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## Determination of the Structure and Effective Dielectric Constant of Hydrated Ions\*

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### SUMMARY

Debye's equation for the salting in or out of nonpolar compounds, such as benzene, in aqueous salt solutions was expanded so as to determine the effective dielectric decrement and constant of the hydrated domain of an ion. For ions having an electrostatic charge per surface area less than or equal to that of the  $K^+$  or  $Cl^-$  ions, this domain consists of a single layer of water molecules loosely or negatively hydrated to the ion; i.e., the domain consists of a monomolecular B region. For ions having an electrostatic charge per unit surface area approximately equal to that of the  $Na^+$  and  $F^-$  ions, there exists no B region and only one layer of tightly bound or positively hydrated water (a monomolecular A region). Since the electrostatic field does not appreciably influence water molecules beyond this A region, such ions have an effective dielectric constant that is near zero, as in relatively inert molecules such as hydrocarbons. For all other ions, such as  $H^+$ ,  $Li^+$ ,  $Mg^{2+}$ ,  $Cr^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ , and other multivalent ions, there exists only one monomolecular A region followed by one monomolecular B region. The effective value of the dielectric constant of such an ion is obtained from its B region, since its A region cannot be penetrated. The effective dielectric decre-

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ment or constant of any B region as measured by benzene solubility goes through a maximum as the electrostatic charge per unit surface area ( $C/A$ ) is decreased because a large  $C/A$  restricts the orientation of the hydrated water molecules and a low value of  $C/A$  allows competitive interaction between surrounding water molecules. Thus both small and large values of  $C/A$  decrease the solubility of benzene, i.e., decrease its ability to penetrate into the medium. A decrease in the macroscopic dielectric constant of water upon the addition of salt is due to the destruction of the clusters of water by the ions, or to the addition of ions which have effective dielectric constants less than that of water, or both. All hydrated ions or molecules which salt-in or salt-out benzene have, respectfully, effective dielectric constants greater or less than that of water.

## INTRODUCTION

At present it is not known why salts or polar compounds in aqueous solutions denature or solubilize proteins, DNA, starch, or other polymers that have hydrophobic, polar, or electrostatically charged groups. Why is one salt more effective in converting a random coil into a helix or vice versa? Why does the solubility of starch granules [1] or proteins [2] reach a maximum as the molarity of a lithium salt is increased, whereas no such maximum in dispersing power is obtained for guanidinium salts [1]? These questions and others are related to structure and effective dielectric constant ( $D$ ) of the water surrounding an ion or polar group.

But what determines the value of the dielectric constant? Robinson and Stokes [3] in their review have shown that for polar molecules such as water the dielectric constant is a function of the polarization of these molecules. This polarization is the sum of two factors [3]: (1) the distortion of the electronic distributions of atoms or molecules (distortion polarization or induced dipoles such as in ion-water interactions) and (2) the partial lining up of molecules which already have permanent molecular dipoles (orientation polarization).

The above conclusions are applied to physical measurements made over relatively large distances for a particular solution [3]. However, factor (1) is also applicable for explaining the microscopic (or "effective") dielectric constant of the medium as seen by a particular molecule, such as the benzene molecule. Factor 2 would apply only to the macroscopic dielectric constant. If the benzene molecule is surrounded by hydrated ions as well as by unhydrated water, then the microscopic dielectric constant will be determined by the interaction of the benzene molecule with the hydrated ions as well as with the free water molecules. Consequently, the effective value of  $D$ , as obtained from benzene solubility studies, measures

dipole-dipole and ion-dipole interactions between water molecules and between ions and associated water molecules. The effective or microscopic value of  $D$  differs from the macroscopic dielectric constant in that large structures such as "clusters" or "icebergs" of hydrogen-bonded water molecules will greatly increase the macroscopic value of  $D$  but will decrease or will have little effect on the microscopic value of  $D$ .

Equations have been derived to explain the salting in or out of various low molecular weight hydrocarbons [4-8]. The equation developed by Debye [5] and extended by Givon et al. [6] relates the salting-in or salting-out property of an aqueous salt solution to the effective dielectric decrement of an ion. Such an equation gives the opportunity to determine the effective dielectric constant of a hydrated ion and to apply such information to explain the properties of hydrated ions. The Debye equations as modified by Givon et al. [6] will be extended further in calculating the effective dielectric decrement of a specific anion or cation.

Other equations that attempt to explain the salting out of hydrocarbons, such as the equation developed by McDevit and Long [7] and modified by Deno and Spink [8], cannot be used to determine the effective dielectric constant. Their equation relates the extent of "electrostriction" of the solvent by the salt to the salting-out constant. Moreover, the equation is hindered by the fact that it must be modified by an unknown factor of 0.3 in order to obtain good agreement between theoretical and experimental values. Their compression [7, 8] or electrostriction of volume is due to an orientation of water molecules around an ion, because Padova [9] has shown that the compressibility of the solvent in the neighborhood of an ion is essentially the same as that in the absence of an ion.

Present theoretical values of the dielectric constant only consider the electrostatic field of an ion and not the induced dipole of hydrated water molecules. Hence the values given by Padova [9], Noyes [10], Debye and McAulay [12], Hasted et al. [13], and Schellman [14] (see review by Robinson and Stokes [3], Chap. 1) are too low, being about  $D = 3$  for all ions. In the Debye equation [5, 6] it is assumed that the dielectric constant does not vary with distance. Therefore, this dielectric constant is actually the effective value in the medium surrounding the ion and hence is quite different from that calculated by theoretical equations which only consider the electrostatic field of the ion and not the induced dipole on hydrated water.

### Calculation of $k_s$ from the Dielectric Decrement

At a specific temperature the maximum molar solubility of a compound such as benzene in water ( $S_0$ ) divided by its solubility in a salt solution ( $S$ ) equals its activity coefficient [7]:  $f_3 = S_0/S$ . From the Setschenow equation, the limiting slope of the line in a plot of  $\log$

$f_3$  versus the molar concentration ( $C_2$ ) of the salt gives a characteristic constant  $k_S$  for the salt:  $\log f_3/C_2 = k_S$ . A correlation of this constant  $k_S$  with the dielectric decrement of the ions can be obtained by expanding the derivation given by Givon et al. [6].

According to the Debye theory, the activity coefficient  $f_3$  of a non-electrolyte is given as [6]

$$f_3 = 1 \left/ \left[ 1 - \frac{4\pi N_0}{1000} (J_+ C_+ + J_- C_-) \right] \right. \quad (1)$$

where  $J_{\pm} = \bar{R}^4 Z_{\pm}^2 / b_{\pm}$ . Here  $N_0$  is Avogadro's number and  $C_{\pm}$ ,  $b_{\pm}$ , and  $Z_{\pm}$  are the molar concentrations, radii, and electrostatic charges of the ions. The value of  $\bar{R}$  as given by Debye is [6]

$$\bar{R}^4 = N_0 e^2 [v_3 (\partial D / \partial n_1)_{n_3} - v_1 (\partial D / \partial n_3)_{n_1}] / 8\pi R T v_1 D^2 \quad (2)$$

where  $v_i$  is the molal volume of component  $i$  per molecule ( $V_i/N_0$ ),  $R$  the gas constant,  $n_i$  the number of molecules of component  $i$  per milliliter, and  $D$  the dielectric constant of the solution.

The terms  $(\partial D / \partial n_3)_{n_1}$  and  $(\partial D / \partial n_1)_{n_3}$  of Eq. (2) can be evaluated as follows. The dielectric constant  $\bar{D}$  is expressed as a function of its components [11]:

$$D = D_1 - \delta_2 C_2 - \delta_3 C_3 \quad (3)$$

where  $D_1$  is the dielectric constant of pure water,  $\delta_2$  and  $\delta_3$  the dielectric decrements of the salt and the nonelectrolyte, and  $C_2$  and  $C_3$  the molar concentrations of salt and nonelectrolyte, respectively. According to Hasted et al., [13] the dielectric constant  $D$  of a salt may be expressed as a function of its ions. Hence

$$D = D_1 - \delta_+ C_+ - \delta_- C_- - \delta_3 C_3 \quad (4)$$

When  $C_+ = C_-$ , then  $\delta_+ + \delta_- = \delta_2$ .

At concentrations of 2 M or less, the dielectric decrements  $\delta_+$  and  $\delta_-$  of the positive and negative ions appear to be independent [13]. Thus even though the molar concentrations  $C_+$  and  $C_-$  of the positive and negative ions are present in the solution at a constant ratio, they can be considered as being independent of one another with respect to the dielectric constant of the solution. The quantity  $(\partial D / \partial n_1)_{n_3}$  in Eq. (2) can therefore be expressed as

$$\left( \frac{\partial D}{\partial n_1} \right)_{n_3} = \left( \frac{\partial D}{\partial C_+} \right) \left( \frac{\partial C_+}{\partial n_1} \right) + \left( \frac{\partial D}{\partial C_-} \right) \left( \frac{\partial C_-}{\partial n_1} \right) \quad (5)$$

From Eq. (4) the value of  $(\partial D/\partial C_{\pm})$  is  $-\delta_{\pm}$  if  $C_3$  is sufficiently small. Also  $(\partial C_i/\partial n_1) = -1000 v_1/(V_i^{\phi} + h_i V_1)$ , where  $V_i^{\phi}$  is the apparent molal volume of the component  $i$  in solution and  $h_i$  its hydration number [5]. Thus Eq. (5) becomes

$$\left(\frac{\partial D}{\partial n_1}\right)_{n_3} = \delta_+ \left(\frac{1000v_1}{V_+^{\phi} + h_+V_1}\right) + \delta_- \left(\frac{1000v_1}{V_-^{\phi} + h_-V_1}\right) \tag{6}$$

Moreover, from Eq. (3) the value of  $1/D^2$  can be approximated as  $D^2 = D_1^2/[1 + (2C_2\delta_2/D_1)]$  for small values of  $C_3$  and for  $C_2\delta_2 \ll D_1$ .

Using the above results, the value of  $\bar{R}^4$  in Eq. (2) can be expressed as

$$\bar{R}^4 = 1000e^2[1 + (2C_2\delta_2/D_1)] \left[ \left(\frac{V_3\delta_+}{V_+^{\phi} + h_+V_1}\right) + \left(\frac{V_3\delta_-}{V_-^{\phi} + h_-V_1}\right) - \left(\frac{N_0}{1000}\right) \left(\frac{\delta D}{\delta n_3}\right)_{n_1} \right] / 8\pi RTD_1^2 \tag{7}$$

In Eq. (1) the term  $(J_+C_+ + J_-C_-)$  is equal to  $[J_+(C_+/C_2) + J_-(C_-/C_2)]C_2$ . Now  $C_2 = C_-/\gamma_- = C_+/\gamma_+$ , where  $\gamma_{\pm}$  is the number of ions of the cation or anion per molecule of salt and is always positive. Thus we have

$$(J_+C_+ + J_-C_-) = (J_+\gamma_+ + J_-\gamma_-)C_2. \tag{8}$$

Substitution of  $J_{\pm} = \bar{R}^4 Z_{\pm}^2/b_{\pm}$  and of Eq. (8) into Eq. (1) gives

$$\frac{1}{f_3} = 1 - \frac{4\pi N_0 \bar{R}^4}{1000} \left[ \left(\frac{Z_+^2\gamma_+}{b_+}\right) + \left(\frac{Z_-^2\gamma_-}{b_-}\right) \right] C_2 \tag{9}$$

where  $\bar{R}^4$  is defined as given in Eq. (7). The salting coefficient  $k_S = \lim_{C_2 \rightarrow 0} d \log f_3/dC_2$  may be obtained by the procedure given by Givon<sup>2</sup> et al. [6], where  $\log f_3$  of Eq. (9) is expanded as  $\log (1/1 - X) = \log (1 + X) = X$ , where  $X = 1 - (1/f_3)$ . Also  $V_+^{\phi} + h_+V_1 = \bar{V}_+^0 + h_+^0\bar{V}$  as  $C_2 \rightarrow 0$ , where the superscript zero refers to infinite dilution. Substituting these expressions into Eq. (7) and determining  $k_S$  as  $\lim_{C_2 \rightarrow 0} dX/dC_2$ , the value of  $k_S$  becomes

$$k_S = \left(\frac{0.4343N_0e^2V_3}{2RTD_1^2}\right) \left[ \left(\frac{\delta_+}{\bar{V}_+^0 + h_+^0V_1}\right) + \left(\frac{\delta_-}{\bar{V}_-^0 + h_-^0V_1}\right) - \left(\frac{N_0}{1000V_3}\right) \left(\frac{\partial D}{\partial n_3}\right)_{n_1} \right] \left[ \frac{Z_+^2\gamma_+}{b_+} + \frac{Z_-^2\gamma_-}{b_-} \right] \tag{10}$$

where  $V_3 = M_3/\rho_3$  or the molecular weight of component 3 divided by its density. For benzene,  $V_3 = 89.4$  ml at  $25^\circ\text{C}$ . The values of  $b_{\pm}$  are in angstrom units and refer to the hydrated radii.

## CALCULATIONS AND DISCUSSION

### Approximate Values of $D_1$ and $(\partial D/\partial n_3)_{n_1}$

Before theoretical calculations of  $k_S$  can be made from Eq. (10), one must first know the value of the effective dielectric constant ( $D_1$ ) in the vicinity of the hydrocarbon (component 3) in pure water. Water exists as a mixture of water "clusters" or "icebergs" and partially or totally unbonded water [15-17]. A hydrocarbon cannot exist inside these water clusters but is confined to those domains where relatively unbonded water molecules exist. The dielectric constant of the water in these domains should be markedly different from the macroscopic dielectric constant of water.

The observed dielectric constant of pure water decreases from  $D_1 = 88.0$  at  $0^\circ\text{C}$  to  $D_1 = 55.3$  at  $100^\circ\text{C}$ . Yet from  $25$  to  $100^\circ\text{C}$  the dipole moment of water in the vapor state remains constant at  $\mu = 1.85$  Debye units [18]. Therefore the decrease in the values of  $D_1$  cannot result from the constant dipole moment. Indeed, all theoretical equations that attempt to explain the temperature dependence of the dielectric constant of water incorporate various types of hydrogen bonding [19]. A small change in  $D_1$  with temperature will occur even for water molecules that are not hydrogen-bonded to neighbors, since the rotation of the permanent dipoles is opposed by thermal agitation [3, p. 7]. This small change in  $D_1$  will be neglected.

All evidence points to hydrocarbons not being surrounded by clathrated water structures [20]. Since hydrocarbons cannot exist inside the water clusters and since they have no clathrated water structures surrounding them, they must exist in those pockets or domains in the water that consist of relatively unassociated or free water. The water in these domains should have a dielectric constant approximately equal to that of boiling water where water clusters are nearly absent.  $D_1$  must be approximately equal to  $55.3$  in Eq. (10), since this is the value at  $100^\circ\text{C}$  for pure water [18].

The quantity  $(\partial D/\partial n_3)_{n_1}$  in Eq. (10) is the change in the dielectric constant with a change in the concentration of component 3. Taking the derivative of Eq. (2) with respect to  $n_3$  at constant  $n_1$  gives  $(\partial D/\partial n_3)_{n_1} = -1000 \delta_3/N_0$ . For inert substances, such as benzene, that cannot induce polarization into surrounding water molecules, the macroscopic dielectric decrement,  $\delta_3$ , becomes a volume correction. Therefore the approximation  $\delta_3 = V_3 (D_1 - D_3)10^{-3}$  made by Butler [21, p. 5] is valid for the macroscopic value of  $D$ . Here  $V_3$  is the molar volume of component 3 and  $D_3$  is its dielectric constant. In

other words, the macroscopic value of the dielectric constant becomes  $D = D_1 - \delta_3 C_3 = D_1 - D_1(V_3 C_3)10^{-3} + D_3 (V_3 C_3)10^{-3}$ . The dielectric constant of the displaced fraction of water [ $D_1(V_3 C_3)10^{-3}$ ] is subtracted and the dielectric constant of that fraction of benzene [ $D_3(V_3 C_3)10^{-3}$ ] which displaces the water is added to the value of  $D$  for pure water. The correction is then one concerning the displacement of the volume of water by another component and is only applicable to substances like benzene which do not change the value of  $D$  in the surrounding medium.

But the solubility of benzene and other inert hydrocarbons in water is determined by the dielectric constant of the medium in its immediate vicinity and not by the macroscopic value. The macroscopic value of  $D$  would include the contribution of benzene to the volume of water, while the effective value of  $D$  would only include the interaction of benzene with other benzene molecules. The value of  $(\delta D/\partial n_3)_{n_1}$  therefore becomes a value seen by an individual benzene molecule and not by macroscopic measurements. Since the concentration of benzene will always be extremely low in aqueous solutions, then the value of  $(\partial D/\partial n_3)_{n_1}$  will be approximately zero. In other words, because of the low interaction between benzene molecules with respect to their interaction with surrounding water and hydrated ions, Eq. (4) becomes  $D = D_1 - \delta_+ C_+ - \delta_- C_-$  and  $(\partial D/\partial n_3)_{n_1} \equiv 0$ . As the microscopic value of  $D_1$  in the vicinity of the hydrocarbon is different from that of the macroscopic value, so also the value of  $(\partial D/\partial n_3)_{n_1}$  will be different.

From the above discussions the approximate microscopic values  $D_1 = 55.3$  and  $(\partial D/\partial n_3)_{n_1} = 0$  can be substituted into Eq. (10) for the solubility of benzene or other inert, slightly soluble substances in water for all temperatures of water at 1 atm pressure. The components of Eq. (10) which vary with temperature ( $T$ ) are  $\bar{V}_\pm^0, h_\pm^0, b_\pm$ , and  $\delta_\pm$ , since the hydration of an ion and its influence on the surrounding water molecules changes with temperature. At 25°C for aqueous salt solutions of inert components such as benzene, Eq. (10) becomes

$$k_S = 0.0397V_3 \left[ \left( \frac{\delta_+}{V_+^0 + 18 h_+^0} \right) + \left( \frac{\delta_-}{V_-^0 + 18 h_-^0} \right) \right] \left[ \left( \frac{Z_+^2 \gamma_+}{b_+} \right) + \left( \frac{Z_-^2 \gamma_-}{b_-} \right) \right] \quad (11)$$

### Comparison of Theoretical and Observed Values of $k_S$

To calculate theoretical values for  $k_S$ , values for  $\delta_\pm, b_\pm, h_\pm$ , and  $\bar{V}_\pm^0$  must be known. Observed values for these constants have been reported in the literature. The partial specific volume of an ion has been obtained by Padova [9, 22], Mukerjee [23], and Hepler [24]. A comparison of their results shows that  $\bar{V}_\pm^0$  does not vary significantly. Moreover, the term  $h_\pm^0 V_1$  in Eq. (10) is much larger than the value of the partial specific volume. Therefore, any small error



introduced into the value of  $\bar{V}_{\pm}^0$  will be insignificant. Padova's values [9, 22] for  $\bar{V}_{\pm}^0$  are listed in Table 1.

The extent of hydration of an ion is usually obtained by physical measurements. As pointed out by Samoilov [25], "negative" hydration can occur and therefore the average number of water molecules associated at a specific time with an ion may not be readily detectable. In aqueous salt solutions where negative hydration exists, the viscosity of the water is lower than that of pure water because (1) hydrogen bonds between some water molecules have been destroyed by the ions, and (2) the attractive forces between the ion and a hydrated water molecule for a specific distance  $\Delta r$  are less than those between two water molecules [25]. Because of the negative hydration effect, most values of the hydrated radii ( $b_{\pm}$ ) listed in the literature are too small. However, Nightengale's [26] data, which are based on the large "unhydrated" tetraethylammonium ion, are probably the most accurate and are listed in Table 1.

Using Nightengale's values for the hydrated radii ( $b_{\pm}$ ) and Pauling's value for the ionic or crystal radii ( $r_{\text{X}}$ ), one can calculate a theoretical average hydration number in the following manner. Subtract the volume of the ion from the volume of the hydrated ion to give the volume of hydrated water. It can be assumed that the volume of space occupied by the water equals its weight. That is, the error introduced because of a change in density of the water in the vicinity of an ion is neglected. If one divides this volume for 1 mole of hydrated ion by the molecular weight of water, then the hydration number  $h_{\pm}^0$  or the number of molecules of water associated with one ion at infinite dilution is obtained. Thus  $h_{\pm}^0$  can be obtained from the following equation:

$$h_{\pm}^0 = 6.023 \times 10^{23} \frac{4}{3}\pi (b_{\pm}^3 - r_{\text{X}}^{*3})/M_{\text{H}_2\text{O}} \quad (12)$$

or

$$h_{\pm}^0 = 0.1402(b_{\pm}^3 - r_{\text{X}}^3) \quad (13)$$

where  $b_{\pm}$  and  $r_{\text{X}}$  are in angstrom units and  $b_{\pm}^*$  and  $r_{\text{X}}^*$  are in centimeter units. Most values of  $h_{\pm}^0$  calculated from Eq. (13) compare favorably with the minimum hydration numbers obtained by Hasted et al. [12] (see Table 1). In calculating the value of  $h_{\pm}^0$  for the hydronium ion, the value of  $b_{\pm}$  was obtained by extrapolating Nightengale's [26] data for the  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Li}^+$  ions to  $r_{\pm} = 0$ . The calculated values of  $h_{\pm}^0$  can be fractional because, as shown by Samoilov [25] and Hertz and Zeidler [27], the hydrated water molecules are exchangeable with those of the medium.

Theoretical values for  $k_{\text{S}}$  were calculated from Eq. (11) by using  $\delta_{\pm}$  values from the data of Hasted et al. [13],  $\bar{V}_{\pm}^0$  values from Padova [9, 22],  $b_{\pm}$  values from Nightengale [26], and  $h_{\pm}^0$  values from either Eq. (13) or from Hasted et al. [13]. A comparison of the theoretical

Table 1. Radii, Hydration Numbers, Dielectric Decrements, and Partial Specific Volumes of Various Ions<sup>a</sup>

Ion	$r_x$ (Pauling)	$b_{\pm}$ (Nightingale)	$h_{\pm}^0$ (Hasted)	$h_{\pm}^0$ (calc.)	$\delta_{\pm}$ (Hasted)	$\delta_{\pm}$ (theoret.)	$\bar{V}_{\pm}^0$ (Padova)	$\frac{\delta_{\pm} \times 10^2}{(V_{\pm}^0 + h_{\pm}^0 V_1)}$	$V_{\pm}$ , ml
H <sup>+</sup>	—	4.23	10	10.6	17	-1.2	-0.40	-0.6	191
Li <sup>+</sup>	0.60	3.82	6	7.8	11	5.5	-1.60	3.9	141
Na <sup>+</sup>	0.95	3.58	4	6.3	8	7.0	-2.20	6.3	116
K <sup>+</sup>	1.33	3.31	4	4.8	8	4.4	8.20	4.6	92
Rb <sup>+</sup>	1.48	3.29	4	4.5	7	3.2	13.37	3.4	90
Cs <sup>+</sup>	1.69	3.29	—	4.3	—	0.9	20.55	1.0	90
NH <sub>4</sub> <sup>+</sup>	1.48	3.31	—	4.6	—	1.7	17.40	1.7	92
Ba <sup>2+</sup>	1.35	4.04	14	8.9	22	4.1	-13.60	4.1	166
F <sup>-</sup>	1.36	3.52	—	5.8	5	6.1	-1.60	5.9	110
Cl <sup>-</sup>	1.81	3.32	—	4.3	3	2.2	18.60	2.3	92
Br <sup>-</sup>	1.95	3.30	—	4.0	—	0.3	25.68	3.1	91
I <sup>-</sup>	2.16	3.31	—	3.7	7	-2.7	37.10	-2.6	92
OH <sup>-</sup>	1.76	3.00	—	3.0	13	2.7	-5.30	4.6	68
SO <sub>4</sub> <sup>2-</sup>	2.90	3.79	—	4.2	7	2.2	15.87	2.4	137

<sup>a</sup> Values of  $h_{\pm}^0$  (Hasted) and  $\delta_{\pm}$  (Hasted) were obtained from the data of Hasted et al. [13]. Values of  $\delta_{\pm}$  (theoret.) and  $\delta_{\pm}/(V_{\pm}^0 + h_{\pm}^0 V_1)$  were obtained from  $k_S$  values of the sodium or chloride salt and assuming  $\delta_{+} = 8.0$  for Na<sup>+</sup> and  $\delta_{-} = 3.0$  for Cl<sup>-</sup>, and using  $h_{\pm}^0$  (calc.). The value of  $b_{+}$  for the hydronium ion was obtained by extrapolating the K<sup>+</sup>, Na<sup>+</sup>, and Li<sup>+</sup> data in Fig. 2 of Nightengale [26] to  $r_x = 0$ .  $V_{\pm}$  represents the volume in milliliters that 1 mole of a hydrated ion will occupy ( $V_{\pm} = N(4/3)\pi b_{\pm}^3 = 2.523 b_{\pm}^3$ , where  $b_{\pm}$  is in angstrom units).

values with some observed values of McDevit and Long [7] and Saylor et al. [28] is made in Table 2. The theoretical value  $k_S$  (Nightengale) obtained for sodium fluoride solutions is in excellent agreement with the corresponding experimental values [0.241 compared to 0.254 (Saylor)]. The  $k_S$  values obtained by employing Eq. (13) for  $h_{\pm}^0$  give much better agreement than those based on the minimum hydration values of Hasted et al. [13]. This agreement suggests that the  $h_{\pm}^0$  values obtained from Eq. (13) are more nearly correct. While the theoretical values of  $k_S$  for both NaF and NaCl are within reasonable agreement with the observed values, the theoretical values of HCl, LiCl, KCl, and RbCl are much too large. For example, the  $k_S$  (Nightengale) value of 0.185 for HCl is about five times greater than the observed values of  $k_S = 0.048$  and 0.041. These discrepancies suggest that for salts other than NaF or NaCl, the values for the constants  $\delta_{\pm}$ ,  $h_{\pm}^0$ , or  $b_{\pm}$  listed in Table 1 are not correct.

### Elimination of $h_{\pm}^0$ and $b_{\pm}$ as Variables

Theoretical values of  $b_{\pm}$  or  $h_{\pm}^0$  for ions other than  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{F}^-$  can be obtained from Eq. (11) by using  $\text{Na}^+$  and  $\text{Cl}^-$  ions as standards and by taking observed values of  $k_S$  (McDevit and Long [7]),  $\delta_{\pm}$  (Hasted et al. [13]),  $\bar{V}_{\pm}^0$  (Padova [9, 22]), and calculated values of  $h_{\pm}^0$  from Eq. (13). The fluoride ion cannot be used as a standard because  $k_S$  values for fluoride salts other than NaF are not given in the literature. Figure 1 gives a plot of these hydrated radii versus their respective crystal radii. For the iodide and hydronium ions, the hydrated radii are infinitely large. For the hydroxide ion it is approximately 14 Å, and for the lithium, potassium, rubidium, and bromide ions the hydrated radii are approximately 6-8 Å. Because these values are too large, it can be concluded that the discrepancies between the observed and calculated values of  $k_S$  are not due to experimental errors in the hydrated radii.

Similarly, theoretical values for  $h_{\pm}^0$  were calculated from values of  $k_S$ ,  $\delta_{\pm}$ , and  $b_{\pm}$  (Nightengale [26]) as given in Tables 1 and 2. The respective calculated values were -219, 27, 12, and 31 for  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$ . These large negative and positive values of  $h_{\pm}^0$  show that the discrepancies between observed and calculated values for  $k_S$  are not due to variations in the hydration numbers.

Further proof can be seen in Table 1 by examining the values of  $\delta_{\pm}/(\bar{V}_{\pm}^0 + h_{\pm}^0 V_1)$ , which were calculated from observed  $k_S$  values of the standards  $\text{Na}^+$  and  $\text{Cl}^-$ . Values of  $\delta_{\pm}/(\bar{V}_{\pm}^0 + h_{\pm}^0 V_1)$  for the ions  $\text{H}^+$  and  $\text{I}^-$  are negative. If  $\delta_{\pm}$  is always positive, as implied by Hasted et al. [13], then the hydration number  $h_{\pm}^0$  for these ions must be negative. Such values are unreal, and hence some  $\delta_{\pm}$  values must be negative. Substitution of Eq. (12) into Eq. (10) and calculation of  $h_{\pm}$  or  $b_{\pm}$  from observed values of  $k_S$  and  $\delta_{\pm}$  also give unreal positive and negative values for either  $h_{\pm}$  or  $b_{\pm}$ . Consequently, it can be concluded

Table 2. Observed<sup>a</sup> and Theoretical<sup>b</sup> Values of  $k_s = \log f_3/C_2$  for Benzene in Aqueous Salt Solutions

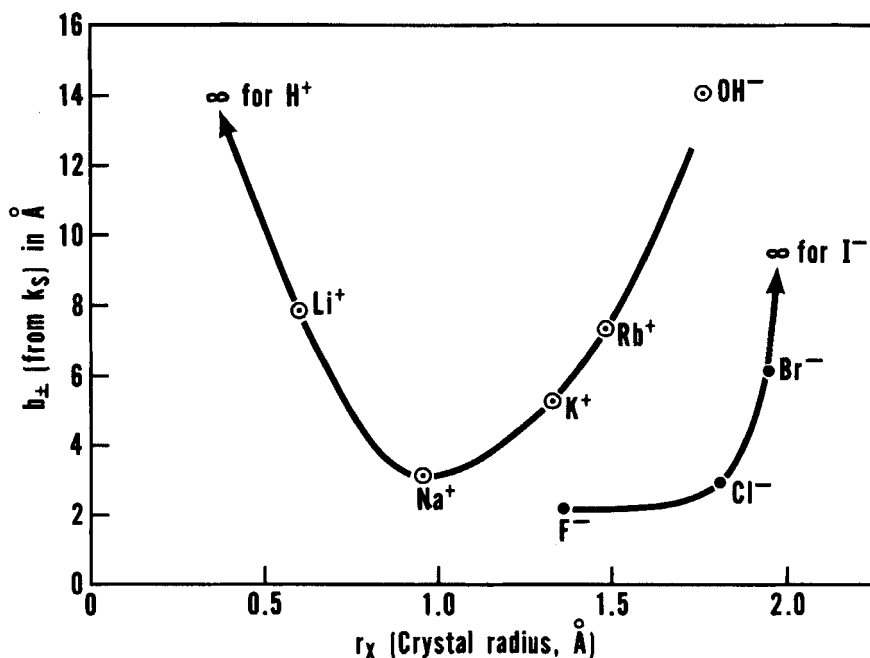
Salt	Observed			Theoretical			
	$k_s$ (McDevit)	$k_s$ (Saylor)	$k_s$ (av.)	$k_s$ (Hasted)	$(\Delta k_s)c$	$k_s$ (Nightengale)	$(\Delta k_s)c$
HCl	0.048	0.041	0.045	0.240	(0.195)	0.230	(0.185)
LiCl	0.141	0.136	0.139	0.269	(0.130)	0.221	(0.082)
NaCl	0.195	0.178	0.187	0.300	(0.113)	0.212	(0.025)
NaF	0.262 <sup>d</sup>	0.254	0.258	0.326	(0.068)	0.241	(-0.017)
KCl	0.166	0.163	0.165	0.281	(0.116)	0.248	(0.083)
RbCl	0.140	—	0.140	0.243	(0.103)	0.227	(0.087)

<sup>a</sup>Observed values for  $k_s$  were obtained from Table I of McDevit and Long [7] and from Table I of Saylor et al. [28] after converting from molality to molarity.

<sup>b</sup>Values of  $k_s$  (Nightengale) and  $k_s$  (Hasted) were calculated using  $\delta_{\pm}$  values from Hasted et al. [13],  $\bar{V}_X^0$  values from Padova [9, 22],  $b_{\pm}$  values from Nightengale [26], and  $h_{\pm}^0$  values from either Hasted et al. [13] or from Eq. (13) using Nightengale's  $b_{\pm}$  and Pauling's  $r_X$  values.

<sup>c</sup> $\Delta k_s = k_x$  (calc.) -  $k_s$  (obs.) using the average value for  $k_s$  (obs.).

<sup>d</sup>Estimated by comparing the  $k_s$  values of McDevit and Long (at 25°C) [7] with those of Saylor et al. (at 30°C) [28].



**Fig. 1.** Calculated hydrated radius plotted versus the crystal radius for different ions. The hydrated radius was obtained from Eq. (10) using the  $k_s$  values of Long and McDevit [4, 7] concerning the solubility of benzene in aqueous salt solutions. Values for the constants used in Eq. (10) for determining  $b_{\pm}$  are listed in Table 1.

that the discrepancies between the theoretical and calculated values of  $k_s$  must be due to differences between the macroscopic and effective dielectric decrement of ions other than  $Na^+$ ,  $F^-$ , and possibly  $Cl^-$ .

#### Calculation of the Dielectric Decrement

Values for  $\delta_{\pm}$  were calculated using Eqs. (11) and (13) and using the values of  $b_{\pm}$ ,  $\bar{V}_{\pm}^0$ , and  $h_{\pm}^0$  (calc.) listed in Table 1. The results are given in Table 1 and Fig. 2. In the calculations it was assumed that the values of  $\delta_{\pm}$  given by Hasted et al. [13] for the ions  $Na^+$ ,  $F^-$ , and  $Cl^-$  were correct. The value of  $\delta_+ = 8.0$  was inserted into Eq. (11) to calculate the corresponding  $\delta_-$  from values of  $k_s$  for the sodium salts as given by McDevit and Long [7]. Likewise, the value of  $\delta_- = 3.0$  was used to calculate the corresponding values of  $\delta_+$  for all chloride salts using the  $k_s$  values of McDevit and Long. The slight differences between  $\delta_+$  (Hasted) = 8.0 and  $\delta_+$  (calc.) = 7.0 and be-

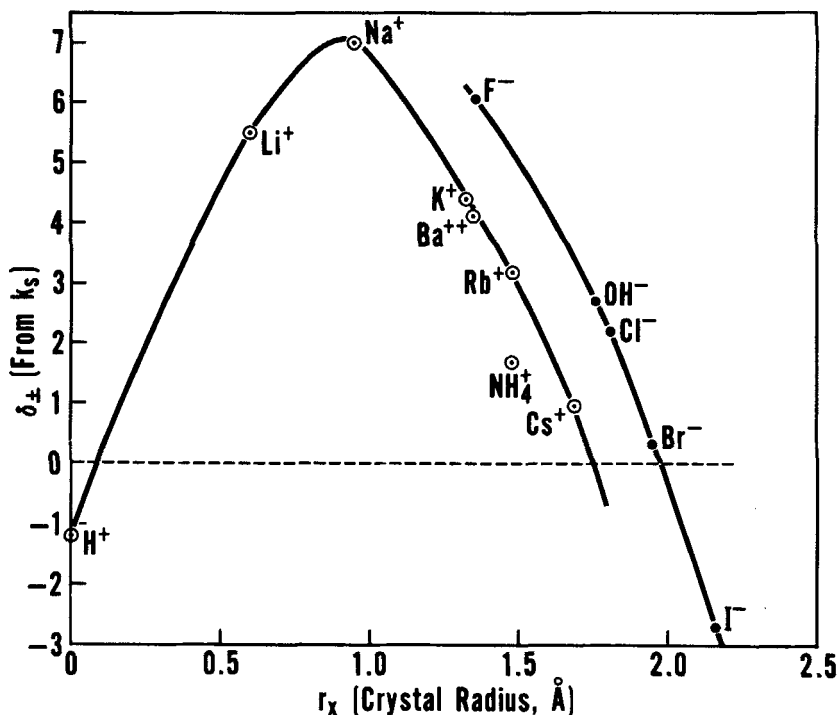


Fig. 2. Dielectric decrement for various ions is plotted versus the corresponding crystal radii. Results were obtained using Eq. (11) and the data listed in Table 1.

tween  $\delta_-$  (Hasted) = 3.0 and  $\delta_-$  (calc.) = 2.2 for the  $Na^+$  and  $Cl^-$  ions are due to the slight discrepancies between the theoretical value of  $k_s$  (Nightengale) = 0.212 and the observed value of  $k_s$  (McDevit) = 0.195 as shown in Table 2.

### Structural Models for the Hydrated Ions

To understand why the theoretical values of  $\delta_{\pm}$  for the  $Na^+$ ,  $F^-$ , and  $Cl^-$  ions agree with their corresponding observed macroscopic values, the properties and structure of these and the other hydrated ions must be examined. Several studies [15, 17, 29, 30] suggest that both the sodium and fluoride ions have single hydration shells and that these hydrated ions do not appreciably influence the water molecules surrounding them. In other words, they behave similarly to inert molecules. The structural entropy values obtained by Frank

and Evans [30] suggest that the sodium ion has a tightly bound layer of water molecules surrounding it, as does the lithium ion. These tightly bound water molecules have been termed "positive hydration" by Samoilov [25]. Kaminsky [29] has shown that viscosity B-coefficient for the positively hydrated sodium ion is independent of temperature. In regard to this observation, Kaminsky [29] and others referred to by him state that the first hydration shell (the positively hydrated water) for strongly hydrated ions such as  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Li}^+$ , and  $\text{Ce}^{3+}$  is essentially temperature-independent. Kaminsky's data [29] thus suggest that the hydrated sodium ion possesses only one hydration shell, and that this hydration shell has little influence on the surrounding water molecules. Furthermore, this hydration shell is tightly bound (positive hydration). In terms of the nomenclature of Frank and Wen [15], the sodium ion must possess only the A region, which consists of one monomolecular layer of water molecules.

For lithium ions, Hindman [31, p. 61] found evidence for the presence of a complete first hydration shell and an additional outer hydration shell. Other evidence, such as that of Kaminsky [29], supports the conclusion that two hydration shells exist on the lithium ion. Thus the lithium ion possesses a monomolecular A region (first hydration shell) and a monomolecular B region (second hydration shell). Examination of the literature [29, 32] also suggests that such a structure of two hydration shells exists not only for the  $\text{Li}^+$  ion but also for the  $\text{H}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  ions. The results of Samoilov [25], Kaminsky [29], and Frank and Wen [15] show that the  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and other monovalent cations having a charge density equal to or less than that of the  $\text{K}^+$  ion have only one monovalent hydration shell which is negatively hydrated (possesses the B region only). Thus the hydrated  $\text{Na}^+$  is the only cation which does not possess negatively hydrated water, i.e., a B region.

Examination of the properties [7, 17, 20, 25, 29, 33] of the anions  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$  show that these anions possess only negatively hydrated water, i.e., only B regions. Hence it can be concluded that those hydrated anions having a surface charge density equal to or less than that of the  $\text{Cl}^-$  ion possess only a monomolecular layer of negatively hydrated water molecules, just as in the case of the cations  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ .

Hindman [31] observed that for the halide ions, only the fluoride ion forms a hydrate in the "chemical sense" [17]. In other words, while the  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions possess only negatively hydrated water, the  $\text{F}^-$  ion possesses positively hydrated water. The salting-out properties [6, 33] and the structural entropy values [30] ( $\Delta S^{\text{st}}$ ) for the fluoride and phosphate ions, and possibly hydroxide ions, also show that these ions possess positively hydrated water molecules in aqueous solutions.

Yet the crystal radius of the fluoride ion (and hence the electrostatic charge on its surface) is approximately equal to the potassium

ion (Table 1). But the potassium ion forms negatively hydrated water and the fluoride ion forms positively hydrated water. This difference is due to the position in which the water molecule hydrates to the anion or cation. In other words, the center of the hydrogen atoms of the water molecules can get closer to the anion than the center of the oxygen atom to its cation. When the electrostatic charges of the water molecule and ion are closer, it will take more energy to separate them, and hence their association will last for a longer time.

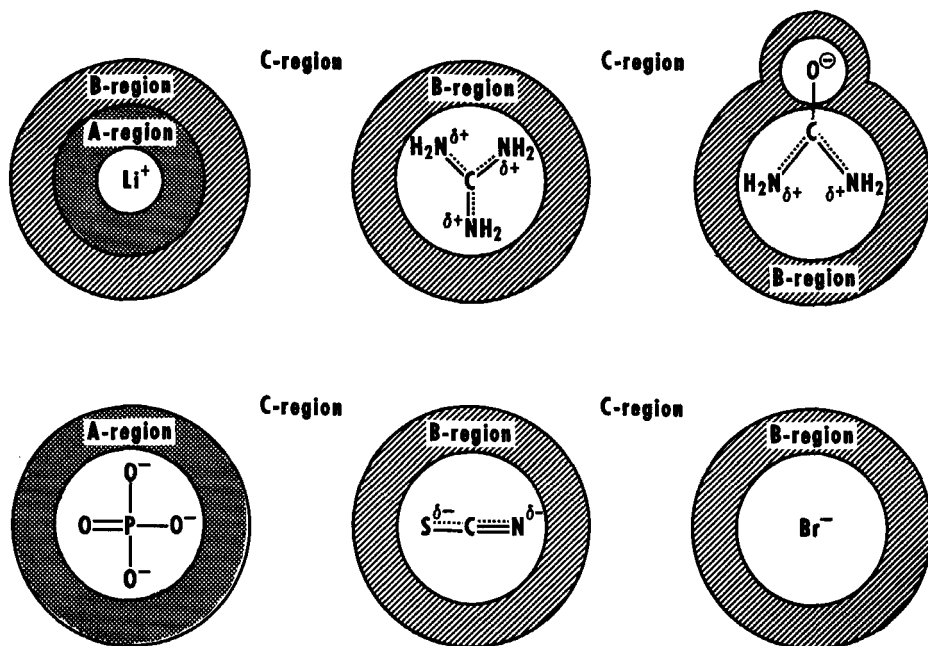
The existence of this stronger interaction between an anion and a water molecule is proved by the observed length of time for reorientation of water molecules in various hydrated shells. According to Hertz and Zeidler [27], the reorientation time of water on the fluoride ion is  $6 \times 10^{-11}$  sec, which is even longer than that on the lithium ion ( $4 \times 10^{-11}$  sec) or sodium ion ( $3 \times 10^{-11}$  sec). (The orientation time on the lithium ion is, of course, an average of the two hydration shells.) In contrast, those water molecules hydrated to the chloride and potassium ions have the same reorientation time,  $1 \times 10^{-11}$  sec, which is shorter than that of the  $F^-$  ion. Both the  $K^+$  and  $Cl^-$  ions are negatively hydrated [25] and both have the same viscosity B-coefficient [29]. Hence the extent of hydration of the  $Cl^-$  ion and not that of the  $F^-$  ion is the same as that of the  $K^+$  ion, despite the differences in the crystal radii of  $K^+$  and  $Cl^-$ . Thus the above observations show the  $F^-$  is positively hydrated because of its stronger interaction with water molecules. Further verification is illustrated by the greater enthalpy of hydration for anions than for cations [9, 34]. The observed and theoretical values for the dielectric decrement (Table 1 and Fig. 2) for the fluoride ion also show that the  $F^-$  ion, just as in the case of the  $Na^+$  ion, does not have a second hydration shell or B region. Hence in aqueous solutions the anions  $F^-$ ,  $PO_4^{3-}$ , and possibly  $OH^-$  have a monomolecular, positively hydrated shell but possess no further hydration, whereas the anions which have a charge density equal to or less than that of the  $Cl^-$  ion (such as  $Br^-$ ,  $I^-$ , and  $SCN^-$ ), have a single hydrated (B region).

The above model can also be applied to polar groups where a separation of electrostatic charge occurs. In polar groups it is unlikely that the density of the electrostatic charge on the surface of the atoms will be greater than that of the  $Na^+$  or  $F^-$  ions. Generally speaking, it can thus be concluded that all polar groups produce a single hydration shell which is negatively hydrated (B region). Some polar groups such as the oxygen atom on DMSO may have A regions. Examples of the proposed models are depicted in Fig. 3.

#### Explanation for Discrepancies between Theoretical and Observed Values of $\delta_{\pm}$

The work of several investigators [15, 25, 27] has shown that the negative hydration shell is not static but rather is dynamic. Hydrated





**Fig. 3.** Proposed hydration models for various ions. The different structural water associated with ions is given by Frank and Wen's [15] terminology. The A region represents highly polarized water which is positively hydrated to the ion. The B region represents negatively hydrated water. For each of the ions  $H^+$ ,  $Li^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Ra^{2+}$ , and other multivalent cations having similar charge densities, there exists a monomolecular A region as well as a monomolecular B region. For each of the ions  $Na^+$ ,  $F^-$ ,  $PO_4^{3-}$ , and possibly  $OH^-$ , there exists a monomolecular A region but no B region in the proposed model. Ions such as  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $SCN^-$ , and guanidinium, in addition to dipolar molecules such as urea and hydrocyanic acid, have monomolecular B regions but no A regions (see the text).

ted water molecules are continually being exchanged with the surrounding aqueous medium. In positive hydration, the interaction between the ion and the water molecules is great enough to reduce such an exchange. This reduction is so great for the hydrated  $Na^+$  and  $F^-$  ions that these ions behave as inert molecules to the surrounding structural water. It will be shown that these factors can explain the discrepancies between the observed and theoretical values of  $\delta_{\pm}$ .

The reduction in the macroscopic dielectric constant of pure water in going from 0 to 100°C is due to a destruction of water clusters or icebergs of water and their aggregates [20]. When a salt is added to water, there is also a reduction in the dielectric constant of the medium. Two factors can contribute to such a reduction in the macroscopic value of  $D$  for water:

1. If one adds an inert molecule such as benzene to water, the macroscopic value of  $D$  will be reduced because of a volume displacement. In other words, Butler's [21] correction, as discussed above, would apply. The same effect would be true for the addition of an ion that has a value of  $D$  slightly above zero. The resulting reduction in  $D$  would be purely a volume displacement. As shown above, an aqueous solution of NaF consists of two hydrated ions which do not influence the structure of water. Hence, from the observed values of  $\delta_{\pm}$  the addition of hydrated NaF to water reduces the experimental macroscopic value of  $D$  in the same manner as the addition of benzene.

2. If a hydrated ion contains a B region, the water molecules in this region will be exchanged with the surrounding medium. Such an exchange will cause the destruction of neighboring water clusters, since, as pointed out in the review by Kavanau [17], when water molecules are broken away from a cluster, the entire cluster will collapse. Consequently, an ion with a B region can reduce the macroscopic dielectric constant in the same manner as an increase in temperature, i.e., by destruction of water clusters.

Examination of Table 1 shows that for all ions with B regions or negatively hydrated water, the observed value of  $\delta_{\pm}$  is always greater than the theoretical value. This discrepancy becomes greater as the charge per unit surface area ( $C/A$ ) on the ion is reduced. A reduction in this charge density increases the rate at which water molecules are exchanged between the ion and the medium. The faster the rate of exchange, the greater will be the destruction of water clusters. Hence, as the charge per unit surface area of an ion is reduced, the greater will be the lowering of the macroscopic dielectric constant, as shown above in point 2. The increase in the ability of an ion to destroy a water cluster with respect to a decrease in charge per unit surface area will, however, reach a maximum, since zero charge has no effect. This maximum in the effective value of  $D$  will be discussed below.

The reason for the discrepancies between the observed and theoretical values of  $\delta_{\pm}$  is now apparent. The macroscopic value of the dielectric constant considers the dielectric constant of the water clusters, the unassociated water, and the added hydrated ions. But hydrated ions other than those similar to  $\text{Na}^+$  or  $\text{F}^-$  are capable of destroying nearby water clusters. Hence the greater values of  $\delta_{\pm}$  observed experimentally for ions with B regions is due to the reduction in the macroscopic value of  $D$  for pure water; i.e., it is due

to a reduction in the number of water clusters in the water. Even though an ion may have an effective dielectric constant greater than that of water, its observed value of  $\delta_{\pm}$  may be positive instead of negative, because of its ability to destroy the water clusters or icebergs. The macroscopic value of  $\delta_{+}$  should agree with that obtained from Eq. (11) when the water clusters do not exist, i.e., at the boiling point of water.

### Effective Dielectric Constant of a Hydrated Ion

As shown by Kaminsky [29] and others [15, 17, 30], sodium and fluoride ions do not significantly influence the structure of water (the formation or destruction of water clusters) past their first hydration shell. Moreover, the agreement between theoretical and experimental values of  $\delta_{\pm}$  also shows that the electrostatic fields of these hydrated ions do not influence those water molecules past their monomolecular hydration shell. Since the diameter of a water molecule is 2.76 Å and the radius of the sodium ion is 0.95 Å, the distance from the center of the  $\text{Na}^{+}$  ion to the edge of the outer shell is approximately 3.7 Å. Hence, when the charge per unit surface area of an electrostatic field becomes equal to or less than that obtained at an approximate distance of 3.7 Å from the center of a monovalent cation, then this electrostatic field becomes equivalent in character to that obtained from a relatively inert compound such as a hydrocarbon. It follows that the value of the electrostatic field past the B region of any hydrated ion is equal to or less than this value. Hence a hydrated ion has no influence on the surrounding water molecules past its negatively hydrated shell.

For the  $\text{Li}^{+}$  and  $\text{H}^{+}$  ions, the charge per unit surface area at the surface of the first hydration shell is greater than that for the  $\text{Na}^{+}$  ion. Consequently, for these ions there will be two hydration shells. Based on the calculations for the hydrated  $\text{Na}^{+}$  ion, an ion must have an extremely large electrostatic charge in order to have three hydration shells. For example, if the ion has a crystal radius of about 0.5 Å, it must have an electrostatic charge of +12 or more in order to have three hydration shells. Hence all ions must have at most one monomolecular A region and only one monomolecular B region. Consequently, the A region or B region can never be greater than the diameter of one water molecule (2.76 Å), and the effective dielectric decrement of an ion or dipolar molecule must be a measurement of the water molecules within its monomolecular B region. In other words, the effective value of D cannot be in the monomolecular A region because benzene or other molecules cannot penetrate this region. Moreover, it cannot be outside the B region, because the electrostatic field of the ion is too weak outside the B region.

Further information can be obtained by determining the apparent dielectric constant of an ion. Such a calculation can be done by

obtaining the molar concentration of an ion necessary to make 1 liter of hydrated ion. In such a hypothetical solution there would exist no "free" water, and hence the calculated dielectric constant would represent that value at the surface of the hydrated ion. This calculation involves extrapolation from dilute to very concentrated salt solutions. However, as shown in another paper [33], the Setschenow constant,  $k_s$ , is within experimental error the same at these high concentrations for all salts or compounds tested: NaCl, LiBr, urea, and guanidinium chloride. The results therefore show that such an extrapolation is valid. The apparent nonlinearity in  $D$  versus salt concentration for NaCl solutions greater than 2 M, as observed by Hasted et al. [13], is due to a difference in values of the macroscopic and microscopic dielectric constant. As noted above, the macroscopic value of  $D$  is effected by a change in the number of water clusters as well as by the addition of hydrated ions having dielectric constants different from that of the water. Hence the results of Hasted et al. [13] are not applicable to the effective (microscopic) dielectric constant.

From Eq. (4) we can write the theoretical expressions  $D_+ = D_1 - \delta_+ C_+$  and  $D_- = D_1 - \delta_- C_-$ . The value of  $C_{\pm}$  is equal to the volume of 1 mole of hydrated ion divided into 1 liter, or  $1000/V_{\pm}$ , where  $V_{\pm}$  is obtained from Table 1. Substitution of  $C_{\pm} = 1000/V_{\pm}$ ,  $D_1 = 55.3$ , and values of  $\delta_{\pm}$  obtained from Eq. (11) (Table 1) into these expressions for  $D_{\pm}$  yields the results given in Fig. 4.

The physical measurements described above show that the hydrated  $\text{Na}^+$  and  $\text{F}^-$  ions do not significantly influence the structure of the surrounding water molecules outside their A region. In this respect they behave as inert compounds such as hydrocarbons. Their dielectric constants should be similarly low. As shown in Fig. 4, the value of  $D_{\pm}$  for  $\text{Na}^+$  ions is  $D_+ = -5$ , while that for  $\text{F}^-$  ions is  $D_- = 0$ . In other words, since  $D_{\pm}$  can never be zero or negative, the values of  $D_{\pm}$  for the  $\text{Na}^+$  and  $\text{F}^-$  are near zero. Considering the possible experimental errors, these values are in good agreement with my conclusions.

It follows from the above discussion and the results that the effective dielectric constant is a measurement of not only the water-water interactions but also the ion-water interactions involved in the B regions. The effective dielectric constant of the B region will be large if the charge on the ion's surface is great enough to considerably reduce water-water interactions and yet not large enough to drastically restrict the movement of the water dipole. Under such circumstances the hydrated water molecule can readily form a loose structure which can enable a greater solubilization of relatively inert molecules such as benzene and which can also destroy clusters of water molecules. In other words, Samoilov [25] has shown that the displacement distance  $\Delta r$  for the movement of the water dipole

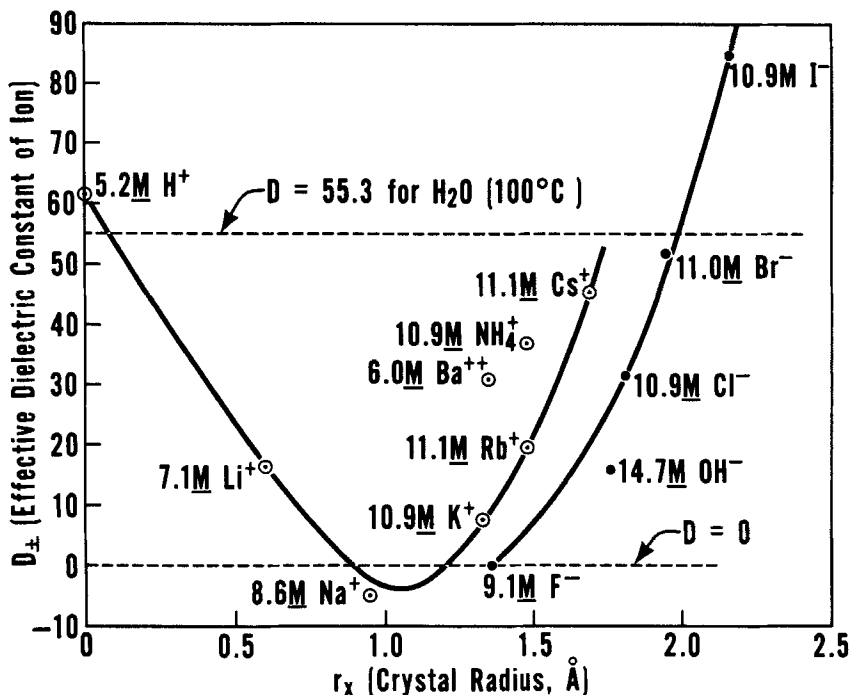


Fig. 4. Effective dielectric constant  $D_{\pm}$  versus the crystal radius  $r_x$ . Values of  $D_{\pm}$  were calculated from the relationship  $D_{+} = D_1 - \delta_{+} C_{+}$  or  $D_{-} = D_1 - \delta_{-} C_{-}$ . The molar concentration  $C_{\pm}$  of a specific ion was obtained by letting the volume of the hydrated ion equal 1 liter (see the text).

away from the ion is greater than that involved in dipole-dipole interactions of water. This  $\Delta r$  increases with a decrease in charge per unit surface area. Consequently, this increase enables the B region to have a looser structure, as shown by Samoilov [25], but also it must increase the ability of the B region to exchange water molecules with the surrounding medium. This exchange would destroy water clusters. Both factors would increase the solubility of benzene by producing a less rigid water structure and thus enable benzene to increase its concentration. The effective dielectric constant is therefore a function of the ion-dipole interactions of the B region and the B region's ability to destroy water clusters.

#### Maximum Effective Dielectric Constant

To determine where the maximum in the value of  $D_{\pm}$  occurs, a

plot of  $D_{\pm}$  versus the electrostatic charge per unit surface area was made (Fig. 5). The radii for those ions that have positive hydration ( $H^+$ ,  $Li^+$ ,  $Na^+$ , and  $F^-$  in Fig. 5) were obtained by adding the diameter of a water molecule to the crystal radii ( $r = r_x + 2.76 \text{ \AA}$ ). Figure 5

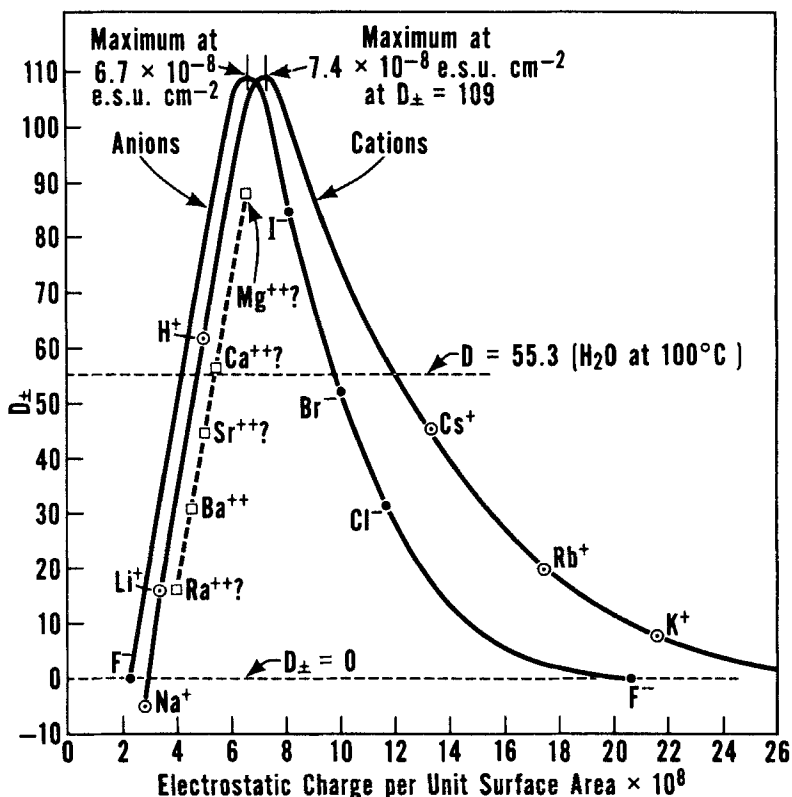


Fig. 5. Effective dielectric constant of an anion or cation versus the electrostatic charge per unit surface area in esu per square angstrom. The latter quantity was calculated from the formula  $(e/4\pi r^2)$ , where  $e = 4.803 \times 10^{-10}$  esu and  $r = r_x$  (the crystal radius) for ions having only a single hydrated shell or  $r = r_x + 2.76$  for ions having positive hydration (an A region). The  $Na^+$  and  $F^-$  ions fall into both categories of ions. The maximum in  $D_{\pm}$ , i.e., the entire curve in the figure, occurs in a single hydrated shell (B region). The question mark after  $Ra^{2+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  indicates that the value of  $D_{\pm}$  was not obtained for these ions, since their experimental values of  $k_s$  are not given in the literature.

shows that a maximum value in  $D_{\pm}$  is obtained for cations at a charge density of  $7.4 \times 10^{-8}$  esu/cm<sup>2</sup> and for anions at a value of  $6.7 \times 10^{-8}$  esu/cm<sup>2</sup>. It can be shown [33] that the guanidinium ion has an effective radius of about 2.3 Å (or a charge density of  $7.2 \times 10^{-8}$  esu/cm<sup>2</sup>). Hence its value of  $D$  is approximately at the maximum shown in Fig. 5 ( $D \equiv 109$ ). The anions produce a maximum at a greater radius than the cations, because for the same radii they have a greater attraction for the water molecules. The two curves shown in Fig. 5 represent the B regions of all ions.

Studies with the tetraethyl or tetramethyl ammonium ion appear to contradict the results given in Fig. 5. According to Saylor et al. [28], and Deno and Spink [7], the value of  $k_s$  for  $(\text{CH}_3)_4\text{NBr}$  or  $(\text{C}_2\text{H}_5)_4\text{NBr}$  is negative. The value of  $D$  for the tetramethyl or tetraethyl ammonium ion must therefore be greater than that of water, since  $D_-$  for the  $\text{Br}^-$  ion is approximately equal to that of the surrounding water (Fig. 4). But according to Fig. 5, the values of  $D_+$  for  $(\text{C}_2\text{H}_5)_4\text{N}^+$  and  $(\text{CH}_3)_4\text{N}^+$  should be approximately zero, as for  $\text{Na}^+$  and  $\text{F}^-$  ions, since the values of  $r_x$  are 3.47 Å for  $(\text{CH}_2)_3\text{N}^+$  and 4.00 Å for  $(\text{C}_2\text{H}_5)_4\text{N}^+$  [14, 26]. However, these ions most likely act as detergents in solubilizing the benzene. Consequently, the solubility of benzene cannot be used in such cases to determine the effective dielectric decrement. Hence there is no contradiction to the conclusions concerning a maximum value for  $D_+$  at an effective spherical radius of 2.2 Å.

The point for  $\text{Ba}^{2+}$  in Fig. 5 does not fall on the curve obtained for the monovalent cations. This discrepancy may be due to differences in orientation of water molecules in the first hydration shell and hence to differences in the electrostatic charge per unit surface area of the A region as calculated from  $r = r_x + 2.76$ . Assuming that the same discrepancy occurs for other divalent ions, their approximate values of  $D_+$  can be obtained from Fig. 5, since  $r_x$  is known. For  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Ra}^{2+}$  the respective approximate values of the effective dielectric constants are 88, 56, 44, 31, and 16. In contrast with the monovalent cations, these divalent cations all have monomolecular A and B regions. The  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions should salt-in hydrocarbons, whereas,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Ra}^{2+}$  should salt-out hydrocarbons according to their respective values of  $D_+$ .

### Association of the Thickness of the Hydration Shell with $D$

The difference between the hydrated radius and the crystal radius ( $b_{\pm} - r_x$ ) can be compared with the diameter of a water molecule (2.76 Å). For the  $\text{Na}^+$  ion the thickness of its single hydration shell should be close to that of the water molecule because physical measurements [17] show that if the charge per unit surface area is increased as in the  $\text{Li}^+$  ion, two hydration shells are formed. Examination of Table 1 shows that the thickness of the hydration shell for

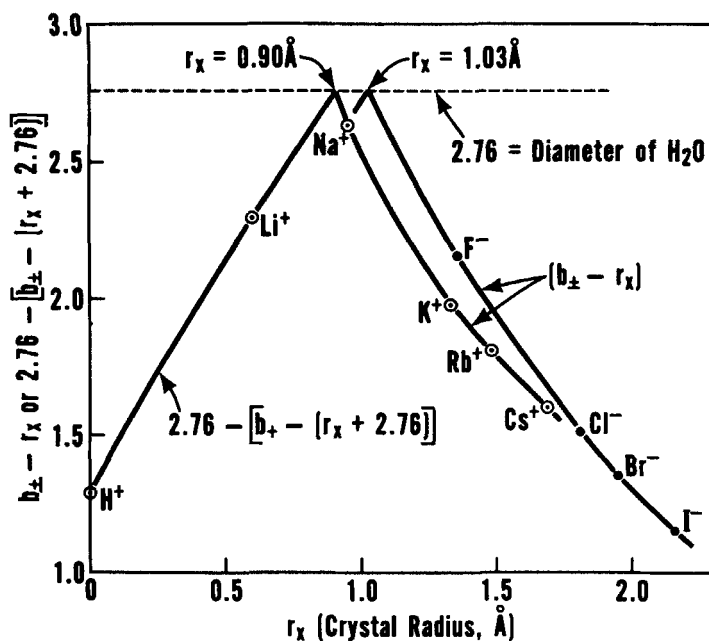
the  $\text{Na}^+$  ion is  $(b_+ - r_x) = 2.63 \text{ \AA}$ , which is very close to the diameter of a water molecule ( $2.76 \text{ \AA}$ ). In addition, the thickness of the two hydration shells for the smaller  $\text{Li}^+$  or  $\text{H}^+$  ion is greater than the diameter of a water molecule ( $b_+ - r_x = 2.76 + 0.46 \text{ \AA}$  for the  $\text{Li}^+$ ). These results support the hydration radii reported by Nightengale [26].

The corresponding differences  $(b_{\pm} - r_x)$  for the other ions should be associated with their effective dielectric constant or decrement. The maximum in  $D_{\pm}$  given in Fig. 5 can be correlated with the thickness of the B region of the hydrated ion. On the right side of the maximum value of  $D_{\pm}$  shown in Fig. 5, the decrease in  $D_{\pm}$  is due to an increase in the electrostatic charge per unit surface area, while on the left side, the decrease in  $D_{\pm}$  is due to a decrease in the charge per unit surface area of the ion. The thickness of the B region increases with an increase in charge density. Therefore, for the ions  $\text{H}^+$  and  $\text{Li}^+$ , the effective value of the dielectric constant should increase with an increase in the thickness of the B region ( $b_+ - [r_x + 2.76]$ ). In contrast with this, for ions having a surface charge density, slightly less than that of the  $\text{Na}^+$  or  $\text{F}^-$  ion, the effective value of the dielectric constant should increase with a decrease in the thickness of the B region ( $b_{\pm} - r_x$ ). The maximum thickness of a single hydration shell surrounding any ion is approximately  $2.76 \text{ \AA}$ , the diameter of a water molecule. As the difference between this value and the thickness of the B shell for ions such as  $\text{Li}^+$  or  $\text{H}^+$  approaches zero, the value of  $D_{\pm}$  will increase as shown in Fig. 5. That is, when  $2.76 - (b_+ - [r_x + 2.76]) = 0$ , then  $D_{\pm} \equiv 0$ . For ions having only a single hydration shell, when  $b_{\pm} - r_x = 0$ , then  $D_{\pm} \equiv 0$ . Hence, to have both ions on a comparative basis, one must plot  $b_{\pm} - r_x$  versus  $r_x$  for those ions having only one shell and  $2.76 - (b_{\pm} - [r_x + 2.76])$  versus  $r_x$  for those ions having two shells. Such a plot is given in Fig. 6. It is seen that these functions of the observed radii of hydration give a plot similar to that for the dielectric decrement or constant (Figs. 2 and 4). From Fig. 6 it can be deduced that when the charge density of an anion becomes equivalent to that of a spherical anion having a radius less than  $r_x = 1.03 \text{ \AA}$ , the anion will have two hydration shells.

## CONCLUSIONS

This study shows that the effective dielectric constant of a hydrated ion at  $25^\circ\text{C}$  can have values ranging from near zero to much greater than that of unbonded water. This result is in direct contrast with that obtained from theoretical equations for the unhydrated ion. The small and large values of  $D_{\pm}$  are thus associated with how the ion interacts with the surrounding water molecules. Thus in the case of the hydrated  $\text{Na}^+$  ion, where there is no B region, the value





**Fig. 6.** Thickness of the hydrated shell ( $b_{\pm} - r_x$ ) for ions having only one shell or the difference between the maximum thickness minus the actual thickness [ $2.76 - (b_{\pm} - [r_x + 2.76])$ ] for ions having two shells is plotted versus the corresponding crystal radius for specific ions.

of  $D_+$  is near zero and consequently behaves as an inert molecule such as benzene. In other words, the hydrated  $\text{Na}^+$  ion can still attract anions by long-range electrostatic forces. However, just as in the case of inert molecules, its electrostatic force past the impenetrable, strongly positioned A region is not great enough to influence the structure of water and thus cannot form a hydrated B region. Consequently, the hydrated  $\text{Na}^+$  ion, just as inert compounds, can only influence the macroscopic dielectric constant by the fraction of water molecules that is displaced (the Butler effect). Moreover, when the value of  $D_{\pm}$  is greater than that of unbonded water, the water in the B region has a greater fluidity than the unbonded water molecules. Unlike pure water which consists mainly of rigid water clusters, the loose structure of the B region therefore increases the solubility of hydrocarbons. This is because in comparison to pure water, these hydrated water molecules can be

more readily repositioned and hence more readily allow the insertion of a molecule which does not interact with them. In addition, the induced dipole and the greater freedom of movement of these hydrated water molecules enables them to more effectively destroy a hydrogen bond by competing with one of the groups involved in the hydrogen bond. Previous calculations [1] have illustrated, however, that the volume of the hydrated ions must equal that of the solution before hydrogen bonds can be permanently destroyed, since such conditions prohibit the reformation of these bonds. Consequently, hydrogen bonds both in water clusters and in polymers—as well as hydrophobic bonds—can be readily destroyed by B regions of ions if the value of  $D_{\pm}$  for the hydrated ion is greater than that of unbonded water. The results presented here therefore explain the peculiar properties of aqueous salt solutions.

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