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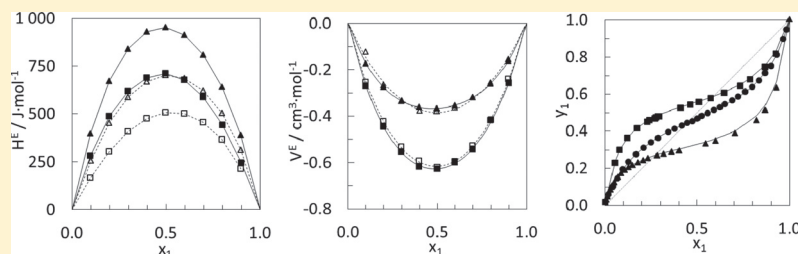
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Vapor–Liquid Equilibrium, Excess Molar Enthalpies, and Excess Molar Volumes of Binary Mixtures Containing 2-Ethoxy-2-methylpropane or 2-Ethoxy-2-methylbutane and Acetonitrile or Propanenitrile

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ABSTRACT: Vapor–liquid equilibrium (VLE), excess molar enthalpies (H^E), and excess molar volumes (V^E) provide complementary data for thermodynamic models. In this work, new data of binary mixtures of acetonitrile (ACN) or propanenitrile (PPN) with 2-ethoxy-2-methylpropane (ETBE) or 2-ethoxy-2-methylbutane (TAEE) are reported. Isothermal VLE data were measured by using a circulation still at 333 K for ETBE + ACN, at 343 K for TAEE + ACN, and at 363 K for TAEE + PPN. H^E were measured by using a SETARAM C80 calorimeter equipped with a flow mixing cell at 298 K for all four binary systems. V^E were measured by using an Anton Paar DMA 512P densimeter at 298 K for all four binary systems. H^E data and measured VLE data, or literature VLE data for the binary system of ETBE and PPN, were used for the optimization of Wilson model parameters by using VLEFIT software. Redlich–Kister equation parameters were separately regressed for the V^E data.

INTRODUCTION

C_4 and C_5 cuts from fluid catalytic cracking (FCC) units are used in the preparation of fuel oxygenates such as 2-ethoxy-2-methylpropane so-called *tert*-butyl ethyl ether (ETBE) and 2-ethoxy-2-methylbutane so-called *tert*-amyl ethyl ether (TAEE). However, this feedstock typically contains nitriles such as acetonitrile (ACN) and propanenitrile (PPN) which poison the etherification catalyst.¹ The nitriles together with metal cations cause neutralization of the acidic sites of the ion-exchange resin catalyst.¹ Experimental thermodynamic data are needed for the development of exact process models. If the components, such as nitriles and ethers, form azeotropic mixtures, accurate modeling of the phase equilibrium is crucial since one of the components may accumulate in the process.

The combined use of excess molar enthalpies (H^E) and vapor–liquid equilibrium (VLE) data in thermodynamic modeling makes the model more reliable and permits extrapolation outside the conditions of the measurements as shown in our previous work.²

The thermodynamic properties of the binary mixtures of these ethers and nitriles are scarcely studied. Only for the binary system of ETBE + PPN isothermal VLE data have been published at 312.85 K and at 358.32 K and isobaric data at 102.6 kPa and at 65.2 kPa.³ For the binary systems of ETBE + ACN, TAEE + ACN, and TAEE + PPN no data are reported in open literature.

MATERIALS

The purities, water contents, densities, and sources of the used chemicals are listed in Table 1. The purity of the chemicals was checked by gas chromatography. ETBE was obtained from Neste Oil Oyj and purified by extraction with distilled water and by distillation. TAEE was synthesized by using a micro plant developed in our laboratory⁴ and further purified by extraction with water. TAEE was dried by adding a molecular sieve (pore size 3 Å) prior to final purification by distillation. ACN was purchased from Merck and purified by distillation. ACN was dried by adding a molecular sieve (pore size 3 Å) to the chemical. PPN was purchased from Fluka and used without further purification. The water content of the chemicals was determined using the Karl Fischer titrator (Mettler-Toledo DL38) applying one-component reagents (Hydrapoint Solvent G and Titrant 2 mgH₂O·cm⁻³) technique. The pure component densities were measured by using the DMA512P density measuring cell (Anton Paar) thermostatted with a Lauda E200 water immersion

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Table 1. Purity, Water Content, and Density ρ at Temperature T , and Source of Pure Liquid Components^a

| initial purity | purification method | final purity | water content | ρ_{exp} | ρ_{lit} | T | source |
|----------------|---|---------------|---------------|---------------------|---------------------|-------|-----------------------------|
| | | mole fraction | wt % | kg·dm ⁻³ | kg·dm ⁻³ | K | |
| ETBE | extraction with distilled water, distillation | 0.9960 | 0.004 | 0.735 | 0.736 | 298.4 | Neste Oil Oyj |
| TAAE | distillation, drying over molecular sieves | 0.9986 | 0.026 | 0.761 | 0.761 | 298.4 | own production ⁴ |
| ACN | 0.998 distillation, drying over molecular sieves | 0.9989 | 0.010 | 0.776 | 0.776 | 298.4 | Merck |
| PPN | 0.999 none | | 0.026 | 0.776 | 0.777 | 298.4 | Fluka |

^a ρ_{exp} is the measured density, kg·dm⁻³; ρ_{lit} is the density from DIPPR⁵, kg·dm⁻³; T is the temperature at which the density was measured, K.

thermostat. The literature⁵ values of densities for the pure chemicals are shown for comparison in Table 1.

EQUIPMENT

Excess Molar Enthalpy. Excess molar enthalpies were measured at 298.15 K with a SETARAM C80 calorimeter equipped with a flow mixing cell.⁶ The temperature accuracy of the calorimeter was 0.1 K. The flows of the chemicals into the calorimeter were controlled by syringe pumps ISCO 260D and ISCO 500D of which the accuracies of the flow rates were 0.5 % of the set point. The calorimeter was calibrated by using two well-known recommended chemical reference systems: cyclohexane–hexane and methanol–water.⁷ The calibration procedure indicated for this type of equipment^{7,8} was utilized. The cyclohexane–hexane binary system was used to determine the sensitivity of the calorimeter and methanol–water binary system was used to check the accuracy of the calibration. The average accuracy of the calorimeter was found to be 2.6 %.

Excess Molar Volume. Densities of the binary mixtures were measured with the DMA 512 P vibrating tube densimeter that was located at the outflow of the calorimeter unit. The uncertainty of the densimeter was ± 0.00016 kg·dm⁻³. The densimeter temperature was controlled with a Lauda E200 water immersion thermostat. Temperature of the vibrating tube block was measured with a Thermolyzer S2541 temperature meter equipped with a Pt-100 probe calibrated at the Finnish National Standards Laboratory. The calibration uncertainty was ± 0.015 K, and the uncertainty of temperature was estimated to be ± 0.02 K. The densimeter was calibrated based on deionized and degassed water⁹ and dry air¹⁰ reference systems. The measured pure component densities corresponded well to the literature data as can be seen from Table 1.

Vapor–Liquid Equilibrium. The vapor–liquid equilibrium (VLE) was measured using a circulation still of Yerazunis-type¹¹ with minor modifications to the original design.^{12,13} The liquid volume needed for running the apparatus was approximately 80 cm³. Pressure was measured with a pressure transducer PMP 4070 (Druck) connected to Red Lion panel meter with accuracy of 0.04 kPa. The pressure meter was compared against the Beamex MC2-PE field calibrator calibrated at the Finnish National Standards Laboratory. The uncertainty of the whole pressure measurements system including the calibration uncertainty was less than ± 0.17 kPa. The temperature meter was a F200 precision thermometer (Automatic Systems Laboratories ASL) with an uncertainty of ± 0.02 K calibrated at Finnish National Standards Laboratory at calibration uncertainty of 0.015 K. The uncertainty of the whole temperature measurement system was less than ± 0.05 K.

An Agilent 6850 gas chromatograph with a flame ionization detector (FID) was used for VLE composition analysis.

Table 2. The Physical Properties⁵ and Parameters^{15,16} Used in the Hayden–O’Connell Correlation with Chemical Theory^a

| | ETBE | TAAE | ACN | PPN |
|--|---------|----------|----------|----------|
| RGYR/10 ⁻¹⁰ m | 3.79 | 4.07 | 1.82 | 2.65 |
| DMOM/D | 1.20 | 1.10 | 3.93 | 4.02 |
| Association η_{ii} and Solvation Parameters η_{ij} | | | | |
| ACN | 1.65 | 1.65 | 1.00 | 1.00 |
| PPN | 1.65 | 1.65 | 1.00 | 1.00 |
| ETBE | 1.00 | 1.00 | 0.00 | 0.00 |
| TAAE | 1.00 | 1.00 | 0.00 | 0.00 |
| Critical Properties | | | | |
| ω | 0.29567 | 0.338192 | 0.337886 | 0.324267 |
| Z_c | 0.273 | 0.273 | 0.184 | 0.204 |
| P_c /kPa | 2934 | 2740 | 4830 | 4180 |
| T_c /K | 509.4 | 544 | 545.5 | 561.3 |
| V_c /m ³ ·kmol ⁻¹ | 0.382 | 0.435 | 0.173 | 0.225 |

^aRGYR is the radius of gyration, 10⁻¹⁰ m; DMOM is the dipole moment, D; η_{ii} are the association parameters (located in the diagonal of the table); η_{ij} are the solvation parameters.

EXPERIMENTAL PROCEDURE

Excess Molar Enthalpy. The feed pumps were let to equilibrate to the feed temperature for 60 min prior to starting the experiments. The total flow rate to the calorimeter was kept at 0.5 cm³·min⁻¹ by varying the flow rates of the feed pumps as recommended.^{6,8} The calorimeter signal stabilized in approximately 20 min, after which at least 10 min was waited prior to recording the values of the experimental point.

Excess Molar Volume. Since the densimeter was located after the calorimeter unit, it also provided information whether the mixing in the calorimeter flow mixing cell was complete. The thermostat of the densimeter was activated one hour prior to the measurements to guarantee the temperature in demand. The densimeter signal was let to stabilize (30 to 45) min in which the calorimeter signal stabilized even though it took only approximately 10 min to get a stabilized mixed flow from the densimeter.

Vapor–Liquid Equilibrium. The procedure is described in detail in our previous work.¹³ Pure component 1 was introduced in the circulation still, and its vapor pressure was measured. Then, component 2 was introduced into the cell, and it took approximately 30 min to achieve a constant temperature. The temperature was held constant for (30 to 45) min before sampling. After the pressure was measured, the vapor and liquid samples were simultaneously withdrawn with a 1 cm³ Hamilton Sample Lock syringe. Approximately 0.5 cm³ of the syringe volume was used for a sample into a GC vial.

Gas Chromatography. Compositions of liquid and condensed vapor phases of the circulation still measurements were determined by gas chromatography. Liquid samples of 1 mm³

Table 3. Excess Molar Enthalpy H^E , Excess Molar Volume V^E , and Density ρ at 298 K and at 0.1 MPa of Binary Systems of (ETBE or TAAE) + (ACN or PPN)^a

| x_1 | H^E | ρ | V^E | T |
|-----------------|---------------------|---------------------|------------------------------------|---------------|
| | J·mol ⁻¹ | kg·dm ⁻³ | cm ³ ·mol ⁻¹ | K |
| | | ETBE (1) + ACN (2) | | |
| 0.0996 ± 0.0054 | 281.3 ± 3.6 | 0.7701 ± 0.0002 | -0.26968 ± 0.04433 | 298.41 ± 0.02 |
| 0.1989 ± 0.0058 | 485.2 ± 6.3 | 0.7645 ± 0.0002 | -0.44366 ± 0.04247 | 298.41 ± 0.02 |
| 0.2993 ± 0.0053 | 617.6 ± 8.0 | 0.7595 ± 0.0002 | -0.55358 ± 0.03679 | 298.41 ± 0.02 |
| 0.3982 ± 0.0045 | 689.2 ± 8.9 | 0.7551 ± 0.0002 | -0.61690 ± 0.03197 | 298.41 ± 0.02 |
| 0.4984 ± 0.0037 | 709.8 ± 9.2 | 0.7510 ± 0.0002 | -0.62670 ± 0.02841 | 298.42 ± 0.02 |
| 0.5994 ± 0.0029 | 677.3 ± 8.7 | 0.7473 ± 0.0001 | -0.59983 ± 0.02627 | 298.42 ± 0.02 |
| 0.6994 ± 0.0021 | 588.1 ± 7.6 | 0.7441 ± 0.0001 | -0.54220 ± 0.02534 | 298.42 ± 0.02 |
| 0.8010 ± 0.0014 | 441.8 ± 5.7 | 0.7408 ± 0.0001 | -0.41679 ± 0.02525 | 298.42 ± 0.02 |
| 0.9009 ± 0.0007 | 243.4 ± 3.1 | 0.7378 ± 0.0001 | -0.25728 ± 0.02612 | 298.42 ± 0.02 |
| | | ETBE (1) + PPN (2) | | |
| 0.0991 ± 0.0029 | 166.5 ± 2.1 | 0.7712 ± 0.0002 | -0.25417 ± 0.03319 | 298.43 ± 0.02 |
| 0.1986 ± 0.0038 | 305.0 ± 3.9 | 0.7663 ± 0.0002 | -0.42273 ± 0.03629 | 298.44 ± 0.02 |
| 0.2986 ± 0.0038 | 407.8 ± 5.3 | 0.7617 ± 0.0002 | -0.53250 ± 0.03449 | 298.43 ± 0.02 |
| 0.3984 ± 0.0035 | 474.0 ± 6.1 | 0.7572 ± 0.0002 | -0.59138 ± 0.03168 | 298.43 ± 0.02 |
| 0.4986 ± 0.0030 | 505.3 ± 6.5 | 0.7532 ± 0.0002 | -0.62098 ± 0.0291 | 298.43 ± 0.02 |
| 0.5986 ± 0.0024 | 498.8 ± 6.4 | 0.7492 ± 0.0001 | -0.59438 ± 0.02724 | 298.43 ± 0.02 |
| 0.6982 ± 0.0018 | 455.7 ± 5.9 | 0.7455 ± 0.0001 | -0.52685 ± 0.02616 | 298.43 ± 0.02 |
| 0.7978 ± 0.0012 | 366.7 ± 4.7 | 0.7419 ± 0.0001 | -0.41840 ± 0.02592 | 298.44 ± 0.02 |
| 0.8990 ± 0.0006 | 215.0 ± 2.8 | 0.7383 ± 0.0001 | -0.24022 ± 0.02645 | 298.43 ± 0.02 |
| | | TAAE (1) + ACN (2) | | |
| 0.0990 ± 0.0067 | 397.6 ± 5.1 | 0.7745 ± 0.0002 | -0.17416 ± 0.02887 | 298.40 ± 0.02 |
| 0.1996 ± 0.0067 | 670.5 ± 8.6 | 0.7726 ± 0.0002 | -0.27630 ± 0.02834 | 298.40 ± 0.02 |
| 0.2996 ± 0.0058 | 839.7 ± 10.8 | 0.7707 ± 0.0002 | -0.33253 ± 0.02633 | 298.40 ± 0.02 |
| 0.3985 ± 0.0049 | 928.6 ± 12.0 | 0.769. ± 0.0002 | -0.36066 ± 0.02520 | 298.41 ± 0.02 |
| 0.4976 ± 0.004 | 951.4 ± 12.3 | 0.7675 ± 0.0002 | -0.36865 ± 0.02468 | 298.41 ± 0.02 |
| 0.5980 ± 0.0031 | 911.9 ± 11.8 | 0.7661 ± 0.0002 | -0.35419 ± 0.02491 | 298.41 ± 0.02 |
| 0.6974 ± 0.0023 | 809.5 ± 10.4 | 0.7648 ± 0.0002 | -0.31990 ± 0.02570 | 298.41 ± 0.02 |
| 0.7984 ± 0.0015 | 641.1 ± 8.3 | 0.7635 ± 0.0002 | -0.25797 ± 0.02691 | 298.40 ± 0.02 |
| 0.8971 ± 0.0007 | 386.7 ± 5.0 | 0.7623 ± 0.0002 | -0.16232 ± 0.02849 | 298.40 ± 0.02 |
| | | TAAE (1) + PPN (2) | | |
| 0.1000 ± 0.0039 | 257.3 ± 3.3 | 0.7743 ± 0.0002 | -0.12333 ± 0.02503 | 298.40 ± 0.02 |
| 0.1991 ± 0.0046 | 451.0 ± 5.8 | 0.7731 ± 0.0002 | -0.26602 ± 0.02728 | 298.40 ± 0.02 |
| 0.2988 ± 0.0045 | 586.3 ± 7.6 | 0.7715 ± 0.0002 | -0.33601 ± 0.02719 | 298.39 ± 0.02 |
| 0.3991 ± 0.004 | 668.4 ± 8.6 | 0.7699 ± 0.0002 | -0.37737 ± 0.02665 | 298.40 ± 0.02 |
| 0.4975 ± 0.0033 | 702.3 ± 9.1 | 0.7683 ± 0.0002 | -0.38008 ± 0.02626 | 298.39 ± 0.02 |
| 0.5990 ± 0.0027 | 686.6 ± 8.9 | 0.7667 ± 0.0002 | -0.36329 ± 0.02634 | 298.39 ± 0.02 |
| 0.6987 ± 0.0020 | 621.5 ± 8.0 | 0.7653 ± 0.0002 | -0.31972 ± 0.02676 | 298.40 ± 0.02 |
| 0.7991 ± 0.0013 | 502.0 ± 6.5 | 0.7638 ± 0.0002 | -0.25722 ± 0.02765 | 298.40 ± 0.02 |
| 0.8976 ± 0.0007 | 312.3 ± 4.0 | 0.7624 ± 0.0002 | -0.15504 ± 0.02889 | 298.41 ± 0.02 |

^a x_1 is the mole fraction of the ether; H^E is the excess molar enthalpy at 298 K, J·mol⁻¹; ρ is the density, kg·dm⁻³; V^E is the excess molar volume, cm³·mol⁻¹; T is the temperature at which the excess volumes have been measured, K.

were injected into GC. Prior to GC analysis, the condensed vapor and liquid phase samples of the circulation still equipment were diluted with (0.7 to 0.6) cm³ of toluene. Agilent GC 2 cm³ glass vials with aluminum grimp caps with PTFE/red rubber septa were used.

The following settings were used for the GC analysis for all measurements related to the circulation still apparatus. The front inlet temperature was set to 523 K and the pressure to 171.5 kPa over pressure; the split ratio was 50:1. The separation capillary column was a HP-1, (methyl siloxane: length 60 m, inner diameter 250 μ m, film thickness 1 μ m). Helium was the carrier gas, and its flow rate in the GC column was 22 cm³·s⁻¹. The GC oven temperature was programmed to increase after 14 min of isothermal operation at 381 K at a rate of 50 K·min⁻¹ to the final temperature of 463 K, which was kept for 0.5 min. The FID

temperature was set at 523 K, hydrogen flow was set to 40 cm³·min⁻¹, and air flow was set to 450 cm³·min⁻¹.

MODELING

The VLEFIT software¹⁴ was used to obtain the model parameters. The Hayden–O'Connell (HOC) method was used for the modeling of the vapor phase fugacity coefficients.^{15,16} For ethers and nitriles, the association parameters η_{ii} and solvation parameters η_{ij} were directly available only for ACN and diethylether. Therefore, the ACN parameter values were used for PPN, and the diethylether parameter values were used for ETBE and TAAE based on the chemical similarity.¹⁶ The modeling parameters and critical properties of the components are presented in Table 2.

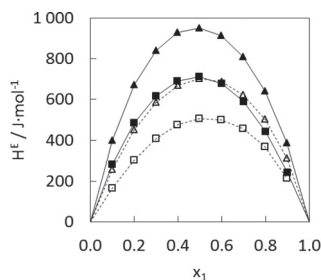


Figure 1. Excess molar enthalpies H^E at 298 K of binary systems of ■, ETBE (1) and ACN (2); □, ETBE (1) + PPN (2); ▲, TAE (1) + ACN (2); and △, TAE (1) + PPN (2); —, comparison with the model presented in this work for the binary systems with ACN; - - -, comparison with the model presented in this work for the binary systems with PPN.

Table 4. Parameters A_i of the Redlich–Kister Equation for the Excess Molar Volume V^E ^a

| | A_0 | A_1 | A_2 | S |
|--------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| | $\text{cm}^3 \cdot \text{mol}^{-1}$ | $\text{cm}^3 \cdot \text{mol}^{-1}$ | $\text{cm}^3 \cdot \text{mol}^{-1}$ | $\text{cm}^3 \cdot \text{mol}^{-1}$ |
| ETBE (1) + ACN (2) | -2.507 | 0.112 | -0.611 | 0.004 |
| ETBE (1) + PPN (2) | -2.461 | 0.059 | -0.436 | 0.004 |
| TAE (1) + ACN (2) | -1.465 | 0.098 | -0.578 | 0.002 |
| TAE (1) + PPN (2) | -1.538 | 0.023 | -0.130 | 0.010 |

^a A_0 to A_4 are the Redlich–Kister equation parameters for excess molar volume V^E , $\text{cm}^3 \cdot \text{mol}^{-1}$; S is the standard deviation $S = (1/N \sum_{i=1}^N (V_{\text{experiments}}^E - V_{\text{Redlich-Kister}}^E)^2)^{1/2}$, $\text{cm}^3 \cdot \text{mol}^{-1}$; N is the number of experiments.

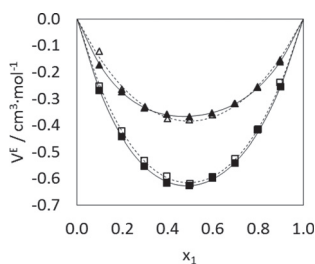


Figure 2. Excess molar volumes V^E at 298 K of binary systems of ■, ETBE (1) and ACN (2); □, ETBE (1) + PPN (2); ▲, TAE (1) + ACN (2); and △, TAE (1) + PPN (2); —, comparison with the model presented in this work for the binary systems with ACN; - - -, comparison with the model presented in this work with the binary systems for PPN.

The liquid activity coefficients were regressed by using the Wilson model¹⁷ where the temperature dependence was given by the polynomials 1 and 2

$$\lambda_{12} - \lambda_{11} = a_{0,12} + a_{1,12}T + a_{2,12}T^2 \quad (1)$$

$$\lambda_{21} - \lambda_{22} = a_{0,21} + a_{1,21}T + a_{2,21}T^2 \quad (2)$$

where λ_{ij} are the Wilson model parameters (K), $a_{0,ij}$ (K), $a_{1,ij}$ and $a_{2,ij}$ (K^{-1}) are the binary interaction parameters of the Wilson model, and T is the temperature (K).

Table 5. Vapor Pressures p at Temperature T of ETBE, TAE, ACN, and PPN^a

| ETBE | | acetonitrile | |
|---------------|----------------|---------------|----------------|
| T/K | p/kPa | T/K | p/kPa |
| 345.99 ± 0.05 | 101.42 ± 0.17 | 354.12 ± 0.05 | 99.40 ± 0.17 |
| 342.76 ± 0.05 | 91.51 ± 0.17 | 351.76 ± 0.05 | 92.16 ± 0.17 |
| 340.37 ± 0.05 | 84.63 ± 0.17 | 349.69 ± 0.05 | 86.34 ± 0.17 |
| 338.60 ± 0.05 | 79.89 ± 0.17 | 347.55 ± 0.05 | 80.49 ± 0.17 |
| 336.69 ± 0.05 | 74.94 ± 0.17 | 345.58 ± 0.05 | 75.40 ± 0.17 |
| 334.21 ± 0.05 | 68.91 ± 0.17 | 343.86 ± 0.05 | 71.24 ± 0.17 |
| 332.17 ± 0.05 | 64.24 ± 0.17 | 341.07 ± 0.05 | 64.81 ± 0.17 |
| 330.26 ± 0.05 | 60.07 ± 0.17 | 339.20 ± 0.05 | 60.76 ± 0.17 |
| 328.05 ± 0.05 | 55.57 ± 0.17 | 336.56 ± 0.05 | 55.46 ± 0.17 |
| 324.77 ± 0.05 | 49.34 ± 0.17 | 333.51 ± 0.05 | 49.76 ± 0.17 |
| 322.38 ± 0.05 | 45.18 ± 0.17 | 329.94 ± 0.05 | 43.71 ± 0.17 |
| 319.61 ± 0.05 | 40.71 ± 0.17 | 326.03 ± 0.05 | 37.80 ± 0.17 |
| 311.54 ± 0.05 | 29.66 ± 0.17 | 317.53 ± 0.05 | 27.19 ± 0.17 |
| | | 308.32 ± 0.05 | 18.59 ± 0.17 |

| TAE | | propanenitrile | |
|---------------|----------------|----------------|----------------|
| T/K | p/kPa | T/K | p/kPa |
| 373.71 ± 0.05 | 98.94 ± 0.17 | 371.23 ± 0.05 | 103.78 ± 0.17 |
| 368.16 ± 0.05 | 83.80 ± 0.17 | 368.88 ± 0.05 | 96.66 ± 0.17 |
| 367.36 ± 0.05 | 81.79 ± 0.17 | 367.21 ± 0.05 | 91.88 ± 0.17 |
| 366.44 ± 0.05 | 79.62 ± 0.17 | 364.69 ± 0.05 | 84.93 ± 0.17 |
| 364.42 ± 0.05 | 74.90 ± 0.17 | 363.02 ± 0.05 | 80.76 ± 0.17 |
| 362.13 ± 0.05 | 69.66 ± 0.17 | 360.86 ± 0.05 | 75.34 ± 0.17 |
| 359.96 ± 0.05 | 65.08 ± 0.17 | 358.53 ± 0.05 | 69.91 ± 0.17 |
| 357.39 ± 0.05 | 59.91 ± 0.17 | 356.17 ± 0.05 | 64.72 ± 0.17 |
| 355.12 ± 0.05 | 55.54 ± 0.17 | 353.63 ± 0.05 | 59.51 ± 0.17 |
| 351.71 ± 0.05 | 49.52 ± 0.17 | 351.26 ± 0.05 | 54.93 ± 0.17 |
| 349.21 ± 0.05 | 45.43 ± 0.17 | 349.02 ± 0.05 | 50.91 ± 0.17 |
| 345.82 ± 0.05 | 40.29 ± 0.17 | 346.17 ± 0.05 | 46.11 ± 0.17 |
| 343.83 ± 0.05 | 37.59 ± 0.17 | 340.70 ± 0.05 | 37.95 ± 0.17 |
| 331.83 ± 0.05 | 23.98 ± 0.17 | 332.31 ± 0.05 | 27.73 ± 0.17 |
| 324.31 ± 0.05 | 17.73 ± 0.17 | 325.79 ± 0.05 | 21.46 ± 0.17 |
| | | 322.25 ± 0.05 | 18.58 ± 0.17 |

^a T is the temperature, K; p is the pressure, kPa.

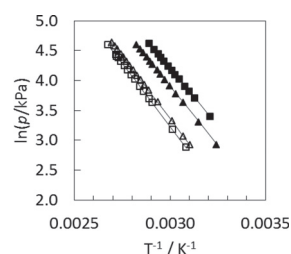


Figure 3. Vapor pressure of pure components: ■, ETBE; □, TAE; ▲, ACN; and △ PPN; —, DIPPR³ correlation.

The objective functions (OF) of the data regression were based on measured quantities

$$\text{OF}_{\text{circ}} = \sum_{i=1}^{NP} \left(\frac{(p_{\text{calc},i} - p_{\text{meas},i})}{p_{\text{meas},i}} \right)^2 \quad (3)$$

Table 6. Coefficients *A* to *C* for the Vapor Pressure Correlation and the Absolute Average Pressure Deviation $|\Delta p|$ from the Literature⁵ from Temperature T_{\min} to T_{\max} ^a

| this work | ETBE | TAEE | ACN | PPN |
|-------------------------|---------|---------|--------|--------|
| <i>A</i> | 7.4606 | 6.5986 | 8.9392 | 9.0194 |
| <i>B</i> | 3001.3 | 2720.0 | 3999.9 | 4200.0 |
| <i>C</i> | -38.104 | -68.498 | 1.605 | 1.143 |
| T_{\min}/K | 311.5 | 324.3 | 308.3 | 322.3 |
| T_{\max}/K | 346.0 | 373.7 | 354.1 | 371.2 |
| $ \Delta p /\text{kPa}$ | 0.75 | 0.44 | 0.42 | 0.42 |

^a*A*, *B*, and *C* are the parameters for eq 7 in this work, T_{\min} (K) is the minimum temperature for the vapor pressure correlation; T_{\max} is the maximum pressure for the vapor pressure correlation; $|\Delta p|$ (kPa) is the absolute average pressure deviation from the DIPPR⁵ reference.

Table 7. Measured *xyTp* Data for the Binary System of ETBE (1) + ACN (2)^a

| x_1 | y_1 | T/K | p/kPa |
|----------------|----------------|---------------|----------------|
| 1.0000 | 1.0000 | 332.26 ± 0.05 | 64.28 ± 0.17 |
| 0.9270 ± 0.001 | 0.8188 ± 0.001 | 333.12 ± 0.05 | 75.33 ± 0.17 |
| 0.8693 ± 0.001 | 0.7457 ± 0.001 | 333.14 ± 0.05 | 79.26 ± 0.17 |
| 0.7883 ± 0.001 | 0.6781 ± 0.001 | 333.04 ± 0.05 | 82.15 ± 0.17 |
| 0.7355 ± 0.001 | 0.6425 ± 0.001 | 333.05 ± 0.05 | 83.45 ± 0.17 |
| 0.6466 ± 0.001 | 0.6057 ± 0.001 | 333.03 ± 0.05 | 84.32 ± 0.17 |
| 0.5742 ± 0.001 | 0.5775 ± 0.001 | 333.08 ± 0.05 | 84.76 ± 0.17 |
| 0.5118 ± 0.001 | 0.5572 ± 0.001 | 333.07 ± 0.05 | 84.53 ± 0.17 |
| 0.4640 ± 0.001 | 0.5430 ± 0.001 | 333.09 ± 0.05 | 84.29 ± 0.17 |
| 0.4106 ± 0.001 | 0.5247 ± 0.001 | 333.07 ± 0.05 | 83.65 ± 0.17 |
| 0.2959 ± 0.001 | 0.4795 ± 0.001 | 333.08 ± 0.05 | 81.58 ± 0.17 |
| 0.2891 ± 0.001 | 0.4788 ± 0.001 | 333.06 ± 0.05 | 81.29 ± 0.17 |
| 0.2788 ± 0.001 | 0.4729 ± 0.001 | 333.09 ± 0.05 | 81.12 ± 0.17 |
| 0.2719 ± 0.001 | 0.4674 ± 0.001 | 333.04 ± 0.05 | 80.74 ± 0.17 |
| 0.2712 ± 0.001 | 0.4677 ± 0.001 | 333.06 ± 0.05 | 80.75 ± 0.17 |
| 0.2437 ± 0.001 | 0.4575 ± 0.001 | 333.14 ± 0.05 | 79.94 ± 0.17 |
| 0.2307 ± 0.001 | 0.4500 ± 0.001 | 333.12 ± 0.05 | 79.42 ± 0.17 |
| 0.1745 ± 0.001 | 0.4147 ± 0.001 | 333.07 ± 0.05 | 76.44 ± 0.17 |
| 0.1229 ± 0.001 | 0.3625 ± 0.001 | 333.01 ± 0.05 | 72.14 ± 0.17 |
| 0.0808 ± 0.001 | 0.2977 ± 0.001 | 333.05 ± 0.05 | 67.20 ± 0.17 |
| 0.0560 ± 0.001 | 0.2279 ± 0.001 | 333.07 ± 0.05 | 63.11 ± 0.17 |
| 0.0025 ± 0.001 | 0.0164 ± 0.001 | 333.08 ± 0.05 | 49.85 ± 0.17 |
| 0.0000 | 0.0000 | 333.57 ± 0.05 | 49.76 ± 0.17 |

^a x_1 is the ETBE liquid phase mole fraction; y_1 is the ETBE vapor phase mole fraction; T is the temperature, K; p is the pressure, kPa.

at bubble point pressure at x_{meas} and T_{meas}

$$\text{OF}_{\text{HE}} = \sum_{i=1}^{\text{NP}} \left(\frac{(H_{\text{calc},i}^{\text{E}} - H_{\text{meas},i}^{\text{E}})^2}{H_{\text{meas},i}^{\text{E}}} \right) \quad (4)$$

at x_{meas} and T_{meas} ; where p is the pressure (kPa), x is the liquid mole fraction, T is the temperature (K), and H^{E} is the excess molar enthalpy ($\text{J}\cdot\text{mol}^{-1}$).

RESULTS AND DISCUSSION

Excess Molar Enthalpy, Density, and Excess Molar Volume. Results of excess molar enthalpies, densities, and excess molar volumes for the mixtures of an ether (ETBE or TAEE) and a nitrile (ACN or PPN) are given in Table 3.

The experimental excess molar enthalpies H^{E} ($\text{J}\cdot\text{mol}^{-1}$) were regressed together with the measured VLE data by using the Wilson model¹⁷ for liquid phase activities and Hayden O'Connell

Table 8. Measured *xyTp* Data for the Binary System of TAEE (1) + ACN (2)^a

| x_1 | y_1 | T/K | p/kPa |
|----------------|----------------|---------------|----------------|
| 0.0000 | 0.0000 | 343.94 ± 0.05 | 71.24 ± 0.17 |
| 0.0092 ± 0.001 | 0.0299 ± 0.001 | 343.08 ± 0.05 | 71.13 ± 0.17 |
| 0.0154 ± 0.001 | 0.0477 ± 0.001 | 343.08 ± 0.05 | 72.27 ± 0.17 |
| 0.0221 ± 0.001 | 0.0648 ± 0.001 | 343.11 ± 0.05 | 73.32 ± 0.17 |
| 0.0290 ± 0.001 | 0.0806 ± 0.001 | 343.11 ± 0.05 | 74.34 ± 0.17 |
| 0.0364 ± 0.001 | 0.0952 ± 0.001 | 343.04 ± 0.05 | 75.06 ± 0.17 |
| 0.0510 ± 0.001 | 0.1219 ± 0.001 | 343.10 ± 0.05 | 76.75 ± 0.17 |
| 0.0704 ± 0.001 | 0.1494 ± 0.001 | 343.05 ± 0.05 | 78.18 ± 0.17 |
| 0.0891 ± 0.001 | 0.1705 ± 0.001 | 343.06 ± 0.05 | 79.35 ± 0.17 |
| 0.1086 ± 0.001 | 0.1879 ± 0.001 | 343.05 ± 0.05 | 80.19 ± 0.17 |
| 0.1288 ± 0.001 | 0.2026 ± 0.001 | 343.11 ± 0.05 | 81.05 ± 0.17 |
| 0.1499 ± 0.001 | 0.2150 ± 0.001 | 343.06 ± 0.05 | 81.41 ± 0.17 |
| 0.1790 ± 0.001 | 0.2293 ± 0.001 | 343.06 ± 0.05 | 81.85 ± 0.17 |
| 0.2067 ± 0.001 | 0.2410 ± 0.001 | 343.09 ± 0.05 | 82.23 ± 0.17 |
| 0.2342 ± 0.001 | 0.2510 ± 0.001 | 343.08 ± 0.05 | 82.27 ± 0.17 |
| 0.2825 ± 0.001 | 0.2654 ± 0.001 | 343.08 ± 0.05 | 82.38 ± 0.17 |
| 0.3192 ± 0.001 | 0.2755 ± 0.001 | 343.09 ± 0.05 | 82.27 ± 0.17 |
| 0.3619 ± 0.001 | 0.2857 ± 0.001 | 343.11 ± 0.05 | 82.06 ± 0.17 |
| 0.4028 ± 0.001 | 0.2932 ± 0.001 | 343.06 ± 0.05 | 81.54 ± 0.17 |
| 0.5447 ± 0.001 | 0.3296 ± 0.001 | 343.01 ± 0.05 | 79.17 ± 0.17 |
| 0.6016 ± 0.001 | 0.3436 ± 0.001 | 343.05 ± 0.05 | 77.93 ± 0.17 |
| 0.7063 ± 0.001 | 0.3865 ± 0.001 | 343.12 ± 0.05 | 74.04 ± 0.17 |
| 0.8216 ± 0.001 | 0.4556 ± 0.001 | 343.11 ± 0.05 | 66.37 ± 0.17 |
| 0.8680 ± 0.001 | 0.5092 ± 0.001 | 343.03 ± 0.05 | 62.18 ± 0.17 |
| 0.9296 ± 0.001 | 0.6325 ± 0.001 | 343.16 ± 0.05 | 53.60 ± 0.17 |
| 1.0000 | 1.0000 | 343.12 ± 0.05 | 36.56 ± 0.17 |

^a x_1 is the TAEE liquid phase mole fraction; y_1 is the TAEE vapor phase mole fraction; T is the temperature, K; p is the pressure, kPa.

with chemical theory correlation^{15,16} for vapor phase fugacities. The values of H^{E} are highly positive in the entire mole fraction range for all of the studied binary mixtures as can be seen in Figure 1. The model corresponds well to the experimental values. The highest deviations are observed close to the H^{E} maximum of each system. For the binary systems containing ACN the highest discrepancy between the measured and modeled H^{E} values is 4 %, and for the binary systems containing PPN the highest discrepancy is only 1 %.

The excess molar volumes V^{E} ($\text{cm}^3\cdot\text{mol}^{-1}$) were regressed using the Redlich–Kister equation¹⁸ (eq 5)

$$V^{\text{E}} = x_1(1 - x_1) \sum_{i=0}^m A_i(2x_1 - 1)^i \quad (5)$$

where x_i is the mole fraction of the ether. The values of the parameters A_i determined by least-squares analysis are listed in Table 4 together with the standard deviations. The correspondence of the Redlich–Kister equation with the experimental excess molar volumes is shown in Figure 2. The definition of the excess molar volume is given in eq 6

$$V^{\text{E}} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (6)$$

where x_i is the molar fraction, M_i is the molar mass ($\text{g}\cdot\text{mol}^{-1}$), and ρ_i is the density ($\text{g}\cdot\text{cm}^{-3}$) of the component i .

The excess molar volumes are negative for all studied binary systems. The change from the ACN to PPN seems to have a negligible effect on the V^{E} in comparison to the change from ETBE to TAEE: the V^{E} for the binary systems of ETBE + ACN

Table 9. Measured $xyTp$ Data for the Binary System of TAAE (1) + PPN (2)^a

| x_1 | y_1 | T/K | p/kPa |
|----------------|----------------|---------------|---------------|
| 0.0000 | 0.0000 | 363.10 ± 0.05 | 80.66 ± 0.17 |
| 0.0218 ± 0.001 | 0.0582 ± 0.001 | 363.09 ± 0.05 | 84.24 ± 0.17 |
| 0.0434 ± 0.001 | 0.1029 ± 0.001 | 363.09 ± 0.05 | 87.02 ± 0.17 |
| 0.0675 ± 0.001 | 0.1453 ± 0.001 | 363.09 ± 0.05 | 89.78 ± 0.17 |
| 0.0964 ± 0.001 | 0.1936 ± 0.001 | 363.09 ± 0.05 | 92.62 ± 0.17 |
| 0.1294 ± 0.001 | 0.2342 ± 0.001 | 363.09 ± 0.05 | 95.24 ± 0.17 |
| 0.1709 ± 0.001 | 0.2756 ± 0.001 | 363.12 ± 0.05 | 97.77 ± 0.17 |
| 0.2094 ± 0.001 | 0.3090 ± 0.001 | 363.13 ± 0.05 | 99.54 ± 0.17 |
| 0.2511 ± 0.001 | 0.3385 ± 0.001 | 363.13 ± 0.05 | 100.95 ± 0.17 |
| 0.2907 ± 0.001 | 0.3635 ± 0.001 | 363.12 ± 0.05 | 101.81 ± 0.17 |
| 0.3440 ± 0.001 | 0.3931 ± 0.001 | 363.14 ± 0.05 | 102.43 ± 0.17 |
| 0.3798 ± 0.001 | 0.4108 ± 0.001 | 363.10 ± 0.05 | 102.61 ± 0.17 |
| 0.4178 ± 0.001 | 0.4296 ± 0.001 | 363.08 ± 0.05 | 102.74 ± 0.17 |
| 0.4478 ± 0.001 | 0.4444 ± 0.001 | 363.09 ± 0.05 | 102.78 ± 0.17 |
| 0.4743 ± 0.001 | 0.4536 ± 0.001 | 363.12 ± 0.05 | 102.83 ± 0.17 |
| 0.5007 ± 0.001 | 0.4682 ± 0.001 | 363.10 ± 0.05 | 102.72 ± 0.17 |
| 0.5261 ± 0.001 | 0.4814 ± 0.001 | 363.07 ± 0.05 | 102.42 ± 0.17 |
| 0.5568 ± 0.001 | 0.4953 ± 0.001 | 363.03 ± 0.05 | 102.01 ± 0.17 |
| 0.5913 ± 0.001 | 0.5126 ± 0.001 | 363.06 ± 0.05 | 101.68 ± 0.17 |
| 0.6235 ± 0.001 | 0.5286 ± 0.001 | 363.08 ± 0.05 | 101.11 ± 0.17 |
| 0.6518 ± 0.001 | 0.5437 ± 0.001 | 363.02 ± 0.05 | 100.33 ± 0.17 |
| 0.6909 ± 0.001 | 0.5660 ± 0.001 | 363.04 ± 0.05 | 99.23 ± 0.17 |
| 0.7220 ± 0.001 | 0.5854 ± 0.001 | 363.02 ± 0.05 | 98.16 ± 0.17 |
| 0.7620 ± 0.001 | 0.6114 ± 0.001 | 363.08 ± 0.05 | 96.65 ± 0.17 |
| 0.7979 ± 0.001 | 0.6383 ± 0.001 | 363.01 ± 0.05 | 94.61 ± 0.17 |
| 0.8370 ± 0.001 | 0.6739 ± 0.001 | 363.05 ± 0.05 | 92.39 ± 0.17 |
| 0.8704 ± 0.001 | 0.7143 ± 0.001 | 363.13 ± 0.05 | 90.33 ± 0.17 |
| 0.9007 ± 0.001 | 0.7519 ± 0.001 | 363.11 ± 0.05 | 87.34 ± 0.17 |
| 0.9329 ± 0.001 | 0.8112 ± 0.001 | 363.09 ± 0.05 | 83.52 ± 0.17 |
| 0.9690 ± 0.001 | 0.8948 ± 0.001 | 363.12 ± 0.05 | 77.82 ± 0.17 |
| 0.9858 ± 0.001 | 0.9471 ± 0.001 | 363.04 ± 0.05 | 74.64 ± 0.17 |
| 1.0000 | 1.0000 | 363.10 ± 0.05 | 71.73 ± 0.17 |

^a x_1 is the TAAE liquid phase mole fraction; y_1 is the TAAE vapor phase mole fraction; T is the temperature, K; p is the pressure, kPa.

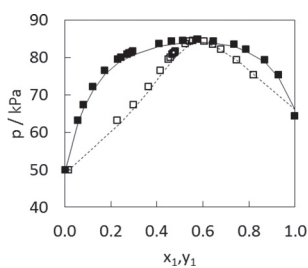


Figure 4. Pressure–composition diagram for ETBE (1) + ACN (2); ■, liquid mole fraction; □, vapor mole fraction at 333 K; —, liquid phase comparison with the model presented in this work; - - -, vapor phase comparison with the model presented in this work.

and ETBE + PPN are of the same order as well as the V^E for TAAE + ACN and TAAE + PPN.

Pure Component Vapor Pressure. Pure component vapor pressures were measured with the Yerazunis type apparatus before the VLE measurements of the binary systems. The measured vapor pressures of ETBE, TAAE, ACN, and PPN are presented in Table 5 and graphically in Figure 3.

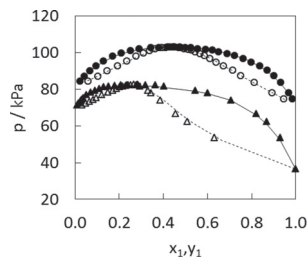


Figure 5. Pressure–composition diagram for binary systems containing TAAE: ▲, liquid mole fraction, Δ, vapor mole fraction for TAAE (1) + ACN (2) at 343 K; ●, liquid mole fraction, ○, vapor mole fraction for TAAE (1) + PPN (2) at 363 K; —, liquid phase comparison with the model presented in this work; - - -, vapor phase comparison with the model presented in this work.

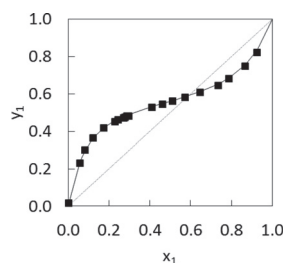


Figure 6. Composition diagram for ETBE (1) + ACN (2) at 333 K; ■, measurements; —, comparison with the model presented in this work.

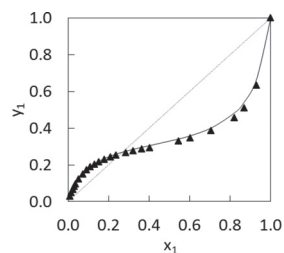


Figure 7. Composition diagram for TAAE (1) + ACN (2) at 343 K; ▲, measurements; —, comparison with the model presented in this work.

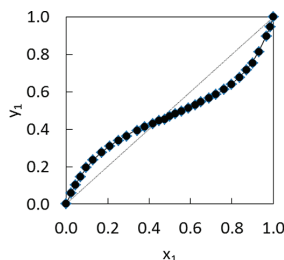


Figure 8. Composition diagram for TAAE (1) + PPN (2) at 363 K; ◆, measurements; —, comparison with the model presented in this work.

The vapor pressure correlation is presented in eq 7

$$\ln(p/\text{MPa}) = A - \frac{B}{(T/\text{K}) + C} \quad (7)$$

Table 10. Experimental and Modeled Azeotropic Mole Fractions x for the Binary Systems of ETBE (1) + ACN (2), TAAE (1) + ACN (2), and TAAE (1) + PPN (2) at Temperature T^a

| | T/K | experiments | | model |
|--------------------|-------|-------------|--------|-------|
| | | x_1 | x_1 | x_1 |
| ETBE (1) + ACN (2) | 333 | 0.5927 | 0.5908 | |
| TAAE (1) + ACN (2) | 343 | 0.2559 | 0.2674 | |
| TAAE (1) + PPN (2) | 363 | 0.4402 | 0.4459 | |

^a x is the ether liquid phase mole fraction; T is the temperature, K.

Table 11. Results of the Consistency Tests (Area, Infinite Dilution, Point) for Circulation Still Measurements of the Binary Systems of an Ether (ETBE or TAAE) + a Nitrile (ACN or PPN) by Using the Hayden–O'Connell Method^a

| | ETBE (1) + ACN (2) | TAAE (1) + ACN (2) | TAAE (1) + PPN (2) |
|-------------------------------|--------------------|--------------------|--------------------|
| Area Test | | | |
| area | -0.055 | -0.067 | -0.013 |
| deviation/% | 7.60 | 8.16 | 2.21 |
| Infinite Dilution Test | | | |
| $x_1 \rightarrow 0/\%$ | 25.50 | 9.11 | 7.15 |
| $x_1 \rightarrow 1/\%$ | 5.91 | 26.80 | 0.35 |
| Point Test | | | |
| $ \Delta \bar{y} $ | 0.008 | 0.008 | 0.003 |
| $ \Delta \bar{p} /\text{kPa}$ | 0.749 | 0.677 | 0.226 |

^a x_1 is the ether liquid mole fraction; y is the ether vapor mole fraction; $|\Delta \bar{p}|$ is the absolute average pressure deviation between the measured and the calculated pressure, kPa.

Table 12. Wilson Model Parameters $a_{i,j}$ and Model Deviations of Vapor Mole Fraction y , Pressure p , and Excess Molar Enthalpy H^E from the Measured Values for the Binary Systems of an Ether (ETBE or TAAE) + a Nitrile (ACN or PPN)^a

| | ETBE (1) + ACN (2) | ETBE (1) + PPN (2) | TAAE (1) + ACN (2) | TAAE (1) + PPN (2) |
|---|--------------------|--------------------|--------------------|--------------------|
| $a_{0,12}$ | 358.788 | 243.951 | 534.695 | 218.589 |
| $a_{0,21}$ | 286.297 | 146.387 | 484.072 | 343.537 |
| $a_{1,12}$ | -0.886186 | 0.842796 | -1.28688 | -0.767329 |
| $a_{1,21}$ | 0.904209 | -0.596211 | 0.469156 | 0.431987 |
| $ \bar{y} $ | 0.008 | 0.005 | 0.008 | 0.003 |
| $ \bar{p} /\text{kPa}$ | 0.75 | 0.41 | 0.68 | 0.24 |
| $ \Delta \bar{H}^E /\text{J}\cdot\text{mol}^{-1}$ | 22.7 | 5.9 | 22.7 | 4.2 |

^a $a_{0,ij}$ and $a_{1,ij}$ are the Wilson model binary interaction parameters for eqs 1 and 2; y is the vapor phase mole fraction; T is the temperature, K; p is the pressure, kPa; H^E is the excess molar enthalpy, $\text{J}\cdot\text{mol}^{-1}$.

where p is the vapor pressure (MPa), T is the temperature (K), and A , B , and C are the parameters of the equation. The coefficients (A to C) are given in Table 6. Equation 7 with these parameters was used as the vapor pressure correlation of the VLE model presented in this work. The objective function (eq 3) used for the vapor pressure correlation (eq 7) was the minimum of the sum of the absolute relative deviations between measured and correlated values.

The correlation of DIPPR⁵ was used for the comparison of the measured vapor pressures. Within the used temperature ranges, the vapor pressure correlation based on measured vapor pressures agreed well with the DIPPR⁵ vapor pressure correlation as can be seen from Table 6.

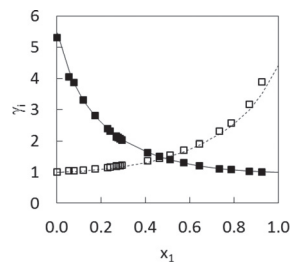


Figure 9. Activity coefficients for ETBE (1) + ACN (2) at 333 K: ■, ETBE; □, ACN; —, comparison of the ether activity coefficients with the model presented in this work; - - -, comparison of the nitrile activity coefficients with the model presented in this work.

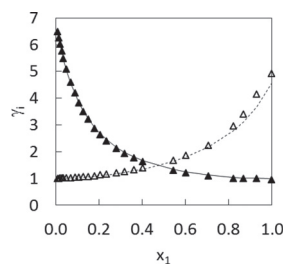


Figure 10. Activity coefficients for TAAE (1) + ACN (2) at 343 K: ▲, TAAE; △, ACN; —, comparison of the ether activity coefficients with the model presented in this work; - - -, comparison of the nitrile activity coefficients with the model presented in this work.

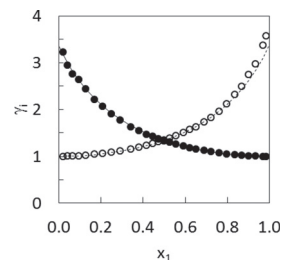


Figure 11. Activity coefficients for TAAE (1) + PPN (2) at 363 K: ●, TAAE; ○, PPN; —, comparison of the ether activity coefficients with the model presented in this work; - - -, comparison of the nitrile activity coefficients with the model presented in this work.

Vapor–Liquid Equilibrium. The measured VLE results are presented in Tables 7, 8, and 9. The sampling at the circulation still technique is dependent on the stability of the boiling. A stainless-steel cylinder (approximate volume 0.03 m³, height 0.9 m) was installed between the vacuum pump and the circulation still to keep the pressure stable within 0.01 kPa. The pressure–composition diagrams are presented in Figures 4 and 5, and the composition diagrams are presented in Figures 6, 7, and 8. These figures clearly show that all measured systems exhibit a maximum-pressure azeotrope. The determined azeotropic points based on experiments and the used VLE model are presented in Table 10.

The consistency of the measured VLE data was first evaluated by using the area test.^{19–21} Second, the infinite dilution test^{19–21} was applied to the measured data. Third, the point test was applied.²²

The results of the consistency tests for the circulation still measurements are given in Table 11.

The regressed Wilson model parameters and the deviations of the objective functions are listed in Table 12. Modeled activity coefficients based on the VLE measurements and the excess molar enthalpy measurements are presented in Figures 9, 10, and 11. As seen in the figures, the model describes the measured data very accurately.

The literature data³ of the binary system of ETBE + PPN was used in the regressing of H^E of this binary system. Both isobaric and isothermal data together with the new H^E data agreed well with the model as seen from the reported model deviations in Table 12.

CONCLUSIONS

Excess molar enthalpies (H^E) and excess molar volumes (V^E) have been measured at 298.15 K for the systems consisting of an ether (ETBE or TAEE) and a nitrile (ACN or PPN). Redlich–Kister equation parameters are provided for V^E .

Isothermal VLE has been measured for the systems ETBE + ACN at 333 K, TAEE + ACN at 343 K, and TAEE + PPN at 363 K by using a circulation still. All systems showed a maximum-pressure azeotrope.

The chemical theory was applied to vapor phase fugacity coefficients and the Wilson model to liquid phase activity coefficients. The VLE model was capable of correlating the VLE and H^E data for all of the binary systems. Furthermore, VLE data from literature³ for the binary system ETBE + PPN was successfully used to regress the measured H^E data of the same system at lower temperature.

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Notes

The authors declare no competing financial interest.

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