Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Erlander, Stig R.(1968) 'Interaction of Aqueous Ions: A Correlation between the Hydration and Solubility Properties of Inorganic, Organic, and Polymeric Salts Having Mono- or Polyatomic Ions', Journal of Macromolecular Science, Part A, 2: 3, 623 — 643

To link to this Article: DOI: 10.1080/10601326808051430

URL: http://dx.doi.org/10.1080/10601326808051430

J. MACROMOL. SCI.—CHEM., **A2**(3), pp. 623-643, May, 1968

Interaction of Aqueous Ions: A Correlation between the Hydration and Solubility Properties of Inorganic, Organic, and Polymeric Salts Having Mono- or Polyatomic Ions*

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SUMMARY

It is concluded that the solubility of many salts in water is determined by the interaction of hydrated water molecules on the anion and cation. In other words, the solubility sequences of salts can be explained by using previously developed models for hydrated ions and calculated values of the effective dielectric constant ($D_{\pm}$) even though such sequences cannot be explained on the bases of polarization of the ions. Salts were divided into three groups: Group I represents those salts which have no tightly bound water (A regions) on their ions. Group II contains salts which consist of one ion having an A region and a counterion which does not. Group III consists of salts where both anion and cation have an A region. The solubility of salts in groups I and II depends primarily on the value of $D_{\pm}$ of the B region. If both ions have high or if both have low values of $D_{\pm}$, then the stability of the hydrates are similar and the solubility of the salt is relatively low compared to dissimilar $D_{\pm}$ values. For group III salts the solubility of the salt is determined primarily by the strength of the induced dipole on the positively hydrated water. A comparison of the maximum solubility of the salt with its theoretical maximum molarity based on values of the hydrated radii sub-

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stantiates the conclusions. From cationic sequences it is possible to determine whether the value of D_- for the anion is greater or less than that of water and whether positive or negative hydration exists. From anionic sequences it should be possible to determine what cationic groups on protein molecules bind counterions and what cations have positive hydration (A regions). Some polyatomic ions can form chelation structures with the counterion. Such complexes reduce the solubility of the salt if a two-or three-dimensional network can be formed or increase the solubility if such a network cannot be formed.

INTRODUCTION

The salting-in or salting-out of various polar and nonpolar molecules in aqueous solutions has been studied extensively [1-7]. Such interactions can be grouped into specific ionic sequences according to the ability of the ions to salt-out or salt-in the molecule the most effectively [7]. The cationic salting-out sequence [1, 7] for nonpolar molecules is $Na^+ > K^+ > Li^+ > Cs^+$. In other words, for the same molarity of salt, NaCl will reduce the solubility of benzene more than KCl, and so on. In contrast with this sequence, it is observed [1, 7] that the salting-out sequence for basic molecules such as ammonia is $K^+ > Na^+ > Li^+ > Cs^+$ and that sequence for acidic molecules such as benzoic acid is $Li^+ > Na^+ > K^+ > Cs^+$. The change in sequences is readily explainable if the strong interactions between the base or the acid and the hydrated water molecules of the A region of Li^+ or Na^+ are considered [7]. In contrast with these changes in sequences, the same salting-out sequences $K^+ > Rb^+ > Cs^+$ and $Cl^- > Br^- > I^-$ are obtained for all nonpolar, basic, and acidic types of molecules. Thus in the absence of A regions the ionic sequences are the same. But these constant sequences for ions having no A regions can also be explained on the basis of the effective dielectric constant ($D_\pm$) of the hydration sphere of the ion; the lower the values of $D_\pm$, the greater will be the salting-out effect.

Just as in the above example for nonpolar, basic, and acidic molecules, solubility sequences can be obtained for various anions or cations by examining the maximum solubilities of salts in water. Such sequences should also be dependent on the presence or absence of A regions and the value of $D_\pm$ and should yield information concerning the interaction of salts with polyelectrolytes. In both the salting-out of molecules and the solubility of salts, the first encounter is with the hydration sphere of the ion and not with that of the ion itself. Proof that the interaction of ions is a function of their hydration shell has recently been given by Petrucci [8] and by Eigen and Tamm [9]. It is the purpose of this paper to show that the maximum solubility of a salt in water is due to the attraction and repulsion forces of the hydrated water molecules on the cation and anion.

As pointed out by Petrucci [8] and by Eigen and Tamm [9], this conclusion does not mean that other electrostatic forces between the cation and anion are not important in determining the final degree of hydration or the crystal structure of the precipitated salt. Rather, the solubility results of salts show the minimum amount of water that is required to destroy the ionic bond between the particular cation and anion. In other words, it is concluded that the electrostatic interaction of a cation and an anion in an aqueous medium does not depend on the polarizability of the cation or anion but on the value of $D_\pm$ in the B region of the ion and on the strength of its A region of hydration if such a region is present. Thus, if the interactions between the hydrated water molecules of a cation and anion are strong, then the solubility of the salt will be low, or vice versa. Consequently, the solubilities of most salts are governed by the interaction of their hydration shells.

Recently Pearson [10, 11] introduced the concept of hard and soft acids and bases. Soft bases and soft acids have high polarizability, large size, and low electronegativity. Hard bases and acids have the opposite properties. According to Fajans [12], the new terms hard and soft acids and bases may be useful and convenient, but the fact that one ion has a greater polarizability than another has been recognized for some time. This concept may explain the formation of convalent bonds and their relative strengths. But the concept of polarization fails to explain some ionic solubility sequences between ions which do not form covalent bonds. For example, why is the solubility sequence $F^- < Cl^- < Br^- < I^-$ for Na^+, whereas it is $Cl^- < Br^- < I^- < F^-$ for K^+, even though both Na^+ and K^+ are hard acids? Also why does the solubility sequence $Li^+ < Na^+ < K^+ < Cs^+$ for F^- shift to $K^+ < Na^+ < Cs^+ < Li^+$ for Cl^-, even though both anions would presumably be in the same classification? Using the above nomenclature, the sequence for the F^- ion is "acidic," whereas the sequence for the Cl^- ion is "basic."

These results can be explained if the interaction of the hydration shells of the anion and cation are considered. In other words, just as in the salting out of polar or partially charged molecules, the interaction of an anion with a cation is determined by the interaction of its hydrated water molecules. To explain such interactions, the effective value of $D_\pm$ and the absence or presence of A regions on the ions must be known. Therefore, the results obtained previously [6, 7] will be applied. In addition, for a polyatomic ion, the effect of chelation must also be considered [13] and in many cases may be more important than its value of $D_\pm$.

EFFECTIVE DIELECTRIC CONSTANT AND HYDRATION MODELS FOR VARIOUS IONS

The results of Petrucci [8] and of Eigen et al. [9, 14] show that in the interaction of cations and anions, the hydrated water of B regions as well as that of the more tightly bound A regions, must be considered. (For definition of A and B regions and positive and negative hydration, see the previous paper [6] and also Frank and Wen [15] and Samoilov [16].) For example, as shown below, the SO_4^{2-}, K^+, and Cl^- ions are negatively hydrated (have B regions), and yet from the sound absorption spectra their B regions are apparently involved in the interaction with other ions. But the sound absorption technique will most likely not be able to detect the interaction of B regions having values of $D_\pm$ close to that of water. Consequently, the models of Eigen et al. [9, 14] must be extended to include such interactions. Thus it is here proposed that in aqueous solutions for monovalent anions (X^-) and cations (M^+) having only B regions, the interaction can be written

$$M^+(H_2O) + (H_2O)X^- \underset{\text{step A}}{\rightleftharpoons} M^+(H_2O)(H_2O)X^- \underset{\text{step B}}{\rightleftharpoons} M^+(H_2O)X^- \underset{\text{step C}}{\rightleftharpoons} M^+X^- \qquad (1)$$

and for divalent cations or monovalent cations (Me^+) having both A regions and B regions, the interaction can be written

$$Me^+(H_2O)(H_2O) + (H_2O)X^- \underset{\text{step A}}{\rightleftharpoons} Me^+(H_2O)(H_2O)(H_2O)X^- \underset{\text{step B}}{\rightleftharpoons}$$

$$Me^+(H_2O)(H_2O)X^- \underset{\text{step B}'}{\rightleftharpoons} Me^+(H_2O)X^- \underset{\text{step C}}{\rightleftharpoons} Me^+X^- \qquad (2)$$

Those cations which can form both an A and a B region are designated as Me^+, those which can form only one hydration shell as M^+. In these equations the total number of water molecules involved in the hydration shells (or that water lost from such shells) is not shown. Rather, the formation of $(H_2O)(H_2O)$ in step A of both Eqs. (1) and (2) illustrates the interaction and partial overlapping of the B regions. The salt, of course, can have in some cases water of hydration and therefore can precipitate at either step B or B .

The initial interaction (step A) and also the sharing of a common B region (step B) must involve the effective dielectric constant of the anion and cation. Consequently, the values of this quantity for various ions will now be considered. The effective value of $D_\pm$ for hydrated ions can be calculated using an equation relating the Setchenow constant, k_S, for inert molecules such as benzene to the effective dielectric decrement of the ions [6]. This effective dielectric constant of an ion ($D_\pm$) pertains only to the domain of the loosely hydrated, penetrable B region (negatively hydrated shell) of an ion [6]. For each of the ions such as Cl^-, Br^-, I^-, K^+, Rb^+, and Cs^+ there is only a single loosely bound hydration shell (B region), whereas for each ion such as Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} there are two hydration shells (an A and a B region). Moreover, for Na^+ and F^- there exists only a single A region [6].

A few values of $D_\pm$ calculated previously using Nightengale's [17] hydrated radii are listed in Table 1. For ions which do not have B regions, the value of $D_\pm$ should be positive and close to zero. The value of D_+ for Na^+ is slightly less than zero, owing to errors in the experimental values of k_s and to the use of Cl^- as a standard [6]. Consequently, the values of D_+ for K^+, Rb^+, and Cs^+ will also be greater than those listed in Table 1. The value given for NH_4^+ is actually much greater than its true value, because other studies [18] conducted at low and high concentrations of NH_4Cl show that the high value of D_+ is due to the partial formation of the polar complex $NH_4^{\delta+}Cl^{\delta-}$. The charge per unit surface area on this complex is reduced, which results in an increase in the effective value of D_+ for the NH_4^+ ion. .

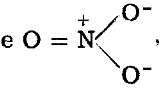
Table 1. Approximate Values for the Effective Dielectric Constant of Various Ions Using $D_1 = 55.3$ for Unbonded Water[a]

	Anions							
	F^-	OH^-	Cl^-	SO_4^{2-}	Br^-	NO_3^-	ClO_4^-	I^-
δ_-	6.1	2.7	2.2	2.2	0.3	−1.1	−1.7	−2.7
D_-	0	11	31	39	52	67	73	84

	Cations									
	Na^+	K^+	Ra^{2+}	Rb^+	Ba^{2+}	NH_4^+	Sr^{2+}	Cs^+	Ca^{2+}	Mg^{2+}
δ_+	7.0	4.4	–	3.2	4.1	1.7	–	0.9	–	–
D_+	−5	8	16	20	31	37	45	45	56	88

[a] Results were calculated by using equations developed in a previous paper [6]. The values of D_+ for Ra^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+} were estimated from a plot of $D_\pm$ versus charge per unit surface area [6].

To understand the solubility properties of various polyatomic anions, the values of dielectric decrement δ- and the effective dielectric constant D_- were calculated for SO_4^{2-}, NO_3^-, and ClO_4^- by the method described previously [6] using k_s values of 0. 548, 0. 119, and 0. 106 for Na_2SO_4, $NaNO_3$, and $NaClO_4$, respectively, for the solubility of benzene in the aqueous salt solutions [1-3]. The partial molar volumes ($\overline{V}$) for SO_4^{2-} and NO_3^- were obtained from the data of Padova [19], and that for ClO_4^- was obtained from the data of Mukerjee [20]. Pauling's crystal radii, r_x, and Nightengale's [17] hydrated radii, $b_\pm$, were used in these calculations.

The results in Table 1 show that the sulfate ion has a value of D_- between that of Cl^- and Br^-. Because of the chelation effect (see below), the actual value of D_- for SO_4^{2-} is most likely about equal to that of the chloride ion. Nevertheless, unlike the positively hydrated fluoride and hydroxide ions, the SO_4^{2-} ion is negatively hydrated just as in the case of the Cl^- ion. Further proof of this will be given below in the examination of solubility sequences. The nitrate ion has an extremely high value of D_-, assuming that its oxygen atoms have an electrostatic charge density approximately equal to that on the oxygen atoms of OH^- ions. Considering the structure of NO_3^- to be , the high value of D_- may be due to its positively charged nitrogen atom or to a lower charge per unit surface area on its oxygen atoms than on the OH^- ion.

CHELATION EFFECTS IN POLYATOMIC IONS

Before examining the solubility sequences, it is first pertinent to establish the existence of stable ion-ion complexes for polyatomic ions in relatively dilute solutions. Chelation of NH_4^+ ions with anions must occur by means of ion-ion or ion-dipole interactions instead of dipole-dipole water interactions, because hydration of the NH_4^+ ion would completely mask or engulf the structure of the NH_4^+ ion. In other words, the hydrate of the NH_4^+ ion would be similar in structure to that of the Rb^+ ion, since both ions have the same crystal radius ($r_x = 1.48$ Å) and both have about the same hydrated radius [b_+ (NH_4^+) = 3. 31 and b_+ (Rb^+) = 3. 29]. Hence the hydrated tetrahedral structure of the NH_4^+ ion, just as the hydrated Rb^+, could not lend itself to any chelation effect.

The tetrahedral structure of the NH_4^+ ion could lead to ion-ion interactions with partially unhydrated counterions because the positive charge on NH_4^+ is distributed to its hydrogen atoms [21]. In other words, hydration of an ion is a continuous and dynamic process, especially if the ion is negatively hydrated, as in this case. At some instant one of the tetrahedral faces of the NH_4^+ ion could come in contact with the surface of a nearby negatively hydrated anion if the approaching sides of both the NH_4^+ ion and anion became unhydrated at the same time. The formation of such ion-ion interactions follows directly from the model of Eigen and Tamm [9] for the interaction of divalent ions.

The resulting salt complex would be more stable than a normal ion-ion interaction because of the chelating effect of the NH_4^+ ion. However, unlike a salt structure, the ions will not be surrounded on all sides by ion-ion interactions. Moveover, because the salt complex will not be surrounded by other ions, there may be a tendency to share electrons between the NH_4^+ and its counterion, which, in turn, will lower the electrostatic charge per unit surface area on the NH_4^+-anion complex. The result will be an increase in the value of the effective dielectric constant of the aqueous salt.

Such a model for aqueous ammonium salts is supported by the observation that the effective value of D_+, as obtained for NH_4Cl solutions, increases as the concentration of NH_4Cl increases [18]. The only plausible explanation for this variation in D_+ is a reduction in the charge per unit surface area with an increase in the formation of the $NH_4^{\delta+}Cl^{\delta-}$ complex. The same type of reduction in charge occurs with NH_4OH, where it is known that this salt does not readily dissociate in aqueous solutions (pK = 4. 7) [18]. In this case, the $NH_4^{\delta+}OH^{\delta-}$ complex (rather than $NH_3 \cdot H_2O$) has salting-in properties comparable to that of the urea molecule or guanidinium ion [18].

Further support for the proposal that NH_4^+ salts form ion-ion complexes in aqueous solutions is the unique behavior of dilute aqueous ammonium halides, nitrate, and sulfate solutions. Scatchard and Prentiss [22] (see also Harned and Owen [4, p. 527]) observed that the conductance and freezing-point data for these NH_4^+ salts behaved as if ionic association between NH_4^+ and its counterion was occurring.

The tetrahedral SO_4^{2-} ion should form a relatively stable ion-ion interaction just as in the case of NH_4^+ ion. However, because of its divalent character, the sulfate ion will be capable of interacting with other surrounding counterions, while in the case of NH_4^+-anion complexes the resulting electrostatic charge will most likely be too low to form extended two- or three-dimensional interactions. Such a model would explain the low solubility of some sulfate salts and the high solubility of ammonium salts.

Chelation effects should also be present in such ions as NO_3^- and $R{-}CO_2^-$. However, the planar structure of the NO_3^- ion prohibits the interaction of its three oxygen atoms with an approaching cation. In the case of SO_4^{2-} and NH_4^+ the chelation could occur through the interaction of three atoms and the approaching counterion rather than only two. Consequently, the chelation effect will not be as great in NO_3^- and RCO_2^- as those for SO_4^{2-} and NH_4^+ ions.

CORRELATION OF A REGIONS AND B REGIONS WITH SOLUBILITY SEQUENCES

Most ions, particularly the monoatomic ions, do not form chelation structures with coions. The solubility of such salts must therefore be governed by the dipole-dipole interactions of their hydrated water molecules. When a salt is dissolved in water, it interacts to form ion-hydrates. These hydrated ions separate from their coion because the hydrated water molecules reduce the electrostatic attraction of the cation and anion by increasing the distance between the ions. If the mobility of the hydrated water molecules on both the anion and cation are similar, then there will be a greater resistance to the penetration of one hydrated water molecule into the hydration domain of the other ion [6]. Consequently, steps A and B in the above modified Eigen and Tamm [9] interaction sequence are governed by the value of $D_\pm$ of the B region and by the influence of the induced dipoles of the A region of an ion.

Examination of ionic solubility sequences will now be made with regard to such interactions. All salts can be placed into three main divisions: (1) those where both ion and coion have only B regions, (2) those salts where one ion has only a B region while the coion has an A region, and (3) those salts where both ion and coion have A regions. Solubility sequences for these three sequences are given in Table 2 and are based on moles of salt per liter of solution. The data in this table can be summarized as follows.

Group I

Both ions having only B regions. If both anion and cation have either high or low values of $D_\pm$, then the solubility of the salt will be relatively low; e.g., when $D_+ > D_1$ and $D_- > D_1$ or when $D_+ < D_1$ and $D_- < D_1$, the solubility of the salt is low. Thus if a specific cation or anion has a high value of $D_\pm$, then the solubility of its salt will decrease as the value of $D_\pm$ of its counterion increases. Conversely, if the value of $D_\pm$ of the cation or anion is low, then the solubility of the salt will increase as the value of $D_\pm$ of its counterion increases. A comparison of the anionic sequence for the NH_4^+ ion with those of Cs^+, Rb^+, and K^+ ions shows that the sequence for NH_4^+ agrees with that for the K^+ ion even though the value of D_+ for NH_4^+ is almost equal to that of Cs^+ (see Table 1). The position of NH_4^+ in the sequence is further proof that ionic association or chelation between NH_4^+ and the halides occurs and that this association is accompanied by a reduction in charge per unit surface area of the $NH_4^{\delta+} \cdot X^{\delta-}$

complex. If it did not occur, then the sequence would have to be the same as that of the Cs^+ or Rb^+ ion, which it is not. The change in the sequence order occurs at the Rb^+ ion, where the value of D_+ is less than that of D_1, and at the Br^- ion, where the value of D_- is equal to that of D_1. The data therefore show that the sequences are only approximately associated with the properties of the surrounding water or that $D_{Rb} = D_1$; i.e., there is a slight error in the values of D_+.

Group II

One ion has an A region while the coion has only a B region. Just as in group I, if $D_+ > D_1$, then the solubility of its salt will decrease as the value of D_- of its coion increases ($MgCl_2 > MgI_2$ in solubility). Likewise, if $D_+ < D_1$, then the solubility of the salt decreases with an increase in the value of D_- of the coion ($BaCl_2 < BaI_2$ in solubility). A study of the sequences for the anion of group II salts shows that the A region also influences the solubility of the salt. Thus for the Br^- and Cl^- ions, the divalent sequence $Ca^{2+} > Sr^{2+} > Ba^{2+}$ and the monovalent cation sequence $Li^+ > Na^+$ follow that expected for a decrease in the effective dielectric constant of the cation's B region. However, the solubility of NaCl or NaBr is equal to or greater than that of $CaCl_2$ or $CaBr_2$, even though the value of D_+ for Na^+ is essentially zero, i.e., even though $D_{Na} < D_{Ca}$. Consequently, the attractive forces of the A region decrease the solubility of the salt. That is, they enhance the effect of the B region if this region has a value of D_+ less than that of pure water (D_1).

The influence of the A region is further shown by examining the Na^+ and Li^+ sequences of this group. Because $D_{Cl} < D_1$ and $D_I > D_1$, then as shown in group I the sequence $Li^+ > Na^+$ for the chloride salts should change to $Li^+ < Na^+$ for the iodide salts if the sequence is only influenced by the value of $D_\pm$ of the B region. Furthermore, the cation sequence $Ca^{2+} > Sr^{2+} > Ba^{2+}$ for I^- salts should change to $Ca^{2+} < Sr^{2+} < Ba^{2+}$ for the I^- salts based on the values of $D_\pm$. However, the solubility sequences for the I^- salts are not $Li^+ < Na^+$ and $Ca^{2+} < Sr^{2+} < Ba^{2+}$ but rather are $Li^+ = Na^+$ and $Ca^{2+} > Sr^{2+} > Ba^{2+}$. Consequently, these observations show that the A region, with its tightly bound, polarized water molecules, enhances the effect of a B region if $D_+ < D_1$ or counteracts the effect of those B regions which have $D_+ > D_1$. Examination of the sequences for the K^+, Rb^+, and Cs^+ salts further verifies this. That is, even though $D_K < D_1$ and $D_{Cs} > D_1$, the same sequence $OH^- > F^-$ is obtained for K^+, Rb^+, and Cs^+ salts. The switch in the position of the CO_3^{2-} ion in this sequence may be due to its chelating properties.

Table 2. Relative Molar Solubilities of Salts in Water as a Function of Their Effective Dielectric Constant and Type of Hydration[a]

Cations			Anions		
Coion		Sequence	Coion		Sequence
Group I. Intermediate: both ions having only B regions					
G^+	$(D_G > D_1)$	$Cl^- > Br^- > I^-$			
Cs^+	$(D_{Cs} = D_1)$	$Cl^- > Br^- > I^-$	I^-	$(D_I > D_1)$	$K^+ > Rb^+ > Cs^+$
Rb^+	$(D_{Rb} < D_1)$	$Cl^- = Br^- = I^-$	Br^-	$(D_{Br} = D_1)$	$K^+ < Rb^+ > Cs^+$
K^+	$(D_K < D_1)$	$Cl^- < Br^- < I^-$	Cl^-	$(D_{Cl} < D_1)$	$K^+ < Rb^+ < Cs^+$
NH_4^+	$(D_{NH_4} < D_1)$	$Cl^- < Br^- < I^-$	SO_4^{2-}	$(D_{SO_4} < D_1)$	$K^+ < Rb^+ < Cs^+$
Group II. Most soluble salts: one Ion having an A region; coion having only a B region					
Mg^{2+}	$(D_{Mg} > D_1)$	$Cl^- > Br^- > I^-$	I^-	$(D_I > D_1)$	$Li^+ = Na^+ > Ca^{2+} > Sr^{2+} > Mg^{2+} > Ba^{2+}$
Ca^{2+}	$(D_{Ca} = D_1)$	$Cl^- < Br^- = I^-$	Br^-	$(D_{Br} = D_1)$	$Li^+ > Na^+ > Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$
Sr^{2+}	$(D_{Sr} < D_1)$	$Cl^- < Br^- < I^-$	Cl^-	$(D_{Cl} < D_1)$	$Li^+ > Na^+ = Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$
Ba^{2+}	$(D_{Ba} < D_1)$		OH^-	$(D_{OH} < D_1)$	$Rb^+ < K^+ < Cs^+$
Na^+	$(D_{Na} < D_1)$		F^-	$(D_F < D_1)$	
Cs^+	$(D_{Cs} = D_1)$	$CO_3^{2-} < F^- < OH^-$	CO_3^{2-}	$(D_{CO_3} < D_1)$	$K^+ = Cs^+ < Rb^+$
K^+	$(D_K < D_1)$				
Rb^+	$(D_{Rb} < D_1)$	$F^- < OH^- = CO_3^{2-}$			

Group III. Least soluble salts: both ions having A regions

Mg^{2+}	$(D_{Mg} > D_1)$	$CO_3^{2-} = F^- > OH^-$	OH^-	$(D_{OH} < D_1)$	$Na^+ > Li^+ > Sr^{2+} > Ba^{2+} > Ca^{2+} > Mg^{2+}$
Ca^{2+}	$(D_{Ca} = D_1)$	$F^- = OH^- > CO_3^{2-}$	F^-	$(D_F < D_1)$	$Na^+ > Li^+ > Ca^{2+} > Ba^{2+} > Mg^{2+} > Sr^{2+}$
Sr^{2+}	$(D_{Sr} < D_1)$	$CO_3^{2-} < F^- < OH^-$	CO_3^{2-}	$(D_{CO_3} < D_1)$	$Na^+ > Li^+ > Mg^{2+} > Ca^{2+} > Ba^{2+} > Sr^{2+}$
Ba^{2+}	$(D_{Ba} < D_1)$		PO_4^{3-}	$(D_{PO_4} < D_1)$	$Na^+ > Li^+ > Mg^{2+} > Ca^{2+}$
Li^+	$(D_{Li} < D_1)$				
Na^+	$(D_{Na} < D_1)$	$F^- < CO_3^{2-} < OH^-$			

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[a] Data obtained from *Handbook of Chemistry and Physics* [23] and *Handbook of Chemistry* [24]. The columns of ions (the coion listings) are given according to the value of their dielectric constant; those listed first having the greater value, e.g., $D_G > D_{Cs} > D_{Rb} > D_K$. The G^+ refers to guandinium salts. The greater sign (>) designates a greater solubility; e.g., CsCl is more soluble (in moles/liter) than CsBr. The SO_4^{2-} ion is negatively and not positively hydrated; i.e., it has no A region. However, CO_3^{2-} and PO_4^{3-} are positively hydrated (see the text). D_1 is the dielectric constant of water at 100°C, i.e., water relatively free of iceberg structures.

The position of the Mg^{2+} ion in the sequences for the Cl^-, Br^-, and I^- ions is shifted because its B region ($D_+ > D_1$) counteracts its A region. Hence $SrI_2 < MgI_2$ in solubility, but $SrCl_2 > MgCl_2$ because the B region of Mg^{2+} decreases the solubility of the I^- salt and increases the solubility of the Cl^- salt. The position of the other divalent cations in these sequences, i.e., the Ca^{2+}, Ba^{2+}, and Sr^{2+} ions, does not change, since in these cases all their values for D_+ are equal to or less than that of D_1, whereas that for Mg^{2+} is greater than D_1.

Group III

Both ions have A regions. As in groups I and II, the solubility sequence for a specific cation is determined in part by the effective dielectric constant of its B region. Furthermore, as in group II, the A region behaves in the same manner as a B region if the B region has a value of $D_\pm$ less than that of D_1. As seen in Table 1, the value of D_- for the F^- ion is less than that for the OH^- ion, because the charge per unit surface area is greater for the F^- ion. Consequently, the solubility sequence $F^- > OH^-$ for the Mg^{2+} ion and $F^- < OH^-$ for the Sr^{2+}, Ba^{2+}, Li^+, and Na^+ ions is what one would expect based on the values of D_+ and D_-. The calcium ion, where $D_+ = D_1$ is an intermediate ion, just as the Rb^+ and Br^- ions, are intermediate. Hence the sequence for Ca^{2+} salts is irregular.

A comparison of the cationic sequences for the positively hydrated anions PO_4^{3-}, CO_3^{2-}, and F^- shows that there is a marked difference between the behavior of an A region of an anion as compared to a B region. The sequence $Ba^{2+} > Sr^{2+}$, as obtained for the F^- and CO_3^{2-} and presumably for the PO_4^{3-} ion, is opposite to that of the OH^-, Cl^-, Br^-, and I^- ions. This difference can be explained on the basis that the A region is more important in group III salts than in group II. In group III salts the greater A region of the Sr^{2+} ion as compared to that of the Ba^{2+} ion interacts more strongly with the A region of the F^-, CO_3^{2-}, and PO_4^{3-} ions. Conversely, in group II salts, the Sr^{2+} ion will not interact as strongly as the Ba^{2+} ion with anions having only B regions because the value of D_+ for Sr^{2+} is greater than that for Ba^{2+}. Thus for group III the strength of A regions is most important because both anion and cation have A regions. In group II the strength of the B regions on positively and negatively hydrated ions is most important because the counterion possesses only a B region and not an A region.

The above results given in Table 2 and in the above discussion show that the solubility of various salts is determined by the attraction or repulsion of the hydrated water molecules on the ion and counterion. Thus the solubility of a salt for groups I and II are governed by the values of $D_\pm$, which in turn determine the ability of an ion to hold its hydrated water molecules. If these abilities are similar, the solubility of the salt will be relatively low. Conversely, if they are quite different, then the solubility of the salts will be relatively high. Thus the solubility of a salt is a direct function of the effective dielectric constant of the B region. For group III, the solubility of the salts is determined mostly by the strength of the induced dipole of the strongly hydrated A regions. In other words, the solubility of the salt is governed almost entirely by the attraction of the A region of the cation to the A region of the anion.

COMPARISON OF THE DEGREE OF HYDRATION WITH MAXIMUM SOLUBILITY OF A SALT

Because the solubility of a salt in water will depend on the interaction between hydrated water molecules of the cation and anion, the concentration at which the salt precipitates should be related to the disappearance of free or unhydrated water in the medium. According to the mechanism given in Eq. (1), the salt complex formed in the saturated solution may be $M^+(H_2O)X^-$. By using Nightengale's [17] hydrated radii ($b_\pm$) for various ions, the theoretical volume that a hydrated salt would occupy was calculated from the molar volume of the hydrated ions ($V_\pm = N(4/3)\pi b_\pm^3$), as discussed in a previous paper [25]. In Table 3 these theoretical volumes are compared to the maximum molarities observed experimentally for various salts. For those salts in group I the theoretical volumes of the hydrated salts are closely associated with the observed solubilities. The theoretical volumes of 5.4 and 5.5 moles/liter for KCl and CsI are larger than the respective observed maximum solubilities of 4.6 and 3.9 moles/liter. Conversely, the theoretical volumes of 5.4 and 5.5 moles/liter for KI and CsCl are less than the observed maximum solubilities (9.6 M KI and 11 M CsCl). The results therefore illustrate that (1) the mechanism depicted in Eq. (1) must occur because the salt precipitates when the unhydrated water disappears, and that (2) greater concentrations than that predicted from the theoretical volumes are required for ions having dissimilar values of $D_\pm$ because of the greater instability of the $M^+(H_2O)X^-$ complex.

The chelation effects of the SO_4^{2-} ion can be readily seen for both groups I and II salts. As noted above, the SO_4^{2-} should be capable of forming three-dimensional chelates. Strong chelation effects occur only when the counterion has tightly bound water and low values of D_-, as in the case of the Ba^{2+} ion. In such cases the reorientation rates of the hydrated water molecules are extremely low and hence promote more permanent chelate complexes.

Table 3 shows that in general the maximum molarity of a group II salt is greater than that of the theoretical volume. This phenomena may be due to the ability of strongly hydrated water (A region)

Table 3. Number of Moles of Hydrated Salt Required to Occupy 1 Liter Divided by the Maximum Observed Molarity of the Salt[a]

	Group I salts		
	K^+	Rb^+	Cs^+
SO_4^{2-}	3.1/0.7	3.2/1.7	3.2/4.6
Cl^-	5.4/4.6	5.5/7.4	5.5/11
Br^-	5.5/5.5	5.6/7.3	5.6/5.8
I^-	5.4/9.6	5.5/7.2	5.5/3.9

	Group II salts									
	Li^+	Na^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}		K^+	Rb^+	Cs^+
Cl^-	4/15	5/6	3/6	3/7	3/3	3/2	CO_3^{2-}	4/8	4/19	4/8
Br	4/17	5/11	3/6	3/7	3/4	3/4	F^-	5/16	5/12	5/24
I^-	4/12	5/12	3/5	3/7	3/6	3/4	OH^-	6/20	6/19	6/26
SO_4^{2-}	2/2	3/1	3/3	3/0.01	3/0.08	3/0.00001				

	Group III salts					
	Li^+	Na^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
CO_3^{2-}	4/0.2	5/2	3/0.001	3/0.0001	3/0.0001	3/0.0001
F^-	4/0.1	4/1	2/0.001	3/0.02	3/0.001	3/0.007
OH^-	5/5	5/29	3/0.0002	3/0.02	3/0.4	3/0.1

[a] The theoretical number of moles of hydrated salt required to fill a volume of 1 liter (M) was obtained from the expression $M = 1000/(V_+ + V_-)$, where V_+ and V_- equal $(4/3)N\pi b_\pm^3 = 2.523b_\pm^3$, where $b_\pm$ is the hydrated radii of anion or cation in angstrom units as obtained from Nightengale [17]. Solubility data were obtained from [23] and [24].

of the one ion to be shared by the B region of the other ion. For salts such as $BaCl_2$, the ratio is reversed because the values of $D_\pm$ are similar and hence the complex $Ba^{2+}(H_2O)(H_2O)Cl^-$ is more stable.

In group III the phenomenon observed in group II is reversed. That is, the theoretical volumes are much greater than the maximum molarities of the corresponding aqueous salt solutions. This reversal is due to the fact that the more tightly held and greater polarized water molecules of an A region form more stable attractive forces, as concluded above.

The above comparison of theoretical and experimental molarities therefore substantiates the conclusion that the solubility of a salt is determined by the interaction of its hydrated water. These interactions can be predicted from the calculated effective dielectric constant of an ion and the presence or absence of positively hydrated water (A regions).

COMPARISON OF IONIC SEQUENCES FOR THE SOLUBILITY OF SALTS AND NONIONIC MOLECULES

As noted in the introduction and elsewhere [7], the cationic solubility sequence for basic compounds such as ammonia is $K^+ < Na^+ < Li^+ < Cs^+$, whereas that for acidic compounds such as o-phthalic acid is $Li^+ < Na^+ < K^+ < Cs^+$. The sequence does not change for those ions such as K^+, Rb^+, Cs^+, Cl^-, Br^-, and I^- because these ions do not possess A regions (positively hydrated water) and consequently only the value of $D_\pm$ is important.

A comparison can be made between the above cationic sequences for acids and bases and those sequences observed for the solubility of different salts. In Table 4 the cationic sequences for I^-, Br^-, Cl^-, and SO_4^{2-} ions are given. If the effective value of D_- is greater than or less than that of water (D_1), the sequence will be acidic or basic, respectively. Thus as the value of D_- on the anion increases, the position of the Na^+ and Li^+ will change from the basic to the acidic sequence. Table 4 thus shows that various ions can have either acidic or basic sequences, just as various nonionic molecules. Both uncharged and charged groups on polyelectrolytes are therefore capable of producing the same sequences.

The solubility sequences for some polyatomic anions is given in Table 5. Just as shown in Table 4, an acidic-type sequence is obtained for those anions that are negatively hydrated and have D_- values greater than that of pure unbonded water. Likewise, the basic sequence is obtained for negatively hydrated anions if the effective value of D_- for these anions is greater that D_1. Such sequences occur despite the fact that chelation effects may be present, since the ion-ion interaction occurs after that of the dipole-dipole inter-

Table 4. Cationic Solubility Sequences for Various Negatively Hydrated Anions[a]

Coion	Sequence	Type of sequence and reason	
I^- salts	$Li^+ = Na^+ = NH_4^+ > K^+ > Rb^+ > Cs^+$	Acidic	$(D_- > D_1)$
Br^- salts	$Li^+ > Na^+ > NH_4^+ > K^+ < Rb^+ > Cs^+$	Acidic and basic	$(D_- = D_1)$
Cl^- salts	$K^+ < Na^+ < Rb^+ < NH_4^+ < Cs^+ < Li^+$	Basic	$(D_- < D_1)$
SO_4^{2-} salts	$K^+ < Na^+ < Rb^+ < Li^+ < Cs^+ < NH_4^+$	Basic	$(D_- < D_1)$

[a] The type of sequence is based on the results given in Table 1. The greater sign (>) indicates greater solubility; i.e., Cs_2SO_4 is more soluble than K_2SO_4. Solubility data obtained from *Handbook of Chemistry and Physics* [23], and *Handbook of Chemistry* [24].

Table 5. Cationic Solubility Sequences for Various Polyatomic Anions Having Either A or B Regions[a]

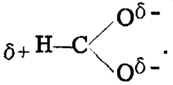
Coion	Sequence	Type	Reason
ClO_4^-	$Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$	Acidic	Negatively hydrated anions; $D_- > D_1$
NO_3^-	$Li^+ > Na^+ > K^+ > Rb^+$		
$(PO_3^-)_n$	$Li^+ < Na^+ < K^+ < Cs^+$	Acidic	Positively hydrated anions $(D_- < D_1)$; attraction of A regions
PO_4^{3-}	$Li^+ < Na^+ < K^+$		
$H_2PO_4^-$	$Li^+ < Na^+ < K^+ < Rb^+$		
CO_3^{2-}	$Li^+ < Na^+ < K^+ < Rb^+$		
F^-	$Li^+ < Na^+ < Rb^+ < K^+ < Cs^+$		
Formate	$Li^+ < Na^+ < K^+ < Cs^+$		
Acetate	$Rb^+ < Na^+ < K^+ < Li^+ < Cs^+$	Basic	Negatively hydrated anions; $D_- < D_1$
HCO_3^-	$Na^+ < K^+ < Rb^+ < Li^+ < Cs^+$		
SO_4^{2-}	$K^+ < Na^+ < Rb^+ < Li^+ < Cs^+$		

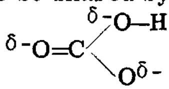
[a] Data were obtained from *Handbook of Chemistry and Physics* [23], and *Handbook of Chemistry* [24]. The sequence for $(PO_3^-)_n$ was obtained from the binding studies of Strauss and Ross [26] (see also Rice and Nagasawa [27]). The type of sequence ("acidic" or "basic") is in reference to salting in or out of nonionic acids (benzoic) or bases (NH_3).

action between the hydrated H_2O molecules. Moreover, the sequences can be used to determine whether an anion has an effective value of D_- greater than that of pure water.

If positively hydrated anions such as the F^- ion are examined, it is seen that they produce an acidic-type sequence just as negatively hydrated anions having $D_- > D_1$. However, the solubilities are reversed. Instead of the Li^+ ion being the most soluble cation, it becomes the least soluble. Moreover, the cationic sequence $K^+ < Rb^+ < Cs^+$ for these salts is the same as that obtained for anions which have $D_- < D_1$ and which possess negatively rather than positively hydrated water. The increase in the insolubility of the Li^+ and Na^+ for salts having positively hydrated anions (A regions) occurs because the A regions of both the anion and cation strongly interact as discussed above for group III salts. Hence, if $D_- < D_1$, then both a basic and an acidic-type sequence can be obtained. These sequences are maintained even for polyelectrolytes as is indicated in the sequence for $(PO_3^-)_n$. If an acidic cationic sequence is observed for anions having $D_- < D_1$, it can be predicted that the anion is positively hydrated. Conversely, if a basic sequence is observed, the anion is negatively hydrated. The cationic sequence can therefore be used to determine whether an anion is positively or negatively hydrated as well as whether $D_- > D_1$ or $D_- < D_1$.

The acidic sequence obtained for the formate ion indicates that this anion is positively hydrated, whereas the similar acetate anion is negatively hydrated. The pK's of the formate and acetate ions are, respectively, 3.75 and 4.76. Consequently, as one would expect, the positive hydration on the formate ion is due to an increase in the electrostatic charge on the oxygen atoms of the carboxylate group. This increase is caused by the increase in the positive character of the hydrogen atom attached to the carbon atom, i.e.,



If the phosphate ion PO_4^{3-} is titrated to give the dihydrogen phosphate ion $H_2PO_4^-$, the cationic sequence of the ion remains acidic. However, if the carbonate ion is titrated to give the bicarbonate ion HCO_3^-, the sequence is changed from acidic to basic. The only plausible explanation is that just as in the case of changing from the formate to the acetate ion, the electrostatic charge per unit surface area on the CO_3^{2-} is reduced when the HCO_3^- ion is formed. This reduction is great enough to change the positively hydrated oxygen atom to a negatively hydrated oxygen atom. Part of the electrostatic charge on the oxygen atoms must therefore be shared by the other two oxygen atoms through resonance, i.e.,  . In the case of the $H_2PO_4^-$ ion, this resonance effect may be the same. However, the $H_2PO_4^-$ ion is most likely positively hydrated because of the greater positive charge on the phosphate atom in $H_2PO_4^-$ as compared to that on the carbon atom in HCO_3^-. In other words, the oxygen atoms can draw the electrons more readily from the phosphate atom than they can from the carbon atom, and thus the charge per unit surface area on the oxygen atoms of $H_2PO_4^-$ is greater than that on HCO_3^-.

DETECTION OF POSITIVELY HYDRATED CATIONS AND CHELATION EFFECTS

Just as in the comparison of positively hydrated anions such as F^-, CO_3^{2-}, and $(PO_3^-)_n$ with negatively hydrated anions, ionic sequences for positively hydrated cations should also be different than those for negatively hydrated cations. Examples of cationic sequences for various anions are given in Table 6. The A regions of the positively hydrated F^- ion interacts strongly with the A region of the positively hydrated Na^+ ion. Hence the NaF salt is less soluble than the NaCl, NaBr, or NaI salt. However, the solubility of the fluoride salt is increased for negatively hydrated cations such as K^+, NH_4^+, Rb^+, and Cs^+. Consequently, the position of the F^- ion, with respect to that of the Cl^-, Br^-, and I^- ions, can be used to detect the presence of positively hydrated water (A regions) on various polymeric or monomeric cations.

Both the sulfate and acetate (Ac^-) ions can produce chelation effects, because their electrostatic charge is spread over two or more atoms which are attached to each other by covalent bonds.

Table 6. Anionic Solubility Sequences for Various Cations[a]

Coion	Sequence
Na^+ ($D_{Na} < D_1$)	$F^- < SO_4^{2-} < [Cl^- < Br^- < I^-] < Ac^-$
K^+ ($D_K < D_1$)	$SO_4^{2-} < [Cl^- < Br^- < I^-] < F^- < Ac^-$
NH_4^+ ($D_{NH_4} < D_1$)	$SO_4^{2-} < [Cl^- < Br^- < I^-] < Ac^- < F^-$
Rb^+ ($D_{Rb} < D_1$)	$SO_4^{2-} < Ac^- < [Cl^- = Br^- = I^-] < F^-$
Cs^+ ($D_{Cs} = D_1$)	$I^- < SO_4^{2-} < [Br^- < Cl^-] < F^- < Ac^-$

[a] Data obtained from [23] and [24].

Examination of their salting-out constants for the solubility of benzene shows that both the SO_4^{2-} and the Ac^- ions have effective dielectric constants which are approximately equal to each other and to that of the Cl^- ion, i.e., $D_- < D_1$. The SO_4^{2-} and Ac^- ions should therefore follow the Cl^- ion in the ionic sequences given in Table 6. In comparing the solubility of the salts of these two anions, it is seen that the Ac^- salts are always more soluble, whereas the SO_4^{2-} salts are always more insoluble than the corresponding Br^- and Cl^- salts even though they both have approximately the same value of D_-. Moreover, if the SO_4^{2-} and Ac^- anions behaved as normal negatively hydrated anions, their position in the sequences should be reversed when the value of D_+ of their counterion is increased, as in going from K^+ to Cs^+ salts. As seen in Table 6, their position with respect to themselves and with respect to Br^- and Cl^- remains unchanged for K^+ and Cs^+ salts. However, the slight change of $SO_4^{2-} < I^-$ for K^+ salts to $SO_4^{2-} > I^-$ for Cs^+ salts shows an attempt to change in the manner expected for negatively hydrated anions.

The position of the SO_4^{2-} and Ac^- anions in the sequences given in Table 6 can be explained based on their chelation effects. As discussed above, the SO_4^{2-} ion with its tetrahedral structure and large electrostatic charge can produce three-dimensional chelate structures and hence it will produce abnormally low solubilities. Conversely, the acetate ion cannot form three-dimensional networks of ion-ion aggregates, because there are only two negatively charged oxygen atoms in the acetate ion. These planar oxygen atoms can only complex with, at most, one metallic ion. Moreover, the methyl group blocks the formation of any ion-ion chain structures. Consequently, the solubilities of the acetate salts will be abnormally high because of its ability to chelate with only one cation. The Rb^+ ion promotes a more insoluble salt, possibly because the Ac^- cannot form a stable ion-ion complex with the Rb^+ ion due to the intermediate value of D_+ for the Rb^+ ion. Consequently, the solubility of sulfate and acetate salts are peculiar because of their ability to form chelate structures with their counterion.

Chelation does not always occur and may be selective. For example, the $MgSO_4$ precipitate does not form until the molar volume of the hyrated ions equals the saturation molarity (see Table 3). Hence in $MgSO_4$ the interaction must be between the hydrated water molecules (dipole-dipole interactions) rather than the formation of chelate structures (ion-ion interactions). This same variation in ability to form chelates may also be true for ions such as NH_4^+ and NO_3^-. Thus their position in an ionic sequence is determined by the ability to form chelate structures with a particular coion. Consequently, NH_4^+ in Table 4 is not in any fixed position in the sequence. Polyatomic ions such as the thiocyanate ion, where $D_- > D_1$, would most likely have no chelating properties, not because of their high values of D_- but because of their linear structure.

APPLICATION TO POLYELECTROLYTES

As seen in Table 5, the cationic sequence for the polymer $(PO_3^-)_n$ is the same as that for monomers. A more detailed comparison of properties of monomers with those of polyelectrolytes will be given in subsequent papers. The data presented in these papers as well as that given above for $(PO_3^-)_n$ show that the results for the interaction of inorganic or organic ions can be applied to polyelectrolytes.

An interesting conclusion can be made when the results are applied to proteins. In Table 2 the guanidinium ion G^+ has the solubility sequence $Cl^- > Br^- > I^-$, whereas the NH_4^+ ion has the sequence $Cl^- < Br^- < I^-$. From the reversal of charge phenomena [28] it is seen that the more soluble counterion "binds" the most to the polyelectrolyte. In other words, considering the guanidinium ion, the Cl^- will "bind" to a greater extent than the I^- ion. Moreover, considering the positively charged amino group on proteins, the reverse of this will be true (I^- will be more strongly "bound" than Cl^-). Thus if a positively charged protein has a greater affinity for those anions having high values of D_- such as I^- and SCN^- ions, then one can conclude that it is the amino groups and not the guanidinium groups of the protein that are binding or associating the counterions. Moreover, the carboxylate group on proteins should interact with cations by either an acidic (as in the formate ion) or basic (as in the acetate ion) sequence depending on its pK.

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Accepted by editor December 4, 1967
Submitted for publication January 23, 1968