Excess Volume of Electrolytes in the Mean Spherical Approximation[†]

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An expression for the excess partial molar volume of electrolyte solutions was derived in the framework of the mean spherical approximation (MSA). This integral theory, an extension of the Debye−Hückel theory, includes the effect of the ion size in the radial ion−ion distribution function, and it allows the description of excess thermodynamic properties of electrolytes over a wide range of concentration. The general pressure and temperature dependence of the excess volume predicted by the model were analyzed for model electrolytes, and the results for NaCl aqueous solutions at temperatures up to 300 °C were compared with experimental data over a wide range of concentrations (up to 4 $\text{mol}\cdot\text{kg}^{-1}$). Crystallographic and adjustable ion diameters were used in the calculations, allowing reasonable predictions of the NaCl(aq) excess volume over different concentration regions. The effect of ion association, excluded volume, and reference system conversion were also analyzed.

Introduction

The equation of state (EOS) of electrolytes, particularly for aqueous systems, is of practical and theoretical interest. The knowledge of the EOS of electrolyte solutions is essential to estimate the speciation or solubility of brines in the hydrothermal system under pressure conditions far from ambient conditions. While these estimations can be performed if the activity coefficients of the species are known as a function of pressure, temperature, and salt concentration, it is experimentally simpler to access the excess volume of the electrolyte than its equivalent, the change of the activity coefficient with pressure. Nowadays, the use of vibrating tube densimeters (VTD)[1] allows us to perform very precise measurement of high temperature and high pressure volumetric properties of aqueous solutions as a function of pressure and temperature over a wide range of concentrations, including the very dilute region where the Debye−Hückel limiting law[2] (DHLL) should be obeyed. Thus, numerous authors[3−12] have studied the densities of aqueous electrolytes at temperatures close to or above the water critical temperature (647 K) and pressures up to 40 MPa, and the resulting density data were used to describe the behavior of the electrolyte partial molar volume with concentration over a wide range of p and T. Basically, the partial molar volume, V_2, can be split into a standard state term, V_2^{o}, plus an excess term, V_2^{E}, which depends on the solute concentration. The standard state partial molar volume is the value of V_2 at infinite dilution and represents the solute−solvent interaction, while the excess partial molar volume accounts for the nonideality of the mixture. It is a measure of the solute−solute interaction, and the concentration dependence is substantially different for electrolyte and nonelectrolyte solutes.

The calculation of V_2^{o} as a function of p and T requires a model for the effect of the local electric field of the ions upon the packing of the solvent molecules around them. Most of the models to estimate the standard state volume of the electrolyte are based on the classical equation for the electrostriction effect proposed by Born[13] with the modifications introduced by other authors.[14−17]

The semiempirical equations developed by Shock and Helgeson[17] for the standard partial molar volume and other properties of aqueous ionic species to 500 MPa and 1000 °C provide a relatively good estimation of V_2^{o} at least within the range of T and p where experimental data are available for comparison.[18]

On the contrary, the estimation of the excess volume at high temperature and pressure beyond the validity range of the DHLL is far from being acceptable and in all cases relies on the knowledge of empirical parameters. The so call *pVTx* properties of electrolyte solutions, where x stands for the concentration of the salt in the solution, have been studied using different approaches, including semiempirical equations, analyzed by Millero in a classical review.[19] One of the commonly used for hydrothermal electrolyte systems is the Redlich−Mayer equation,[20] having two empirical parameters which account for the short-range interactions not considered in the DH model. Most of the empirical equations were formualted to describe room-temperature data, but an equation having five adjustable parameters has also been recently reported[21] that predicts the density of one or more electrolytes in water as a function of concentration and temperature, below 110 °C, with an average deviation of 0.1 $\text{kg}\cdot\text{m}^{-3}$.

A way to extend the DH approach to higher electrolyte concentrations is to combine the long-range Coulombic potential with the hard sphere (short-range) potential, as in the Pitzer model of ion interaction.[22] The Pitzer equation for the excess partial molar volume describes quite well the experimental data over a wide range of temperatures, pressures, and concentrations provided that its three empirical coefficients are fitted as a function of pressure and temperature. For instance, to describe the volumetric properties of NaCl up to 250 °C and 40 MPa,[5] 14 parameters are needed for fitting the coefficients, while up to 24 parameters are needed for $CaCl_2$ up to 250 °C and 40 MPa.[23] Thus, the extrapolation of the volumetric properties

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beyond the temperature and pressure range where these parameters where adjusted is not reliable.

It is possible to take into account the short-range ion−ion interaction effect on the volumetric properties of electrolytes by resorting to integral equation theories, such as the mean spherical approximation (MSA). The MSA model renders an analytical solution[24] for the unrestricted primitive model of electrolytes (ions of different sizes immersed in a continuous solvent). Thus, the excess Gibbs energy (activity coefficients) of electrolytes can be described in terms of an electrostatic contribution given by the MSA expression[25,26] and a hard sphere contribution obtained from the excess pressure of a hard sphere (HS) mixture.[27,28] The only parameters of the model are the ionic diameters and numerical densities.

A MSA + hard sphere model has been developed by Perry et al.[29] based on fluctuation solution theory,[30] expressed in terms of the direct correlation function integrals.[31] The model includes the diameter of the solvent molecule as an adjustable parameter; that is, the model is primitive for the electrostatic contribution and nonprimitive for hard sphere contribution. The authors only tested the model for the excess Gibbs energy for NaCl and NaBr aqueous solutions at 25 °C and pressures up to 25 MPa. Lu et al.[32] developed a modified MSA + hard sphere model to describe the activity coefficients of 85 aqueous electrolytes at 25 °C. They introduced an effective diameter which accounts for the change of solvation with the ionic strength; however, the calculations were restricted to this single temperature, and the volumetric properties of the electrolyte solutions were not analyzed.

The purpose of this work is to obtain an expression for the electrostatic contribution of the excess partial molar volume of electrolyte solutions based on the MSA and compare it with the existing models. In the case of electrolyte solutions at moderate concentrations, it is expected that the short-range or excluded volume contribution to the excess partial molar volume could be neglected. The effect of ion association on the excess volume of real 1:1 electrolytes at high temperatures, not considered in the simple MSA model, which would deteriorate the agreement between the experimental and calculated excess volume at high concentration and temperatures, needs also be analyzed.

Theories for the Excess Volume of Electrolyte Solutions

We briefly summarize here the main theories of the volumetric properties of electrolyte solutions assuming that the electrolyte is fully dissociated. For a binary solution containing a solvent (1) and a single electrolyte (2), the total molar volume of the solution is given by

$$V = (1 - x)V_1 + xV_2 \tag{1}$$

where x represents the molar fraction of the solute and V_i is the partial molar volume of component i. As any partial molar property, V_2 can be split into a standard state term plus an excess term, which depends on the solute concentration

$$V_2(m, T) = V_2^{\mathrm{o}}(T) + V_2^{\mathrm{E}}(m, T) \tag{2}$$

The standard state partial molar volume, V_2^{o}, is obtained by extrapolation of V_2 at infinite dilution, and it represents the solute−solvent interaction and is related to the salt−solvent direct correlation function, $c_{12}(r)$, through the relationship[33]

$$\frac{V_2^{\mathrm{o}}}{\nu RT\kappa_1^{\mathrm{o}}} = 1 - 4\pi\rho\int c_{12}^{\infty}(r)r^2\mathrm{d}r = 1 - C_{12}^{\infty} \tag{3}$$

κ_1^{o} being the isothermal compressibility of the pure solvent; $\nu = \nu_+ + \nu_-$ is the number of ions resulting from the electrolyte dissociation; ρ is the total density of the solution; and C_{12}^{∞} is the direct correlation function integral evaluated in the limit of infinite dilution of the electrolyte.

On the other hand, V_2^{E} accounts for the nonideality of the mixture. It is a measure of the solute−solute interaction, and the concentration dependence is different for electrolyte and nonelectrolyte solutes.

The classical theory of Debye−Hückel[2] (DH) gives a simple description for the electrostatic contribution to the excess properties of electrolyte solutions in the framework of the primitive model, that is, point charges immersed in a continuum, structureless, solvent characterized by its macroscopic dielectric permittivity. The DH model neglects not only the short-range interaction between ions but also the hard core effect of the ions in the ionic atmosphere. For this reason, the DH model is valid in the dilute region of concentration, where the Debye−Hückel limiting law (DHLL) for the excess thermodynamic properties represents the exact physical limit.

The excess volume of the electrolyte in the DH model is given by

$$V_{2\ \mathrm{DH}}^{\mathrm{E}} = \frac{3\nu|z_+z_-|}{2}A_{\upsilon}I^{1/2} \tag{4}$$

where z_+ and z_- are the charges of the ions (in electron charge units); I is the ionic strength ($1/2\Sigma m_i z_i^2$), and A_{υ} is the DH limiting slope for the partial molar volume, given by

$$A_{\upsilon} = -4RT\left(\frac{\partial A_{\phi}}{\partial p}\right)_T \tag{5}$$

with

$$A_{\phi} = \frac{1}{3}(2\pi N_{\mathrm{A}}\rho_1^{\mathrm{o}})^{1/2}\left(\frac{e^2}{\varepsilon_1^{\mathrm{o}}kT}\right)^{3/2} \tag{6}$$

where ρ_1^{o} is the density of the pure solvent; N_{A} is the Avogadro constant; $\varepsilon_1^{\mathrm{o}}$ is the solvent relative permittivity; k is the Boltzmann constant; and e is the electron charge.

Different extensions of the DH theory were proposed to extend the model to higher concentrations, the Stokes and Robinson ionic hydration model[34] being a remarkable contribution to the description of the thermodynamic properties of very concentrated electrolyte solutions.

Other theories introduced corrections due to the repulsive short-range interactions or to overcome the problem of the linearization of the Poisson−Boltzmann equation. The most successful of these extensions is the Pitzer model of ion interaction,[21] which combines the long-range Coulombic potential with the hard sphere, short-range potential. The expression for the electrostatic contribution to the excess apparent partial molar volume of the electrolyte, $\phi_{\mathrm{V}}^{\mathrm{E}}$, is

$$\phi_{\mathrm{V}}^{\mathrm{E}} = \frac{\nu|z_+z_-|A_{\mathrm{v}}}{2b}\ln(1 + bI^{1/2}) + 2\nu_+\nu_-RT(mB^{\mathrm{v}} + m^2C^{\mathrm{v}}) \tag{7}$$

where $b = 1.2\ (\mathrm{kg \cdot mol^{-1}})^{1/2}$ and B^{v} and C^{v} are the second and third virial coefficients, the first one being dependent on the ionic strength, I, of the solution, according to

$$B^{\mathrm{v}} = \beta^{(0)\mathrm{v}} + \frac{\beta^{(1)\mathrm{v}}}{2I}[1 - (1 + 2I^{1/2})\exp(-2I^{1/2})] \tag{8}$$

It should be noted that the excess partial molar volume and the excess apparent partial molar volume of the electrolyte are linked through

$$V_2^{\mathrm{E}} = \phi_{\mathrm{v}}^{\mathrm{E}} + m\left(\frac{\partial \phi_{\mathrm{v}}^{\mathrm{E}}}{\partial m}\right)_{T,p,x} \tag{9}$$

Equations 7 and 8 describe quite well the experimental data over a wide range of temperatures, pressures, and concentrations provided that the coefficients $\beta^{(0)\mathrm{v}}$, $\beta^{(1)\mathrm{v}}$, and C^{v} are fitted as a function of pressure and temperature. Usually, the precision of the high temperature volumetric data does not justify the use of a second virial coefficient dependent on the concentration, and $\beta^{(1)\mathrm{v}}$ is taken as zero. However, the predictive value of the Pitzer model is scarce because these coefficients are complex functions of temperature and pressure.

A model of electrolyte solutions based on the fluctuation solution theory was developed by Perry et al.[29] using the direct correlation function integrals derived from the mean spherical approximation for mixtures of charged hard spheres for the electrostatic contribution and the hard spheres mixture theory for the excluded volume. The expression for the partial molar volume at infinite dilution, V_2^{o}, of the electrolyte is

$$\frac{V_2^{\mathrm{o}}}{RT\kappa_T} = (1 - x)(1 - \nu_+ C_{1+} - \nu_- C_{1-}) + \nu x\left(1 - \nu_+^{\,2} C_{++} - 2\nu_+\nu_- C_{+-} - \nu_-^2 C_{--}\right) \tag{10}$$

where κ_T is the isothermal compressibility of the solution and C_{1i} and C_{ij} are the direct correlation function integrals for the solvent−ion and the ion−ion, respectively. Each $C_{\alpha\beta}$ can be written as the sum of the electrostatic part and a short-range or excluded volume part. Besides, C_{1i} includes a correction term which accounts for the fact that the limit of C_{1i} does not tend to the right limit at infinite dilution, so it is the experimental partial molar volume at infinite dilution that is used as a correction factor.

The expressions for the electrostatic parts of $C_{12} = \nu_+ C_{1+} + \nu_- C_{1-}$ and $C_{22} = \nu_+^{\,2} C_{++} + 2\nu_+\nu_- C_{+-} + \nu_-^{\,2} C_-$ were evaluated for these authors using the Debye−Hückel and the mean spherical approximation (MSA). Only the activity coefficients and the osmotic coefficient of electrolytes were tested, but no reference to the calculation of volumetric properties is found for this model.

Finally, we can describe the properties of electrolytes in terms of integral theories based on the Ornstein−Zernike equation,[35] which relates the ion−ion pair distribution function, g_{ij}, with the direct correlation function, c_{ij}, defined as

$$g_{ij} - 1 = c_{ij} + \sum_k \rho_k \int (g_{ik} - 1) c_{kj} \mathrm{d}r_k \tag{11}$$

and can be linked to the ion−ion interaction potential through a closure relationship. The hypernetted chain closure (HNC) describes the ion−ion interaction in electrolyte solutions at the same level of accuracy as the McMillan−Mayer theory,[30] but HNC does not have an exact solution and requires numerical integration of the OZ eq 11. By contrast, the mean spherical closure[36]

$$\begin{aligned} g_{ij}(r) &= 0 \qquad & r &< \sigma_{ij} \\ c_{ij}(r) &= -\frac{z_i z_j e^2}{\varepsilon kT} \qquad & r &> \sigma_{ij} \end{aligned} \tag{12}$$

has an analytical solution, given by Waisman and Leibowitz[37,38] in the restricted primitive model, that is, a mixture of cations and anions of the same size. Blum[24] generalized the solution of the MSA closure for charged spheres of arbitrary diameters (unrestricted primitive model).

The MSA result for the excess of Gibbs energy, related to the activity coefficient of the electrolyte, is given in terms of a screening parameter, Γ, whose physical meaning is identical to that of the DH parameter κ_{D}. Other parameters are the charges, diameters, and concentrations (densities) of the ions in the solution. The expression for Γ is

$$4\Gamma^2 = \alpha^2 \sum_{i=1}^{s} \frac{\rho_i a_i^2}{b_i} \tag{13}$$

where

$$\alpha^2 = \frac{4\pi e^2}{\varepsilon kT} \tag{14}$$

$$a_i = z_i - \frac{\pi}{2\Delta} P_n \sigma_i^2 \tag{15}$$

$$b_i = 1 + \sigma_i \Gamma \tag{16}$$

$$P_n = \frac{1}{\Omega} \sum_{i=1}^{s} \frac{\rho_i \sigma_i z_i}{b_i} \tag{17}$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_{i=1}^{s} \frac{\rho_i \sigma_i^3}{b_i} \tag{18}$$

$$\Delta = 1 - \frac{\pi}{6} \sum_{i=1}^{s} \rho_i \sigma_i^3 \tag{19}$$

In eqs 17 to 19, the sums are over the s ionic species with density ρ_i and diameter σ_i. The excess Gibbs energy is given by[39,40]

$$\frac{G^{\mathrm{E}}}{\nu RT} = \ln \gamma_\pm = -\frac{\alpha^2 \Gamma}{4\pi\nu} \sum_{i=1}^{s} \frac{\nu_i z_i^2}{b_i} - \frac{\alpha^2}{8\nu\rho_2}\left(\frac{P_n^2 \Omega}{\Delta} + \frac{P_n^2}{\Delta^2}\right) \tag{20}$$

$\gamma_\pm$ being the electrolyte mean activity coefficient and ρ_2 being the density of the electrolyte, that is, the sum of the ionic densities.

The excess partial molar volume of the electrolyte, V_2^{E}, can be obtained from the pressure derivative of the excess Gibbs energy at fixed temperature and composition

$$V_2^{\mathrm{E}} = \left(\frac{\partial G^{\mathrm{E}}}{\partial p}\right)_{T,x_1,x_2} \tag{21}$$

In the next section, we will derive an expression for the electrostatic contribution of the excess partial molar volume using the MSA equations.

Electrostatic Contribution to the Excess Volume in the MSA

The pressure derivative of the excess Gibbs energy, eq 21, can be expressed in the more convenient form

$$\left(\frac{\partial G^{\mathrm{E}}}{\partial p}\right)_{T,x_1,x_2} = \left(\frac{\partial G^{\mathrm{E}}}{\partial p}\right)_{T,\rho_2} + \left(\frac{\partial \rho_2}{\partial p}\right)_{T,x_1,x_2}\left(\frac{\partial G^{\mathrm{E}}}{\partial \rho_2}\right)_{T,p} \tag{22}$$

At fixed temperature and electrolyte density, only the dielectric constant of the solvent in the expression of α (eq 14) is a function of pressure, and observing that

$$\frac{G^{\mathrm{E}}}{\nu RT} = \ln \gamma_{\pm} = -\alpha^3 f(\rho_2) \tag{23}$$

it follows that the first term on the right side of eq 22 is

$$\left(\frac{\partial G^{\mathrm{ex}}}{\partial p}\right)_{T,\rho_2} = -\frac{3}{2}\nu RT \ln \gamma_{\pm}\left(\frac{\partial \ln \varepsilon}{\partial p}\right)_{T,\rho_2} \tag{24}$$

The second term can be calculated resorting to the relationship

$$\left(\frac{\partial \rho_2}{\partial p}\right)_{T,x_1,x_2} = \rho_2 \kappa_T \tag{25}$$

and derivating G^{E} in eq 20 with respect to ρ_2

$$\frac{1}{\nu RT}\frac{\partial G^{\mathrm{ex}}}{\partial \rho_2} = -\frac{\alpha^2}{4\pi\nu}\frac{\partial \Gamma}{\partial \rho_2}\sum_{i=1}^{s}\frac{\nu_i z_i^2}{b_i^2} + \frac{\alpha^2 P_n^2}{8\nu\Delta\rho_2^2}\left(\Omega + \frac{1}{\Delta}\right) - \frac{\alpha^2}{8\nu\rho_2}\left[\frac{P_n}{\Delta}\frac{\partial(P_n\Omega)}{\partial \rho_2} - \left(\frac{P_n^2\Omega}{\Delta^2} + \frac{2P_n^2}{\Delta^3}\right)\frac{\partial \Delta}{\partial \rho_2} + \left(\frac{P_n\Omega}{\Delta} + \frac{2P_n}{\Delta^2}\right)\frac{\partial P_n}{\partial \rho_2}\right] \tag{26}$$

Then, resorting to the relationships obtained by deriving eqs 13 and 17 to 19

$$\frac{\partial \Delta}{\partial \rho_2} = \frac{\Delta - 1}{\rho_2} \tag{27}$$

$$\frac{\partial \Omega}{\partial \rho_2} = \frac{\Omega - 1}{\Delta\rho_2} - \frac{\pi\rho_2}{2\Delta}\frac{\partial \Gamma}{\partial \rho_2}\sum_{i=1}^{s}\frac{\nu_i\sigma_i^4}{b_i^2} \tag{28}$$

$$\frac{\partial P_n}{\partial \rho_2} = \frac{P_n}{\rho_2} - \frac{P_n}{\Omega}\frac{\partial \Omega}{\partial \rho_2} - \frac{\rho}{\Omega}\frac{\partial \Gamma}{\partial \rho_2}\sum_{i=1}^{s}\frac{\nu_i z_i\sigma_i^2}{b_i^2} \tag{29}$$

$$\frac{\partial \Gamma}{\partial \rho_2} = \frac{\Phi}{\Psi} \tag{30}$$

where

$$\Phi = \frac{4\Gamma^2}{\rho_2} - \frac{\pi\alpha^2 P_n}{\Delta^2\Omega}\sum_{i=1}^{s}\frac{\nu_i a_i\sigma_i^2}{b_i^2} \tag{31}$$

$$\Psi = 8\Gamma + 2\alpha^2\sum_{i=1}^{s}\frac{\nu_i\sigma_i a_i^2}{b_i^3} - \frac{\pi\alpha^2}{\Delta\Omega}\left(\sum_{i=1}^{s}\frac{\rho_i a_i\sigma_i^2}{b_i^2}\right) \tag{32}$$

In eqs 31 and 32, we have used the same notation as Perry et al.,[29] who derived similar expressions in calculating the direct correlation function integrals used to calculate thermodynamic properties of electrolyte solutions using the fluctuation theory.

Therefore

$$\frac{1}{\nu RT}\frac{\partial G^{E}}{\partial \rho_2} = -\frac{\alpha^2 P_n^2}{4\nu\rho_2^2\Delta^3\Omega} - \frac{\Phi^2}{4\pi\nu\Psi} \tag{33}$$

and the final expression for the excess volume in the MSA is

$$V_2^{\mathrm{E}} = -\frac{3}{2}\nu RT \ln \gamma_{\pm}\left(\frac{\partial \ln \varepsilon}{\partial p}\right)_{T,\rho_2} - RT\kappa_T\left(\frac{\alpha^2 P_n^2}{4\nu\rho_2^2\Delta^3\Omega} - \frac{\Phi^2}{4\pi\nu\Psi}\right) \tag{34}$$

The first term is identical to the Debye−Hückel expression for V^{E}, while the second term represents the ion size effect on the electrostatic contribution to the excess volume. This term becomes negligible at infinite dilution, and the MSA limiting slope for the partial molar volume agrees with the Debye−Hückel limiting law.

Results and Discussion

Figure 1 shows the electrostatic contribution to the excess partial molar volume given by eq 34 for a univalent ($z_+ = |z_-| = 1$) model electrolyte with diameters $\sigma_+ = 0.2$ nm and σ_- between (0.1 and 0.3) nm (note that the results are equivalent if we exchange the anion and cation sizes). The calculations have been performed for aqueous solutions at 25 °C and 0.1 MPa, using the density of the water substance[41] and the dielectric constant and its pressure derivative as reported by IAPWS.[42]

The excess volume is almost insensitive to the ion size when the concentration is lower than about 1 mol·kg^{-1}, and it changes only 20 % when the diameter of one of the ions changes from (0.1 to 0.3) nm at the highest concentration. As expected on the basis of the experimental results,[7] the smaller the ion size, the larger the calculated excess partial molar volume is.

The effect of pressure on the calculated excess partial molar volume is shown in Figure 2, where V_2^{E} is reported at 25 °C, as a function of the concentration, for an electrolyte with $\sigma_+ = \sigma_- = 0.2$ nm. It is observed that V_2^{E} decreases as the pressure increases, as observed for real electrolytes. The isothermal compressibility of the solution in eq 34 can be obtained self-consistently by iterative calculation of the solution volume at two pressures close to the desired one. Since this property is much less sensitive to the model parameters than the partial molar volumes, the calculated compressibility for NaCl (aq) is always in very good agreement with the experimental reported values.[43]

In Figure 3, the temperature dependence of V_2^{E} is reported at saturation pressure, as a function of concentration. The MSA expression captures the real behavior of aqueous electrolytes; that is, the excess volume exhibits a strong increase with temperature.

The MSA model was finally applied to describe the behavior of the excess partial molar volume of aqueous NaCl at high temperature. Figure 4 shows the results obtained for NaCl (aq) at (150 and 300) °C at saturation pressure, as compared to experimental data.[43] The Debye−Hückel limiting law and the Pitzer limiting law at 300 °C are also plotted for comparison. It is observed that the Pitzer limiting law improves the prediction of the excess volume in the dilute region, but both limiting laws fail at concentrations as low as 0.01 mol·kg^{-1}.

The simplest choice for the model parameters is to fix the ion diameters as $\sigma_- = 0.36$ nm for the chloride ion and $\sigma_+ = 0.19$ nm for the sodium ion (crystallographic values). It is observed that the prediction of the MSA model without adjustable parameters agrees with the experimental results within the standard deviation of the data (around ± 2 cm^3·mol^{-1}) up to concentrations of about 0.5 mol·kg^{-1} at 300 °C, while it extends over the entire range of concentrations at 150 °C. This remarkable result is probably fortituous because at 25 °C the MSA model underestimates the experimental excess volumes beyond the uncertainties at concentrations above 0.5 mol·kg^{-1}.

The best fit diameter for the sodium ion at 300 °C (fixing $\sigma_- = 0.36$ nm) was $\sigma_+ = 0.30$ nm, and the predicted excess volumes agree with the experimental data within the experimental error up to concentrations close to 2 mol·kg^{-1}; however, the MSA model overestimates the excess volume for higher concentrations. At 150 °C, this effective sodium ion diameter underestimates the experimental excess volumes beyond the experimental uncertainties for salt concentrations above 1 mol·kg^{-1}, and the same behavior is observed at 25 °C (not shown in Figure 4).

The underestimation of the excess volume by the MSA model at (25 and 150) °C and high concentrations is mainly due to the fact that the hard sphere excluded volume contribution has not been taken into account in our simple MSA model. However,

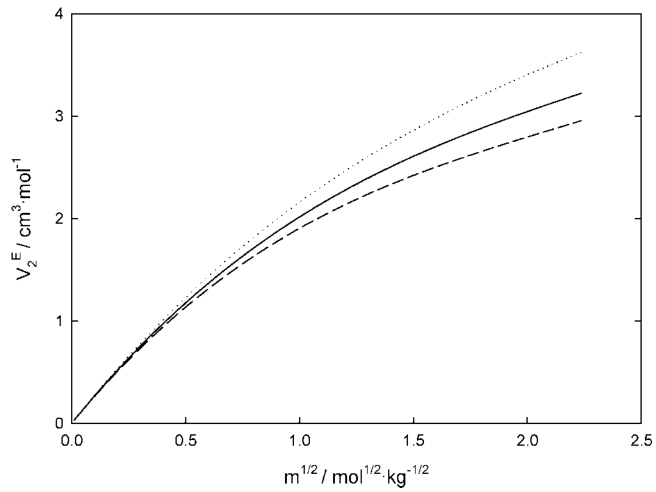

Figure 1. Excess partial molar volume at 25 °C and 0.1 MPa for an electrolyte with dotted line, $\sigma_+ = 0.2$ nm and $\sigma_- = 0.1$ nm; solid line, $\sigma_- = 0.2$ nm; and dashed line, $\sigma_- = 0.3$ nm.

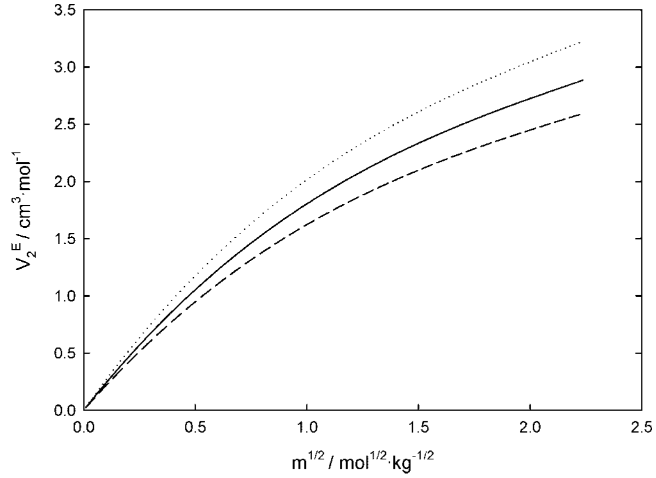

Figure 2. Excess partial molar volume at 25 °C and for an electrolyte with $\sigma_+ = 0.2$ nm and $\sigma_- = 0.2$ nm at dotted line, $p = 0.1$ MPa; solid line, $p = 50$ MPa; and dashed line, $p = 100$ MPa.

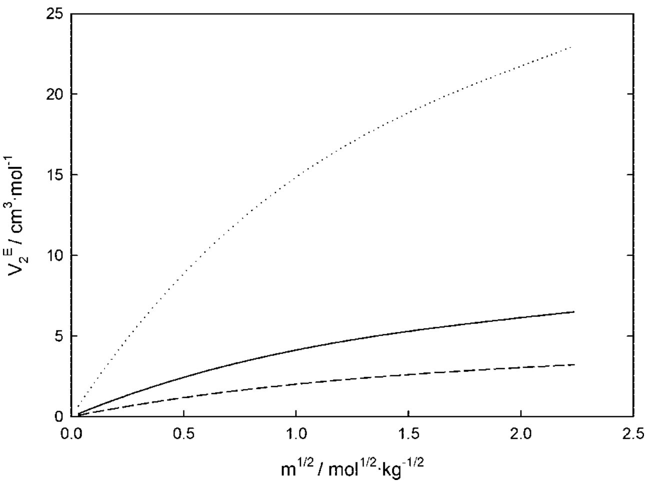

Figure 3. Excess partial molar volume at saturation pressure for an electrolyte with $\sigma_+ = 0.2$ nm and $\sigma_- = 0.2$ nm at dotted line, $T = 200$ °C; solid line, $T = 100$ °C; dashed line, and $T = 25$ °C.

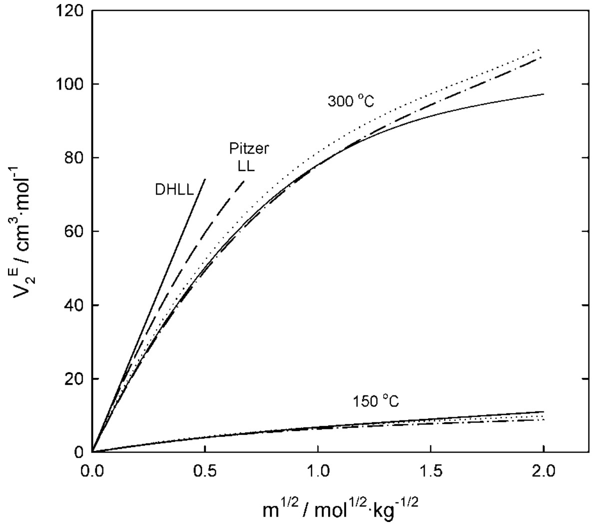

Figure 4. Excess partial molar volume of aqueous NaCl as a function of concentration at 300 °C (8.6 MPa) and at 150 °C (0.4 MPa). The diameter of the chloride was fixed at 0.36 nm. The dotted and dot-dashed lines correspond to the crystallographic diameter (0.19 nm), and the diameter $\sigma_+ = 0.30$ nm for the sodium ion, respectively. The experimental results[43] correspond to the solid lines.

the overestimation of the excess volume at high concentrations at 300 °C is probably due to the effect of ion association, which becomes important even in 1:1 electrolytes in high temperature aqueous solutions, and reduces the fraction of free ions in very concentrated solutions.

The conversion of the excess volumes from the McMillan (MM) to the Lewis−Randall (LR) reference system[44] should also be taken into account in a comprehensive calculation of excess volume of electrolytes. Svarc[45] has shown that the diferences $V_2^{MM} - V_2^{LR}$ for NaCl (aq) are almost constant (0.3 cm^3·mol^{-1}) at 25 °C in the range from (1 to 5) mol·kg^{-1}, while they increase from (4 to 9) cm^3·mol^{-1} at 300 °C. Thus, it is reasonable to ignore this correction when dealing with strong electrolyte at temperatures and concentrations where the ion association is negligeable because it could be implicitly included in the adjustable parameters of the model, as in the case of the Pitzer ion interaction model.

Sedlbauer and Wood[46] have used the MSA expression for the electrostatic excess Helmholtz energy along with the hard sphere contribution[47] to calculate the apparent molar properties of NaCl solutions near the critical point of water. In addition to the hard sphere (HS) repulsion, these authors include in the calculation the conversion from the MM to the LR reference system. Due to the low density of the solution near the critical point, they include the NaCl ion pair in the calculation, using experimental association constants from conductance measurements in the critical region. They compared the experimental excess volume for aqueous NaCl at temperatures between (331 and 430) °C, pressures between (28 and 38) MPa, and concentrations between (0.05 and 1) mol·kg^{-1}, with those calculated with the MSA−HS model using the effective diameters for the ions and the ion pair reported by Tikanen and Fawcett[48] by adjusting activity coefficient data (range of temperatures not reported). The agreement is reasonable taking into account the experimental dispersion of the experimental data near critical conditions and the fact that the diameters of the species were not adjusted. It should be emphasized that Sedlbauer and Wood calculate the molar volumes by numerical derivation of the excess free energy, and consequently an explicit expression for the excess volume was not provided by the authors.

More recently, Trevani et al.[49] used the MSA−HS model to describe the apparent partial molar volumes of NaCl, NaOH, and HCl in water and heavy water at high temperature [(250 and 300) °C]. They compared the experimental excess volume for NaCl, NaOD, and DCl in D_2O, at concentrations between

(0.25 and 2.5) mol·kg^{-1}, calculated with the model using the crystallographic diameters of the ions. They found a good agreement for the three electrolytes at 250 °C, but at 300 °C, the MSA−HS model overpredicts the experimental excess volumes at concentrations above 1 mol·kg^{-1}, probably because of the ion-association effect, as found in this work for NaCl in water at 300 °C.

In summary, it is shown that the simple MSA model with an adjustable parameter (the sodium ion diameter in this case) is able to describe the excess volume of NaCl aqueous solutions up to 300 °C and moderate concentrations [(1 to 2) mol·kg^{-1}]. The performance of the MSA model without adjustable parameters (using the crystallographic diameters of the ions) for predicting volumetric properties of NaCl is still very good up to 300 °C if the concentration is restricted to (0.3 to 0.5) mol·kg^{-1}.

The calculation of *pVTx* properties of aqueous NaCl using the simple MSA model is really encouraging and prompts us to undertake a most comprehensive analysis of its performance over a complete set of data for 1:1 or even asymmetric electrolytes on the temperature, pressure, and concentration ranges where ion association can be neglected. The addition of a hard sphere term could improve the predictions at very high concentrations, but it should be first analyzed whether the increasing complexity of the calculation related to this contribution could be avoided by including a concentration-dependent ionic diameter in the MSA model.

Conclusions

An expression for the electrostatic part of the excess partial molar volume was derived from the mean spherical approximation in its unrestricted primitive version. This equation yields the Debye−Hückel limiting law at infinite dilution, and it is able to describe with accuracy the excess volume of NaCl aqueous solutions at high temperatures and concentrations up to (1 to 2) mol·kg^{-1}, by adjusting one of the ionic diameters. Even when the ionic crystallographic diameters are used, the MSA model gives a reasonable estimation of the excess partial molar volume of electrolytes over a wide range of concentration, pressure, and temperatures, provided that the electrolyte is fully dissociated.

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