Supporting Information

# Selecting Critical Properties of Terpenes and Terpenoids through Group-Contribution Methods and Equations of State

Mónia A. R. Martins,[1,2] Pedro J. Carvalho,[1] André M. Palma,[1] Urszula Domańska,[2] João A. P. Coutinho[1] and Simão P. Pinho[3*]

[1]CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

[2]Physical Chemistry Department, Warsaw University of Technology, 00-661 Warsaw, Poland.

[3]Associate Laboratory LSRE/LCM, Departamento de Tecnologia Química e Biológica, Instituto Politécnico de Bragança, 5301-857 Bragança, Portugal.

*Corresponding author: Phone: +351 273303086; Fax: +351 273313051; E-mail: spinho@ipb.pt.

**Table S1.** Joback group-contributions used in this work.

| Group *k* | *tck* / K | *pck* / bar |
|---|---|---|
| =C | 0.0117 | 0.0011 |
| =C(ds) | 0.0143 | 0.0008 |
| =CH | 0.0129 | -0.0006 |
| =CH(ds) | 0.0082 | 0.0011 |
| $=CH_2$ | 0.0113 | -0.0028 |
| ACOH (phenol) | 0.024 | 0.0184 |
| C | 0.0067 | 0.0043 |
| C (ss) | 0.0042 | 0.0061 |
| C=O (ss) | 0.0284 | 0.0028 |
| CH | 0.0164 | 0.002 |
| CH (ss) | 0.0122 | 0.0004 |
| $CH_2$ | 0.0189 | 0 |
| $CH_2$ (ss) | 0.01 | 0.0025 |
| $CH_3$ | 0.0141 | -0.0012 |
| O | 0.0168 | 0.0015 |
| O (ss) | 0.0098 | 0.0048 |
| OH | 0.0741 | 0.0112 |

**Table S2.** Constantinou and Gani group-contributions used in this work.

| Group *k* | First Order | |
|---|---|---|
| | ***tc1k* / K** | ***pc1k* / bar** |
| AC | 14.6409 | 0.0021 |
| ACCH | 10.4664 | 0.0028 |
| $ACCH_2$ | 10.3239 | 0.0122 |
| $ACCH_3$ | 8.2130 | 0.0194 |
| ACH | 3.7337 | 0.0075 |
| ACOH | 25.9145 | -0.0074 |
| C | 4.8823 | -0.0104 |
| C=C | 11.3764 | 0.002 |
| C=CH | 8.9582 | 0.0126 |
| $C=CH_2$ | 6.5081 | 0.0223 |
| CH | 4.0330 | 0.0013 |
| CH=CH | 7.3691 | 0.0179 |
| $CH=CH_2$ | 5.0146 | 0.0250 |
| $CH_2$ | 3.4920 | 0.0106 |
| $CH_2CO$ | 14.6273 | 0.0178 |
| $CH_3$ | 1.6781 | 0.0199 |
| $CH_3O$ | 6.4737 | 0.0204 |
| CH-O | 5.0663 | 0.0099 |
| OH | 9.7292 | 0.0051 |
| | **Second Order** | |
| | ***tc2j* / K** | ***pc2j* / bar** |
| 6 membered ring | 0.8479 | 0.002257 |
| 7 membered ring | 3.6714 | -0.009800 |
| AC-O-$CH_m$ | -5.3307 | -0.002250 |
| C-$CH_m$=$CH_n$ | -0.3850 | 0.005675 |
| $C_{cyclic}$=O | 2.9571 | 0.003818 |
| $CH_2$-$CH_m$=$CH_n$ | -0.5231 | 0.003538 |
| $CH_3$-$CH_m$=$CH_n$ | 0.0167 | -0.000180 |
| $CH_{m,\ cyclic}$-OH | 0.3233 | 0.006917 |
| $CH_n$=$CH_m$-$CH_p$=$CH_k$ | 0.4402 | 0.004186 |
| COH | -3.5442 | 0.000178 |

**Table S3.** Wilson-Jasperson atomic contributions used in this work.

| Atom | *Δtck* | *Δpck* |
|---|---|---|
| C | 0.008532 | 0.72983 |
| H | 0.002793 | 0.12660 |
| O | 0.020341 | 0.43360 |

| Group | *Δtcj* | *Δpcj* |
|---|---|---|
| OH ($C_5$ or more) | 0.0100 | 0 |
| >CO | -0.0550 | 0 |
| -O- | -0.0075 | 0 |

**Table S4.** Density, $\rho$, of pure components at different temperatures and at $p$ = 0.1 MPa.[a]

| $T$ / K | (−)-menthone | $T$ / K | (1R)-(−)-fenchone | $T$ / K | (S)-(+)-carvone | $T$ / K | Carvacrol | $T$ / K | Eucalyptol | $T$ / K | DL-citronellol | $T$ / K | Eugenol | $T$ / K | Geraniol |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 278.16 | 0.90567 | | | 278.16 | 0.97352 | 279.51 | 0.98626 | 278.16 | 0.93784 | 279.85 | 0.86708 | 278.16 | 1.07987 | | |
| 283.14 | 0.90178 | 283.16 | 0.95343 | 283.14 | 0.96954 | 283.14 | 0.98353 | 283.14 | 0.93355 | 283.14 | 0.86479 | 283.14 | 1.07548 | | |
| 288.14 | 0.89787 | 288.14 | 0.94923 | 288.14 | 0.96553 | 288.14 | 0.97977 | 288.14 | 0.92925 | 288.14 | 0.86133 | 288.14 | 1.07107 | 288.16 | 0.88386 |
| 293.14 | 0.89397 | 293.14 | 0.94501 | 293.14 | 0.96152 | 293.14 | 0.97600 | 293.14 | 0.92494 | 293.14 | 0.85786 | 293.14 | 1.06666 | 293.14 | 0.88027 |
| 298.14 | 0.89007 | 298.14 | 0.9408 | 298.14 | 0.95750 | 298.14 | 0.97222 | 298.14 | 0.92064 | 298.14 | 0.85438 | 298.14 | 1.06225 | 298.14 | 0.87665 |
| 303.14 | 0.88617 | 303.14 | 0.93658 | 303.14 | 0.95349 | 303.14 | 0.96843 | 303.14 | 0.91633 | 303.14 | 0.85088 | 303.14 | 1.05783 | 303.14 | 0.87302 |
| 308.14 | 0.88227 | 308.14 | 0.93236 | 308.14 | 0.94948 | 308.14 | 0.96461 | 308.14 | 0.91202 | 308.14 | 0.84736 | 308.14 | 1.05341 | 308.14 | 0.86937 |
| 313.14 | 0.87837 | 313.14 | 0.92814 | 313.14 | 0.94546 | 313.14 | 0.96078 | 313.14 | 0.9077 | 313.14 | 0.84382 | 313.14 | 1.04899 | 313.14 | 0.86571 |
| 318.14 | 0.87447 | 318.14 | 0.92392 | 318.14 | 0.94145 | 318.14 | 0.95693 | 318.14 | 0.90339 | 318.14 | 0.84027 | 318.14 | 1.04456 | 318.14 | 0.86203 |
| 323.14 | 0.87057 | 323.14 | 0.9197 | 323.14 | 0.93743 | 323.14 | 0.95305 | 323.14 | 0.89907 | 323.14 | 0.83669 | 323.14 | 1.04013 | 323.14 | 0.85832 |
| 328.14 | 0.86667 | 328.14 | 0.91548 | 328.14 | 0.9334 | 328.14 | 0.94915 | 328.14 | 0.89474 | 328.14 | 0.83308 | 328.14 | 1.03570 | 328.14 | 0.85459 |
| 333.14 | 0.86276 | 333.14 | 0.91125 | 333.14 | 0.92938 | 333.14 | 0.94523 | 333.14 | 0.89040 | 333.14 | 0.82946 | 333.14 | 1.03126 | 333.14 | 0.85084 |
| 338.14 | 0.85885 | 338.14 | 0.90701 | 338.14 | 0.92534 | 338.14 | 0.94129 | 338.14 | 0.88605 | 338.14 | 0.8258 | 338.14 | 1.02681 | 338.14 | 0.84706 |
| 343.14 | 0.85494 | 343.14 | 0.90277 | 343.14 | 0.92131 | 343.14 | 0.93733 | 343.14 | 0.88169 | 343.14 | 0.82211 | 343.14 | 1.02236 | 343.14 | 0.84326 |
| 348.14 | 0.85102 | 348.14 | 0.89853 | 348.14 | 0.91727 | 348.14 | 0.93334 | 348.14 | 0.87732 | 348.14 | 0.81838 | 348.14 | 1.01790 | 348.14 | 0.83942 |
| 353.14 | 0.84708 | 353.14 | 0.89427 | 353.14 | 0.91322 | 353.14 | 0.92933 | 353.14 | 0.87293 | 353.14 | 0.81462 | 353.14 | 1.01344 | 353.14 | 0.83555 |
| 358.14 | 0.84314 | 358.14 | 0.89001 | 358.14 | 0.90916 | 358.14 | 0.9253 | 358.14 | 0.86854 | 358.14 | 0.81082 | 358.14 | 1.00897 | 358.14 | 0.83166 |
| 363.14 | 0.83917 | 363.14 | 0.88573 | 363.14 | 0.90509 | 363.14 | 0.92124 | 363.14 | 0.86413 | 363.14 | 0.80699 | 363.14 | 1.00449 | 363.14 | 0.82772 |
| 368.14 | 0.83520 | 368.14 | 0.88145 | 368.14 | 0.90101 | 368.14 | 0.91717 | 368.14 | 0.85971 | 368.14 | 0.80312 | 368.14 | 1.00000 | 368.14 | 0.82375 |

[a]Standard uncertainties, $u$, are $u(T)$ = 0.01 K and $u(\rho) = 5 \cdot 10^{-5}$ g·cm$^{-3}$. For (R)-(+)-limonene and $p$-cymene are $u(T)$ = 0.02 K, $u(\rho) = 1 \cdot 10^{-4}$ g·cm$^{-3}$.

**Table S4.** Density, $\rho$, of pure components at different temperatures and at $p$ = 0.1 MPa.[a] *(cont.)*

| $T$ / K | (-)-isopulegol | $T$ / K | Linalool | $T$ / K | L(-)-menthol | $T$ / K | Thymol | $T$ / K | α-pinene oxide | $T$ / K | (R)-(+)-Limonene | $T$ / K | α-pinene | $T$ / K | β-pinene | $T$ / K | *p*-cymene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 278.16 | 0.92212 | 280.01 | 0.87279 | | | | | 278.16 | 0.97773 | 278.15 | 0.8565 | 278.16 | 0.87153 | 278.16 | 0.88281 | 278.15 | 0.8689 |
| 283.14 | 0.91806 | 283.14 | 0.87025 | | | | | 283.14 | 0.97358 | 283.15 | 0.8525 | 283.14 | 0.86743 | 283.14 | 0.87881 | | |
| 288.14 | 0.91395 | 288.14 | 0.86617 | | | | | 288.14 | 0.96941 | 288.15 | 0.8486 | 288.14 | 0.86332 | 288.14 | 0.87478 | 288.15 | 0.8608 |
| 293.14 | 0.90983 | 293.14 | 0.86205 | | | | | 293.14 | 0.96525 | 293.15 | 0.8446 | 293.14 | 0.85920 | 293.14 | 0.87076 | | |
| 298.14 | 0.90570 | 298.14 | 0.85790 | | | | | 298.14 | 0.96108 | 298.15 | 0.8406 | 298.14 | 0.85507 | 298.14 | 0.86673 | 298.15 | 0.8527 |
| 303.14 | 0.90155 | 303.14 | 0.85371 | | | | | 303.14 | 0.95690 | 303.15 | 0.8367 | 303.14 | 0.85093 | 303.14 | 0.86270 | | |
| 308.14 | 0.89739 | 308.14 | 0.84948 | | | | | 308.14 | 0.95272 | 308.15 | 0.8327 | 308.14 | 0.84679 | 308.14 | 0.85866 | 308.15 | 0.8446 |
| 313.14 | 0.89322 | 313.14 | 0.84521 | | | | | 313.14 | 0.94854 | 313.15 | 0.8288 | 313.14 | 0.84263 | 313.14 | 0.85461 | | |
| 318.14 | 0.88904 | 318.14 | 0.84091 | 318.16 | 0.87951 | | | 318.14 | 0.94435 | 318.15 | 0.8249 | 318.14 | 0.83847 | 318.14 | 0.85055 | 318.15 | 0.8365 |
| 323.14 | 0.88485 | 323.14 | 0.83659 | 323.16 | 0.87579 | | | 323.14 | 0.94016 | 323.15 | 0.8209 | 323.14 | 0.83429 | 323.14 | 0.84649 | | |
| 328.14 | 0.88066 | 328.14 | 0.83223 | 328.16 | 0.87203 | 328.16 | 0.94624 | 328.14 | 0.93596 | 328.15 | 0.8170 | 328.14 | 0.83009 | 328.14 | 0.84242 | 328.15 | 0.8284 |
| 333.14 | 0.87646 | 333.14 | 0.82785 | 333.16 | 0.86823 | 333.16 | 0.94223 | 333.14 | 0.93175 | 333.15 | 0.8130 | 333.14 | 0.82589 | 333.14 | 0.83834 | | |
| 338.14 | 0.87226 | 338.14 | 0.82344 | 338.16 | 0.86438 | 338.16 | 0.93820 | 338.14 | 0.92754 | 338.15 | 0.8091 | 338.14 | 0.82167 | 338.14 | 0.83424 | 338.15 | 0.8203 |
| 343.14 | 0.86805 | 343.14 | 0.81901 | 343.16 | 0.86050 | 343.16 | 0.93415 | 343.14 | 0.92331 | 343.15 | 0.8051 | 343.14 | 0.81743 | 343.14 | 0.83014 | | |
| 348.14 | 0.86385 | 348.14 | 0.81456 | 348.16 | 0.85657 | 348.16 | 0.93008 | 348.14 | 0.91907 | 348.15 | 0.8011 | 348.14 | 0.81317 | 348.14 | 0.82601 | 348.15 | 0.8121 |
| 353.14 | 0.85964 | 353.14 | 0.81009 | 353.16 | 0.85259 | 353.16 | 0.92600 | 353.14 | 0.91481 | 353.15 | 0.7970 | 353.14 | 0.80889 | 353.14 | 0.82188 | | |
| 358.14 | 0.85543 | 358.14 | 0.80560 | 358.14 | 0.84859 | 358.16 | 0.92189 | 358.14 | 0.91055 | 358.15 | 0.7930 | 358.14 | 0.80459 | 358.14 | 0.81772 | 358.15 | 0.8039 |
| 363.14 | 0.85121 | 363.14 | 0.80109 | | | 363.16 | 0.91776 | 363.14 | 0.90627 | 363.15 | 0.7890 | 363.14 | 0.80027 | 363.14 | 0.81355 | | |
| 368.14 | 0.84699 | 368.14 | 0.79657 | | | 368.14 | 0.91363 | 368.14 | 0.90199 | 368.15 | 0.7849 | 368.14 | 0.79593 | 368.14 | 0.80936 | 368.15 | 0.7954 |

[a]Standard uncertainties, $u$, are $u(T)$ = 0.01 K and $u(\rho) = 5 \cdot 10^{-5}$ g·cm$^{-3}$. For (R)-(+)-limonene and *p*-cymene are $u(T)$ = 0.02 K, $u(\rho) = 1 \cdot 10^{-4}$ g·cm$^{-3}$.

**Table S5.** Average relative deviation between the experimental and the predicted densities and vapor pressures, calculated using the PR and SRK EoS, with critical properties estimated by Joback, Constantinou and Gani, and Wilson and Jasperson methods.

| %ARD | SRK | | | | | | PengRobinson | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Joback | | CG | | WJ | | Joback | | CG | | WJ | |
| | Density | Pvap | Density | Pvap | Density | Pvap | Density | Pvap | Density | Pvap | Density | Pvap |
| Non-cyclic | | | | | | | | | | | | |
| Geraniol | 16.49 | 26.20 | 40.34 | 52.89 | 26.90 | 41.26 | 4.32 | 12.31 | 24.97 | 55.15 | 12.98 | 47.82 |
| DL-citronellol | 17.79 | 18.05 | 34.15 | 61.07 | 26.74 | 47.31 | 6.29 | 8.18 | 19.43 | 63.37 | 12.79 | 54.00 |
| Linalool | 7.91 | 54.80 | 33.42 | 51.86 | 24.97 | 21.48 | 4.10 | 33.82 | 18.79 | 58.52 | 11.26 | 29.98 |
| Monocyclic | | | | | | | | | | | | |
| (−)-menthone | 21.97 | 3.07 | 28.29 | 9.34 | 20.32 | 26.15 | 8.61 | 2.88 | 14.24 | 2.57 | 7.10 | 30.03 |
| (−)-isopulegol | 10.42 | 113.05 | 35.29 | 87.68 | 21.16 | 10.23 | 2.73 | 79.08 | 20.46 | 54.22 | 7.89 | 9.83 |
| L(−)-menthol | 11.14 | 18.94 | 28.86 | 30.81 | 20.63 | 19.87 | 1.01 | 8.50 | 14.74 | 38.71 | 7.41 | 17.94 |
| (S)-(+)-carvone | | | 45.81 | 25.74 | 23.80 | 24.29 | | | 28.08 | 18.27 | 10.26 | 23.12 |
| (R)-(+)-limonene | | | 32.55 | 14.06 | 18.76 | 12.76 | | | 17.91 | 29.95 | 5.66 | 27.38 |
| Aromatic monocyclic | | | | | | | | | | | | |
| Thymol | 3.97 | 15.66 | 30.72 | 56.53 | 22.53 | 11.03 | 7.38 | 1.70 | 16.38 | 61.73 | 20.33 | 22.42 |
| Eugenol | 13.56 | 111.86 | 45.87 | 79.59 | 37.46 | 20.63 | 16.17 | 69.49 | 29.89 | 83.19 | 14.56 | 8.99 |
| Carvacrol | 8.35 | 7.79 | 32.46 | 24.55 | 26.20 | 5.78 | 5.20 | 4.48 | 17.93 | 24.06 | 12.23 | 10.01 |
| *p*-cymene | 15.52 | 5.92 | 38.62 | 22.83 | 18.20 | 5.48 | 2.78 | 7.18 | 23.26 | 26.01 | 5.16 | 7.54 |
| Tricyclic | | | | | | | | | | | | |
| α-pinene | | | 0.50 | 28.29 | 22.41 | 7.21 | | | 11.11 | 36.88 | 8.81 | 7.06 |
| β-pinene | | | 4.14 | 16.77 | 23.33 | 16.64 | | | 7.38 | 2.36 | 9.67 | 1.81 |
| (1R)-(−)-fenchone | 8.59 | 16.91 | | | 25.80 | 67.67 | 3.34 | 5.14 | | | 11.92 | 73.08 |
| Eucalyptol | 5.31 | 2.18 | | | 25.25 | 32.72 | 6.31 | 16.75 | | | 11.44 | 9.60 |
| **Average** | **11.41** | **35.32** | **30.18** | **41.48** | **24.42** | **24.34** | **5.95** | **22.03** | **18.56** | **40.69** | **10.95** | **24.87** |

**Table S6.** Average relative deviation of experimental and calculated vapor pressures using the EoS SRK and PR at different temperatures for substances presenting higher deviations.

| **DL-citronellol** | | | **Geraniol** | | | **(–)-isopulegol** | | | ***p*-cymene** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *T* / K | SRK | PR | *T* / K | SRK | PR | *T* / K | SRK | PR | *T* / K | SRK | PR |
| 293.17 | -27.37 | -33.45 | 293.11 | -7.43 | -14.98 | 260.00 | -15.84 | -23.95 | 273.15 | 14.29 | 13.89 |
| 298.18 | -23.07 | -28.57 | 298.15 | -5.97 | -12.59 | 263.50 | -14.04 | -21.57 | 298.15 | -0.38 | -0.51 |
| 303.16 | -19.41 | -24.25 | 303.17 | -4.75 | -10.44 | 270.00 | -10.83 | -17.28 | 323.15 | -7.80 | -7.78 |
| 308.19 | -15.78 | -19.90 | 308.19 | -4.13 | -8.89 | 280.00 | -6.29 | -11.02 | 348.15 | -10.90 | -10.79 |
| 313.20 | -12.90 | -16.23 | 313.16 | -2.67 | -6.55 | 290.00 | -2.23 | -5.21 | 373.15 | -11.16 | -10.99 |
| 318.23 | -9.24 | -11.77 | 318.16 | -1.60 | -4.61 | 298.15 | 0.71 | -0.84 | 398.15 | -9.42 | -9.23 |
| 323.22 | -5.48 | -7.20 | 323.17 | -0.23 | -2.39 | 300.00 | 1.34 | 0.10 | 423.15 | -6.21 | -6.03 |
| 328.20 | -1.56 | -2.43 | 328.17 | 1.56 | 0.22 | 310.00 | 4.43 | 4.89 | 448.15 | -1.89 | -1.78 |
| 333.23 | 1.98 | 2.00 | 333.16 | 2.21 | 1.69 | 320.00 | 7.05 | 9.15 | 473.15 | 3.26 | 3.24 |
| 338.19 | 5.10 | 6.01 | 338.14 | 3.28 | 3.56 | 330.00 | 9.23 | 12.87 | 498.15 | 9.03 | 8.78 |
| 343.19 | 7.97 | 9.79 | 343.13 | 4.22 | 5.28 | 339.82 | 10.95 | 16.01 | 523.15 | 15.23 | 14.63 |
| 348.14 | 11.03 | 13.77 | 348.10 | 4.80 | 6.60 | 340.00 | 10.98 | 16.06 | | | |
| 353.10 | 13.71 | 17.35 | 353.07 | 5.60 | 8.13 | | | | | | |
| 358.01 | 16.34 | 20.88 | 358.04 | 5.69 | 8.90 | | | | | | |
| 362.97 | 19.05 | 24.50 | 362.92 | 6.07 | 9.93 | | | | | | |
| | | | 362.94 | 5.88 | 9.73 | | | | | | |
| Average | 12.67 | 15.87 | | 4.13 | 7.15 | | 7.83 | 11.58 | | 8.14 | 7.97 |

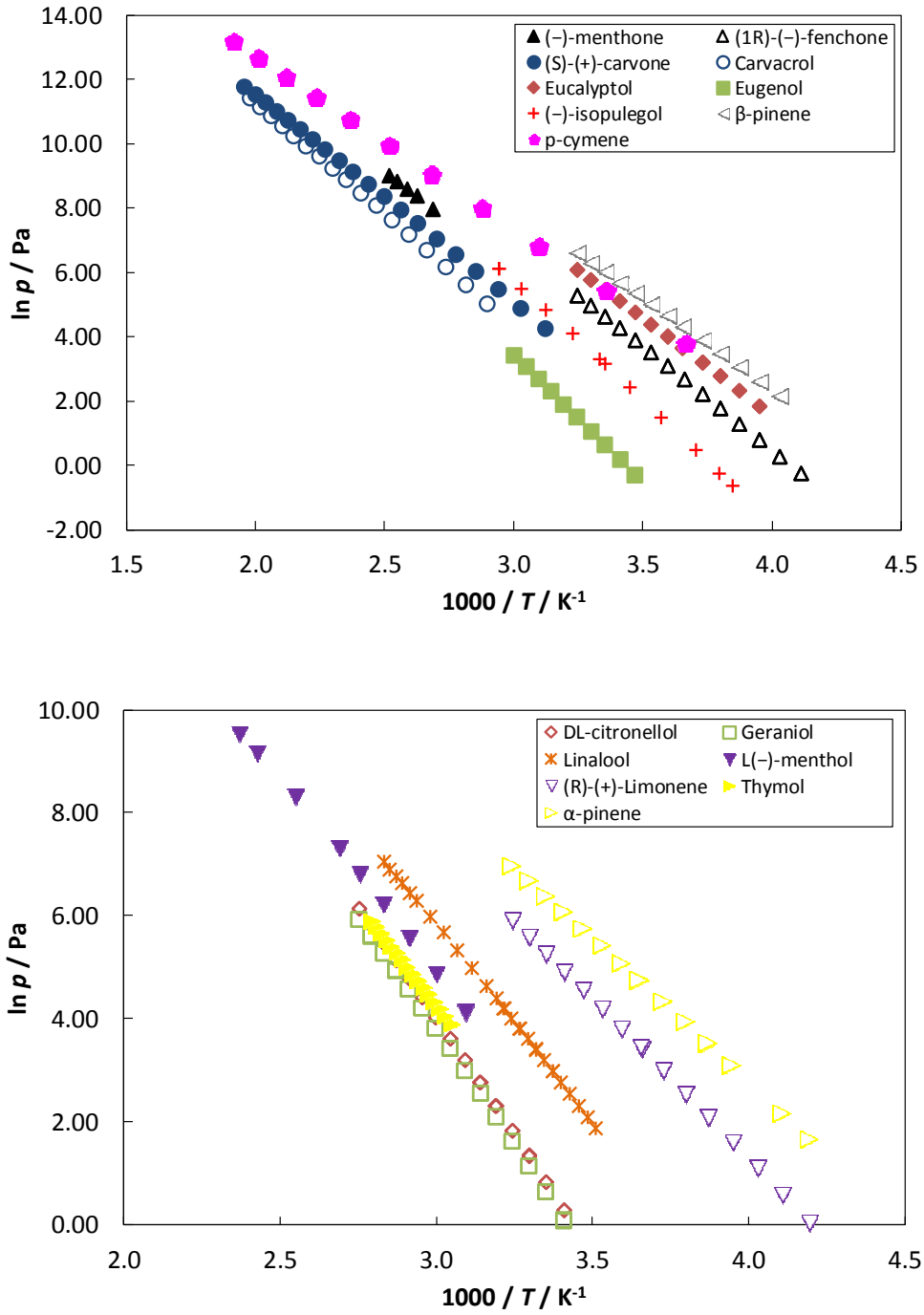


**Figure S1.** Vapor pressures, *p*, of pure terpenes and terpenoids as a function of temperature collected from literature: (−)-menthone,[61] (1R)-(−)-fenchone,[62] (S)-(+)-carvone,[63] carvacrol,[64] eucalyptol,[65] eugenol,[66] (−)-isopulegol: not published yet, β-pinene,[67] *p*-cymene,[68] DL-citronellol,[69] geraniol,[69] linalool,[70] L(−)-menthol,[71] (R)-(+)-limonene,[65] thymol,[72] and α-pinene.[67]

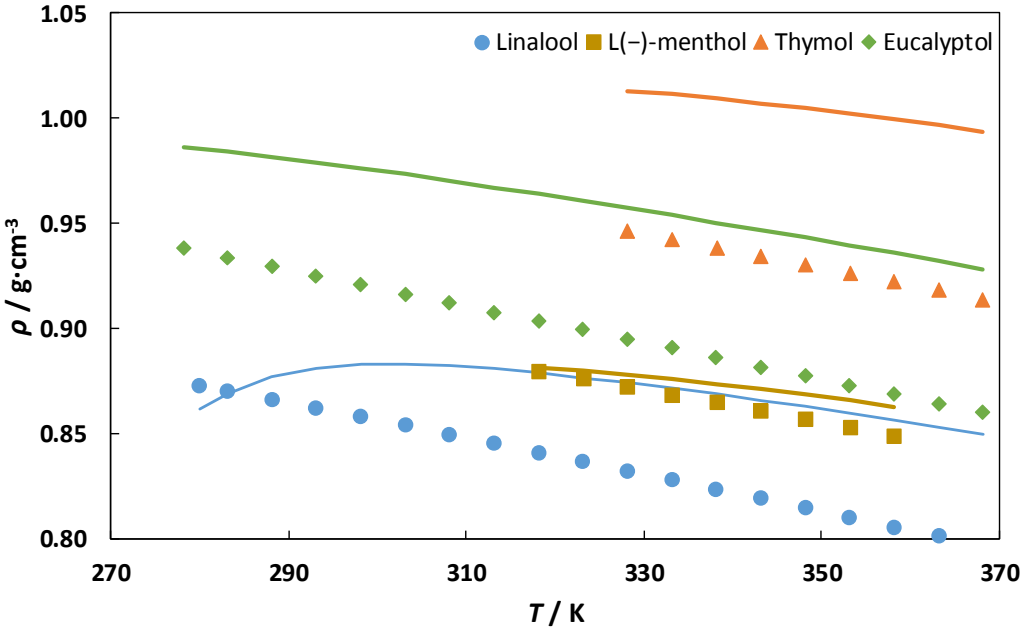


**Figure S2.** Experimental density (symbols) and calculated (lines) by PR EoS using critical properties estimated by Joback method at different temperatures and at $p$ = 0.1 MPa.

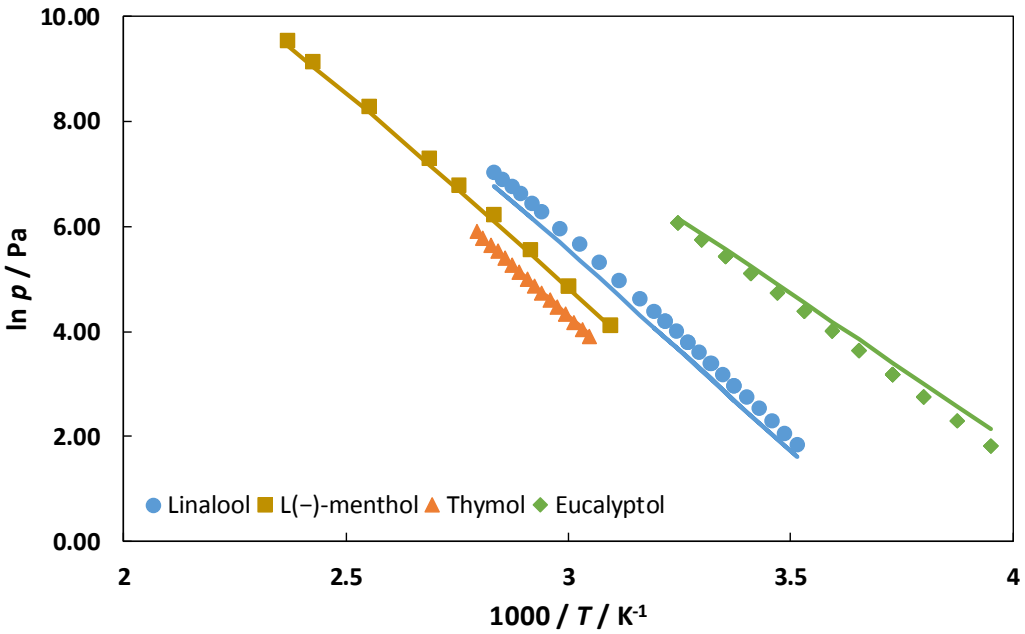


**Figure S3.** Experimental vapor pressures (symbols) and calculated (lines) by PR EoS using critical properties estimated by Joback method at different temperatures.

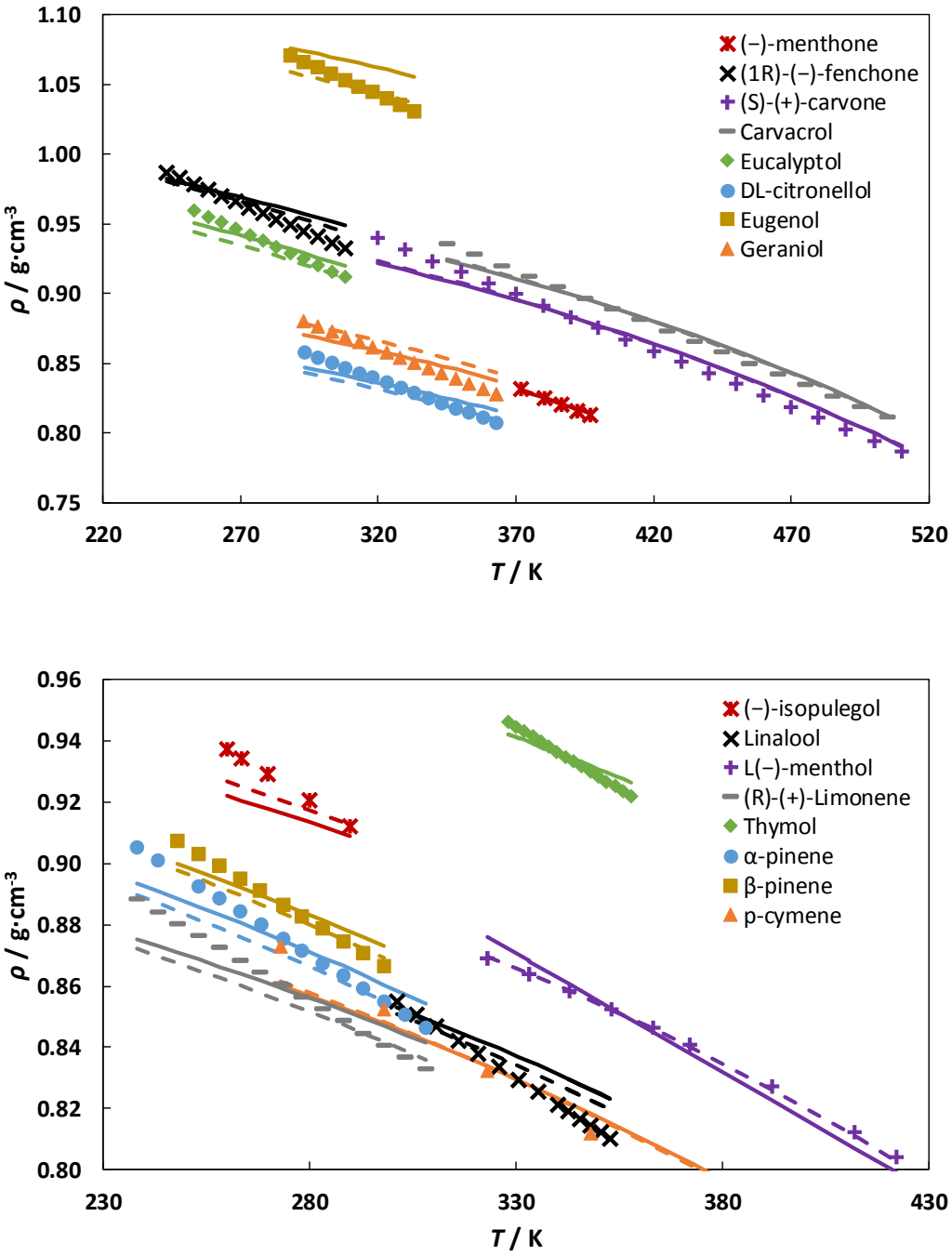


**Figure S4.** Experimental density (symbols) and calculated (lines) by EoS using critical properties estimated using the same EoS and experimental density and vapor pressure data. Dotted and full lines correspond to SRK and PR EoS, respectively.

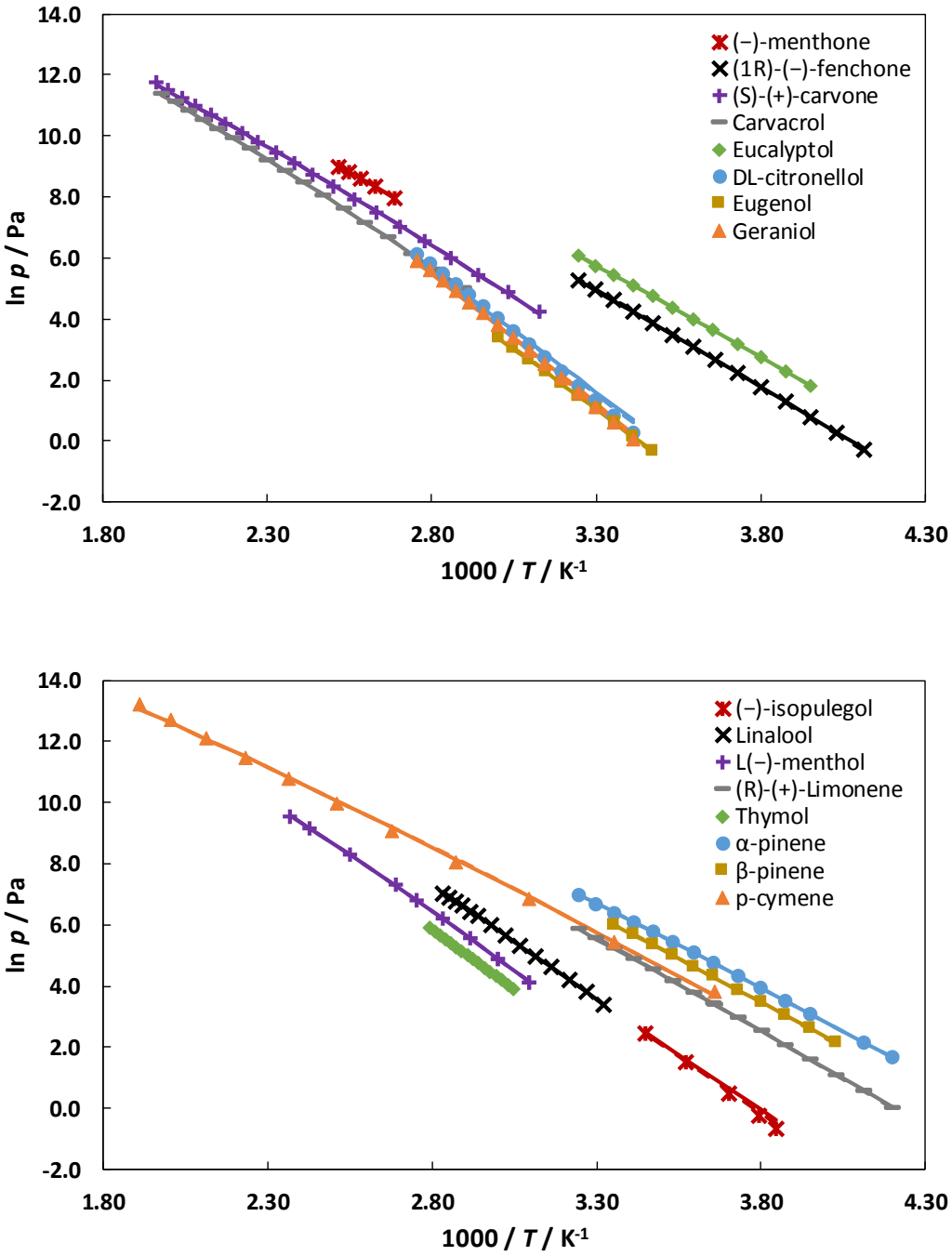


**Figure S5.** Experimental vapor pressures (symbols) and calculated (lines) by PR EoS using critical properties estimated using the same EoS and experimental density and vapor pressure data. Dotted and full lines correspond to SRK and PR EoS, respectively.