VOLUMETRIC EFFECTS DUE TO ION-SOLVENT INTERACTION IN AQUEOUS ELECTROLYTE SOLUTIONS

by

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The apparent volume of a series of chlorides dissolved in water – including hydrochloric acid and chlorides of divalent cations – is calculated from available data on the density of the aqueous solutions.

The concentration dependence of the volume of the electrolytes illustrates the long range electrostriction of water by the ions. The volume of the cations, at infinite dilution, reveals that the electrostriction observed, is composed of two opposite volume effects. The experimental data supports the view that bulky, “icelike” water structures predominate near the surface of a small ion, and dense structures, less organized than bulk water, are present at a distance from the ionic center.

1. INTRODUCTION

Volumetric properties of aqueous solutions of alkali halides were considered in a previous paper (11). Available experimental data indicates that a progressive hydration of the ions in aqueous solution occurs upon dilution, giving rise to negative volume changes (electrostriction of water). A peculiar behaviour of the Li^+ -salts, compared with other alkali halides, was tentatively associated with the small size of the Li^+ -ion compared with a water molecule.

The aim of the present paper is to further elucidate the volumetric behavior of aqueous electrolyte solutions. The volume of a series of chlorides, including HCl and chlorides of divalent cations, is discussed in relation to the concentration of the electrolytes and the radius of the cation.

In ref. 11 the hypothetical state of the molten salts at room temperature was chosen as a reference. The volume in the molten state was

estimated by extrapolation from data on the density at higher temperatures. A similar procedure for HCl is not described in the literature, and in the present paper, the volume of the electrolytes in solution has therefore been compared with the so-called intrinsic volume of the ions calculated from the ionic radius, R , as $4\pi R^3/3$. This intrinsic volume is different from the hypothetical volume of molten salts at room temperature used in ref. 11 and for this reason the extrinsic volume used in the present paper differs from the excess volume used previously.

2. THE VOLUME OF A SERIES OF CHLORIDES

The apparent molar volume of solute, V_1^{app} , is calculated from the density of a solution in the following way

$$V_1^{\text{app}} = M_1 [1/d^* + (1/d - 1/d^*)/w_1] \quad (1)$$

In this expression d is the density. The subscripts

Figure 1. The apparent molar volume of chlorides in aqueous solution at 291 K, calculated from available data (5) according to eqn. (1). x_1 is the mole fraction of the electrolyte.

Figure 2. The extrinsic molar volume of chlorides in aqueous solution at 291 K, $V_l^{\text{extr}} = V_l^{\text{app}} - V_l^{\text{intr}}$. V_l^{app} is from Figure 1, and $V_l^{\text{intr}} = 4\pi R^3/3$, where R is the ionic radius, reported in Table I. x_1 is the mole fraction of the electrolyte.

Table I

The radius, $R(\text{\AA})$, taken from ref. 1, of the cations, and the intrinsic molar volume, V_l^{intr} ($\text{cm}^3 \text{mole}^{-1}$), of their chlorides.

R of cation		V_l^{intr} of chlorides	
H ⁺	0	HCl	14.98
Li ⁺	.68	LiCl	15.77
Na ⁺	.98	NaCl	17.36
K ⁺	1.33	KCl	20.94
Rb ⁺	1.48	RbCl	23.14
Cs ⁺	1.69	CsCl	26.76
Be ²⁺	.30	BeCl ₂	30.02
Mg ²⁺	.65	MgCl ₂	30.65
Ca ²⁺	.94	CaCl ₂	32.05
Sr ²⁺	1.10	SrCl ₂	33.32
Ba ²⁺	1.29	BaCl ₂	35.38

0 and 1 refer to the solvent and the solute, respectively; w is weight fraction, and the superscript* denotes the pure liquid state.

Figure 1 illustrates the concentration dependence of V_l^{app} of a series of chlorides, calculated according to eqn. (1) from data interpolated to 291 K from available density measurement on aqueous solutions (5).

Table I reports the radius of the cations considered and the intrinsic molar volume of their chlorides.

Figure 2 shows the concentration dependence of the extrinsic volume of the electrolytes, de-

Figure 3. The extrinsic molar volume of cations at infinite dilution in aqueous solution at 291 K. The abscissa is the intrinsic volume of the cations. ($\text{cm}^3 \cdot \text{mol}^{-1}$).

defined as the difference between the apparent volume in solution and the intrinsic volume, $V_1^{\text{extr}} = V_1^{\text{app}} - V_1^{\text{intr}}$.

The molar volume of the chloride ion, at infinite dilution, is $23.0 \text{ cm}^3 \text{ mol}^{-1}$ (6, 10), and the intrinsic volume is $15.0 \text{ cm}^3 \text{ mol}^{-1}$ (see Table I). The extrinsic volume of the chloride ion, $V_{\text{Cl}^-}^{\text{extr}} = 23.0 - 15.0 = 8.0 \text{ cm}^3 \text{ mol}^{-1}$, is subtracted from the extrinsic volume of the salts, at infinite dilution (Figure 2), in order to give the extrinsic volume of the cations. This volume is presented in Figure 3 as a function of the intrinsic volume.

3. DISCUSSION

Electrostriction of a liquid is defined as the volume change caused by an electric field (1, 8).

Figure 4. The strength of the electrostatic field around an ion, calculated according to eqn. (2). a is the distance from the center of the ion.

The field strength around an ion may be expressed as

$$E = -q/\epsilon a^2, \quad (2)$$

where q is the ionic charge ($q = Z 4.8 \cdot 10^{-10} \text{ e.s.u.}$), ϵ is the dielectric constant of the medium, and a is the distance from the center of the ion. Figure 4 illustrates the variation of the field strength with the distance from the charge. The increase of the strength with decreasing values of a is remarkable in the range relevant of the interaction of an ion with neighbouring water molecules, and for this reason an increase of the electrostriction of water, with decreasing ion radius, might be anticipated.

The interaction of the electrostatic field of an ion with water tends to align the dipolar water molecules in the direction of the field. In this way the field tends to disrupt hydrogen bonded structures in liquid water, and to compress the water molecules surrounding an ion. These electrostatic effects give rise to a shrinkage of the water. The extent of the alignment of the water molecules depends on the ratio $\mu E/kT$, where μ is the dipole moment of water, $\mu = 1.83 \text{ Debye}$. The alignment is perfect if $\mu E \gg kT$, i.e. if $E \gg 2 \cdot 10^4 \text{ e.s.u.}$ ($6 \cdot 10^6 \text{ V cm}^{-1}$). This condition is only fulfilled for the proton, but a consideration

Figure 5. Model for structure modifications of water produced by a small cation. U, S and V stands for molar energy, entropy and volume, respectively.

of eqn. (2), or of Figure 4, shows that very high electric fields do exist near the surface of the smaller ions.

There can hardly be any doubt that water molecules are most strongly attracted to, and oriented towards the smaller ions. However, Figure 3 demonstrates the very fact that a positive contribution to the electrostriction is observed for the smaller ions. This *positive* volume effect is illustrated in Figure 3 by the difference between the fully drawn curve and the dashed extrapolation. The experimental data thus brings up the question whether the strong attraction between a small ion and water is compatible with a positive volume change.

In the case of the Li^+ -ion the positive volume effect (about $7 \text{ cm}^3 \text{ mole}^{-1}$, see Figure 3) was in ref. 11 tentatively ascribed to a void volume between the ion and the first shell of surrounding water molecules. The corresponding effect observed for H^+ and for Be^{++} is, however, so large, that this explanation is insufficient to explain the observations.

According to the model of structure modifications of water by small ions, originally proposed by FRANK and coworkers (3, 4), an ion dissolved

Figure 6. The extrinsic molar volume of monovalent cations in aqueous solutions at infinite dilution at 283, 298 and 353 K, calculated from available data (5). The abscisse is the intrinsic molar volume of the cations. ($\text{cm}^3 \cdot \text{mol}^{-1}$).

in water is surrounded by two concentric regions of structurally different types of water. Water molecules in the innermost region (a) are assumed to be immobilized, whereas molecules in the outermost region (b) are even more randomly organized than the molecules in bulk water.

On the basis of this suggested picture of structured water the present volumetric data indicates (see Figure 5) that region *a* of water (characterized by low energy and entropy) has a *larger*, and region *b* (characterized by high energy and entropy) has a *smaller* specific volume than pure water.

This volumetric behaviour is in accordance with the unusual volumetric properties of water, such as the unique temperature dependence of the volume of liquid water (the negative expansivity below 4°C), or the expansion accompanying the freezing of liquid water to ice, and the structural changes of water introduced by non-polar solutes (7). The temperature dependence of the extrinsic volume of monovalent cations

(5), illustrated in Figure 6, supports the view that bulky, "icelike" water structures surrounding the smaller ions "melt" upon heating.

These peculiar volume effects are associated with hydrogen bonding between water molecules. They reflect the fact that although hydrogen bonding diminishes the distance between neighbouring water molecules, it gives rise to an expansion, due to the directional character of the hydrogen bond. Hydrogen bonding decreases the number of nearest neighbours to a given water molecule, and in this way relatively large void spaces are created between the molecules (2). In ice the coordination number of the water molecules is 4; the apparent volume of small cations in aqueous solution suggests that tetrahedral ("icelike") water structures exist in the immediate surroundings of the ions. Convincing experimental evidence is available that a proton binds a water molecule in a proton-water complex, H_3O^+ , which is coordinated through hydrogen bonding with three or four water molecules in an open structure (1).

The over-all negative electrostriction of water originates from the dielectric polarization of more distant water molecules (region b). Figures 1 and 2 illustrate how the extent of this effect increases upon dilution. The absence of any inflection point of the volume curves, even at the lowest electrolyte concentrations studied ($x \approx 10^{-3}$), reflects the electrostriction as an extremely long range effect.

In summary, the suggested model of water structures around an ion as composed of two distinguishable regions is undoubtedly a crude oversimplification of the conditions in an electrolyte solution, but it elucidates essential features of the solute-solvent interaction. The structural changes of water, introduced by an ion, occur as a result of two competing orienting influences on any water molecule. One is the influence from neighbouring water molecules; the other is the influence from the spherically symmetrical ionic field. The first is present in bulk water, and the latter predominates near the surface of a small, or multiply charged ion. In between there is a region of more orientational disorder than exists in pure water. The volumetric data, here discussed, supports this picture of water, taking into consideration the character-

istic thermodynamics of structural equilibria in liquid water. The formation of *ordered, low-energy structures* among water molecules is accompanied by an *expansion* ($\Delta H \cdot \Delta V < 0$, and $\Delta S \cdot \Delta V < 0$). The long range structural changes of water introduced by ions, and drastically reflected in volumetric properties, may play an essential role in cell physiology, particularly in the mechanism of the Na^+ pump, extensively discussed by LING (9).

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