Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information
# Fluid phase interface properties of acetone, oxygen, nitrogen and their binary mixtures by molecular simulation

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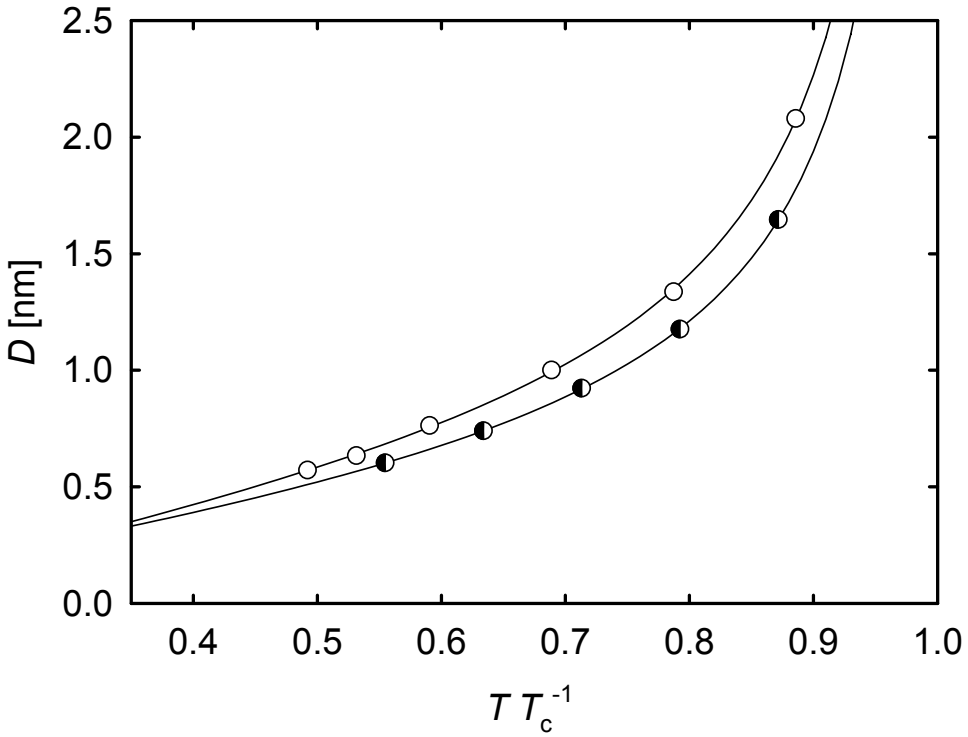


**Figure 1** Width of the interface over the reduced temperature $T\,T_c^{-1}$ of acetone and nitrogen. The results for nitrogen are only given as comparison. ○ acetone; ◐ nitrogen. The lines represent the empirical correlation[1] $D = a(1-T/T_c)^b + c(1-T/T_c)^{-0.63}$ fitted to the data. For the determination of the critical temperatures, the parameters of the corresponding EOS were applied.[2,3] The statistical uncertainties of the simulation data are considered as the standard error on a 95 % confidence interval and are within the symbol size.

**Table 1** Parameters of the force field models of acetone,[4] oxygen[5] and nitrogen.[5] The position of the interaction site is refered to as $x$, $y$ and $z$ with respect to the center of mass. The Lennard–Jones size and energy parameters $\sigma$ and $\varepsilon$ as well as the dipole and quadrupole moments $\mu$ and $Q$ are given. Lennard–Jones interaction sites are denoted by the modeled atoms or atomic groups and electrostatic interaction sites are denoted by dipole or quadrupole, respectively. Orientations of the electrostatic sites are defined in standard Euler angles, where $\varphi$ is the azimuthal angle with respect to the $x$–$z$ plane and $\theta$ is the inclination angle with respect to the $z$ axis

| site | $x$ | $y$ | $z$ | $\sigma$ | $\varepsilon/k_\mathrm{B}$ | $\theta$ | $\varphi$ | $\mu$ | $Q$ |
|---|---|---|---|---|---|---|---|---|---|
| | Å | Å | Å | Å | K | deg | deg | D | DÅ |
| acetone | | | | | | | | | |
| C | 0 | 0 | 0 | 2.9307 | 9.8216 | | | | |
| O | 0 | 1.2095 | 0 | 3.3704 | 106.9873 | | | | |
| CH3 | 0 | -0.8031 | 1.2853 | 3.6225 | 111.9795 | | | | |
| CH3 | 0 | -0.8031 | -1.2853 | 3.6225 | 111.9795 | | | | |
| dipole | 0 | 0 | 0 | | | 90 | 90 | 3.4448 | |
| quadrupole | 0 | -0.8031 | 0 | | | 90 | 90 | | 0.7308 |
| oxygen | | | | | | | | | |
| O | 0 | 0 | -0.48495 | 3.1062 | 43.183 | | | | |
| O | 0 | 0 | 0.48495 | 3.1062 | 43.183 | | | | |
| quadrupole | 0 | 0 | 0 | | | 0 | 0 | | -0.8081 |
| nitrogen | | | | | | | | | |
| N | 0 | 0 | -0.5232 | 3.3211 | 34.897 | | | | |
| N | 0 | 0 | 0.5232 | 3.3211 | 34.897 | | | | |
| quadrupole | 0 | 0 | 0 | | | 0 | 0 | | -1.4397 |

**Table 2** The binary interaction parameter $\xi_{AB}$ for oxygen + nitrogen,[6] oxygen + acetone[4] and nitrogen + acetone.[4] This parameter was used to modify the Lorentz–Berthelot combining rule to adjust the Lennard–Jones energy parameter $\varepsilon_{AB} = \xi_{AB}\sqrt{\varepsilon_A \varepsilon_B}$ between two unlike molecules $A$ and $B$ in preceding work to one experimental data point of vapor pressure or the Henry's law constant

| molecule | | $\xi_{AB}$ |
|---|---|---|
| $A$ | $B$ | |
| oxygen | nitrogen | 1.007 |
| oxygen | acetone | 0.905 |
| nitrogen | acetone | 0.96 |

**Table 3** Details of the initial simulation setup for the pure substances acetone, oxygen and nitrogen. The temperature $T$, the molar densities of the liquid and vapor bulk phase $\rho_\mathrm{l}$ and $\rho_\mathrm{v}$, the number of molecules $N$ as well as the dimensions of the simulation volume $l_{\mathrm{x/y}}$ and $l_\mathrm{z}$ are given

| $T$ | $\rho_\mathrm{l}$ | $\rho_\mathrm{v}$ | $N$ | $l_{\mathrm{x/y}}$ | $l_\mathrm{z}$ |
|---|---|---|---|---|---|
| K | $\mathrm{mol\,l^{-1}}$ | $\mathrm{mol\,l^{-1}}$ | | nm | nm |
| acetone | | | | | |
| 250 | 14.41 | 0.00115 | 32 000 | 15.45 | 51.89 |
| 270 | 14.04 | 0.00354 | 32 000 | 15.58 | 46.72 |
| 300 | 13.47 | 0.0137 | 32 000 | 15.79 | 47.11 |
| 350 | 12.46 | 0.0732 | 32 000 | 16.15 | 48.71 |
| 400 | 11.29 | 0.255 | 32 000 | 16.51 | 49.73 |
| 450 | 9.80 | 0.735 | 32 000 | 16.77 | 50.49 |
| oxygen | | | | | |
| 60 | 40.06 | 0.00446 | 32 000 | 10.99 | 35.89 |
| 80 | 37.20 | 0.0459 | 32 000 | 11.25 | 33.74 |
| 100 | 34.09 | 0.326 | 32 000 | 11.52 | 34.76 |
| 120 | 30.43 | 1.23 | 32 000 | 11.73 | 35.40 |
| 140 | 25.42 | 3.65 | 32 000 | 11.76 | 35.46 |
| nitrogen | | | | | |
| 70 | 29.93 | 0.0677 | 32 000 | 12.09 | 36.46 |
| 80 | 28.34 | 0.217 | 32 000 | 12.27 | 37.03 |
| 90 | 26.60 | 0.538 | 32 000 | 12.43 | 37.47 |
| 100 | 24.61 | 1.14 | 32 000 | 12.55 | 37.85 |
| 110 | 22.18 | 2.23 | 32 000 | 12.59 | 37.96 |

**Table 4** Details of the initial simulation setup for the mixture oxygen + nitrogen with an equimolar liquid bulk composition. The temperature $T$, the oxygen mole fraction of the vapor bulk phase $y_{\mathrm{O2}}$, the molar densities of the liquid and vapor bulk phase $\rho_\mathrm{l}$ and $\rho_\mathrm{v}$, the number of molecules $N$ as well as the dimensions of the simulation volume $l_{\mathrm{x/y}}$ and $l_\mathrm{z}$ are given

| $T$ | $y_{\mathrm{O2}}$ | $\rho_\mathrm{l}$ | $\rho_\mathrm{v}$ | $N$ | $l_{\mathrm{x/y}}$ | $l_\mathrm{z}$ |
|---|---|---|---|---|---|---|
| K | $\mathrm{mol\,mol^{-1}}$ | $\mathrm{mol\,l^{-1}}$ | $\mathrm{mol\,l^{-1}}$ | | nm | nm |
| 70 | 0.146 | 34.04 | 0.0405 | 32 000 | 11.59 | 34.97 |
| 80 | 0.191 | 32.54 | 0.134 | 32 000 | 11.74 | 35.51 |
| 90 | 0.235 | 30.94 | 0.337 | 32 000 | 11.89 | 35.89 |
| 100 | 0.278 | 29.20 | 0.712 | 32 000 | 12.02 | 36.25 |
| 110 | 0.318 | 27.25 | 1.35 | 32 000 | 12.11 | 36.52 |
| 120 | 0.358 | 24.93 | 2.42 | 32 000 | 12.13 | 36.59 |
| 130 | 0.401 | 21.87 | 4.31 | 32 000 | 12.03 | 36.30 |

**Table 5** Details of the initial simulation setup for the mixture oxygen + acetone. The temperature $T$, the oxygen mole fraction of the liquid and vapor bulk phase $x_{O2}$ and $y_{O2}$, the molar densities of the liquid and vapor bulk phase $\rho_l$ and $\rho_v$, the number of molecules $N$ as well as the dimensions of the simulation volume $l_{x/y}$ and $l_z$ are given

| $T$ | $x_{O2}$ | $y_{O2}$ | $\rho_l$ | $\rho_v$ | $N$ | $l_{x/y}$ | $l_z$ |
|---|---|---|---|---|---|---|---|
| K | $mol\,mol^{-1}$ | $mol\,mol^{-1}$ | $mol\,l^{-1}$ | $mol\,l^{-1}$ | | nm | nm |
| 400 | 0.00 | 0.000 | 11.29 | 0.255 | 32 000 | 16.51 | 49.73 |
| 400 | 0.05 | 0.813 | 11.44 | 1.73 | 32 000 | 15.28 | 46.03 |
| 400 | 0.10 | 0.882 | 11.71 | 3.21 | 32 000 | 14.31 | 43.13 |
| 400 | 0.15 | 0.892 | 12.01 | 4.83 | 32 000 | 13.48 | 40.65 |
| 400 | 0.20 | 0.905 | 12.25 | 6.15 | 32 000 | 12.94 | 39.01 |
| 400 | 0.24 | 0.899 | 12.52 | 7.40 | 32 000 | 12.48 | 37.65 |
| 400 | 0.26 | 0.901 | 12.60 | 7.78 | 32 000 | 12.36 | 37.27 |
| 450 | 0.00 | 0.000 | 9.80 | 0.735 | 32 000 | 16.77 | 50.49 |
| 450 | 0.04 | 0.471 | 9.70 | 1.58 | 32 000 | 16.05 | 48.35 |
| 450 | 0.05 | 0.508 | 9.87 | 1.88 | 32 000 | 15.74 | 47.42 |
| 450 | 0.10 | 0.648 | 9.89 | 2.75 | 32 000 | 15.11 | 45.54 |
| 450 | 0.15 | 0.697 | 9.94 | 3.71 | 32 000 | 14.52 | 43.76 |
| 450 | 0.20 | 0.733 | 9.96 | 4.41 | 48 000 | 14.14 | 63.85 |
| 450 | 0.24 | 0.757 | 10.11 | 5.08 | 48 000 | 13.79 | 62.25 |
| 450 | 0.26 | 0.771 | 9.99 | 4.92 | 48 000 | 13.89 | 62.70 |

**Table 6** Details of the initial simulation setup for the mixture nitrogen + acetone. The temperature $T$, the nitrogen mole fraction of the liquid and vapor bulk phase $x_{N2}$ and $y_{N2}$, the molar densities of the liquid and vapor bulk phase $\rho_l$ and $\rho_v$, the number of molecules $N$ as well as the dimensions of the simulation volume $l_{x/y}$ and $l_z$ are given

| $T$ | $x_{N2}$ | $y_{N2}$ | $\rho_l$ | $\rho_v$ | $N$ | $l_{x/y}$ | $l_z$ |
|---|---|---|---|---|---|---|---|
| K | $mol\,mol^{-1}$ | $mol\,mol^{-1}$ | $mol\,l^{-1}$ | $mol\,l^{-1}$ | | nm | nm |
| 400 | 0.00 | 0.000 | 11.29 | 0.255 | 32 000 | 16.51 | 49.73 |
| 400 | 0.05 | 0.837 | 11.50 | 2.07 | 32 000 | 15.03 | 45.30 |
| 400 | 0.10 | 0.870 | 11.75 | 3.99 | 32 000 | 13.91 | 41.94 |
| 400 | 0.16 | 0.891 | 12.07 | 6.02 | 32 000 | 13.01 | 39.24 |
| 400 | 0.24 | 0.870 | 12.56 | 8.70 | 32 000 | 12.10 | 36.51 |
| 400 | 0.32 | 0.849 | 13.00 | 10.70 | 48 000 | 11.56 | 52.22 |
| 450 | 0.00 | 0.000 | 9.80 | 0.735 | 32 000 | 16.77 | 50.49 |
| 450 | 0.04 | 0.487 | 9.67 | 1.69 | 32 000 | 15.96 | 48.09 |
| 450 | 0.05 | 0.527 | 9.65 | 1.88 | 32 000 | 15.82 | 47.67 |
| 450 | 0.10 | 0.640 | 9.94 | 3.21 | 32 000 | 14.81 | 44.63 |
| 450 | 0.15 | 0.670 | 10.07 | 4.38 | 48 000 | 14.13 | 63.79 |
| 450 | 0.22 | 0.670 | 10.20 | 6.00 | 48 000 | 13.38 | 60.40 |
| 450 | 0.26 | 0.650 | 10.30 | 6.70 | 48 000 | 13.09 | 59.10 |

**Table 7** Simulation results of acetone, oxygen and nitrogen for given temperature. The number in brackets indicates the standard error on a 95 % confidence interval in the last digit

| $T$ | $\rho_\mathrm{l}$ | $\rho_\mathrm{v}$ | $D$ | $\gamma$ |
|---|---|---|---|---|
| K | $\mathrm{mol\,l^{-1}}$ | $\mathrm{mol\,l^{-1}}$ | nm | $\mathrm{mN\,m^{-1}}$ |
| | | acetone | | |
| 250 | 14.478 (2) | 0.0010 (3) | 0.57 (1) | 32.1 (5) |
| 270 | 14.090 (2) | 0.0027 (4) | 0.63 (1) | 29.5 (5) |
| 300 | 13.496 (2) | 0.019 (1) | 0.76 (1) | 24.7 (5) |
| 350 | 12.434 (3) | 0.084 (1) | 1.000 (7) | 17.7 (4) |
| 400 | 11.206 (8) | 0.279 (3) | 1.34 (1) | 11.3 (4) |
| 450 | 9.65 (1) | 0.834 (8) | 2.08 (3) | 5.0 (3) |
| | | oxygen | | |
| 60 | 40.156 (5) | 0.0086 (6) | 0.348 (6) | 23.6 (6) |
| 80 | 37.222 (6) | 0.044 (3) | 0.511 (6) | 17.6 (4) |
| 100 | 34.029 (7) | 0.349 (8) | 0.722 (8) | 12.1 (3) |
| 120 | 30.35 (2) | 1.24 (1) | 1.07 (2) | 7.0 (3) |
| 140 | 25.46 (6) | 3.63 (4) | 1.86 (5) | 2.6 (2) |
| | | nitrogen | | |
| 70 | 29.962 (5) | 0.067 (2) | 0.602 (7) | 11.8 (3) |
| 80 | 28.307 (6) | 0.244 (3) | 0.740 (7) | 9.1 (3) |
| 90 | 26.516 (8) | 0.57 (1) | 0.92 (1) | 6.9 (2) |
| 100 | 24.51 (2) | 1.19 (1) | 1.18 (2) | 4.5 (2) |
| 110 | 22.13 (3) | 2.30 (1) | 1.65 (3) | 2.5 (2) |

# References


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