Supporting Information for: ’Solvation and Ion-Pairing Properties of the Aqueous Sulfate Anion: Explicit versus Effective Electronic Polarization’

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1 Kirkwood-Buff Analysis

The Kirkwood-Buff (KB) integrals, \( G_{ij} \)

\[
G_{ij} = 4\pi \int_0^\infty (g_{ij}(r) - 1)r^2dr,
\]

(1)

can be related to measurable thermodynamic properties.\(^1\) As these quantities can feasibly be calculated both from simulations and experimental data, they provide an opportunity to test force field models against experiments. A binary salt has to be formally treated as a single species, a fact that is due to the electroneutrality condition.\(^2\) For such an electrolyte, all relations become formally equivalent to those for a neutral compound if all ions are treated as indistinguishable.\(^3\) This convention is adopted here. The product

\[
N_{ij} = n_j G_{ij},
\]

(2)

where \( n_j \) is the molar concentration of \( j \), has the physical interpretation of the excess number of particles of species \( j \) in a sufficiently large volume containing a particle of species \( i \) over to the average number of particles of species \( j \) in the same volume. For instance, \( N_{cc} \) is the excess number of water molecules in the vicinity of any ion. \( N_{cc} \) and \( N_{ww} \) should therefore be thought of as properties of the salt rather than of individual ions. Species \( c \) should be interpreted as having the average properties of the salt. \( N_{cw} \) can be interpreted as the average number of solvent molecules displaced by each ion.

1.1 Analysis of Experimental Data

The KB integrals can be calculated from experimental data through the relations\(^3,4\)

\[
G_{cw} = RT \kappa_T - \frac{\bar{V}_c \bar{V}_w}{DV_m},
\]

(3)

\[
G_{cc} = G_{cw} + \left( \frac{\bar{V}_w}{D} - V_m \right) \frac{1}{x_c},
\]

(4)

\[
G_{ww} = G_{cw} + \left( \frac{\bar{V}_w}{D} - V_m \right) \frac{1}{x_w},
\]

(5)

where \( x_i \) and \( \bar{V}_i \) are mole fraction and partial molar volume, respectively, of species \( i \). \( V_m \) is the solution molar volume. \( D \) is the mole fraction activity derivative, see eq. 8 below, and \( \kappa_T \) is the isothermal compressibility of the solution. Quantities with subscripts \( c \) are calculated on a per-formula unit basis where applicable, effectively treating all ions as the same species, see section 1 above. When referring to the normal convention of reporting quantities on a per-formula unit basis, the subscript \( s \) is used.

The molar and partial molar volumes were calculated from the polynomial fitting function for the mass density, \( \rho \), of sodium sulfate solutions reported in ref.\(^5\), through the relations

\[
V_m = \frac{x_c M_c + x_w M_w}{\rho} = x_c \bar{V}_c + x_w \bar{V}_w,
\]

(6)

\[
\bar{V}_c = \frac{1}{V} \left( M_s - m_s M_s + 1000 \frac{dp}{d m_s} \right),
\]

(7)

where \( m_s \) is the molal salt concentration, \( M_s, M_c \) and \( M_w \) are salt, average ion and water molar masses, respectively, and \( V \) is the number of ions in a formula unit of salt.

The activity derivative was calculated as

\[
D = \left. \frac{\partial \ln \gamma_c}{\partial \ln x_c} \right|_{P,T,N_{cw}} = \frac{1}{x_w} \left( 1 + m_i \left. \frac{\partial \ln \gamma}{\partial m_s} \right|_{P,T} \right),
\]

(8)

where \( \gamma \) is the molar mean activity coefficient of the salt. \( \frac{\partial \ln \gamma}{\partial m_s} \) was evaluated from the analytical fitting function given in ref.\(^6\).
\( \kappa_f \) was calculated from the isothermal compressibility of pure water from ref. \(^7\) and the fitting functions for the apparent molar compressibilities for sodium sulfate solutions given as eq. 11 in ref. \(^8\). The coefficients were interpolated linearly to get the value appropriate for 25°C. While this procedure is unlikely to give a high-accuracy estimate of \( \kappa_f \), the KB integrals are insensitive to this quantity. The total contribution of \( \kappa_f \) to \( N_{ij} \) is typically in the order of a few percent, so even a relatively large relative error in \( \kappa_f \) will be of little consequence for the total error of the Kirkwood-Buff integrals.

The resulting excess coordination numbers are shown in Figure 1. \( N_{cc} \) is a measure of ion-association. This number is positive over the whole concentration range which implies that the enrichment of oppositely charged ions around any given ion is greater than the depletion of similarly charged ions. Note, for comparison, that \( N_{cc} \) goes from positive to negative with increasing concentration for most of the alkali halides, with sodium fluoride being the only exception.\(^9\)

\( N_{cw} \) is the excess number of water molecules around a given ion. There are two principal contributions to this number: The water molecules displaced due to the excluded volume of the ions and the change in number density of the surrounding water, integrated over the whole space. That \( N_{cw} \) is close to zero at infinite dilution indicates that these contributions are of comparable magnitude. Presumably, the fact that \( N_{cw} \) is less negative at low concentrations is largely due to the fact that the regions in which each ion appreciably affects the water density tend to overlap at high concentration. The marginal effect of each additional ion thus decreases with increasing concentration.

Note that (anhydrous) crystalline sodium sulfate has a molar volume similar to water on a per-ion basis.\(^10\) The excluded volume contribution to \( N_{ij} \) from these compounds should be similar and it is not surprising that \( N_{cw} \) and \( N_{ww} \) have similar values at higher concentrations. The fact that \( N_{cw} \) goes through a shallow minimum can be ascribed to a decrease in the water concentration with increasing salt concentration. The number of water molecules displaced due to a given excluded volume, therefore, decreases. Interestingly, \( N_{cw} \) for the alkali halides display a quantitatively different concentration dependence, with only a modest decrease with increasing concentration at low concentrations.\(^9\) This suggests that for sodium sulfate, the sulfate ions are responsible for a large portion of the initial decrease in \( N_{cw} \) with concentration. \( N_{ww} \) increases slightly with concentration, but the variation over the concentration range shown is small.

### 1.2 Kirkwood-Buff Analysis of Simulation Trajectories

Strictly, the KB integrals are defined in the grand canonical ensemble.\(^1\) These quantities can, however, be approximated from standard \( NPT \) simulations. The reason why this is possible is that, for sufficiently large system size, the simulation box can, effectively, be divided into two regions that mimic a \( \mu VT \) system and its environment, respectively. The \( N_{ij} \) were evaluated from

\[
N_{ij}(R) = \bar{N}_{ij}(R) - \frac{4\pi}{3} R^3 n_j
\]  

where \( \bar{N}_{ij}(R) \) is the average total number of particles of species \( j \) within \( R \) of a particle of species \( i \). For sufficiently large system size, \( N_{ij}(R) \) approaches \( N_{ij} \) for large \( R \). Here, we take \( R \) to be 15 Å. \( n_j \) is the concentration of species \( j \), calculated as

\[
n_j = \frac{N_j - \bar{N}_{ij}(R) - \delta_{ij}}{V - \frac{4\pi}{3} R^3},
\]

where \( N_j \) is the total number of particles of species \( j \) in the system, \( V \) is the average system volume, \( \delta_{ij} = 1 \) if \( i = j \) and zero otherwise. Thus, the concentration is identified with the concentration in the complementary volume to the spherical region around the central particle corresponding to \( R \). \( N_{ij}(R) \) thus corresponds to the excess number of particles of species \( j \) in this volume over the number of particles of species \( j \) in the corresponding volume of bulk solution at the same chemical potential, conforming to the physical interpretation of \( N_{ij} \) for large \( R \). Note that this procedure is not strictly equivalent to evaluation of 1 with \( g_{ij}(r) \) calculated in a constant \( N \) ensemble, because \( g_{ij}(r) \) from such an ensemble will not in general approach unity for large \( r \) for finite systems. This deviation results in a systematic error that increases in magnitude with the upper limit of the integral that is supposed to approach 1.
Fig. 2 Average absolute value of the induced dipole moment of water molecules as a function of distance to the sulfate sulfur atom for the SM version of the sulfate model presented in Table 1 of the paper (green curve). Full curves correspond to a 20% increase (red) and decrease (blue) in the magnitude of $q_O$ and dashed curves correspond to a 5% increase (red) and decrease (blue) in $\sigma_O$.

Table 1 Kirkwood-Buff excess coordination numbers for the variations of the ECC model at 0.5 m concentration. The estimated error in $N_{cc}$ is typically within 0.1 and that in $\Gamma$ is within 0.05 as determined by block averages.

<table>
<thead>
<tr>
<th>Models</th>
<th>$N_{cc}$</th>
<th>$N_{cw}$</th>
<th>$\Gamma$</th>
<th>$\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>0.34</td>
<td>-0.87</td>
<td>0.45</td>
<td>1.051</td>
</tr>
<tr>
<td>EC, $q_O$ -20%</td>
<td>0.64</td>
<td>-1.10</td>
<td>0.56</td>
<td>1.052</td>
</tr>
<tr>
<td>EC, $q_O$ +20%</td>
<td>0.32</td>
<td>-0.81</td>
<td>0.45</td>
<td>1.052</td>
</tr>
<tr>
<td>EC, $\sigma_O$ -5%</td>
<td>0.34</td>
<td>-0.68</td>
<td>0.45</td>
<td>1.054</td>
</tr>
<tr>
<td>EC, $\sigma_O$ +5%</td>
<td>0.34</td>
<td>-1.09</td>
<td>0.45</td>
<td>1.047</td>
</tr>
<tr>
<td>$\exp$</td>
<td>0.55</td>
<td>-0.64</td>
<td>0.52</td>
<td>1.057</td>
</tr>
</tbody>
</table>

3 Effect of Sulfate Parameter Variations on the Kirkwood-Buff integrals for the ECC model.

$N_{cc}$ and $N_{cw}$ for the variants of the ECC model are shown in Table 1. $N_{cw}$ shows a considerable variation with $\sigma_O$, that can probably be ascribed to the change in excluded volume of the sulfate ion. $N_{cc}$ shows relatively moderate variation. The exception is the variant with reduced $|q_O|$, which gives a significantly larger value. This model also gives a significantly more negative value of $N_{cw}$, which can be rationalized by replacement of solvation water molecules by ions.

In Figure 3 the $S_r$-$Na$ radial distribution functions for the ECC model variants are shown. The most conspicuous difference is in the shoulder on the first peak, which changes dramatically in height between the model variants. For the model with $|q_O|$ reduced by 20% it has turned into a peak, which explains the high value of $N_{cc}$. The physical reason for this difference can be appreciated by noting that the change in the sulfur charge, that must accompany a decrease in the magnitude of the oxygen charge, causes the field in the region between the oxygen atoms to change so that these positions can more easily accommodate cations. In effect, this makes the “bidentate” ion-pairs more stable. This observation also...
Fig. 3 First two peaks of the $S_t$-$Na$ radial distribution functions for 0.5 m sodium sulfate solutions with the variations of the ECC sulfate. Full colored curves correspond to a 20% increase (red) and decrease (blue) in the magnitude of $q_0$ and dashed curves correspond to a 5% increase (red) and decrease (blue) in $\sigma_0$. The curves have been sorted according to peak height and shifted for clarity.

gives a hint towards why the corresponding SM sulfate variant shows clustering, as the same mechanism should be present in the polarizable model. The weaker polarization of the first solvation shell for the same model is likely to contribute to this tendency.

References