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The Solvation Thermodynamic Functions In The Mean Spherical Approximation (MSA): Behaviour Near The Solvent Critical Region

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Abstract

Explicit expressions of the MSA solvation thermodynamic functions, the Gibbs free energy, energy, enthalpy, entropy, apparent molar heat capacities and partial molar volume are derived starting from the Helmholtz free energy. The thermodynamic consistency of the MSA solvation thermodynamic functions are discussed. Some limiting behaviours of the MSA solvation thermodynamic functions are compared with the Born theory. The effect of explicit solvent structures in the MSA theory on the Gibbs and the Helmholtz free energy is given special attention. Model Calculations of alkali and halide ions in water are carried out and compared with experimental data. The apparent molar heat capacities at constant volume and pressure, and the partial molar volume are calculated along an isobaric line to the critical region of a dipolar liquid. A great deal of insight has been gained on the behaviour of the solvation thermodynamic properties near the critical region of dipolar solvent. It helps to explain some of the recent experimental observations.

I. Introduction

The theory of electrolyte solution has been an active research subject for a long time^{1,2}. Recent efforts are focused on obtaining structures and thermodynamic functions starting from molecular models of solvents which are treated explicitly^{3,4}. There is little doubt that ion solvation in a molecular solvent is a complicated process. Sophisticated modeling which implies extensive numerical solution of integral equations⁴ and large scale simulations are needed to get accurate structural information and thermodynamic properties^{5,6,7}. However we believe that some simple analytical theories can still capture some of the dominant features in the solvation process, of which the Born⁸ theory is a beautiful example. It is the propose of this paper to show that an analytical theory known as the Mean Spherical Approximation(MSA) is valuable to gain insight on the solvation thermodynamics.

Indeed, the detailed theoretical and simulation studies^{5,6,7} show that in spite of sophisticated solvent re-organization and polarization around ions the Helmholtz solvation free energy of an ion in a polar solvent is approximately a quadratic function of ion charge. This observation is strongly supported by experimental data^{9,10}. One can understand it by examing a well known effects, such as, the dielectric saturation^{11,12,13} near the ion. For some systems, the dielectric saturation of solvent around the ion may not be very important or may be cancelled by an opposing effect, for example, the electrostriction¹⁴. There are simple relations between the internal energy and the Helmholtz free energy in some simple theories such as that due to Born⁹, which hold approximately as shown by the simulation and sophisticated theories. For example, the Helmholtz free energy is half of the internal energy. Having these basic features the simple Born equation may somehow be able to give a good representation of the solvation free energy. It seems that there are indeed ways to find a consistent set of radii to fit experimental data of some solvation thermodynamics using the Born equation^{15,16}. On the other hand, the Born theory is, after all, an over simplified theory, in which the solvent is treated as dielectric continuum. The solvent reorientation and structure breaking that occurs

when an ion is dissolved can not be properly accounted by the continuum model. The MSA is an analytically tractable Hamiltonian models which may provide useful information on the solvation of ion in dipolar solvent^{17,18}. Basically the MSA is a linear theory but it treats the excluded volume consistently³. It has also the remarkable property of satisfying the infinite charge, large density limits of Onsager¹⁹. The MSA Helmholtz free energy of charging a cavity in a dipolar hard sphere liquid was calculated by Chan et al²⁰. The result is of the form of the Born formula with a modified ion size dependent on solvent properties. In this paper, we will obtain other thermodynamic functions based on the Helmholtz free energy. Indeed, the MSA gives new physical interpretation to some of the solvation thermodynamic functions, for example, the MSA Gibbs free energy has two terms, one due to the ion-dipole interaction, and another due to the solvent re-organization, i.e., the structure breaking effect. As was shown by Garisto and Patey²¹ that the MSA Helmholtz free energy is very close to the LHNC in a wide range of dipole densities. This is consistent with earlier observations that the MSA gives reasonable thermodynamic properties though the structure may not be very good³. Recently, Blum and Fawcett²² find the MSA is quite useful in estimating the outer-sphere contribution to the activation parameters for homogeneous electron-transfer reactions, and also in calculating solvation Gibbs free energy in various solvents.

Experimental data of electrolyte solutions at high temperature and pressure has recently become available^{23,24}. The heat capacities and partial molar volume show very interesting behavior near the critical region of water. There have been attempts²⁵ to apply the Born theory to understand experimental observations. It is found that the Born theory does reasonably well. In this paper, the newly obtained formulas are used to explain the experimental observations using the MSA.

In the first section, we derive expressions for thermodynamic functions, such as, the Gibbs free energy, internal energy, entropy, heat capacities from the Helmholtz free energy. The thermodynamic consistency of the MSA solvation thermodynamic functions is discussed. In

the second part, the free energy and entropy are calculated and compared with experimental data of alkali and halide ions in water at 298K. The dipole moment is adjusted to fit the MSA dielectric constant to the experimental value, and the dipole moment so obtained is considered to be the effective liquid phase dipole moment of water. We also calculate the heat capacities and partial molar volume at temperatures and pressures near the critical point of a dipolar liquid.

II. Theory

A. The solvation Helmholtz and Gibbs free energies, entropies and chemical potentials

The solvation Gibbs free energy is the standard free energy change of transferring an ion from the gas phase at 1 atm to solvent (mole fraction standard state). We assume that the standard free energy change for such a process can be broken down as,

$$\Delta G^0 = \Delta G^{n,0} + \Delta G^{el,0}, \quad (1)$$

where $\Delta G^{n,0}$ is the free energy of solvation of a non-polar gaseous solute of the same size as a given ion and $\Delta G^{el,0}$ is the electrostatic free energy of solvation. The other thermodynamic excess functions such as the Helmholtz free energy, entropy, enthalpy and energy are of the same form. $\Delta G^{n,0}$ can be estimated by various theoretical models²⁶. In this paper, we only consider the electrostatic contribution. The electrostatic part of the Helmholtz free energy have been derived by constructing a thermodynamic charging process²⁰. Using the notation of Blum and Wei²⁷, it can be written as^{20,21,27}

$$\Delta A_i^{el,0} = \frac{-Z_i^2 e^2 (1 - 1/\epsilon^0)}{\sigma_i + \sigma_d/\lambda^0} \quad (2a)$$

where $Z_i e$ is the charge of an ion of species i , σ_i , σ_d are the diameters of ion and dipole respectively. The equilibrium dielectric constant, ϵ^0 , of the MSA is given by a single parameter λ^0

$$\epsilon^0 = \frac{(\lambda^0(1 + \lambda^0)^2)^2}{16} \quad (2b)$$

λ^0 is a solution of following algebraic equation^{22,27}

$$d_2^2 = \left(\frac{\lambda^0(\lambda^0 + 2)}{3} \right)^2 \left(1 - \frac{1}{\epsilon^0} \right), \quad (3a)$$

where d_2 is a parameter determined by the solvent dipole moment

$$d_2^2 = \frac{4\pi}{3} \rho_d \mu^2 / kT \quad (3b)$$

ρ_d and μ are the density and dipole moment of solvent.

The entropy is given by the temperature derivative of the Helmholtz free energy at constant volume. To calculate such a derivative we have to calculate $(\frac{\partial \lambda^0}{\partial T})_V$. From (3a), we get

$$\left(\frac{\partial \lambda^0}{\partial T} \right)_V = \frac{-(\epsilon^0 - 1)\lambda^0(1 + \lambda^0)(2 + \lambda^0)}{2T(2\epsilon^0(1 + \lambda^0)^2 + \lambda^0(\lambda^0 + 3))} \quad (4a)$$

and

$$\frac{\partial \epsilon^0}{\partial \lambda^0} = \frac{2\epsilon^0(1 + 3\lambda^0)}{\lambda^0(1 + \lambda^0)} \quad (4b)$$

The solvation entropy is therefore given by

$$\Delta S_i^{el,0} = - \left(\frac{\partial \Delta A_i^{el,0}}{\partial T} \right)_V = - \frac{\partial \Delta A_i^{el,0}}{\partial \lambda^0} \left(\frac{\partial \lambda^0}{\partial T} \right)_V \quad (5a)$$

Using the fact that $\Delta A_i^{el,0}$ is a unique function of b_2 , from (2) and (4), we have explicitly

$$\Delta S_i^{el,0} = \frac{-Z_i^2 e^2 \lambda^0 (2 + \lambda^0) (1 - 1/\epsilon^0) (2(3\lambda^0 + 1)(\sigma_i \lambda^0 + \sigma_d) + (\epsilon^0 - 1)(1 + \lambda^0)\sigma_d)}{2TW_3} \quad (6)$$

where for later convenience, we defined a set of three W parameters

$$W_1 = 4 \frac{\sigma_i}{\sigma_d} \lambda^0 (1 + \lambda^0) + 2 + 3\lambda^0, \quad (7a)$$

$$W_2 = \lambda^0 (1 + \lambda^0) \sigma_d (1 - 1/\epsilon^0)^2 \epsilon^0 W_1, \quad (7b)$$

$$W_3 = (\sigma_i \lambda_0 + \sigma_d)^2 (2\epsilon^0(1 + \lambda^0)^2 + \lambda^0(3 + \lambda^0)) . \quad (7c)$$

From the standard thermodynamics relation, the solvation energy is given by

$$\Delta E_i^{el,0} = \Delta A_i^{el,0} + T \Delta S_i^{el,0} . \quad (8a)$$

According to Garisto and Patey²⁰, the solvation energy consists of two terms, ion-dipole, $\Delta E_{id}^{el,0}$, and dipole-dipole, $\Delta E_{dd}^{el,0}$, contributions:

$$\Delta E_i^{el,0} = \Delta E_{id}^{el,0} + \Delta E_{dd}^{el,0} . \quad (8b)$$

As it was shown^{20,21,27}

$$\Delta E_{id}^{el,0} = 2\Delta A_i^{el,0} . \quad (8c)$$

Equation (8c) holds precisely for the continuum solvent model. Accurate theory^{7,20} and simulations^{5,6} also show that the Helmholtz free energy is approximately half of the solute-solvent contribution to the solvation energy. Then from (8a),

$$\Delta E_i^{el,0} = \frac{1}{2} \Delta E_{id}^{el,0} + T \Delta S_i^{el,0} \quad (8d)$$

and

$$\Delta E_{dd}^{el,0} = \frac{1}{2} \Delta E_{id}^{el,0} + T \Delta S_i^{el,0} . \quad (8e)$$

Explicitly we have

$$\Delta E_{id}^{el,0} = \frac{-2Z_i^2 e^2 (1 - 1/\epsilon^0)}{\sigma_i + \sigma_d / \lambda^0} \quad (8f)$$

and

$$\Delta E_{dd}^{el,0} = T \Delta S_i^{el,0} - \Delta A_i^{el,0} = \frac{Z_i^2 e^2 W_2}{2W_3} . \quad (8g)$$

(8g) has been obtained by Garisto and Patey²⁰ by evaluating the energy integral. $\Delta A_i^{el,0}$ is obtained essentially by calculating the virial type integral, ie, by the virial route. As was pointed out by Garisto and Patey the MSA result of the solvation thermodynamics is consistent at this stage because one gets the same result from the energy and the virial route. As we see from (8g) that $\Delta E_{dd}^{el,0}$ is always positive, which corresponds to solvent structure breaking in charging an ion .

In order to calculate the Gibbs free energy, one starts with the thermodynamic relation

$$\Delta G_i^{el,0} = \frac{\partial \rho_d \Delta A_i^{el,0}}{\partial \rho_d} . \quad (9a)$$

Following the same procedures as in (5) we have

$$\Delta G_i^{el,0} = \Delta A_i^{el,0} + \rho_d \frac{\partial \Delta A_i^{el,0}}{\partial \lambda^0} \frac{\partial \lambda^0}{\partial \rho_d} . \quad (9b)$$

From (3b), it can be shown that

$$\left(\frac{\partial \lambda^0}{\partial \rho_d} \right)_T / \left(\frac{\partial \lambda^0}{\partial T} \right)_V = -T / \rho_d . \quad (9c)$$

We then get

$$\Delta G_i^{el,0} = \Delta A_i^{el,0} + T \Delta S_i^{el,0} , \quad (9d)$$

that is,

$$\Delta G_i^{el,0} = \Delta E_i^{el,0} . \quad (9e)$$

This is, in fact, a known result of the MSA^{28,29}. This shows again that the MSA solvation thermodynamic functions are thermodynamically consistent at this level. From (8g) and (8f), we have explicitly,

$$\Delta G_i^{el,0} = \frac{-2Z_i^2 e^2 (1 - 1/\epsilon^0)}{\sigma_i + \sigma_d / \lambda^0} + \frac{Z_i^2 e^2 W_2}{2W_3} . \quad (9f)$$

Comparing with (1) and (9), we find

$$\Delta G_i^{el,0} \neq \Delta A_i^{el,0} . \quad (9g)$$

If one charges a cavity in a dielectric continuum the work needed is the same at constant pressure as constant volume as long as ϵ^0 remains unchanged, ie,

$$\Delta G_i^{el,0} = \Delta A_i^{el,0} . \quad (9h)$$

When a cavity is charged in a molecular solvent the work is different. The complexity of the solvation is reflected in equation (9f). The first term is due to the electrostatic interaction between the ion and the dipoles. The second term is the change in the dipole-dipole energy due

to the ion. As we pointed out before, it is always positive, which corresponds to a structure breaking effect²⁶. The Helmholtz free energy is half of the first term in (9f). Only if the second term equals half of the first term the Helmholtz free energy is not equal to the Gibbs free energy.

Consider some limiting cases. In the high coupling limit^{19,27}, where the dipole-dipole interaction becomes infinitely strong, $\epsilon^0 \rightarrow \infty$, from (2a), (9f), we get

$$\Delta G_i^{el,0} = \Delta A_i^{el,0} = \frac{-Z_i^2 e^2}{\sigma_i}, \quad (10a)$$

This is equivalent to the classical Born result⁸ in the same limit, and

$$\Delta S_i^{el,0} = 0. \quad (10b)$$

This shows that strong coupling between solvent molecules makes the re-organization of the solvent around the ion impossible, and therefore the entropy change which is the measure of the microscopic order is zero.

When the solvent diameter becomes infinitely small, $\sigma_d = 0$, we recover the continuum limit results. We find the the Helmholtz free energy is given by

$$\Delta A_i^{el,0} = \frac{-Z_i^2 e^2 (1 - 1/\epsilon^0)}{\sigma_i} \quad (11a)$$

which is precisely the classical Born free energy. However the Gibbs free energy is found to be different from the Helmholtz free energy in this limit,

$$\Delta G_i^{el,0} = \frac{-Z_i^2 e^2 (1 - 1/\epsilon^0)}{\sigma_i} \left(2 - \frac{1 - 1/\epsilon^0}{1 + \frac{\lambda^0(3+\lambda^0)}{2\epsilon^0(1+\lambda^0)^2}} \right) \quad (11b)$$

and the entropy is given by

$$\Delta S_i^{el,0} = \frac{-Z_i^2 e^2 (1 - 1/\epsilon^0) (2 + \lambda^0) (3\lambda^0 + 1)}{\sigma_i T (\lambda^0(3 + \lambda^0) + 2\epsilon^0(1 + \lambda^0)^2)}. \quad (11c)$$

This indicates that the solvent effect, in this limit, is still different from that of the continuum dielectric media. One can calculate the entropy by taking derivative of $\Delta A_i^{el,0}$ in equation (11a) with respect to T. The same result should be obtained.

From Blum and Wei²⁷, the electrostatic part of the excess chemical potential of the MSA can be written as for an ion-dipole mixture of equal ion size ($\sigma = \sigma_i$, $Z = Z_i$, $\rho = \rho_i$)

$$\mu_i^{el}/(kT) = \frac{Z_i^2 d_0 (d_0 b_0 - d_2 b_1 \sigma_i / \sigma_d)}{4\pi\eta\sigma_i^3}, \quad (12a)$$

$$\mu_d^{el}/(kT) = \frac{-d_2 (2d_2 b_2 + d_0 b_1 \sigma_d^2 / \sigma_i^2)}{4\pi\rho_d \sigma_d^3} \quad (12b)$$

where

$$d_0^2 = 4\pi\eta\sigma_i^2 e^2 / (kT), \quad (12c)$$

$$\eta = \sum_i \rho_i Z_i^2. \quad (12d)$$

The b parameters can be obtained explicitly in the low density limit as

$$b_0 = -\kappa/2 \quad (13a)$$

$$b_1 = b_1^1 \kappa + b_1^2 \kappa^2 / 2 \quad (13b)$$

$$b_2 = b_2^0 + b_2^2 \kappa^2 / 2 \quad (13c)$$

where κ is the Debye screening length

$$\kappa = \frac{d_0}{\sqrt{\epsilon^0}} \quad (13d)$$

and

$$b_1^1 = \frac{9d_2(1 + \lambda^0)^2}{4(1 + \sigma_i \lambda_0 / \sigma_d)(2 + \lambda^0)^2}, \quad (13e)$$

$$b_1^2 = \frac{-9d_2(1 + \lambda^0)^2 \sigma_d}{4\sigma_i \lambda_0 (2 + \lambda^0)^2} \quad (13f)$$

$$b_2^2 = \frac{-\epsilon^0 W_2 \sigma_d^3 / \sigma^2}{2W_3 d_2^2}. \quad (13g)$$

After some algebra, we have

$$\mu_i^{el} = \frac{1}{2} \Delta G_{id}^{el,0} - \frac{Z_i^2 e^2 \kappa}{2\sigma_i \epsilon^0}, \quad (14a)$$

$$\mu_d^{el} = \frac{\eta(\frac{1}{2} \Delta G_{id}^{el,0} + \Delta G_{dd}^{el,0})}{Z_i^2 \rho_d} - \frac{d_2^2 b_2^0 kT}{2\pi \rho_d \sigma_d^3}. \quad (14b)$$

The first term of (14a) is simply the solvation Helmholtz free energy. The second one gives the Debye-Huckel limiting law. The second term in (14b) is the chemical potential of the pure

dipole liquid and terms inside the bracket of the first term are related to the solvation entropy, that is,

$$\mu_i^{el} = \Delta A_i^{el,0} - \frac{Z_i^2 e^2 \kappa}{2\sigma_i \epsilon^0}, \quad (14c)$$

$$\mu_d^{el} = \frac{\eta T \Delta S_i^{el,0}}{Z_i^2 \rho_d} - \frac{d_2^2 b_2^0 k T}{2\pi \rho_d \sigma_d^3}. \quad (14d)$$

The total solvation Gibbs free energy can be obtained making use of the thermodynamic relation

$$\Delta G^{el,0} = \sum_i \rho_i \mu_i^{el} - \Delta G_d \quad (15)$$

where ΔG_d is the Gibbs free energy of the pure dipole. This result agrees with what we obtained previously, ie, (9b). The cavity and ideal parts of the standard chemical potential are discussed by Zhou et al³⁰.

B. The apparent molar heat capacity at constant volume and pressure, $\bar{C}_{v,i}^{el,0}$, $\bar{C}_{p,i}^{el,0}$, enthalpy, $\Delta H_i^{el,0}$ and partial molar volume, $\bar{V}_i^{el,0}$

To calculate $\bar{C}_{v,i}^{el,0}$, $\bar{C}_{p,i}^{el,0}$ we have to take second temperature derivative of $\Delta A_i^{el,0}$ or first derivative of $\Delta E_i^{el,0}$. From a standard thermodynamic formula, $\bar{C}_v^0$ is given by

$$\bar{C}_{v,i}^{el,0} = \left(\frac{\partial \Delta E_i^{el,0}}{\partial T} \right)_v = \frac{\partial \Delta E_i^{el,0}}{\partial \lambda^0} \left(\frac{\partial \lambda^0}{\partial T} \right)_v. \quad (16a)$$

After considerable algebra, we have

$$\begin{aligned} \bar{C}_{v,i}^{el,0} = & -2\Delta S_i^{el,0} + \frac{Z_i^2 e^2 \left(\frac{\partial \lambda^0}{\partial T} \right)_v}{2W_3^2} (\sigma_d W_3 \epsilon^0 ((1 - 1/\epsilon^0)^2 ((1 + 2\lambda^0) W_1 \\ & + \lambda^0 (1 + \lambda^0) (4\sigma_i (1 + 2\lambda^0)/\sigma_d + 3)) + 2W_1 (1 - 1/(\epsilon^0)^2) (3\lambda^0 + 1)) \\ & - W_2 (2W_3 \frac{\sigma_i}{\sigma_d + \lambda^0 \sigma_i} + (\sigma_d + \lambda^0 \sigma_i)^2 (2\lambda^0 + 3 + 4\epsilon^0 (1 + \lambda^0) (4\lambda^0 + 1)/\lambda^0))) \end{aligned} \quad (16b)$$

However $\bar{C}_{p,i}^{el,0}$ and $\bar{V}_i^{el,0}$ are not very easy to calculate because they involve temperature derivative at constant pressure and pressure derivative at constant temperature which can not be calculated unless the equation of state is known. Explicitly,

$$\bar{C}_{p,i}^{el,0} = \left(\frac{\partial \Delta H_i^{el,0}}{\partial T} \right)_P = \frac{\partial \Delta H_i^{el,0}}{\partial \lambda^0} \left(\frac{\partial \lambda^0}{\partial T} \right)_P, \quad (17a)$$

$$\bar{V}_i^0 = \left(\frac{\partial \Delta G_i^{el,0}}{\partial P} \right)_T = \frac{\partial \Delta G_i^{el,0}}{\partial \lambda^0} \left(\frac{\partial \lambda^0}{\partial P} \right)_T \quad (17b)$$

where $\Delta H_i^{el,0}$ is the enthalpy

$$\Delta H_i^{el,0} = \Delta G_i^{el,0} + T \Delta S_i^{el,0} = \Delta E_i^{el,0} + T \Delta S_i^{el,0} \quad (17c)$$

and we have used the fact that for the MSA, $\Delta G_i^{el,0} = \Delta E_i^{el,0}$. From (16a), we have

$$\bar{V}_i^{el,0} = \bar{C}_{v,i}^{el,0} \left(\frac{\partial \lambda^0}{\partial P} \right)_T / \left(\frac{\partial \lambda^0}{\partial F} \right)_V. \quad (17d)$$

There are actually a few ways to calculate $\Delta H_i^{el,0}$ and hence, $\bar{C}_{p,i}^0$. If the entropy is given by (5a), which is obtained by taking the constant volume temperature derivative of the Helmholtz free energy, from (8a) and (17c), then

$$\Delta H_i^{el,0} = 2\Delta E_i^{el,0} - \Delta A_i^{el,0}, \quad (18a)$$

$$\frac{\partial \Delta H_i^{el,0}}{\partial \lambda^0} = (2\bar{C}_{v,i}^{el,0} + \Delta S_i^{el,0}) / \left(\frac{\partial \lambda^0}{\partial T} \right)_V. \quad (18b)$$

We can also use (17c) and calculate the entropy by taking the constant pressure derivatives of $\Delta G_i^{el,0}$ with respect to temperature,

$$\Delta S_i^{el,0} = - \left(\frac{\partial \Delta G_i^{el,0}}{\partial T} \right)_P. \quad (18c)$$

It can also be calculated using the thermodynamic relation

$$\Delta H_i^{el,0} = \Delta E_i^{el,0} + P \bar{V}_i^{el,0} \quad (18d)$$

where $\bar{V}_i^{el,0}$ is given by (17d). If the MSA is a thermodynamically consistent theory, these three routes should give the same result. Unfortunately the MSA is not a thermodynamically consistent theory for $\Delta H_i^{el,0}$ in this level, as we can see only some routes give reasonable results.

As a first step, $(\frac{\partial \lambda^0}{\partial T})_P$ and $(\frac{\partial \lambda^0}{\partial P})_T$ should be calculated. Taking temperature and pressure derivatives of both sides of (3a), keeping pressure and temperature constant respectively, we get

$$\left(\frac{\partial \lambda^0}{\partial T} \right)_P = \left(\frac{\partial V}{\partial T} \right)_P / V + \frac{1}{T} T \left(\frac{\partial \lambda^0}{\partial T} \right)_V, \quad (19a)$$

$$\left(\frac{\partial \lambda^0}{\partial P}\right)_T = \frac{(\frac{\partial V}{\partial P})_T}{V} T \left(\frac{\partial \lambda^0}{\partial T}\right)_V, \quad (19b)$$

Using the definition of the compressibilities,

$$\alpha = \frac{(\frac{\partial V}{\partial T})_P}{V}, \quad (20a)$$

$$\beta = -\frac{(\frac{\partial V}{\partial P})_T}{V}, \quad (20b)$$

equation (19) can be simplified

$$\left(\frac{\partial \lambda^0}{\partial T}\right)_P = (\alpha T + 1) \left(\frac{\partial \lambda^0}{\partial T}\right)_V, \quad (21a)$$

$$\left(\frac{\partial \lambda^0}{\partial P}\right)_T = -\beta T \left(\frac{\partial \lambda^0}{\partial T}\right)_V. \quad (21b)$$

To calculate α and β we need a state equation for the pure dipole liquid which has been given by Rushbrooke et al³¹

$$PV = nRT \left(\frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} + \frac{b_2^0(2 + \lambda^0)^2}{18\pi\rho^*} \left(\frac{b_2^0}{3} \left(\frac{(1 + \lambda^0)^2}{2} + \frac{(3 + \lambda^0)^2}{(1 + \lambda^0)^4} \right) - (\lambda^0)^2 + \frac{16}{(1 + \lambda^0)^4} \right) \right). \quad (22a)$$

The excess Helmholtz free energy with respect to the hard sphere system is given by

$$\beta \Delta A = \frac{-(b_2^0(2 + \lambda^0))^2}{54\pi\rho^*} \left(\frac{(1 + \lambda^0)^2}{2} + \frac{(3 + \lambda^0)^2}{(1 + \lambda^0)^4} \right) \quad (22b)$$

where

$$n = \rho_d V / N_A, \quad (22c)$$

$$\rho^* = \rho_d \sigma_d^3, \quad (22d)$$

$$\xi = \frac{\pi}{6} \rho^*, \quad (22e)$$

$$b_2^0 = \frac{6(\lambda^0 - 1)}{2 + \lambda^0}, \quad (22f)$$

$$\frac{\partial b_2^0}{\partial \lambda^0} = \frac{18}{(2 + \lambda^0)^2}. \quad (22g)$$

N_A is the Avogadro number. (22a) has a critical point characterized by

$$T_c^* = .225, \quad (23a)$$

$$P_c^* = .106 , \quad (23b)$$

$$\rho_c^* = .00704 \quad (23c)$$

and

$$\frac{P_c^*}{\rho_c^* T_c^*} = .295 \quad (23d)$$

where the reduced parameters are defined

$$P^* = \frac{P \sigma_d^6}{\mu^2} , \quad (24a)$$

$$T^* = \frac{kT \sigma_d^3}{\mu^2} . \quad (24b)$$

From (22), the isothermal and isobaric compressibilities can be calculated, the details of which are given in the appendix, and the results are

$$\alpha = \frac{\frac{PV}{nRT^2} + W_4 \left(\frac{\partial b_2^0}{\partial T} \right)_V}{\frac{P^0 V}{nRT} + D_p^0 \xi - W_4 T \left(\frac{\partial b_2^0}{\partial T} \right)_V} , \quad (25a)$$

$$\beta = \frac{\frac{V}{nRT}}{\frac{P^0 V}{nRT} + D_p^0 \xi - W_4 T \left(\frac{\partial b_2^0}{\partial T} \right)_V} \quad (25b)$$

where

$$W_4 = -\frac{d_2^2}{2\pi\rho^*} , \quad (25c)$$

$$\frac{P^0 V}{nRT} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} , \quad (25d)$$

$$D_p^0 = \frac{2(2 + 2\xi - \xi^2)}{(1 - \xi)^4} , \quad (25f)$$

$$\left(\frac{\partial b_2^0}{\partial T} \right)_V = \frac{18}{(2 + \lambda^0)^2} \left(\frac{\partial \lambda^0}{\partial T} \right)_V . \quad (25g)$$

The explicit formulas for the $\bar{C}_{p,i}^{el,0}$ and $\bar{V}_i^{el,0}$ can be now written out. From (17d) and (21b), we get

$$\bar{V}_i^{el,0} = -\beta T \bar{C}_{v,i}^{el,0} \quad (26)$$

From (18a),

$$\bar{C}_{p,i}^{el,0} = (2\bar{C}_{v,i}^{el,0} + \Delta S_i^{el,0})(\alpha T + 1) . \quad (27)$$

Using (17c) and (18c), we have

$$\Delta H_i^{el,0} = \Delta G_i^{el,0} - T \left(\frac{\partial \Delta G_i^{el,0}}{\partial T} \right)_P, \quad (28a)$$

and (17a) gives,

$$\bar{C}_{p,i}^{el,0} = -T \left(\frac{\partial^2 \Delta G_i^{el,0}}{\partial T^2} \right)_P. \quad (28b)$$

From (16a) and (21a), we get

$$\left(\frac{\partial \Delta G_i^{el,0}}{\partial T} \right)_P = \frac{\partial \Delta G_i^{el,0}}{\partial \lambda^0} \left(\frac{\partial \lambda^0}{\partial T} \right)_P = \bar{C}_{v,i}^{el,0} (\alpha T + 1), \quad (28c)$$

Then the entropy from this route is

$$\Delta S_i^{el,0} = -\bar{C}_{v,i}^{el,0} (\alpha T + 1) \quad (.)$$

and

$$\bar{C}_{p,i}^{el,0} = \bar{C}_{v,i}^{el,0} - T(\alpha T + 1) \left(\frac{\partial \bar{C}_{v,i}^{el,0}}{\partial \lambda^0} \right)_T \left(\frac{\partial \lambda^0}{\partial T} \right)_P - T^2 \bar{C}_{v,i}^{el,0} \left(\frac{\partial \alpha}{\partial T} \right)_P. \quad (28e)$$

where we have used the fact that $\bar{C}_{v,i}^{el,0} T$ is a unique function of b_2^0 .

We now consider another route, starting from (18d) and (26), we have

$$\Delta H_i^{el,0} = \Delta E_i^{el,0} - P\beta T \bar{C}_{v,i}^{el,0}, \quad (29a)$$

$$\Delta S_i^{el,0} = -P\beta \bar{C}_{v,i}^{el,0} \quad (29b)$$

and

$$\bar{C}_{p,i}^{el,0} = \bar{C}_{v,i}^{el,0} (\alpha T + 1) - PT\beta \left(\frac{\partial \bar{C}_{v,i}^{el,0}}{\partial \lambda^0} \right)_T \left(\frac{\partial \lambda^0}{\partial T} \right)_P - PT \bar{C}_{v,i}^{el,0} \left(\frac{\partial \beta}{\partial T} \right)_P \quad (29c)$$

where

$$\left(\frac{\partial \beta}{\partial T} \right)_P = \beta \left(\alpha - 1/T + \frac{\xi \alpha (D_p^0 + D_p^1) + W_4 T \left(\frac{\partial^2 b_2^0}{\partial T^2} \right)_{V,P}}{\frac{P^0 V}{nRT} + D_p^0 \xi - W_4 T \left(\frac{\partial b_2^0}{\partial T} \right)_V} \right), \quad (30a)$$

$$\begin{aligned} \left(\frac{\partial \alpha}{\partial T} \right)_P &= \left(\frac{PV}{nRT} (\alpha/T - 2/T^2) + W_4 \left(\left(\frac{\partial^2 b_2^0}{\partial T^2} \right)_{V,P} - \left(\frac{\partial b_2^0}{\partial T} \right)_V / T \right) \right. \\ &\quad \left. + \alpha (\xi \alpha (D_p^0 + D_p^1) + W_4 T \left(\frac{\partial^2 b_2^0}{\partial T^2} \right)_{V,P}) \right) / \left(\frac{P^0 V}{nRT} + D_p^0 \xi - W_4 T \left(\frac{\partial b_2^0}{\partial T} \right)_V \right) \end{aligned} \quad (30b)$$

which are obtained from (a6) and (a8). We have used following notation

$$D_P^1 = \frac{2(2 + 10\xi + \xi^2 - \xi^3)}{(1 - \xi)^5}, \quad (30c)$$

$$\begin{aligned} \left(\frac{\partial^2 b_2^0}{\partial T^2}\right)_{V,P} = & \frac{-54(\sigma_d + \sigma_i \lambda^0)^4 \left(\frac{\partial \lambda^0}{\partial T}\right)_P}{(2 + \lambda^0)^2} \left(\frac{W_3}{(\sigma_i \lambda^0 + \lambda_d)^2} (2\epsilon^0(3\lambda^0 + 1) + (\epsilon^0 - 1) \left(\frac{2}{3}\beta_6^0(1 + \lambda^0) + \lambda^0\right)) \right. \\ & \left. - (4\epsilon^0(\lambda^0 + 1)(1 + 4\lambda^0)/\lambda^0 + 2\lambda^0 + 3)(\epsilon^0 - 1)(1 + \lambda^0)\lambda^0 / (2\beta_6^0 W_3^2 T) - \left(\frac{\partial b_2^0}{\partial T}\right)_V / T \right), \quad (30d) \end{aligned}$$

All the solvation thermodynamic functions are now given in terms of explicit expressions. They can be calculated by only solving an algebra equation (3a). The MSA solvation energy, free energy and entropy given in section A are thermodynamically consistent. However others involve second derivatives and equation of states are not, only some give reasonable results.

III. Model calculations and discussions

Jansoone and Franck³² found that the equilibrium dielectric constant of water could be fitted fairly well by the MSA formula, (2b). We pick 2.8 Å as diameter of water and adjust the dipole moment so that the dielectric constant given by (2b) agrees with experimental data, i.e., 78.7 at 298K. The density of the liquid is chosen as 1.0 gram per cm³, and the effective dipole movement so obtained is about 2.22 Debye. The solvation Gibbs free energy, enthalpy and entropy of alkalis and halides is listed in Table I, where the energy is in kJ and the entropy is in J/K. The second column are the ion diameters used in the current calculations which are from the X-ray electron density measurements³³. Comparison between the experimental data^{34,35,15} at 298K and the calculations shows that agreement for halides are much better than for alkalis. Corresponding Born calculations were carried out with $\left(\frac{\partial \ln \epsilon}{\partial \ln T}\right)_P = -1.357$, which is the experimental value for water at 298K¹⁵. As can be seen from (9f) MSA correction to the Born Gibbs free energy is more than an effective diameter of the central ion. The

structure breaking, ie, solvent re-organization, cancels almost half of the ion-dipole term giving a Gibbs free energy close to the Helmholtz free energy which are listed in the seventh column. Agreement between the MSA entropy and the experimental data is much better than that of the Born approximate. In the MSA theory, the solvation entropy has contributions from the solvent structure breaking and also solvent re-organization around the ion. In the Born theory, the entropy is determined by the temperature derivative of the dielectric constant. It is probably too simple to reflect the complexity of the solvation process. Table I shows that the MSA solvation entropy may give better description of the structure change associated with introducing an ion from gas phase to liquid. However the structure breaking and solvent re-organization contributions in the ion-dipole model, may be over-estimated comparing with those in the hydrogen bonded water. So good agreement with experimental may result from cancellation of errors.

The apparent molar heat capacities and partial molar volume are calculated along an isobaric line to the region near the critical point with the pressure being kept at 139 bars. Calculations were done for an ion of $z_i = 1$, $\sigma_i = 3.27A^0$ and solvent of $\mu = 2.2$ Debye, $\sigma_d = 2.5A^0$. As we pointed out before, the MSA is not a thermodynamically consistent theory for these thermodynamic quantities, and only some routes give reasonable results. We find that for the system we have chosen (28e) is found to give better results. Since the equation of state for of the MSA hard sphere dipole has a very different critical point and isobaric line to the critical point from that of water we are not able to compare our calculation with experimental observation²³. As it is shown in Fig. 1 and 2, some of the basic features are well reproduced by the MSA. The $\bar{V}_i^{el,0}$ and $\bar{C}_{p,i}^{el,0}$ diverge near the critical point while $\bar{C}_{v,i}^{el,0}$ changes slowly with temperature. Just like the Born calculation of Wood et al²⁴ the $\bar{C}_{v,i}^{el,0}$ tends to increase near the critical point, but we do not see any evidence that it is diverging. As we can see from (26), (27), (28e) and (29c) $\bar{V}_i^{el,0}$ and $\bar{C}_{p,i}^{el,0}$ are related to the compressibilities that diverge at the critical point. This has to be physical reason why $\bar{V}_i^{el,0}$ and $\bar{C}_{p,i}^{el,0}$ diverge in the critical region. From (16a) $\bar{C}_{v,i}^{el,0}$ is related to some well behaved variables at the critical point. The MSA theory give a good clue

to the question Wood et al²⁴ raised in their Born calculation on the critical behaviour of $\bar{C}_{v,i}^{el,0}$. The MSA dipole model has a set of classical critical exponents³⁰. It would be very interesting to make detailed comparison with recent thermodynamic data³⁶. We would like also to apply our theory to other ions, polar and non-polar solutes³⁷.

Appendix: Derivation of α and β

(22a) can be rewritten as

$$PV = P^0V + Q(b_2^0)nRT/\rho^* \quad (a1)$$

where P^0 is defined by (25d) and $Q(b_2^0)$

$$Q(b_2^0) = \frac{b_2^0(2 + \lambda^0)^2}{18\pi} \left(\frac{b_2^0}{3} \left(\frac{(1 + \lambda^0)^2}{2} + \frac{(3 + \lambda^0)^2}{1 + \lambda^0^4} \right) - (\lambda^0)^2 + \frac{16}{(1 + \lambda^0)^2} \right) \quad (a2)$$

Taking the derivative with respect to temperature, and keeping P constant, we have

$$P\left(\frac{\partial V}{\partial T}\right)_P = PV/T + nRT(-D_P^0\xi \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P + \frac{Q(b_2^0)}{\rho^*} \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P + \frac{\partial Q(b_2^0)}{\partial b_2^0} \left(\frac{\partial b_2^0}{\partial T}\right)_P / \rho^*) \quad (a3)$$

We have used

$$\left(\frac{\partial \frac{P^0V}{nRT}}{\partial T}\right)_P = \left(\frac{\partial \frac{1+\xi+\xi^2-\xi^3}{(1-\xi)^3}}{\partial \xi}\right)_V \left(\frac{\partial \xi}{\partial T}\right)_P = -D_P^0\xi \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad (a4)$$

and

$$\left(\frac{\partial \xi}{\partial T}\right)_P = -\xi \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad (a5)$$

From (20a) and (21a), that is,

$$\alpha = \frac{(\frac{\partial V}{\partial T})_P}{V}$$

$$\left(\frac{\partial b_2^0}{\partial T}\right)_P = (\alpha T + 1)\left(\frac{\partial b_2^0}{\partial T}\right)_V$$

we have

$$PV\alpha = PV/T + nRT(-D_P^0\xi\alpha + \frac{Q(b_2^0)}{\rho^*}\alpha + \frac{\partial Q(b_2^0)}{\partial b_2^0}(\alpha T + 1)\left(\frac{\partial b_2^0}{\partial T}\right)_V / \rho^*) \quad (a6)$$

It can be shown after tedious algebra that

$$\left(\frac{\partial Q(b_2^0)}{\partial b_2^0}\right)_V / \rho^* = W_4 \quad (a7)$$

where W_4 is defined by (25c). Solving for α we get

$$\alpha = \frac{\frac{PV}{nRT} + W_4\left(\frac{\partial b_2^0}{\partial T}\right)_V}{\frac{P^0V}{nRT} + D_P^0\xi - W_4T\left(\frac{\partial b_2^0}{\partial T}\right)_V} \quad (a8)$$

Let us keep T constant and take the derivative with respect to pressure to obtain

$$V + P\left(\frac{\partial V}{\partial P}\right)_T = nRT(-D_P^0 \xi \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T + \frac{Q(b_2^0)}{\rho^*} \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T + \frac{\partial Q(b_2^0)}{\partial b_2^0} \left(\frac{\partial b_2^0}{\partial P}\right)_T / \rho^*) . \quad (a9)$$

Using (20b), (21b) and (a7), that is,

$$\beta = -\frac{(\frac{\partial V}{\partial P})_T}{V}$$

$$\left(\frac{\partial b_2^0}{\partial P}\right)_T = -\beta T \left(\frac{\partial b_2^0}{\partial T}\right)_V$$

we have

$$\beta = \frac{\frac{V}{nRT}}{\frac{P^0 V}{nRT} + \xi D_P^0 - W_4 T \left(\frac{\partial b_2^0}{\partial T}\right)_V} . \quad (a10)$$

At the critical point,

$$\frac{P^0 V}{nRT} + \xi D_P^0 - W_4 T \left(\frac{\partial b_2^0}{\partial T}\right)_V = 0 , \quad (a11)$$

$$\alpha \longrightarrow \infty , \quad (a12)$$

$$\beta \longrightarrow \infty . \quad (a13)$$

We have shown numerically that at the critical point found by Rushbrooke et al²⁹ this is correct.

Calculation of $(\frac{\partial \alpha}{\partial T})_P$ and $(\frac{\partial \beta}{\partial T})_P$ is straightforward, but one has to remember that

$$W_4 T = -\frac{d_2^2 T}{2\pi \rho^*} = -\frac{2\mu^2}{3k\sigma_d^3} \quad (a14)$$

which is independent of temperature, pressure and volume, and

$$D_P^1 = \frac{\partial \xi D_P^0}{\partial \xi} . \quad (a15)$$

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Captions

Table I: The experimental data of the ΔS_i^0 is from Abraham and Liszi^{33,34}, ΔH_i^0 from Rashin and Honig¹⁶ and ΔG_i^0 calculated based upon these two. The energy is in kJ and the entropy in J/K.

Figure 1: The MSA $\bar{C}_{v,i}^{el,0}$ and $\bar{C}_{p,i}^{el,0}$ as functions of temperature.

Figure 2: The MSA $\bar{V}_i^{el,0}$ as a function of temperature.

Table I

Solvation thermodynamics of single ions

Ions	$\sigma_i(A^\circ)$	Experimental			The MSA				The Born		
		$\Delta G_i^{ex,0}$	$\Delta H_i^{ex,0}$	$\Delta S_i^{ex,0}$	$\Delta G_i^{ex,0}$	$\Delta A_i^{ex,0}$	$\Delta H_i^{ex,0}$	$\Delta S_i^{ex,0}$	$\Delta G_i^{ex,0}$	$\Delta H_i^{ex,0}$	$\Delta S_i^{ex,0}$
<i>Li</i> ⁺	1.904	-470	-526	-187	-525	-464	-585	-204	-720	-733	-42
<i>Na</i> ⁺	2.352	-366	-412	-154	-450	-402	-497	-157	-583	-593	-34
<i>K</i> ⁺	3.024	-292	-328	-120	-370	-336	-404	-113	-453	-461	-27
<i>Cs</i> ⁺	3.584	-286	-283	-105	-322	-296	-349	-90	-382	-389	-23
<i>F</i> ⁻	2.352	-453	-499	-155	-450	-402	-497	-157	-583	-593	-34
<i>Cl</i> ⁻	3.278	-328	-357	-97	-347	-316	-377	-102	-418	-425	-25
<i>Br</i> ⁻	3.584	-305	-329	-81	-322	-296	-349	-90	-382	-389	-23
<i>I</i> ⁻	4.032	-270	-288	-60	-292	-270	-315	-76	-340	-346	-20



