

Partial Molar Volume and Compressibility of Alkali–Halide Ions in Aqueous Solution: Hydration Shell Analysis with an Integral Equation Theory of Molecular Liquids

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The partial molar volume and partial molar compressibility of alkali–halide ions in aqueous solution at infinite dilution are calculated based on the RISM–Kirkwood–Buff theory. The theoretical results are in qualitative agreement with the corresponding experimental data. The volume and compressibility values are decomposed into the volume-exclusion and electrostriction contributions. The volume-exclusion effect qualitatively determines the dependence of the partial molar volume on the ion size, whereas the electrostriction effect dominates in the size dependence of the partial molar compressibility. The partial molar volume and compressibility are further analyzed by using the hydration shell model which enables us to distinguish a contribution from each hydration shell. For the primary hydration shell, we can make contact with the classical models of ion hydration proposed by Frank–Wen and Samoilov. Water molecules in the immediate vicinity of an ion always give a negative contribution to its partial molar volume. The first hydration shell makes a negative contribution to the partial molar compressibility for the ions classified with the “positive hydration” in terms of Samoilov’s model and does the opposite contribution for those with the “negative hydration”. The reason the water structure around a negatively hydrated ion is more compressible is explained in terms of density fluctuations around the ions from a viewpoint of the Landau fluctuation formula for the thermodynamic response functions.

Introduction

Hydration of the alkali–halide ions in aqueous solution has been one of the most important subjects as a fundamental physicochemical process.^{1–3} The ion hydration is of interest also in close connection with many fields including biophysical chemistry. Most biomolecules have ionized groups, for example, some side chains in protein and phosphate groups in DNA. Irrespective of whether a solute has ionic centers or not, dissolved ions affect stability of the solute in solution through changes of the hydration structure perturbed by the ions.^{4,5}

The volumetric properties of ions are known as quantities in which ions manifest their specificity of hydration. It is very interesting that the partial molar volume is negative in cases for some small ions such as Li⁺.⁶ The phenomenon cannot be explained only by considering the ionic volume based on molecular geometry, i.e., the van der Waals volume or the intrinsic volume.⁷ The negative volume has been attributed to the so-called “electrostriction”, or a volume contraction in the

hydration shell due to the electrostatic field produced by an ion. The outstanding propensity of the partial molar compressibility of the ions to be negative has also been attributed to the electrostriction. The electrostriction thus must be directly related to the hydration structure around an ion.

The integral equation theory of liquids⁸ is a robust means which relates thermodynamic properties to the density pair correlation functions representing solvation structure. The partial molar volume of some solutes such as ions,^{9–11} hydrocarbons,^{12,13} and biomolecules^{13–17} in aqueous solutions has been calculated by means of the Kirkwood–Buff (KB) theory¹⁸ coupled with the integral equation theories of molecular liquids, the reference interaction site model (RISM) theory,¹⁹ and the reference hypernetted-chain (RHNC) theory.²⁰ However, the integral equations have not been applied to the calculation of the partial molar compressibility for any species. Only a few studies based on the molecular simulation have been reported for some organic molecules such as methane²¹ and alcohol^{22,23} but not for ions. In this paper, we calculate both the partial molar volume and the partial molar compressibility of alkali–halide ions in aqueous solution by means of the RISM–KB theory.

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For some alkali and halide ions, Li^+ , Na^+ , K^+ , F^- , and Cl^- , the partial molar volume has been obtained by the RISM-KB theory.¹¹ The results have shown that the electrostriction effect on the partial molar volume diminishes as the ionic size increases, and the degree of the electrostriction of a cation in water is smaller than that of an anion of the same size. Based on those results for the partial molar volume, we raise the following questions in the present paper. How does the electrostriction affect the partial molar compressibility of ions? What is the relation between the electrostriction of water in the vicinity of an ion (which probes the local density fluctuation of the solvent around a solute) and the partial molar volume and compressibility (which are thermodynamic properties)? To answer these questions, we calculate the partial molar volume and compressibility of alkali and halide ions (Li^+ , Na^+ , K^+ , Cs^+ , F^- , Cl^- , Br^- , and I^-) and examine their electrostriction effects. We also analyze them in terms of the hydration shell model²¹ which relates the hydration thermodynamic properties to the radial distribution functions characterizing hydration structure.

In connection with the hydration shell model, it is worthwhile to briefly explain two classical models proposed by Frank-Wen²⁴ and Samoilov,²⁵ which have been widely used in the interpretation of ion hydration. Suppose there is an ion in water. The electrostatic field of the ion tends to attract water molecules orienting them in accord with the ion charge sign. On the other hand, water molecules around the ion have orientational preference to form a hydrogen-bonding network. Therefore, hydration structure varies amply because of the interplay between the hydrogen bonding and the orientational force of the ion decreasing with separation from it. Let's divide the radial distance from the ion center into three concentric regions: small, medium, and large. When the distance is small, the electrostatic force is large enough to bind water molecules in the immediate vicinity of the ion. Such water molecules become less mobile than in the bulk. At a large distance, the ionic field is just a small perturbation to water-water interactions, and so it polarizes water in ordinary fashion. Between those two cases, there is an intermediate region where the two orientational forces balance each other to make water molecules in that region more "disordered" or more "fluid" compared to bulk water. Frank and Wen referred to these regions as A, C, and B regions, respectively. Which region appears in the primary hydration shell depends on the ion size. Small ions, such as Li^+ , Na^+ , and F^- , are known to have "region A" as the primary hydration shell, whereas the other alkali-halide ions have "region B" in their immediate vicinity because "region A" is hidden inside their cores. At the same time, Samoilov proposed essentially the same view of ion hydration, based on the dynamic property. Suppose that water molecules in the immediate vicinity of an ion are exchanging their positions with those in the bulk and that the exchange process is activated barrier crossing. The activation barrier will become higher for water molecules in "region A" compared to that in the bulk. Samoilov called ions having "region A" in their immediate vicinity as "positively" hydrated, because the activation energy change due to the ionic field is "positive". On the other hand, the activation energy should be reduced for water molecules in "region B", because the water molecules there are more "fluid". Such ions are called "negatively" hydrated.

The two models mentioned above have been successful in explaining the curiosity appeared in many experimental data of ion hydration, except for the partial molar volume and compressibility. The latter quantities were not so effective to

resolve the difference in hydration structure around ions. For example, it is reasonable to consider that "region A" contributes negatively to the partial molar volume, because the ion firmly binds water molecules to make the void space between the ion and solvent less. The contribution from "region B" seems to be also negative in an intuitive consideration based on the two states model of water structure: water is regarded as an equilibrium mixture of the ice-like tetrahedral and close packed structures, and the equilibrium seems to shift in "region B" toward the close packed structure in which water-water hydrogen bonds are weakened or distorted. So, it appears from the intuitive consideration that both "regions A and B" contribute in the same direction to the partial molar volume. Is such an intuitive consideration correct? How do those hydration regions contribute to the partial molar compressibility? These are the questions we study in the present paper.

2. Theory

2.1. Partial Molar Volume and Compressibility. According to the Kirkwood-Buff solution theory,¹⁸ the partial molar volume, \bar{V} , can be expressed in terms of the density pair correlation functions. The Kirkwood-Buff formula can be extended to a system consisting of polyatomic (site) molecules by being coupled with the RISM theory.¹⁹ The RISM-based expression (RISM-KB equation) for the partial molar volume at infinite dilution, \bar{V}^0 , is given in terms of the site-site direct correlation functions of solute(u)-solvent(v) pairs:^{14,26}

$$\bar{V}^0 = \chi_T^0 k_B T (1 - \rho_v C^{uv}) \quad (1)$$

where ρ_v and χ_T^0 are respectively the number density and the isothermal compressibility of solvent. The RISM-KB theory allows us to express χ_T^0 as

$$\chi_T^0 = [k_B T \rho_v (1 - \rho_v C^{vv})]^{-1} \quad (2)$$

In the above equations, $C^{mm'}$ denotes the sum of the site-site direct correlation functions integrated over the infinite volume space:

$$C^{mm'} = \sum_{\alpha, \gamma} \int_0^\infty C_{\alpha\gamma}^{mm'}(r) dr \quad (3)$$

where the subscripts in Greek label sites of molecule m of either solute or solvent.

The partial molar compressibility, $\bar{\beta}_T$, is defined as a pressure derivative of the partial molar volume:

$$\bar{\beta}_T = -\frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial P} \right)_{T,N} \quad (4)$$

We have obtained the RISM-based expression for the partial molar compressibility at infinite dilution, $\bar{\beta}_T^0$, by differentiating eq 1 with respect to the pressure:

$$\bar{\beta}_T^0 = \chi_T^0 \left[1 - \chi_T^0 k_B T \rho_v \left(1 + \rho_v^2 \left(\frac{\partial C^{vv}}{\partial \rho_v} \right) \right) + \chi_T^0 k_B T (\bar{V}^0)^{-1} \left(1 + \rho_v^2 \left(\frac{\partial C^{uv}}{\partial \rho_v} \right) \right) \right] \quad (5)$$

in which we employ the thermodynamic relation

$$\left(\frac{\partial f}{\partial P} \right)_{T,N} = \chi_T^0 \rho_v \left(\frac{\partial f}{\partial \rho} \right)_{T,\chi=0} \quad (6)$$

As is seen from eq 5, in such particular cases as a “solute” water molecule in “solvent” water, the partial molar compressibility $\bar{\beta}_T^0$ is reduced to the compressibility of pure solvent χ_T^0 , because $c^{uv} = c^{vv}$ and $\bar{V}^0 = 1/\rho_v$ in this case.

Although the definition of the partial molar compressibility by eq 4 is general, we are reluctant to adopt it in the case of alkali-halide ions for the following reason. As has been well regarded, the partial molar volume of some small ions, such as Li^+ , is negative. In this case, the partial molar compressibility does not purely represent the volume response to pressure because the factor $1/\bar{V}$ is negative. Therefore, we adopt another definition of the partial molar compressibility to avoid the confusion:

$$\bar{\beta}_T^* = -\frac{1}{|V|} \left(\frac{\partial \bar{V}}{\partial P} \right)_{T,N} \quad (7)$$

It is worthwhile to mention about additivity of the partial molar volume and compressibility. The partial molar volume at infinite dilution is an additive quantity. In other words, the partial molar volume of alkali halide \bar{V}_{MX}^0 is the sum of the volumes of alkali cation (\bar{V}_{M+}^0) and halide anion (\bar{V}_{X-}^0): $\bar{V}_{MX}^0 = \bar{V}_{M+}^0 + \bar{V}_{X-}^0$. On the other hand, the additivity does not hold for the partial molar compressibility. The partial molar compressibility of alkali halides $\bar{\beta}_{MX}^0$ is given as follows:

$$\bar{\beta}_{MX}^0 = \frac{\bar{V}_{M+}^0 \bar{\beta}_{M+}^0 + \bar{V}_{X-}^0 \bar{\beta}_{X-}^0}{\bar{V}_{MX}^0} \quad (8)$$

An alternative definition of the partial molar compressibility may be considered:

$$\bar{K}_T = -\left(\frac{\partial \bar{V}}{\partial P} \right)_{T,N} \quad (9)$$

In this article, we refer to \bar{K}_T as “partial molar volume-compressibility” to distinguish it from $\bar{\beta}_T$. Unlike the latter, \bar{K}_T is an additive quantity.

2.2. RISM Theory. As described in the previous subsection, calculation of the partial molar volume and compressibility requires the site-site pair correlation functions. They can be obtained from the RISM theory.^{8,19} For a two-component system consisting of solvent (v) and solute (u) at the infinite dilution limit, the RISM equation is decomposed into the solvent-solvent and solute-solvent equations:²⁷

$$h_{\alpha\gamma}^{vv}(r) = \sum_{\alpha',\gamma'} w_{\alpha\alpha'}^{vv} * c_{\alpha'\gamma'}^{vv} * (w_{\gamma'\gamma}^{vv} + \rho_v h_{\gamma'\gamma}^{vv}) \quad (10)$$

$$h_{\alpha\gamma}^{uv}(r) = \sum_{\alpha',\gamma'} w_{\alpha\alpha'}^{uu} * c_{\alpha'\gamma'}^{uv} * (w_{\gamma'\gamma}^{vv} + \rho_v h_{\gamma'\gamma}^{vv}) \quad (11)$$

where h , c , and w are the total, direct, and intramolecular correlation functions, respectively, the subscripts in Greek indicate site labels of a molecule, and “*” denotes a convolution integral in the real space. The intramolecular correlation function specifies the molecular geometry. These equations are iteratively solved with the closure relations, such as the HNC approximation

$$g_{\alpha\gamma}(r) = \exp \left[-\frac{u_{\alpha\gamma}(r)}{k_B T} + h_{\alpha\gamma}(r) - c_{\alpha\gamma}(r) \right] \quad (12)$$

where $u_{\alpha\gamma}$ is the pair potential between interaction sites of molecules and $g_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) - 1$ is the radial distribution function.

It is well documented that the RISM/HNC theory yields trivial results for the dielectric properties of a polar liquid.^{8,29} Therefore, we employ the DRISM theory,^{28,29} which ensures dielectric consistency for solution comprising ionic and polar molecular species. In the DRISM theory in the infinite dilution limit, the solute-solvent equation is identical to eq 11, whereas eq 10 is replaced by

$$h_{\alpha\gamma}^{vv}(r) = \sum_{\alpha',\gamma'} (w_{\alpha\alpha'}^{vv} + \rho_v D_{\alpha\alpha'}^{vv}) * c_{\alpha'\gamma'}^{vv} * (w_{\gamma'\gamma}^{vv} + \rho_v h_{\gamma'\gamma}^{vv}) + D_{\alpha\gamma}^{vv} \quad (13)$$

In the solvent-solvent equation, $D_{\alpha\gamma}$ is the term affecting the dielectric constant, which is expressed in the Fourier space as

$$\tilde{D}_{\alpha\gamma}(k) = -j_0(-kd_{\alpha x})j_0(-kd_{\alpha y})j_1(-kd_{\alpha z})j_0(-kd_{\gamma x})j_0(-kd_{\gamma y})j_1(-kd_{\gamma z})\rho_v \tilde{h}_c(k) \quad (14)$$

$$\rho_v \tilde{h}_c(k) = \left(\frac{\epsilon - 1}{y} - 3 \right) \exp(-0.1k^2) \quad (15)$$

where j_n is the n th order spherical Bessel function, ϵ is the dielectric constant of solvent, and $y = 4\pi\rho_v\mu^2/9k_B T$ is the dipole density.

The density derivatives of the pair correlation functions can be obtained by means of the Yu-Karplus method³⁰ as well as numerical differentiation. In the former, the density derivatives of pair correlation functions are calculated by using the analytical derivatives of the DRISM/HNC equation with respect to the density. In the latter, they are numerically calculated from the DRISM/HNC theory at several densities. The two approaches have been checked to provide quantitatively the same result. In this study, we calculate the density derivative by using the first-order finite difference:

$$\left(\frac{\partial f}{\partial \rho_v} \right) \approx \left(\frac{f(\rho_v + \Delta\rho_v/2) - f(\rho_v - \Delta\rho_v/2)}{\Delta\rho_v} \right) \quad (16)$$

2.3. Models. For the site-site pair potential $u_{\alpha\gamma}(r)$, we employ the standard model which consists of the Lennard-Jones and electrostatic interaction terms:

$$u_{\alpha\gamma}(r) = 4\epsilon_{\alpha\gamma} \left[\left(\frac{\sigma_{\alpha\gamma}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\gamma}}{r} \right)^6 \right] + \frac{q_{\alpha}q_{\gamma}}{r} \quad (17)$$

For water, we employ the SPC/E model,³¹ modified with the O-H repulsive term of Pettitt and Rossky³² to optimize the RISM description of hydrogen bonding. For the ion-water interaction, we use the parameters proposed by Kinoshita and Hirata³³ which are based on the parametrization of Pettitt and Rossky.³⁴ The site charges and the Lennard-Jones size and energy for all of the species are listed in Table 1.

Other input data to the DRISM/HNC theory are the number density $\rho_v = 0.03333 \text{ \AA}^{-3}$, temperature $T = 298.15 \text{ K}$, and dielectric constant $\epsilon = 78.4$ of ambient water. The density derivatives are calculated using density step $\Delta\rho_v = 3 \times 10^{-5} \text{ \AA}^{-3}$.

3 Results and Discussion

3.1. Partial Molar Volume and Compressibility of Alkali Halides. Table 2 lists the partial molar volume and compressibility of the individual ions of the alkali and halide series at

TABLE 1: Site Charges and Lennard-Jones Potential Parameters for Water–Water and Ion–Water Interactions

α	$\sigma_{\alpha\text{O}}$ (Å)	$\epsilon_{\alpha\text{O}}$ (kcal/mol)	$\sigma_{\alpha\text{H}}$ (kcal/mol)	$\epsilon_{\alpha\text{H}}$ (kcal/mol)
O	3.166	0.156	1.6 ^a	0.2 ^a
H	1.6 ^a	0.2 ^a	0.0	0.0
Li ⁺	2.28	0.14	0.87	0.14
Na ⁺	2.72	0.13	1.31	0.13
K ⁺	3.16	0.13	1.75	0.13
Cs ⁺	3.45	0.13	2.04	0.13
F [−]	2.95	0.29	1.54	0.29
Cl [−]	3.55	0.36	2.14	0.36
Br [−]	3.75	0.36	2.34	0.36
I [−]	4.03	0.36	2.61	0.36

^a Only for the repulsive term**TABLE 2: Partial Molar Volume (cm³ mol^{−1}) and Compressibility (10^{−9} Pa^{−1}) of Alkali–Halide Ions**

	$V^0(V_{\text{MX}}^0)^a$		$\beta_T^{*0}(\beta_{T,\text{MX}}^{*0})^a$	
	theor	expt ^b	theor	expt ^c
Li ⁺	−8.5 (12.8)	−11.2 (17.0)	−2.79 (−2.83)	
Na ⁺	4.4 (25.6)	−7.4 (16.4)	−1.07 (−0.67)	(−3.02)
K ⁺	19.0 (40.3)	3.4 (26.5)	0.58 (−0.04)	(−1.56)
Cs ⁺	30.3 (51.6)	15.5 (39.2)	0.67 (−0.15)	(−0.89)
F [−]	1.7 (5.8)	3.3 (−3.5)	−14.84 (−4.46)	(−20.46)
Cl [−]	21.2 (25.6)	23.7 (16.4)	−0.59 (−0.67)	(−3.02)
Br [−]	28.2 (32.6)	30.2 (23.5)	−0.48 (−0.56)	(−1.69)
I [−]	39.8 (44.2)	41.4 (35.1)	−0.41 (−0.47)	(−0.79)

^a The values in parentheses are of alkali chloride (MCl) for alkali cation and of sodium halide (NaX) for halide anion. ^b Reference 35
^c Calculated from the data in refs 35 and 36

infinite dilution in aqueous solution, calculated from the RISM-KB theory along with the corresponding experimental data.^{35,36} The values for salts, or pairs of alkali and halide ions, are also exhibited in the parentheses for direct comparison with the experimental results in order to avoid some ambiguity associated with the experimental determination of the contribution from an individual ion. The counteranion is fixed to the sodium ion for the series of halide ions, whereas the anion is fixed to the chloride ion for the series of alkali ions. The contribution from an individual ion to the partial molar volume can be obtained experimentally from the ultrasonic vibration potentials³⁵ without any assumption as to the value for a given ion or the ratio of values for any pair of ions.^{6,37} However, the experimental determination of the individual partial molar compressibility requires such assumptions that are not free from some ambiguity. Considering the situation, it is more reasonable to compare our results with the experimental data for alkali halide pairs. The theoretical results for the partial molar volume are in fair agreement with experiment. For the partial molar compressibility, the agreement is worse. Compared to the partial molar volume, the partial molar compressibility is apparently more sensitive to the quality of models and approximations employed in the theory, because it is a higher order property with respect to the density derivative of the free energy. Apart from the quantitative aspect, the theory reproduces the features of the partial molar compressibility observed in experimental fairly well: the propensity to be negative and the same dependence on the ionic radius.

The small, negative in some cases, values for the partial molar volume and the negative values for the partial molar compressibility of ions have been often attributed to the electrostriction due to the ionic field. To extract the electrostriction effects of ions, we calculated the partial molar volume and compressibility of hypothetical solutes obtained from the ions by removing their charge. The partial molar volume and compressibility of such

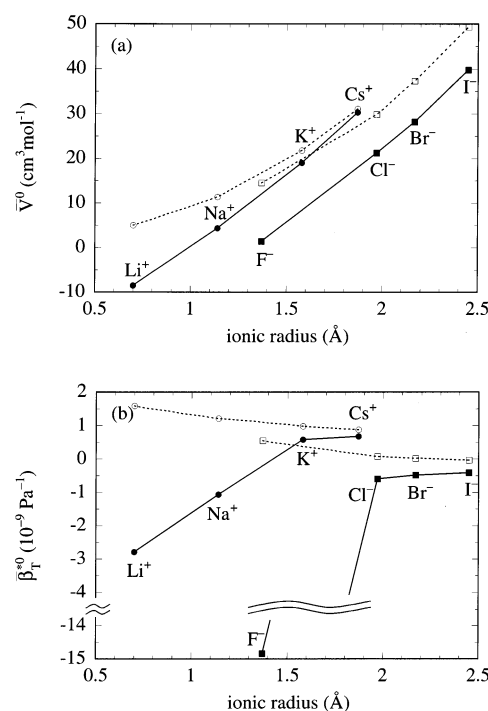


Figure 1. (a) partial molar volume \bar{V}^0 and (b) compressibility β_T^{*0} of the individual alkali and halide ions plotted against the ionic radius (solid lines with solid symbols). Contributions from the volume-exclusion effects (dotted lines with open symbols). The differences between solid and open symbols correspond to the electrostriction effect.

a solute originate essentially from the volume-exclusion effect. In Figure 1, the partial molar volume (a) and compressibility (b) of the individual ions are plotted against their ionic radius, and those of the hypothetical solutes are shown as well. The difference in the value for the hypothetical solutes derived from a cation and an anion of the same ionic radius arises from the difference in their Lennard-Jones potentials and is not essential in discussing the volume-exclusion effect. The difference of the partial molar volume and compressibility for the ion from those for the corresponding hypothetical solute is regarded as the electrostriction effect.

Figure 1a shows that the volume-exclusion effect on the partial molar volume becomes larger as the ion size increases, whereas the electrostriction effect is always negative and becomes smaller with the increase of the ionic size. The dependence of the electrostriction effect on the ionic radius is consistent with the corresponding change in the strength of the ion electrostatic field. By comparison between cations and anions of the same ionic radius, it is seen that the electrostriction effect for an anion is greater than that for a cation. This is explained as follows: because a water molecule has a negative partial charge at the center (at the oxygen) and positive partial charges on the periphery (at the hydrogen sites), it is more sensitive to the negative than to positive electrostatic field. The partial molar volume, the sum of the volume-exclusion and electrostriction effects, becomes larger as the ionic size increases. The electrostriction affects the magnitude of partial molar volume, but it does not affect the dependence on the ionic size.

As is seen in Figure 1b, the volume-exclusion effect on the partial molar compressibility becomes smaller as the ionic size increases, whereas the electrostriction effect is always negative and becomes smaller as the ionic size increases. Similarly to the case of the partial molar volume, the electrostriction effect on the partial molar compressibility for an anion is greater than that for a cation of the same ionic radius. The volume-exclusion

and electrostriction effects compensate each other, or rather, the electrostriction dominates over the volume-exclusion effect. As a result, the electrostriction not only affects the magnitude of the partial molar compressibility but also determines its dependence on the ionic size, unlike the partial molar volume. This is the origin of the common understanding that the partial molar compressibility is often more sensitive to solute–solvent interactions than the partial molar volume.³⁸

3.2. Hydration Shell Analysis. In this subsection, we analyze the partial molar volume and compressibility by using the hydration shell model proposed by Matubayasi and Levy,²¹ which enables us to make investigation with respect to each solvation shell. The partial molar volume can be expressed in terms of the radial distribution function $g^{uv}(r)$ between two arbitrary sites of solute and solvent (instead of the direct correlation functions summed over all solute and solvent sites):

$$\bar{V}^0 = \chi_T^0 k_B T - \int_0^\infty (g^{uv}(r) - 1) dr \quad (18)$$

The local partial molar volume $\bar{V}^0(\lambda)$ is defined by introducing a cutoff at the distance λ :

$$\bar{V}^0(\lambda) = \bar{V}^{id} - \int_0^\lambda (g^{uv}(r) - 1) dr \quad (19)$$

where the ideal part $\bar{V}^{id} = \chi_T^0 k_B T$ at temperature $T = 298.15$ K amounts to $1.4 \text{ cm}^3 \text{ mol}^{-1}$. For a local value of the partial molar compressibility, it is convenient to employ the partial molar volume-compressibility \bar{K}^0 rather than the partial molar compressibility β^0 , because β^0 does not have the additivity with respect to the volume space. The local partial molar volume-compressibility $\bar{K}^0(\lambda)$ is defined by differentiating eq 19 with respect to the pressure:

$$\bar{K}^0(\lambda) = \bar{K}^{id} + \int_0^\lambda \left(\frac{\partial g^{uv}(r)}{\partial P} \right) dr, \quad (20)$$

where the ideal part, $\bar{K}^{id} = -k_B T (\partial \chi_T^0 / \partial P)$, has the value of $4.0 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$.

Here, we should comment on the difference between the two definitions of the partial molar volume given by eqs 1 for $\bar{V}_{(C)}^0$ and 18 for $\bar{V}_{(G)}^0$. Their difference T^0 expressed by the equation^{10,11} $\bar{V}_{(G)}^0 = \bar{V}_{(C)}^0 - T^0$ is a product of the solute charge and such solvent properties as the dielectric constant. For 1–1 electrolytes such as alkali halides (MX), the relation $T_{M+}^0 = -T_{X-}^0$ holds, and T^0 does not contribute to the partial molar volume of the ion pair \bar{V}_{MX}^0 . In the present system, the difference is $T_{M+}^0 = -2.2 \text{ cm}^3 \text{ mol}^{-1}$ and $\partial T_{M+}^0 / \partial P = -6.4 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$. We omit these terms in the following discussion because they do not depend on the ionic species.

In Figure 2, we depict the local partial molar volume $\bar{V}^0(\lambda)$ of the ions as a function of the cutoff distance λ . The term $\bar{V}^0(0)$ is the ideal contribution to the partial molar volume. The first-peak rise in $\bar{V}^0(\lambda)$ is due to the volume exclusion by ion itself, i.e., $4/3\pi\lambda^3$. The subsequent oscillations reflect the local density fluctuation of water around the ion. There is no difference in the features between positively hydrated (Li^+ , Na^+ , and F^-) and negatively hydrated ions (K^+ , Cs^+ , Cl^- , Br^- , and I^-). For all of the ions, the water molecules in the primary hydration shell contribute negatively to the partial molar volume.

Figure 3 shows the local partial molar volume-compressibility \bar{K}^0 of the ions. The value of $\bar{K}^0(0)$ is of the ideal term of partial molar volume compressibility. In the present model, in which the solute itself is not compressed by pressure, the solute core

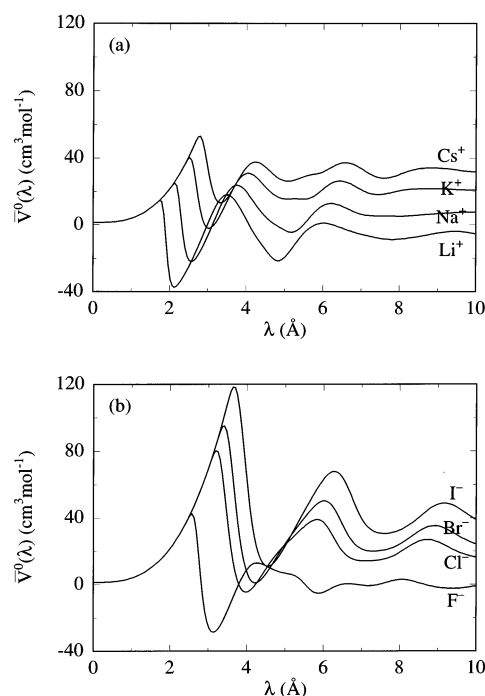


Figure 2. Local partial molar volume $\bar{V}^0(\lambda)$ defined by eq 20 plotted against the cutoff radius λ : (a) alkali cations and (b) halide anions.

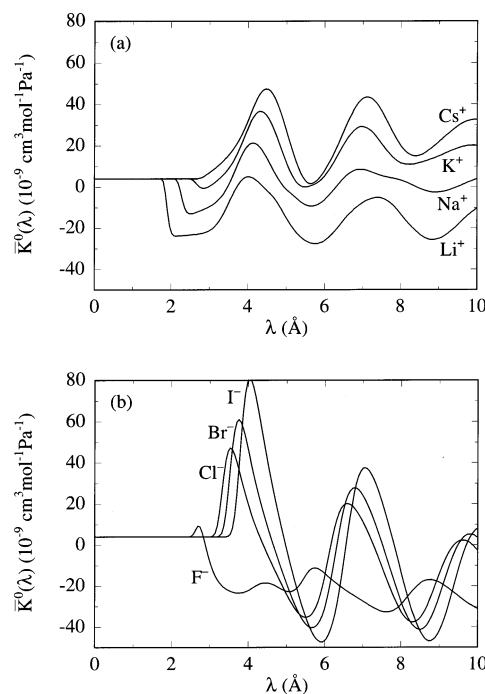


Figure 3. Local partial molar volume compressibility $\bar{K}^0(\lambda)$ defined by eq 20 plotted against the cutoff radius λ : (a) alkali cations and (b) halide anions.

does not contribute to the partial molar volume-compressibility. A clear distinction between positively and negatively hydrated ions is found in the contribution from the water molecules in the primary hydration shell to the partial molar volume compressibility. The primary hydration shell of the positively hydrated ions makes negative contribution, or is less compressible, whereas that for the negatively hydrated ions is more compressible. In naive consideration, the behavior exhibited in the compressibility by the negatively hydrated ions is contradictory to that observed in the partial molar volume: if the partial molar volume is less, the compressible space should also be

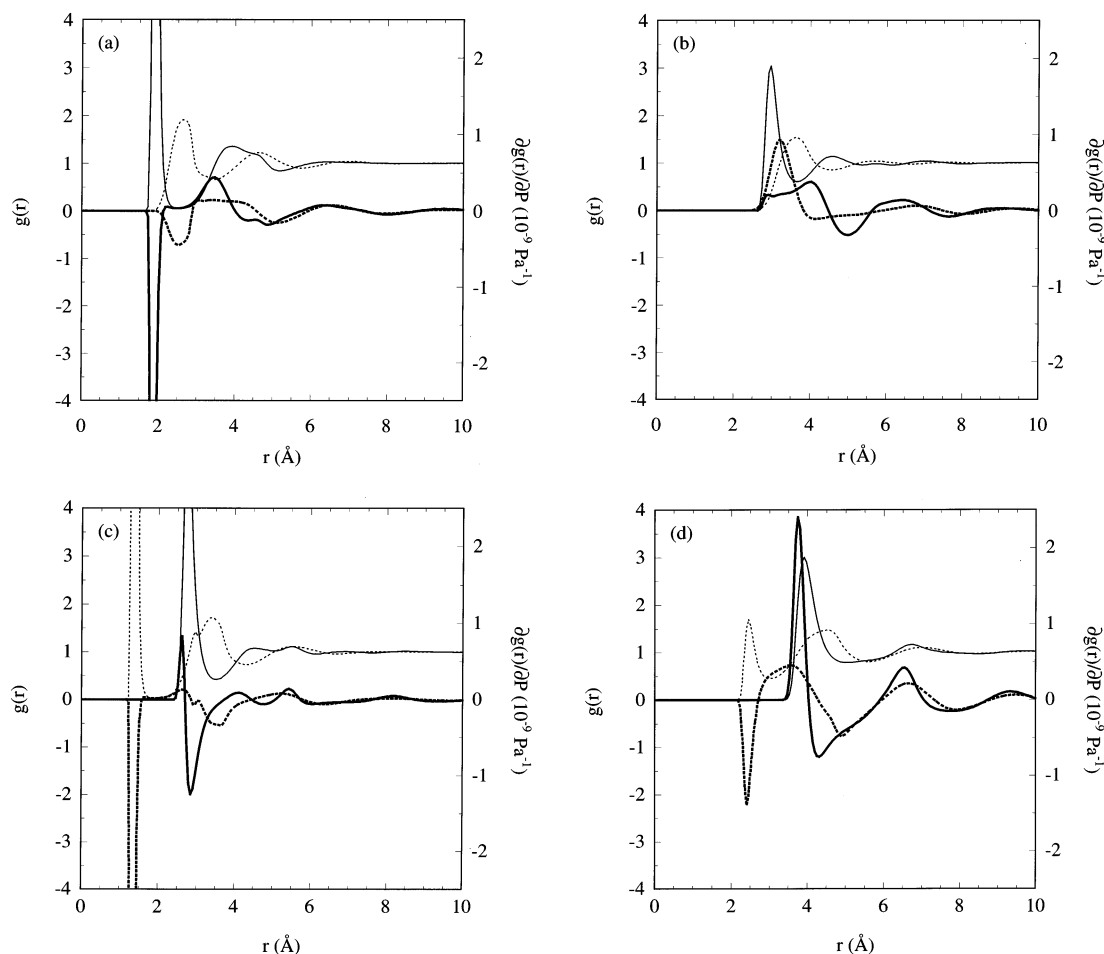


Figure 4. Ion–water oxygen (solid lines) and hydrogen (dotted lines) radial distribution functions $g_{\alpha\gamma}(r)$ (thin lines) and their pressure derivatives $\partial g_{\alpha\gamma}(r)/\partial P$ (thick lines): (a) positively hydrated cation Li^+ , (b) negatively hydrated cation Cs^+ , (c) positively hydrated anion F^- , and (d) negatively hydrated anion I^- .

less. The question may not be solved by just considering the average density around the region. Its fluctuation must be taken into account, because the compressibility is closely related to the dispersion of the density fluctuation according to Landau.³⁹

The density fluctuation around an ion is probed by the radial distribution functions, and the local partial molar volume-compressibility is related directly to their derivative with respect to the pressure given by eq 20. In the following subsection, we look into the radial distributions and their pressure derivatives and discuss the microscopic origin of the difference manifested in the volumetric properties between positively and negatively hydrated ions.

3.3. Hydration Structure and Its Response to Pressure.

Shown in Figure 4 are the radial distribution functions of water around the ions and their derivatives with respect to the pressure. We pick out the four ions, (a) Li^+ , (b) Cs^+ , (c) F^- , and (d) I^- , as the representatives of the positively hydrated cations (Li^+ , Na^+), the negatively hydrated cations (K^+ , Cs^+), the positively hydrated anions (F^-), and negatively hydrated anions (Cl^- , Br^- , and I^-), respectively. The features of radial distribution functions and their derivatives with respect to the pressure of the ions belonging to the same group are similar to each other.

As is the case with the local partial molar volume discussed in the preceding subsection, there is no qualitative difference between the structural features of the radial distribution functions for positively and negatively hydrated ions. However, the peaks of water oxygen and hydrogen become lower with the increase of the ionic size, both for cations and anions. The cation is

hydrated primarily by the oxygen and electrostatically repels the hydrogen, whereas the anion has such a hydration structure that one of the hydrogens faces the ion because of the anion–hydrogen electrostatic attraction.

The derivatives of the radial distribution function with respect to the pressure exhibit a clear difference between positively and negatively hydrated ions. For the positively hydrated cation Li^+ , the distribution of water molecules in the primary hydration shell decreases with increasing pressure. On the other hand, for the negatively hydrated cation Cs^+ , it somewhat increases. This can be explained according to the concept of ion hydration by Frank and Wen²⁴ as follows. The water molecules in the vicinity (“region A”) of the positively hydrated ion are highly compressed and aligned along the electrostatic field directed radially from the ion. Pressure primarily causes an increase in the density of water; however, the water molecules in “region A” are resistant to pressure because of the steric and dipole–dipole repulsions between themselves. On the other hand, “region A” is hidden for the negatively hydrated ion, and the first solvation shell for those ions becomes “region B” which is considered to be more “disordered” or “fluid”. The first peak corresponding to “region B” is characterized by the larger second moment or dispersion as compared to that of “region A”. The increased dispersion of the local density fluctuation would be compressed by pressure to cause a positive change in the first peak, as can be observed in Figure 4 parts b and d. Thus, the increased local compressibility in “region B” is caused not by the static density change of water due to the ions but by the increased density

fluctuation. This interpretation for the compressibility corresponds to Landau's fluctuation formula for thermodynamic response functions³⁹ and represents its microscopic realization for ion hydration.

Conclusion

In this paper, we have presented a theoretical study for the partial molar volume and compressibility of alkali-halide ions in aqueous solution by means of the RISM–Kirkwood–Buff theory. We have shown that the partial molar compressibility is more sensitive to ion–water interactions than the partial molar volume in the following macroscopic and microscopic respects. Macroscopically, the difference between the partial molar volume and compressibility is found in the effects of electrostriction on those quantities. The electrostriction affects the magnitude of the partial molar volume, but it does not change the qualitative dependence on the ionic size, which is essentially determined by the volume-exclusion effect. For the partial molar compressibility, the electrostriction dominates over the volume-exclusion effect so that it determines the dependence on the ionic size. The effect would be more significant for some series of organic ions such as alkylammonium ions. In the microscopic aspect, water molecules in the primary hydration shell always make a negative contribution to the partial molar volume irrespective of whether the ions are hydrated positively or negatively. Thus, the partial molar volume does not resolve the characteristics of ion hydration. On the other hand, the local compressibility can resolve such characteristics. Positively hydrated ions make water molecules in their immediate vicinity less compressible, whereas negatively hydrated ions give opposite contributions. These results give us an interesting picture of ion hydration: a positively hydrated ion is surrounded by a denser and more “rigid” hydration shell as compared to bulk water, whereas a negatively hydrated ion is surrounded by a denser but more “fluctuating” hydration shell.

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