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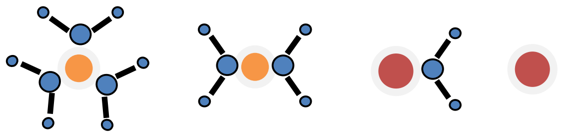
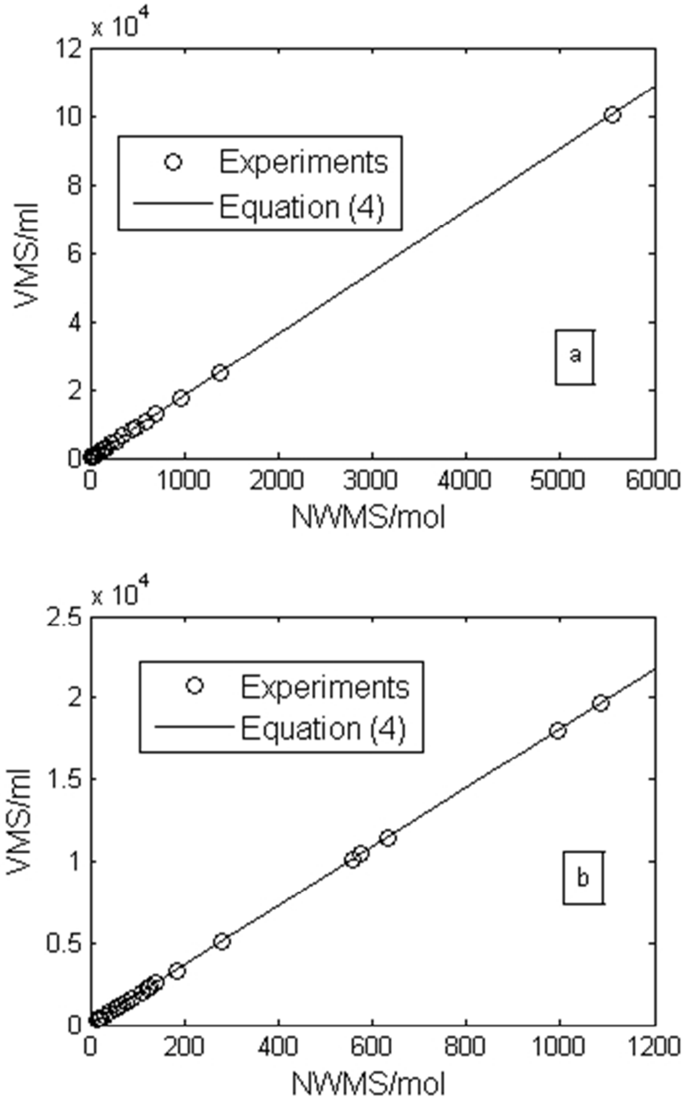


The structures of hydrated sodium (yellow) and potassium (red) ions



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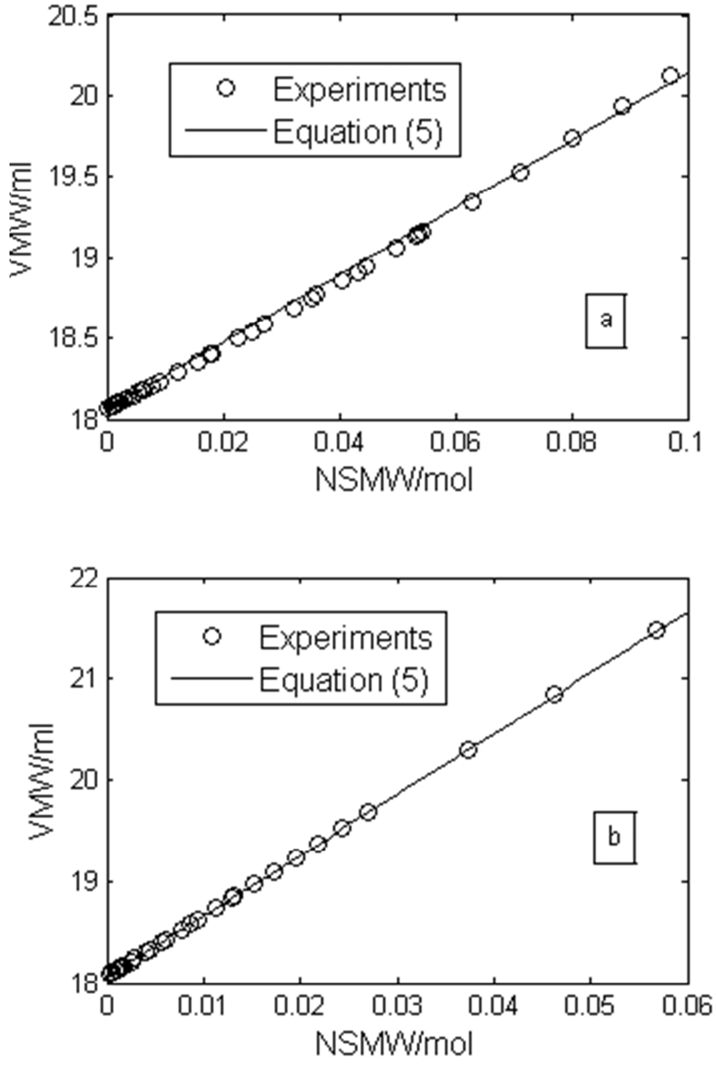

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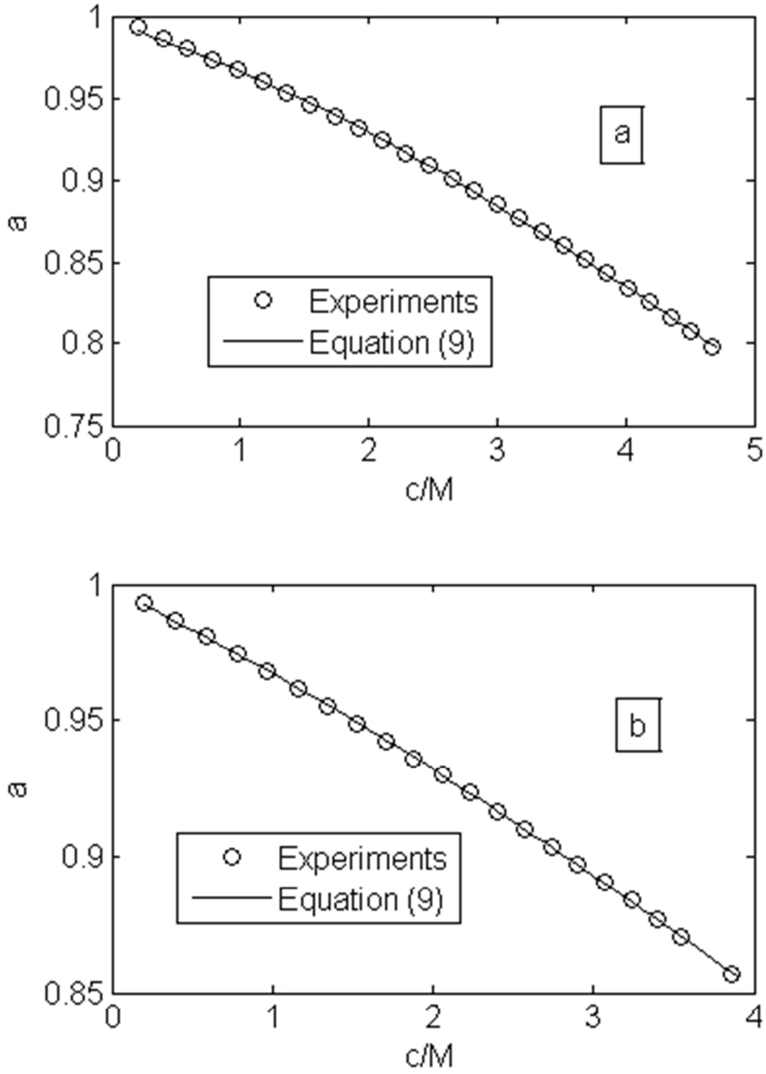

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# The size and structure of some hydrated ions and the ions channels selectivity

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## Abstract

In this work we present that part of the coordinated water around an ion in aqueous solution is so strongly bound to the ion that they can't be dissociated as part of the ion, the unable-dissociated water is called as hydration water and the combination of the ion and the hydration waters is called as the hydrated ion, and establish an approach to determine the average volume and hydration number of a hydrated ions. Applying the approach, the both quantities of some alkali metal and halogen hydrated ions are determined by the water activities, the densities and the salt volume concentrations of aqueous solutions reported in the literatures. The results show that the effective radii and the structures of hydrated $Na^+$, $K^+$, $Rb^+$ and $Cs^+$ play a key role in ion transport properties, such as the ions channels selectivity.

## Keywords

hydrated ion; ions transport; potassium ions, sodium ions, water activity

## 1. Introduction

Aqueous solutions in living systems contain appreciable amounts of ions, such as sodium and potassium ions. In studies of the ions selectivity in membrane transport, the prevailing view[1] has been that inside the selectivity filter, $K^+$ ions are coordinated by oxygen atoms from the protein, which replace the water molecules that normally surround the ion. However, the field generated by ion, such as sodium ion is $138.4 GV \cdot m^{-1}$ right near its surface at 0.102 nm from its center[2], as a result the coordination waters of an ion can be only dissociated partly due to the high electric field and the strong polarity of water molecule and the unable-dissociated waters in fact become part of the ion. Therefore, the total dissociation equilibrium of a coordinated ion, $\mathrm{I(H_2O)}_m$ is, $\mathrm{I(H_2O)}_m = \mathrm{I(H_2O)}_n + (m-n)\mathrm{H_2O}$, where $\mathrm{I(H_2O)}_n$ is called as a hydrated ion, m and n (an integer from 0 to m) are the coordination number and the hydration number respectively. The experimental observations, that potassium ions and water in narrow ion channels are together transported[3-4] and the partial molar volumes of small or/and multivalent metal ions in aqueous solutions are negative values[5], support the existence of hydration water. Physically, the transport properties of an ions in aqueous solution must be closely related to the average volume and hydration number of its hydrated ions. However, the scattering method [6-7] and molecular dynamics simulations[8-10] were only capable of telling us how many the first shell coordination number for water around an ion and what size the volume of the coordinated ion. So far the absolute volumes of hydrated ions have not been reported in the literatures. There is very important difference between the hydration numbers of an ion reported in the literatures [11-13]. The hydration number reported by Stokes and Robinson [11] is 3.5, 4.2, 5.5, 1.9, 2.1 and 2.5 for NaCl, NaBr, NaI, KCl, KBr and KI respectively. Dielectric relaxation measurements [12] shown that the hydration number of $Na^+$ is 2.6 and the one of $K^+$, $Cs^+$, $Cl^-$, $Br^-$ and $I^-$ is all 0. Zavitsas [13] indicated that the hydration number is 3.4, 3.5, 3.9, 1.3, 1.1, 1.4 and 0 for NaCl, NaBr, NaI, KCl, KBr, KI and CsCl (assigned hydration number 0 to $Cl^-$, $Br^-$ and $I^-$) respectively. However, the experiments [14] shown the B coefficients of these ions in the Jones–Dole expression for the viscosity of aqueous ionic solutions are (in parentheses): $Cs^+$ (-0.047) < $K^+$ (-0.009) < $Na^+$ (0.085) and $Cl^-$ (-0.005) > $Br^-$ (-0.033) > $I^-$ (-0.073) with units of $dm^3 \cdot mol^{-1}$. Obviously the orders for the hydration numbers of these ions are not consistent with the ones for their B coefficients.

In this work, the partial molar volume of a salt in aqueous solution refers to the sum of the partial molar volumes of hydrated ions from the salt. First we demonstrate the collective formula of partial molar volume can be changed into a linear equation due to the partial molar volumes of a salt and the solvent water in aqueous solution are independent of the salt concentrations over very large range. Second an equation that correlate the activities of water in aqueous solution of a salt with the molarities of the salt is established and the partial molar volume of the salt is a parameter of the equation. Third applying the equations, the average volume and hydration number of some alkali metal and halogen hydrated ions are determined by the water activities, the densities and the salt volume concentrations of aqueous solutions reported in the literatures. Finally the relation between the volumes and the structures of hydrated ions and the ions transport properties is investigated.

## 2. Approach

Since the hydration waters of an ion become effectively part of the ion without increasing the number of the ion, the number of free water molecules that are called as the solvent water should be decreased. According to the thermodynamic principle,

$$v = n_w v_w + \sum_i n_i v_i \quad (1)$$

where $v$ is the volume of aqueous solution of salts, $n_w$, $n_i$, $v_w$ and $v_i$ are the mole numbers and the partial molar volumes of the solvent water and the hydrated ion $i$ respectively. For a single salt, equation (1) is replaced by

$$v = n_w v_w + n_s v_s \quad (2)$$

where $n_s$ and $v_s$ are the mole number and the partial molar volume of the salt respectively. If $H$ is the average hydration number of a salt, equation (2) is changed to

$$\frac{m_w + m_s}{d} = \left(\frac{m_w}{M_w} - H\frac{m_s}{M_s}\right)v_w + \frac{m_s}{M_s}v_s \quad (3)$$

where $m_w$ and $m_s$ are the total mass of the solvent water and the hydration water with the molar mass $M_w$ and the mass of salt with the molar mass $M_s$ respectively, and $d$ is the density of the solution. A large number of diffraction experiments [15-24] shown that the length for ion-O (from water) distance and the average coordination number of ions are almost independent of the $H_2O$/salt molar ratio. This fact implies that $v_s$ and $H$ in equation (3) are independent of the salt concentration over very large range. According to the Gibbs-Duhem equation, $x_w dv_w + x_s dv_s = 0$, where $x_w$ and $x_s$ are the mole fractions of the solvent water and the salt, $v_w$ is also independent of the salt concentration. Interestingly, the recent measurements[25-26] shown that ions have no effect on water structure beyond the first sphere of surrounding water molecules. Similarly, this fact implies that $v_w$ is nearly independent of salt concentration, and supports that $v_s$ and $H$ are independent of the salt concentration. Since $v_s$, $H$ and $v_w$ are constant in aqueous solution of a salt over a very large range of concentration, equation (3) can be changed into linear ones in terms $\frac{M_s(m_w+m_s)}{m_s d}$ (the volume of solution per mole salt, VMS) and $\frac{m_w M_s}{m_s M_w}$ (the number of water per mole salt, NWMS) or $\frac{M_w(m_w+m_s)}{m_w d}$ (the volume of solution per mole water, VMW) and $\frac{m_s M_w}{m_w M_s}$ (the number of salt per mole water, NSMW) ,

$$VMS = v_w \times NWMS + (v_s - H \times v_w) \quad (4)$$

or

$$VMW = (v_s - H \times v_w) \times NSMW + v_w \quad (5)$$

Once $v_s$ is determined, the $H$ will be obtained by the intercept $(v_s - H \times v_w)$ of equation (4) or the slop $(v_s - H \times v_w)$ of equation (5) and the molar volume of pure water $v_w^*$.

Statistically, at the liquid-gas equilibrium there must be a few water molecules on the hydrated ions at the surface of aqueous solution of a salt. Therefore, the vapor pressure results from the evaporation of the surface water and the water on the surface hydrated ions. The former is nearly direct proportion to the surface quantities $(c_w)^{\frac{2}{3}}$, where $c_w$ is the volume concentrations of the solvent water and the latter are direct proportion to the surface quantities $(c)^{\frac{2}{3}}$, where $c$ is the volume concentration of the salt, thus

$$\frac{p_w}{p_w^*} = (\frac{c_w}{c_w^*})^{\frac{2}{3}} + bc^{\frac{2}{3}} \quad (6)$$

where $p_w$, $p_w^*$ and $c_w^*$ are the vapor pressure over the solution, the saturated vapor pressure and the volume concentration of pure water respectively, and $b$ is the parameter that measures the volatility of the water on the surface hydrated ions. Generally the relative vapor pressure ($\frac{p_w}{p_w^*}$) is the activity $a$ of the solvent water in aqueous solution of a salt. Due to the field generated by hydrated ions, the volatility of the water at the side of the surface hydrated ions is somewhat smaller than the one of the surface water away from the hydrated ions, so the first term of right side in equation (6) is slightly larger than the real contribution of the surface water to pressure, but the deviation is reduced with the salt concentration increased. The parameter $b$ also is dependent of the salt concentration and is increased with the salt concentration increased. In theory, if there is not the interaction between hydrated ions and the solvent water molecules, $b$ should vanishes zero, then equation (6) is reduced to

$$\frac{p_w}{p_w^*} = \left(\frac{c_w}{c_w^*}\right)^{\frac{2}{3}} \quad (7).$$

Based the above analysis, equation (6) is empirically changed into

$$\frac{p_w}{p_w^*} = \left(\frac{c_w}{c_w^*}\right)^{\frac{2}{3}} + b_1(1-\exp(-b_2 c))c^{\frac{2}{3}} \quad (8)$$

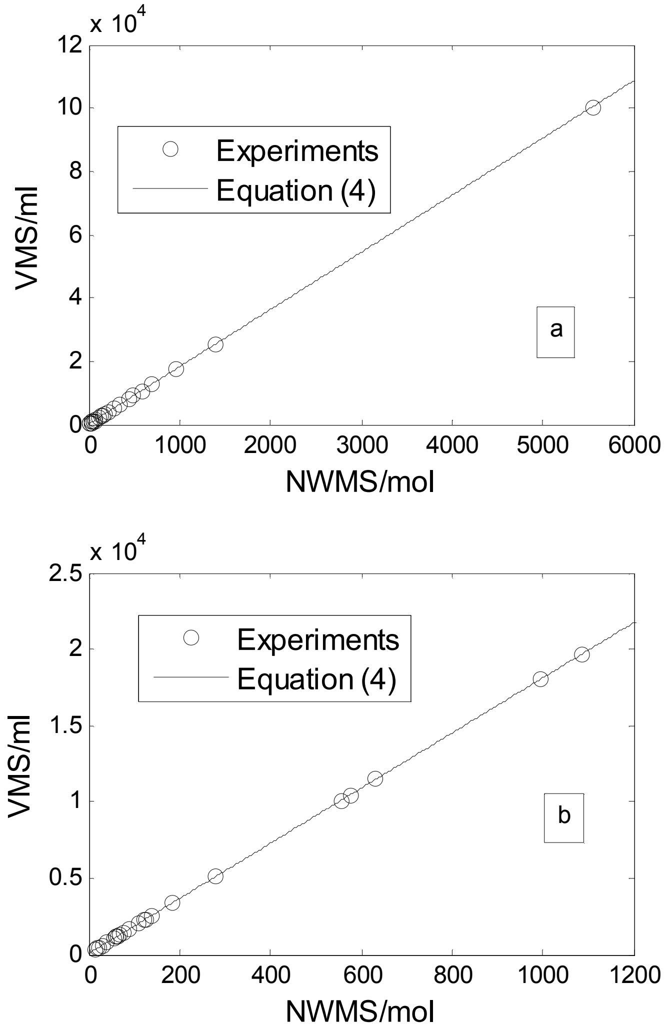
where $b_1$ and $b_2$ are salt-dependent parameters. Substituting $c_w = \frac{1-cv_s}{v_w}$ from equation (2) into equation (8), and combining $v_w = v_w^*$ and $c_w^* v_w^* = 1$, equation (8) is finally changed into

$$\frac{p_w}{p_w^*} = (1-v_s c)^{\frac{2}{3}} + b_1(1-\exp(-b_2 c))c^{\frac{2}{3}}. \quad (9)$$

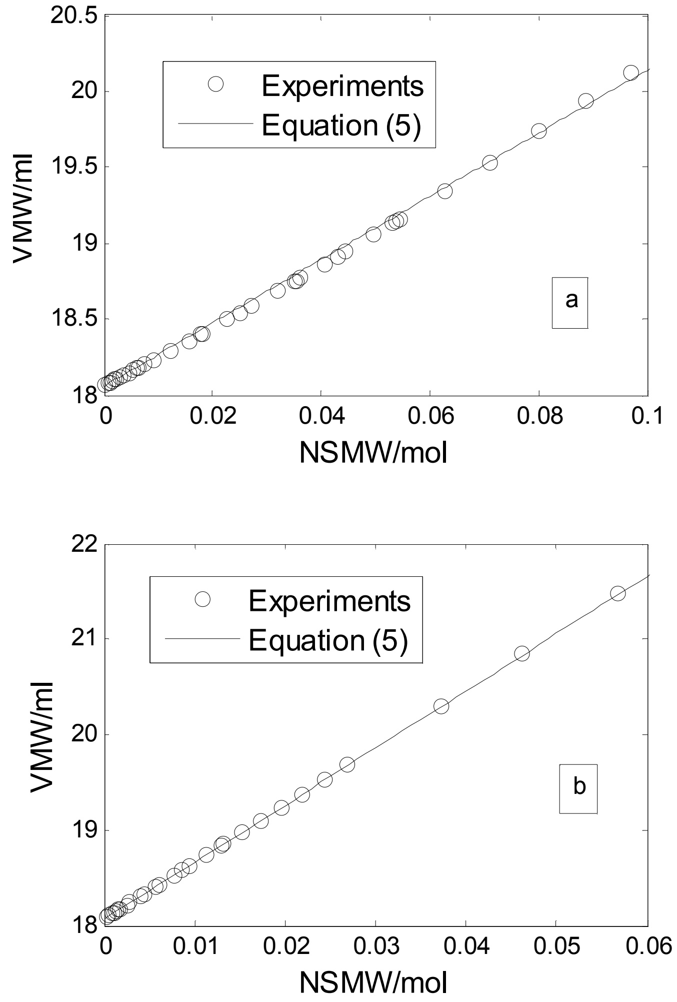
When the coordination shells of cation and anion interpenetrate, equation (9) probably is no longer valid due to the water molecules push each other on the surface hydrated ions. Therefore, to determine the volume $v_s$ of a salt in aqueous solution by fitting the experimental data of $\frac{p_w}{p_w^*}$ and $c$ with equation (9), the $\frac{p_w}{p_w^*}$ should be the ones below a critical concentration $c_{cr}$ (see the Supplementary Material).

## 3. Results and Discussion

Using the densities [27-33] for aqueous solutions of NaCl, KCl, NaBr, KBr, RbCl, CsCl, RbBr, CsBr, RbI, and CsI at 25℃, we determine their NWMS, VMS, NSMW and VMW at molalities (m) in the very large ranges, which successively from 0.01 to 5.95, from 0.1 to 4.4, from 0.03 to 5.2, from 0.06 to 4.4, from 0.02 to 6.8, from 0.01 to 5.9, from 0.04 to 6.0, from 0.04 to 4.7, from 0.01 to 4.7, and from 0.02 to 3.1 (see the Supplementary Material), and fitting the data of VMS and NWMS, VMW and NSMW for each salt solution with equation (4) and (5) respectively, the multiple fitted $v_w$ and $(v_s - N_{cw}v_w)$ are shown in table 1. The R-squares of the resulting linear regression with equation (4) are generally unity with confidence level 99% and the fitted slops $v_w$ are generally $18.07\,cm^3 \cdot mol^{-1}$, and the $v_w^*$ from the density [34] $997.047\,kg \cdot m^{-3}$ of pure water at 25℃ is $18.0687\,cm^3 \cdot mol^{-1}$. Fig.1 shows plots of VMS vs. NWMS for NaCl and KCl solutions respectively.



Obviously, the experimental data drop almost in the fit lines with equation (4). The facts strongly indicate that the partial molar volumes of a salt and the solvent water are independent of the salt concentration over a very large range. The poorest and best R-squares of the resulting linear regression with equation (5) are 0.9985 for NaCl and 1 for CsI respectively and the fitted intercepts $v_w$ closest to 18.07 $cm^3 \cdot mol^{-1}$ are in the range from 18.05 to 18.07 $cm^3 \cdot mol^{-1}$. Fig.2 shows plots of VMW vs. NSMW for NaCl and CsI solutions

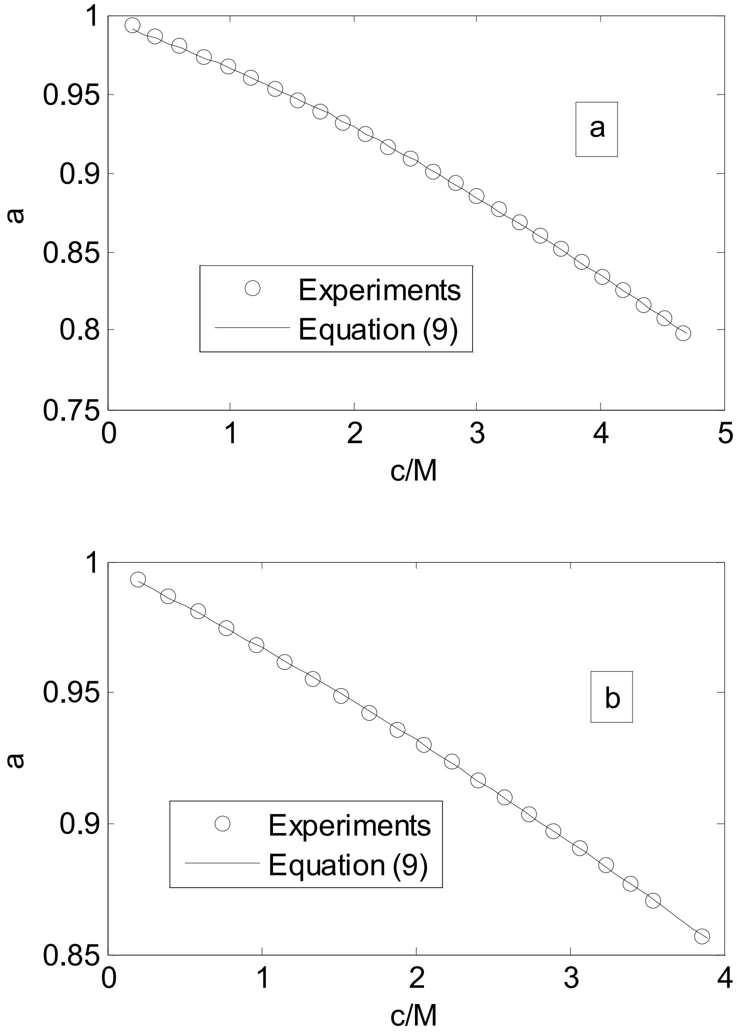


respectively. The experimental data of CsI drop almost in the fit line but some of experimental data for NaCl drop somewhat aside the fit line. The numerical value comparison of NWMS with NSMW and VMS with VMW in Fig.1a and 2a indicates that the magnitudes of NSMW and VMW are much smaller than NWMS and VMS respectively, so relatively the larger experimental error results in that the fit with equation (5) is a bit poor.

Using the densities [28] of aqueous solutions of $CaCl_2$ from 0.05 to 6.46 m at 25℃, the NWMS and VMS are determined, and fitting the data of VMS and NWMS with equation (4) with confidence level 99%, the multiple fitted $v_w$ and the R-square are

18.06 (18.05, 18.07) $cm^3 \cdot mol^{-1}$ and 1 respectively (see the Supplementary Material). The fact shows equation (4) also is fit to a multivalent salt over a very wide range of concentration.

Correlating the experimental densities [27-33] with the molalities, we determine the molarities $c$ corresponding to $\frac{p_w}{p_w^*}$ over aqueous solutions [35-38] at molalities from 0.2 to 5.2 for NaCl, from 0.2 to 4.4 molality for KCl, from 0.1 to 4.5 for NaBr, from 0.1 to 4.0 for KBr, RbCl, CsCl, RbBr, CsBr, from 0.1 to 3.5 for RbI and from 0.1 to 3.0 for CsI at 25℃ (see the Supplementary Material) and fitting the data of $\frac{p_w}{p_w^*}$ and the molarities $c$ for each salt solution with equation (9), the multiple fitted $v_s$ are shown in table 2. The R-squares of the resulting multiple non linear regression with confidence level 99% are from 0.9996 to 1. Fig.3 shows plots of $\frac{p_w}{p_w^*}$ vs. $c$ for aqueous solutions of NaCl and KCl respectively.



The experimental data drop almost in the fit lines. The facts strongly indicate that the equation (9) can be used to obtain the volume of a salt in aqueous solution over a large range of concentration.

Correlating the experimental densities [28] with the molalities, we determine the molarities $c$ corresponding to $a$ over aqueous solution [39] of $CaCl_2$ at molalities from 0.1 to 4.5 at 25℃, and fitting the data of $\frac{p_w}{p_w^*}$ and $c$ with equation (9), the R-square of the resulting multiple non linear regression with confidence level 99% is 0.9996 (see the Supplementary Material). The fact shows equation (9) also is fit to a multivalent salt over a wide range of concentration.

Since the partial molar volumes of a salt is independent of the salt concentration over very wide ranges, the additivity is also applicable at high salt concentrations. On application of the additivity, the $v_s$ of NaCl minus the $v_s$ of KCl should equal the $v_s$ of NaBr minus the $v_s$ of KBr and the $v_s$ of NaBr minus the $v_s$ of NaCl should equal the $v_s$ of KBr minus the $v_s$ of KCl or the $v_s$ of CsBr minus the $v_s$ of CsCl. Therefore, 0.08327, 0.06534, 0.08422, 0.06627, 0.06372, 0.06111, 0.06467, 0.06209, 0.06206 and 0.05944 $dm^3 \cdot mol^{-1}$ in table 2 are the most close to the absolute molar volume of NaCl, KCl, NaBr, KBr, RbCl, CsCl, RbBr, CsBr, RbI and CsI in aqueous solution respectively.

The multiple calculated hydration number by the $v_s$ for each salt and the multiple intercepts $(v_s - N_{cw}v_w)$ of equation (4) in table 1 ($v_w$ is all taken as $v_w^*$, 18.07 $cm^3 \cdot mol^{-1}$) are presented in table 3. Again on application of the additivity, it is known that the hydration number $H$ of NaCl, KCl, NaBr, KBr, RbCl, CsCl, RbBr, CsBr, RbI and CsI in aqueous solution is 3.5, 2.0, 3.2, 1.7, 1.6, 1.1, 1.3, 0.8, 0.5 and 0 respectively, consequently the average hydration numbers $H_i$ for each hydrated ions is (in parentheses): $Na^+$ (2.4) > $K^+$ (0.9) > $Rb^+$ (0.5) > $Cs^+$ (0) and $Cl^-$ (1.1) > $Br^-$ (0.8) > $I^-$ (0) respectively. The hydration number sequences of $Na^+ > K^+ > Rb^+ > Cs^+$ and $Cl^- > Br^- > I^-$ are consistent with the sequences for the absolute hydration enthalpies[41] and the B-coefficient, the $B_{NMR}$ and the negative water structural entropy $-\Delta S_{struct}$ [14] of $Na^+ > K^+ > Rb^+ > Cs^+$ and $Cl^- > Br^- > I^-$. At 298.15K the absolute hydration enthalpies [40] of $Na^+$, $K^+$, $Rb^+$, $Cs^+$ and $Cl^-$, $Br^-$, $I^-$ are -391, -308, -283, -258 and -392, -361,

-321($kJ \cdot mol^{-1}$) and the B-coefficients [14] are 0.085, -0.009, -0.033, -0.047 and -0.005, -0.033, -0.073 with unit of $\mathrm{dm}^3 \cdot mol^{-1}$ respectively. The crystal radii [41] of the above ions are: $Na^+$ (0.102) > $K^+$ (0.138) > $Rb^+$ (0.152) > $Cs^+$ (0.167) and $Cl^-$ (0.181) > $Br^-$ (0.196) > $I^-$ (0.220) with unit of nanometer respectively. The comparison between the orders of the B-coefficients and the crystal radii indicates that an ion transport properties depend strongly on the hydration number of the ion.

The further analysis of $H_i$ is summarized in table 4. According table 4, it is known that $Cs^+$ and $I^-$ ions are bare and one-fold spherical structure, sixty and forty percent of $Na^+$ ions are hydrated with two and three water molecules, ninety and ten percent of $K^+$ ions are hydrated with one and zero water molecules, fifties percent of $Rb^+$ ions are hydrated with one and zero water molecules, ninety and ten percent of $Cl^-$ ions are hydrated with one and two water molecules and eighty and twenty percent of $Br^-$ ions are hydrated with one and zero water molecules respectively. As compared with the structures of hydrated potassium ions, the complex structures of hydrated sodium ions lead to $Na^+$ limiting molar conductivity smaller than $K^+$ one [42].

In facts, the hydration numbers of $Cl^-$ (0), $Br^-$ (0), $K^+$ (0) and $Na^+$ (2.6) from dielectric relaxation measurements[12] don't contradict the structures of hydrated ions in table 4. There can be still the two movements for hydration water: round motion on the surface of the ion and rotation around the axle of bond between the ion and the hydration water. According to table 4, $Na^+(\mathrm{H_2O})_3$ is trigonal planar molecular geometry and $Na^+(\mathrm{H_2O})_2$ is linear molecular geometry. The external field will make the two of dipoles (hydration water) on the surface of $Na^+$ round in opposite direction, while the solvent water molecules between the hydration waters must be stop the round motion, so the two or three dipole on the surface of $Na^+$ can't free move round. In addition, owing to symmetry the rotation of hydration waters around the $Na^+$-O axle can't generate the change of the dipole orientation. The facts imply the hydration number of $Na^+$ equals the number of irrotationally bound solvent molecules [26]. In contrast to $Na^+$, the sole hydration water on the surface of $K^+$ can free move round and the movement can lead to the change of the dipole orientation, so the number of irrotationally bound solvent molecules is zero. The sole hydration water on the surface of $Br^-$ or 90% $Cl^-$ can free rotate around the $Br^-$-H axle and the movement must be lead to the change of the dipole orientation, so the number of irrotationally bound solvent molecules is zero.

Equation (9) can represent the vapor pressures over aqueous solutions of alkali-halide up to several molarities with confidence level 99% as shown in fig.3. In contrast to this, Raoults's law, $\frac{p_w}{p_w^*} = x_w$, can only represent the vapor pressure over very dilute aqueous solutions of salt. In the ideal condition, physically the vapor pressure over the solution should be proportional to the surface quantity $(\frac{c_w}{c_w^*})^{\frac{2}{3}}$, not the bulk quantity $x_w$, so equation (7) is more reasonable than Raoults's law. However, the correctness of equation (9) don't exclude the colligative properties of dilute solutions derived from Raoults's law, because in the limit of low concentration the values of $\frac{p_w}{p_w^*}$ calculated with equation (9) equals practically the values of $x_w$. When $c$ is 0.1M, $x_w(\frac{1/v_w}{1/v_w + 2c})$ is 0.9964, and the calculated $\frac{p_w}{p_w^*}$ with equation (9) is 0.9953 and 0.9961 for NaCl and KCl solutions respectively, where $v_s$, $b_1$ and $b_2$ of NaCl and KCl are given respectively in the caption of fig.3; when $c$ are 0.01M, $x_w$ are 0.9996, and the calculated $\frac{p_w}{p_w^*}$ is 0.9995 and 0.9996 for NaCl and KCl solutions respectively. Zavitsas[13] claimed the activity $a$ of the solvent water in aqueous solution of a salt $a = (55.509 - mH_T)/(55.509 - mH_T + mi_e)$ over wide concentration ranges, where m, $H_T$ and i are the molality, the thermodynamic hydration number and the stoichiometric number of particles produced per mole of the salt respectively and obtained the hydration number from the freezing-point depressions of aqueous solutions of salt: NaI (3.9) > NaBr (3.5) > NaCl (3.4), which is not in agreement with the order of B-coefficients for these anion. There are several main defects for the work by Zavitsas. First, the strategy of using freezing-point depressions of the "ideal" aqueous solution of a salt to determine the thermodynamic hydration number in reality implies that the hydration number of an ion is independent of temperatures! It is hard to believe the hydration number at 25°C is same with the one at -25°C. Second, the equilibrium constant $K_e$ for ion-pair was miscalculated as $K_e = \alpha^2/(1-\alpha)^2$ to support that the degree $\alpha$ of association to ion pairs independent of concentration of salt over wide concentration ranges. However, according to the definition of $K_e$, $K_e = (1 + c_w/\alpha c)\cdot\alpha^2/(1-\alpha)^2$. In addition, the existence of the univalent ion pair require the relative permittivity of solvent be below 30[43], so it is questioned that 31% NaCl is in the form of ion pairs in water. Three, the $H_T = 0$ of CsCl is incompatible with the hypothesis: Ion-pair formation would replace at least one of the water molecules strongly bound to cation by anion to form ion pair.

According to the thermodynamic principles, the hydration numbers for NaCl (3.5), NaBr (4.2), NaI (5.5), KCl (1.9), KBr (2.1), KI (2.5) reported by Stokes and Robinson[11] should be consistent with the ones found in the present approach, but it's not the truth. Although Stokes and Robinson also assumed that some molecules of solvent are strongly bound to the ions and then the remaining "free" water molecules are considered to be the solvent, they disregarded unreasonably the hydration in the process of deriving the Debye-Hückel equation with two parameters.

The coordination numbers for $Na^+$, $K^+$, and $Cl^-$ are 4.5, 3.5 and 2.0 from the standard molar ionic compression[44] and within the range of 5.0-5.8, 6.0-7.0, and 6.0-6.5 from molecular dynamics simulations [8-10] respectively. According to the present theory, the coordination number of an ion must be larger than the hydration number of the ion. The smaller the radius of an ion or/and the higher the valence, the larger the hydration number, and then the hydrated ions seem to be a cluster of water. Because hydration water can strongly shield the field of the ion, even the field of a multivalent hydrated ion is not too strong. In addition, the hydration waters can block the concentric contraction of the coordination water, simultaneously the coordination waters each other also blocks the concentric contraction. These facts cause the volume of coordination water maintain nearly unchanged as in the bulk, so the molar volume of free water is the same with the one of pure water until the hydrated ions interpenetrate.

The $Cs^+$-$H_2O$ bond length from Neutron diffraction[6-7] is 0.295nm and the radius of a water molecule is generally taken as 0.138nm [45], so the radius of $Cs^+$ in aqueous solution is taken as 0.157nm. If the molar volume of a spherical shape ion is taken as the sum of the volume of closely packed spheres and the void space between closely packed spheres, according to the cubic closet packing the molar volume of $Cs^+$ in aqueous solution should be $0.0132\,dm^3 \cdot mol^{-1}$. Applying the additivity, the molar volumes of $Na^+$, $K^+$, $Rb^+$ and $Cl^-$, $Br^-$, $I^-$ in aqueous solution are about 0.0354, 0.0174, 0.0159 and 0.0479, 0.0489, $0.0462\,dm^3 \cdot mol^{-1}$, and their effective radii are 0.218, 0.172, 0.167 and 0.242, 0.243, 0.239 nm.

Because the hydration number of $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ in aqueous solution are 2.4, 0.9, 0.5, and 0 respectively, in contrast to the order of their crystal radius [41], the order of their effective radii in aqueous solution is $Na^+ > K^+ > Rb^+ > Cs^+$. In spite of this, according to table 4 the transverse radii of hydrated $K^+$ , $Rb^+$ and $Cs^+$ are still their crystal radii. These facts are closely related to the ions channels selectivity [46-47]. The structures of hydrated sodium ions with larger volume are more complicated, so the ions are hard to go into the narrow potassium channel [48]. In addition, the existence of hydrated ions don't exclude that the crown ethers of more high affinity than water for some cations (M) strongly bind the cations, forming complexes, $\mathrm{M(H_2O)_n} + crown = \mathrm{M(H_2O)}_n \cdot crown = \mathrm{M}crown + n\mathrm{H_2O}$ . Similarly, shedding some or all hydration water, hydrated ion, such as $Na^+(\mathrm{H_2O})_3$ or $Na^+(\mathrm{H_2O})_2$ is coordinated by oxygen atoms from suitable protein due to the entropy gain arising through release of water molecules from the hydrated ion, i.e., $Na^+(\mathrm{H_2O})_{2.4} + protein = Na^+(\mathrm{H_2O})_1 \cdot protein + 1.4\mathrm{H_2O}$ and $Na^+(\mathrm{H_2O})_{2.4} + protein = Na^+ \cdot protein + 2.4\mathrm{H_2O}$ , where 2.4 are the average hydration number of hydrated sodium ions. According to the reactions, ones know that a significant effect of entropy gain also restricts the sodium ion hydrated with one or zero water molecule inside the selectivity filter to move. In contrast to hydrated sodium ions, the structures of hydrated potassium, rubidium and cesium ions with smaller volume are simpler, so they can all enter into the $K^+$ channels. However, to pass through the selectivity filter, an ion must shed a certain number water molecules from the first coordination shell of the ion. Because the greater the effective radius of an ions, the smaller the de-coordination energy, all $K^+$ channels show a selectivity sequence [46] of $K^+ > Rb^+ > Cs^+$. As the same reason, $Na^+$ channels show a selectivity sequence [47] of $Na^+ > K^+$.

## 4. Conclusions

The measurements for physical quantities, such as the water activities in aqueous solution of a salt and the densities of the solution, yield the average volume and hydration number of a hydrated ions. The difference of volume and structure between hydrated ions results in their different behaviors, such as the ions transport properties. In addition, the existence of hydration water implies that the interactions between hydration water and the solvent water are a important component part of hydrated ion-the solvent water interaction.

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## Captions

Figure 1. Plots of VMS vs. NWMS at 25 °C. **(a)** Open circles: The experimental data from aqueous solutions [27, 28] of NaCl at molalities (m) from 0.01 to 5.95 m; Solid line: Plot of equation (4), in which the slope $v_w$ and the intercept $(v_s - H \times v_w)$ are taken as 18.07 and 19.53 (ml/mole) respectively. **(b)** Open circles: The experimental data from aqueous solutions [29, 30] of KCl at molalities from 0.1 to 4.4 m; Solid line: Plot of equation (4), in which the slopes $v_w$ and the intercepts $(v_s - H \times v_w)$ are taken as 18.07 and 29.66 (ml/mole) respectively.

Figure 2. Plot of VMW vs. NSMW at 25 °C. **(a)** Open circles: The experimental data from aqueous solutions [27, 28] of NaCl at molalities from 0.01 to 5.95 m; Solid line: Plot of equation (5), in which the slopes $(v_s - H \times v_w)$ and the intercepts $v_w$ are taken as 20.8 and 18.06 (ml/mole) respectively. **(b)** Open circles: The experimental data from aqueous solutions [27, 33] of CsI at molalities from 0.02 to 3.15 m; Solid line: Plot of equation (5), in which the slope $(v_s - H \times v_w)$ and the intercept $v_w$ are taken as 59.93 and 18.06 (ml/mole) respectively.

Figure 3. Plot of $a$ vs. $c$ at 25 °C. **(a)** Open circles: $a$ from aqueous solution [36] of NaCl at molalities from 0.2 to 5.2 m and the corresponding $c$ obtained by correlating the experimental densities [27, 28] with the molalities; Solid line: Plot of equation (9), in which the $v_s$, $b_1$ and $b_2$ are taken as $v_s = 0.08327 dm^3 \cdot mol^{-1}$, $b_1 = 0.02852 molarity^{-2/3}$ and $b_2 = 1.532 molarity^{-1}$ respectively. **(b)** Open circles: $a$ from aqueous solution [36] of

KCl at molalities from 0.2 to 4.4 m and the corresponding $c$ obtained by correlating the experimental densities [29, 30] with the molalities; Solid line: Plot of equation (9), in which the $v_s$, $b_1$ and $b_2$ are taken as $v_s = 0.06534 dm^3 \cdot mol^{-1}$, $b_1 = 0.01368 molarity^{-2/3}$ and $b_2 = 1.713 molarity^{-1}$ respectively.

## Tables and the titles

**Table 1 The fitted $v_w$ and $(v_s - H \times v_w)$ for aqueous solutions of some alkali halide with equation (4) and (5) respectively**

| Salt | Equation | $v_w / cm^3 \cdot mol^{-1}$ | $(v_s - H \times v_w) / cm^3 \cdot mol^{-1}$ | R-square |
|---|---|---|---|---|
| NaCl | (4) | 18.07 (18.07, 18.07) | 18.97 (18.42, 19.53) | 1 |
| | (5) | 18.04 (18.03, 18.06) | 20.8 (20.43, 21.17) | 0.9985 |
| KCl | (4) | 18.07 (18.06, 18.07) | 29.66 (29.08, 30.24) | 1 |
| | (5) | 18.04 (18.03, 18.05) | 31.23 (30.92, 31.54) | 0.9996 |
| NaBr | (4) | 18.06 (18.07, 18.07) | 25.68 (24.97, 26.39) | 1 |
| | (5) | 18.05 (18.04, 18.06) | 27.48 (27.2, 27.75) | 0.9998 |
| KBr | (4) | 18.07 (18.07, 18.07) | 35.37 (34.43, 36.32) | 1 |
| | (5) | 18.06 (18.04, 18.07) | 37.14 (36.75, 37.53) | 0.9997 |
| RbCl | (4) | 18.07 (18.07, 18.07) | 34.41 (33.74, 35.08) | 1 |
| | (5) | 18.04 (18.02, 18.06) | 36.68 (36.19, 37.17) | 0.9993 |
| CsCl | (4) | 18.07 (18.07, 18.07) | 41.45 (40.77, 42.13) | 1 |
| | (5) | 18.04 (18.02, 18.05) | 43.72 (43.26, 44.18) | 0.9997 |
| RbBr | (4) | 18.07 (18.07, 18.07) | 41.07 (40.52, 41.63) | 1 |
| | (5) | 18.04 (18.03, 18.06) | 42.93 (42.54, 43.32) | 0.9997 |
| CsBr | (4) | 18.07 (18.07, 18.07) | 48.21 (47.74, 48.68) | 1 |
| | (5) | 18.05 (18.04, 18.06) | 49.73 (49.38, 50.08) | 0.9998 |
| RbI | (4) | 18.07 (18.07, 18.07) | 51.92 (51.45, 52.38) | 1 |
| | (5) | 18.05 (18.04, 18.06) | 53.46 (53.13, 53.78) | 0.9999 |
| CsI | (4) | 18.07 (18.07, 18.07) | 59.12 (58.77, 59.46) | 1 |
| | (5) | 18.06 (18.06, 18.06) | 60.12 (59.93, 60.32) | 1 |

**Table 2 The multiple fitted $v_s$ for aqueous solutions of some alkali halide with equation (9)**

| Salt | $v_s / dm^3 \cdot mol^{-1}$ | R-square |
|---|---|---|
| NaCl | *0.08327* (0.07994, 0.08661) | 0.9998 |
| KCl | *0.06534* (0.06256, 0.06811) | 0.9999 |
| NaBr | 0.08892 (*0.08422*, 0.09361) | 0.9996 |
| KBr | *0.06627* (0.06380, 0.06875) | 0.9999 |
| RbCl | 0.06168 (0.05964, *0.06372*) | 0.9999 |
| CsCl | 0.06395 (*0.06111*, 0.06679) | 0.9999 |
| RbBr | 0.06224 (0.05981, *0.06467*) | 0.9999 |
| CsBr | 0.06617 (*0.06209*, 0.07025) | 0.9998 |
| RbI | 0.06484 (*0.06206*, 0.06761) | 0.9999 |
| CsI | 0.05677 (0.05409, *0.05944*) | 1 |

**Table 3 The multiple calculated $H$ of alkali halide by $(v_s - H \times v_w)$ and $v_s$**

| Salt | $H$ |
|---|---|
| NaCl | 3.5584 (3.5888, *3.5274*) |
| KCl | 1.9745 (*2.0066*, 1.9424) |
| NaBr | 3.2396 (3.2789, *3.2003*) |
| KBr | *1.7100* (1.7620, 1.6574) |
| RbCl | *1.6220* (1.6591, 1.5849) |
| CsCl | *1.0880* (1.1256, 1.0504) |
| RbBr | *1.3060* (1.3362, 1.2750) |
| CsBr | *0.7681* (0.7941, 0.7421) |
| RbI | 0.5612 (0.5872, *0.5357*) |
| CsI | 0.0177 (0.0371, *-0.0011*) |

**Table 4 The hydration number ($H_i$) and percentage ($P$) of hydrated ions**

| Aqueous Ions | $H_1$ and $P_1$ | $H_2$ and $P_2$ |
|---|---|---|
| $Na^+$ | 2 and 60 | 3 and 40 |
| $K^+$ | 1 and 90 | 0 and 10 |
| $Rb^+$ | 1 and 50 | 0 and 50 |
| $Cs^+$ | 0 and 100 | |
| $Cl^-$ | 1 and 90 | 2 and 10 |
| $Br^-$ | 1 and 80 | 0 and 20 |
| $I^-$ | 0 and 100 | |