Aqueous Partial Molar Volumes from Simulation

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ABSTRACT

The partial molar volume of a solute is a thermodynamic property that not only describes the size of a molecule, but also the response of that solute to changes in the bulk pressure. Here, we evaluate the partial molar volumes (PMV) of organic solutes in water at infinite dilution, compare the results with experimental data, and then use two alternate methods to PMVs: A group additivity correlation of Kirkwood-Buff theory. The models enable the estimation of the PMVs of large and complex molecules without running experiments or simulations.

PARTIAL MOLAR VOLUME

Partial molar volume is the response of the free energy to changes in pressure. It is an important thermodynamic property that gives insights into molecular size and intermolecular interactions in solution. It tells us how solvents molecules pack around the solute to fill space. The PMV is important to understand;

- pressure denaturation of protein
- critical micelle concentrations
- solvation of enzymatic pockets that regulate binding

SIMULATION DETAILS

- Simulations were performed using GROMACS 2016.3
- PMVs was calculated for 14 classes of organic compounds (alkanes, alkenes, alkynes, aromatics, amines, amides, nitrides, thiols, alcohols, ketones etc.) totaling 120 individual molecules
- Water was modelled using Tip4p2005
- The molecules were modelled using the GAFF⁴, loplsa³ and opls⁶ forcefields
- Each molecule was simulated for 400ns, and 200,000 configurations were saved for further analysis
- Temperature and pressure were held constant using the Nose-Hoover thermostat and the Parrinello-Rahman Barostat Respectively

- Simulations were performed to calculate the;
  - PMVs of organic solutes in water at infinite dilution
  - Radial distribution functions (rdf) between the heavy atoms of the solute and solvent
  - The isothermal compressibility of the solute-solvent mixture

EXPT. VS SIM. PMV

KIRKWOOD-BUFF THEORY

From a molecular point of view, the PMV ($\bar{V}$) can be written as:

$$\bar{V} = RTX + \int_{V} (1 - g(r)) dr$$

$$T = \sum_{i} \int_{0}^{\infty} (1 - g_{prox}^{pmv}(r)) \cdot \kappa \cdot 4 \pi r^{2} dr$$

$x$ = isothermal compressibility

$g_{prox}^{pmv} = $ proximal distribution function

$\kappa(r) = $ Fractional area

This is more physically relevant because it draws a correlation between how water packs around a solute to the physical volume.

GROUP ADDITIVITY

We split up each molecule into groups as shown above to get an array of groups.

Groups worked on so far:

- CH₄
- CH₂
- CH
- C

We fit the individual functional groups to the equation:

$$\bar{V}_i = RTX + \sum_{j} n_{ij} \bar{V}_j$$

where,

$$\kappa = \frac{\partial \ln V}{\partial P} X$$

CONCLUSION

- Molecular simulation accurately reproduce the partial molar volumes of a wide range of solutes in water
- Group additivity correlations accurately fits the data but may have unphysical contributions, thereby making it impossible to draw a relationship to how solvent molecules pack around a solute.
- Kirkwood-Buff theory provides molecular rational for the partial molar volumes calculated using proximal correlation function.

REFERENCES


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