### Subscripts

| | |
|---|---|
| a | adsorbate |
| l | liquid phase |
| m | maximum concentration |
| s | solid phase |
| 1 | solute |
| 2 | solvent |
| 12 | solute and solvent |
| 0 | independent of solute and solvent |

### Superscripts

| | |
|---|---|
| ° | standard state |
| ∞ | infinite dilution |

**Registry No.** Phenol, 108-95-2; *o*-chlorophenol, 95-57-8; *m*-chlorophenol, 108-43-0; *p*-chlorophenol, 106-48-9; 2,4,6-trichlorophenol, 88-06-2; 2,3-dichlorophenol, 576-24-9; 2,4-dichlorophenol, 120-83-2; 2,5-dichlorophenol, 583-78-8; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5; 2,3-dimethylphenol, 526-75-0; 2,4-dimethylphenol, 105-67-9; 2,6-dimethylphenol, 576-26-1; 3,4-dimethylphenol, 95-65-8; 3,5-dimethylphenol, 108-68-9; *p*-isopropylphenol, 99-89-8; *o*-nitrophenol, 88-75-5; *p*-nitrophenol, 100-02-7; *o*-methoxyphenol, 90-05-1; *p*-methoxyphenol, 150-76-5; *o*-hydroxybenzoic acid, 69-72-7; *o*-isopropylphenol, 88-69-7; 2,6-dichlorophenol, 87-65-0; carbon, 7440-44-0.

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Received for review May 16, 1991. Revised December 2, 1991. Accepted December 21, 1991. The research work was supported by a grant from Hindustan Lever Research Foundation (Sanction No. 47/86).

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# Vapor–Liquid Equilibria in the Systems of Toluene/Aniline, Aniline/Naphthalene, and Naphthalene/Quinoline

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**Vapor–liquid equilibria for the aniline/naphthalene, toluene/aniline, and naphthalene/quinoline systems have been determined at 0–1500 kPa and 490–623 K by using a static equilibrium cell. The data can be accurately correlated with the modified Peng–Robinson equation of state by using density-dependent mixing rules. The binary interaction parameters and correction factors for the equation of state are reported at each isotherm. The presence of coal-derived solids in these binary systems did not influence any of the binary bubble pressures.**

## Introduction

Thermodynamic property correlations and equations of state have been developed for the petroleum industry largely on the basis of measurements in highly paraffinic systems. However, the liquids produced in coal liquefaction are highly aromatic and may contain heteroatoms such as sulfur, oxygen, and nitrogen. Since there is a scarcity of vapor–liquid equilibrium data for mixtures containing aromatic or heterocyclic compounds, additional data on such systems are needed.

Our goal of this study is to obtain vapor–liquid equilibria (VLE) data for model mixtures, representative of coal-derived liquids. Such compounds include polycyclic aromatics, cyclic alkanes, and compounds containing heteroatoms. These results contribute to a data base for aromatic compounds which may be present in coal liquefaction processes (*1*–*13*) so that coal liquids processing equipment can be accurately designed. A second goal of the study is to determine if the separation of coal liquids by distillation might be affected by the differential adsorption of these compounds on the solids (insoluble organic matter and ash) which may be present in coal liquefaction streams (*14*). The effect of the adsorption can be studied through measurement of the properties of heavy liquid model compounds with and without coal solids. Any variation of bubble pressure of a binary liquid mixture upon the addition of solids can reflect the preferential adsorption of one of the components of the liquid.

## Experimental Section

The following list of chemicals were available with a purity of 99% or greater. Aldrich supplied toluene (27,037; 99.9+%), naphthalene (18,450; 99+%), aniline (24,228-4; 99.5+%), and quinoline (25,401-0; 99%). The purity of all chemicals, as measured by gas chromatography (Hewlett-Packard 5880A), was greater than 99%. All chemicals were used without further purification.

The coal solids were obtained from Gulf Research and Technology Center (Extracts P-99-65-25 Vacuum Coal Bottoms). The charcoal, a model coal solid, was available from Aldrich (24,227-6; Darco). Coal solids were extracted by a tetrahydrofuran (THF) solvent in a Soxhlet extraction unit to remove all organic compounds which may be adsorbed on the coal solid surface and to leave a solid composed of ash and insoluble organic matter (IOM). This ensures that any vapor pressure deviation which may result is not due to the extraction of organic compounds from the solid.

The experimental apparatus has been described previously (*15*). Prausnitz et al. measured the vapor–liquid equilibrium of a coal-derived mixture by using a recirculating still which can measure vapor and liquid composition without condensation (*16*, *17*). However, in this study a stainless steel static equilibrium cell with a volume of 70 mL was used to determine the vapor–liquid equilibria and the effect of the differential adsorption of coal-derived mixtures on the solids. A sample of pure or binary liquid was gravimatically mixed and analyzed by GC and then charged to the evacuated stainless steel vessel such that the vapor space was quite small (5–20 mL). The vessel was then immersed in a high-temperature sand bath. The

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**Table I. Comparison of Direct Experimental Vapor Pressures $P_{expt}$ of Pure Aniline and Pure Quinoline with Values $P_{calc}$ Calculated Using the Coefficients $A$, $B$, and $C$, for Equation 1, as a Function of Temperature $T$, and Percentage Mean Relative Deviations, PMRD, Equation 2**

| | | $P_{calc}$/kPa | |
|---|---|---|---|
| $T$/K | $P_{expt}$/kPa | this work | lit. (*18*) |
| | Aniline | | |
| 429.4 | 45.2 | 45.9 | 46.3 |
| 470.9 | 143 | 142 | 143 |
| 479.1 | 172 | 172 | 174 |
| 512.4 | 361 | 356 | 358 |
| 552.1 | 740 | 744 | 745 |
| 591.4 | 1387 | 1387 | 1386 |
| this work: $A$ = 15.09; $B$ = 4208.16; $C$ = −55.86; PMRD = 0.78<br>ref 18: PMRD = 0.86 | | | |
| | Quinoline | | |
| 503.9 | 89.6 | 89.6 | 87.1 |
| 523.3 | 132 | 135 | |
| 544.9 | 207 | 207 | |
| 563.2 | 292 | 288 | |
| 583.2 | 400 | 402 | |
| 603.6 | 558 | 554 | |
| 615.6 | 661 | 661 | |
| this work: $A$ = 14.91; $B$ = 4897.23; $C$ = −33.44; PMRD = 0.83 | | | |

**Table II. Experimental Bubble Pressure $P_{expt}$ of the Toluene (1)/Aniline (2) System at Mole Fraction $x_1$ of Toluene as a Function of Temperature $T$, Coefficients $A$, $B$, and $C$, Equation 1, and Percentage Mean Relative Deviations, PMRD, Equation 2**

| $T$/K | $P_{expt}$/kPa | $T$/K | $P_{expt}$/kPa |
|---|---|---|---|
| $x_1$ = 0.200 71 | | $x_1$ = 0.397 44 | |
| 394.6 | 41.7 | 390.0 | 62.1 |
| 434.6 | 108 | 431.8 | 172 |
| 512.5 | 439 | 472.2 | 380 |
| | | 513.3 | 781 |
| | | 549.8 | 1307 |
| $A$ = 13.96<br>$B$ = 4034.95<br>$C$ = 0<br>PMRD = 0.19 | | $A$ = 14.93<br>$B$ = 4351.14<br>$C$ = 12.78<br>PMRD = 0.95 | |
| $x_1$ = 0.592 26 | | $x_1$ = 0.809 40 | |
| 390.1 | 81.7 | 331.6 | 15.5 |
| 429.4 | 207 | 412.4 | 179 |
| 471.0 | 494 | 453.4 | 445 |
| 511.7 | 982 | 495.5 | 917 |
| 547.5 | 1662 | 530.9 | 1684 |
| $A$ = 14.91<br>$B$ = 4117.00<br>$C$ = 1.70<br>PMRD = 0.69 | | $A$ = 15.44<br>$B$ = 4329.77<br>$C$ = 9.29<br>PMRD = 1.34 | |

bubble pressure *P* exerted by this liquid mixture was measured as a function of temperature *T* in the range of 490–625 K. Pressures were measured using a Viatran pressure transmitter (±0.25%) with remote high-temperature diaphragm. Temperatures were measured with type K thermocouples to ±0.05 K. The accuracy of the apparatus was verified by its ability to produce vapor pressures of pure components within 0.83% maximum error.

Equilibrium conditions were assumed when constant temperature and pressure were obtained for 15 min or longer. The pressure exerted by this mixture was then measured as a function of temperature. At the relatively low pressures reported in this study, the amount of the material in the vapor phase was negligible. This was verified by varying the amount of liquid charged to the cell and noting that the same bubble pressure was obtained. The accuracy of the data was limited by the purity of the liquids. The reported pressures are within 2% of the true values at the reported temperature and compositions.

**Table III. Experimental Bubble Pressure $P_{expt}$ of the Aniline (1)/Naphthalene (2) System at Mole Fraction $x_1$ of Aniline as a Function of Temperature $T$, Coefficients $A$, $B$, and $C$, Equation 1, and Percentage Mean Relative Deviations, PMRD, Equation 2**

| $T$/K | $P_{expt}$/kPa | $T$/K | $P_{expt}$/kPa |
|---|---|---|---|
| $x_1$ = 0.224 46 | | $x_1$ = 0.406 20 | |
| 494.3 | 135 | 493.3 | 159 |
| 514.1 | 199 | 515.7 | 248 |
| 533.4 | 276 | 531.7 | 340 |
| 553.5 | 390 | 552.9 | 494 |
| 573.5 | 540 | 572.1 | 665 |
| 593.0 | 728 | 592.5 | 919 |
| 611.5 | 942 | 615.2 | 1262 |
| $A$ = 15.34<br>$B$ = 5287.36<br>$C$ = −13.04<br>PMRD = 0.24 | | $A$ = 15.09<br>$B$ = 4985.53<br>$C$ = −26.58<br>PMRD = 0.34 | |
| $x_1$ = 0.603 62 | | $x_1$ = 0.800 04 | |
| 490.8 | 187 | 492.2 | 205 |
| 510.4 | 277 | 511.0 | 304 |
| 572.6 | 801 | 531.8 | 453 |
| 593.7 | 1100 | 570.6 | 876 |
| 613.8 | 1469 | 591.2 | 1191 |
| | | 610.5 | 1562 |
| $A$ = 15.07<br>$B$ = 4953.24<br>$C$ = −27.04<br>PMRD = 0.51 | | $A$ = 14.92<br>$B$ = 4819.51<br>$C$ = −28.35<br>PMRD = 0.36 | |

**Table IV. Experimental Bubble Pressure $P_{expt}$ of the Naphthalene (1)/Quinoline (2) System at Mole Fraction $x_1$ of Naphthalene as a Function of Temperature $T$, Coefficients $A$, $B$, and $C$, Equation 1, and Percentage Mean Relative Deviations, PMRD, Equation 2**

| $T$/K | $P_{expt}$/kPa | $T$/K | $P_{expt}$/kPa |
|---|---|---|---|
| $x_1$ = 0.200 40 | | $x_1$ = 0.400 85 | |
| 522.2 | 142 | 523.2 | 157 |
| 543.1 | 212 | 542.8 | 228 |
| 563.1 | 306 | 562.8 | 325 |
| 586.5 | 454 | 583.6 | 461 |
| 604.1 | 596 | 604.1 | 634 |
| 621.3 | 768 | 620.9 | 815 |
| $A$ = 15.34<br>$B$ = 5287.36<br>$C$ = −13.04<br>PMRD = 0.24 | | $A$ = 15.09<br>$B$ = 4985.53<br>$C$ = −26.58<br>PMRD = 0.34 | |
| $x_1$ = 0.499 02 | | $x_1$ = 0.739 93 | |
| 505.1 | 113 | 503.3 | 119 |
| 523.3 | 161 | 523.0 | 177 |
| 543.2 | 237 | 543.7 | 259 |
| 562.8 | 338 | 563.4 | 367 |
| 583.0 | 474 | 583.4 | 508 |
| 603.0 | 645 | 603.6 | 693 |
| 622.8 | 853 | 621.5 | 891 |
| $A$ = 15.07<br>$B$ = 4953.24<br>$C$ = −27.04<br>PMRD = 0.51 | | $A$ = 14.92<br>$B$ = 4819.51<br>$C$ = −28.35<br>PMRD = 0.36 | |

## Results and Discussion

The vapor pressure and the bubble pressure measurements of all the systems are shown in Tables I–IV. All pure components and constant mole fraction composition $x_i$ binary *P*–*T* data were fitted with a three-constant Antoine equation (1) with

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

$$\mathrm{PMRD} = \left( \sum_{i}^{N} \frac{|P_{\mathrm{expt}} - P_{\mathrm{calc}}|}{P_{\mathrm{expt}}} \right) \frac{100}{N} \tag{2}$$

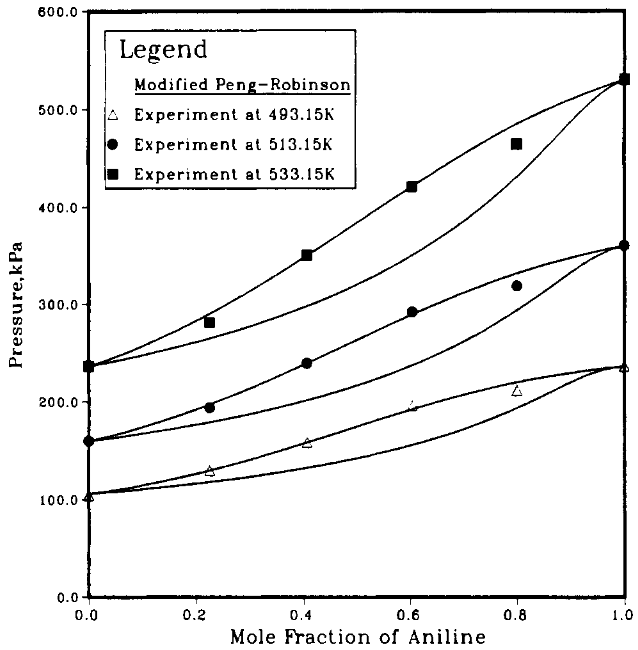

**Figure 1.** Equilibrium pressure vs composition diagram for the aniline/naphthalene system.

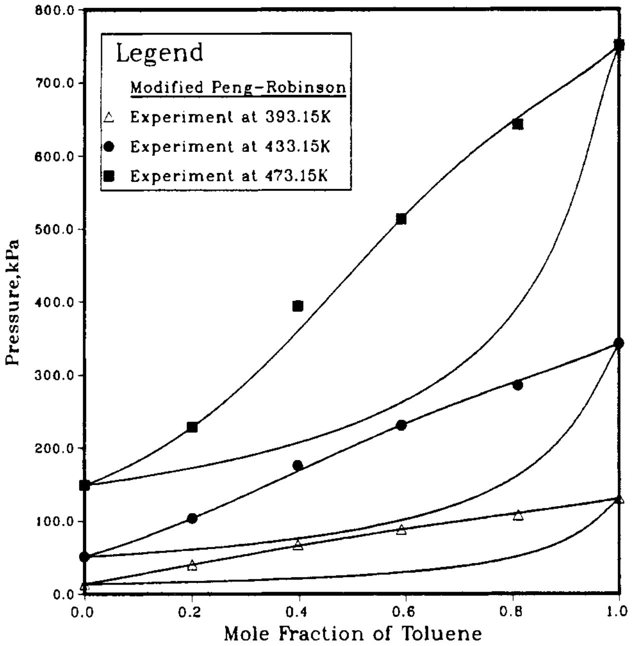

**Figure 2.** Equilibrium pressure vs composition diagram for the toluene/aniline system.

a percentage mean relative deviation (PMRD), eq 2, of less than 1% between correlated and experimental pressures. Comparison with literature (*18*) indicates that the experimental errors in pure systems were less than 1%.

In this work, the $P$-$x$-$T$ data were regressed to determine the binary interaction parameters for the Peng-Robinson equation of state (P-R EOS) by using the density-dependent mixing rules (*19*, *20*). The P-R EOS (*21*) was given by

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b) + b(V-b)} \tag{3}$$

where $V$ is molar volume and $R$ is gas constant. The $a$ and $b$ are the parameters representing the attractive force between molecules and hard sphere molecular volume, respectively, and

$$a = a(T_c)\,\alpha(T_r,\omega) \tag{4}$$

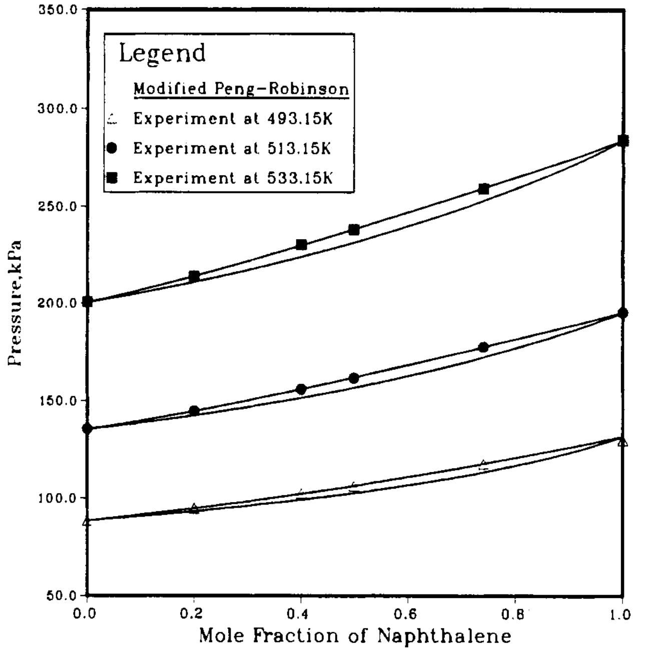

**Figure 3.** Equilibrium pressure vs composition diagram for the naphthalene/quinoline system.

**Table V. Correction Factors $C_a$ and $C_b$, Equations 7 and 8, for the Pure Component Vapor Pressures and Molar Volumes as a Function of Temperature $T$**

| $T$/K | $C_a$ | $C_b$ | $T$/K | $C_a$ | $C_b$ |
|---|---|---|---|---|---|
| | | Aniline | | | |
| 393.15 | 0.9934 | 0.9977 | 533.15 | 1.0002 | 0.9984 |
| 433.15 | 1.0094 | 1.0024 | 553.15 | 0.9785 | 0.9936 |
| 473.15 | 1.0191 | 1.0044 | 573.15 | 0.9413 | 0.9866 |
| 493.15 | 1.0188 | 1.0038 | 593.15 | 0.8819 | 0.9777 |
| 513.15 | 1.0134 | 1.0019 | 613.15 | 0.7846 | 0.9667 |
| | | Naphthalene | | | |
| 493.15[a] | 0.9643 | 0.9885 | 563.15 | 0.9639 | 0.9885 |
| 503.15[a] | 0.9644 | 0.9889 | 573.15 | 0.9567 | 0.9876 |
| 513.15 | 0.9769 | 0.9889 | 583.15 | 0.9474 | 0.9847 |
| 523.15 | 0.9767 | 0.9899 | 593.15 | 0.9355 | 0.9828 |
| 533.15 | 0.9754 | 0.9899 | 603.15 | 0.9204 | 0.9806 |
| 543.15 | 0.9730 | 0.9897 | 613.15 | 0.9020 | 0.9780 |
| 553.15 | 0.9692 | 0.9893 | 623.15 | 0.9794 | 0.9752 |
| | | Toluene | | | |
| 393.15 | 1.0200 | 1.0051 | 513.15 | 0.8231 | 0.9750 |
| 433.15 | 1.0104 | 1.0027 | 553.15[a] | 0.2205 | 0.9453 |
| 473.15 | 0.9629 | 0.9932 | | | |
| | | Quinoline | | | |
| 503.15[a] | 1.1425 | 1.0103 | 583.15 | 1.3123 | 1.0204 |
| 523.15 | 1.1791 | 1.0135 | 603.15 | 1.3683 | 1.0213 |
| 543.15 | 1.2188 | 1.0162 | 623.15 | 1.4378 | 1.0223 |
| 563.15 | 1.2627 | 1.0185 | | | |

[a] Literature data (*18*).

$$a(T_c) = 0.45724(R^2T_c^{\,2}/P_c) \tag{5}$$

$$\alpha(T_r,\omega) = [1 + \kappa(1 - T_r^{\,1/2})]^2 \tag{6}$$

$$\begin{aligned}\kappa &= C_a(0.379642 + 1.48503\omega - \\ &\qquad 0.164423\omega^2 + 0.016666\omega^3) \quad \text{at} \quad \omega > 0.5\\ &= C_a(0.37464 + 1.54426\omega - 0.2699\omega^2) \quad \text{at} \quad \omega \le 0.5\end{aligned} \tag{7}$$

$$b = C_b[0.0778(RT_c/P_c)] \tag{8}$$

where critical pressure $P_c$ is in kilopascals and critical temperature $T_c$ in kelvin. $T_r$ and $\omega$ are reduced temperature and acentric factor, respectively. In this study the correction fac-

**Table VI. Interaction Parameters[a] for the Peng–Robinson Equation of State**

| $T$/K | $\alpha_{12}$ | $\beta_{12}$/(cm$^3$/mol) | PMRD |
|---|---|---|---|
| | Aniline (1)/Naphthalene (2) | | |
| 493.15 | −0.227 830 | 66.016 7 | 1.20 |
| 513.15 | −0.205 075 | 60.542 2 | 1.50 |
| 533.15 | −0.204 219 | 61.239 2 | 1.31 |
| 553.15 | −0.205 439 | 61.808 6 | 1.51 |
| 573.15 | −0.143 432 | 42.955 5 | 1.63 |
| 593.15 | −0.122 200 | 36.511 7 | 1.75 |
| 613.15 | −0.152 412 | 46.826 3 | 1.93 |
| | Toluene (1)/Aniline (2) | | |
| 393.15 | 0.118 931 | −30.891 7 | 0.82 |
| 433.15 | 0.189 996 | −53.610 1 | 1.61 |
| 473.15 | 0.379 911 | −107.884 0 | 1.74 |
| 513.15 | 0.542 766 | −153.194 0 | 3.08 |
| 553.15 | 0.649 937 | −181.690 0 | 4.91 |
| | Naphthalene (1)/Quinoline (2) | | |
| 503.15 | −0.042 9070 | 4.698 80 | 0.28 |
| 523.15 | −0.016 9750 | −1.736 44 | 0.08 |
| 543.15 | −0.017 0500 | −1.454 48 | 0.09 |
| 563.15 | −0.015 5000 | −1.390 00 | 0.12 |
| 583.15 | −0.015 8906 | −0.559 805 | 0.14 |
| 603.15 | −0.016 0000 | 0.321 104 | 0.15 |
| 623.15 | 0.076 0000 | −23.627 7 | 1.2 |

[a] $\delta_{12} = \alpha_{12} + \beta_{12}/V$.

**Table VII. Isothermal Vapor–Liquid Equilibrium Data**

| $x_{1\,\mathrm{expt}}$ | $y_{1\,\mathrm{calc}}$ | $P_{\mathrm{expt}}$/kPa | $P_{\mathrm{calc}}$/kPa |
|---|---|---|---|
| | Aniline (1)/Naphthalene (2) at $T$ = 533.15 K | | |
| 0.0 | 0.0 | 237 | 236 |
| 0.224 46 | 0.368 44 | 281 | 290 |
| 0.406 20 | 0.602 83 | 350 | 350 |
| 0.603 62 | 0.779 97 | 422 | 422 |
| 0.800 04 | 0.895 81 | 465 | 485 |
| 1.0 | 1.0 | 530 | 530 |
| | Toluene (1)/Aniline (2) at $T$ = 473.15 K | | |
| 0.0 | 0.0 | 149 | 149 |
| 0.200 71 | 0.487 67 | 229 | 229 |
| 0.397 44 | 0.772 04 | 394 | 360 |
| 0.592 26 | 0.898 23 | 513 | 513 |
| 0.809 40 | 0.957 39 | 642 | 652 |
| 1.0 | 1.0 | 750 | 750 |
| | Naphthalene (1)/Quinoline (2) at $T$ = 563.15 K | | |
| 0.0 | 0.0 | 289 | 288 |
| 0.200 40 | 0.249 57 | 308 | 308 |
| 0.400 85 | 0.475 20 | 330 | 329 |
| 0.499 02 | 0.575 84 | 341 | 341 |
| 0.739 94 | 0.796 90 | 368 | 369 |
| 1.0 | 1.0 | 402 | 402 |

tors, $C_a$ and $C_b$, were used in eqs 6 and 7 so that the pure component vapor pressure and liquid molar volumes were accurately predicted.

The following mixing rules were used for the parameters $a$ and $b$

$$b = \sum_i x_i b_i \tag{9}$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{10}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - \delta_{ij}) \tag{11}$$

$$\delta_{ij} = \alpha_{ij} + \beta_{ij}/V \tag{12}$$

Equation 11 requires that the interaction parameter $\delta_{ij}$ vary linearly with the phase molar volume of the mixture. Using the above equations, the modified P–R EOS can be written as a fourth-order (quartic) equation in compressibility. The fugacity coefficient expressions are correspondingly changed (*19, 20*).

The interaction parameters were taken as those values which minimized the following objective function

$$Q = \sum_i^N \frac{|P_{\mathrm{expt}} - P_{\mathrm{calc}}|}{P_{\mathrm{expt}}} \tag{13}$$

The data can be accurately correlated with the modified P–R EOS, as shown in Figures 1–3. The Peng–Robinson parameters and correction factors at several temperatures are given in Tables V and VI, and isothermal data at a single temperature per system are given in Table VII. Note that the results are insensitive to the values used for $C_a$ and $C_b$. These parameters could be set to 1.0, but the values reported allow the pure component vapor pressures to be accurately reproduced. The isothermal data are obtained using eq 1 to correct for slight deviations in temperature from the specified value.

Experiments were conducted with up to 50 wt % solids (coal-derived IOM and charcoal). The solids did not influence any of the binary bubble pressures to a measurable degree. This indicates that no differential adsorption occurs. Thus, the presence of coal solids on these systems does not affect the degree of separation of the components by distillation in an equilibrium still.

## Glossary

| | |
|---|---|
| $A,B,C$ | vapor pressure parameters, eq 1 |
| $a$ | energy parameter in eq 4, atm cm$^6$/mol$^2$ |
| $b$ | size parameter in eq 8, cm$^3$/mol |
| $C_a$ | correction factor, eq 7 |
| $C_b$ | correction factor, eq 8 |
| $N$ | number of data |
| $P$ | pressure, kPa |
| $R$ | gas constant |
| $T$ | temperature, K |
| $V$ | molar volume, cm$^3$/mol |
| $x$ | liquid-phase mole fraction |
| $y$ | vapor-phase mole fraction |

### *Greek Letters*

| | |
|---|---|
| $\alpha$ | adjustable binary parameter |
| $\beta$ | adjustable binary parameter, cm$^3$/mol |
| $\delta$ | Peng–Robinson binary interaction parameter |
| $\omega$ | acentric factor |

### *Subscripts*

| | |
|---|---|
| c | critical point |
| calc | calculated value |
| expt | experimental value |
| $i$ | component $i$ |
| $j$ | component $j$ |
| r | reduced property |

**Registry No.** Toluene, 108-88-3; aniline, 62-53-3; naphthalene, 91-20-3; quinoline, 91-22-5.

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Received May 21, 1990. Revised August 12, 1991. Accepted November 11, 1991. We thank the Department of Energy/Fossil Energy for support of this research under Grant No. DE-PS22-86PC90501.

# Vapor–Liquid Equilibria in the Systems of *n*-Decane/Tetralin, *n*-Hexadecane/Tetralin, *n*-Decane/1-Methylnaphthalene, and 1-Methylnaphthalene/Tetralin

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**Vapor–liquid equilibrium data for the binary systems of *n*-decane/tetralin, *n*-hexadecane/tetralin, *n*-decane/1-methylnaphthalene, and 1-methylnaphthalene/tetralin were measured at a low to moderate pressure (0–1123 kPa) by using a static equilibrium cell. The binary *P*–*x* data were isothermally correlated using the modified Peng–Robinson equation of state to describe both vapor and liquid phases at 473.15, 533.15, and 573.15 K. Interaction parameters for density-dependent mixing rules are reported at each isotherm.**

## Introduction

The need for vapor–liquid equilibrium (VLE) data for mixtures of coal-derived liquids has been discussed previously (*1*–*14*). Such data would be invaluable in the design of process equipment involving the reaction or separation of coal liquids.

This present study is a continuation of efforts to develop a data base for aromatic and aromatic/aliphatic mixtures which may be present in coal liquefaction processes (*1*–*13*). High-temperature vapor–liquid equilibrium data for model mixtures representing coal-derived liquids are relatively scarce. In this paper the use of the modified Peng–Robinson equation of state (*15*, *16*) for correlating the data is presented.

## Experimental Section

The experimental apparatus has been described previously (*18*, *19*). A 70-mL static equilibrium cell was used. A 50-mL sample of pure or binary liquid was charged to the evacuated stainless steel vessel such that the vapor space was quite small (5–20 mL). The pressure *P* exerted by this mixture was then measured as a function of temperature *T*. At the pressures reported in this study, the amount of material in the vapor phase was negligible, as verified by varying the amount of liquid charged to the cell. The accuracy of the data was limited by the purity of the liquids. The reported pressures are within 2% of the true values at the reported temperatures and compositions.

Table I. Comparison of Direct Experimental Vapor Pressures $P_{\mathrm{expt}}$ of Pure *n*-Decane, 1-Methylnaphthalene, Tetralin, and *n*-Hexadecane with Values $P_{\mathrm{calc}}$ Calculated Using the Coefficients *A*, *B*, and *C*, for Equation 1, as a Function of Temperature *T*, and Percentage Mean Relative Deviation, PMRD, Equation 2

| | | $P_{\mathrm{calc}}$/kPa | |
|---|---|---|---|
| *T*/K | $P_{\mathrm{expt}}$/kPa | this work | lit. (*19*, *20*) |
| | *n*-Decane | | |
| 409.0 | 34.0 | 34.0 | 34.3 |
| 449.0 | 103 | 103 | 106 |
| 488.1 | 254 | 253 | 259 |
| 526.8 | 533 | 532 | 539 |
| 566.4 | 1016 | 1016 | 1023 |
| 584.3 | 1320 | 1320 | 1332 |
| this work: $A = 14.86$; $B = 4172.08$; $C = -40.99$; PMRD = 0.19<br>refs 19 and 20: PMRD = 1.38 | | | |
| | 1-Methylnaphthalene | | |
| 485.0 | 45.2 | 45.2 | 47.2 |
| 523.6 | 113 | 113 | 116 |
| 559.5 | 228 | 231 | 234 |
| 580.6 | 336 | 335 | 337 |
| 594.8 | 423 | 424 | 425 |
| this work: $A = 14.36$; $B = 4306.56$; $C = -76.87$; PMRD = 0.33<br>refs 19 and 20: PMRD = 2.02 | | | |
| | Tetralin | | |
| 464.8 | 71.7 | 71.7 | 74.3 |
| 498.6 | 155 | 155 | 159 |
| 516.0 | 221 | 221 | 224 |
| 532.3 | 300 | 300 | 303 |
| 562.4 | 503 | 503 | 503 |
| 579.7 | 659 | 659 | 655 |
| this work: $A = 14.39$; $B = 4138.32$; $C = -56.01$; PMRD = 0.10<br>refs 19 and 20: PMRD = 1.60 | | | |
| | *n*-Hexadecane | | |
| 504.5 | 25.6 | 25.6 | 25.6 |
| 532.8 | 55.0 | 54.7 | 54.0 |
| 546.8 | 76.9 | 76.9 | 75.4 |
| 566.1 | 119 | 119 | 115 |
| 589.0 | 188 | 191 | 182 |
| this work: $A = 15.00$; $B = 4817.50$; $C = -94.61$; PMRD = 0.46<br>refs 19 and 20: PMRD = 2.06 | | | |

The following chemicals were used: *n*-hexadecane (29,631-7; 99+%), *n*-decane (D90-1; 99+%), tetralin (10,241-5; 99%), and 1-methylnaphthalene (M5680-8; 99%). All were supplied by Aldrich. As a secondary measure, the

0021-9568/92/1737-0183$03.00/0