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# Isothermal Binary and Ternary VLE for the Mixtures of Propyl Vinyl Ether + Ethanol + Isooctane at 323.15 K and $V^E$ at 293.15 K

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Isothermal vapor−liquid equilibrium (VLE) data at 323.15 K are reported for the binary systems of propyl vinyl ether (PVE) + ethanol, ethanol + isooctane, and PVE + isooctane and also for ternary system of PVE + ethanol + isooctane by using headspace gas chromatography. For the computation of VLE, vapor pressure of PVE was determined and fitted to the Antoine equation. The experimental binary and ternary VLE data were correlated with different $G^E$ models. Additionally the new excess volume data are reported for the same binary systems at 293.15 K and correlated with the Redlich−Kister polynomial. Ternary $V^E$ data are also calculated with correlated parameters by the Radojkovič equation.

## Introduction

Recently, alkyl vinyl ethers are increasingly produced as industrial solvents and chemical intermediates in the chemical or pharmaceutical industry. However their reasonable volatility caused significant emission into the urban atmosphere. Consequently, they will be oxidized by OH and $NO_3$ radicals. For the synthesis and separation of these compounds, reliable data of the physical properties and phase equilibrium behavior are required. However, relatively few investigations were reported for alkyl vinyl ether compounds, and there are no data for propyl vinyl ether (PVE) as far as we know.[1]

We have studied the phase equilibria and mixture properties systematically for several ether compounds because the accurate data of such properties are strongly related to the processing of their compounds and application of group contribution method. We reported previously phase equilibria and excess properties for various binary and ternary systems involving MTBE (methyl *tert*-butyl ether), ETBE (ethyl *tert*-butyl ether), TAME (*tert*-amyl methyl ether), DME (dimethyl ether), and DBE (dibutyl ether).[2−7]

In this work, the isothermal VLE data are reported at 323.15 K for the binary systems of PVE + ethanol, PVE + isooctane, and ethanol + isooctane and for the ternary system of PVE + ethanol + isooctane by using headspace gas chromatography (HSGC). We report also vapor pressures for PVE and regressed Antoine constants. While the experimental binary VLE data were correlated using Margules, van Laar, Wilson, NRTL, and UNIQUAC equations, the ternary VLE data were correlated with Wilson and NRTL models. The excess molar volumes ($V^E$) for the same binary systems were also calculated with directly measured density. The $V^E$ data were correlated with the Redlich−Kister polynomial. Isoclines of $V^E$ for the ternary system were also calculated by using the Radojkovič equation.

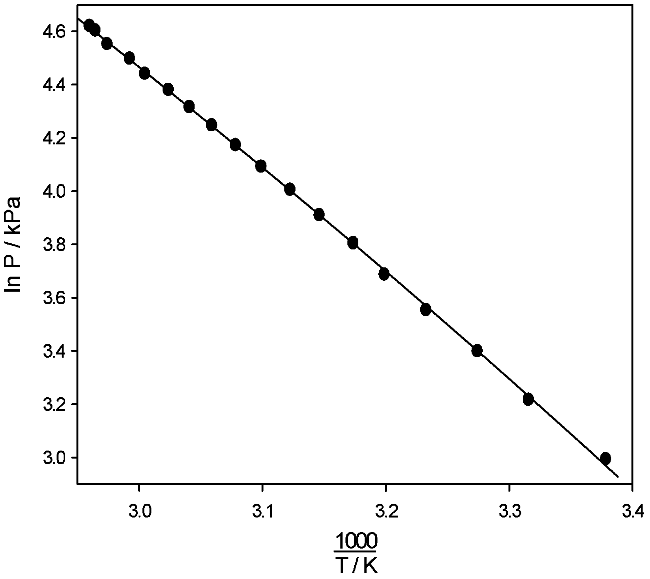

**Figure 1.** Experimental vapor pressure data vs temperature for PVE. ●, experimental data. Solid line calculated from Antoine equation.

**Table 1. Experimental Vapor Pressure vs Temperature Data and Coefficients in Vapor Pressure Correlation for PVE**

| $P^{sat}$/kPa | $\Delta P$ | $T$/K | $P^{sat}$/kPa | $\Delta P$ | $T$/K |
|---|---|---|---|---|---|
| Antoine Coefficients $A = 11.8597$, $B = 1640.5297$, $C = -111.4676$ | | | | | |
| 20.00 | 0.3 | 296.02 | 65.00 | 0.3 | 324.90 |
| 25.00 | −0.4 | 301.62 | 70.00 | 0.3 | 326.95 |
| 30.00 | 0.0 | 305.44 | 75.00 | 0.3 | 328.89 |
| 35.00 | −0.4 | 309.37 | 80.00 | 0.3 | 330.76 |
| 40.00 | −0.5 | 312.65 | 85.00 | −0.7 | 332.86 |
| 45.00 | 0.3 | 315.13 | 90.00 | 0.2 | 334.22 |
| 50.00 | 0.3 | 317.88 | 95.00 | −1.3 | 336.28 |
| 55.00 | 0.5 | 320.29 | 100.00 | 0.2 | 337.38 |
| 60.00 | 0.3 | 322.72 | 101.70 | 0.1 | 337.90 |

## Experimental Section

***Materials.*** The chemicals of analytical commercial grade of purity were used in this work. Before the measurement, all the chemicals were dried using molecular sieves with a pore diameter of 0.4 nm. The purity of the chemicals was checked by gas chromatography and by comparing the density with reported values in the literatures. By gas chromatographic analysis, the impurity of each chemical was found to be less than 0.02 %. The measured densities of PVE, ethanol, and isooctane at 293.15 K were (0.76897, 0.78938, and 0.69205)

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**Table 2. Isothermal VLE for Binary Systems of PVE (1) + Ethanol (2), PVE (1) + Isooctane (2), and Ethanol (1) + Isooctane (2) at 323.15 K**

| $P_{\mathrm{cal}}$/kPa | $x_1$ | $y_1$ | $P_{\mathrm{cal}}$/kPa | $x_1$ | $y_1$ | $P_{\mathrm{cal}}$/kPa | $x_1$ | $y_1$ |
|---|---|---|---|---|---|---|---|---|
| PVE (1) + Ethanol (2) | | | PVE (1) + Isooctane (2) | | | Ethanol (1) + Isooctane (2) | | |
| 34.81 | 0.0201 | 0.1681 | 20.89 | 0.0199 | 0.0839 | 22.69 | 0.0045 | 0.1432 |
| 38.64 | 0.0398 | 0.2625 | 22.14 | 0.0393 | 0.1522 | 25.51 | 0.0097 | 0.2414 |
| 40.33 | 0.0592 | 0.2997 | 23.42 | 0.0596 | 0.2147 | 30.01 | 0.0210 | 0.3604 |
| 43.85 | 0.0797 | 0.3702 | 24.32 | 0.0783 | 0.2555 | 34.12 | 0.0601 | 0.4435 |
| 49.03 | 0.1193 | 0.4554 | 26.40 | 0.1184 | 0.3413 | 35.12 | 0.0808 | 0.4624 |
| 53.51 | 0.1688 | 0.5189 | 29.17 | 0.1698 | 0.4373 | 36.50 | 0.1197 | 0.4878 |
| 57.23 | 0.2290 | 0.5670 | 32.15 | 0.2289 | 0.5231 | 37.56 | 0.1701 | 0.5081 |
| 60.53 | 0.2898 | 0.6081 | 34.97 | 0.2881 | 0.5922 | 38.70 | 0.2303 | 0.5313 |
| 61.86 | 0.3490 | 0.6253 | 37.65 | 0.3494 | 0.6495 | 39.36 | 0.2903 | 0.5463 |
| 63.41 | 0.4086 | 0.6476 | 40.20 | 0.4090 | 0.6984 | 39.84 | 0.3501 | 0.5592 |
| 64.30 | 0.4686 | 0.6621 | 42.58 | 0.4684 | 0.7397 | 40.16 | 0.4114 | 0.5699 |
| 65.39 | 0.5294 | 0.6837 | 44.82 | 0.5287 | 0.7759 | 40.33 | 0.4699 | 0.5775 |
| 66.46 | 0.5894 | 0.7087 | 46.88 | 0.5886 | 0.8076 | 40.48 | 0.5305 | 0.5891 |
| 67.19 | 0.6512 | 0.7311 | 48.85 | 0.6492 | 0.8373 | 40.57 | 0.5907 | 0.6028 |
| 67.75 | 0.7088 | 0.7562 | 50.93 | 0.7091 | 0.8676 | 40.54 | 0.6504 | 0.6155 |
| 68.03 | 0.7700 | 0.7799 | 52.93 | 0.7679 | 0.8956 | 40.37 | 0.7109 | 0.6329 |
| 67.93 | 0.8287 | 0.8009 | 54.76 | 0.8303 | 0.9216 | 40.12 | 0.7700 | 0.6467 |
| 67.43 | 0.8778 | 0.8297 | 56.46 | 0.8783 | 0.9458 | 39.54 | 0.8302 | 0.6699 |
| 66.70 | 0.9195 | 0.8549 | 58.01 | 0.9205 | 0.9656 | 38.56 | 0.8806 | 0.7007 |
| 65.86 | 0.9416 | 0.8772 | 58.55 | 0.9401 | 0.9728 | 36.83 | 0.9201 | 0.7532 |
| 64.61 | 0.9601 | 0.9087 | 59.28 | 0.9599 | 0.9826 | 35.89 | 0.9406 | 0.7816 |
| 63.34 | 0.9784 | 0.9397 | 59.96 | 0.9795 | 0.9912 | 34.28 | 0.9602 | 0.8309 |
| | | | | | | 32.30 | 0.9802 | 0.8964 |

g·cm$^{-3}$, respectively. The literature values of ethanol and isooctane are (0.78930 and 0.69192) g·cm$^{-3}$.[8,9] The density of PVE is not available in the literature.[1]

***Apparatus and Procedure.*** For the measurement of the vapor pressure, Sieg and Roeck type recirculating glass still was used. Details on this apparatus were described previously.[10] The HSGC was used for the measurement of isothermal VLE data for all the binary and ternary systems. The HSGC consists of a gas chromatograph (HP 6890N) and a headspace sampler (HP19395A), in which the precision thermostat having an accuracy of ± 0.1 K is equipped. The HP-5 (5 % diphenyl/95 % dimethylsiloxane, 30 m × 0.32 mm × 0.25 $\mu$m) capillary column and a thermal conductivity detector were used for the analysis. The uncertainty of the measured equilibrium mole fraction is about ± 1 × 10$^{-4}$. The procedure of measurement has been described in detail elsewhere.[2] The excess volume was calculated directly from measured pure and mixture density using the Anton-Paar model 5000 vibrating-tube digital density meter. The accuracy of this density meter is ± 5 × 10$^{-6}$ g·cm$^{-3}$. The measuring procedure can be found elsewhere.[11]

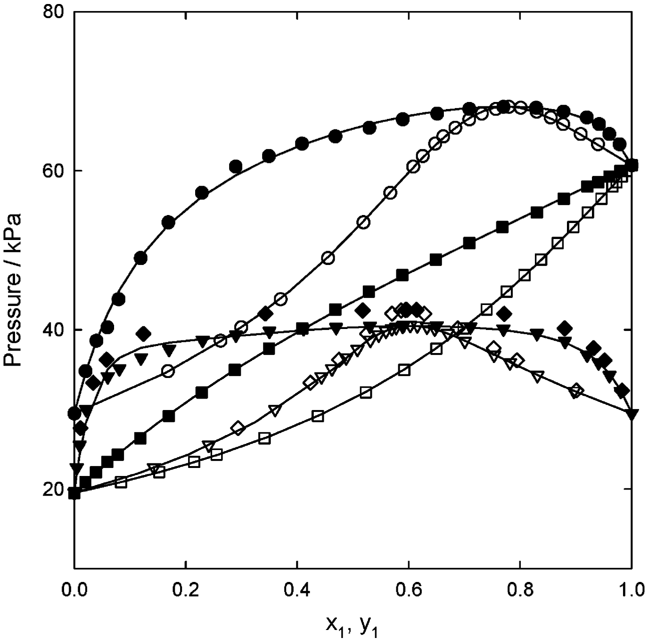

**Figure 2.** VLE for the three binary systems of PVE, ethanol, and isooctane at 323.15 K. Filled symbols, liquid phase; open symbols, vapor phase; ●, PVE (1) + ethanol (2); ■, PVE (1) + isooctane (2); ◆, ethanol (1) + isooctane (2) by Kretschmer et al.;[12] ▼, ethanol (1) + isooctane(2). Solid curves were calculated from NRTL equation.

**Table 3. $G^{\mathrm{E}}$ Model Parameters and Mean Deviation between the Calculated and Experimental Vapor-Phase Mole Fraction ($\Delta y_1$) for the Binary Systems at 323.15 K**

| model equation | $A_{12}$ | $A_{21}$ | α | $\Delta y_1$ |
|---|---|---|---|---|
| PVE (1) + Ethanol (2) | | | | |
| Margules | 1.3965 | 1.5987 | | 0.0132 |
| van Laar | 1.3930 | 1.6162 | | 0.0129 |
| Wilson | 77.87164 | 1182.4323 | | 0.0096 |
| NRTL | 907.1678 | 722.0531 | 0.7135 | 0.0062 |
| PVE (1) + Isooctane (2) | | | | |
| Margules | 0.3418 | 0.3235 | | 0.0024 |
| van Laar | 0.3419 | 0.3237 | | 0.0024 |
| Wilson | 396.7821 | −172.5167 | | 0.0024 |
| NRTL | 51.9412 | 168.8991 | 0.3000 | 0.0024 |
| Ethanol (1) + Isooctane (2) | | | | |
| Margules | 2.3152 | 1.9037 | | 0.0373 |
| van Laar | 2.3655 | 1.8959 | | 0.0364 |
| Wilson | 2053.7658 | 148.9483 | | 0.0163 |
| NRTL | 1080.7518 | 1499.3400 | 0.5322 | 0.0107 |
| UNIQUAC | −203.8005 | 1129.6486 | | 0.0350 |

## Results and Discussion

***Vapor Pressure.*** The measured vapor pressure of PVE was correlated using Antoine equation, which is expressed by

$$\ln P^{\mathrm{sat}}/\mathrm{kPa} = A - \frac{B}{C + T/\mathrm{K}} \qquad (1)$$

Table 1 presents the measured vapor pressure and boiling temperature of PVE with prediction results using the Antoine equation. Figure 1 shows the measured vapor pressure and the predicted one. As shown in the Figure 1, the vapor pressure was correlated relatively well with the Antoine equation. The correlation linearity ($r^2$) with fitted Antoine constants for PVE was found to be 0.9996.

**Table 4. Isothermal VLE for the Ternary System of PVE (1) + Ethanol (2) + Isooctane (3) at 323.15 K**

| $P_{cal}$/kPa | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $P_{cal}$/kPa | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $P_{cal}$/kPa | $x_1$ | $x_2$ | $y_1$ | $y_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 44.16 | 0.0606 | 0.5391 | 0.1258 | 0.5411 | 43.04 | 0.0413 | 0.5990 | 0.0982 | 0.5597 | 59.59 | 0.4337 | 0.0668 | 0.5039 | 0.2586 |
| 43.12 | 0.0497 | 0.4503 | 0.0972 | 0.5435 | 42.25 | 0.0301 | 0.7001 | 0.0850 | 0.5827 | 61.07 | 0.4983 | 0.0502 | 0.5923 | 0.2099 |
| 42.20 | 0.0413 | 0.3597 | 0.0780 | 0.5423 | 49.71 | 0.1504 | 0.4994 | 0.2561 | 0.4783 | 63.67 | 0.5994 | 0.0402 | 0.6705 | 0.1596 |
| 41.09 | 0.0298 | 0.2704 | 0.0524 | 0.5129 | 48.33 | 0.1198 | 0.5998 | 0.2284 | 0.5100 | 64.88 | 0.6994 | 0.0301 | 0.7552 | 0.1122 |
| 39.84 | 0.0198 | 0.1800 | 0.0362 | 0.5091 | 46.52 | 0.0892 | 0.7006 | 0.2023 | 0.5476 | 64.48 | 0.8003 | 0.0189 | 0.8389 | 0.0696 |
| 50.94 | 0.1801 | 0.4194 | 0.2793 | 0.4518 | 39.85 | 0.0308 | 0.8993 | 0.1297 | 0.6800 | 60.65 | 0.3986 | 0.1816 | 0.4726 | 0.3190 |
| 46.51 | 0.1209 | 0.2801 | 0.1968 | 0.4744 | 57.91 | 0.3009 | 0.3990 | 0.4131 | 0.3939 | 64.73 | 0.5005 | 0.1485 | 0.5510 | 0.2769 |
| 44.30 | 0.0900 | 0.2118 | 0.1463 | 0.4685 | 55.97 | 0.2493 | 0.5012 | 0.3829 | 0.4262 | 67.75 | 0.5989 | 0.1216 | 0.6219 | 0.2413 |
| 36.73 | 0.0302 | 0.0707 | 0.0566 | 0.4434 | 53.73 | 0.1999 | 0.6001 | 0.3561 | 0.4571 | 69.30 | 0.6978 | 0.0921 | 0.6948 | 0.2018 |
| 56.75 | 0.2997 | 0.3002 | 0.3969 | 0.3757 | 50.97 | 0.1505 | 0.6997 | 0.3182 | 0.5034 | 62.04 | 0.3993 | 0.3004 | 0.4819 | 0.3488 |
| 53.59 | 0.2497 | 0.2498 | 0.3404 | 0.3895 | 47.21 | 0.0996 | 0.8006 | 0.2744 | 0.5583 | 66.13 | 0.4985 | 0.2514 | 0.5520 | 0.3111 |
| 50.45 | 0.1990 | 0.1998 | 0.2837 | 0.4024 | 64.67 | 0.4197 | 0.4005 | 0.5288 | 0.3498 | 69.31 | 0.5984 | 0.2022 | 0.6215 | 0.2732 |
| 47.13 | 0.1485 | 0.1518 | 0.2319 | 0.4363 | 62.27 | 0.3507 | 0.5016 | 0.4947 | 0.3865 | 71.07 | 0.7007 | 0.1497 | 0.6880 | 0.2338 |
| 43.04 | 0.1005 | 0.1015 | 0.1641 | 0.4201 | 59.07 | 0.2795 | 0.6005 | 0.4669 | 0.4196 | 70.76 | 0.7993 | 0.1012 | 0.7586 | 0.1897 |
| 57.99 | 0.3503 | 0.1502 | 0.4329 | 0.3244 | 55.26 | 0.2095 | 0.7003 | 0.4321 | 0.4578 | 67.99 | 0.4994 | 0.3512 | 0.5780 | 0.3283 |
| 53.88 | 0.2798 | 0.1183 | 0.3712 | 0.3438 | 43.13 | 0.0693 | 0.9010 | 0.2749 | 0.6411 | 71.07 | 0.6004 | 0.2795 | 0.6398 | 0.2891 |
| 49.09 | 0.2092 | 0.0913 | 0.3032 | 0.3568 | 71.04 | 0.5392 | 0.4004 | 0.6382 | 0.3197 | 72.74 | 0.6986 | 0.2115 | 0.6945 | 0.2551 |
| 33.86 | 0.0703 | 0.0310 | 0.1404 | 0.3352 | 68.19 | 0.4498 | 0.5003 | 0.6163 | 0.3435 | 68.75 | 0.8986 | 0.0706 | 0.8258 | 0.1600 |
| 53.17 | 0.3601 | 0.0401 | 0.4941 | 0.2327 | 64.40 | 0.3603 | 0.6002 | 0.5673 | 0.3933 | 73.00 | 0.5983 | 0.3620 | 0.6679 | 0.3052 |
| 45.84 | 0.2703 | 0.0281 | 0.4269 | 0.2274 | 59.60 | 0.2700 | 0.6999 | 0.5235 | 0.4378 | 74.53 | 0.7003 | 0.2699 | 0.7146 | 0.2685 |
| 38.51 | 0.1829 | 0.0202 | 0.3388 | 0.2280 | 53.50 | 0.1794 | 0.8005 | 0.4571 | 0.5069 | 73.86 | 0.7990 | 0.1807 | 0.7565 | 0.2326 |

***Isothermal VLE.*** According to our HSGC measurement of VLE, the equilibrium pressure cannot be measured but calculated from experimental vapor-phase mole compositions and thermodynamic equations.[2] The true liquid mole compositions can be calculated from vapor-phase equilibrium composition with mass balance. The experimental VLE compositions and calculated pressures for the binary systems of PVE (1) + ethanol (2), PVE (1) + isooctane (2), and ethanol (1) + isooctane (2) at 323.15 K are listed and plotted in Table 2 and Figure 2.

**Table 5. Fitted $G^E$ Model Parameters and Standard Deviations for the Ternary System of PVE (1) + Ethanol (2) + Isooctane (3) at 323.15 K**

| $G^E$ model | $A_{ij}$ | $A_{ji}$ | α | Δ$y$ |
|---|---|---|---|---|
| | | Wilson | | |
| 1 + 2 | −48.8374 | 1259.2615 | | 0.0145 |
| 2 + 3 | 2179.6625 | 281.7181 | | |
| 1 + 3 | 178.7169 | −61.4718 | | |
| | | NRTL | | |
| 1 + 2 | 1530.4911 | −647.8497 | 0.0226 | 0.0121 |
| 2 + 3 | 1374.1801 | 1551.9482 | 0.5379 | |
| 1 + 3 | −56.0864 | 160.4998 | 0.3000 | |

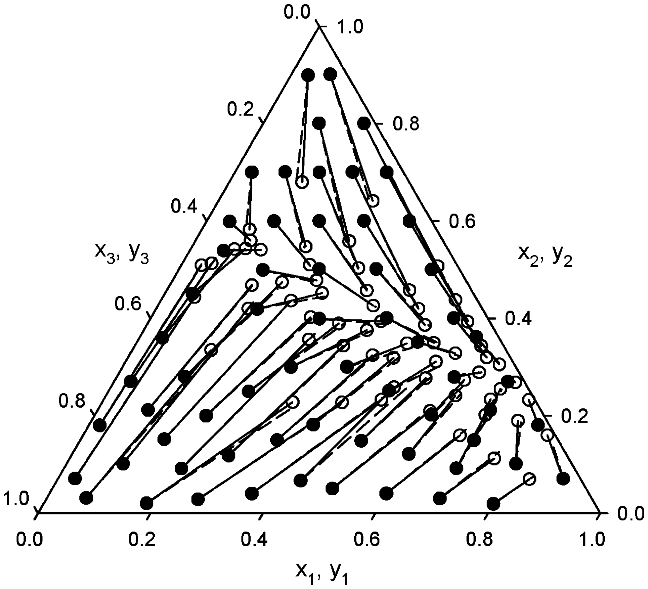

**Figure 3.** VLE for the ternary system of PVE (1) + ethanol (2) + isooctane (3) at 323.15 K. ●, liquid phase; ○, vapor phase. Dashed lines were calculated from the NRTL equation.

There is no azeotrope in the binary VLE for the PVE + isooctane system, while a minimum boiling azeotrope was observed in the PVE + ethanol and ethanol + isooctane systems as in the many cases observed for ether and alcohol mixtures. The azeotropic point determined by interpolation for the PVE + ethanol system is $x_1 = 0.785$ and $P = 68.00$ kPa, and for the ethanol + isooctane system it is $x_1 = 0.606$ and $P = 40.56$ kPa, respectively. The measured binary VLE for ethanol + isooctane was compared with the reference data[12] as shown in Figure 2. The experimental binary VLE data were correlated with Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. The adjustable binary parameters are listed in Table 3 along with the mean deviations between experimental and calculated data. The mean deviation of vapor-phase mole fraction ($\Delta y_1$) was calculated from

$$\Delta y_1 = \frac{|\Delta y_{1,\mathrm{exp}} - \Delta y_{1,\mathrm{cal}}|}{N} \tag{2}$$

where $N$ is the number of experimental data points. The binary parameters ($A_{ij}$) for calculation of ln $\gamma$(activity coefficient) of Wilson, NRTL, and UNIQUAC models means

$$A_{ij} = (\lambda_{ij} - \lambda_{ii})/\mathrm{J{\cdot}mol^{-1}} \quad \text{(Wilson)}$$

$$A_{ij} = (g_{ij} - g_{ii})/\mathrm{J{\cdot}mol^{-1}} \quad \text{(NRTL)}$$

$$A_{ij} = (u_{ij} - u_{ii})/\mathrm{J{\cdot}mol^{-1}} \quad \text{(UNIQUAC)}$$

The ternary VLE data of the PVE (1) + ethanol (2) + isooctane (3) system at 323.15 K are listed in Table 4 and illustrated in Figure 3. The ternary VLE data were correlated with the Wilson and NRTL models. Among them, the NRTL model provided the best correlation result. Dashed lines in Figure 3 represent the calculated values by NRTL equation. We compared the calculated data using binary parameters with ternary correlation data. The mean deviation of comparing the results was $\Delta y = 0.0247$. Each $G^E$ model parameter and the mean deviation of vapor-phase mole fraction ($\Delta y_{\mathrm{mean}}$) are given in the Table 5. $\Delta y_{\mathrm{mean}}$ can be determined by following eqution:

$$\Delta y_{\mathrm{mean}} = \frac{\Delta y_1 + \Delta y_2 + \Delta y_3}{3} \tag{3}$$

**Table 6. Densities and Excess Molar Volumes for the Binary Systems of PVE (1) + Ethanol (2), Ethanol (1) + Isooctane (2), and PVE (1) + Isooctane (2) at 293.15 K**

| $x_1$ | $\rho$/(g·cm$^{-3}$) | $V^E$/(cm$^3$·mol$^{-1}$) | $x_1$ | $\rho$/(g·cm$^{-3}$) | $V^E$/(cm$^3$·mol$^{-1}$) |
|---|---|---|---|---|---|
| | | PVE (1) + Ethanol (2) | | | |
| 0.0499 | 0.78789 | −0.0302 | 0.6005 | 0.77444 | −0.0401 |
| 0.1000 | 0.78634 | −0.0467 | 0.7005 | 0.77261 | −0.0087 |
| 0.2002 | 0.78337 | −0.0591 | 0.8002 | 0.77101 | 0.0207 |
| 0.2996 | 0.78078 | −0.0649 | 0.8997 | 0.76967 | 0.0346 |
| 0.4004 | 0.77849 | −0.0692 | 0.9492 | 0.76918 | 0.0246 |
| 0.5006 | 0.77639 | −0.0612 | | | |
| | | Ethanol (1) + Isooctane (2) | | | |
| 0.0520 | 0.69345 | 0.1058 | 0.6006 | 0.72337 | 0.3453 |
| 0.1002 | 0.69499 | 0.1671 | 0.7002 | 0.73360 | 0.3056 |
| 0.1990 | 0.69869 | 0.2525 | 0.8006 | 0.74691 | 0.2396 |
| 0.2992 | 0.70317 | 0.3129 | 0.8998 | 0.76431 | 0.1595 |
| 0.3991 | 0.70852 | 0.3541 | 0.9503 | 0.77579 | 0.0863 |
| 0.5005 | 0.71522 | 0.3594 | | | |
| | | PVE (1) + Isooctane (2) | | | |
| 0.0503 | 0.69447 | 0.0591 | 0.6003 | 0.72849 | 0.4220 |
| 0.1011 | 0.69692 | 0.1323 | 0.7004 | 0.73699 | 0.3703 |
| 0.2002 | 0.70216 | 0.2286 | 0.7998 | 0.74625 | 0.3081 |
| 0.3002 | 0.70768 | 0.3546 | 0.9002 | 0.75695 | 0.1655 |
| 0.3995 | 0.71380 | 0.4282 | 0.9503 | 0.76256 | 0.1123 |
| 0.4998 | 0.72072 | 0.4507 | | | |

***Excess Molar Volumes.*** The excess molar volumes ($V^E$) for the mixtures were calculated from the measured densities of pure substances and mixtures by using

$$V^E = \frac{\sum_i x_i M_i}{\rho_m} - \sum_i \left(\frac{x_i M_i}{\rho_i}\right) \qquad (4)$$

where $x_i$, $M_i$, $\rho_i$, and $\rho_m$ are the mole fraction, molar mass, pure component density, and mixture density, respectively. The measured binary $V^E$ data were correlated with the Redlich−Kister polynomial of[13]

$$V^E_{12}/\mathrm{cm^3{\cdot}mol^{-1}} = x_1 x_2 \sum_{i=1}^{4} A_i (x_1 - x_2)^{i-1} \qquad (5)$$

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

$$\sigma_{st}/\mathrm{cm^3{\cdot}mol^{-1}} = \left[\frac{\sum_i ((V^E)_{cal} - (V^E)_{exp})_i^2}{(N - n)}\right]^{1/2} \qquad (6)$$

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

The experimental densities and excess molar volumes ($V^E$) for the binary systems of PVE (1) + ethanol (2), PVE (1) + isooctane (2), and ethanol (1) + isooctane (2) at 293.15 K are listed in Table 6 and depicted in Figure 4. $V^E$ of PVE + ethanol at 293.15 K shows negative deviation in the ethanol rich region according to strong polarity of ethanol, while it shows positive deviation in the PVE-rich region. The systems of PVE + isooctane and ethanol + isooctane show positive deviations. The positive deviation may be attributed due to the hydrogen bond rupture and dispersive interactions between dislike molecules, while the negative deviation due to the intermolecular dipolar interactions and geometrical fitting as mentioned by Chen and Tu.[14] This dependence of positive and negative deviation is therefore caused by the magnitude of positive and negative reason. The binary $V^E$ data were correlated with the Redlich−Kister polynomial, and the calculated values (solid line) with each correlated parameters are in good agreement with experimental values as shown in Figure 4. The adjusted parameters of Redlich−Kister are given in Table 7 along with standard deviations between calculated and experimental data. Besides the isoclines of $V^E$ was calculated using Radojkovič equation[15] and plotted in Figure 5. As shown in the figure, the ternary system shows positive values of $V^E$ at almost all the composition range, except at some compositions close to those of the system PVE + ethanol.

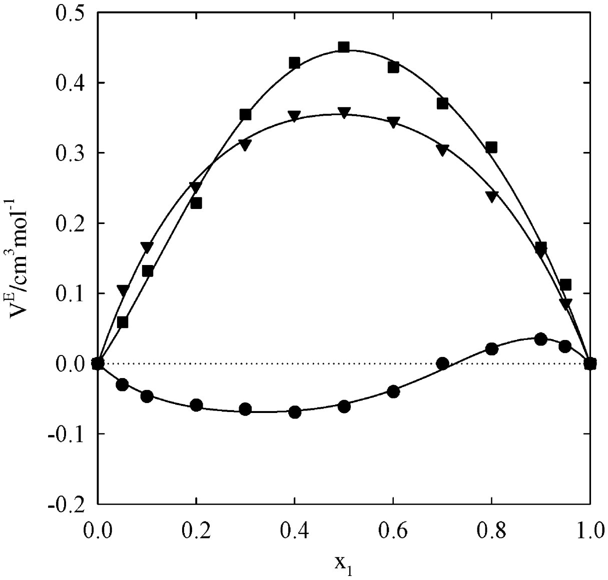

**Figure 4.** $V^E$ for three binary systems of PVE, ethanol, and isooctane mixture at 293.15 K: ●, PVE (1) + ethanol (2); ■, PVE (1) + isooctane (2); ▼, ethanol (1) + isooctane (2). Solid curves were calculated from the Redlich−Kister polynomial.

**Table 7. Fitted Parameters for the Redlich−Kister Equation and Standard Deviations for $V^E$ of PVE (1), Ethanol (2), and Isooctane (3) at 293.15 K**

| system | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma_{st}$ |
|---|---|---|---|---|---|
| (1) + (2) | −0.2293 | 0.2955 | 0.2867 | 0.4039 | 0.0047 |
| (2) + (3) | 1.4189 | −0.0438 | 0.5030 | −0.0705 | 0.0089 |
| (1) + (3) | 1.7823 | 0.0868 | −0.2594 | 0.4413 | 0.0117 |

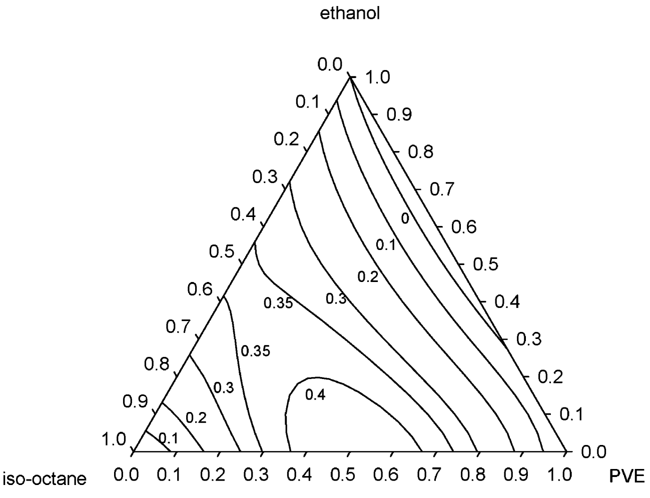

**Figure 5.** Constant line of $V^E$ at 293.15 K for the ternary system of PVE + ethanol + isooctane, calculated by the Radojkovič equation.

## Conclusions

New vapor pressures for the PVE were determined and fitted to the Antoine equation. The linearity of correlations result was 0.9996. Isothermal vapor−liquid equilibrium (VLE) data at 323.15 K were experimentally determined for the binary and ternary systems of PVE, ethanol, and iso-octane. The binary VLE of PVE + ethanol and ethanol + isooctane showed minimum boiling azeotrope. The binary and ternary data were correlated with some $G^E$ models, and the NRTL model provided the best result. Among the measured binary $V^E$ at 293.15 K, PVE + ethanol system showed negative and positive deviation from the ideality according to the content of ethanol. The other two binary systems have positive deviations, and, the isoclines were calculated using the Radojkovič equation. They show positive values of $V^E$ at almost all the compositions.

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