

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}

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

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

$$N_{ij} = n_j G_{ij}, \quad (2)$$

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_{cw} is the excess number of water molecules in the vicinity of any ion. N_{cc} and N_{cw} 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}

$$G_{cw} = RT \kappa_T - \frac{\bar{V}_c \bar{V}_w}{DV_m}, \quad (3)$$

$$G_{cc} = G_{cw} + \left(\frac{\bar{V}_w}{D} - V_m \right) \frac{1}{x_c}, \quad (4)$$

$$G_{ww} = G_{cw} + \left(\frac{\bar{V}_c}{D} - V_m \right) \frac{1}{x_w}, \quad (5)$$

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 κ_T is the isothermal compressibility of the solution. Quantities with subscripts c are calculated on a per-ion 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, ρ , of sodium sulfate solutions reported in ref.⁵, through the relations

$$V_m = \frac{x_c M_c + x_w M_w}{\rho} = x_c \bar{V}_c + x_w \bar{V}_w, \quad (6)$$

$$\bar{V}_c = \frac{1}{\nu} \left(\frac{M_s}{\rho} - \frac{m_s M_s + 1000}{\rho^2} \frac{d\rho}{dm_s} \right), \quad (7)$$

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 ν is the number of ions in a formula unit of salt.

The activity derivative was calculated as

$$D = \frac{\partial \ln a_c}{\partial \ln x_c} \Big|_{P,T,N_w} = \frac{1}{x_w} \left(1 + m_s \frac{\partial \ln \gamma_s}{\partial m_s} \Big|_{P,T} \right), \quad (8)$$

where γ_s is the the *molal* mean activity coefficient of the salt. $\frac{\partial \ln \gamma_s}{\partial m_s}$ was evaluated from the analytical fitting function given in ref.⁶.

κ_T 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 κ_T , the KB integrals are insensitive to this quantity. The total contribution of κ_T to N_{ij} is typically in the order of a few percent, so even a relatively large relative error in κ_T 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 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

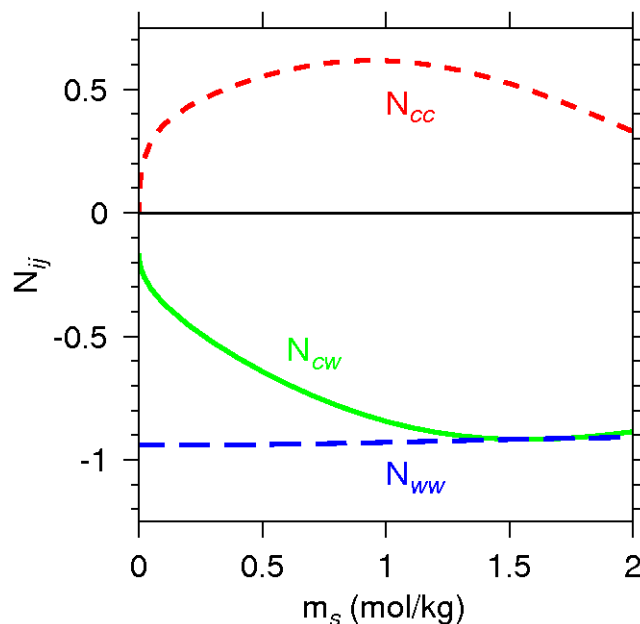


Fig. 1 N_{cc} , N_{cw} and N_{ww} , see Eq. 2, as a function of molal concentration.

box can, effectively, be divided into two regions that mimic a μVT system and its environment, respectively. The N_{ij} were evaluated from

$$N_{ij}(R) = \bar{N}_{ij}(R) - \frac{4\pi}{3}R^3 n_j \quad (9)$$

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

$$n_j = \frac{N_j - \bar{N}_{ij}(R) - \delta_{ij}}{V - \frac{4\pi}{3}R^3}, \quad (10)$$

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

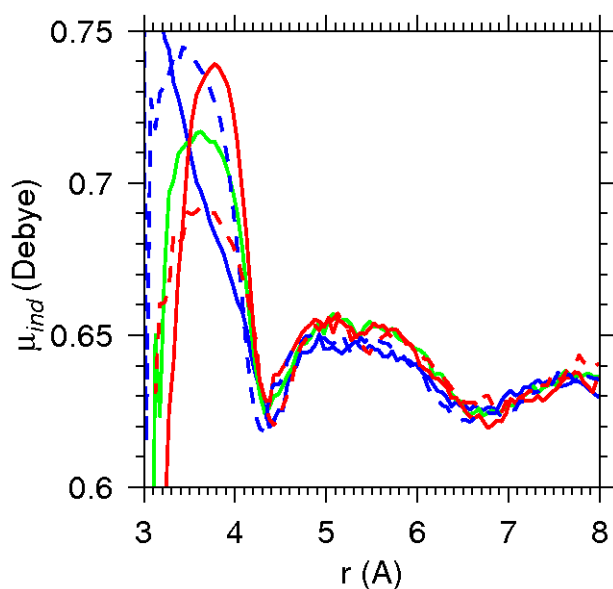


Fig. 2 Average absolute value of the induced dipole moment of water molecules as a function of distance to the sulfate sulfur atom for the SM version of the sulfate model presented in Table 1 of the paper (green curve). Full curves correspond to a 20% increase (red) and decrease (blue) in the magnitude of q_O and dashed curves correspond to a 5% increase (red) and decrease (blue) in σ_O .

in the limit of large r . This problem is clearly illustrated by Figure 4 of ref.¹¹, though its origin is not discussed explicitly in that work. Eq. 9 is, on the other hand, equivalent to the integration of 1 with the finite size correction from¹² applied to $g_{ij}(r)$.

2 Dependence of the Polarization Profile on the Force Field Parameters

In Figure 2, the average induced dipole moment of water molecules in the first solvation shells of the SM sulfate is shown. Making the oxygen partial charges more negative increases the height of the peak and decreasing σ_O has a similar effect, except that the maxima occur at slightly different r . These observations are easy to reconcile as the solvation shell water molecules are subjected to higher fields in both cases. Increasing σ_O results, not surprisingly, in a decrease in the average dipole moment of water molecules in the first solvation shell. Making the oxygen partial charges less negative, however, results in a qualitative change: The maximum disappears and is replaced by a seemingly monotonic increase in dipole moment as the water molecules approach the sulfate ion. This behavior is not in itself surprising, but, in fact, what would be expected for a spherically symmetric ion. Making the oxygen atoms less negatively charged, and, correspond-

	N_{cc}	N_{cw}	Γ	ρ (g/cm ³)
EC	0.34	-0.87	0.45	1.051
EC, q_O -20%	0.64	-1.10	0.56	1.052
EC, q_O +20%	0.32	-0.81	0.45	1.052
EC, σ_O -5%	0.34	-0.68	0.45	1.054
EC, σ_O +5%	0.34	-1.09	0.45	1.047
exp	0.55	-0.64	0.52	1.057

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 Γ is within 0.05 as determined by block averages.

ingly, the sulfur atom less positive, makes the sulfate ion more similar to such an ion with respect to the electric field in its vicinity. It is important to note that even though the average water dipole moment reaches large values for the model with reduced oxygen partial charges, the solvation shell is not on average strongly polarized. The reason is that large values are reached only for distances where the S_s - O_w radial distribution function is small. Note that the above calculations refer to a system with just 64 water molecules to ensure comparability with the AIMD simulation. Analogous calculations for a system with 512 water molecules indicate that the polarization is too small by about 0.04 D in the first solvation shell and 0.02 D elsewhere. Overall, the polarization behavior is very similar to that of the point polarizable model in ref¹³.

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 σ_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_s - 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

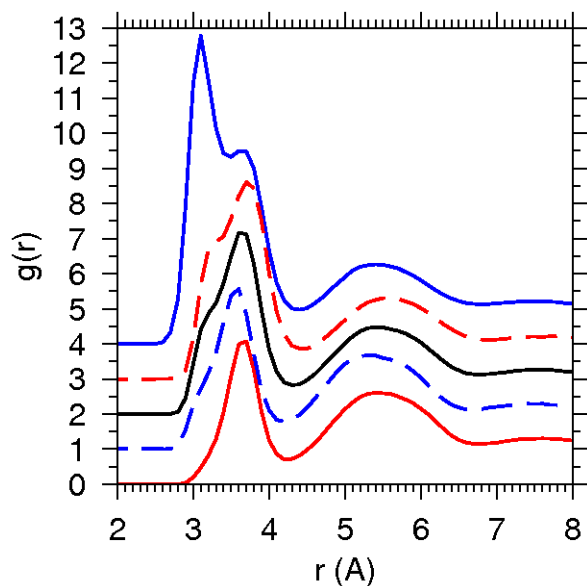


Fig. 3 First two peaks of the S_y - Na radial distribution functions for 0.5 m sodium sulfate solutions with the variations of the ECC sulfate. Full colored curves correspond to a 20% increase (red) and decrease (blue) in the magnitude of q_O and dashed curves correspond to a 5% increase (red) and decrease (blue) in σ_O . 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.

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