Example 3: Calculating Mean Activity Coefficients of Salt Solutions

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# Example file folders

Uncompress the files listed in the table below, using the command

$ tar –zxvf {filename}.tar.gz

|  |  |
| --- | --- |
| Simulation Examples | Compressed files |
| Example 3 A: Mean activity coefficient of sodium chloride versus concentration based on the unrestricted primitive model (UPM) | ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_1M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_1PT5M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_2M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_3M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_4M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_10mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_25mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_50mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_100mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_200mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM/ CONC\_500mM.tar.gz |
| Example 3 B: Mean activity coefficient of sodium chloride versus concentration based on the solvent primitive model (SPM) | ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_1M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_1PT5M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_2M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_3M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_4M.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_10mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_25mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_50mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_100mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_200mM.tar.gz  ./gibs/Simulation\_Examples/ excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM/ CONC\_500mM.tar.gz |

# Equations

The chemical potential of a salt in solution can be expressed as a function of the chemical potential of its dissociated ionic species in solution. Let’s consider the following stoichiometric reaction equation for the dissociation of a salt in solution, into its individual cationic and anionic species:

, (1)

where represents the cationic species with valence , represent the anionic species with valence , and are the stoichiometric numbers. The salt system is consider to be charge neutral, i.e.,

. (2)

The concentrations of the individual ions must also obey the charge neutrality condition,

. (3)

At equilibrium, the chemical potential of the salt is given by the equation,

, (4)

where The chemical potentials of the cation and of the anion are given by the relationships,

(5)

(6)

Hence, the chemical potential of the salt solution can written as

. (7)

The values for and are calculated from the GCMC simulations for the target concentration of cations and anions, and , respectively.

The activity coefficient of each ion species, , is computed from the excess chemical potential using the formula,

. (8)

The mean activity coefficient of the salt can be expressed in terms of the individual activity coefficients of the cationic and anionic species, as

. (9)

# Example 3 A: Mean activity coefficient of sodium chloride versus concentration based on the unrestricted primitive model (UPM)

In this example, we calculate the mean activity coefficients of sodium chloride for concentrations ranging from 10 mM to 4M, using the PID method and the UPM model.

Simulation file directory:

The simulation files for each concentration are provided in the directory: ./gibs/Simulation\_Examples/excess\_chempot\_vs\_conc\_NaCl\_PID\_UPM

## Setting up inputfiles/inputparameters.in file

The parameters are set up in the same way as in Example 2A, except for the following

USE\_SPM NO

USE\_PID YES

NUM\_ITER 1

NUM\_STEPS 8000000

## Excess chemical potential values calculated for Na+ at different salt concentrations

Run each simulation and compute the excess chemical potentials. The values should be close to those listed in the table below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Salt Concentration (M) | (average) (kcal/mol) | (s.d.) (kcal/mol) | Number (average) | Number (s.d.) |
| 0.01 | -0.00724 | 0.120369 | 5.846044 | 1.12081 |
| 0.025 | -0.07543 | 0.061704 | 14.88597 | 1.446126 |
| 0.05 | -0.11944 | 0.040943 | 29.9437 | 1.829729 |
| 0.1 | -0.16483 | 0.029681 | 60.06469 | 2.391149 |
| 0.2 | -0.21367 | 0.023576 | 120.2983 | 3.155749 |
| 0.5 | -0.28093 | 0.019743 | 300.9638 | 4.365415 |
| 1 | -0.32381 | 0.018604 | 602.07 | 5.2435 |
| 1.5 | -0.33841 | 0.01847 | 903.1707 | 5.734246 |
| 2 | -0.34134 | 0.018197 | 1204.277 | 5.948074 |
| 3 | -0.32829 | 0.0183 | 1806.49 | 6.305428 |
| 4 | -0.29756 | 0.018421 | 2408.676 | 6.477844 |

## Excess chemical potential values calculated for Cl- at different salt concentrations

The values should be close to those listed in the table below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Salt Concentration (M) | (average) (kcal/mol) | (s.d.) (kcal/mol) | Number (average) | Number (s.d.) |
| 0.01 | -0.0117 | 0.121715 | 5.829545 | 1.117861 |
| 0.025 | -0.07518 | 0.063636 | 14.8736 | 1.44556 |
| 0.05 | -0.11824 | 0.043352 | 29.93752 | 1.825659 |
| 0.1 | -0.16333 | 0.032709 | 60.06244 | 2.370983 |
| 0.2 | -0.21026 | 0.027663 | 120.3052 | 3.124834 |
| 0.5 | -0.27117 | 0.025646 | 300.9762 | 4.338187 |
| 1 | -0.30404 | 0.025754 | 602.0711 | 5.217129 |
| 1.5 | -0.30782 | 0.026205 | 903.1824 | 5.680741 |
| 2 | -0.29545 | 0.026204 | 1204.289 | 5.893618 |
| 3 | -0.24613 | 0.026836 | 1806.501 | 6.246005 |
| 4 | -0.17315 | 0.02723 | 2408.693 | 6.428903 |

## Mean activity coefficient of NaCl at different salt concentrations (UPM)

Calculate the activity coefficient based on Equation 9. The values should be close to those listed in the table below.

|  |  |
| --- | --- |
| Salt Concentration () |  |
| 0.1 | -0.015998619 |
| 0.158113883 | -0.127164654 |
| 0.223606798 | -0.200686011 |
| 0.316227766 | -0.277075232 |
| 0.447213595 | -0.357943642 |
| 0.707106781 | -0.466160776 |
| 1 | -0.530114821 |
| 1.224744871 | -0.545641946 |
| 1.414213562 | -0.537664683 |
| 1.732050808 | -0.484998026 |
| 2 | -0.397439371 |

# Example 3 B: Mean activity coefficient of sodium chloride versus concentration based on the solvent primitive model (SPM)

In this example, we calculate the mean activity coefficients of sodium chloride for concentrations ranging from 10 mM to 4M, using the PID method and the SPM model (water with solvent packing fraction of 0.3 in a 100 Angstrom cube box).

**Simulation run directory:**

The simulation files for each concentration are provided in the directory: ./gibs/Simulation\_Examples/excess\_chempot\_vs\_conc\_NaCl\_PID\_SPM

## Setting up inputfiles/inputparameters.in file

The parameters are set in the same way as in Example 3A, except for the following

USE\_SPM YES

In a 100 Angstrom cube box, a solvent packing fraction of 0.3 corresponds to 22.693 M concentration of water.

## Excess chemical potential values calculated for Na+ at different salt concentrations

The values should be close to those listed in the table below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Salt Concentration (M) | (average) (kcal/mol) | (s.d.) (kcal/mol) | Number (average) | Number (s.d.) |
| 0.01 | 0.599403 | 0.140089 | 5.919969 | 1.303963 |
| 0.025 | 0.535476 | 0.075668 | 14.94625 | 1.771772 |
| 0.05 | 0.492886 | 0.051078 | 29.99466 | 2.282718 |
| 0.1 | 0.448447 | 0.037235 | 60.133 | 3.000885 |
| 0.2 | 0.399889 | 0.029264 | 120.3624 | 3.911616 |
| 0.5 | 0.338621 | 0.023993 | 301.0125 | 5.291484 |
| 1 | 0.308901 | 0.022471 | 602.1073 | 6.270452 |
| 1.5 | 0.305978 | 0.021963 | 903.2152 | 6.715788 |
| 2 | 0.320153 | 0.02198 | 1204.321 | 6.989228 |
| 3 | 0.37065 | 0.021944 | 1806.502 | 7.304079 |
| 4 | 0.442367 | 0.022012 | 2408.719 | 7.506751 |

## Excess chemical potential values calculated for Cl- at different salt concentrations (SPM)

The values should be close to those listed in the table below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Salt Concentration (M) | (average) (kcal/mol) | (s.d.) (kcal/mol) | Number (average) | Number (s.d.) |
| 0.01 | 1.642734 | 0.142697 | 5.879614 | 1.298646 |
| 0.025 | 1.586753 | 0.077359 | 14.94765 | 1.756388 |
| 0.05 | 1.547784 | 0.05386 | 30.01327 | 2.267656 |
| 0.1 | 1.50852 | 0.041024 | 60.13584 | 2.976667 |
| 0.2 | 1.471711 | 0.034527 | 120.367 | 3.897778 |
| 0.5 | 1.445939 | 0.031197 | 301.0425 | 5.270281 |
| 1 | 1.472 | 0.030868 | 602.1407 | 6.227023 |
| 1.5 | 1.534227 | 0.031055 | 903.2335 | 6.66896 |
| 2 | 1.611042 | 0.031314 | 1204.365 | 6.95042 |
| 3 | 1.801064 | 0.031596 | 1806.55 | 7.259296 |
| 4 | 2.021506 | 0.032027 | 2408.779 | 7.466246 |

## Excess chemical potential values calculated for Water at different salt concentrations

The values should be close to those listed in the table below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Salt Concentration (M) | (average) (kcal/mol) | (s.d.) (kcal/mol) | Number (average) | Number (s.d.) |
| 0.01 | 1.039552 | 0.028773 | 13665.8 | 13.88172 |
| 0.025 | 1.041002 | 0.028586 | 13665.85 | 13.76463 |
| 0.05 | 1.045091 | 0.02847 | 13665.84 | 13.69715 |
| 0.1 | 1.052018 | 0.028422 | 13665.84 | 13.71411 |
| 0.2 | 1.06605 | 0.028642 | 13665.84 | 13.79189 |
| 0.5 | 1.107417 | 0.028661 | 13665.84 | 13.82196 |
| 1 | 1.180442 | 0.029002 | 13665.84 | 13.9873 |
| 1.5 | 1.254973 | 0.028902 | 13665.85 | 13.93265 |
| 2 | 1.333058 | 0.02894 | 13665.83 | 13.95959 |
| 3 | 1.495662 | 0.029135 | 13665.86 | 14.01853 |
| 4 | 1.670574 | 0.029089 | 13665.81 | 14.04189 |

## Mean activity coefficient of NaCl at different salt concentrations

The values should be close to those listed in the table below. Note, the listed values were obtained after subtracting the mean activity values at zero concentration (found by extrapolation at the lower concentrations)

|  |  |
| --- | --- |
| Concentration () |  |
| 0.1 | -0.092488164 |
| 0.158113883 | -0.193730174 |
| 0.223606798 | -0.262593596 |
| 0.316227766 | -0.333267101 |
| 0.447213595 | -0.405345492 |
| 0.707106781 | -0.478836031 |
| 1 | -0.481925954 |
| 1.224744871 | -0.431853428 |
| 1.414213562 | -0.355027856 |
| 1.732050808 | -0.151948919 |
| 2 | 0.094730221 |

## Compare mean activity versus concentration plots from GCMC simulations and experiment

The figure below shows the mean activity coefficient versus NaCl concentration from experiment (black) and from GCMC simulations with the UPM (red) and SPM (blue) models. Experimental values are taken from Haynes, CRC Handbook of Chemistry and Physics (2014).

