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Explanation of Ionic Sequences in Various Phenomena. I. Salting-Out of Uncharged Molecules

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SUMMARY

Theoretical models for hydrated ions and their calculated effective dielectric constants obtained previously were used to explain the salting-in or salting-out of nonionic molecules. Three types of salting-out sequences were obtained: nonpolar ($\text{Na}^+ > \text{K}^+ > \text{Li}^+ \geq \text{Rb}^+ > \text{Cs}^+$), basic ($\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Li}^+$), and acidic ($\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$). The nonpolar sequence is not influenced by the A region of a cation, and therefore the ability to salt-out is great if the effective dielectric constant of the ion is small. The A region on hydrated Li^+ ions (the tightly bound water) salts-in basic compounds because of the interaction of its positively charged hydrogen atoms with the negative dipolar charge of the base. Conversely, the A region of a cation salts-out acidic compounds because the hydroxyl group on carboxylic acids behaves as a similar cationic A region. A sulfonic polymer will cause the salting-in of the base *p*-nitroaniline because the addition of salts to an aqueous solution of the base and polymer destroys hydrogen bonds in the polymer and in so doing releases hydronium ions from the polymer. This release of H^+ , in turn, produces a positive charge on part of the *p*-nitroaniline molecules, which produces a salting-in effect.

INTRODUCTION

Ionic sequences pertaining to various physical phenomena have been observed for a number of years. The Hofmeister series, reversal of charge phenomenon, helix-coil transitions of DNA, and

retrogradation of amylose are some of the phenomena that have been examined with respect to the relative effects of various mono- or divalent ions. In this paper the salting-in and salting-out of various inorganic and organic compounds will be examined. The other phenomena will be examined in subsequent papers. Conclusions drawn from the present study will be applied to polymers or polyelectrolytes in another paper [1]. It will then be shown that ionic sequences are an important tool in determining the presence of hydrogen, hydrophobic, and ionic bonding. In the present paper, the effective dielectric constants and the structure of hydrated ions as set forth in a previous paper [2], and as applied to the solubility of inorganic, organic, and polymeric salts [3], will be used to explain various ionic sequences connected with the salting-in or salting-out of polar and nonpolar molecules.

Some time ago Harned and Owen [6] recognized that the induced dipole of a cation's hydrated water molecules effects the solubility of basic and acidic molecules such as ammonia and carboxylic acids. They proposed their "localized hydrolysis" theory and considered that all hydrated water molecules interact with acidic and basic molecules by the same mechanism. That is, the water molecules reacted differently only because of the change in the strength of their induced dipole. But all hydrated cations do not have the same structure as shown previously [2] and hence cannot interact in the same manner as they [6] proposed. An ion has either a loosely bound, penetrable hydration shell ("negative hydration" as defined by Samoilov [4] or "B regions" as defined by Frank and Wen [5]) or it has a tightly bound, impenetrable shell ("positive hydration" or "A region") plus possibly a loosely bound hydration shell [2]. From the ionic sequence studies [3] made on the solubility of various salts, it was seen that only the A regions can interact in a manner similar to that proposed by Harned and Owen [6]. The solubility of ions which do not have A regions is dependent only upon their effective dielectric constant. It will be shown in this and subsequent papers that the same principle applies to the salting-in and salting-out of various polar or nonpolar molecules, to the reversal of the charge on a colloid, and to the ability of an ion to bind to a polyelectrolyte. In other words, only the A regions alter the ability of an ion to salt-in or salt-out nonpolar, acidic, or basic molecules.

Salting-Out Sequences for Polar and Nonpolar Molecules

Nonpolar and Acidic Sequences. Table 1 lists the salting-out sequences for various organic and inorganic molecules. It is seen that the cationic and anionic salting-out sequences for all ions which do not have A regions, such as K^+ , Rb^+ , Cs^+ , Cl^- , Br^- , and I^- , always remain the same ($K^+ > Rb^+ > Cs^+$ and $Cl^- > Br^- > I^-$) and depend

Table 1. Salting-Out Sequences for Organic and Inorganic Compounds Using Anions and Cations with Similar Cations^a

Type of sequence	Solute	k_s (KCl)	Cationic sequence	Anionic sequence
Nonpolar	Benzene	0.166	$\text{N}^+ > \text{K}^+ > \text{Li}^+, \text{Rb}^+ > \text{Cs}^+ > \text{H}^+$	$\frac{1}{2} \text{SO}_4^{2-} > \text{F}^- > \text{OH}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$
	Diacetone alcohol	0.142	$\text{Na}^+ > \text{K}^+ > \text{Li}^+$	$\frac{1}{2} \text{SO}_4^{2-} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{SCN}^-$
	Aniline	0.13	$\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Li}^+ > \text{Cs}^+$	$\frac{1}{2} \text{SO}_4^{2-} > \text{OH}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$
	H ₂	0.102	$\text{Na}^+ > \text{K}^+ > \text{Li}^+$	$\text{OH}^- > \text{Cl}^-$
	Acetone	0.101	$\text{Na}^+ > \text{K}^+ > \text{Li}^+$	$\text{Cl}^- > \text{Br}^- > \text{I}^-$
	Trimethylamine	0.20	$\text{K}^+ > \text{Na}^+ > \text{Li}^+$	$\frac{1}{2} \text{SO}_4^{2-} > \text{Cl}^- > \text{Br}^- > \text{I}^-$
Basic	NH ₃	0.057	$\text{K}^+ > \text{Na}^+ > \text{Li}^+$	$\text{OH}^- > \frac{1}{2} \text{SO}_4^{2-} > \text{Cl}^- > \text{Br}^- > \text{I}^-$
	Helium	0.053	$\text{K}^+ > \text{Na}^+ > \text{Li}^+$	$\text{Cl}^- > \text{I}^- > \text{ClO}_4^-$
Intermediate: acidic and nonpolar	Phenol	0.133	$\text{Na}^+ > \text{Li}^+ > \text{K}^+$	
Acidic	Benzoic acid (pK 4.2)	0.152	$\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{H}^+$	$\text{Cl}^- > \text{Br}^- > \text{I}^-$
	o-Phthalic acid (pK 2.9)	0.093	$\text{Li}^+ > \text{Na}^+ > \text{H}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$	$\text{Cl}^- > \text{Br}^-$
	Acetic acid (pK 4.8)	0.026	$\text{Li}^+ > \text{Na}^+ > \text{K}^+$	$\text{Cl}^- > \text{Br}^-$
	Chloroacetic acid (pK 2.9)	0.026	$\text{Na}^+ > \text{K}^+$	$\text{Cl}^- > \text{Br}^-$
	Succinic acid (pK 4.2)	0.018	$\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$	$\text{Cl}^- > \text{Br}^- > \text{I}^-$
	HCN	—	$\text{Li}^+ > \text{K}^+ > \text{Cs}^+$	—

^aData obtained from Long and McDevit [7] or Harned and Owen [6]. The salting-out sequences were determined by comparing k_s values of different anions or cations having the same cation.

entirely on the value of D_{\pm} of the ion's B region. Furthermore, if the molecule is inert as in the case of benzene, then the molecule's solubility is not influenced by the A regions of such ions as H^+ , Li^+ , and Na^+ , but rather Table 1 shows that it is determined by the value of D_{\pm} of the penetrable B region. That is, the salting-in sequence observed for these inert molecules agrees with the value [2] of D_{\pm} ; the greater the value of D_{\pm} , the greater is the salting-in ability of the ion.

In the case of acidic substances such as phthalic acid, the polarized $-OH$ group of the carboxylic acid will have the same effect as an A region of a cation to any approaching hydrated ion. In other words, the positively charged proton on the oxygen atom of the carboxylic acid will extend into the medium just as in the case of the positively charged protons on a water molecule in an A region of a cation. The greater the polarization of the $-OH$ group, the greater will be the A region effect. The polarization of the $-OH$ group on the carboxylic acid will increase as the pK of the acid decreases. That is, the greater the polarization, the greater will be the tendency for the carboxylic acid to release its proton and hence the lower will be its pK . Consequently, *o*-phthalic acid with a pK of 2.9 will have a stronger "A region" than benzoic acid (pK 4.2). As the A region of a cation approaches the carboxylic acid, the positively charged hydrogen atoms of the A region will repel the positively charged hydrogen atom of the acid. Consequently, cations having A regions will have a greater ability to salt-out the carboxylic acid than they had previously with inert molecules. Thus the cationic sequence is changed from $Na^+ > K^+ > Li^+ \geq Rb^+ > Cs^+ > H^+$ for benzene to $Li^+ > Na^+ > H^+ > K^+ > Rb^+ > Cs^+$ for *o*-phthalic acid (Table 1).

Let us now examine the position of the H^+ ion in the sequences of Table 1. Because of its greater charge per unit surface area, the Li^+ ion is able to induce greater polarization into the water molecules of its A region and hence has a stronger A region than that of the hydrated Na^+ ion. But by the same reasoning the H^+ ion has a more polarized A region than the Li^+ ion. From this viewpoint, one would expect it to have greater salting-out properties toward acids than the Li^+ ion. But as seen in Table 1, the salting-out property of the H^+ ion is less than both the Li^+ and the Na^+ ion. This apparent discrepancy can be explained if one considers the effect of the B region as well as that of the A region. The previous paper [2] showed that the value of D_+ for the H^+ ion is much greater than that for the Li^+ ion. As seen above, the solubility of any molecule will be increased as the value of D_+ increases. Consequently, even though the A region of H^+ is stronger than that of the Li^+ ion, the hydronium ion's high value of D_+ for its B region partially counteracts the A region effect [$D_+ = 62$ for H^+ and $D_+ = 16$ for Li^+ for $D_1(H_2O) = 55$] [2]. Thus the hydrated H^+ ion would salt-out an acid more than

the Li^+ ion if both had the same value of D_+ . Consequently, in determining the position of a positively hydrated cation, both the A and B regions must be considered. Therefore, Li^+ salts-out benzene more than H^+ .

This effect of the B region also occurs as shown previously in the study of the solubility of various salts [3]. However, it must be emphasized again that the reason for the shift in the cationic sequence is due entirely to the repulsion effects of the A region. Moreover, as expected, the shift in the position of H^+ in the sequence is greater for *o*-phthalic acid ($\text{H}^+ > \text{K}^+$) than it is for benzoic acid ($\text{K}^+ > \text{H}^+$) because of the lower pK of the *o*-phthalic acid (see Table 1) and the consequent production of greater repulsive forces toward the A regions on cations.

Basic Sequence. Besides the nonpolar and acidic sequences described above, a "basic" sequence is also obtained which involves an interaction of extremely polar substances with an A region. The unshared electrons of the NH_3 or $(\text{CH}_3)_3\text{N}$ molecules produce a dipole, so that electrons are concentrated more on one side than the other side of the almost tetrahedral sp^3 hybrid molecule. This negative charge of the dipole can interact with the positively charged hydrogens of the A region of a cation. Since this interaction involves an attraction rather than a repulsion of the solute molecules, the A regions of H^+ , Li^+ , and Na^+ will increase the solubility of the solute rather than decrease it as in the case of the carboxylic acids. Consequently, the K^+ ion salts-out more than the Na^+ and the Na^+ more than the Li^+ , as shown in Table 1.

Possible Polarity of Helium and the Production of Intermediate Sequences by Partially Polar Molecules. As seen in Table 1, helium behaves as a polar substance while hydrogen does not. This sequence was obtained from the studies of Åkerlöf [8]. Other sequences [9, 10] obtained for helium indicate that helium and argon behave the same as hydrogen. However, there is still the possibility that Åkerlöf may be correct. If he is correct, then the helium atom's 1s electrons must go through the same "north" and "south" poles. In this manner, the electrons would be concentrated at these poles and thus produce a polar atom. The position of the poles most likely cannot change more than approximately once every 10^{-11} sec, since this is the approximate reorientation time of water or hydrated water. Argon would be less polar than helium because of a swamping-out of the polar s orbital by the many p orbitals. The model would explain why the solubility and conductivity of helium in fused NaNO_3 is greater than that of argon [11]. Further studies are, however, needed to verify Åkerlöf's results.

Even though acetone is considered as a polar molecule, its cationic salting-out sequence is the same as the relatively inert benzene molecule. Acetone does not behave as NH_3 or $(\text{CH}_3)_3\text{N}$ because the separation of charges on the $\text{C}=\text{O}$ groups is not great

enough. However, a comparison of salting-out constants (k_s) does show that the sequence for acetone approaches that for basic molecules such as ammonia. The value of k_s is $(1/C) \log (S_0/S)$, where C is the molarity of the salt and S_0 and S are the solubilities of the molecule in pure water and an aqueous salt solution, respectively [7]. The value of k_s remains constant to extremely high molarities [12]. The ratio of k_s values for the solubility of benzene and acetone in different aqueous salt solutions is:

Benzene: $k_s(\text{KCl})/k_s(\text{LiCl}) = 1.18$; $k_s(\text{KCl})/k_s(\text{NaCl}) = 0.85$

Acetone: $k_s(\text{KCl})/k_s(\text{LiCl}) = 1.60$; $k_s(\text{KCl})/k_s(\text{NaCl}) = 0.92$

Using the KCl as a standard, since it has no A regions, the results show that the Li^+ and Na^+ ions salt-out acetone less than they salt-out benzene; i.e., their relative k_s values are smaller. Hence there is a trend toward the sequence $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ as obtained for the more polar NH_3 molecule. A more complete sequence showing the position of the Li^+ ion with respect to the Rb^+ and Cs^+ ions would most likely reveal that acetone has an intermediate sequence between that of the nonpolar and basic sequences.

As seen in Table 1, phenol also has an intermediate sequence. However, in this case, the polar nature of the hydroxyl group on phenol interacts as a carboxylic acid group toward the A regions of cations. Consequently, the sequence for phenol is intermediate between that of a nonpolar molecule (because of its benzyl group) and that of an acidic molecule (because of its polar hydroxyl group).

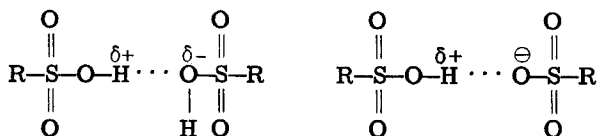
The A region of anions such as those of the F^- ion are not as influential in reversing the sequence as those of a cation's because the induced dipole of the hydrated water molecules is weaker. In other words, the close proximity of the center of the hydrogen atoms on H_2O to the surface of some anions causes positive hydration, even though there is a relatively low charge per unit surface area [2]. This weak charge per unit surface area reduces the induced dipole, so that the A regions of these anions do not have as great an effect as those of cations. Consequently, as seen in Table 1, the anionic sequence remains the same for all anions, just as in the case of those cations such as K^+ , Rb^+ , and Cs^+ which contain only B regions. An exception is where a chemical reaction such as between NH_4^+ and OH^- involving sharing of electrons can occur [3].

Salting-In Effects of Polyelectrolytes

Steigman and Lando [13] observed that in the presence of poly(*p*-styrene sulfonic acid) the basic hydrocarbon *p*-nitroaniline is salted-in, whereas in its absence, the base is salted-out. They explain these results assuming that salting-in occurs by incorporating the basic hydrocarbon in a cage of organized water molecules. Their order of cation effectiveness in the presence of the polymer was observed to be $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < (\text{CH}_3)_4\text{N}^+$. Their [13]

results and conclusions present two interesting problems. First, the sequence they obtained is acidic and therefore must be related to the salting-in of an acid and not the base *p*-nitroaniline. In other words, Long and McDevit [7] have shown that the salting-out sequence for *p*-nitroaniline is basic, not acidic: $K^+ > Na^+ > Li^+ > Cs^+$. Therefore, the salting-in sequence should have been $K^+ < Na^+ < Li^+ < Cs^+$ and not $Li^+ < Na^+ < K^+ < Cs^+$ if *p*-nitroaniline is the only group effected by the salt. Second, the previous paper [14] shows that hydrocarbons do not enter a caged water structure but rather exist in domains of relatively free or unbonded water molecules. Consequently, their conclusions do not seem valid. Why then does the addition of this polyelectrolyte (A) salt-in nitroaniline and (B) change the ionic sequence from acidic to basic?

Their [13] experimental results can be readily explained using the above observations and relationships on salting-in and out of different compounds and using the proposed model [14] for the structure of water. In the poly(*p*-styrene sulfonic acid) there must exist hydrogen bonds between untitrated sulfonic acid groups and between sulfonate and sulfonic acid groups:



If a salt is added to the polymer solution, the hydrated water molecules on the ions will tend to break the above hydrogen bonds by competitive interaction with the polar or charged groups. However, the A regions on the lithium and sodium ions will tend to salt-out rather than salt-in the acid group for the same reasons given above for the salting-out of organic acids. Consequently, Li^+ will be least effective in breaking such bonds and the acidic sequence will be obtained. And it must be remembered that for ions which do not have A regions, the effectiveness of the ion to salt-out the molecule will increase as the value of D_{\pm} increases. Consequently, the observed acidic sequence for the salting-in of *p*-nitroaniline refers to the destruction of hydrogen bonds in the above polymer by competitive electrostatic interactions. In other words, when the sulfonic acid group is released by destruction of hydrogen bonds, its pK value increases with the result that hydronium ions are released into the medium. The release of the H^+ ions causes the protonation of more *p*-nitroaniline molecules, which in turn increases its solubility. Consequently, the addition of the polyelectrolyte poly(*p*-styrene sulfonic acid) causes salt to salt-in rather than salt-out the *p*-nitroaniline by ionizing the *p*-nitroaniline. Thus the above proposed mechanisms concerning ionic sequences and the structure of water

are in complete agreement with the results of Steigman and Lando [13]. It is the acidic polymer which produces the observed sequence, and it is the release of H^+ ions which increases the solubility of the p-nitroaniline.

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