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Hydration of Kr(aq) in Dilute and Concentration Solutions

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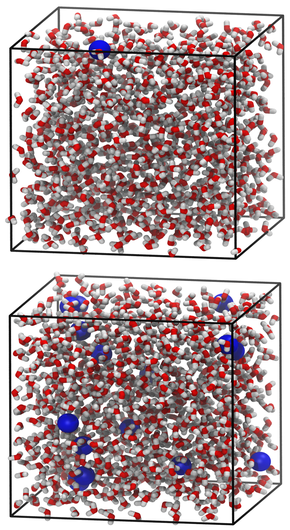
INTRODUCTION

Molecular dynamics simulations of water with both multi-Kr and single Kr atomic solutes are carried out to implement quasi-chemical theory evaluation of the hydration free energy of Kr(aq). This approach obtains free energy differences reflecting Kr-Kr interactions at higher concentrations. Those differences are negative changes in hydration free energies with increasing concentrations at constant pressure. The changes are due to a slight reduction of packing contributions in the higher concentration case. The observed Kr-Kr distributions, analyzed with the extrapolation procedure of Krüger et al, yield a modestly attractive osmotic second virial coefficient, B_2~ -60 cm³/mol. The thermodynamic analysis interconnecting these two approaches shows that they are closely consistent with each other, providing support for both approaches.

SIMULATION DETAILS

- GROMACS molecular dynamics software
  - System I: Single ion in 1000 SPC/E water molecules, NPT, T= 300 K, p=1 atm
  - System II: 16 Kr atoms in 1000 SPC/E water, NPT, T=300 K, p=1 atm
  - LJ parameters for Kr
    - σ = 3.935 Å, ε = 0.4342 kcal/mol
  - Production run = 20 ns sampled every 0.5 ps
- Packing contribution was calculated from 30000 random insertions of radius 3.5 Å



PUBLICATION

"Hydration of Kr(aq) in dilute and concentrated solutions" Mangesh. I. Chaudhari, Dubravko Sabo, Lawrence R. Pratt and Susan B. Rempe, ***J. Phys. Chem. B.,*** Branka M. Ladanyi festschrift, Article ASAP, **(2014).**

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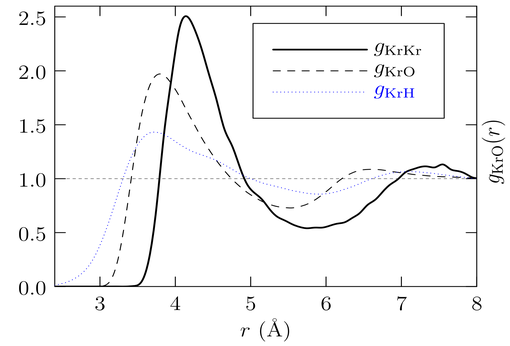
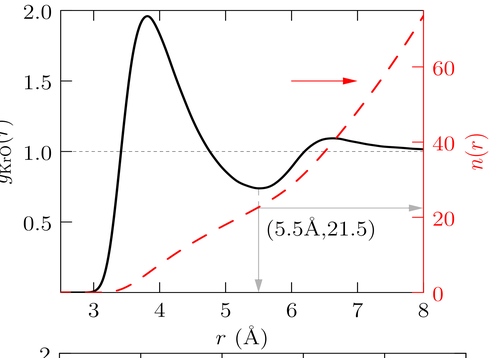
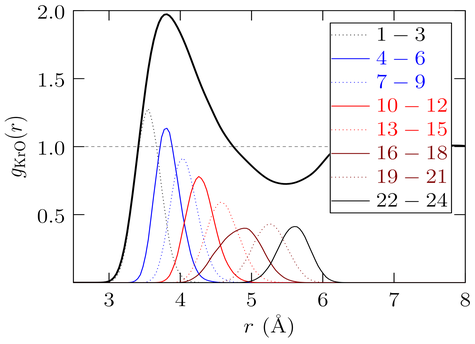
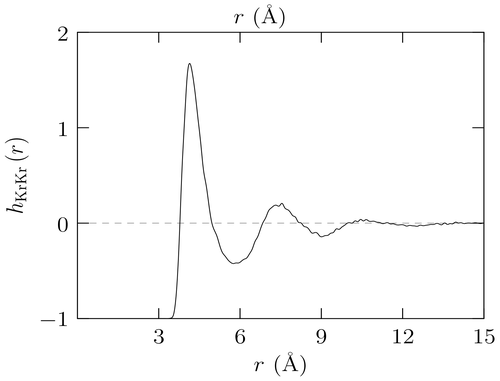
STRUCTURAL ANALYSIS



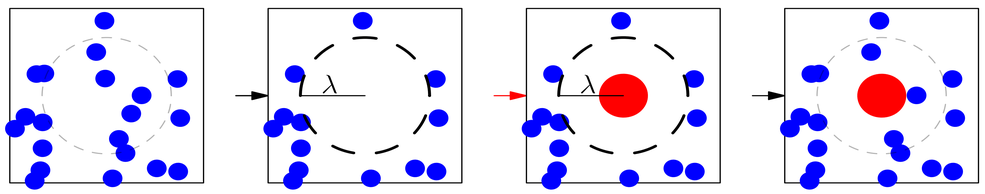




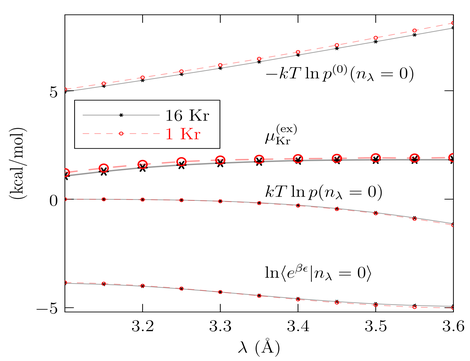


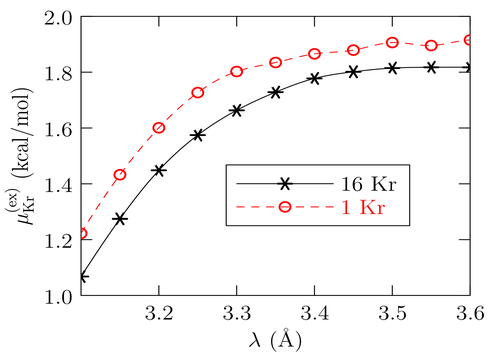
QUASI-CHEMICAL THEORY

$$\beta\mu^{(\mathrm{ex})} = -\ln p^{(0)}(n_\lambda = 0) + \ln\left\langle e^{\beta\varepsilon} | n_\lambda = 0\right\rangle + \ln p(n_\lambda = 0)$$



$$\approx \beta\left\langle \varepsilon \mid n_\lambda = 0\right\rangle + \beta^2\left\langle \delta\varepsilon^2 \mid n_\lambda = 0\right\rangle/2$$





SECOND VIRIAL COEFFICIENT

$$B_2 = -\frac{1}{2}\lim_{\rho_{\mathrm{Kr}\to 0}}\int h_{\mathrm{KrKr}}(r)\,\mathrm{d}^3 r$$

$$2B_2 = \lim_{\rho_{\mathrm{Kr}\to 0}}\left(\frac{\partial\beta\mu_{\mathrm{Kr}}^{(\mathrm{ex})}}{\partial\rho_{\mathrm{Kr}}}\right)_{T,\mu_{\mathrm{W}}}$$

$$2B_2 = \lim_{\rho_{\mathrm{Kr}\to 0}}\left[\left(\frac{\partial\beta\mu_{\mathrm{Kr}}^{(\mathrm{ex})}}{\partial\rho_{\mathrm{Kr}}}\right)_{T,p} + \left(\frac{\partial\beta\mu_{\mathrm{Kr}}^{(\mathrm{ex})}}{\partial p}\right)_{T,\rho_{\mathrm{Kr}}}\left(\frac{\partial p}{\partial\rho_{\mathrm{Kr}}}\right)_{T,\mu_{\mathrm{W}}}\right]$$

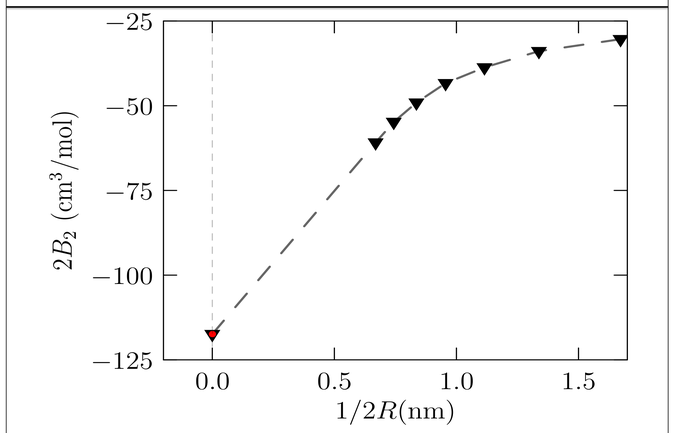
$$\lim_{\rho_{\mathrm{Kr}\to 0}}\left(\frac{\partial\beta p}{\partial\rho_{\mathrm{Kr}}}\right)_{T,\mu_{\mathrm{W}}} = \lim_{\rho_{\mathrm{Kr}\to 0}}\left(\frac{\partial}{\partial\rho_{\mathrm{Kr}}}[\beta p_{\mathrm{W}}(T,\mu_{\mathrm{W}}) + \rho_{\mathrm{Kr}} + O(\rho_{\mathrm{Kr}}{}^2)]\right)_{T,\mu_{\mathrm{W}}} = 1$$

$$\nu_{\mathrm{Kr}}^{(\mathrm{ex})} = \lim_{\rho_{\mathrm{Kr}\to 0}}\left(\frac{\partial\mu_{\mathrm{Kr}}^{(\mathrm{ex})}}{\partial p}\right)_{T,\rho_{\mathrm{Kr}}}$$

$$2B_2 = \lim_{\rho_{\mathrm{Kr}\to 0}}\left(\frac{\partial\beta\mu_{\mathrm{Kr}}^{(\mathrm{ex})}}{\partial\rho_{\mathrm{Kr}}}\right)_{T,p} + \nu_{\mathrm{Kr}}^{(\mathrm{ex})}$$

$$-2B_2 = \lim_{R\to\infty} 4\pi\int_0^{2R} h_{\mathrm{KrKr}}(r)\, w\left(\frac{r}{2R}\right) r^2\,\mathrm{d}r$$

with $$w(x) = 1 - \left(\frac{3}{2}\right)x + \left(\frac{1}{2}\right)x^3$$



CONCLUSIONS

- QCT evaluates the hydration free energy of Kr(aq) successfully and in physical terms.
- It also captures Kr-Kr interactions affecting hydration free energy differences in dilute and concentrated solutions.
- Negative differences in hydration free energy due to increased concentration are due to a slight reduction of unfavorable packing contributions.
- Kruger et al. procedure yields B_2 ~ -60 cm³/mol
- This analysis shows both approaches are consistent with each other.