# Supplementary material: Additive polarizabilities in ionic liquids

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## DESIGNED REGRESSION

The Designed regression in MATHEMATICA[1] is a classical one-way analysis of variance (ANOVA) method.[2–5] Basically, it decomposes data into statistically averaged contributions of some moieties. For example, the molecular volume $V_{\mathrm{mol}}$ of the ionic liquids under investigation is correlated via the Design matrix $\mathbf{X}$ with the atomic contributions of the constituting atoms, i.e. $\{ V_{\mathrm{H}}, V_{\mathrm{B}}, V_{\mathrm{Csp^3}}, V_{\mathrm{Csp^2}}, V_{\mathrm{Csp}}, V_{\mathrm{N}}, V_{\mathrm{O}}, V_{\mathrm{F}}, V_{\mathrm{P}}, V_{\mathrm{S}}, V_{\mathrm{Cl}}\}$.

$$\begin{pmatrix} V^1_{\mathrm{mol}} \\ V^2_{\mathrm{mol}} \\ \vdots \\ V^m_{\mathrm{mol}} \end{pmatrix} = \begin{pmatrix} X^1_{\mathrm{H}} & X^1_{\mathrm{B}} & X^1_{\mathrm{C(sp^3)}} & X^1_{\mathrm{C(sp^2)}} & X^1_{\mathrm{C(sp)}} & X^1_{\mathrm{N}} & X^1_{\mathrm{O}} & X^1_{\mathrm{F}} & X^1_{\mathrm{P}} & X^1_{\mathrm{S}} & X^1_{\mathrm{Cl}} \\ X^2_{\mathrm{H}} & X^2_{\mathrm{B}} & X^2_{\mathrm{C(sp^3)}} & X^2_{\mathrm{C(sp^2)}} & X^2_{\mathrm{C(sp)}} & X^2_{\mathrm{N}} & X^2_{\mathrm{O}} & X^2_{\mathrm{F}} & X^2_{\mathrm{P}} & X^2_{\mathrm{S}} & X^2_{\mathrm{Cl}} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ X^m_{\mathrm{H}} & X^m_{\mathrm{B}} & X^m_{\mathrm{C(sp^3)}} & X^m_{\mathrm{C(sp^2)}} & X^m_{\mathrm{C(sp)}} & X^m_{\mathrm{N}} & X^m_{\mathrm{O}} & X^m_{\mathrm{F}} & X^m_{\mathrm{P}} & X^m_{\mathrm{S}} & X^m_{\mathrm{Cl}} \end{pmatrix} \cdot \begin{pmatrix} V_{\mathrm{H}} \\ V_{\mathrm{B}} \\ V_{\mathrm{C(sp^3)}} \\ V_{\mathrm{C(sp^2)}} \\ V_{\mathrm{C(sp)}} \\ V_{\mathrm{N}} \\ V_{\mathrm{O}} \\ V_{\mathrm{F}} \\ V_{\mathrm{P}} \\ V_{\mathrm{S}} \\ V_{\mathrm{Cl}} \end{pmatrix} \tag{1}$$

This equation corresponds to Eq.(2) in the manuscript. The index in the upper right corner indicate the corresponding experimental data. For instance, ionic liquid 1 and 2 may be two measurements of 1-ethyl-3-methylimidazolium tetrafluoroborate from different scientific groups. In this case, $V^1_{\mathrm{mol}}$ and $V^2_{\mathrm{mol}}$ differ slighty from each other. However, the $X$-values are the very same for both ionic liquids 1 and 2 since the composition has not changed: $X^1_{\mathrm{H}} = X^2_{\mathrm{H}} = 11$, $X^1_{\mathrm{B}} = X^2_{\mathrm{B}} = 1$, $X^1_{\mathrm{C(sp^3)}} = X^2_{\mathrm{C(sp^3)}} = 3$, $X^1_{\mathrm{C(sp^2)}} = X^2_{\mathrm{C(sp^2)}} = 3$, ... As a result, the Design matrix $\mathbf{X}$ has linearly dependent lines which results in a determinant of zero. Consequently, $\mathbf{X}$ cannot be inverted (which would have been difficult since $\mathbf{X}$ is also not a square matrix). Please also note, that we make no discrimination, if the atoms are part of the cation or anion.

The Designed Regression tries to find the optimal values $V_{\mathrm{H}}$, $V_{\mathrm{B}}$, ..., $V_{\mathrm{Cl}}$ to match the molecular volumes $V_{\mathrm{mol}}$ on the left hand side of Eq. (1) with the lowest possible mean-squared deviation as visible in Fig. 1.

ParameterTable →

| | Estimate | SE | TStat | PValue |
|---|---|---|---|---|
| H | 5.91444 | 0.377247 | 15.6779 | $1.09092\times10^{-48}$ |
| Csp3 | 15.8402 | 0.796532 | 19.8865 | $3.28762\times10^{-72}$ |
| Csp2 | 15.2741 | 0.370137 | 41.2659 | $6.80115\times10^{-203}$ |
| Csp | 20.0398 | 1.41915 | 14.121 | $1.02365\times10^{-40}$ |
| N | 14.3484 | 0.914869 | 15.6835 | $1.01895\times10^{-48}$ |
| O | 9.27549 | 0.399537 | 23.2156 | $3.56658\times10^{-92}$ |
| B | 18.1527 | 1.89715 | 9.56842 | $1.21608\times10^{-20}$ |
| F | 13.2603 | 0.417227 | 31.7819 | $1.98238\times10^{-145}$ |
| P | 22.99 | 2.6582 | 8.6487 | $2.68733\times10^{-17}$ |
| S | 37.2829 | 0.992203 | 37.5759 | $5.86125\times10^{-181}$ |
| Cl | 26.0849 | 2.10029 | 12.4197 | $1.35846\times10^{-32}$ |

,

RSquared → 0.999566, AdjustedRSquared → 0.99956,

EstimatedVariance → 85.4161, ANOVATable →

| | DF | SumOfSq | MeanSq |
|---|---|---|---|
| Model | 11 | $1.62341\times10^{8}$ | 1.4758 |
| Error | 826 | 70553.7 | 85.416 |
| U Total | 837 | $1.62411\times10^{8}$ | |

FIG. 1. Result of the Designed Regression on the molecular volumes of the 837 ionic liquids under investigation. U Total is the total number of experimental data and SE is the standard error for the atomic volumes which are the "Degrees of freedom"(DF).

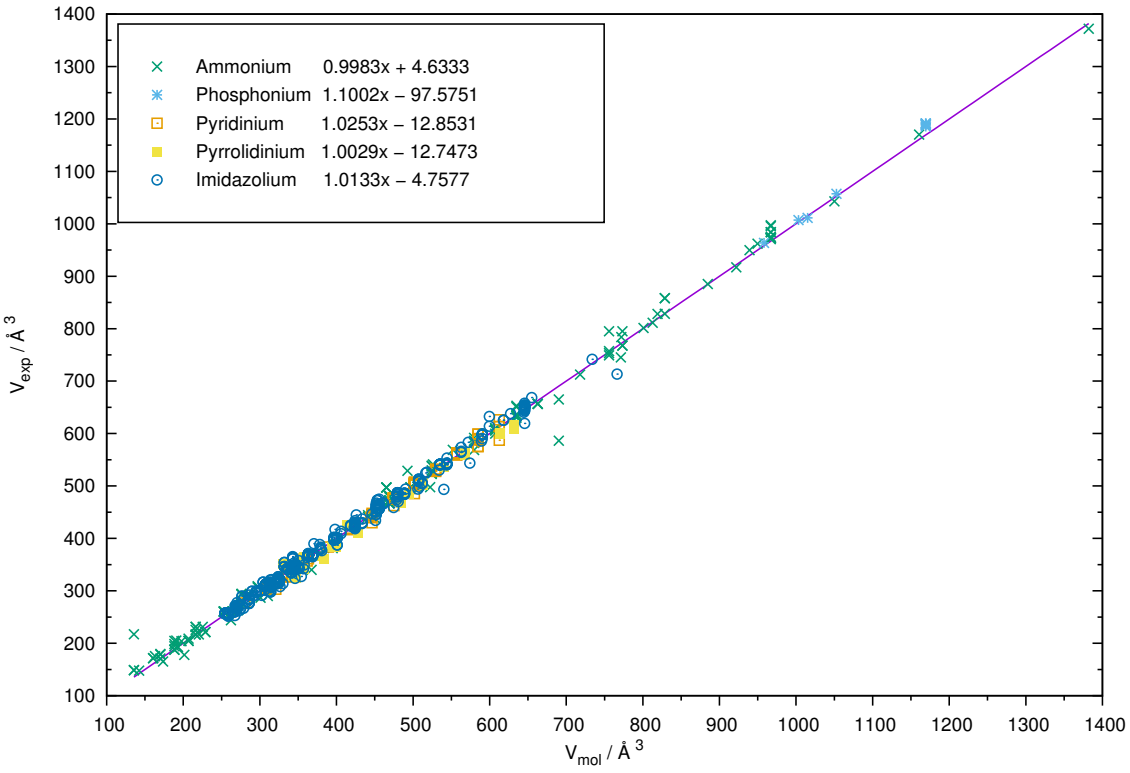



FIG. 2. Comparison between experimental and computational molecular volumes.

Fig. 2 correlates experimental molecular volumes with the predictions based on the Designed regression values of the atomic volumes. The magenta line represents 100% agreement. The legend also contains linear regression of the corresponding ionic liquid classes. A slope of 1.0 and an axis intercept of 0.0 would correspond to 100% agreement.

In a second step, the Lorentz-Lorenz equation is used to compute experimental molecular polarizabilities.

$$\frac{n_{\mathrm{D}}^2 - 1}{n_{\mathrm{D}}^2 + 2} = \frac{4\pi}{3} \frac{\alpha_{\mathrm{mol}}}{V_{\mathrm{mol}}} \tag{2}$$

Since many groups report the density or the refractive index of an ionic liquid but seldom both values, the set of ionic liquids to compute the molecular volume differs from that to evaluate the molecular polarizabilities. Therefore, the values of $V_{\mathrm{mol}}$ in Eq. (2) are predicted by the Designed Regression. Afterwards, the Designed Regression is applied to the molecular polarizabilities:

$$\begin{pmatrix} \alpha_{\mathrm{mol}}^1 \\ \alpha_{\mathrm{mol}}^2 \\ \vdots \\ \alpha_{\mathrm{mol}}^m \end{pmatrix} = \begin{pmatrix} X_{\mathrm{H}}^1 & X_{\mathrm{B}}^1 & X_{\mathrm{C(sp^3)}}^1 & X_{\mathrm{C(sp^2)}}^1 & X_{\mathrm{C(sp)}}^1 & X_{\mathrm{N}}^1 & X_{\mathrm{O}}^1 & X_{\mathrm{F}}^1 & X_{\mathrm{P}}^1 & X_{\mathrm{S}}^1 & X_{\mathrm{Cl}}^1 \\ X_{\mathrm{H}}^2 & X_{\mathrm{B}}^2 & X_{\mathrm{C(sp^3)}}^2 & X_{\mathrm{C(sp^2)}}^2 & X_{\mathrm{C(sp)}}^2 & X_{\mathrm{N}}^2 & X_{\mathrm{O}}^2 & X_{\mathrm{F}}^2 & X_{\mathrm{P}}^2 & X_{\mathrm{S}}^2 & X_{\mathrm{Cl}}^2 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ X_{\mathrm{H}}^m & X_{\mathrm{B}}^m & X_{\mathrm{C(sp^3)}}^m & X_{\mathrm{C(sp^2)}}^m & X_{\mathrm{C(sp)}}^m & X_{\mathrm{N}}^m & X_{\mathrm{O}}^m & X_{\mathrm{F}}^m & X_{\mathrm{P}}^m & X_{\mathrm{S}}^m & X_{\mathrm{Cl}}^m \end{pmatrix} \cdot \begin{pmatrix} \alpha_{\mathrm{H}} \\ \alpha_{\mathrm{B}} \\ \alpha_{\mathrm{C(sp^3)}} \\ \alpha_{\mathrm{C(sp^2)}} \\ \alpha_{\mathrm{C(sp)}} \\ \alpha_{\mathrm{N}} \\ \alpha_{\mathrm{O}} \\ \alpha_{\mathrm{F}} \\ \alpha_{\mathrm{P}} \\ \alpha_{\mathrm{S}} \\ \alpha_{\mathrm{Cl}} \end{pmatrix} \tag{3}$$

yielding the following atomic polarizabilities:

ParameterTable →

| | Estimate | SE | TStat | PValue |
|---|---|---|---|---|
| H | 0.388649 | 0.0291522 | 13.3317 | $7.60488\times10^{-34}$ |
| Csp3 | 1.0813 | 0.0611446 | 17.6844 | $3.2632\times10^{-52}$ |
| Csp2 | 1.29038 | 0.0320951 | 40.2049 | $4.0955\times10^{-143}$ |
| Csp | 1.29165 | 0.110219 | 11.7189 | $1.70283\times10^{-27}$ |
| N | 1.08463 | 0.071505 | 15.1685 | $1.95626\times10^{-41}$ |
| O | 0.353941 | 0.0276127 | 12.8181 | $8.72538\times10^{-32}$ |
| B | 0.242837 | 0.137951 | 1.76032 | 0.0791128 |
| F | 0.345808 | 0.0317926 | 10.877 | $2.46478\times10^{-24}$ |
| P | 1.09758 | 0.190508 | 5.76135 | $1.65901\times10^{-8}$ |
| S | 2.77091 | 0.0711402 | 38.9501 | $1.06837\times10^{-138}$ |
| Cl | 2.42837 | 0.132329 | 18.351 | $4.13099\times10^{-55}$ |

RSquared → 0.99967, AdjustedRSquared → 0.999661,
EstimatedVariance → 0.203444, ANOVATable →

| | DF | SumOfSq | MeanSq | FRatio | PValue |
|---|---|---|---|---|---|
| Model | 11 | 248641. | 22603.7 | 111105. | $1.148436604804\times10^{-693}$ |
| Error | 403 | 81.9878 | 0.203444 | | |
| U Total | 414 | 248723. | | | |

FIG. 3. Result of the Designed Regression on the molecular polarizabilities of the 414 ionic liquids under investigation.

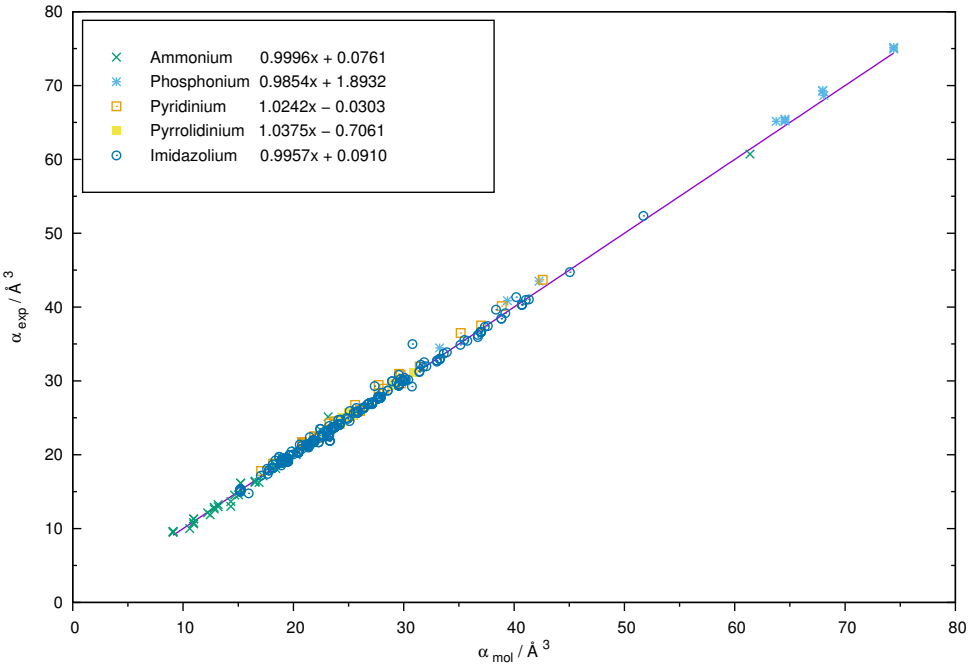



FIG. 4. Comparison between experimental and computational molecular polarizabilities.

## MODEL OF THE EXCESS ELECTRON

The molecular polarizabilities $\alpha_{\mathrm{mol}}$ in Table I were computed by MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVQZ for neutral and charged ionic liquid related compounds. The agreement between the quantum-chemical results indicates that MP2/aug-cc-pVDZ seems to be sufficient to compute reasonable molecular polarizabilities as visible in Fig. 5. Ref. 6 showed that using HF or smaller basis sets, e.g. 6-311+G(3df,2p), result in lower predictions of $\alpha_{\mathrm{mol}}$.

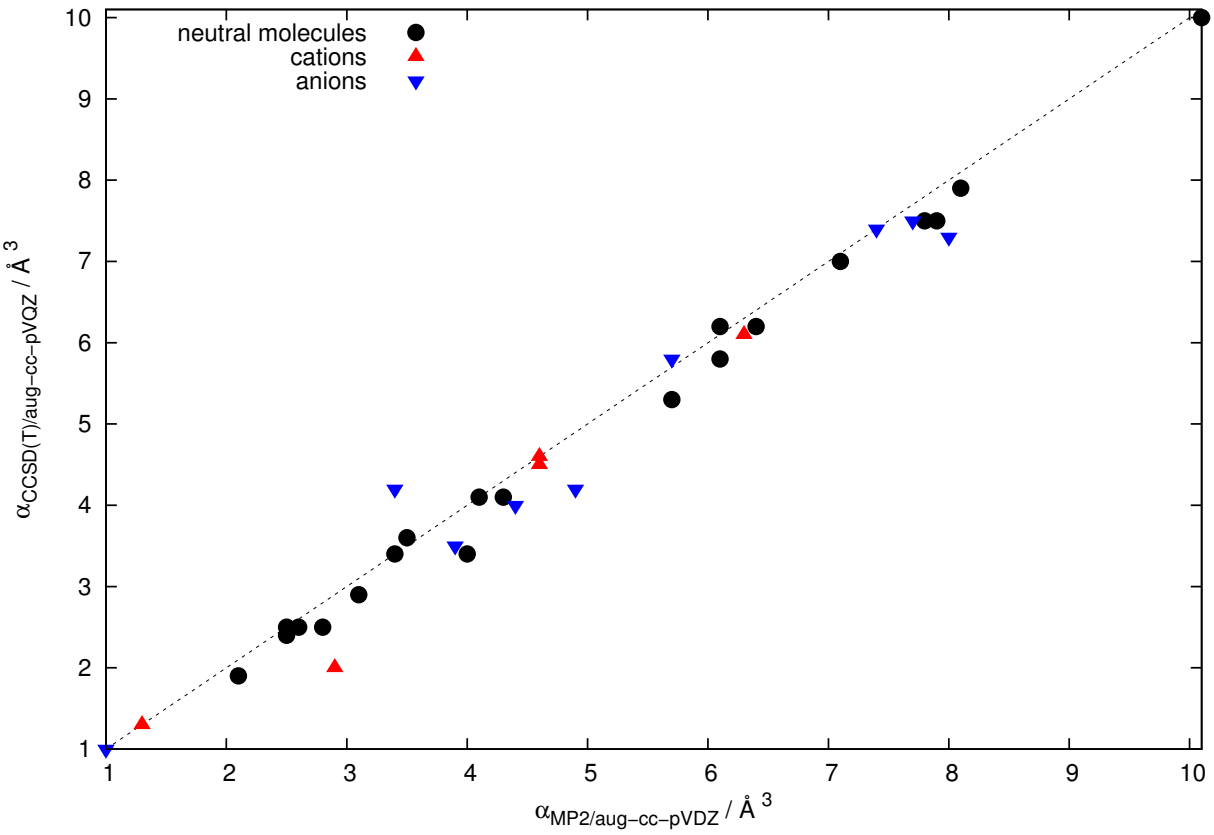



FIG. 5. Comparison between quantum-chemical calculations of the molecular polarizability at MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVQZ level. The dashed line represents 100% agreement.

TABLE I. Predicted and computed molecular polarizabilities of selected compounds.

| Molecule | Abbreviation | MP2 aug-cc-pVDZ $\alpha_{\mathrm{mol}}/\mathrm{Å}^3$ | CCSD(T) aug-cc-pVQZ $\alpha_{\mathrm{mol}}/\mathrm{Å}^3$ | Designed Regression $\alpha_{\mathrm{mol}}/\mathrm{Å}^3$ |
|---|---|---|---|---|
| methane | | 2.5 | 2.4 | 2.3 |
| ethane | | 4.3 | 4.1 | 4.1 |
| ethylene | | 4.1 | 4.1 | 3.6 |
| ethyne | | 3.4 | 3.4 | 2.9 |
| propane | | 6.1 | 5.8 | 6.0 |
| butane | | 7.9 | 7.5 | 7.8 |
| isobutylene | | 7.8 | 7.5 | 7.3 |
| isobutane | | 7.9 | | 7.8 |
| $H_2S$ | | 3.5 | 3.6 | 2.5 |
| HCN | | 2.5 | 2.5 | 2.6 |
| HSCN | | 6.1 | 6.2 | 6.5 |
| $CF_4$ | | 2.8 | 2.5 | 2.8 |
| $CCl_4$ | | 10.1 | 10.0 | 12.1 |
| $CF_2Cl_2$ | | 6.4 | 6.2 | 7.4 |
| $NH_3$ | | 2.1 | 1.9 | 1.9 |
| $NH(CH_3)_2$ | | 5.7 | 5.3 | 5.6 |
| $PF_5$ | | 4.0 | 3.4 | 3.3 |
| $PCl_3$ | | 10.2 | 10.4 | 9.6 |
| $H_2C{=}O$ | | 2.6 | 2.5 | 2.4 |
| $CH_3OH$ | | 3.1 | 2.9 | 2.9 |
| imidazole | [im] | 7.1 | 7.0 | 7.4 |
| methylimidazole | [$C_1$im] | 9.3 | | 9.3 |
| pyrrol | | 8.1 | 7.9 | 7.8 |
| pyrrolidin | [pyrr] | 8.5 | | 8.8 |
| pyridin | [py] | 9.6 | | 9.1 |
| $CN^-$ | | 4.4 | 4.0 | 2.7 |
| $SCN^-$ | | 7.7 | 7.5 | 4.9 |
| $N(CN)_2^-$ | | 8.0 | 7.3 | 6.2 |
| $PCl_6^-$ | | 18.5 | 18.0 | 19.4 |
| $NO_3^-$ | | 4.9 | 4.2 | 3.1 |
| $Cl^-$ | | 3.4 | 4.2 | 3.0 |
| $F^-$ | | 1.0 | 1.0 | 0.4 |
| $HCOO^-$ | | 3.9 | 3.5 | 3.0 |
| acetate | [$C_1COO^-$] | 5.7 | 5.8 | 4.9 |
| propionate | [$C_2H_5COO^-$] | 7.4 | 7.4 | 6.7 |
| $NTf_2^-$ (trans) | | 15.2 | | 13.0 |
| imidazolium$^+$ | [im$^+$] | 6.3 | 6.1 | 7.3 |
| methylimidazolium$^+$ | [$C_1$im$^+$] | 8.2 | | |
| 1-ethyl-3-methylimidazolium | [$C_2C_1$im$^+$] | 11.9 | | 12.9 |
| 1-butyl-3-methylimidazolium | [$C_4C_1$im$^+$] | 13.9 | | 16.6 |
| pyridinium$^+$ | [py$^+$] | 8.6 | | 9.2 |
| pyrrolidinium$^+$ | [pyrr$^+$] | 7.4 | | 8.9 |
| $NH_4^+$ | | 1.3 | 1.3 | 2.1 |
| $CH_3NH_3^+$ | [$C_1NH_3^+$] | 2.9 | 2.0 | 4.0 |
| $C_2H_5NH_3^+$ | [$C_2NH_3^+$] | 4.6 | 4.6 | 5.8 |
| $(CH_3)_2NH_2^+$ | [$C_1C_1NH_3^+$] | 4.6 | 4.5 | 5.8 |

## COMPUTATION OF THE ATOMIC POLARIZABILITIES

For the computation of atomic polarizabilities in case of 1-ethyl-3-methyl-imidazolium, the Designed regression values of $\alpha_H$=0.389 Å$^3$, $\alpha_{C(sp^2)}$=1.290 Å$^3$, $\alpha_{C(sp^3)}$=1.081 Å$^3$ and $\alpha_N$=1.085 Å$^3$ are used. Following our common setup for polarizable molecular dynamics simulations using Drude oscillators,[7] the polarizability of the hydrogens should be merged with that of the attached non-hydrogen atom.[8] Consequently, terminal carbons of the alkyl chains will be assigned $\alpha_C^{\text{term}} = 1.081\mathring{A}^3 + 3 \cdot 0.389\mathring{A}^3 = 2.248\mathring{A}^3$. The $CH_2$-group has a polarizability of $\alpha_C^{\text{CH2}} = 1.081\mathring{A}^3 + 2 \cdot 0.389\mathring{A}^3 = 1.859\mathring{A}^3$. The ring-nitrogen and carbons have a polarizability of $\alpha_N = 1.085\mathring{A}^3$ and $\alpha_C^{\text{CH}} = 1.290\mathring{A}^3 + 0.389\mathring{A}^3 = 1.679\mathring{A}^3$, respectively.

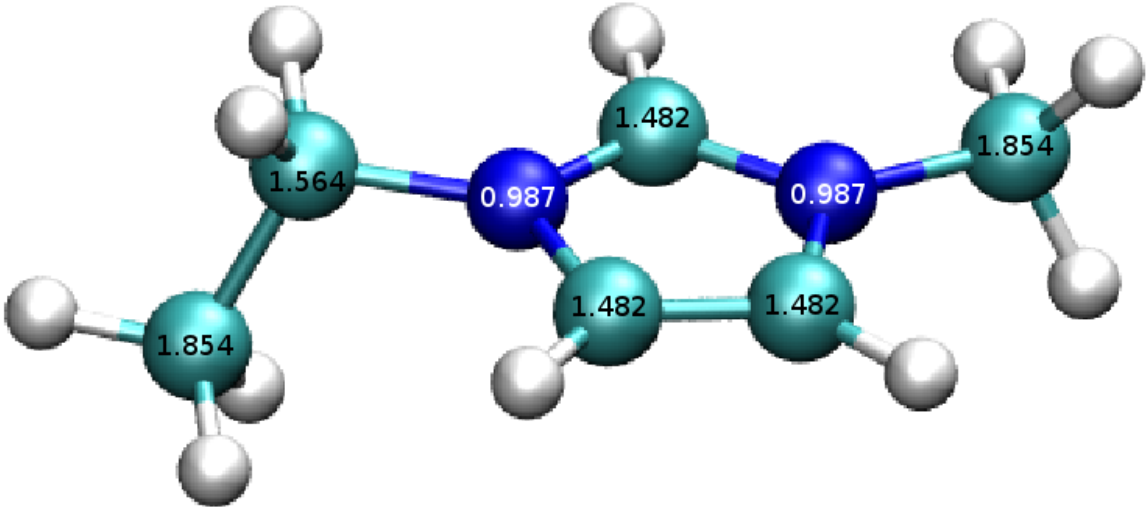
These polarizabilities have to be corrected by the polarizability of the excess electron $\alpha_e = 1.87\mathring{A}^3$, yielding:

$$\alpha_C^{\text{term}} = 2.248\mathring{A}^3 - \frac{4}{19}\alpha_e = 1.854\mathring{A}^3 \tag{4}$$

$$\alpha_C^{\text{CH2}} = 1.859\mathring{A}^3 - \frac{3}{19}\alpha_e = 1.564\mathring{A}^3 \tag{5}$$

$$\alpha_N = 1.085\mathring{A}^3 - \frac{1}{19}\alpha_e = 0.987\mathring{A}^3 \tag{6}$$

$$\alpha_C^{\text{CH}} = 1.679\mathring{A}^3 - \frac{2}{19}\alpha_e = 1.482\mathring{A}^3 \tag{7}$$



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