

Supporting Information

Optimized Unlike-pair Interactions for Water-Carbon Dioxide Mixtures
described by the SPC/E and EPM2 Model (Lukas Vlcek, Ariel A. Chialvo,
and David R. Cole)

Alternative derivation of the polarization contribution to the solubility of
SPC/E water in a carbon dioxide-rich phase

Here we consider the condition of equilibrium for the water species in a two
phases equilibrium system, *i.e.*, a carbon dioxide-rich water phase in liquid-liquid
equilibrium with the corresponding water-rich carbon dioxide phase,

$$\mu_W^C(PTx_W^C) = \mu_W^W(PTx_W^W) \quad \text{SI-1}$$

where the superscripts ^C and ^W identify the carbon dioxide-rich and water-rich phases,
respectively. This condition of equilibrium can be rewritten in terms of the so-called
pseudo-chemical potentials $\mu_W^{*\beta}(PTx_W^\beta)$ in the following equivalent form ¹,

$$\begin{aligned} \mu_W^{*C}(PTx_W^C) - \mu_W^{*W}(PTx_W^W) &= \Delta G_W^{*C} - \Delta G_W^{*W} \\ &= kT \ln \left[\rho_W^W / \rho_W^C \right]_{pe} \end{aligned} \quad \text{SI-2}$$

where $\Delta G_W^{*\beta} = \left[\mu_W^{*\beta}(PTx_W^\beta) - \mu_W^{*IG}(T) \right]$ is the solvation Gibbs free energy for the water
species in the liquid phase β (either W or C), ρ_W^β is the equilibrium density of water in
phase β , and subscript *pe* denotes phase equilibrium. The microscopic interpretation is
given by the following statistical mechanics expression ¹,

$$\Delta G_W^{*\beta} = -kT \ln \left\langle \exp(-B_W/kT) \right\rangle \quad \text{SI-3}$$

which relates the binding energy B_W between the molecule of species “W” and the surrounding system, where the angle brackets denote an ensemble average over all possible system configurations.

While Eqns. SI-2 and SI-3 are completely general expressions; their application to the system of current interest, *i.e.*, the solvation of water in the carbon dioxide-rich phase when water is described by the SPC/E model requires some additional analysis. By invoking the following approximation for the free energy of solvation of water as a fixed-charge non-polarizable model ², *i.e.*,

$$\begin{aligned}\Delta G_W^{*C} &\cong \mu_{W,SPC/E}^{*C}(PTx_{W,SPC/E}^C) - \mu_W^{*IG}(T) - W_{W,pol} \\ &= \Delta G_{W,SPC/E}^{*C} - W_{W,pol}\end{aligned}\tag{SI-4}$$

then,

$$\begin{aligned}W_{W,pol} &= [\Delta G_{W,FC}^{*C} - \Delta G_{wat}^{*W}] - [\Delta G_W^{*C} - \Delta G_W^{*W}] \\ &= kT \ln \left[\rho_W^W / \rho_{W,SPC/E}^C \right]_{pe} - kT \ln \left[\rho_W^W / \rho_W^C \right]_{pe} \\ &= kT \ln \left[\rho_W^C / \rho_{W,SPC/E}^C \right]_{pe} \cong kT \ln \left[x_W^C / x_{W,SPC/E}^C \right]_{pe}\end{aligned}\tag{SI-5}$$

where we have invoked the accurate approximation $\rho_W^C \cong x_W^C \rho_C^C$ for a highly dilute water solute in a carbon dioxide-rich phase. Note that SI-4 might be obtained from SI-3 by assuming that the binding energy $B_W \cong B_{W,SPC/E} - \Delta B_{W,pol}$ so that,

$$\begin{aligned}
\Delta G_W^{*\beta} &= -kT \ln \left\langle \exp \left(- \left[B_{W,SPC/E} - \Delta B_{W,pol} \right] / kT \right) \right\rangle \\
&= -kT \ln \left\langle \exp \left(- B_{W,SPC/E} / kT \right) \right\rangle - kT \ln \left\langle \exp \left(\Delta B_{W,pol} / kT \right) \right\rangle \quad \text{SI-6} \\
&= \Delta G_{W,SPC/E}^{*\beta} - W_{W,pol}
\end{aligned}$$

For SPC/E we have that $\Delta H_{pol}^{SPC/E} = 0.5 \left(\vec{\mu}_W^{SPC/E} - \vec{\mu}_W^{vac} \right)^2 / \alpha_m$, where $\Delta H_{pol}^{SPC/E}$ is the change of enthalpy involved in the polarization of an isolated water molecule to increase its original permanent dipole moment $|\vec{\mu}_W^{vac}| = 1.85D$ to that of the SPC/E water molecule, $|\vec{\mu}_W^{SPC/E}| = 2.35D$, and α_m is the molecular polarizability of water (see schematic Figure 1a). Consequently, from SI-5 we can estimate the effect of the ‘over-polarized’ solute water on the water solubility in the carbon dioxide-rich phase as follows,

$$\left[x_W^C / x_{W,SPC/E}^C \right]_{pe} = \exp \left(\Delta H_{pol}^{SPC/E} / kT \right) \quad \text{SI-7}$$

where x_W^C is the corrected solubility (mole fraction) of the water in the carbon dioxide-rich phase (C), while $x_{W,SPC/E}^C$ is the corresponding uncorrected solubility directly obtained from the Gibbs Ensemble Monte Carlo simulation.

The polarization correction SI-6 was first included in Hermans *et al.*’s estimation of the solvation free energy of water models³, resulting in a satisfactory prediction by the SPC/E model. On the other hand, disregarding this correction led to the exclusion of the SPC/E model for a more detailed study of the vapor-liquid equilibria of the CO₂/H₂O mixture by Gibbs ensemble Monte Carlo simulations⁴.

REFERENCES:

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