correlated using the NRTL model.

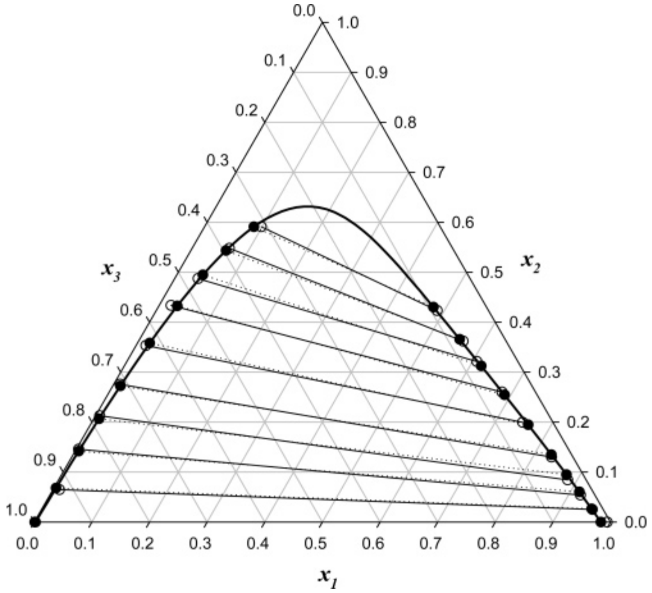

**Figure 2.** LLE for the ternary system of PVE (1) + methanol (2) + water (3) at 298.15 K: ○, experimental value; ●, calculation value. Dashed lines were calculated from the NRTL equation.

**Table 4. Experimental LLE Data of the System PVE (1) + Methanol or Ethanol (2) + Water (3) at 298.15 K (Mole Fraction)**

| | organic phase | | aqueous phase | |
|---|---|---|---|---|
| | $x_{11}$ | $x_{21}$ | $x_{13}$ | $x_{23}$ |
| PVE + methanol + water | 0.9560 | 0.0251 | 0.0115 | 0.0648 |
| | 0.9208 | 0.0541 | 0.0042 | 0.1459 |
| | 0.8835 | 0.0844 | 0.0075 | 0.2126 |
| | 0.8325 | 0.1301 | 0.0108 | 0.2759 |
| | 0.7476 | 0.1996 | 0.0171 | 0.3534 |
| | 0.6815 | 0.2602 | 0.0206 | 0.4336 |
| | 0.6077 | 0.3211 | 0.0407 | 0.4874 |
| | 0.5634 | 0.3619 | 0.0648 | 0.5478 |
| | 0.4877 | 0.4233 | 0.0985 | 0.5911 |
| PVE + ethanol + water | 0.9184 | 0.0422 | 0.0199 | 0.0266 |
| | 0.8088 | 0.1034 | 0.0203 | 0.0540 |
| | 0.6590 | 0.1868 | 0.0198 | 0.0800 |
| | 0.5685 | 0.2324 | 0.0220 | 0.1107 |
| | 0.4487 | 0.2845 | 0.0265 | 0.1363 |
| | 0.3276 | 0.3188 | 0.0337 | 0.1624 |
| | 0.2018 | 0.3440 | 0.0364 | 0.2148 |

**Table 5. NRTL Model Parameters for the Ternary Systems of PVE (1) + Methanol or Ethanol (2) + Water (3) at 298.15 K**

| | NRTL parameters (K) | | | | |
|---|---|---|---|---|---|
| | $i - j$ | $(g_{ij} - g_{ii})/R$ | $(g_{ji} - g_{jj})/R$ | $\alpha_{ij}$ | RMSD |
| PVE + methanol + water | 1 − 2 | −290.79 | 893.77 | 0.20 | |
| | 2 − 3 | −458.41 | 473.87 | 0.20 | 0.0065 |
| | 1 − 3 | 720.50 | 1366.80 | 0.20 | |
| PVE + ethanol + water | 1 − 2 | 1117.90 | −485.42 | 0.20 | |
| | 2 − 3 | 370.54 | −8.57 | 0.20 | 0.0095 |
| | 1 − 3 | 553.74 | 1544.20 | 0.20 | |

The binary parameters were determined by minimizing the differences between the experimental and calculated mole fractions for each component over all the measured tie-lines of the ternary systems. The objective function (OF) used was

$$\mathrm{OF} = \min \sum_i \sum_j \sum_k (X_{ijk} - X^{c}_{ijk})^2 \qquad (1)$$

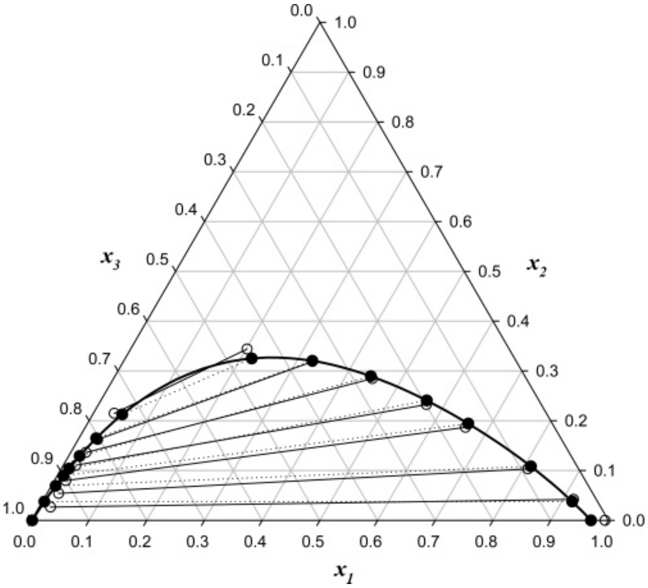

**Figure 3.** LLE for the ternary system of PVE (1) + ethanol (2) + water (3) at 298.15 K: ○, experimental value; ●, calculation value. Dashed lines were calculated from the NRTL equation.

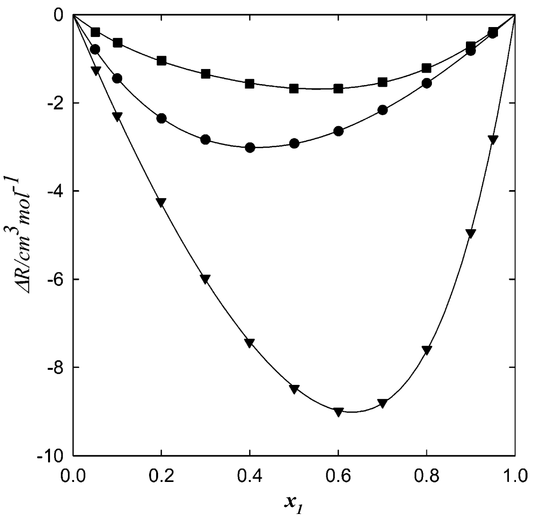

**Figure 4.** $\Delta R$ ($\mathrm{cm^3 \cdot mol^{-1}}$) for the three binary systems at 293.15 K: ●, PVE (1) + ethanol (2); ▼, ethanol (1) + 2,2,4-trimethylpentane (2); ■, PVE (1) + 2,2,4-trimethylpentane (2). Solid curves were calculated from the Redlich−Kister polynomial.

where $X$ and $X^c$ are the experimental and calculated mole fractions, respectively. The subscripts $i$, $j$, and $k$ denote component, phase, and tie-line, respectively. The correlated parameters are listed in Table 5, together with the root-mean-square deviation (RMSD) values between experimental and calculated data, defined as

$$\mathrm{RMSD} = \left[\frac{\sum_i \sum_j \sum_k (X_{ijk} - X_{ijk}^{c})^2}{6N}\right]^{1/2} \tag{2}$$

where $N$ is the number of tie-lines.

The ternary LLE of each system at 298.15 K are plotted in Figures 2 and 3. They were categorized as type 1, having only one pair of partially miscible components according to the classification of Treybal.[8] The dashed lines are calculated tie-lines. The experimental and calculated LLE data agreed relatively well as shown in the figures. Their root-mean-square deviations between calculated and measured values are less than 1 % for both systems. The slopes of the tie-lines presented in the figures show that methanol is more soluble in water than in PVE, whereas ethanol is more soluble in PVE than in water.

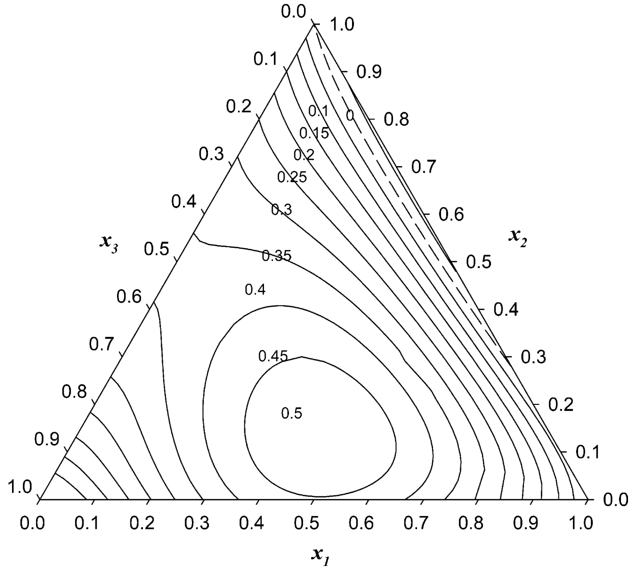

**Figure 5.** Lines of constant $V^E$ ($\mathrm{cm^3 \cdot mol^{-1}}$) for the ternary system of PVE (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at 293.15 K.

**Table 6. Refractive Indices and Deviations in Molar Refractivity for Binary Systems of PVE (1) + Ethanol (2), Ethanol (1) + 2,2,4-Trimethylpentane (2), and PVE (1) + 2,2,4-Trimethylpentane (2) at 293.15 K**

| $x_1$ | $n_D$ | $\Delta R$ / $\mathrm{cm^3 \cdot mol^{-1}}$ | $x_1$ | $n_D$ | $\Delta R$ / $\mathrm{cm^3 \cdot mol^{-1}}$ |
|---|---|---|---|---|---|
| | | PVE (1) + Ethanol (2) | | | |
| 0.0000 | 1.36161 | 0.0000 | 0.6005 | 1.38262 | −2.6417 |
| 0.0499 | 1.36372 | −0.7898 | 0.7005 | 1.38517 | −2.1625 |
| 0.1000 | 1.36550 | −1.4457 | 0.8002 | 1.38724 | −1.5547 |
| 0.2002 | 1.36949 | −2.3535 | 0.8997 | 1.38925 | −0.8200 |
| 0.2996 | 1.37356 | −2.8329 | 0.9492 | 1.39010 | −0.4260 |
| 0.4004 | 1.37689 | −3.0175 | 1.0000 | 1.39094 | 0.0000 |
| 0.5006 | 1.38018 | −2.9217 | | | |
| | | Ethanol (1) + 2,2,4-Trimethylpentane (2) | | | |
| 0.0000 | 1.39267 | 0.0000 | 0.6006 | 1.37947 | −8.9893 |
| 0.0520 | 1.39087 | −1.2536 | 0.7002 | 1.37613 | −8.7939 |
| 0.1002 | 1.38995 | −2.2982 | 0.8006 | 1.37214 | −7.5893 |
| 0.1990 | 1.38855 | −4.2400 | 0.8998 | 1.36728 | −4.9435 |
| 0.2992 | 1.38682 | −5.9790 | 0.9503 | 1.36436 | −2.8189 |
| 0.3991 | 1.38458 | −7.4283 | 1.0000 | 1.36161 | 0.0000 |
| 0.5005 | 1.38228 | −8.4756 | | | |
| | | PVE (1) + 2,2,4-Trimethylpentane (2) | | | |
| 0.0000 | 1.39267 | 0.0000 | 0.6003 | 1.38967 | −1.6794 |
| 0.0503 | 1.39117 | −0.3984 | 0.7004 | 1.38964 | −1.5303 |
| 0.1011 | 1.39096 | −0.6366 | 0.7998 | 1.38978 | −1.2127 |
| 0.2002 | 1.39064 | −1.0431 | 0.9002 | 1.39013 | −0.7206 |
| 0.3002 | 1.39044 | −1.3395 | 0.9503 | 1.39035 | −0.3901 |
| 0.3995 | 1.39004 | −1.5678 | 1.0000 | 1.39094 | 0.0000 |
| 0.4998 | 1.38988 | −1.6774 | | | |

***Excess Molar Volumes and Deviations in Molar Refractivity.*** The measured refractive indices and $\Delta R$ at 293.15 K for the binary systems of PVE + ethanol, ethanol + 2,2,4-trimethylpentane, and PVE + 2,2,4-trimethylpentane are presented in Table 6. $\Delta R$ was calculated from the molar refractivity ($R_m$) of each of the pure and mixture components, which

**Table 7. Densities, Excess Molar Volumes, Refractive Indices, and Deviations in Molar Refractivity for the Ternary System of PVE (1) + Ethanol (2) + 2,2,4-Trimethylpentane (3) at 293.15 K**

| $x_1$ | $x_2$ | $\rho$ / g·cm$^{-3}$ | $V^E$ / cm$^3$·mol$^{-1}$ | $n_D$ | $\Delta R$ / cm$^3$·mol$^{-1}$ | $x_1$ | $x_2$ | $\rho$ / g·cm$^{-3}$ | $V^E$ / cm$^3$·mol$^{-1}$ | $n_D$ | $\Delta R$ / cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.0604 | 0.5402 | 0.72411 | 0.3410 | 1.38073 | −8.3622 | 0.3503 | 0.4992 | 0.75283 | 0.2419 | 1.38037 | −5.4121 |
| 0.0500 | 0.4506 | 0.71598 | 0.3555 | 1.38313 | −7.8549 | 0.2804 | 0.5998 | 0.75797 | 0.1797 | 1.37774 | −5.4323 |
| 0.0405 | 0.3594 | 0.70937 | 0.3291 | 1.38533 | −6.8669 | 0.2102 | 0.6998 | 0.76386 | 0.1210 | 1.37493 | −5.0422 |
| 0.0303 | 0.2690 | 0.70367 | 0.3186 | 1.38721 | −5.5204 | 0.0700 | 0.9001 | 0.77923 | 0.0274 | 1.36673 | −2.5440 |
| 0.0200 | 0.1798 | 0.69918 | 0.2314 | 1.38907 | −3.9129 | 0.5400 | 0.4003 | 0.76490 | 0.1168 | 1.38287 | −3.5428 |
| 0.1198 | 0.2797 | 0.71026 | 0.3840 | 1.38648 | −5.7151 | 0.4494 | 0.5007 | 0.76778 | 0.0754 | 1.38043 | −3.8319 |
| 0.0895 | 0.2090 | 0.70454 | 0.3326 | 1.38784 | −4.6111 | 0.3601 | 0.5995 | 0.77093 | 0.0431 | 1.37718 | −3.9023 |
| 0.0287 | 0.0710 | 0.69551 | 0.1594 | 1.39038 | −1.7978 | 0.2698 | 0.7004 | 0.77472 | 0.0170 | 1.37426 | −3.6003 |
| 0.2997 | 0.3000 | 0.72584 | 0.4447 | 1.38511 | −5.5763 | 0.1799 | 0.7999 | 0.77894 | −0.0089 | 1.36987 | −2.9939 |
| 0.2502 | 0.2497 | 0.71855 | 0.3535 | 1.38646 | −5.2130 | 0.4001 | 0.0609 | 0.71714 | 0.4750 | 1.38947 | −2.5053 |
| 0.2003 | 0.1995 | 0.71108 | 0.4536 | 1.38756 | −4.5312 | 0.4976 | 0.0548 | 0.72385 | 0.5057 | 1.38920 | −2.4239 |
| 0.1001 | 0.1004 | 0.70058 | 0.2294 | 1.38944 | −2.6855 | 0.6000 | 0.0394 | 0.73114 | 0.4633 | 1.38935 | −2.1199 |
| 0.3497 | 0.1489 | 0.71910 | 0.4451 | 1.38793 | −3.7956 | 0.6996 | 0.0309 | 0.73922 | 0.4216 | 1.38937 | −1.7981 |
| 0.2813 | 0.1181 | 0.71258 | 0.3733 | 1.38865 | −3.3531 | 0.8002 | 0.0201 | 0.74809 | 0.3239 | 1.38964 | −1.3329 |
| 0.2109 | 0.0881 | 0.70611 | 0.4022 | 1.38933 | −2.7146 | 0.4006 | 0.1789 | 0.72481 | 0.5171 | 1.38732 | −4.0607 |
| 0.0703 | 0.0302 | 0.69674 | 0.0502 | 1.39087 | −1.1445 | 0.5002 | 0.1502 | 0.73114 | 0.4997 | 1.38765 | −3.5041 |
| 0.3604 | 0.0390 | 0.71329 | 0.4350 | 1.39002 | −2.1143 | 0.5986 | 0.1218 | 0.73773 | 0.4650 | 1.38799 | −2.9143 |
| 0.2697 | 0.0307 | 0.70736 | 0.3346 | 1.39015 | −1.8252 | 0.6988 | 0.0911 | 0.74484 | 0.3788 | 1.38851 | −2.2616 |
| 0.1809 | 0.0186 | 0.70160 | 0.2786 | 1.39051 | −1.3207 | 0.9012 | 0.0293 | 0.76023 | 0.1738 | 1.38989 | −0.7924 |
| 0.0400 | 0.6004 | 0.72759 | 0.3320 | 1.37913 | −8.6384 | 0.3996 | 0.3012 | 0.73516 | 0.4485 | 1.38478 | −5.0807 |
| 0.0306 | 0.7000 | 0.73738 | 0.2933 | 1.37591 | −8.3630 | 0.4983 | 0.2517 | 0.74039 | 0.4204 | 1.38563 | −4.2410 |
| 0.0194 | 0.8008 | 0.74983 | 0.2332 | 1.37204 | −7.1651 | 0.5991 | 0.2012 | 0.74587 | 0.3696 | 1.38658 | −3.3855 |
| 0.1508 | 0.4996 | 0.72930 | 0.3697 | 1.38124 | −7.5495 | 0.6990 | 0.1508 | 0.75137 | 0.3042 | 1.38760 | −2.5367 |
| 0.1197 | 0.6005 | 0.73658 | 0.3074 | 1.37850 | −7.7949 | 0.7987 | 0.1016 | 0.75701 | 0.2339 | 1.38867 | −1.6893 |
| 0.0907 | 0.6994 | 0.74529 | 0.2618 | 1.37545 | −7.4169 | 0.5001 | 0.3491 | 0.75209 | 0.2677 | 1.38349 | −4.3575 |
| 0.0300 | 0.8999 | 0.77040 | 0.1112 | 1.36707 | −3.9614 | 0.5988 | 0.2814 | 0.75556 | 0.2482 | 1.38502 | −3.4768 |
| 0.3000 | 0.4001 | 0.73488 | 0.3983 | 1.38298 | −6.1420 | 0.6998 | 0.2101 | 0.75882 | 0.2175 | 1.38661 | −2.5857 |
| 0.2505 | 0.4995 | 0.74019 | 0.3384 | 1.38065 | −6.6302 | 0.9012 | 0.0694 | 0.76534 | 0.1168 | 1.38956 | −0.8333 |
| 0.1995 | 0.6005 | 0.74663 | 0.2581 | 1.37829 | −6.7225 | 0.5996 | 0.3601 | 0.76715 | 0.1016 | 1.38347 | −3.0635 |
| 0.1504 | 0.6995 | 0.75405 | 0.2048 | 1.37528 | −6.3115 | 0.7004 | 0.2695 | 0.76754 | 0.0864 | 1.38596 | −2.3576 |
| 0.1002 | 0.7998 | 0.76323 | 0.1417 | 1.37153 | −5.2422 | 0.8006 | 0.1797 | 0.76793 | 0.0734 | 1.38789 | −1.6091 |
| 0.4198 | 0.4003 | 0.74863 | 0.2938 | 1.38276 | −5.0569 | | | | | | |

**Table 8. Fitted Parameters for the Redlich−Kister or Cibulka Equation and Standard Deviations for $V^E$ and $\Delta R$ for the Ternary System of PVE (1) + Ethanol (2) + 2,2,4-Trimethylpentane (3) at 293.15 K**

| | systems | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma_{st}$ |
|---|---|---|---|---|---|---|
| $V^E$ | (1) + (2)[a] | −0.2293 | 0.2955 | 0.2867 | 0.4039 | 0.0047 |
| | (2) + (3)[a] | 1.4189 | −0.0438 | 0.5030 | −0.0705 | 0.0089 |
| | (1) + (3)[a] | 1.7823 | 0.0868 | −0.2594 | 0.4413 | 0.0117 |
| | (1) + (2) + (3) | −1.5592 | 9.5513 | 3.2210 | − | 0.0245 |
| $\Delta R$ | (1) + (2) | −11.7156 | 3.8805 | −1.3303 | 0.7014 | 0.0059 |
| | (2) + (3) | −33.7749 | −16.0861 | −9.7012 | −3.5944 | 0.0359 |
| | (1) + (3) | −6.6776 | −1.3414 | −1.2861 | 1.3165 | 0.0210 |
| | (1) + (2) + (3) | 3.6831 | −2.0423 | 7.3894 | − | 0.0318 |

[a] Parameters taken from ref 9.

are derived directly from the measured densities, taken from our previous data,[9] and refractive indices using eqs 3 to 6.[10,11]

$$\Delta R/\text{cm}^3\cdot\text{mol}^{-1} = R_m - \sum_i \phi_i R_i \tag{3}$$

$$R_m = \left(\frac{n_D^{\,2} - 1}{n_D^{\,2} + 1}\right)\left(\frac{\sum_i x_i M_i}{\rho_m}\right) \tag{4}$$

$$R_i = \left(\frac{n_{D,i}^{\,2} - 1}{n_{D,i}^{\,2} + 1}\right)\left(\frac{M_i}{\rho_i}\right) \tag{5}$$

and

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j} \tag{6}$$

where $\phi_i$, $n_D$, $n_{D,i}$, and $V_i$ are the volume fraction of the pure components in the mixture, the refractive index of the mixture, and the refractive index and molar volume of the pure component, respectively.

The calculated binary $\Delta R$ at 293.15 K is plotted in Figure 4. $\Delta R$ values of all the binary systems reveal negative values. The magnitude of negativity of the system follows the order: ethanol + 2,2,4-trimethylpentane > PVE + ethanol > PVE + 2,2,4-trimethylpentane. $\Delta R$ data were correlated with the Redlich−Kister polynomial eq 7.[12] The solid lines in Figure 4 indicate calculated values using correlated parameters.

$$\Delta R/\text{cm}^3\cdot\text{mol}^{-1} = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{7}$$

The standard deviation of the fits, $\sigma_{st}$, is defined as

$$\sigma_{st}/\text{cm}^3\cdot\text{mol}^{-1} = \left[\frac{\sum_i ((V^E \text{ or } \Delta R)_{calcd} - (V^E \text{ or } \Delta R)_{exptl})_i^{\,2}}{(N - n)}\right]^{1/2} \tag{8}$$

where $N$ is the number of experimental data points and $n$ is the number of fitted parameters.

The standard mean deviation of each system according to the comparison between measured and calculated values is (0.0059, 0.0359, and 0.210) cm$^3$·mol$^{-1}$ for PVE + ethanol, ethanol + 2,2,4-trimethylpentane, and PVE + 2,2,4-trimethylpentane, respectively.

The $V^E$ and $\Delta R$ for the ternary system of PVE + ethanol + 2,2,4-trimethylpentane at 293.15 K were derived from measured ternary densities and refractive indices. The densities, $V^E$, refractive indices, and $\Delta R$ for the ternary system are furnished in Table 7.

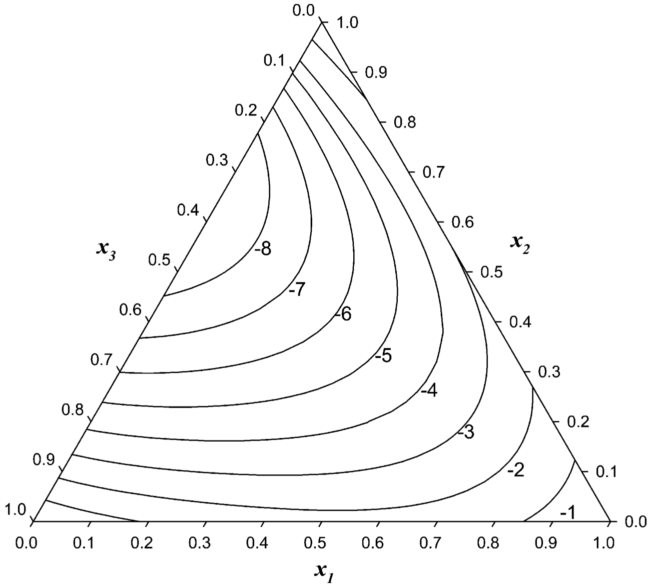

**Figure 6.** Lines of constant $\Delta R$ ($\text{cm}^3\cdot\text{mol}^{-1}$) for the ternary system of PVE (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at 293.15 K.

In the case of the ternary system, $V^E$ and $\Delta R$ were correlated with the Cibulka equation.[13]

$$V^E_{123} = V^E_{12} + V^E_{23} + V^E_{13} + x_1x_2x_3(A_1 + A_2x_1 + A_3x_2) \qquad (9)$$

where $V^E_{12}$, $V^E_{23}$, and $V^E_{13}$represent the excess molar volumes and $x_1$, $x_2$, and $x_3$ are ternary mole fractions.

The correlated values are in good agreement with the experimental data. The correlation results by the Cibulka equation for the ternary $V^E$ and $\Delta R$ are represented as isoclines in Figures 5 and 6, respectively. The adjusted parameters of the Redlich−Kister equation for binary $\Delta R$ and of the Cibulka equation for the ternary $V^E$ and $\Delta R$ are given in Table 8 along with standard deviations between calculated and experimental data. The standard deviations of the ternary system were 0.0245 for $V^E$ and 0.0318 for $\Delta R$, respectively. The ternary data of $V^E$ show positive values for almost all the compositions except a small region of the PVE + ethanol system and $\Delta R$ at 293.15 K which show negative values for all the composition ranges.

## Conclusion

The LLE for the binary system of PVE + water at the temperature range from (288.15 to 323.15) K and also for the ternary systems of PVE + methanol or ethanol + water at 298.15 K were measured by an analytical method. The PVE + water system was supposed to have an upper critical solution temperature and correlated well with the NRTL equation. The ternary LLE data have only one partially miscible system and correlated well with the NRTL equation. Their root-mean-square deviations for the binary and ternary systems between calculated and measured values are less than 1 %. Additionally, the $\Delta R$ data for each of the three binary systems of PVE (1) + ethanol (2) + 2,2,4-trimethylpentane (3) show negative deviation from ideality. These binary data correlated well with the Redlich−Kister equation. The $V^E$ and $\Delta R$ for the ternary system of PVE (1) + ethanol (2) + 2,2,4-trimethylpentane (3) were correlated with the Cibulka equation. The standard deviations were 0.0245 for $V^E$ and 0.0318 for $\Delta R$ and show positive and negative values, respectively, for all the composition ranges.

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