Ion-Dipole Interactions

Ion-Dipole Forces are involved in solutions where an ionic compound is dissolved into a polar solvent, like that of the solution of table salt (NaCl) into water. So these must be for solutions (and not pure substances).

\[ \text{Na}^+ \leftrightarrow (\text{H}_2\text{O})_n \]

Figure \(\PageIndex{1}\): Ion-Dipole interaction. Note the oxygen end of dipole is closer to the sodium than the hydrogen end, and so the net interaction is attractive.

The name "Ion dipole forces" describes what they are, which simply speaking, are the result of the Coulombic electrostatic interactions between an ion and the charged ends of a dipole. Note that here, the term "Intermolecular Force" is a misnomer, even though it is commonly used, as these are the forces between ions with molecules possessing a dipole moment (unequal sharing of valence electrons). To gain an understanding we can start by looking at the Coulombic potential between two ions (Equation 2).

What is the difference between Coulombic Ion-Ion and Ion-Dipole interactions?

In the introduction to this chapter we saw that two charged particles \(q_1\) and \(q_2\) had a potential energy related to Equation 11.2.1

\[
\underbrace{E= k\frac{q_1q_2}{r}}_{\text{ ion-ion potential }} \label{11.2.1}
\]

For ion-dipole interactions the interaction is between a dipole moment \(\langle \mu \rangle\), which is really a vector with a magnitude of \(q' r\), where \(q'\) is the value of the partial charge in the dipole moment \(\langle \delta^+ \rangle\) or \(\langle \delta^- \rangle\), noting they are of the same magnitude, just opposite in sign), with an ion of charge \(q\). (We are using \(q'\) to indicate the partial charge in the dipole just to prevent it from being confused with \(q\), the charge of the ion).

So there are two interactions, with one being attractive and the other repulsive, as shown in Figure \(\PageIndex{2}\).
Now if you think about it, the positive-positive repulsion means the positive end of the dipole is going to be farther away from the cation then the negative end that is attracted. So the net force is attractive since since the radius (in the denominator of Coulomb's Law, Equation \ref{11.2.1}) for the +/- attraction is smaller than the radius for the +/+ repulsion. This difference is greatest when the polar molecule is "touching" the cation, and as they become further separated the relative differences in the radii between the two interactions become less, and at great distances they become equal. This can be understood by looking at Figure \(\PageIndex{4}\).

\[ E \propto \frac{-|q_1|\mu_2}{r^2} \quad \text{(ion-dipole potential)} \]

The result in an inverse square of the distance function \(1/r^2\) for the decrease for ion-dipole interactions as compared to a \(1/r\) effect for ion-ion interactions, as shown in Equation \ref{11.2.2}.

\[ E = -k\frac{|q_1|\mu_2}{r^2} \quad \text{(ion-dipole potential)} \]

\(\alpha\) means "proportional to" (the proportionality constant depends on the medium)

\(r\) is the distance of separation.
• \(q\) is the charge of the ion (only the magnitude of the charge is shown here.)
• \(k\) is the proportionality constant (Coulomb's constant).
• \(\mu\) is the permanent dipole moment of the polar molecule. \(\underbrace{\vec{\mu} = q' \, \vec{d}}_{\text{dipole moment}}\)

Note

Equations \ref{11.2.1} and \ref{11.2.2} are dimensionally equivalent. This is because \(\mu\) has the units charge times distance (Equation \ref{11.2.3}), and to distinguish these, we are using "d" to represent the distance between the dipoles from each other, and "r" to represent the distance between the ion and the polar molecule. Likewise, we are using q to represent the charge of an ion, and q' to represent the partial charge in a dipole (most texts will use q for both of these).

**Key differences between ion/ion and ion/dipole interactions**

1. Ions have integer charges (1, 2, 3... for cations and -1, -2, -3... for anions), while dipole's have partial charges \(\delta^{+\text{ or }-}\)) and the partial charges can be very small fractions.
2. Ion-ion interactions fall off slower than ion-dipole. Tripling the distance between two ions reduces the energy by 1/3, while tripling the distance between the ion and a dipole reduces it by 1/9.

**Exercise \(\PageIndex{1}\)**

Why does the Coulombic ion-dipole equation \(\ref{11.2.2}\) have a negative sign and the absolute value on the charge, while the ion-ion equation \(\ref{11.2.1}\) does not?

**Answer:**

• The ion dipole interactions are always attractive resulting in a lowering of the potential energy. Since \(\mu\) is always positive, and q can be positive (cation) or negative (anion), we use its absolute value and add the negative sign. For ion-ion, they can be attractive (+/-) which results in a negative E, or repulsive (+/+ or -/-), both of which result in a positive E.

**Exercise \(\PageIndex{2}\)**

How does the ion-dipole equation show that ion dipole interactions are shorter range than ion-ion interactions?

**Answer:**

• The ion-ion interaction energy is inversely proportional to the distance between the ions \(1/r\), while the ion-dipole energy is inversely proportional to the square \(1/r^2\). So doubling the distance decreases the first by a factor of 2, and the later by a factor of 4 (and tripling the distance decreases the first by a factor of 3, and the later by a factor of 9). So ion dipole interactions are much shorter ranged.

It also needs to be understood that these equations are based on electrostatic interactions and molecules in a solution are rotating and vibrating and actual systems are quite complicated, with the medium (molecular environment) influencing the actual behavior. Coulombs constant is based on the permittivity of an electric field in a vacuum, and actual chemical systems are not in a vacuum, and so the permittivity will be different. The important thing to realize is that these interactions are Coulombic in nature, and these equations show this in terms of the magnitude of the charges.
and their distances from each other, which are the two major factors influencing the strength of intermolecular forces. In
this course we will not be calculating dipole moments or the magnitudes of them, but understanding how to read the
equations, and developing qualitative understandings that allow us to predict trends.

It should also be understood that not all ion-dipole interactions are in solutions. For example, hydrated salts where the
water is “captured” in a crystal's interstitial regions (holes in the lattice) are ion-dipole in nature. In fact these can be
necessary to form certain crystalline geometries as the polar water molecule can reduce the repulsion of like charges
within a lattice. We will look at crystals in the next chapter.

### Periodic Trends and Hydration Energy

The enthalpy of hydration is often defined as the energy released when a mole of a gaseous cation is dissolved in water,
and is related to ion-dipole forces.

\[M^{+}_{(g)} + \text{water} \rightarrow M^{+}_{(aq)}\]

The smaller the cation, the closer the particles, and for a given charge the stronger the ion-dipole forces and the greater
the enthalpy of hydration (more exothermic). This is exemplified by the enthalpies of hydration in Table \(\PageIndex{1}\)).
It needs to be noted that the above definition aligns with thermodynamic values, where greater means more exothermic
(negative). That is, from the first law of thermodynamics, positive energy is energy added to the system (endothermic) and
negative is when it is released (exothermic), so the small Lithium has a lower value (-515 kJ/mol) than the larger Cesium
(-263 kJ/mol), as forming the hydrated ion is the exothermic process. This may be easier to see by looking at the back
reaction, where you need to add energy to remove the hydrated ion and place it in the gas phase, since that is obviously
endothermic, the reaction as drawn must be exothermic. Since lithium is smaller, it would take more energy to remove it,
so the formation of the hydrated ion is more exothermic (negative) than the large Cesium. You must always correlate the
sign of an energy to its process, and recognize that you can “form” or "break" any bond or intermolecular force. As writen,
this is the formation, which is the exothermic process.

**Table \(\PageIndex{1}\)): Enthalpies of hydration for alkali metals show the smaller the
radi the larger the energy, and this is related to the ion-dipole forces of the solvated
ions.**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic Radius (pm)</th>
<th>Enthalpy of Hydration (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Li}^+))</td>
<td>90</td>
<td>-515</td>
</tr>
<tr>
<td>((\text{Na}^+))</td>
<td>116</td>
<td>-405</td>
</tr>
<tr>
<td>((\text{K}^+))</td>
<td>152</td>
<td>-312</td>
</tr>
<tr>
<td>((\text{Rb}^+))</td>
<td>166</td>
<td>-296</td>
</tr>
<tr>
<td>((\text{Cs}^+))</td>
<td>181</td>
<td>-263</td>
</tr>
</tbody>
</table>

**Hydrated Salts:** Ion-dipole forces also explain why many salts will trap water when they crystallize and form hydrated
salts. This is common for small cations like sodium and lithium, which form hydrates like sodium carbonate decahydrate
$\text{Na}_2\text{CO}_3\cdot10\text{H}_2\text{O}$, while larger salts like rubidium and cesium do not form hydrates.

**References**

1. Chemical Principles: Atkins and Jones