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**Vapor-liquid equilibria and mixture densities for 2,2,4,4,6,8,8-heptamethylnonane + N<sub>2</sub> and  
n-hexadecane + N<sub>2</sub> binary mixtures to 535 K and 135 MPa**

**Supplemental Information**

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This document contains data tables for BP/DP transitions and mixture densities for 2,2,4,4,6,8,8-heptamethylnonane (HMN) + N<sub>2</sub> and n-hexadecane (HxD) + N<sub>2</sub> binary mixtures.

Table S1. Isopleths with bubble (BP) and dew points (DP) obtained in this study for HMN + N<sub>2</sub> at varying compositions listed with the N<sub>2</sub> mole fraction,  $x_{N_2}$ , the N<sub>2</sub> weight fraction,  $w_{N_2}$ , the pressure, and the temperature. BP data are listed without an asterisk and DP data are marked with an asterisk.

| $x_{N_2}$ | $w_{N_2}$ | $p/\text{MPa}$ | $T/\text{K}$ | $x_{N_2}$ | $w_{N_2}$ | $p/\text{MPa}$ | $T/\text{K}$ |
|-----------|-----------|----------------|--------------|-----------|-----------|----------------|--------------|
| 0.149     | 0.021     | 11.6           | 297.8        | 0.671     | 0.201     | 114.6          | 356.2        |
|           |           | 9.9            | 374.8        |           |           | 81.5           | 415.4        |
|           |           | 8.4            | 467.2        |           |           | 63.5           | 473.4        |
|           |           | 7.9            | 526.8        |           |           | 104.5          | 423.3        |
| 0.29      | 0.048     | 24.5           | 299.8        | 0.773     | 0.296     | 89.4           | 452.1        |
|           |           | 19.4           | 380.6        |           |           | 77.6           | 478.4        |
|           |           | 15.8           | 463.5        |           |           | 96.5           | 441.4        |
|           |           | 12.2           | 575.6        |           |           | 81.4           | 470.2        |
| 0.392     | 0.074     | 42.5           | 305.7        | 0.874     | 0.463     | 67.5           | 503.7        |
|           |           | 33.3           | 375.2        |           |           | 56.5           | 533.2        |
|           |           | 25.7           | 469.1        |           |           | 101.3          | 492.6        |
|           |           | 21.8           | 527.1        |           |           | 90.0           | 511.5        |
| 0.571     | 0.141     | 91.0           | 298.0        | 0.894     | 0.511     | 76.6           | 533.3        |
|           |           | 67.7           | 352.1        |           |           | 95.8*          | 474.8        |
|           |           | 52.5           | 416.8        |           |           | 83.3*          | 495.5        |
|           |           | 43.4           | 474.8        |           |           | 74.4*          | 510.9        |
|           |           | 38.7           | 519.4        |           |           | 64.0*          | 531.4        |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and 0.41 MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K. The combined expanded uncertainties  $U_c$  are  $U_c(x_{N_2}) = 0.001$  with a coverage factor,  $k = 2$ . \*Dew point pressure

Table S2. Isopleths with BP data obtained in this study for HXD + N<sub>2</sub> at varying compositions listed with the N<sub>2</sub> mole fraction,  $x_{N_2}$ , the N<sub>2</sub> weight fraction,  $w_{N_2}$ , the pressure, and the temperature. Only BP data are observed for this system at the conditions shown here.

| $x_{N_2}$ | $w_{N_2}$ | $p/\text{MPa}$ | $T/\text{K}$ | $x_{N_2}$ | $w_{N_2}$ | $p/\text{MPa}$ | $T/\text{K}$ |
|-----------|-----------|----------------|--------------|-----------|-----------|----------------|--------------|
| 0.209     | 0.032     | 19.2           | 323.2        | 0.686     | 0.212     | 127.5          | 394.7        |
|           |           | 15.4           | 387.0        |           |           | 95.3           | 438.5        |
|           |           | 12.3           | 466.9        |           |           | 76.9           | 478.1        |
|           |           | 10.9           | 525.4        |           |           | 59.7           | 529.4        |
| 0.29      | 0.048     | 27.3           | 325.3        | 0.816     | 0.354     | 127.0          | 469.0        |
|           |           | 21.0           | 397.1        |           |           | 110.3          | 487.6        |
|           |           | 17.6           | 468.4        |           |           | 96.4           | 508.8        |
|           |           | 14.7           | 535.8        |           |           | 85.5           | 527.2        |
| 0.453     | 0.093     | 59.8           | 327.1        | 0.902     | 0.533     | 127.6          | 498.5        |
|           |           | 41.9           | 396.2        |           |           | 110.2          | 517.3        |
|           |           | 34.3           | 458.6        |           |           | 99.1           | 531.4        |
| 0.581     | 0.147     | 106.7          | 324.9        |           |           |                |              |
|           |           | 71.3           | 391.3        |           |           |                |              |
|           |           | 51.0           | 471.2        |           |           |                |              |
|           |           | 41.6           | 528.9        |           |           |                |              |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and  $0.41$  MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K. The combined expanded uncertainties  $U_c$  are  $U_c(x_{N_2}) = 0.001$  with a coverage factor,  $k = 2$ .

Tables S3 and S4 list densities for HMN + N<sub>2</sub> mixtures and HXD + N<sub>2</sub> mixtures, respectfully. The first pressure-density data point at each fixed composition and temperature listed in these tables represents the limit of the single phase region, which is the two phase boundary for a given isopleth. These density data are obtained to pressures as high as ~135 MPa and temperatures as high as ~535 K.

Table S3. Liquid densities,  $\rho$ , obtained in this study for single-phase, HMN + N<sub>2</sub> mixtures at varying compositions listed with the N<sub>2</sub> mole fraction,  $x_{N_2}$ , the N<sub>2</sub> weight fraction,  $w_{N_2}$ , the pressure, and the temperature. Nearly all the isotherms are held at a constant temperature within 0.2 K, except for the 526.9 K isotherm, which is held within 0.3 K, and the 528.0 K isotherm, which is held within 0.5 K.

| $p/\text{MPa}$                     | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ |
|------------------------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| $x_{N_2} = 0.149; w_{N_2} = 0.021$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K} = 297.8$               |                                    | $T/\text{K} = 374.8$ |                                    | $T/\text{K} = 467.1$ |                                    | $T/\text{K} = 526.6$ |                                    |
| 11.6                               | 759                                | 9.9                  | 706                                | 8.4                  | 638                                | 7.9                  | 594                                |
| 24.6                               | 774                                | 20.6                 | 726                                | 17.3                 | 664                                | 17.2                 | 625                                |
| 34.9                               | 781                                | 34.9                 | 743                                | 31.3                 | 688                                | 31.3                 | 653                                |
| 44.4                               | 789                                | 51.8                 | 758                                | 44.9                 | 704                                | 44.7                 | 674                                |
| 51.7                               | 794                                | 62.9                 | 766                                | 58.7                 | 719                                | 58.9                 | 691                                |
| 62.3                               | 800                                | 73.5                 | 773                                | 72.3                 | 732                                | 72.2                 | 705                                |
| 72.1                               | 806                                | 85.7                 | 779                                | 85.3                 | 742                                | 84.0                 | 716                                |
| 84.9                               | 812                                | 98.2                 | 788                                | 98.1                 | 751                                | 97.5                 | 727                                |
| 98.4                               | 819                                |                      |                                    |                      |                                    |                      |                                    |
| $x_{N_2} = 0.392; w_{N_2} = 0.074$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K} = 305.7$               |                                    | $T/\text{K} = 375.2$ |                                    | $T/\text{K} = 469.1$ |                                    | $T/\text{K} = 526.9$ |                                    |
| 42.5                               | 762                                | 33.3                 | 710                                | 25.7                 | 642                                | 21.8                 | 589                                |
| 43.8                               | 764                                | 42.3                 | 717                                | 27.5                 | 647                                | 27.6                 | 600                                |
| 58.7                               | 772                                | 50.9                 | 730                                | 41.6                 | 667                                | 45.5                 | 639                                |
| 59.0                               | 768                                | 62.0                 | 741                                | 55.2                 | 688                                | 45.5                 | 640                                |
| 71.5                               | 782                                | 72.2                 | 748                                | 72.6                 | 708                                | 58.2                 | 661                                |
| 85.2                               | 791                                | 84.7                 | 759                                | 84.7                 | 719                                | 72.1                 | 678                                |
| 98.6                               | 799                                | 98.2                 | 769                                | 97.7                 | 730                                | 84.4                 | 692                                |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and 0.41 MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K with the exclusion of the 526.9 K ( $u(T) = 0.2$  K) and 528.0 K ( $u(T) = 0.5$  K). The combined expanded uncertainties  $U_c$  are  $U_c(x_{N_2}) = 0.001$  and  $U_c(\rho) = 0.008 \cdot \rho$  kg·m<sup>-3</sup> with a coverage factor,  $k = 2$ .

Table S3. Continued: Densities,  $\rho$ , obtained in this study for single-phase, HMN + N<sub>2</sub> mixtures.

| $p/\text{MPa}$                                      | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ |
|-----------------------------------------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| $x_{\text{N}_2} = 0.571$ ; $w_{\text{N}_2} = 0.141$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K}$ K = 298.0                              |                                    | $T/\text{K} = 416.7$ |                                    | $T/\text{K} = 474.8$ |                                    | $T/\text{K} = 519.2$ |                                    |
| 91.0                                                | 786                                | 52.5                 | 663                                | 43.4                 | 615                                | 38.7                 | 569                                |
| 98.2                                                | 793                                | 62.6                 | 684                                | 51.0                 | 630                                | 44.6                 | 586                                |
|                                                     |                                    | 71.5                 | 700                                | 62.4                 | 654                                | 55.1                 | 609                                |
| $T/\text{K} = 352.1$                                |                                    | 85.4                 | 717                                | 73.0                 | 670                                | 73.4                 | 638                                |
| 67.7                                                | 720                                | 97.8                 | 731                                | 84.3                 | 685                                | 86.9                 | 657                                |
| 73.7                                                | 731                                |                      |                                    | 99.0                 | 703                                | 100.5                | 673                                |
| 85.3                                                | 749                                |                      |                                    |                      |                                    |                      |                                    |
| 98.6                                                | 763                                |                      |                                    |                      |                                    |                      |                                    |
| $x_{\text{N}_2} = 0.671$ ; $w_{\text{N}_2} = 0.201$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K} = 356.2$                                |                                    | $T/\text{K} = 415.4$ |                                    | $T/\text{K} = 473.4$ |                                    | $T/\text{K} = 527.0$ |                                    |
| 114.6                                               | 756                                | 81.5                 | 687                                | 63.5                 | 622                                | 51.2                 | 555                                |
| 119.0                                               | 760                                | 91.0                 | 700                                | 74.7                 | 641                                | 58.4                 | 572                                |
| 125.9                                               | 766                                | 96.9                 | 707                                | 88.2                 | 661                                | 71.2                 | 599                                |
|                                                     |                                    | 104.7                | 715                                | 100.9                | 679                                | 84.3                 | 622                                |
|                                                     |                                    | 111.1                | 722                                | 115.0                | 695                                | 98.0                 | 642                                |
|                                                     |                                    | 117.2                | 728                                | 125.3                | 706                                | 111.4                | 659                                |
|                                                     |                                    | 124.4                | 735                                |                      |                                    | 124.5                | 674                                |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and 0.41 MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K with the exclusion of the 526.9 K ( $u(T) = 0.2$  K) and 528.0 K ( $u(T) = 0.5$  K). The combined expanded uncertainties  $U_c$  are  $U_c(x_{\text{N}_2}) = 0.001$  and  $U_c(\rho) = 0.008 \cdot \rho$  kg·m<sup>-3</sup> with a coverage factor,  $k = 2$ .

Table S3. Continued: Densities,  $\rho$ , obtained in this study for single-phase, HMN + N<sub>2</sub> mixtures.

| $p/\text{MPa}$                                         | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ |
|--------------------------------------------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| $x_{\text{N}_2} = 0.760; \quad w_{\text{N}_2} = 0.282$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K} = 423.3$                                   |                                    | $T/\text{K} = 478.4$ |                                    | $T/\text{K} = 502.1$ |                                    | $T/\text{K} = 528.0$ |                                    |
| 104.5                                                  | 696                                | 77.6                 | 610                                | 68.1                 | 575                                | 59.5                 | 535                                |
| 110.0                                                  | 704                                | 83.8                 | 623                                | 74.4                 | 588                                | 73.8                 | 570                                |
| 116.7                                                  | 713                                | 90.0                 | 635                                | 82.0                 | 605                                | 82.1                 | 588                                |
| 128.2                                                  | 727                                | 94.1                 | 643                                | 87.1                 | 614                                | 100.3                | 621                                |
| $T/\text{K} = 452.1$                                   |                                    | 101.0                | 654                                | 95.3                 | 630                                | 116.7                | 647                                |
| 89.4                                                   | 654                                | 109.3                | 666                                | 101.2                | 639                                | 127.0                | 661                                |
| 94.2                                                   | 661                                | 114.0                | 674                                | 109.1                | 651                                |                      |                                    |
| 101.4                                                  | 673                                | 122.7                | 684                                | 114.2                | 659                                |                      |                                    |
| 108.0                                                  | 682                                | 127.8                | 692                                | 122.4                | 669                                |                      |                                    |
| 114.4                                                  | 691                                |                      |                                    | 127.8                | 677                                |                      |                                    |
| 120.6                                                  | 699                                |                      |                                    |                      |                                    |                      |                                    |
| 127.8                                                  | 708                                |                      |                                    |                      |                                    |                      |                                    |
| $x_{\text{N}_2} = 0.773; \quad w_{\text{N}_2} = 0.296$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K} = 441.4$                                   |                                    | $T/\text{K} = 470.2$ |                                    | $T/\text{K} = 503.4$ |                                    | $T/\text{K} = 533.2$ |                                    |
| 96.5                                                   | 669                                | 81.4                 | 621                                | 67.5                 | 565                                | 56.5                 | 515                                |
| 98.8                                                   | 673                                | 85.4                 | 628                                | 72.2                 | 578                                | 58.3                 | 518                                |
|                                                        |                                    | 91.3                 | 640                                | 78.3                 | 592                                | 72.2                 | 557                                |
|                                                        |                                    | 98.9                 | 653                                | 84.7                 | 606                                | 79.0                 | 573                                |
|                                                        |                                    |                      |                                    | 91.6                 | 619                                | 85.2                 | 587                                |
|                                                        |                                    |                      |                                    | 98.3                 | 631                                | 91.6                 | 600                                |
|                                                        |                                    |                      |                                    |                      |                                    | 98.6                 | 613                                |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and  $0.41$  MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K with the exclusion of the  $526.9$  K ( $u(T) = 0.2$  K) and  $528.0$  K ( $u(T) = 0.5$  K). The combined expanded uncertainties  $U_c$  are  $U_c(x_{\text{N}_2}) = 0.001$  and  $U_c(\rho) = 0.008 \rho \text{ kg}\cdot\text{m}^{-3}$  with a coverage factor,  $k = 2$ .

Table S3. Continued: Densities,  $\rho$ , obtained in this study for single-phase, HMN + N<sub>2</sub> mixtures.

| $p/\text{MPa}$                                   | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{kg}\cdot\text{m}^{-3}$ |
|--------------------------------------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------|------------------------------------|
| $x_{\text{N}_2} = 0.874; w_{\text{N}_2} = 0.463$ |                                    |                      |                                    |                      |                                    |                |                                    |
| $T/\text{K} = 492.6$                             |                                    | $T/\text{K} = 511.5$ |                                    | $T/\text{K} = 533.4$ |                                    |                |                                    |
| 101.3                                            | 559                                | 90.0                 | 520                                | 76.6                 | 470                                |                |                                    |
| 105.3                                            | 568                                | 97.5                 | 537                                | 81.6                 | 482                                |                |                                    |
| 112.3                                            | 581                                | 103.9                | 551                                | 88.1                 | 498                                |                |                                    |
|                                                  |                                    | 110.8                | 564                                | 94.5                 | 513                                |                |                                    |
|                                                  |                                    | 119.7                | 580                                | 100.6                | 525                                |                |                                    |
|                                                  |                                    |                      |                                    | 108.1                | 541                                |                |                                    |
|                                                  |                                    |                      |                                    | 113.9                | 551                                |                |                                    |
|                                                  |                                    |                      |                                    | 121.5                | 564                                |                |                                    |
|                                                  |                                    |                      |                                    | 128.0                | 574                                |                |                                    |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and  $0.41$  MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K with the exclusion of the  $526.9$  K ( $u(T) = 0.2$  K) and  $528.0$  K ( $u(T) = 0.5$  K). The combined expanded uncertainties  $U_c$  are  $U_c(x_{\text{N}_2}) = 0.001$  and  $U_c(\rho) = 0.008 \cdot \rho$   $\text{kg}\cdot\text{m}^{-3}$  with a coverage factor,  $k = 2$ .

Table S4. Liquid densities,  $\rho$ , obtained in this study for single-phase, HXD + N<sub>2</sub> mixtures at varying compositions listed with the N<sub>2</sub> mole fraction,  $x_{N_2}$ , the N<sub>2</sub> weight fraction,  $w_{N_2}$ , the pressure, and the temperature. Nearly all the isotherms are held at a constant temperature within 0.2 K, except for the 527.0 K isotherm, which is held within 0.8 K, and the 528.6 K isotherm, which is held within 0.3 K.

| $p/\text{MPa}$                     | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{kg}\cdot\text{m}^{-3}$ |
|------------------------------------|------------------------------------|----------------|------------------------------------|----------------|------------------------------------|----------------|------------------------------------|
| $x_{N_2} = 0.209; w_{N_2} = 0.032$ |                                    |                |                                    |                |                                    |                |                                    |
| T/K = 323.1                        |                                    | T/K = 387.0    |                                    | T/K = 466.9    |                                    | T/K = 527.0    |                                    |
| 19.2                               | 741                                | 15.4           | 688                                | 12.3           | 632                                | 10.9           | 586                                |
| 34.1                               | 760                                | 33.7           | 721                                | 26.0           | 666                                | 31.7           | 638                                |
| 48.0                               | 771                                | 55.0           | 742                                | 46.8           | 694                                | 52.2           | 668                                |
| 61.9                               | 782                                | 76.0           | 758                                | 61.3           | 709                                | 72.2           | 691                                |
| 75.7                               | 791                                | 88.3           | 767                                | 86.1           | 731                                | 91.9           | 708                                |
| 89.5                               | 799                                | 104.6          | 777                                | 106.2          | 746                                | 104.7          | 719                                |
| 102.7                              | 806                                | 125.3          | 789                                | 126.2          | 759                                | 125.2          | 734                                |
| 115.9                              | 812                                |                |                                    |                |                                    |                |                                    |
| 124.3                              | 816                                |                |                                    |                |                                    |                |                                    |
| $x_{N_2} = 0.290; w_{N_2} = 0.048$ |                                    |                |                                    |                |                                    |                |                                    |
| T/K = 325.5                        |                                    | T/K = 397.1    |                                    | T/K = 468.4    |                                    | T/K = 535.8    |                                    |
| 27.3                               | 733                                | 21.0           | 678                                | 17.6           | 628                                | 14.7           | 567                                |
| 40.5                               | 750                                | 30.4           | 696                                | 31.0           | 656                                | 27.2           | 604                                |
| 48.2                               | 758                                | 51.2           | 722                                | 44.6           | 676                                | 42.4           | 630                                |
| 62.6                               | 770                                | 63.7           | 733                                | 58.7           | 692                                | 55.9           | 648                                |
| 77.2                               | 781                                | 84.2           | 750                                | 71.5           | 704                                | 71.4           | 666                                |
| 88.9                               | 789                                | 103.8          | 764                                | 84.9           | 717                                | 86.8           | 680                                |
| 102.3                              | 797                                | 124.2          | 777                                | 97.6           | 727                                | 98.5           | 691                                |
| 114.9                              | 805                                |                |                                    | 111.6          | 737                                | 111.5          | 700                                |
|                                    |                                    |                |                                    | 124.9          | 747                                | 124.6          | 712                                |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and  $0.41$  MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K with the exclusion of the 527.0 K ( $u(T) = 0.8$  K) and 528.6 K ( $u(T) = 0.3$  K). The combined expanded uncertainties  $U_c$  are  $U_c(x_{N_2}) = 0.001$  and  $U_c(\rho) = 0.008 \cdot \rho$  kg·m<sup>-3</sup> with a coverage factor,  $k = 2$ .

Table S4. Continued: Densities,  $\rho$ , obtained in this study for single-phase, HXD + N<sub>2</sub> mixtures.

| $p/\text{MPa}$                                   | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$       | $\rho/\text{kg}\cdot\text{m}^{-3}$ |
|--------------------------------------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| $x_{\text{N}_2} = 0.452; w_{\text{N}_2} = 0.093$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K} = 327.1$                             |                                    | $T/\text{K} = 396.2$ |                                    | $T/\text{K} = 458.4$ |                                    |                      |                                    |
| 59.8                                             | 752                                | 41.9                 | 696                                | 34.3                 | 645                                |                      |                                    |
| 72.2                                             | 764                                | 58.5                 | 716                                | 44.9                 | 663                                |                      |                                    |
| 84.9                                             | 774                                | 71.4                 | 729                                | 58.3                 | 680                                |                      |                                    |
| 98.3                                             | 784                                | 84.4                 | 741                                | 73.3                 | 698                                |                      |                                    |
| 111.6                                            | 793                                | 98.0                 | 752                                | 82.9                 | 707                                |                      |                                    |
| 124.9                                            | 801                                | 111.1                | 762                                | 97.4                 | 721                                |                      |                                    |
|                                                  |                                    | 124.1                | 771                                | 111.8                | 733                                |                      |                                    |
|                                                  |                                    |                      |                                    | 124.3                | 743                                |                      |                                    |
| $x_{\text{N}_2} = 0.581; w_{\text{N}_2} = 0.147$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K} = 324.8$                             |                                    | $T/\text{K} = 391.4$ |                                    | $T/\text{K} = 471.1$ |                                    | $T/\text{K} = 528.6$ |                                    |
| 106.7                                            | 790                                | 71.3                 | 703                                | 51.0                 | 630                                | 41.6                 | 574                                |
| 114.4                                            | 798                                | 77.7                 | 713                                | 62.5                 | 652                                | 52.4                 | 597                                |
| 121.4                                            | 803                                | 84.3                 | 723                                | 75.7                 | 671                                | 61.7                 | 614                                |
| 127.6                                            | 809                                | 92.4                 | 736                                | 89.0                 | 688                                | 68.3                 | 625                                |
|                                                  |                                    | 103.9                | 753                                | 103.0                | 703                                | 84.7                 | 649                                |
|                                                  |                                    | 115.7                | 763                                | 114.7                | 715                                | 95.9                 | 663                                |
|                                                  |                                    | 125.0                | 773                                | 123.9                | 724                                | 103.9                | 673                                |
|                                                  |                                    |                      |                                    |                      |                                    | 113.3                | 683                                |
|                                                  |                                    |                      |                                    |                      |                                    | 125.4                | 696                                |
| $x_{\text{N}_2} = 0.685; w_{\text{N}_2} = 0.212$ |                                    |                      |                                    |                      |                                    |                      |                                    |
| $T/\text{K} = 394.7$                             |                                    | $T/\text{K} = 438.5$ |                                    | $T/\text{K} = 478.3$ |                                    | $T/\text{K} = 529.5$ |                                    |
| 127.5                                            | 730                                | 95.3                 | 676                                | 76.9                 | 630                                | 59.7                 | 566                                |
| 130.8                                            | 732                                | 100.9                | 682                                | 84.3                 | 640                                | 64.6                 | 576                                |
|                                                  |                                    | 107.5                | 690                                | 97.1                 | 657                                | 78.0                 | 600                                |
|                                                  |                                    | 113.9                | 696                                | 110.2                | 672                                | 90.7                 | 620                                |
|                                                  |                                    | 120.8                | 703                                | 120.2                | 682                                | 104.6                | 638                                |
|                                                  |                                    | 128.2                | 709                                | 128.7                | 690                                | 116.9                | 653                                |
|                                                  |                                    |                      |                                    |                      |                                    | 129.9                | 667                                |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and  $0.41$  MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K with the exclusion of the  $527.0$  K ( $u(T) = 0.8$  K) and  $528.6$  K ( $u(T) = 0.3$  K). The combined expanded uncertainties  $U_c$  are  $U_c(x_{\text{N}_2}) = 0.001$  and  $U_c(\rho) = 0.008 \cdot \rho$  kg·m<sup>-3</sup> with a coverage factor,  $k = 2$ .

Table S4. Continued: Densities,  $\rho$ , obtained in this study for single-phase, HXD + N<sub>2</sub> mixtures.

| $p/\text{MPa}$                                   | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{kg}\cdot\text{m}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{kg}\cdot\text{m}^{-3}$ |
|--------------------------------------------------|------------------------------------|----------------|------------------------------------|----------------|------------------------------------|----------------|------------------------------------|
| $x_{\text{N}_2} = 0.816; w_{\text{N}_2} = 0.354$ |                                    |                |                                    |                |                                    |                |                                    |
| T/K = 468.8                                      |                                    | T/K = 487.6    |                                    | T/K = 508.6    |                                    | T/K = 527.1    |                                    |
| 127.0                                            | 668                                | 110.3          | 635                                | 96.4           | 599                                | 85.5           | 566                                |
| 131.6                                            | 673                                | 114.6          | 641                                | 104.1          | 612                                | 91.8           | 579                                |
| 133.8                                            | 677                                | 121.4          | 651                                | 111.6          | 623                                | 97.5           | 589                                |
|                                                  |                                    | 127.5          | 658                                | 117.9          | 633                                | 105.8          | 603                                |
|                                                  |                                    | 133.1          | 665                                | 124.8          | 642                                | 111.2          | 612                                |
|                                                  |                                    |                |                                    | 130.7          | 650                                | 117.7          | 622                                |
|                                                  |                                    |                |                                    |                |                                    | 125.7          | 633                                |
|                                                  |                                    |                |                                    |                |                                    | 131.7          | 641                                |
| $x_{\text{N}_2} = 0.902; w_{\text{N}_2} = 0.533$ |                                    |                |                                    |                |                                    |                |                                    |
| T/K = 498.5                                      |                                    | T/K = 517.3    |                                    | T/K = 531.3    |                                    |                |                                    |
| 127.6                                            | 582                                | 110.2          | 544                                | 99.1           | 515                                |                |                                    |
| 131.4                                            | 592                                | 116.3          | 554                                | 104.7          | 524                                |                |                                    |
|                                                  |                                    | 123.9          | 568                                | 110.6          | 536                                |                |                                    |
|                                                  |                                    | 131.3          | 581                                | 117.6          | 549                                |                |                                    |
|                                                  |                                    |                |                                    | 124.1          | 561                                |                |                                    |
|                                                  |                                    |                |                                    | 131.0          | 572                                |                |                                    |

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.07$  MPa at  $p \leq 68.9$  MPa and  $0.41$  MPa at  $p > 68.9$  MPa and  $u(T) = 0.2$  K with the exclusion of the  $527.0$  K ( $u(T) = 0.8$  K) and  $528.6$  K ( $u(T) = 0.3$  K). The combined expanded uncertainties  $U_c$  are  $U_c(x_{\text{N}_2}) = 0.001$  and  $U_c(\rho) = 0.008 \cdot \rho$  kg·m<sup>-3</sup> with a coverage factor,  $k = 2$ .

Equation S1 is Antoine's equation used to interpolate BP/DP data sets and table S5 lists values for parameters  $A$ ,  $B$ , and  $C$  needed in equation S1.

$$\ln\left(\frac{p}{\text{MPa}}\right) = A - \frac{B}{T+C} \quad (\text{S1})$$

Table S5. Constants for Antoine's equation used to interpolate BP/DP isopleth data for HMN or HXD + N<sub>2</sub> mixtures at each N<sub>2</sub> mole fraction,  $x_{\text{N}_2}$ , and weight fraction,  $w_{\text{N}_2}$ . Refer to tables S1 and S2 for the applicable temperature range of application for Antoine's equation for each isopleth. The average, absolute percent deviation,  $\Delta_{\text{AAD}}$ , and maximum deviation,  $\Delta_{\text{max}}$  are also listed.

| $x_{\text{N}_2}$     | $w_{\text{N}_2}$ | $A$                     | $B$                     | $C$                  | $\Delta_{\text{AAD}}$ | $\Delta_{\text{max}}$ |
|----------------------|------------------|-------------------------|-------------------------|----------------------|-----------------------|-----------------------|
| HMN + N <sub>2</sub> |                  |                         |                         |                      |                       |                       |
| 0.149                | 0.021            | $8.5460 \cdot 10^{-1}$  | $-1.1442 \cdot 10^3$    | $4.2014 \cdot 10^2$  | 0.5                   | 1.0                   |
| 0.290                | 0.048            | $-7.8546 \cdot 10^{-1}$ | $-5.1832 \cdot 10^3$    | 1.0000E+03           | 0.2                   | 0.4                   |
| 0.392                | 0.074            | $-2.5289 \cdot 10^{-1}$ | $-4.4703 \cdot 10^3$    | $8.1203 \cdot 10^2$  | 0.7                   | 1.0                   |
| 0.571                | 0.141            | 2.2256                  | $-8.4731 \cdot 10^2$    | $7.2849 \cdot 10^1$  | 0.3                   | 0.5                   |
| 0.671                | 0.201            | 1.5823                  | $-1.5868 \cdot 10^3$    | $1.4632 \cdot 10^2$  | 0.5                   | 0.8                   |
| 0.760                | 0.282            | -10.625                 | $-4.2002 \cdot 10^4$    | $2.3264 \cdot 10^3$  | 0.2                   | 0.4                   |
| 0.773                | 0.296            | -21.732                 | $-1.1682 \cdot 10^5$    | $4.0000 \cdot 10^3$  | 0.3                   | 0.5                   |
| 0.874                | 0.463            | $-5.4273 \cdot 10^5$    | $-4.2700 \cdot 10^{13}$ | $7.8675 \cdot 10^7$  | 0.5                   | 0.8                   |
| 0.894                | 0.511            | $-3.5627 \cdot 10^5$    | $-1.7732 \cdot 10^{13}$ | $4.9769 \cdot 10^7$  | 0.3                   | 0.4                   |
| HXD + N <sub>2</sub> |                  |                         |                         |                      |                       |                       |
| 0.209                | 0.032            | 1.0993                  | $-8.4884 \cdot 10^2$    | $1.3410 \cdot 10^2$  | 0.3                   | 0.5                   |
| 0.290                | 0.048            | $7.8138 \cdot 10^{-1}$  | $-1.6725 \cdot 10^3$    | $3.3788 \cdot 10^2$  | 0.8                   | 1.3                   |
| 0.453                | 0.093            | 2.6123                  | $-3.2292 \cdot 10^2$    | $-1.0872 \cdot 10^2$ | 0.0                   | 0.0                   |
| 0.581                | 0.147            | 1.9800                  | $-1.0272 \cdot 10^3$    | $5.7106 \cdot 10^1$  | 0.4                   | 0.7                   |
| 0.685                | 0.212            | 1.2685                  | $-1.8005 \cdot 10^3$    | $1.0838 \cdot 10^2$  | 0.3                   | 0.4                   |
| 0.816                | 0.354            | 1.2548                  | $-1.6971 \cdot 10^3$    | 3.9246               | 0.3                   | 0.4                   |
| 0.902                | 0.533            | -3.9896                 | $-9.8479 \cdot 10^3$    | $6.1571 \cdot 10^2$  | 0.0                   | 0.0                   |

Single phase, mixture density data are correlated with the Tait equation, equations S2. This application of the Tait equation uses a reference density,  $\rho_0(T)$ , calculated at  $p_0$  equal to the BP/DP pressure at each  $T$ - $x_{N2}$  value calculated with Antoine's equation. Values for parameters  $C$ ,  $a_0$ ,  $a_1$ ,  $a_2$ ,  $b_0$ ,  $b_1$ , and  $b_2$  are found in tables S5 and S6.

$$\frac{\rho - \rho_0(T)}{\rho} = C \log_{10} \left( \frac{P + B(T)}{P_0 + B(T)} \right) \quad (S2)$$

$$\rho_0(T)/kg \cdot m^{-3} = \sum_{i=0}^2 a_i T^i \quad (S3)$$

$$B(T)/MPa = \sum_{i=0}^2 b_i T^i \quad (S4)$$

Table S6a. Tait parameters for mixture density calculations for HMN + N<sub>2</sub> mixtures for each isopleth listed with the  $\Delta_{AAD}$ ,  $\Delta_{max}$ , and the temperature-pressure ranges fit to the equation. Tait parameters for pure HMN are taken from Rowane et al.<sup>1</sup>

|                   |                         |                         |                         |                         |                         |                        |                        |                        |
|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------------------------|------------------------|------------------------|
| XN <sub>2</sub> : | 0                       | 0.145                   | 0.392                   | 0.571                   | 0.671                   | 0.760                  | 0.773                  | 0.874                  |
| WN <sub>2</sub> : | 0                       | 0.021                   | 0.074                   | 0.141                   | 0.201                   | 0.282                  | 0.296                  | 0.463                  |
| C:                | 0.2166                  | 0.2077                  | 0.2969                  | 0.2387                  | 0.3274                  | 0.4573                 | 0.6048                 | 0.6324                 |
| $a_2$ :           | $-1.9816 \cdot 10^{-4}$ | $-3.1470 \cdot 10^{-4}$ | $-5.3393 \cdot 10^{-4}$ | $4.8878 \cdot 10^{-4}$  | $-3.5305 \cdot 10^{-4}$ | $5.2342 \cdot 10^{-4}$ | $1.8416 \cdot 10^{-4}$ | $8.0139 \cdot 10^{-5}$ |
| $a_1$ :           | $-5.0985 \cdot 10^{-1}$ | $-4.7398 \cdot 10^{-1}$ | $-3.1585 \cdot 10^{-1}$ | -1.3768                 | $-8.6079 \cdot 10^{-1}$ | -2.0549                | -1.8164                | -2.2699                |
| $a_0$ :           | $9.4778 \cdot 10^2$     | $9.3101 \cdot 10^2$     | $9.0605 \cdot 10^2$     | $1.1526 \cdot 10^3$     | $1.1072 \cdot 10^3$     | $1.4757 \cdot 10^3$    | $1.4330 \cdot 10^3$    | $1.6593 \cdot 10^3$    |
| $b_2$ :           | $6.6635 \cdot 10^{-4}$  | $7.5075 \cdot 10^{-4}$  | $7.8070 \cdot 10^{-4}$  | $8.3186 \cdot 10^{-4}$  | $8.6845 \cdot 10^{-4}$  | $4.1145 \cdot 10^{-3}$ | $2.1803 \cdot 10^{-3}$ | $2.2882 \cdot 10^{-3}$ |
| $b_1$ :           | $-8.9215 \cdot 10^{-1}$ | $-8.6166 \cdot 10^{-1}$ | $-9.7974 \cdot 10^{-1}$ | $-7.7500 \cdot 10^{-1}$ | $-9.5265 \cdot 10^{-1}$ | -4.2046                | -2.3543                | -2.3593                |
| $b_0$ :           | $3.1015 \cdot 10^2$     | $2.5144 \cdot 10^2$     | $3.0754 \cdot 10^2$     | $1.5804 \cdot 10^2$     | $2.3909 \cdot 10^2$     | $1.0564 \cdot 10^3$    | $6.3004 \cdot 10^2$    | $5.8430 \cdot 10^2$    |
| $\Delta_{AAD}$ :  | 0.1                     | 0.2                     | 0.2                     | 0.2                     | 0.1                     | 0.2                    | 0.3                    | 0.1                    |
| $\Delta_{MAX}$ :  | 0.4                     | 0.5                     | 0.9                     | 1.1                     | 0.2                     | 0.5                    | 0.4                    | 0.6                    |
| T/K               | 298 - 522               | 298 - 527               | 306 - 527               | 298 - 519               | 356 - 527               | 423 - 529              | 441 - 533              | 493 - 533              |
| p/MPa             | 4 - 174                 | BP* - 99                | BP* - 100               | BP* - 100               | BP* - 127               | BP* - 129              | BP*- 101               | DP* - 129              |

BP\*, DP\* -- The minimum pressure is equal to the BP/DP at a given temperature for each mixture.

Table S6b. Tait parameters for mixture density calculations for HXD + N<sub>2</sub> mixtures for each isopleth listed with the  $\Delta_{\text{AAD}}$ ,  $\Delta_{\text{max}}$ , and the temperature-pressure ranges fit to the equation. Tait parameters for pure HXD are taken from Rowane et al.<sup>1</sup>

|                         |                          |                          |                          |                          |                          |                          |                          |                          |
|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| XN <sub>2</sub> :       | 0                        | 0.209                    | 0.290                    | 0.453                    | 0.581                    | 0.686                    | 0.816                    | 0.902                    |
| WN <sub>2</sub> :       | 0                        | 0.032                    | 0.048                    | 0.093                    | 0.147                    | 0.212                    | 0.354                    | 0.533                    |
| C:                      | 0.21                     | 0.2025                   | 0.2513                   | 0.2793                   | 0.3183                   | 0.3334                   | 0.4023                   | 1.1791                   |
| a <sub>2</sub> :        | -2.2800•10 <sup>-4</sup> | 4.2827•10 <sup>-4</sup>  | -4.5110•10 <sup>-4</sup> | -1.3120•10 <sup>-4</sup> | 1.2020•10 <sup>-3</sup>  | -5.6523•10 <sup>-5</sup> | 3.1774•10 <sup>-4</sup>  | -3.0804•10 <sup>-3</sup> |
| a <sub>1</sub> :        | -5.3980•10 <sup>-1</sup> | -1.1085                  | -3.8873•10 <sup>-1</sup> | -7.0477•10 <sup>-1</sup> | -2.0846                  | -1.1628                  | -2.0540                  | 1.1020                   |
| a <sub>0</sub> :        | 9.5090•10 <sup>2</sup>   | 1.0562•10 <sup>3</sup>   | 9.0966•10 <sup>2</sup>   | 9.9523•10 <sup>2</sup>   | 1.3402•10 <sup>3</sup>   | 1.1979•10 <sup>3</sup>   | 1.5610•10 <sup>3</sup>   | 7.9898•10 <sup>2</sup>   |
| b <sub>2</sub> :        | 9.8970•10 <sup>-4</sup>  | 6.7512•10 <sup>-4</sup>  | 4.1450•10 <sup>-4</sup>  | -8.1536•10 <sup>-5</sup> | 5.2864•10 <sup>-4</sup>  | 1.1140•10 <sup>-3</sup>  | -3.4550•10 <sup>-3</sup> | -6.9053•10 <sup>-3</sup> |
| b <sub>1</sub> :        | -1.191                   | -7.4976•10 <sup>-1</sup> | -5.4141•10 <sup>-1</sup> | -1.2693•10 <sup>-1</sup> | -5.2003•10 <sup>-1</sup> | -1.2490                  | 3.5381                   | 6.7162                   |
| b <sub>0</sub> :        | 3.7410•10 <sup>2</sup>   | 2.0975•10 <sup>2</sup>   | 1.7818•10 <sup>2</sup>   | 8.5495•10 <sup>1</sup>   | 1.1839•10 <sup>2</sup>   | 3.2744•10 <sup>2</sup>   | -9.4192•10 <sup>2</sup>  | -1.5720•10 <sup>3</sup>  |
| $\Delta_{\text{AAD}}$ : | 0.2                      | 0.2                      | 0.2                      | 0.1                      | 0.2                      | 0.0                      | 0.0                      | 0.1                      |
| $\Delta_{\text{MAX}}$ : | 0.5                      | 0.6                      | 0.9                      | 0.2                      | 0.7                      | 0.1                      | 0.1                      | 0.4                      |
| T <sub>range</sub> /K   | 323 - 526                | 323 - 525                | 325 - 536                | 327 - 459                | 325 - 529                | 395 - 529                | 469 - 527                | 499 - 531                |
| p <sub>range</sub> /MPa | 4 - 210                  | BP* - 130                | BP* - 128                | BP* - 128                | BP* - 131                | BP* - 135                | BP* - 138                | BP* - 135                |

BP\* -- The minimum pressure is equal to the BP at a given temperature for each mixture.

## Modeling Mixture Densities

Table S7 lists the results for mixture density calculations for both HXD + N<sub>2</sub> and HMN + N<sub>2</sub> mixtures using the PC-SAFT EoS with T-GC<sup>2</sup> and S-GC<sup>3</sup> pure component parameters and with  $k_{ij} = 0$ . Both sets of GC parameters give identical  $\Delta_{AAD}$  values. However, the values of the  $\Delta_{bias}$  indicate that mixture densities are over predicted using the T-GC method and under predicted using the S-GC method, by almost the same absolute percentages. Although not shown here, better mixture density predictions are found using GC parameters reported by Burgess, et al.<sup>4</sup>, which is not unexpected since Burgess regressed GC parameters from HPHT density data sets, while Sauer and Tihic both regressed parameters from low pressure, vapor pressure and saturated liquid density data. Table 3 also shows that mixture density calculations for the HMN + N<sub>2</sub> system are predicted slightly better using the PC-SAFT EoS with T-GC pure component parameters and with  $k_{ij} = 0$ . With both sets of pure component parameters the bias is negative although the results using the T-GC method are again slightly better than the results using the S-GC method.

Table S7. Results for PC-SAFT predicted mixture densities with GC-calculated pure component parameters and with  $k_{ij} = 0$  for HXD + N<sub>2</sub> mixtures (a) Tihic's GC method and (b) Sauer's GC method and for HMN + N<sub>2</sub> mixtures (c) Tihic's GC method and (d) Sauer's GC method.

| (a) HXD + N <sub>2</sub> (T-GC Method) |       |       |       |       |       |       |       |         |
|----------------------------------------|-------|-------|-------|-------|-------|-------|-------|---------|
| $x_{N_2}$                              | 0.209 | 0.290 | 0.452 | 0.581 | 0.685 | 0.816 | 0.902 | Overall |
| $\Delta_{AAD}$                         | 1.9   | 3.2   | 2.6   | 3.1   | 5.7   | 3.9   | 5.9   | 3.5     |
| $\Delta_{bias}$                        | -1.9  | -3.2  | -2.6  | -3.1  | -5.7  | -3.9  | -5.9  | -3.5    |
| $\Delta_{stdev}$                       | 0.6   | 0.8   | 0.3   | 1.4   | 0.6   | 0.4   | 0.3   | 1.5     |
| $\Delta_{max}$                         | 3.8   | 5.4   | 3.3   | 5.2   | 7.1   | 4.8   | 6.4   | 7.1     |
| Data points                            | 30    | 33    | 21    | 27    | 21    | 22    | 12    | 166     |

(b) HXD + N<sub>2</sub> (S-GC Method)

|                  |       |       |       |       |       |       |       |         |
|------------------|-------|-------|-------|-------|-------|-------|-------|---------|
| $x_{N_2}$        | 0.209 | 0.290 | 0.452 | 0.581 | 0.685 | 0.816 | 0.902 | Overall |
| $\Delta_{AAD}$   | 5.7   | 4.4   | 4.4   | 3.6   | 0.6   | 0.9   | 2.8   | 3.5     |
| $\Delta_{bias}$  | 5.7   | 4.4   | 4.4   | 3.6   | 0.4   | 0.9   | -2.8  | 3.0     |
| $\Delta_{stdev}$ | 0.4   | 0.6   | 0.2   | 1.2   | 0.3   | 0.4   | 0.3   | 1.9     |
| $\Delta_{max}$   | 6.4   | 5.0   | 4.8   | 5.6   | 1.1   | 1.5   | 3.3   | 6.4     |
| Data points      | 30    | 33    | 21    | 27    | 21    | 22    | 12    | 166     |

(c) HMN + N<sub>2</sub> (T-GC Method)

|                  |       |       |       |       |       |       |       |       |         |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|---------|
| $x_{N_2}$        | 0.149 | 0.392 | 0.571 | 0.671 | 0.760 | 0.773 | 0.874 | 0.894 | Overall |
| $\Delta_{AAD}$   | 3.0   | 4.0   | 5.8   | 6.1   | 5.2   | 9.2   | 9.9   | 6.5   | 5.5     |
| $\Delta_{bias}$  | -3.0  | -4.0  | -5.8  | -6.1  | -5.2  | -9.2  | -9.9  | -6.5  | -5.5    |
| $\Delta_{stdev}$ | 0.5   | 0.4   | 1.2   | 1.2   | 1.1   | 1.2   | 1.1   | 0.6   | 2.3     |
| $\Delta_{max}$   | 4.1   | 5.0   | 8.3   | 8.9   | 7.7   | 11.5  | 11.7  | 7.8   | 11.7    |
| Data points      | 33    | 29    | 23    | 10    | 36    | 19    | 17    | 16    | 183     |

(d) HMN + N<sub>2</sub> (S-GC Method)

|                  |       |       |       |       |       |       |       |       |         |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|---------|
| $x_{N_2}$        | 0.149 | 0.392 | 0.571 | 0.671 | 0.760 | 0.773 | 0.874 | 0.894 | Overall |
| $\Delta_{AAD}$   | 7.4   | 8.2   | 9.7   | 9.7   | 8.3   | 9.2   | 9.0   | 6.4   | 8.3     |
| $\Delta_{bias}$  | -7.4  | -8.2  | -9.7  | -9.7  | -8.3  | -9.2  | -9.0  | -6.4  | -8.3    |
| $\Delta_{stdev}$ | 0.6   | 0.5   | 1.4   | 1.4   | 1.2   | 1.2   | 1.41  | 0.8   | 1.6     |
| $\Delta_{max}$   | 9.7   | 9.7   | 12.7  | 12.8  | 11.0  | 11.6  | 11.8  | 7.3   | 12.8    |
| Data points      | 33    | 29    | 23    | 10    | 36    | 19    | 17    | 16    | 183     |

## Modeling VLE

Tables S8a to S8d are the results from a comparison of Antoine-calculated  $p$ - $x_{N_2}$  isotherms at 323, 373, 423, 473, and 523 K for HXD + N<sub>2</sub> mixtures with PC-SAFT-calculated values with pure component parameters calculated with the two GC methods when  $k_{ij} = 0$ . The PC-SAFT-calculated isotherms severely under predict the experimental isotherms using either GC method when  $k_{ij} = 0$ . However, the results listed in tables S9a to S9d demonstrate that the agreement between predicted and observed phase behavior for both mixtures improves considerably with both GC methods when  $k_{ij}$  is set to a nonzero, positive value, reflecting the much higher sensitivity of phase behavior calculations to values of  $\varepsilon/k$ , the energetic parameter.

Table S8. Results for PC-SAFT predictions of BP/DP pressures with GC-calculated pure component parameters and with  $k_{ij} = 0$  for HXD + N<sub>2</sub> mixtures (a) Tihic's GC method and (b) Sauer's GC method and for HMN + N<sub>2</sub> mixtures (c) Tihic's GC method and (d) Sauer's GC method.

| (a) HXD + N <sub>2</sub> (S-GC Method) |     |     |     |     |     |         |
|----------------------------------------|-----|-----|-----|-----|-----|---------|
| T/K                                    | 323 | 373 | 423 | 473 | 530 | Overall |
| $\Delta_{AAD}$                         | 62  | 54  | 50  | 47  | 48  | 51      |
| $\Delta_{bias}$                        | 62  | 54  | 50  | 47  | 48  | 51      |
| $\Delta_{stdev}$                       | 4   | 3   | 6   | 6   | 6   | 7       |
| $\Delta_{Max}$                         | 67  | 58  | 59  | 57  | 59  | 67      |

  

| (b) HXD + N <sub>2</sub> (T-GC Method) |     |     |     |     |     |         |
|----------------------------------------|-----|-----|-----|-----|-----|---------|
| T/K                                    | 323 | 373 | 423 | 473 | 530 | Overall |
| $\Delta_{AAD}$                         | 58  | 48  | 44  | 40  | 38  | 45      |
| $\Delta_{bias}$                        | 58  | 48  | 44  | 40  | 38  | 45      |
| $\Delta_{stdev}$                       | 5   | 4   | 7   | 7   | 5   | 9       |
| $\Delta_{Max}$                         | 64  | 53  | 55  | 51  | 46  | 64      |

  

| (c) HMN + N <sub>2</sub> (S-GC Method) |     |     |     |     |     |         |
|----------------------------------------|-----|-----|-----|-----|-----|---------|
| T/K                                    | 323 | 373 | 423 | 473 | 530 | Overall |
| $\Delta_{AAD}$                         | 56  | 50  | 43  | 36  | 39  | 41      |
| $\Delta_{bias}$                        | 56  | 50  | 43  | 36  | 39  | 41      |
| $\Delta_{stdev}$                       | 4   | 6   | 5   | 5   | 24  | 10      |

|                       |    |    |    |    |     |    |
|-----------------------|----|----|----|----|-----|----|
| $\Delta_{\text{Max}}$ | 62 | 59 | 49 | 46 | 100 | 62 |
|-----------------------|----|----|----|----|-----|----|

  

| (d) HMN + N <sub>2</sub> (T-GC Method) |     |     |     |     |     |         |
|----------------------------------------|-----|-----|-----|-----|-----|---------|
| T/K                                    | 323 | 373 | 423 | 473 | 530 | Overall |
| $\Delta_{\text{AAD}}$                  | 57  | 52  | 45  | 41  | 37  | 44      |
| $\Delta_{\text{bias}}$                 | 57  | 52  | 45  | 41  | 37  | 44      |
| $\Delta_{\text{stdev}}$                | 4   | 6   | 5   | 5   | 5   | 8       |
| $\Delta_{\text{Max}}$                  | 62  | 61  | 51  | 50  | 46  | 62      |

Table S9. Results for PC-SAFT predictions of BP/DP pressures with GC-calculated pure component parameters using the best-fit  $k_{ij}$  for HXD + N<sub>2</sub> mixtures (a) Tihic's GC method and (b) Sauer's GC method and for HMN + N<sub>2</sub> mixtures (c) Tihic's GC method and (d) Sauer's GC method.

| (a) HXD + N <sub>2</sub> (S-GC Method) |     |     |     |     |     |         |
|----------------------------------------|-----|-----|-----|-----|-----|---------|
| T/K                                    | 323 | 373 | 423 | 473 | 530 | Overall |
| $\Delta_{\text{AAD}}$                  | 21  | 8   | 11  | 12  | 18  | 14      |
| $\Delta_{\text{bias}}$                 | -12 | 7   | 11  | 12  | 18  | 9       |
| $\Delta_{\text{stdev}}$                | 25  | 6   | 5   | 6   | 8   | 11      |
| $\Delta_{\text{Max}}$                  | 57  | 17  | 18  | 20  | 26  | 57      |

  

| (b) HXD + N <sub>2</sub> (T-GC Method) |     |     |     |     |     |         |
|----------------------------------------|-----|-----|-----|-----|-----|---------|
| T/K                                    | 323 | 373 | 423 | 473 | 530 | Overall |
| $\Delta_{\text{AAD}}$                  | 11  | 4   | 6   | 6   | 10  | 7       |
| $\Delta_{\text{bias}}$                 | -5  | 3   | 6   | 5   | 10  | 5       |
| $\Delta_{\text{stdev}}$                | 10  | 5   | 5   | 4   | 5   | 6       |
| $\Delta_{\text{Max}}$                  | 24  | 11  | 11  | 12  | 16  | 24      |

  

| (c) HMN + N <sub>2</sub> (S-GC Method) |     |     |     |     |     |         |
|----------------------------------------|-----|-----|-----|-----|-----|---------|
| T/K                                    | 323 | 373 | 423 | 473 | 530 | Overall |
| $\Delta_{\text{AAD}}$                  | 6   | 7   | 5   | 13  | 13  | 10      |
| $\Delta_{\text{bias}}$                 | 6   | 7   | 4   | -8  | -8  | -2      |
| $\Delta_{\text{stdev}}$                | 6   | 6   | 5   | 16  | 14  | 12      |
| $\Delta_{\text{Max}}$                  | 13  | 14  | 14  | 51  | 46  | 51      |

| (d) HMN + N <sub>2</sub> (T-GC Method) |     |     |     |     |     |         |
|----------------------------------------|-----|-----|-----|-----|-----|---------|
| T/K                                    | 323 | 373 | 423 | 473 | 530 | Overall |
| $\Delta_{\text{AAD}}$                  | 7   | 8   | 6   | 13  | 12  | 10      |
| $\Delta_{\text{bias}}$                 | 3   | 8   | 6   | -4  | 2   | 2       |
| $\Delta_{\text{stdev}}$                | 6   | 6   | 7   | 15  | 10  | 10      |
| $\Delta_{\text{Max}}$                  | 14  | 16  | 18  | 49  | 31  | 49      |

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