# Supporting Information

## Viscosities of pure ionic liquids using combinations of free volume theory or friction theory with the cubic, the CPA, and the PC-SAFT equations of state at high pressures

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Table S1. Physical properties of the investigated ionic liquids in this study.

| Compound | MW (g/mol) | $T_c$ (K) | $P_c$ (MPa) | $V_c$ ($cm^3$/mol) | ω | Ref. |
|---|---|---|---|---|---|---|
| $[C_2mim][BF_4]$ | 197.97 | 585.3 | 2.36 | 557.8 | 0.7685 | 69 |
| $[C_4mim][BF_4]$ | 226.02 | 746.1 | 2.68 | 624.6 | 0.4160 | 70 |
| $[C_6mim][BF_4]$ | 254.08 | 679.1 | 1.79 | 786.2 | 0.9258 | 69 |
| $[C_4mim][PF_6]$ | 284.18 | 503.7 | 1.80 | 653.8 | 0.2633 | 70 |
| $[C_6mim][PF_6]$ | 312.24 | 518.6 | 1.63 | 774.4 | 0.2695 | 70 |
| $[C_8mim][PF_6]$ | 340.29 | 533.4 | 1.49 | 895.1 | 0.2773 | 70 |
| $[C_2mim][Tf_2N]$ | 391.31 | 1056.5 | 2.50 | 927.7 | 0.7970 | 70 |
| $[C_4mim][Tf_2N]$ | 419.36 | 1067.1 | 2.20 | 1048.4 | 0.7865 | 70 |
| $[C_6mim][Tf_2N]$ | 447.42 | 1077.8 | 1.96 | 1169.0 | 0.7793 | 70 |

Table S2. The values of optimized parameters for the free volume theory based on the different EoS.

| Compound | $l$ (nm) | | | | $\alpha$ (J.m$^3$.kg$^{-1}$.mol$^{-1}$) | | | | $B\times10^3$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | PR | SRK | PC-SAFT | CPA | PR | SRK | PC-SAFT | CPA | PR | SRK | PC-SAFT | CPA |
| [$C_2$mim][$BF_4$] | 0.022186 | 0.030875 | 0.027705 | 0.019426 | 410.2005 | 315.9939 | 244.8714 | 236.8216 | 1.937991 | 3.514545 | 3.396655 | 3.876440 |
| [$C_4$mim][$BF_4$] | 0.001407 | 0.001263 | 0.001539 | 0.001469 | 455.2505 | 626.8509 | 847.2375 | 364.6877 | 2.774748 | 2.041276 | 0.934752 | 3.702795 |
| [$C_6$mim][$BF_4$] | 0.000657 | 0.000488 | 0.001208 | 0.001011 | 935.4955 | 1400.1648 | 1018.0560 | 352.6647 | 1.387104 | 0.907992 | 0.845291 | 4.702837 |
| [$C_4$mim][$PF_6$] | 0.000468 | 0.000496 | 0.001847 | 0.001738 | 11982.9096 | 19176.1135 | 503.4985 | 230.2277 | 0.013663 | 0.007567 | 1.915484 | 6.887354 |
| [$C_6$mim][$PF_6$] | 0.000909 | 0.003104 | 0.000946 | 0.000910 | 3295.7263 | 3261.8232 | 783.9198 | 420.9727 | 0.113805 | 0.117988 | 1.186128 | 3.242588 |
| [$C_8$mim][$PF_6$] | 0.011694 | 0.035551 | 0.000996 | 0.000616 | 2076.0490 | 1835.9989 | 963.5158 | 860.2328 | 0.182120 | 0.219418 | 0.948023 | 1.204542 |
| [$C_2$mim][$Tf_2N$] | 0.008579 | 0.009807 | 0.014384 | 0.009468 | 247.3007 | 302.7402 | 355.4107 | 192.0327 | 3.792727 | 3.233226 | 1.554536 | 4.858237 |
| [$C_4$mim][$Tf_2N$] | 0.003253 | 0.003086 | 0.005273 | 0.003520 | 364.9497 | 461.2212 | 535.3725 | 341.4107 | 2.801774 | 2.335921 | 1.129885 | 2.568387 |
| [$C_6$mim][$Tf_2N$] | 0.001892 | 0.001901 | 0.003367 | 0.002036 | 438.0647 | 569.2487 | 755.8422 | 331.1033 | 2.575042 | 2.038893 | 0.779259 | 3.288012 |

Table S3. The values of optimized parameters for the friction theory based on the different EoS.

| Compound | EoS | $a_1$ (μP) | $a_2$ (μP) | $a_3$ (μP) | $b_1$ (μP) | $b_2$ (μP) | $b_3$ (μP) | $c_2$ (μP) | $c_3$ (μP) | $c_4$ (μP) | $d_2$ (μP) | $d_3$ (μP) | $d_4$ (μP) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $[C_2mim][BF_4]$ | PR | 0.186 | -0.077 | -0.113 | -0.266 | 0.075 | 0.195 | -10.192557 | 2.382318 | -0.115704 | 21.205160 | -5.418124 | 0.367281 |
| | SRK | 0.951 | -0.261 | -0.874 | -0.549 | 0.050 | -0.302 | -11.735305 | 2.725829 | -0.129833 | 27.476902 | -7.064218 | 0.489812 |
| | PC-SAFT | 0.143 | -0.114 | -0.115 | -0.143 | 0.116 | 0.120 | -1.126472 | 0.170975 | 0.005372 | 2.151172 | -0.4849289 | 0.022600 |
| | CPA | 1.074 | -1.163 | -1.599 | -1.233 | 1.408 | 1.313 | -7.172907 | 1.433893 | -0.045357 | 27.932481 | -7.825346 | 0.620317 |
| $[C_4mim][BF_4]$ | PR | -20.119 | -51.120 | -181.654 | -2.583 | -19.016 | -71.597 | -1.627839 | 0.644293 | -0.040044 | 8.596728 | -1.942266 | 0.121881 |
| | SRK | -15.850 | -41.528 | -149.013 | -1.367 | -10.770 | -41.113 | 0.436639 | 0.277503 | -0.018009 | 9.595238 | -2.185937 | 0.137316 |
| | PC-SAFT | -1022.354 | 166.901 | -611.925 | 4969.830 | -227.373 | 423.638 | 1.884383 | 0.384183 | -0.019398 | 2.798147 | -0.678044 | 0.043457 |
| | CPA | 1066.481 | 662.209 | -514.361 | 2542.941 | -863.321 | -82.867 | -2.24485 | 0.725259 | -0.04593 | 6.317364 | -1.52042 | 0.102743 |
| $[C_6mim][BF_4]$ | PR | -9.950 | -33.090 | -168.213 | -6.4144 | -14.385 | -44.151 | -14.791378 | 3.983982 | -0.250533 | 25.550100 | -6.809543 | 0.473473 |
| | SRK | -13.255 | -31.051 | -97.104 | -1.723 | -14.021 | -45.282 | -14.534028 | 3.8327525 | -0.230856 | 30.030301 | -8.008429 | 0.554611 |
| | PC-SAFT | 2545.606 | -1951.215 | -82.063 | 6422.026 | 1451.446 | -376.064 | -3.083714 | 1.46744 | -0.109514 | 6.779968 | -1.893059 | 0.132372 |
| | CPA | 1442.257 | -1848.26 | -408.498 | 6028.256 | 1872.839 | -479.070 | 1.464402 | 0.889932 | -0.09876 | 9.694933 | -2.49729 | 0.177619 |
| $[C_4mim][PF_6]$ | PR | -3353.972 | 2124.169 | -1853.830 | -6858.80 | -1137.784 | -3385.217 | 227.569210 | -116.36751 | 14.391098 | 450.14846 | -191.612635 | 21.385274 |
| | SRK | -793.736 | 583.806 | -1967.955 | -2332.06 | 1578.947 | -4355.873 | 288.431123 | -137.78302 | 17.237800 | 548.70233 | -233.785554 | 26.018919 |
| | PC-SAFT | -27509.71 | 4998.497 | 1002.556 | -1379.641 | -10930.825 | -1323.090 | -36.023223 | 19.566389 | -2.696944 | 91.749742 | -38.602231 | 4.350179 |
| | CPA | -3746.91 | -3970.61 | -6494.16 | 607.49 | 2056.903 | -6138.78 | -30.2203 | 16.64935 | -2.24555 | 82.04493 | -33.624 | 3.821848 |
| $[C_6mim][PF_6]$ | PR | -1258.951 | -1466.857 | -3249.048 | -1999.59 | -2062.864 | -4184.680 | 499.987899 | -219.08535 | 25.059846 | 425.85885 | -178.888695 | 19.767015 |
| | SRK | -162.849 | 17.760 | 855.437 | -5104.54 | -3822.470 | -6493.342 | 499.999533 | -260.21789 | 31.378088 | 499.99999 | -209.028403 | 22.755254 |
| | PC-SAFT | 11831.637 | 3381.379 | -18305.060 | 43759.47 | -69583.83 | 5195.532 | -27.462724 | 15.453402 | -2.182239 | 85.184462 | -37.244984 | 4.356775 |
| | CPA | -2856.960 | 1039.938 | -5312.078 | 989.264 | 756.069 | -1537.438 | -98.368368 | 47.082074 | -5.307805 | 249.64374 | -105.058300 | 11.733170 |
| $[C_8mim][PF_6]$ | PR | 8.838 | 1.511 | -4.717 | -5.217 | 0.105 | -3.417 | 432.861252 | -193.51803 | 22.959067 | 604.81825 | -236.492189 | 23.924935 |
| | SRK | 8.780 | 1.439 | -4.870 | -5.255 | 0.065 | -3.516 | 429.544960 | -204.42369 | 25.858542 | 604.54990 | -239.577965 | 24.592686 |
| | PC-SAFT | -14639.45 | 11270.641 | -4302.648 | 9619.564 | -49217.46 | -14778.52 | -10.227690 | 2.945336 | -1.225051 | 74.059678 | -29.578575 | 3.3194217 |
| | CPA | 5.422 | 0.663 | -5.646 | -2.760 | 0.075 | -4.316 | 107.475037 | -42.755595 | 4.484656 | 197.13873 | -82.109093 | 8.955433 |
| $[C_2mim][Tf_2N]$ | PR | 0.081 | -0.362 | -3.874 | -0.186 | -0.264 | -0.116 | 0.131522 | -0.007000 | 0.000107 | -0.100552 | 0.008739 | -0.000105 |
| | SRK | -0.093 | -0.970 | -10.457 | -0.044 | -0.146 | -1.406 | 0.227641 | -0.011034 | 0.000205 | -0.152850 | 0.014760 | -0.000181 |
| | PC-SAFT | 97.880 | -4.507 | -20.298 | 124.814 | 0.136 | 4.933 | 0.145952 | -0.002906 | 0.000140 | -0.113168 | 0.009140 | -0.000130 |
| | CPA | 567.676 | -46.155 | -8.999 | 577.452 | -75.293 | -17.543 | -0.141743 | 0.013694 | -0.000165 | 0.214310 | -0.012267 | 0.000179 |
| $[C_4mim][Tf_2N]$ | PR | 0.092 | -0.809 | -6.579 | -0.156 | -0.130 | -5.715 | 0.013901 | -0.000659 | -0.000038 | 0.034981 | -0.000709 | 0.000083 |
| | SRK | -4.350 | -58.995 | -4.203 | -149.872 | 74.871 | 9.798 | 0.284632 | 0.003873 | -0.000006 | 0.035764 | 0.0000725 | 0.000068 |
| | PC-SAFT | 11.638 | -0.094 | -20.892 | 48.378 | 2.343 | 18.076 | 0.032411 | 0.008414 | -0.000005 | 0.002197 | -0.000055 | 0.000014 |
| | CPA | 3.847 | 16.657 | -10.503 | 1.295 | 4.567 | 11.725 | 0.124833 | 0.013052 | -0.000065 | 0.042245 | -0.001677 | 0.000154 |
| $[C_6mim][Tf_2N]$ | PR | -0.089 | -0.670 | -6.351 | -0.028 | -0.095 | -0.9162 | 0.055217 | -0.000227 | -0.000008 | 0.009483 | 0.000522 | 0.000065 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SRK | -0.062 | -0.220 | -4.462 | 0.063 | -0.024 | -0.662 | 0.042445 | 0.001057 | -0.000035 | 0.030990 | -0.001369 | 0.000104 |
| | PC-SAFT | 4.002 | 5.770 | -17.861 | 20.109 | 1.731 | 18.222 | 0.023032 | 0.007286 | 0.0000006 | -0.001607 | 0.000048 | 0.000006 |
| | CPA | 53.950 | -16.374 | -5.649 | 68.664 | -3.971 | -7.142 | 0.044254 | -0.00297 | -0.0000087 | 0.013179 | 0.000514 | 0.000051 |

Table S4. The values of relative deviation percent[1] for the two viscosity models based on the different EoS.

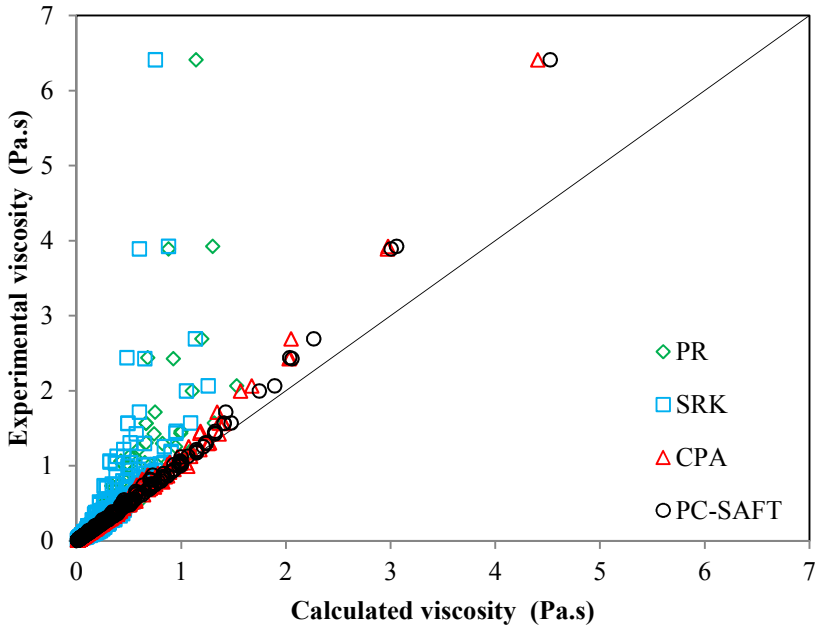
| Compound | Free volume theory | | | | Friction theory | | | |
|---|---|---|---|---|---|---|---|---|
| | PR | SRK | CPA | PC-SAFT | PR | SRK | CPA | PC-SAFT |
| $[C_2mim][BF_4]$ | -1.08 | -0.32 | -0.36 | -1.07 | -0.13 | -0.10 | 0.07 | 0.09 |
| $[C_4mim][BF_4]$ | -3.02 | -2.66 | -3.5 | -2.53 | -0.77 | -0.78 | -0.43 | -0.08 |
| $[C_6mim][BF_4]$ | -4.56 | -4.59 | -3.81 | -1.66 | 0.09 | 0.13 | -0.23 | 0.22 |
| $[C_4mim][PF_6]$ | -5.65 | -9.6 | -2.63 | -1.27 | -1.69 | -3.07 | -3.27 | -1.86 |
| $[C_6mim][PF_6]$ | -11.67 | -13.89 | -2.5 | -0.88 | -1.76 | -2.31 | -1.63 | -1.61 |
| $[C_8mim][PF_6]$ | -7.53 | -14.48 | -1.51 | -1.77 | -1.52 | -4.22 | -2.03 | -0.88 |
| $[C_2mim][Tf_2N]$ | -0.16 | 0.57 | 0.00 | 0.23 | -0.27 | -0.56 | -0.66 | -0.12 |
| $[C_4mim][Tf_2N]$ | -1.55 | -2.18 | -2.49 | -2.14 | -1.42 | -0.67 | -0.50 | -0.12 |
| $[C_6mim][Tf_2N]$ | -0.86 | -1.07 | -0.66 | -1.14 | -0.66 | -0.52 | -0.74 | -0.10 |
| **Average** | **-4.01** | **-5.36** | **-1.94** | **-1.36** | **-0.90** | **-1.34** | **-1.05** | **-0.50** |

[1] relative deviation range = $\frac{100}{NP}\sum_{1}^{NP}\frac{(Viscosity_{calculated} - Viscosity_{experimental})}{Viscosity_{experimental}}$

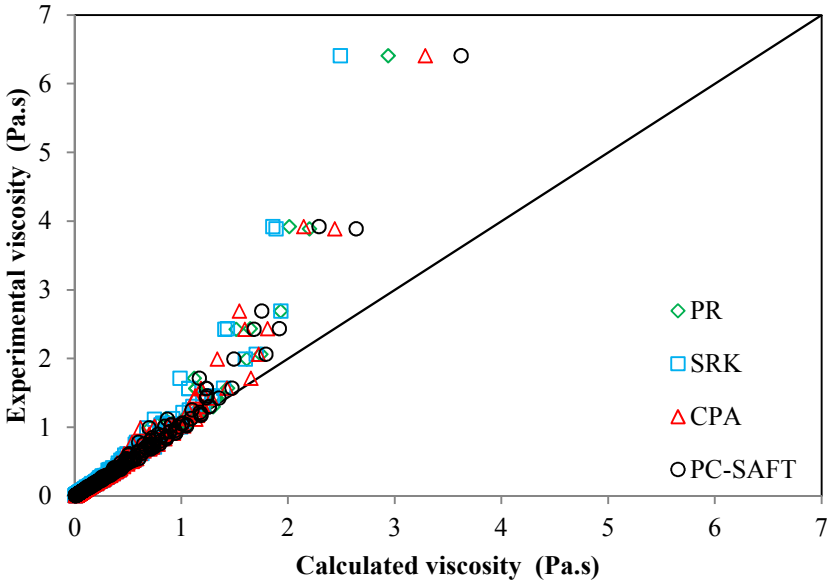
Table S5. The values of absolute deviation[1] for the two viscosity models based on the different EoS.

| Compound | Free volume theory | | | | Friction theory | | | |
|---|---|---|---|---|---|---|---|---|
| | PR | SRK | CPA | PC-SAFT | PR | SRK | CPA | PC-SAFT |
| $[C_2mim][BF_4]$ | -0.0008 | -0.0001 | -0.0003 | -0.0007 | -0.0001 | -0.0001 | 0.0000 | 0.0000 |
| $[C_4mim][BF_4]$ | -0.0111 | -0.0085 | -0.0132 | -0.0104 | -0.0052 | -0.0054 | -0.0051 | -0.0028 |
| $[C_6mim][BF_4]$ | -0.0207 | -0.0184 | -0.0211 | -0.0117 | -0.0019 | -0.0012 | -0.0035 | -0.0012 |
| $[C_4mim][PF_6]$ | -0.0799 | -0.0945 | -0.0290 | -0.0163 | -0.0319 | -0.0431 | -0.0421 | -0.0371 |
| $[C_6mim][PF_6]$ | -0.1144 | -0.1549 | -0.0272 | -0.0175 | -0.0468 | -0.0568 | -0.0439 | -0.0371 |
| $[C_8mim][PF_6]$ | -0.2189 | -0.2643 | -0.0465 | -0.0491 | -0.0846 | -0.1139 | -0.076 | -0.0618 |
| $[C_2mim][Tf_2N]$ | -0.0007 | -0.0005 | -0.0006 | -0.0008 | -0.0007 | -0.0007 | -0.0008 | -0.0005 |
| $[C_4mim][Tf_2N]$ | -0.0032 | -0.0032 | -0.0037 | -0.0025 | -0.0028 | -0.0012 | -0.0009 | -0.0004 |
| $[C_6mim][Tf_2N]$ | -0.0005 | -0.0010 | -0.0002 | -0.0009 | -0.0016 | -0.0011 | -0.0017 | -0.0002 |
| **Average** | **-0.0500** | **-0.0606** | **-0.0157** | **-0.0122** | **-0.0195** | **-0.0248** | **-0.0193** | **-0.0157** |

[1] deviation range $= \frac{1}{NP}\sum_{1}^{NP}(Vis\cos ity_{calc.} - Vis\cos ity_{exp.})$

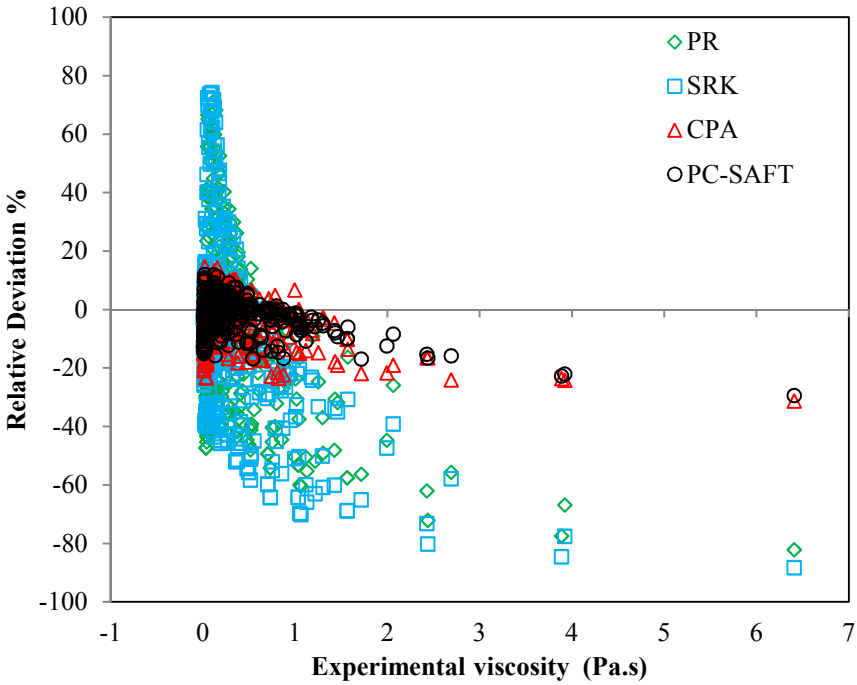



a)

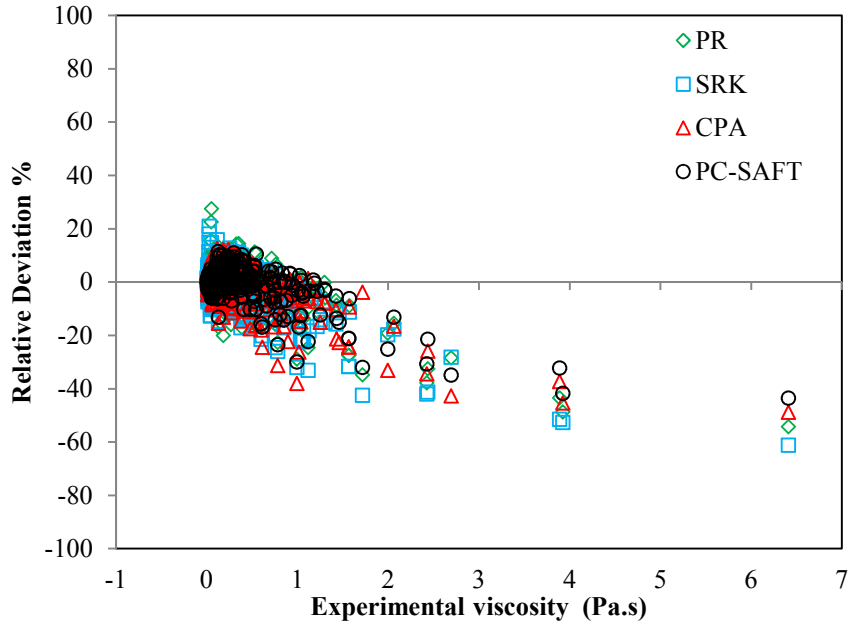



b)

Figure S1. Comparison of experimental versus predicted viscosity (all 583 data points) by the different EoS coupled with a) the free volume theory and b) the friction theory.

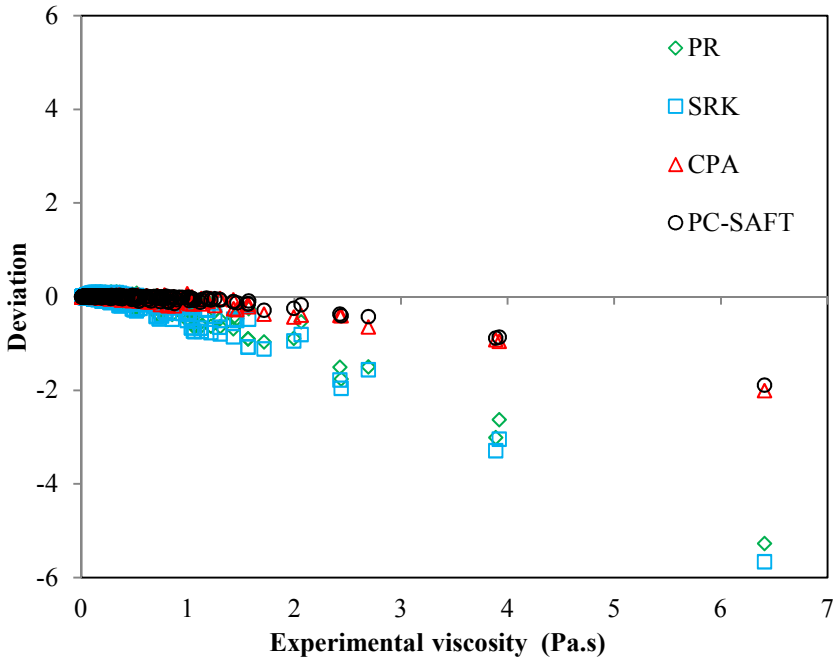



a)

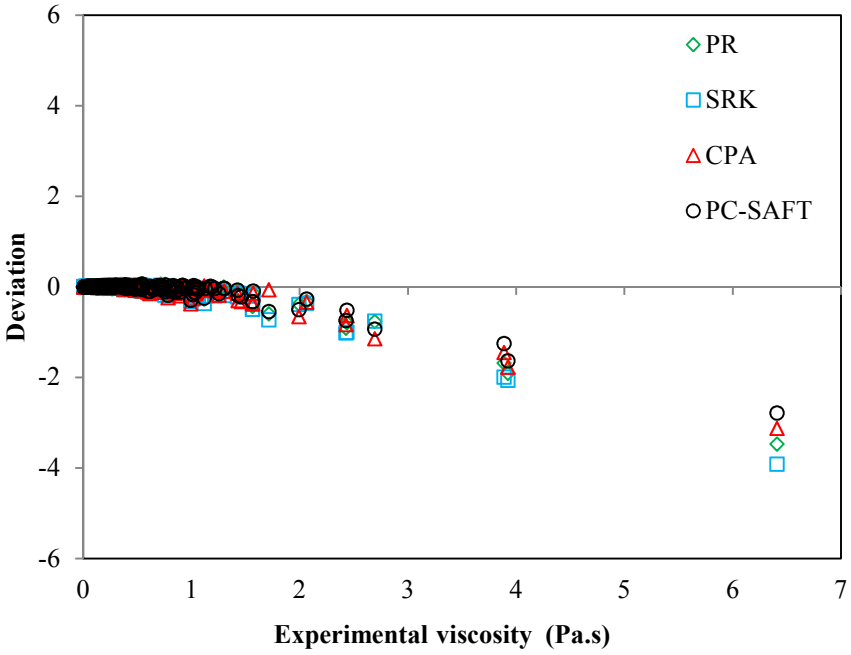



b)

Figure S2. Comparison of experimental viscosity versus relative deviation in predicted viscosity by the different EoS coupled with a) the free volume theory and b) the friction theory.




a)




b)

Figure S3. Comparison of experimental viscosity versus deviation in predicted viscosity by the different EoS coupled with a) the free volume theory and b) the friction theory.