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Choice of the center of water molecules in calculations of partial molar volume of single ions immersed in water: A molecular simulation study

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ABSTRACT

In the Kirkwood–Buff theory, the center of each solvent molecule can be arbitrarily chosen. However, this arbitrariness is not obvious in the calculation of the Kirkwood–Buff integral for a single ion. Actually, the Kirkwood–Buff integral depends on the choice of the center of a solvent molecule, if each solvent molecule has a dipole moment and the solute has a net charge. A few examples based on molecular dynamics simulations are shown. A surrogate definition for the center of a water molecule is also shown. A good agreement between the calculated and experimental values of partial molar volumes for single ions is observed.

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1. Introduction

Hydration is a fundamental process in various chemical processes in aqueous solutions, such as electron-transfer reactions, optical spectra, stabilization of colloidal particles, and conformational changes of biomolecules [1–19]. Partial molar volume is one of the most important thermodynamic quantities related to hydration [20–35]. This quantity is directly correlated to the pressure dependence of system behaviors. For example, the application of pressure to a solution induces association of the solutes if the partial molar volume decreases because of the association process. This type of phenomenon is related to the pressure denaturation of proteins, the pressure dependence of solubility, etc.

The partial molar volume of a single solute in water has been studied using various methods, such as density measurement [36,37], because the partial molar volume is thought to reflect the hydration structure. The partial molar volume of a single ion has been measured by the UVP method [38,39]. In the case of a single ion, the hydration water is compressed by ion-water interactions, and negative volumes are observed for small ions. These phenomena are referred to as electrostriction.

There are some theoretical studies for the partial molar volume of a single ion in water. Kusalik and Patey determined the volumes on the basis of the RHNC theory [33]. Hirata and coworkers calculated the volumes using the RISM–HNC theory [23,34]. The RISM–HNC theory gives the total correlation functions and the direct correlation

functions between solute and solvent molecules. The partial molar volumes are calculated by using the direct correlation functions [20,21,23]. Then, the value for the partial molar volume does not depend on the definition of molecular center, although the value does not become unique when the value is calculated using the total correlation function, as we mention later. On the other hand, the integral equation theories are based on approximations. Actually, Fedorov and co-workers are studying the correction for the RISM theory [29]. So, it is important to discuss the validity of the results obtained from integral equation theories by molecular simulations. Patel et al. calculated the partial molar volumes of a few single ions using molecular dynamics simulation, and showed that their results are in good agreement with experimental values [35]. However, they did not discuss the influence of the choice of the solvent molecular center. In this study, to address the problem of the choice of the molecular center, we attempted to evaluate the partial molar volume of a single ion in water using a combination of molecular dynamics simulations and Kirkwood–Buff-like theory.

In the Kirkwood–Buff theory [40], partial molar volume is related to the integral of the radial distribution function. According to literature, this theory does not depend on the choice of molecular center [41–43]. Here, we briefly discuss the partial molar volume of a neutral solute in water. The shape of the radial distribution function depends on the choice of molecular center. For example, the radial distribution function between a solute and a hydrogen atom of a water molecule differs from that between a solute and the oxygen atom of a water molecule. However, despite this difference, the integrals of the radial distribution functions are independent of the choice of molecular center for neutral solutes, and consequently, partial molar volumes are also independent.

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However, we found that this arbitrariness didn't hold for the system that contained solutes with nonzero net charge and solvent molecules that are polar molecules expressed as an interaction site model such as TIP3P water. In this case, the partial molar volume of these solutes depends on the definition of the solvent molecular center.

In this paper, we indicate this problem with the results for the cases of simple ions and subsequently discuss two questions related to the Kirkwood–Buff theory: (1) Why do partial molar volumes of charged solutes depend on the choice of the water molecule center? (2) How can we calculate the partial molar volumes of charged solutes?

In Section 2, we explain the methods used to calculate the partial molar volume using a molecular simulation with a Kirkwood–Buff-like theory. In Section 3, we present the results and discuss the two previously stated questions.

2. Methods

The Kirkwood–Buff theory [40] is widely used for theoretical calculations of the partial molar volume of a solute under an infinite dilution condition [32,34,35,41,42,44]. According to this theory, the partial molar volume can be expressed by the following equations:

$$\bar{V}_p = \kappa_T k_B T - G, \quad (1)$$

$$G = \int_0^\infty 4\pi r^2 [g(r) - 1] dr \quad (2)$$

where \bar{V}_p is the partial molar volume of the solute, κ_T is the isothermal compressibility of pure solvent, k_B is the Boltzmann constant, T is the temperature, and G is the Kirkwood–Buff integral, which is defined in Eq. (2) as the integral of $g(r) - 1$, where $g(r)$ is a radial distribution function between the solute and solvent. The first term in the right-hand side of Eq. (1) is an ideal term and does not depend on the solute; it depends only on the solvent properties. Therefore, we define the quantity ΔV as follows:

$$\Delta V = \bar{V}_p - \kappa_T k_B T = -G. \quad (3)$$

ΔV is the quantity we are interested in. $g(r)$ in Eq. (2) is defined in a grand canonical ensemble in the Kirkwood–Buff theory. Therefore, $g(r)$ obtained from the NVT ensemble, or the NPT ensemble cannot be used to calculate G [45]. Molecular simulation is usually performed under the NPT condition or the NVT condition, which makes the use of these equations inconvenient.

In this study, we used the following equation instead of the Kirkwood–Buff equation [41,42]:

$$\Delta V = \frac{\int_{r<\lambda} 4\pi r^2 [1 - \rho(r)/\rho_0] dr}{1 - N^{-1} \int_{r<\lambda} 4\pi r^2 \rho(r) dr}, \quad (4)$$

where $\rho(r)$ is the distribution of solvent density at a distance r from the solute and ρ_0 is the bulk solvent density, which is equal to N/V , where N is the number of solvent molecules and V is the volume of the system, and λ is the integral cutoff distance, which is determined so that the obtained ΔV value converges well. Using this equation, we can calculate the value of the partial molar volume from the distribution of solvent molecules' density around a solute molecule. The density distribution is related to $g(r)$ as $\rho(r) = \rho_0 g(r)$. So, using Eq. (4), we can calculate the partial molar volume from radial distribution functions like the Kirkwood–Buff theory, although this radial distribution function is defined in a canonical ensemble unlike the Kirkwood–Buff theory. We performed molecular dynamics simulations to obtain the $g(r)$ between the solute and the solvent.

Molecular dynamics simulations were performed with the GROMACS software, version 4.5.5 [46]. We chose five ions (Na^+ , K^+ , Cl^- , Br^- , and Ca^{2+}) as solutes, and the solvent was water. Water was modeled using the TIP3P potential, which consists of the Lennard–Jones potential, a negative charge on an oxygen atom, and a positive charge on a hydrogen atom; we used the OPLSAA force field [47] for ions. We also prepared a neutral solute labeled as Na^0 that has the same Lennard–Jones potential as Na^+ (OPLSAA), but has no charge. Table 1 shows the force-field parameters used in the simulations. Each simulation box had 1500 water molecules and one solute ion. The temperature was 298 K, and the pressure was 1 atm. We adopted the Nose–Hoover thermostat [48,49] for temperature control and the Parrinello–Raman balostat [50] for pressure control. ρ_0 in Eq. (4) was calculated as $N\langle V \rangle_p$, where $\langle V \rangle_p$ means the average value of the system volume V . Although electroneutrality conditions do not hold for systems that contain a single ion, we used the particle mesh Ewald method [51] to calculate the coulombic interaction. After a 200 ps equilibration time, 100 ns simulations were performed. These simulations provided a trajectory from which we obtained $g(r)$ using a program included in the GROMACS package, and evaluated the partial molar volume of ions using Eq. (4). We defined the centers of water molecules two ways: one method was based on oxygen atoms; and the other was based on hydrogen atoms. Although each water molecule has two hydrogen atoms, only one of them was used to calculate the $g(r)$. Because of the symmetric structure of water molecules, the results do not depend on the choice of hydrogen atom.

3. Results and discussion

Fig. 1 shows the dependence of the partial molar volumes of five ions and one neutral solute on the integral cutoff distance λ obtained using Eq. (4). In each solute's case, two lines are generated that correspond to definitions of the water molecular centers: the oxygen atom and one of the hydrogen atoms. All values of partial molar volumes in Fig. 1 converged well at 15 Å. Two converged values did not agree, except for the values for the neutral solute. These results suggest that the partial molar volume of a single ion depends on the definition of the solvent molecular center. In the case of cations, the partial molar volumes obtained from distributions of hydrogen atoms are larger than those obtained from distributions of oxygen atoms. In contrast, in the case of anions, these relationships are opposite. The absolute values of the differences between the two partial molar volumes are almost same for monovalent ions ($\sim 36 \text{ \AA}^3$), whereas for Ca^{2+} ions, this value ($\sim 72 \text{ \AA}^3$) is twice of that of the monovalent case. Thus, unlike the case of a neutral solute, the values of the partial molar volumes depend on the definition of the molecular center when the solutes have a nonzero net charge.

To facilitate understanding of these differences in the partial molar volumes, Eq. (4) is rewritten in a more intuitive form as

$$\Delta V = V - N \frac{V - V_{\text{sphere}}(\lambda)}{N - N_{\text{sphere}}(\lambda)}, \quad (5)$$

Table 1
Force-field parameters for water molecule and solutes.

Site	σ (Å)	ϵ (kJ mol ⁻¹)	Charge
O	3.15061e+00	6.36386e-01	-0.834
H	0.00000e+00	0.00000e+00	0.417
Na^+	3.33045e+00	1.15980e-02	1.000
K^+	4.93463e+00	1.37235e-03	1.000
Cl^-	4.41724e+00	4.92833e-01	-1.000
Br^-	4.62376e+00	3.76560e-01	-1.000
Ca^{2+}	2.41203e+00	1.88136e+00	2.000
Na^0	3.33045e+00	1.15980e-02	0.000

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