Charge Density Mismatch is a Key Characteristic of Highly Concentrated Electrolyte Solutions and Highly Water-Soluble Salts

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Abstract: Only very soluble electrolytes can form concentrated solutions. Some salts are so soluble that there are less than four water molecules per ion in saturated solution. Ions usually form clusters or networks with more than one counterion in their coordination sphere in these concentrated solutions. Do these ultra-concentrated solutions form because the counterions have high affinity for each other in liquid, or because they have a poor affinity for each other in solids? Here we address this question using the Valence Matching Principle of the Bond Valence Model by comparing the charge density mismatch between counterions to their solubility for a series of alkali fluorides, carboxylates, and oxyanions. The solubilities were plotted against the characteristic average bond valence of the alkali, and the lowest solubilities were those where alkali and anion had matching bond valences. Conversely, the highest solubilities were those with poorly matching bond valences. Available ion-pairing constants indicate that the weakest ion-pairs are those with the largest bond valence mismatch, indicating that the large water solubilities occur despite weak ion-pairing rather than because of strong ion-pairing. Therefore, a key characteristic of highly water-soluble salts is that the counterions have mis-matched charge densities.

Introduction

Concentrated aqueous electrolytes are common in many applications and industries. Examples include batteries, deep eutectic solvents, heat exchanges, and in alkaline nuclear waste.[1-4] With increasing concentration, competition for water molecules occurs and there is a thermodynamic driving force for dissolved ions to form solvent-shared or contact ion-pairs.[5-12] At high concentrations, nearly every ion has a counterion in its immediate vicinity, and formation of ionic clusters or large scale ion-water polyhedron network are expected.[13, 14] Saturated cesium fluoride (CsF) solution is an example of a highly concentrated solution with the solubility of 34.8 m (molality; mole solute per Kg of water) at 25 °C. [15] This amounts to just 0.8 water molecules per dissolved ion, and falls in the stoichiometry range of many hydrated salts that have water molecules in their crystal structure. To characterize the connectivity patterns involving ion-pairs or ionic clusters and understand how certain ion-water polyhedron are more likely to be linked to some polyhedra than to others are part of cluster formation theory, which is still being developed.

Much of the theorical insights into ion solvation and association reactions have been developed from dilute limits where the Debye-Huckel Equation is valid. Solution-phase reactions in highly concentrated conditions, however are not as advanced.[16-19] The Kirkwood transition theory applies to a concentration point where the charge-charge screening between ions switches from purely exponential

decay (at dilute) to a damped oscillation as concentration increases.[20] This implies to a change of reaction length scales from simple charge screening (by solvation) to formation of correlated ion-water networks. For instance, coulombic interactions at high concentrations may thus be very different from dilute solutions.[21]

In the present study, we define an ultra-concentrated aqueous electrolyte as one with less than four water molecules per ion. This assumption is taken from water coordination numbers of some very small ions, such as fluoride[22] (F^-, the smallest anion), hydroxide ion[24] (OH^-, slightly larger than F^-) and lithium ion[24, 25] (Li^+, the smallest metal cation), in which they all have a minimum of four water molecules in the first solvation shell. Therefore, when there are less than four water molecules per dissolved ion in a solution, there is insufficient water for all the ions to be surrounded by water molecules without sharing at least a fraction of them. A solution defined in this way would be greater than 6.94 m for a simple electrolyte with two monovalent ions, or 4.63 m for an electrolyte with one divalent anion and two monovalent cations. Ultra-concentrated solutions might have some domains that still resemble bulk water (see discussion in[26, 27], for instance), but dissolved ions, on average, have counterions separated by the thickness of only one water molecule (as solvent-shared ion-pairs) or none (as contact ion-pairs) in almost every direction.[13] More commonly, ultra-concentrated solutions form ion-clusters or networks where ions are in direct contact with more than one counterions.[28-37]

Only electrolytes that are extremely soluble in water could form these ultra-concentrated solutions. One could assume that these electrolytes form such concentrated solutions because they form strong ion-pairs, stabilizing as ion-paired species in the liquid phase rather than precipitating. However, there have been many reports of electrolytes that form ion-pairs in dilute or moderately concentrated conditions, but these species appear to re-dissociate in ultra-concentrated solutions.[11, 16-19, 37]. For instance, tetra-n-butylammonium picrate acts like an ion-paired species in moderately concentrated solution but acts like free ions in highly concentrated solutions.[19] Thus, an alternative explanation could be that the solid-phase nucleation is so unfavorable and large energy barriers or penalties are incurred that the electrolytes would rather remain in the liquid phase, even when there is little water. Predicting solubility is challenging.[38] Simple guidelines such as "like dissolves like" explain why polar constituents dissolve in polar solvents (such as water) and why non-polar constituents dissolve in non-polar solvents.[39] Given that most of the common small inorganic ions are readily solvated by water, the individual nature of the ions is important, [40-44]

Are there principles derived from the analysis of crystal structures that can help us understand solubility trends in ultra-concentrated solutions? Hawthorne et al. used the Valence Matching Principle and bond valence model to explain how water molecules incorporated into the crystal structure of salts can mitigate a charge-density mismatch between counterions.[45-49] The bond valence model has also been used extensively to identify likely stable crystal structures from a set of candidate structures.[50, 51] Here, we argue that a similar concept may be used to explain why some aqueous electrolytes remain stable as ion-water clustering network rather than precipitate. While there may be ion-specific effects on the relative affinity for water, we show that, using the bond valence model as a tool, the most common cause for high solubility in many alkali-metal salts is likely due to charge-density mismatch effects.

In the following discussion, we first evaluate the extent to which solubilities can be understood in terms of the Valence Matching Principle and the bond valence model for a variety of alkali-metal containing salts. The ease in quantification of charge-density mismatch of involved ions and its intuitive relation to the relative stability of different phases are presented. Below it is shown that this simple approach yields a remarkably consistent picture of solubility in terms of valence matching properties, and can explain why certain salts are extremely soluble. The finding may indicate a path forward for more detailed theoretical interrogation by molecular simulations.

Experimental Section

Valence Matching Principle Theory

The bond valence model grew out of Pauling's bond strength concept. Pauling defined bond strength as the formal charge on an ion divided by the ion's coordination number.[52] Donnay and Allmann found a better empirical correlation between charge per bond length than formal charge, a relationship termed the bond valence to distinguish it from Pauling's bond strength.[53] The bond valence is now regarded as the quantity of charge contributed to a bond. [50, 51]

Though the bond valence model is simplified relative to other theories of bonding, it is consistent with those other theories.[50, 54] Physical bases have been developed for bond valences.[55-59] The larger the bond valence, the more covalent the bond is, and the greater the electron density at the bond critical point.[56] For the oxyanions, the bond between the oxyanion's central cation and the oxygen anions would be largely covalent or intermediate between covalent and ionic.[60] In contrast, bonds between the alkali ions and the oxyanion's oxygen atoms would be largely ionic given the small characteristic bond valences of the alkali and the residual bond valence on the oxygen anions.[65, 66]

Though the bond valence is proportional to the bond length for individual bonds, the sum of the bond valence for all bonds for an ion is equal to the ion's formal charge.[50, 51] This means that Pauling's initial bond strength equation (formal charge divided by coordination number) can approximate the average bond valence per coordinating ion, though individual bonds may vary substantially from this average through their different bond lengths. Characteristic average bond valences reported in valence units (v.u.) per bond have been developed for individual ions.[51] The characteristic bond valences have a relatively narrow range for most cations and many anions.[51]

Bond valence theory predicts that inorganic ions obey the Valence Matching Principle,[50, 51] which states that stable compounds will be formed when the bond valences of the cation and anion closely match; i.e., when the absolute magnitude of the characteristic cation valence matches the absolute magnitude of the anion characteristic valence. For example, F^- has a characteristic valence of -0.25 v.u. and Li^+ has a characteristic valence of +0.22 v.u., which are close to each other in absolute magnitude. Therefore, one would expect LiF to be a stable compound. In contrast, Cs^+ has a characteristic bond valence of 0.08, which is very different from -0.25 v.u. for F^-, which means that CsF would be expected to be much less stable than LiF. In the present study we hypothesize that this is reflected in the relative solubility of LiF and CsF in water. In other words, the Valence Matching Principle is related to thermodynamic quantities such as Gibbs free energies due to its origin in the analysis of stable crystal structures.

If the Valence Matching Principle is applicable to both ion-pairs in solution and to salt solids containing the same electrolytes, then counterions with matching characteristic bond valences might be expected to form both strong ion-pairs and stable salts. However, this is counterintuitive because if the counter-ions had a high affinity for each other they would precipitate instead of forming ion-pairs. This suggests that high solubility and, presumably, the tendency to form ion-clusters in solution stems from a bond valence mismatch. The prospect that bond valence mismatch is a characteristic of highly concentrated solutions would be consistent with the notion that bond valence matching is a characteristic of stable solids while an unstable solid would be very soluble. In the liquid-phase the ions have a larger potential range of coordination numbers and bond lengths. Hawthorne[61] hypothesized that the Valence Matching Principle would predict the relative solubility of solids, but there has been only limited verification of that hypothesis.[62, 63]

The present study will use a simple estimate of the bond valence of ions to determine how bond valence differences between counterions correlate with the solubility of alkali fluorides, small carboxylates, and oxyanions in water. Solubility data was collected from the literature at 25 °C because there is more data available at this temperature than any other. Alkali-bearing salts were studied because there is extensive solubility data available and because alkali salts are often very soluble. Gagne and Hawthorne published estimates of the characteristic bond valence for the alkali ions bonded to oxygen at ambient temperatures, averaged over many crystal structures (Table 1).[64] The radius of fluoride and the oxygen anion are similar, so the characteristic bond valence of the alkali bound to fluoride would be expected to be similar.

Table 1. Characteristic Bond Valences for Alkali Ions. Data from Gagne and Hawthorne[64].

Alkali Ion	Characteristic Bond Valence (v.u.)	Standard Deviation
Li^+	0.215	0.041
Na^+	0.159	0.034
K^+	0.108	0.027
Rb^+	0.099	0.024
Cs^+	0.084	0.020

The oxygen anion has such a large range of potential bond valences that its characteristic bond valence is of little use in the Valence Matching Principle.[45] This is because the charge density at the bond critical point depends on the cation because of electronegativity differences between electropositive cations and oxygen.[57, 58, 65-67] Consequently, oxygen has a variable radius with more covalent bonding having shorter bonds and more ionic bonding having longer bonds.[67, 68] Fortunately, the oxygen atoms within oxyanions have a more constrained range, which can be defined based on the central electropositive element in the oxyanion.[46-49] A reasonable estimate of the bond valence of the oxygen atoms within oxyanions is to take the overall charge of the oxyanion, divide it by the number of oxygen atoms within the oxyanion, and assume that oxygen is coordinated by four cations on average (Equation 1).[45] For instance, sulfate (SO_4^{2-}) has a formal charge of -2 and has four oxygen atoms, so there is a total bond valence available -0.5 per oxygen atom for bonding with cations outside of sulfate. Each oxygen is bound to the sulfur cation, and thus can be coordinated by three additional cations. Therefore, there is an average bond valence of -0.5/3 = -0.17 v.u. per alkali cation per oxygen.[45] This same procedure was used to calculate the bond valence of all the oxyanions and carboxylates in this study, which are shown in Table 2. F^- has a characteristic bond valence of -0.25 v.u.[51]

$$Bond\ valence = {}^{formal\ charge}/_{coordination\ number} \qquad \text{Equation 1}$$

Table 2. Estimated Characteristic Bond Valences for Anions in This Study.

anion	Chemical formula	Bond valence
fluoride	F^-	-0.25
bromate	BrO_3^-	-0.11
acetate	CH_3COO^-	-0.17
carbonate	CO_3^{2-}	-0.22

oxalate	$C_2O_4^{2-}$	-0.17
chlorate	ClO_3^-	-0.11
perchlorate	ClO_4^-	-0.08
chromate	CrO_4^{2-}	-0.17
dichromate	$Cr_2O_7^{2-}$	-0.09
formate	$HCOO^-$	-0.17
iodate	IO_3^-	-0.11
periodate	IO_4^-	-0.08
permanganate	MnO_4^-	-0.08
molybdate	MoO_4^{2-}	-0.17
nitrate	NO_3^-	-0.11
hydroxide	OH^-	-0.33
perrhenate	ReO_4^-	-0.08
sulfite	SO_3^{2-}	-0.22
sulfate	SO_4^{2-}	-0.17
selenite	SeO_3^-	-0.22
selenate	SeO_4^{2-}	-0.17
tellurite	TeO_3^{2-}	-0.22
metavanadate	VO_3^-	-0.11

The oxyanion bond valences in Table 2 can be compared to those few determined by averaging data from many crystal structures reported by previous researchers. Echigo and Mitsuyoshi[69] determined the oxalate anion bond valence is -0.17 v.u., the same as in Table 2. Hawthorne[70] gives the bond valence values of -0.22, -0.17 and -017 v.u. for carbonate, sulfate, and chromate, respectively, which is also identical to the values in Table 2. Hawthorne[70] reports a value of -0.12 v.u. for nitrate, which is only -0.01 v.u. different from the value in Table 2. These comparisons demonstrate that the simplistic method used here to calculate oxyanion bond valences is reasonably accurate compared to those more in-depth methods evaluating many crystal structures, so are likely to be reasonably accurate for the rest of the oxyanions as well.

Limitations of the Bond Valence Approach and Valence Matching Principle

The bond valence model is a somewhat simplistic model of bonding,[71] and the present method of estimating oxyanion bond valences simplifies it further. Obviously, the oxygens in the oxyanions can be coordinated by greater or fewer alkali cations.[72] Three alkali per oxygen were used here for comparison purposes and because it is associated with the most common oxygen coordination number.[45] These comparisons demonstrate that the simple method used here to calculate oxyanion bond valences provides results that are reasonably accurate when compared to more comprehensive approaches that evaluate numerous crystal structures. Therefore, this method is likely to yield similarly reliable results for other oxyanions as well.

Here, some additional limitations with using the bond valence model and the Valence Matching Principle are discussed. The simple method of calculating bond valences does not consider steric factors, where cations of different size may not be able to fit optimally around some oxyanion's oxygens, resulting in longer bonds or smaller coordination numbers than those assumed in the simplistic calculations above. Second, many of the salts evaluated in this study incorporate water into their crystal structure, and many of the experimental solubility studies that we drew from did not mention how many or even if water molecules were incorporated into the salt. As noted earlier, Hawthorne showed that

salts can incorporate water into their structure to mitigate differences in the bond valence between cation and anion.[45-49] When the counterions in a salt have poorly matching characteristic bond valences, water incorporation increases the stability of a salt compared to an anhydrous salt of the same ions. An example would be sodium metavanadate, where the thermodynamically stable dihydrate has a solubility of 1.116 molal but the metastable anhydrous salt has a solubility of 1.530 molal.[73] Thus, water incorporation plays a role in the relative solubility of salts.

Sodium sulfate (Na_2SO_4) has been used to illustrate the Valence Matching Principle in many publications.[45-50] Sulfate's oxygens have a characteristic bond valence of -0.17 and Na^+ has a characteristic bond valence of 0.16, so they match each other. Thus, Na_2SO_4 is a stable phase, and anhydrous Na_2SO_4 is the stable salt precipitated from water above 32.4 °C.[74] However, below 32.4 °C, the hydrated salt $Na_2SO_4 \cdot 10H_2O$ (mirabilite) precipitates. This implies that the Na^+ and SO_4^{2-} valences do not match as well below 32.4 °C, or else water would not need to be incorporated into the salt. There is thus a temperature dependence to the bond valence that is not well understood.
The solubility of hydrated salts depends on the water activity in solution[75] The water activity, in turn, depends on the concentration of dissolved species to the extent that those dissolved ions bind water.[75, 76] The structure of water around ions in salt hydrates is like the structure around ions in water.[27] Sidgewick and Ewbank showed that the likelihood that a salt would form a hydrate was correlated to how strongly the ions bound water in solution.[77]

Water donates and accepts hydrogen bonds both with other water molecules and with ions. Water thus has a bond valence.[78, 79] In crystal structures, water has an average bond valence of approximately 0.2, meaning that the water hydrogen bonds donate about 0.2 v.u. of charge and the oxygens accept an average of two hydrogen bonds each receiving 0.2 v.u. of charge each.[79] There is substantial range around this value, Brown indicates water can form hydrogen bonds with valences between 0.08 and 0.33 v.u.[50] Brown[50] has stated the average bond valence of liquid water is about 0.17, though provided no justification for that value. Regardless, water is willing to accept or donate a wide range of hydrogen bond strengths because the rest of the water molecule can compensate for one strong or weak hydrogen bond.[50] This is likely a contributing factor to salt solubilities.

Note that the alkali ions have a larger range of potential bond valences than many other cations, in part because they can have a large range of coordination numbers and bond lengths.[68] The heavier alkali K^+, Rb^+ and Cs^+ have characteristic bond valences that are close to each other and with ranges that almost completely overlap (Table 1).[64, 68] As will be seen later, these large alkalis usually track together and often exhibit small differences in the order of relative solubility amongst them. Given the overlap in the bond valence ranges for the three heavy alkali, we discounted small differences in the order of their relative solubility.

Solubility Data Collection

The literature was searched for solubility data at 25 °C for fluorides and oxyanions. Table 3 contains the solubility data used in this study in both the original units reported by the literature source and after converting them to molality units. Any special data considerations are listed in the Notes and References column of the table. Table 3 lists the electrolytes/salts in the order they are discussed in the Results section below.

Table 3. Solubility Data Used in This Study.

Electrolyte	Solubility as reported in reference source	Units from original source	Solubility converted to molality (moles/Kg of water)	Notes and Reference
LiF	0.133	wt %	0.051	[80] Note that the temperature was 25.4 °C not 25 °C. We assumed that this was an insignificant temperature difference.
NaF	0.987	molality	0.987	[81]
KF	17.5	molality	17.5	[82]
RbF	74.3	wt %	27.7	[83]
CsF	84.1	wt %	34.8	[15]
$LiNO_3$	22.96	molality	22.96	[84] Note that this is the metastable anhydrous salt solubility, as estimated by this reference. The solubility of $LiNO_3 \cdot 3H_2O$ is 12.81 molality
$NaNO_3$	10.79	molality	10.79	[85]
KNO_3	26.3	wt %	3.53	[86]
$RbNO_3$	41.4	wt %	4.79	[86]
$CsNO_3$	21.5	wt %	1.41	[87]
Li_2CO_3	1.21	wt %	0.166	[88]
Na_2CO_3	22.7	wt %	2.77	[89]
K_2CO_3	52.8	wt %	8.10	[90]
Rb_2CO_3	70.7	wt %	10.4	[91]
Cs_2CO_3	73.27	wt %	8.41	[92]
$Li_2C_2O_4$	5.87	wt %	0.657	[93]
$Na_2C_2O_4$	0.274	molality	0.274	[63]
$K_2C_2O_4$	27.4	wt %	2.97	[93]
$Rb_2C_2O_4$	50.91	wt %	5.98	[94]
$Cs_2C_2O_4$	75.82	wt %	14.2	[93]
CH_3COOLi	31.28	wt %	8.46	[95] Note that the temperature was 25.8 °C not 25 °C. We assumed that this was an insignificant temperature difference.
CH3COONa	6.14	molality	6.14	[96]
CH_3COOK	27.4	molality	27.4	[96]

CH_3COORb	86.987	wt %	46.3	[95] This value was determined by regressing solubility data at other temperatures. See text.
CH_3COOCs	90.857	wt %	51.8	[95] This value was determined by regressing solubility data at other temperatures. See text.
$LiHCO_2$	30.54	wt %	8.46	[97]
NaHCO2	48.55	wt %	13.9	[97]
$KHCO_2$	78.4	wt %	43.2	[97]
$RbHCO_2$	85.13	wt %	44.5	[95] This value was determined by regressing solubility data at other temperatures. See text.
$CsHCO_2$	82.425	wt %	27.1	[95] This value was determined by regressing solubility data at other temperatures. See text.
LiOH	11.1	wt %	5.21	[98]
NaOH	53.2	wt %	28.3	[99]
KOH	54.7	wt %	21.5	[100]
RbOH	69.57	wt %	22.3	[100]
CsOH	80.56	wt %	27.6	[101]
$LiClO_3$	82.6	wt %	52.5	[102]
$NaClO_3$	50.07	wt %	9.42	[103]
$KClO_3$	7.90	wt %	0.699	[103]
$RbClO_3$	6.21	wt %	0.392	[104]
$CsClO_3$	0.359	wt %	0.017	[105]
$LiBrO_3$	65.64	wt %	14.2	[106]
$NaBrO_3$	28.29	wt %	2.61	[103]
$KBrO_3$	7.533	wt %	0.488	[103]
$RbBrO_3$	0.1383	molality	0.1383	[105]
$CsBrO_3$	0.1457	molality	0.1457	[105]
$LiIO_3$	43.82	wt %	4.29	[107]
$NaIO_3$	8.66	wt %	0.479	[108]
KIO_3	8.40	wt %	0.429	[109]
$RbIO_3$	2.39	wt %	0.094	[109]
$CsIO_3$	2.61	wt %	0.087	[110]
$LiClO_4$	60.95	wt %	14.7	[111]
$NaClO_4$	67.7	wt %	17.1	[111]
$KClO_4$	2.02	wt %	0.149	[111]
$RbClO_4$	1.32	wt %	0.072	[111]
$CsClO_4$	1.93	wt %	0.085	[111]
$NaIO_4$	12.62	wt %	0.675	[112]
KIO_4	0.51	wt %	0.022	[112]

$CsIO_4$	2.05	wt %	0.065	[113]
Li_2SeO_3	1.43	wt %	1.43	[114]
Na_2SeO_3	5.15	wt %	5.15	[114]
K_2SeO_3	68.5	wt %	10.6	[114} Note this value was calculated form a regression equation the reference. See text.
Li_2SeO_4	40.1	wt %	4.27	[115]
Na_2SeO_4	36.7	wt %	3.07	[116]
K_2SeO_4	53.35	wt %	5.17	[117]
Rb_2SeO_4	62	wt %	5.20	[118]
Cs_2SeO_4	72.2	wt %	6.35	[119]
Li_2SO_4	3.133	molality	3.133	[120]
Na_2SO_4	1.965	molality	1.965	[121]
K_2SO_4	0.694	molality	0.694	[122]
Rb_2SO_4	33.77	wt %	1.91	[123]
Cs_2SO_4	64.53	wt %	5.03	[123]
Na_2SO_3	2.44	molality	2.44	[114]
K_2SO_3	6.72	molality	6.72	[114]
Li_2TeO_3	13.89	wt %	0.852	[114] Determined from regressing solubilities as a function of temperature. See text.
Na_2TeO_3	3.697	molality	3.697	[114]
$NaVO_3$	1.53	molality	1.53	[73] Note this is the solubility of the metastable anhydrous $NaVO_3$, the more stable dihydrate has a solubility of 1.116 molality.
KVO_3	0.8498	molality	0.8498	[124]
Li_2CrO_4	26.08	wt %	2.72	[125] Calculated from a regression equation as a function of temperature. See text.
Na_2CrO_4	5.17	molality	5.17	[126]
K_2CrO_4	39.5	wt %	3.36	[127]
Rb_2CrO_4	43.41	wt %	2.67	[128]
Cs_2CrO_4	45.5	wt %	2.19	[128]
$Li_2Cr_2O_7$	64.712	wt %	7.98	[129] This value was determined by regressing solubility data at other temperatures. See text.
$Na_2Cr_2O_7$	64.9	wt %	7.06	[130]
$K_2Cr_2O_7$	13	wt %	0.51	[131]
$Cs_2Cr_2O_7$	3.75	wt %	0.080	[131]

Li_2MoO_4	44.33	wt %	6.00	[132]
Na_2MoO_4	40.18	wt %	4.07	[133]
K_2MoO_4	64.58	wt %	9.25	[134]
Rb_2MoO_4	77.05	wt %	11.6	[135]
Cs_2MoO_4	79.8	wt %	10.3	[136]
$LiMnO_4$	36.2	wt %	4.51	[137]
$NaMnO_4$	62	wt %	11.5	[138]
$KMnO_4$	7.1	wt %	0.48	[139]
$LiReO_4$	74.25	wt %	11.2	[139]
$NaReO_4$	1140	g/L of water	4.17	[140] For unit conversion purposes, we approximated one L of water as one kilogram of water.
$KReO_4$	0.041	molality	0.041	[141]
$RbReO_4$	0.037	molality	0.037	[141]
$CsReO_4$	0.002276	molality	0.002276	[142]

For some electrolytes, solubility data was unavailable at 25 °C but was available at other temperatures at more than one temperature. In those cases, the solubility as a function of temperature could be regressed to develop an equation to estimate the solubility at 25 °C. In some of those cases, a literature source already regressed the solubility data and provided an equation describing the solubility as a function of temperature that could be used to estimate the solubility at 25 °C. In other cases, a regression was performed here.

Potassium selenite: solubility data was unavailable at 25 °C for potassium selenite, but Kertes et al.[114] provides the following equation to calculate the solubility (S) in wt % as a function of temperature in Kelvin (T_K).

$$S = 68.42 + 0.00007494(T_K - 273.2)^2 \qquad \text{Equation 2}$$

When this equation was solved for 298.15 K, the solubility of potassium selenite was calculated to be 68.467 wt %, which is 10.58 molality.

Lithium tellurate: solubility data was unavailable at 25 °C for lithium tellurate, but Kertes et al. [114] provides the following equation to calculate the solubility in wt % as a function of temperature in Kelvin.

$$S = 23.5 - 0.505(T_K - 273.2) + 0.00542(T_K - 273.2)^2 \qquad \text{Equation 3}$$

When this equation was solved for 298.15 K, the solubility of lithium tellurate was calculated to be 13.897 wt %, which is 0.852 molality.

Lithium chromate: solubility data was unavailable at 25 °C for lithium chromate, but Hartford et al.[125] provides the following equation to calculate the solubility in wt % as a function of temperature in Celsius (T_C).

$$S = 47.25 + 0.05037(T_C) + 0.0009143(T_C)^2 \qquad \text{Equation 4}$$

When this equation was solved for 25 °C, the solubility of lithium chromate was calculated to be 26.08 wt %, which is 2.72 molality.

Rubidium and cesium acetate: Sidgewick and Gentle[95] did not provide measured solubilities of rubidium and cesium aetate at 25 °C, but they did provide data at other temperatures that could be regressed to estimate the solubility at 25 °C. They reported the solubility of rubidium acetate to be 82.92 wt % at -9.5 °C, 86.2 wt % at 44.7 °C and 89.3 wt % at 99.4 °C. This data was regressed by least square regression to obtain the equation:

$$S = 83.522 + 0.0586(T_C) \qquad \text{Equation 5}$$

The R^2 for this regression was 0.9994. When Equation 5 is solved for 25 °C, the solubility is found to be 86.987 wt %, which is 46.3 molality.

Sidgewick and Gentle[95] reported the solubility of cesium acetate to be 89.71 wt % at -2.5 °C, 91.06 wt % at 21.5 °C and 91.98 wt % at 61.1 °C. This was regressed by least squares regression, with an R^2 of 0.939. While the data is more scattered than one might like, it should be noted how small the temperature dependence is. The solubility of cesium acetate only changes 2.27 wt % between -2.5 and 61.1°C. Thus, there is little actual error in the estimated solubilities at 25 °C using this equation. The resulting equation is Equation 6.

$$S = 89.997 + 0.0344(T_C) \qquad \text{Equation 6}$$

Rubidium and cesium formate: Sidgewick and Gentle[95] did not provide measured solubilities of rubidium and cesium formate at 25 °C, but they did provide data at other temperatures that could be regressed to estimate the solubility at 25 °C. They reported the solubility of rubidium formate to be 83.59 wt % at 14 °C, 84.61 wt % at 16.3 °C, 85.60 wt % at 28.4 °C and 87.7 wt % at 43.6 °C. This data was regressed by least squares linear regression, to obtain Equation 7, with an R^2 of 0.9692.

$$S = 82.082 + 0.1294(T_C) \qquad \text{Equation 7}$$

When Equation 7 is solved for 25 °C, the solubility is found to be 85.13 wt %, which is 44.5 molality.

Sidgewick and Gentle[95] reported the solubility of cesium formate to be 81.69 wt % at 21 °C, 83.25 wt % at 26.2 °C and 84.81 wt % at 32.2 °C. This data was regressed by least squares linear regression, to obtain Equation 8, with an R^2 of 0.9983.

$$S = 75.89 + 0.2781(T_C) \qquad \text{Equation 8}$$

When Equation 8 is solved for 25 °C, the solubility is found to be 82.421 wt %, which is 27.1 molality.

Lithium dichromate: Hartford et al.[129] did not provide solubility data for lithium dichromate at 25 °C, but did provide data at other temperatures that could be regressed and solved at 25 °C. They reported the solubility to be 62.36 wt % at 0.8 °C, 65.11 wt % at 30 °C, 66.08 wt % at 40 °C, 67.28 wt % at 50 °C, and 68.39 wt % at 60 °C. This data was regressed by least squares linear regression, to obtain Equation 9, with an R^2 of 0.997.

$S = 62.177 + 0.1014(T_C)$ Equation 9

When Equation 9 is solved for 25 °C, the solubility was found to be 64.712 wt %, which is 7.98 molality.

Harner et al.[144] measured the solubilities of lithium, sodium, and potassium nitrates and carbonates in methanol. Stenger measured the solubility of rubidium and cesium nitrates and carbonates in methanol.[143] Both of these references reported the data in units of grams per 100 grams of methanol, here converted to molality and shown in Table 4. The data from Strenger[144] was not measured precisely at 25 °C, but we assumed the small temperature difference from 25 °C was insignificant. The temperature of the experiments is shown in Table 4.

Table 4. The Solubilities of Alkali Nitrates and Carbonates in Methanol Used in This Study.

Electrolyte	Solubility (g/100 g of solvent)	Solubility (molality)	Temperature (°C)
$LiNO_3$	42.95	6.23	25
$NaNO_3$	2.936	0.345	25
KNO_3	0.375	0.038	25
$RbNO_3$	0.460	0.031	23.4
$CsNO_3$	0.309	0.016	23.5
$LiCO_3$	0.0555	0.007	25
$NaCO_3$	0.3109	0.029	25
KCO_3	6.165	0.440	25
$RbCO_3$	24.9	1.07	23.3
$CsCO_3$	56.1	1.71	21.1

Results and Discussion

Fluorides

Figure 1 is the solubility of alkali fluorides as a function of the alkali characteristic bond valence at 25 °C. Fluoride and the oxygen anion have similar radius and alkali bond lengths.[72] Li^+ has the closest matching similar bond valence to fluoride's -0.25 v.u. and has the lowest solubility (Figure 1). In contrast, the heavy alkali (K^+, Rb^+, and Cs^+) have a poorly matching bond valence with fluoride and are considerably more soluble (Figure 1). LiF has a solubility of only 0.05 molality, whereas CsF's solubility is > 670 times larger at 34.8 molal.[15, 80] NaF is in between, with solubility of 0.987 molality,[81] and Na^+ bond valence is in between those of Li^+ and K^+. There are only 1.59 moles of water per mole of ion in saturated KF solution, and only 0.8 moles of water per ion in saturated CsF solution. The alkali fluorides containing ions with matching characteristic bond valences are less soluble than those with poorly matching bond valences.

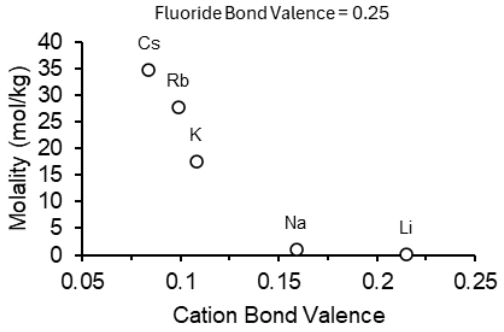

Figure 1. The solubility of fluorides as a function of alkali cation bond valence. The solubility data is from Table 3.

Both potentiometric and electrical conductivity studies indicate that the relative stability of dissolved ion-pairs between the alkali ions and F^- is $Li^+ > Na^+ > K^+$, Rb^+, Cs^+.[145-146] This order is consistent with the Valence Matching Principle: Li^+ matches the valence of F^- well and forms a stronger ion-pair with F^- than the other alkali that do not match as well. If strong ion-pairing between the alkali and F^- were the cause of the high solubilities, one would expect LiF and NaF to be more soluble than KF, RbF and CsF, but the opposite is the case. This is strong evidence that ion-pairing is not causing the high solubilities observed for KF, RbF and CsF in Figure 1, and it is instead the poorly matching charge densities in the solid-phase that are most important. Presumably ion-pairing is enhancing the solubilities of the alkali fluorides, but it is evidently of lower importance than the solid-phase stability.

Nitrate and Carbonate

Nitrate (NO_3^-) and carbonate (CO_3^{2-}) are both planar oxyanions with three oxygens surrounding the center electropositive element. The N-O and C-O bond lengths are nearly identical, comparing radii in references[147-153]. Therefore, nitrate and carbonate are essentially identical in size but differ in charge density. This charge density difference results in a difference in the characteristic bond valence for the oxygens on the oxyanion, -0.11 v.u. for nitrate and -0.22 v.u. for carbonate (Table 2). Figure 2 compares the solubility of alkali nitrates and carbonates. The relative solubility of the alkali carbonates and nitrates is exactly opposite of each other (Figure 2).

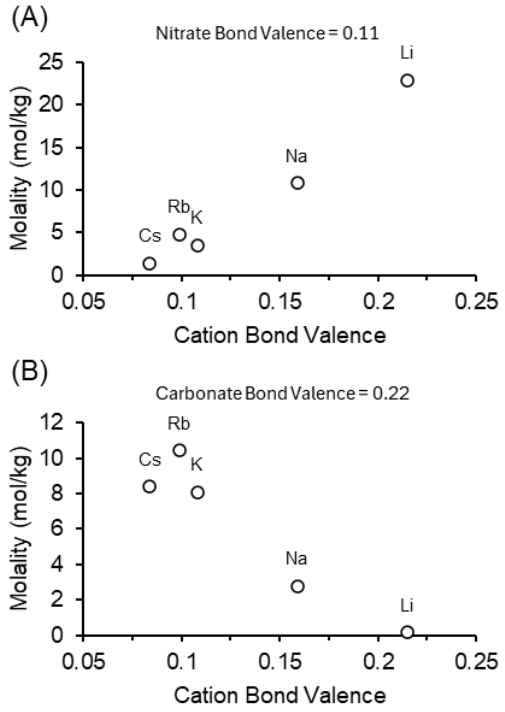

Figure 2. The solubility of nitrates and carbonates as a function of alkali cation bond valence. Solubility data is from Table 3.

The nitrate characteristic bond valence closely matches K^+, Rb^+ and Cs^+ but poorly matches bond valence of Na^+ and Li^+. Correspondingly, the heavy alkali exhibits much lower nitrate solubilities than $NaNO_3$ or $LiNO_3$ (Figure 2a). Saturated $LiNO_3$ solution has only 1.2 water molecules per ion and saturated $NaNO_3$ solution has only 2.57 water molecules per ion, forming ultra-concentrated solutions. The carbonate ion closely matches the bond valence of Li^+, and Li_2CO_3 is thus much less soluble than the heavy alkali carbonates that have poorly matching bond valence (Figure 2b). The bond valence of Na^+ is in-between the heavy alkali and Li^+, and sodium carbonate solubility is correspondingly in-between the two (Figure 2b). The heavy alkali carbonates are so soluble that there are less than 2.5 water molecules per ion in saturated solution forming ultra-concentrated solutions (K^+ = 2.29, Rb^+ = 1.77 and Cs^+ = 2.20).

Xie et al.[154] has determined that the ion-pairing strength between the alkali nitrate solutions they studied increases $K^+ > Na^+ > Li^+$, which is consistent with how well these alkalis match the characteristic bond valence of nitrate, but the opposite of their solubility. Reynolds[62] reviewed the alkali nitrate ion-pairing constants from several independent studies and found that all alkali formed relatively weak ion-pairs with nitrate, even though it is documented that at least Li^+, Na^+ and K^+ form large ion-clusters in solution.[27, 155-158] Thus, the counterions are weakly bound to each other in the clusters. This is consistent with the conclusion that the charge-density mismatch of the most soluble alkali nitrates is driving their high solubility rather than the formation of a strong complexes within the ion-clusters in the liquid phase.

The only alkali nitrate that forms a solid hydrate at 25 °C is lithium nitrate. In Figure 2a, the $LiNO_3$ solubility value is for metastable anhydrous $LiNO_3$. The solubility of the more stable trihydrate is 12.81 molal, which is considerably less soluble than the anhydrous salt at 22.96 molal.[84] The water molecules in crystalline $LiNO_3 \cdot 3H_2O$ partially separate the Li^+ and NO_3^- ions, with four of the six oxygens surrounding Li^+ coming from water molecules.[159] This is consistent with Hawthorne's studies showing that water is incorporated into salt structures to mitigate large bond valence differences, like those of Li^+ and NO_3^-.[45-49] Nonetheless, the trihydrate is still more soluble than all the other alkali nitrates. This indicates that incorporating water into the structure partially mitigate the bond valence discrepancy, which results in a lower solubility, but it does not do so enough to make $LiNO_3 \cdot 3H_2O$ less soluble than the alkali nitrates with more favorable matching bond valences.

Small Carboxylates

Figure 3 shows the solubility of three small organic anions: oxalate, acetate and formate, updating analyses reported previously[63]. All three carboxylates have a characteristic bond valence of -0.17 v.u., matching Na^+ well. Consequently, sodium oxalate and sodium acetate have the lowest solubility of the alkalis (Figure 3). Sodium formate also has a low solubility compared to the heavy alkali, but lithium formate has a slightly lower solubility (Figure 3c). Lithium formate forms a hydrated salt at 25 °C.[160] The low relative solubility of lithium formate may be because the hydration waters helped mitigate the bond valence difference between Li^+ and formate. Sidgwick and Gentle showed graphically that lithium formate is more soluble than sodium formate above 80 °C, which is where anhydrous $LiHCO_2$ precipitates instead of the hydrated salt.[95] The three heavy alkali with poorly matching bond valences form extremely soluble salts for all three carboxylates, as shown in Figure 3.

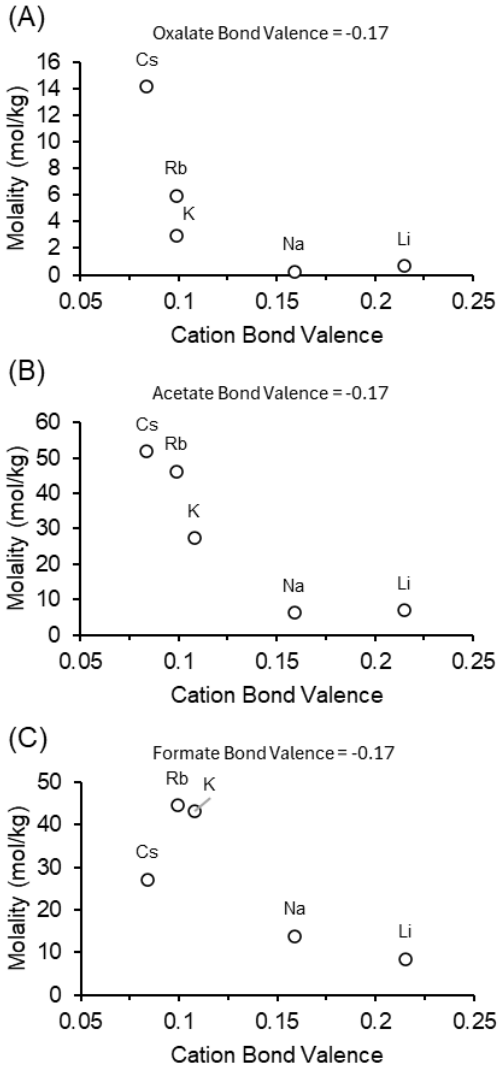

Figure 3. The solubility of oxalates, acetates and formates as a function of alkali cation bond valence. Solubility data is from Table 3.

The relative strength of ion-pairing between the alkali ions and formate has been reported to be $Na^+>Li^+>K^+>Cs^+$.[161] Similarly, the relative strength of ion pairing between the alkali ions and acetate has been reported to be $Na^+>Li^+>K^+$.[162] The Valence Matching Principle explains a previous mystery; why Na^+ forms stronger ion-pair complexes with formate and acetate than Li^+.[5] The Na^+ ion, with a characteristic bond valence of +0.16 v.u., matches the bond valence of acetate and formate (-0.17 v.u.) better than Li^+ (0.22 v.u.) or K^+ (0.11 v.u.).

All the alkali formates and acetates are extremely soluble with less than four water molecules per ion at saturation. While the Valence Matching Principle captures most of the relative solubilities of the alkali formats and acetates, the bond valence by itself does not explain the high solubility of the alkali formates and acetates. Van Der Sluys attributed the high solubility of acetates to the methyl group.[163]

Zhang et al. showed that the thermal vibrations of the methyl group influenced the binding of water to the carboxyl group on acetate.[164]

Hydroxides

The alkali hydroxides are interesting because all the alkali poorly match the bond valence of OH^- (-0.33 v.u.). Concomitantly, all the alkali hydroxides are extremely soluble, forming ultra-concentrated solutions (Figure 4). The Li^+ bond valence (0.22 v.u.) comes closest to matching the OH^- bond valence and has the lowest solubility. The bond valences of the other four alkali are so far from the bond valence of OH^- that there is little differentiation between them. Their saturated hydroxide solutions have less than 2 moles of water per mole of ion. At these low liquid-phase water contents, the remaining water acts as a bridging species to mitigate charge repulsions.[165]

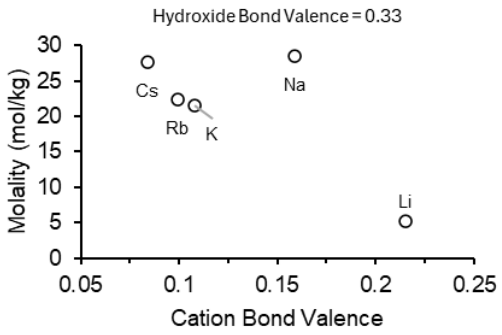

Figure 4. The solubility of hydroxides as a function of alkali cation bond valence. Solubility data is from Table 3.

Halates

The halates ClO_3^-, BrO_3^-, and IO_3^- all have a bond valence of -0.11 v.u., matching well with the three heavy alkali. Consequently, the solubility of the K^+, Rb^+ and Cs^+ halates are much lower than the poorly matching Na^+ and Li^+ halates (Figure 5). Saturated Na^+ and Li^+ chlorate solutions have less than 3 water molecules per ion, and saturated Li^+ bromate has less than 2 water molecules per ion, forming ultra-concentrated solutions. The stability of alkali chlorate ion-pairs is reported to follow the order $Rb^+ > K^+ > Na^+ > Li^+$,[166] the same order as the bond valence match for these ions, and reverse order of their solubility.

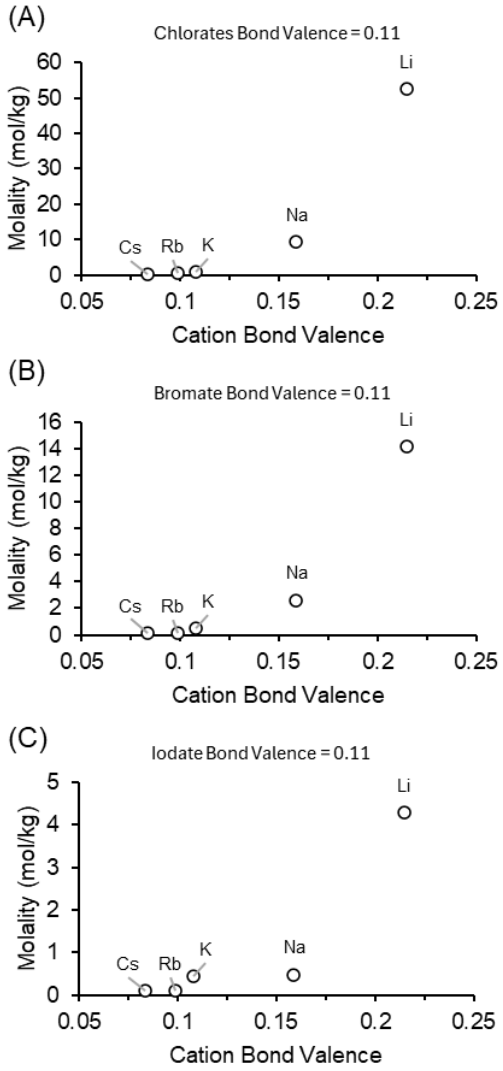

Figure 5. The solubility of chlorates, bromates and iodates as a function of alkali cation bond valence. Solubility data is from Table 3.

The Valence Matching Principle explains the relative solubility of the alkali iodates, but their absolute solubility is very low compared to many other oxyanions in this study. Even Li^+, the poorest matching bond valence and the most soluble, has more than six water molecules per ion in saturated solution. Iodate has unusual behavior in water. The large size of iodate allows water molecules to directly coordinate the iodine atom in iodate, so iodate acts as both a cation and anion.[167, 168] This does not appear to influence the relative solubility of the alkali iodates as shown in Figure 5c, meaning the relative solubility matches the Valence Matching Principle. Nonetheless, it may impact the overall solubility of the iodates.

Perchlorate and Periodate

Perchlorate has a bond valence of -0.08, matching well with the heavy alkali. Consequently, $KClO_4$, $RbClO_4$ and $KClO_4$ have very low solubility compared to $NaClO_4$ and $LiClO_4$ (Figure 6a). While the Na^+ and Li^+ perchlorates are out of order, the Valence Matching Principle successfully predicted that both would be extremely soluble. Saturated lithium and sodium perchlorate solutions have less than two water molecules per dissolved ion. The stability of alkali perchlorate ion-pairs is reported to follow the order $Rb^+ > K^+ > Na^+ > Li^+$,[169] the same order as the bond valence match for these ions, and reverse order of their solubility. This is evidence that the high solubility of sodium and lithium perchlorate is not because of strong ion-pairing.

We only found solubility data for three alkali periodates, and these solubilities were consistent with the electrolytes discussed above: the lowest solubilities were those matching the periodate bond valence of -0.08 v.u. (Figure 6b). Like the alkali iodates, the alkali periodates also exhibit abnormally low solubility, though the Valence Matching Principle predicts the relative solubility well. The low solubility of the periodates may be related to solution phase species, because periodate dimer ($H_2I_2O_{10}^{4-}$) and other protonated species exist in concentrated solutions,[170, 171] which means the liquid phase is not a simple solution of periodate ions. Precipitation of alkali periodate is acidifying because of the release of protons form this species, therefore there is a pH impact on the reaction that may not be captured by the simple solubility studies used here that didn't control solution pH.[70, 171]

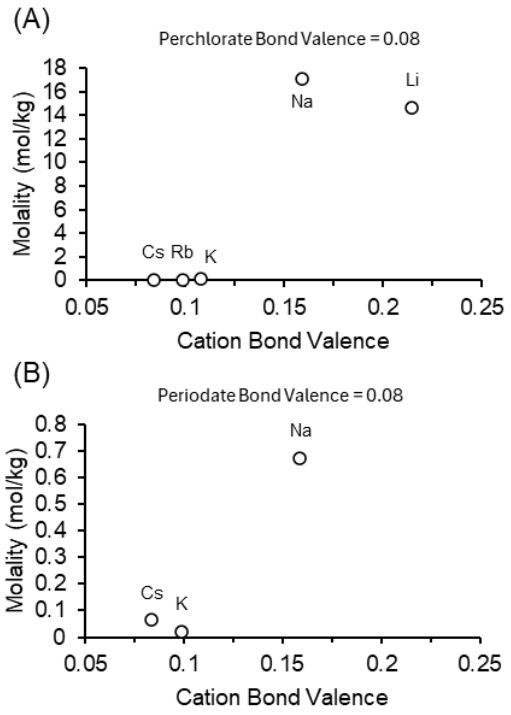

Figure 6. The solubility of perchlorates and periodates as a function of alkali cation bond valence. Solubility data is from Table 3.

Selenite, Selenate, Sulfate, Sulfite, Tellurite, and Metavanadate

The solubility of the selenites and selenates is shown in Figure 7. The characteristic bond valence of selenite (-0.22) matches most closely with Li^+, and the solubility of the alkali selenites increase as the alkali bond valence moves farther from 0.22 (Figure 7a). At saturation, both sodium and potassium selenite solutions have less than four water molecules per ion. The selenate characteristic bond valence (-0.17) most closely matches Na^+, and sodium selenate is the least soluble (Figure 7b).

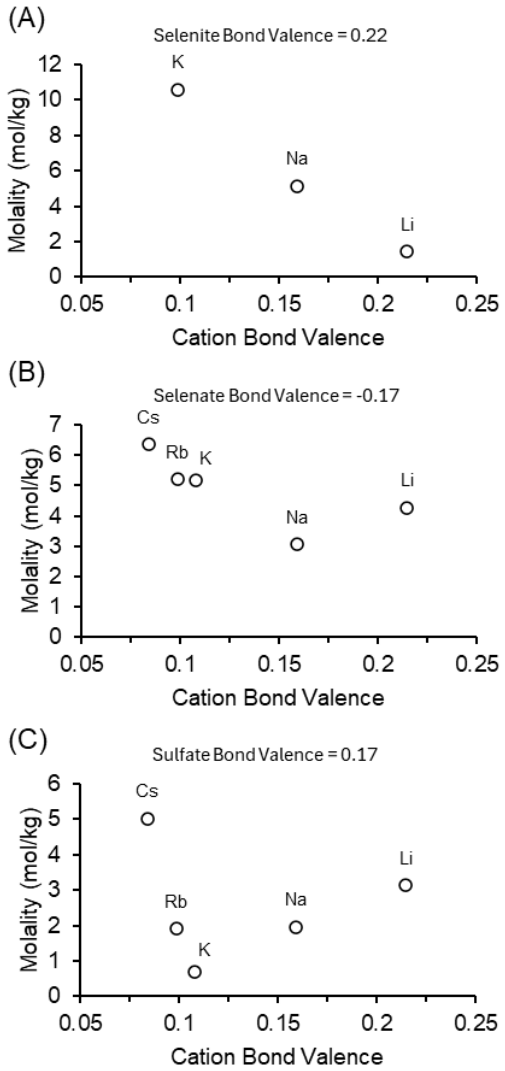

Figure 7. The solubility of selenites, selenates, and sulfates as a function of alkali cation bond valence. Solubility data is from Table 3.

The alkali sulfate solubilities (Figure 7c) are one of the few cases that does not follow the Valence Matching Principle at 25 °C. Sodium sulfate would be expected to be less soluble than potassium sulfate from the Valence Matching Principle, but the opposite is the case (Figure 7c). Reardon studied

the alkali ion-pairs formed with sulfate and found similar results as the solubility data (Figure 8).[172] Even though Na^+ matches the bond valence of SO_4^{2-} better than K^+, the K^+ ion-pair is stronger. The 1/pK is plotted in Figure 8 so that the stronger the ion-pair the smaller the 1/pK so that the solubility data and ion-pairing constants would have the same shape, and comparison between the ion-pairing constants and the solubility can be easily observed. These results indicate that strong ion-pairing is not the reason that sodium sulfate is more soluble than potassium sulfate. K^+ clearly has a stronger affinity for sulfate than Na^+ in both the solid and liquid phase. The reason for this is unknown.
Both Cs^+ and Li^+, with poorly matching bond valence with sulfate, are extremely soluble, as expected from the Valence Matching Principle. Saturated cesium sulfate solution has less than four water molecules per ion.

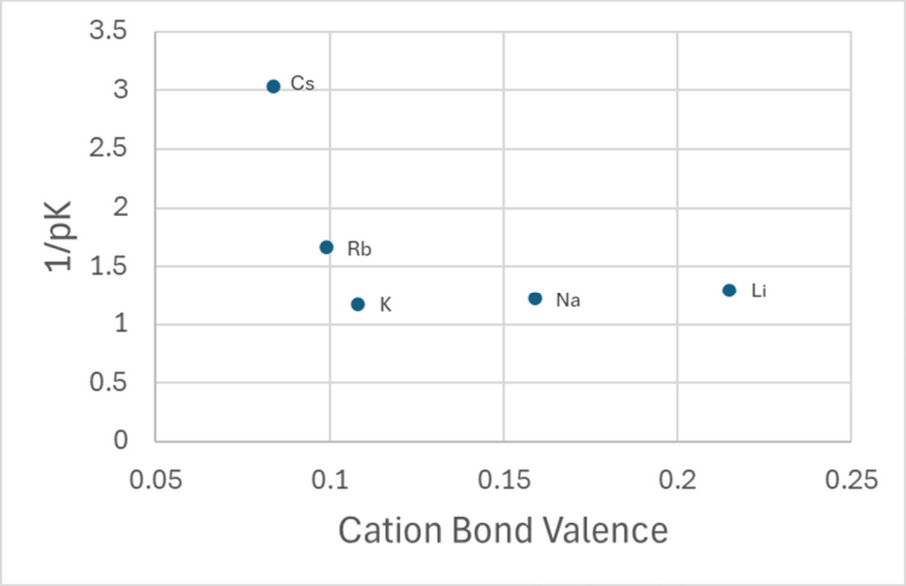

Figure 8, Ion-pairing constant (as 1/pK) versus the cation bond valence for alkali sulfates. The data is from Reardon.[172] Note that the smaller the 1/pK, the stronger complex.

Solubility data for two alkali sulfites (SO_3^{2-}) were found. Sodium sulfite solubility was 2.44 molal and potassium sulfite solubility was 6.72 molal.[114] The relative solubility of these two sulfites is consistent with the cation with the most closely matching bond valence being the least soluble.

Solubility data were found for two alkali tellurites (Li^+ and Na^+).[114] The solubility data for Li^+ was only measured at 30 °C and above, but Kertes et al. [114] provide an empirical equation for lithium tellurite solubility as a function of temperature. When extrapolated to 25 °C the equation calculates a solubility of 0.851 molal. The tellurite bond valence of -0.22 matches the bond valence of Li^+ well (+0.22). Consequently, the solubility of lithium tellurite (0.851 molal) is much less than the solubility of sodium tellurite at 25 °C (3.697 molal). [114]

Solubility data for two alkali metavandates were found, sodium and potassium. K^+ matches the bond valence of metavanadate well (both K^+ and VO_3^- = 0.11) and the KVO_3 solubility in water is reported to be 0.8498 molality.[124] The solubility of metastable anhydrous $NaVO_3$ is reported to be 1.530 molality,[73] which is more soluble than KVO_3, consistent with the more poorly matching bond valence of Na^+.

Chromate and Dichromate

The solubility of the alkali chromates and dichromates as a function of alkali bond valence are shown in Figure 9a,b. Chromates are one of the few oxyanions that do not match the trend of the lowest solubilities equaling the most closely matching bond valence (Figure 9a). Indeed, the alkali chromates behave almost opposite of that predicted by the Valence Matching Principle, with sodium chromate being the most soluble chromate despite having the most closely matching bond valence. This indicates that there are additional factors besides charge density that contribute to the relative solubility, though what is causing this reversal in sodium chromate is unknown.

The dichromates do follow the Valence Matching Principle trend, with the heavy alkali with the most closely matching bond valence being the least soluble (Figure 9b). Saturated Li^+ and Na^+ dichromate solutions have less than four water molecules per dissolved ion.

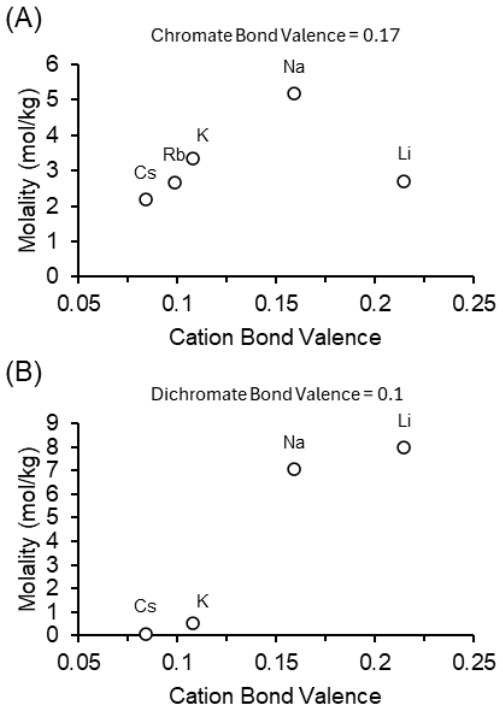

Figure 9. The solubility of chromates and dichromates as a function of alkali cation bond valence. Solubility data is from Table 3.

Molybdates, Permanganates, and Perrhenates

The alkali molybdates are yet another system where the lowest solubility alkali (Na^+) is the one with the most closely matching valence of the anion (Figure 10a). All the other alkali molybdates have less than four water molecules per ion in saturated solution, with the heavy alkali having two or less water molecules per ion.

The alkali permanganate with the closest matching bond valence (K^+) likewise has the lowest solubility (Figure 10b). The relative solubility of Na^+ and Li^+ are somewhat out of order of their bond valence, but both poorly match the bond valence of permanganate and are both very soluble. Both Li^+ and Na^+ permanganate have less than six water molecules per ion at saturation and sodium permanganate has less than 3 water molecules per ion, forming ultra-concentrated solutions.

The last system we evaluate in this study is the alkali perrhenates (Figure 10c). The three heavy alkalis match the bond valence of ReO_4^- well, and thus have lower solubility than sodium and lithium perrhenates. Lithium perrhenate, with poorly matching valence, has less than three water molecules per ion at saturation forming ultra-concentrated solutions. Like most systems discussed above, the solubility of the alkali perrhenates depended on the charge density mismatch.

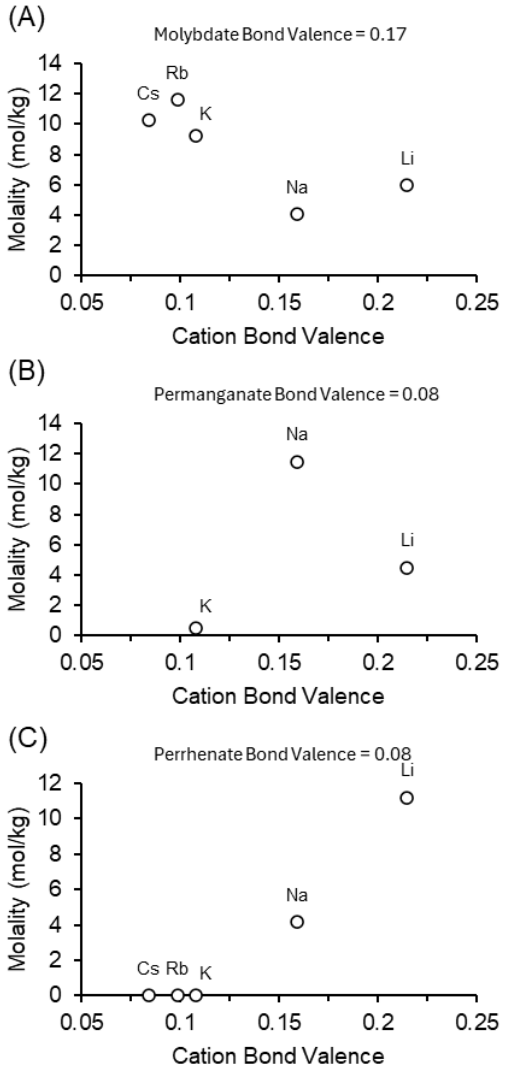

Figure 10. The solubility of molybdates, permanganates, and perrhenates as a function of alkali cation bond valence. Solubility data is from Table 3.

Discussion

This study evaluated 23 anions, 20 of which had solubility data available for three or more alkali. After discounting minor variation in the data for the three heavy alkali that had practically the same bond valence, 20 of the systems showed that the most closely matching bond valence was the lowest solubility salt amongst the alkali, and the highest solubility was those with poorly matching bond valence. We can thus conclude that the Valence Matching Principle will usually correctly predict the relative solubility of the alkali salts, though there are some exceptions that are not fully understood. What can be clearly understood is that the preponderance of the data indicates that matching charge densities is a major factor in the solubility of salts. These results confirm Hawthorne's prediction 40 years ago.[61]

This study reviewed the solubility of small inorganic and carboxylate ions, but we expect the conclusions to hold also for larger inorganic ions such as polyoxometalates. The solubility of some very large alkali polyoxometalates reportedly depends on their charge density.[173-175] Qualitatively, the polyoxometalate anions with large charge density tend to form soluble complexes with the low charge density heavy alkali. In contrast, the large charge density polyoxometalates form lower solubility complexes with Li^+ and Na^+ than with the lower charge density heavy alkali ions.[173-175] Those qualitative results are consistent with the results here for simpler oxyanions.

Collins used alkali fluoride solubility data to develop his "Law of Matching Water Affinities", a Law relating ion-pairing strength to the strength of interaction between ions and water.[176, 177] Collins assumed that alkali fluorides that formed sparingly soluble salts would also form strong ion-pairs.[176] That assumption is consistent with the Valence Matching Principle used here, which assume that ions with matching valences would form stable complexes of all types, including both salts and dissolved ion-pairs. Collin's Law and the Valence Matching Principle are both consistent with the direct measures of the alkali- F^- ion-pair complexation constants reported by references.[176, 177] The primary difference between the present study and Collins' analysis of ion-pairing and alkali fluoride solubility is that no tie to hydration energies were required for the Valence Matching Principle.

If bond-valence mismatch does govern the solubility in water, it should also do so in other highly polar solvents like methanol because other polar solvents should be able to solvate all the common small inorganic ions. The solubility of alkali nitrates (Figure 11a) and alkali carbonates (Figure 11b) in methanol are thus compared. As they are in water, the highest solubilities are those with poor matching bond valence of nitrate and carbonate (Figure 11). These results confirm that charge density matching influences the solubility of salts in polar non-aqueous solvents as well.

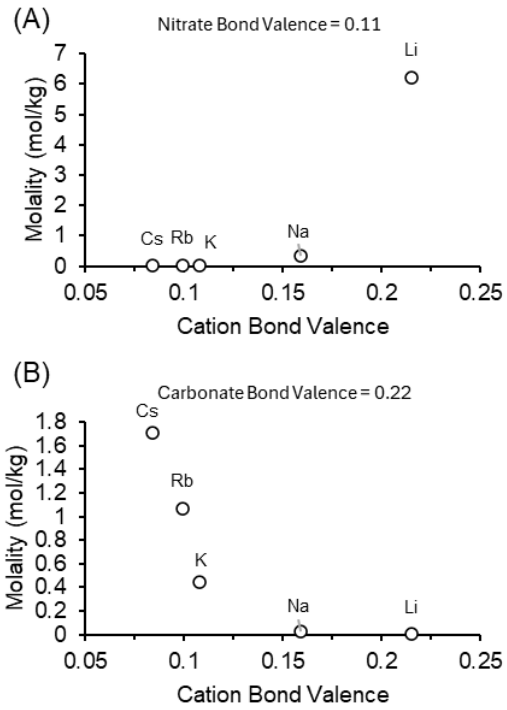

Figure 11. The solubility of alkali nitrates and carbonates in methanol as a function of cation bond valence. Solubility data is from Table 4.

The characteristic bond valence difference between cations and anions can be determined by summing the anion bond valence with the cation bond valence. A value of zero indicates a perfect match. When this difference is 0.06 or larger, the electrolyte usually forms ultra-concentrated solutions with fewer than four water molecules per ion at saturation. In this study, only nine electrolytes exhibited bond valence differences beyond -0.06 or 0.06, yet had more than four water molecules per ion at saturation. Notably, six of these nine electrolytes had less than eight water molecules per ion. Of these six, five contained large anions (e.g., tellurite, sulfite, perrhenate, permanganate, iodate), which coordinate with more than four water molecules in dilute solutions.[42-44,167, 168,178] Consequently, these solutions remain highly crowded, making it challenging to find configurations where all ions are independently hydrated without sharing water molecules. Therefore, there is no precise threshold for the bond valence difference that results in ultra-concentrated solutions, but for most electrolytes, it is typically around 0.06 v.u.

Conclusion

Solubility data indicate that the strongest ion-pairs in the alkali-anion series have closely matching charge densities (e.g., fluorides, formates, acetates, nitrates, chlorates, perchlorates). These ions form the strongest ion-pairs and are the least soluble. In contrast, highly soluble electrolytes exhibit high water solubility despite weak ion-pairing. These observations align with bond valence theory, suggesting that cation/anion combinations with matching charge densities are less likely to achieve high

concentration at equilibrium due to the stability of the anhydrous binary salt. The charge-density mismatch thus provides a predictive upper bound on attainable concentration, while formation of hydrated or metastable phases may reduce it further. Highly soluble salts linked with charge density mismatches are essential for forming ultra-concentrated solutions. Therefore, a key characteristic of highly concentrated solutions is the charge-density mismatch between counterions.

Acknowledgements

This research was supported by IDREAM (Ion Dynamics in Radioactive Environments and Materials), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Science (BES) under FWP 68932. Pacific Northwest National Laboratory (PNNL) is a multiprogram national laboratory operated for DOE by Battelle Memorial Institute operating under Contract No. DE AC05-76RL0-1830.

Keywords: Electrolytes • Ion Pairs • Solubility • Water Chemistry

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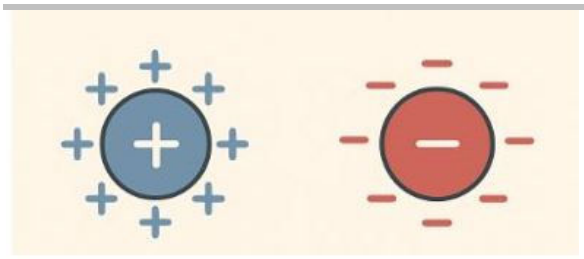
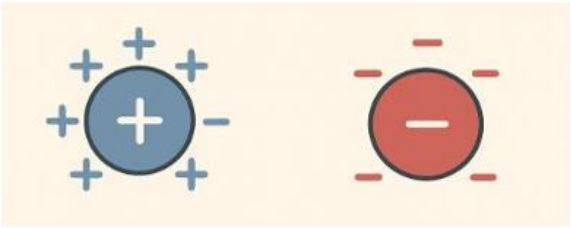
Entry for the Table of Contents

This article proposes that the high solubility of certain salts arises from mismatched charge densities between ions, rather than strong ion pairing. Salts with poorly matched bond valences exhibit higher solubility than those with matching charge densities, suggesting that charge density mismatch significantly influences solubility and stability in concentrated solutions.



Less Soluble



More Soluble