

Dielectric Interpretation of Specificity of Ion Pairing in Water

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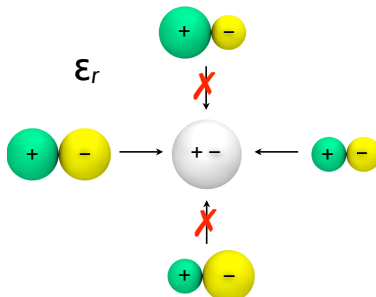
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Abstract

We present a dielectric continuum model that at a semi-quantitative level explains why ion pair formation in water is favored by like sized ions over unlike sized pairs. Using both classical and *ab initio* continuum approaches we show that the now well-established empirical rule, the so called “Law of Matching Water Affinities”, can be rationalized in terms of ion solvation. Namely, pairing of differently sized ions is weakened due to a *shadowing* effect where the larger ion shields the smaller ion from the solvent. It is shown that this empirical law ceases to be valid for less polar solvents where strong ion-ion Coulomb interactions dominate the pairing free energy. The presented model demonstrates that certain ion specific effects, such as those connected with the Hofmeister series, can be qualitatively captured by classical continuum electrostatics although a fully quantitative description would require explicit molecular treatment of the solvent.



Keywords: Ion pairing, Hofmeister series, dielectric continuum, ion specificity, primitive model of electrolytes, solvation, electrolyte solutions.

The degree of ion pairing in solution is the result of a subtle balance between ion-solvent interactions and Coulomb forces between cations and anions.^{1,2} While the former keep the ions isolated in solution, the latter enable ion pairing in the form of contact as well as solvent separated pairs. In solvents with a low dielectric constant this balance tends to be tilted toward strong ion pairing with the extreme case of $\epsilon_r = 1$, where solvent effects disappear. Water as a solvent with $\epsilon_r = 80$, is approaching the other extreme, *i.e.*, infinite dielectric constant, where ion-ion Coulomb interactions (but not solvation!) are scaled to zero. Nevertheless, ion pairing in water does take place insofar as is indicated by the occurrence of distinct peaks in the cation-anion radial distribution functions, hinting at contact and solvent separated pairs.³⁻⁵ While the number of ion pairs obviously grows with increasing salt concentration, the strength of pairing at a given concentration is strongly ion specific. That is, it depends on the chemical nature of cations and anions.^{1,5,6} Phenomenologically, this ion specificity has been formulated as an empirical rule, the so called Law of Matching Water Affinities.^{7,8} It states that monovalent cations and anions of similar hydration energies, *i.e.*, (roughly speaking) of similar size, pair more strongly than dissimilar ions. It is the purpose of the present study to provide, using a dielectric solvation model and *ab initio* calculations, an elementary microscopic interpretation of this remarkably operational empirical rule, which has, however, lacked theoretical justification.

The Law of Matching Water Affinities is reflected in thermodynamic data for bulk electrolyte solutions as shown in Figure 1 e.g., exchanging cesium with sodium in contact with iodide (big-big \rightarrow big-small) is unfavorable while the opposite is true for fluoride (big-small \rightarrow small-small). This behavior is also reflected in explicit solvent molecular dynamics (MD) simulations as shown in Figure 1, right, for the free energy of interaction between NaF, CsF, NaI and CsI. From explicit solvent MD simulations as well as from analysis of ion coordination structures it follows that ion specificity is intimately connected to ion-water and water-water interactions.^{5,9,10}

While explicit solvent models account in molecular detail for solvation changes when ions form a contact ion pair, this is not the case for the widely used primitive model (PM) of electrolytes where ions are described by hard, charged spheres in a uniform dielectric continuum.¹² Here, the

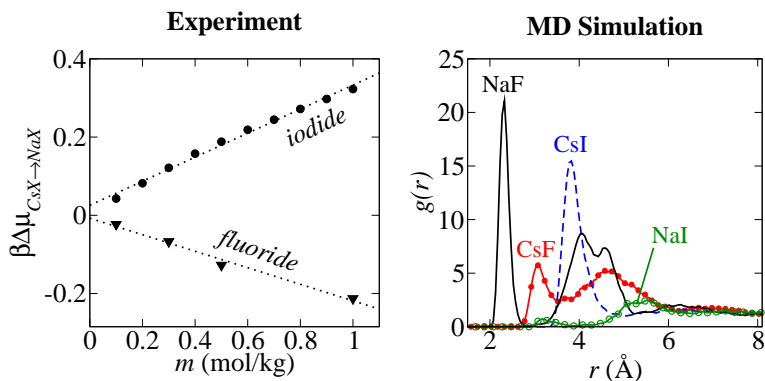


Figure 1: Left: Excess chemical potential difference of replacing iodide with fluoride for cesium and sodium ions in aqueous solutions. Derived from experimental activity coefficients¹¹ ($\beta = 1/kT$ is the inverse thermal energy). Right: Radial distribution functions, $g(r)$, for sodium and cesium halides calculated using explicit solvent MD simulations.

interaction between any two ions is given by a solvent mediated Coulomb potential, $u \propto q_1 q_2 / \epsilon_r r$ where ϵ_r is the relative dielectric constant, q_1 and q_2 are the charges and r is the distance between them. Thus, the critical parameter that determines the ion pairing strength in the PM is the distance of closest approach, *i.e.*, the *sum of ionic radii*, $a_1 + a_2$. In conflict with the idea of matching radii, this implies that big–small combinations will always lead to stronger pairing than big–big combinations. The PM is often employed successfully to describe bulk electrolyte properties and a common, pragmatic, approach is to fit the ionic radii to experimental data. Table 1 shows examples of distances of closest approach that best match experimental osmotic and activity coefficients for two halide salts of sodium and cesium.¹³ These lead to inconsistent bare ionic radii, within the PM, as the sums of the two diagonals in Table 1 are not equal. The observed distances shown in Table 1 are a consequence of the fact that sodium–fluoride (small–small) and cesium–iodide (large–large) pairs are stronger than sodium–iodide (small–large) and cesium–fluoride (large–small) pairs: The Law of Matching Water Affinities.

Can one account at least semi-quantitatively for these observations within a continuum solvent model? Consider a spherical cavity of radius a and dielectric constant ϵ_i immersed in a continuum solvent of dielectric constant ϵ_r . The electrostatic free energy of interaction between a pair of charges q_i and q_j located at positions r_i and r_j inside the sphere is then described by an infinite

Table 1: Typical cation-anion distances of closest approach, found when fitting measured bulk electrolyte data to the primitive model of electrolytes via Metropolis Monte Carlo simulations in the concentration range 0–1 molar.¹³

	Fluoride	Iodide
Sodium	3.4 Å	4.4 Å
Cesium	4.1 Å	3.4 Å

order multipole expansion:^{14–16}

$$w_{ij} = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_i} \left(\frac{1}{r_{ij}} + \sum_{n=0}^{\infty} \frac{(r_i r_j)^n}{a^{2n+1}} \Gamma \right) \quad r_i \wedge r_j < a \quad (1)$$

where ϵ_0 is the permittivity of vacuum, $\Gamma = \frac{(\epsilon_i - \epsilon_r) P_n(\cos \theta)}{\epsilon_r - \epsilon_i n / (n+1)}$ and $P_n(\cos \theta)$ is the Legendre polynomial evaluated for the angle, θ between \mathbf{r}_i and \mathbf{r}_j . The solvation free energy for each charge is given by

$$G_j = \frac{q_j^2}{8\pi\epsilon_0\epsilon_i} \sum_{n=0}^{\infty} \frac{r_j^{2n}}{a^{2n+1}} \Gamma \quad (2)$$

which for $r_j = 0$ reduces to the well-known expression for the Born energy.

Imagine the process of bringing two isolated, solvated ions into the contact distance $r_{12} = a_1 + a_2$ so that they form an ion pair with a common, spherical solvation shell as shown in Figure 2. The pairing free energy change of this process is $\Delta G_{\text{pair}} = w_{12} + G_1 + G_2 - G_1^{\text{Born}} - G_2^{\text{Born}}$, where

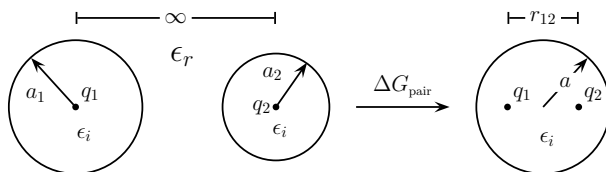


Figure 2: Pairing model where two solvated ions at infinite separation are brought into close contact, sharing a single cavity.

$G_j^{\text{Born}} = G_{j,r_j=0}$ is the Born energy as defined above. The last two terms for ΔG_{pair} thus describe the solvation energies of the two isolated ions. While ΔG_{pair} can be evaluated from Eqs 1 and 2, we can for comparison also approximate the pairing energy by describing the formed ion-pair as a point dipole, with moment $\mu = q_1 r_1 + q_2 r_2$, using Onsager's solvation model.^{17,18} This is

equivalent to neglecting terms in the summations above, for $n > 1$. Following the thermodynamic cycle illustrated in Figure 3 we obtain the pairing free energy:

$$\Delta G_{\text{pair}}^{\text{dipole}} \approx \frac{1}{4\pi\epsilon_0} \left\{ \left(-\frac{\mu^2}{2a^3} + \frac{q_1^2}{2a_1} + \frac{q_2^2}{2a_2} \right) \left(\frac{1}{\epsilon_i} - \frac{1}{\epsilon_r} \right) + \frac{q_1 q_2 |q_1 - q_2|}{2\epsilon_i \mu} \right\} \quad (3)$$

The volume of the ion-pair solvation shell is set according to $a = \sqrt[3]{a_1^3 + a_2^3} \cdot s$ where s is a scaling

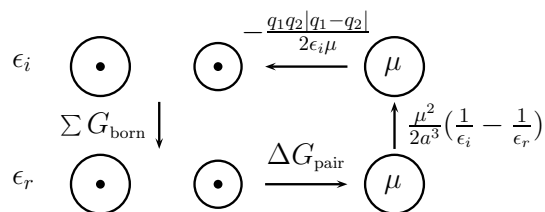


Figure 3: Thermodynamic cycle for obtaining the pairing free energy when the ion-pair is treated as a point dipole.

parameter that, in an approximative manner, accounts for the fact that the shell around the ion pair is not spherical. It should be stressed that the particular choice of s , relatively close to unity, does not influence the qualitative picture provided by the model. Note also that we do not account for the cavitation free energy stemming from changes in sizes and shapes upon pairing.¹⁹ These contributions give only minor corrections and do not change the qualitative picture.

Using our pairing corrected primitive model (PCPM) we investigate the pairing free energy for monovalent ions as a function of the ratio, $\chi = r_A/r_B$, between the individual ion radii. As shown in Figure 4, and in accord with the Law of Matching Water Affinities a free energy minimum is observed when the two ions have the same size ($\chi = 1$). The major effect that is captured by the presented dielectric model is that the solvation shell of the smaller ion is diminished by the presence of the adjacent larger ion (the *shadowing* effect). This effect is missing in the PM. As can be seen in Figure 4, this solvation effect is largely responsible for the minimum occurring when the ionic radii are roughly equal.

Table 2 shows pairing free energies for three different size combinations: small–small, small–

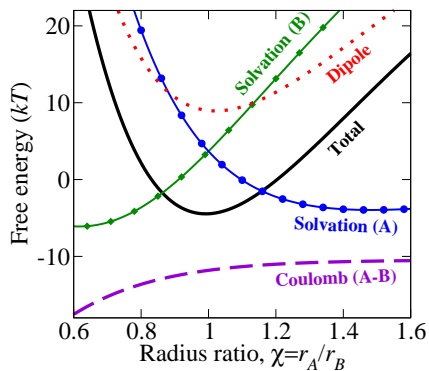


Figure 4: Free energy decomposition of bringing two oppositely charged mono-valent ions, A and B , into a shared solvation shell. The dotted, red line shows the result from the dipole approach cf. Eq. 3. ($a_B = 2.0 \text{ \AA}$, $\epsilon_i = 1$, $\epsilon_r = 80$, $s = 1.31$)

big and big–big. Qualitatively, these combinations correspond to the before mentioned systems of NaF, NaI (or CsF) and CsI, respectively. As in the PM the direct ion-ion term, Eq. 1, monotonically decreases as the radii becomes larger, while for like sized combinations the solvation free energy change is relatively modest. For unlike sized pairs, however, the cost of bringing the small highly solvated ion into contact with a large, poorly solvated ion controls the pairing free energy and gives rise to unfavorable pairing interactions for $\chi \neq 1$. In contrast, as $\epsilon_r \rightarrow \epsilon_0$ the ion-ion interaction term, Eq. 1, becomes increasingly dominant as the solvation contribution goes to zero. This explains why the Law of Matching Water Affinities does not apply for non-polar solvents with dielectric constant approaching that of vacuum.

Table 2: Pairing free energies for differently sized ion-pairs according to Eqns. 1 and 2. $a_{small} = 1.5 \text{ \AA}$, $a_{big} = 2.0 \text{ \AA}$, $|q| = 1e$, $s = 1.3$, $\epsilon_i = 2$. In units of kT .

	$\beta\Delta G_{\text{pair}}$	$\beta\Delta G_1$	$\beta\Delta G_2$	$\beta\Delta w_{12}$	$\beta\Delta G_{\text{pair}}^{gas}$
small–small	-6.2	3.4	3.4	-13.0	-93
small–big	3.5	19	-3.7	-11.8	-80
big–big	-4.7	2.6	2.6	-9.8	-70

Given a fixed value for the radius of one ionic species, ions with radii of similar magnitude, thus have a lower free energy at contact than ions of dissimilar radii. This result is the opposite to that of the PM, which would generally predict greater negative interactions as the ionic radius of one species decreases with respect to the other. The same effect is seen in larger ions, though

the magnitudes of the free energy changes are diminished (roughly proportional to the inverse lengthscale of the ions).

These results are further supported by *ab initio* calculations of ion pair formation using the polarizable continuum model (PCM).²⁰ Similarly to our PCPM approach described above the pairing free energy is calculated from the difference between the isolated ions and the associated pair. As an improvement, the solvation cavity is no longer spherical but reflects the electronic structure of the encompassed ion(s) and, in addition, PCM takes into account cavity free energy in the solvent. Motivated by the experimental backing of calibrated MD force-fields, the contact distances between pairing ions are set equal to the first $g(r)$ maximum from explicit solvent MD simulations as shown in Figure 1. As shown in Table 3 the free energy gain of replacing cesium with sodium is $-3 kT$ for fluoride in water, while it is $+4 kT$ in the case of aqueous iodide. Hence, the PCM indeed captures the big–big preference over big–small but *only* in a highly polar dielectric medium; in vacuum the distance of closest approach again determines the pairing free energy, precisely as in our classical model for non-polar media.

Table 3: Pairing free energy differences between cesium and sodium halides obtained from: MP2-level PCM calculations, the presented PCPM using radii as in the MD simulations²¹ and finally, explicit solvent MD simulations c.f. Figure 1. In units of kT .

	$\beta\Delta\Delta G_{\text{Cs}\rightarrow\text{Na}}$			
	PCM		PCPM	MD
	$\epsilon_r = 80$	$\epsilon_r = 1$	$\epsilon_r = 80$	SPC/E
Fluoride	-3.1	-52	-0.73	-1.5
Iodide	4.4	-29	5.2	3.0
Size rule obeyed	yes	no	yes	yes

The models presented so far – classical as well as quantum mechanical – treat the solvent as a dielectric continuum and, hence, are insensitive to the chemical structure of the solvent molecules. Yet they capture the essential details of the empirical Law of Matching Water Affinities, which suggests that the basic physical mechanism is not specific to the molecular nature of the (polar) solvent. Thus we would anticipate that the proposed “shadowing” mechanism is present in

other polar solvents. Nevertheless, the molecular structure of the solvent does come into play for capturing quantitative details of ion pairing and hydration (such as the different hydration energies of cations vs. anions of the same valency and size^{5,22}).

Calculation Details: MD simulations were performed in the *NPT*-ensemble using Gromacs version 4.0.5²³ with 809 water molecules and one pair of the studied salt (NaF, NaI, CsF, CsI). Simulation lengths were of 150 ns (2 fs time steps), and held at 300 K and 1 atm using the velocity-rescaling thermostat and the Berendsen barostat, respectively. For water we used the SETTLE constrained SPCE model^{24,25} while for ions the forcefield described in our previous paper²¹ was employed. Particle-Mesh Ewald summation was used to account for long-range electrostatic interactions. *Ab initio* calculations were performed at the second-order Møller–Plesset perturbation theory level (MP2), using the aug-cc-pVTZ basis sets for sodium with additional core-valence basis functions (cc-pCVTZ) added for fluorine, aug-cc-pvTZ-PP for iodine²⁶ and optimized valence basis set with effective core potentials for cesium.²⁷ Ion pairing free energies were evaluated as the difference between the free energy of the solvated contact ion pair and the free energies of the separately solvated cation and anion in water. Anion-cation distances were taken from MD simulations for the contact ion pairs in explicit water (see above). Water was described as a polarizable continuum solvent using the PCM model²⁰ within the self-consistent reaction field approach. PCM calculations were performed using the Gaussian 03 program package using default parameters.²⁸

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