Solvation in high-temperature electrolyte solutions. III. Integral equation calculations and interpretation of experimental data

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The solvation of infinitely dilute aqueous Cl\(^-\), Br\(^-\), I\(^-\), Cs\(^+\), K\(^+\), M\(^+\), and the corresponding salts is analyzed by integral equation calculations along three near critical water isotherms according to the recently proposed molecular-based formalism which connects the solvent environment around individual ionic species with their macroscopic solvation behavior. Special emphasis is placed on the temperature dependence of some solvation-related macroscopic properties that are identified as potential candidates for the development of improved engineering correlations. Formal and integral equation calculations are then used to interpret recent experimental data, and some relevant theoretical implications regarding the modeling of high-temperature aqueous electrolyte solutions are discussed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1343875]

I. INTRODUCTION

Hydrothermal solution chemistry reveals a number of potential applications in a wide range of disciplines, including high-temperature microbiology,\(^1,2\) hydrogen-rich fuel gas production from biomass,\(^3\) synthesis of textured materials,\(^4-6\) and oxidation of chemical and biochemical wastes.\(^7,8\) With these applications come also new fundamental and technological challenges, such as metal corrosion,\(^9\) clogging solid deposition on reactor pipes,\(^10,11\) and catalysis of undesired reactions\(^12\) by solvated ions.

Effort has been expended in the study of hydrothermal solutions to determine their thermodynamic, transport, and spectroscopic properties in order to meet these technological challenges in the design of effective processes.\(^13-15\) A major objective behind this enterprise is to generate a fundamentally-based understanding of high-temperature solvation of species over a wide range of molecular asymmetries, including imperfect gases, ionic, polar, and nonpolar compounds.\(^16\) Molecular asymmetry, the actual source of solvation nonideality,\(^17\) translates typically into pronounced gradients of solvent local density around charged species. In turn, these solvent inhomogeneities give rise to electrostriction and dielectric saturation phenomena, which render traditional solvation approaches inadequate.\(^18,19,20\)

The failure of conventional solvation approaches for the description of hydrothermal solutions can be understood by recognizing that the formation of these solutions involved the coexistence of processes with disparate length scales, i.e., short-ranged (solvation) and long-ranged (compressibility-driven) phenomena.\(^21\) In particular, the presence of compressibility-driven phenomena makes near-critical hydrothermal systems extremely challenging to model, unless we sort and isolate the (compressibility-driven) propagation of the density perturbation from the (solvation-related) finite-density perturbation phenomena.\(^22\)

In this paper, part III of a series on ion solvation\(^23,24\) we briefly review the main features of the molecular formalism for high-temperature electrolyte solutions recently proposed to tackle such a challenge\(^24\) (Sec. II). Then, we illustrate the formalism by performing integral equation calculations of model aqueous electrolyte solutions for a variety of alkali metal halides (Sec. III), and use these results to interpret recent experimental data for aqueous alkali halide solutions\(^25\) (Sec. IV). Finally, we discuss a molecular interpretation for the success of the recently proposed regression approach for the solute partial molar volumes,\(^25,26\) and suggest a more appropriate alternative for the modeling of these systems.

II. HIGH-TEMPERATURE SOLVATION OF ELECTROLYTES

The solvation formalism that we have recently presented (part II of this series\(^24\)) is based on the discrimination between the two length-scale phenomena associated with the formation of the solution, i.e., solvation and compressibility-
driven phenomena.\textsuperscript{21,22} This is achieved by splitting the species total correlation functions into their direct and indirect contributions according to the Ornstein–Zernike (OZ) equation.\textsuperscript{24}

The solvation of a salt \( C^{\nu+}A^{\nu-} \) in a solvent at constant state conditions, where \( C^{\nu+} \) is the cation and \( A^{\nu-} \) is the anion, can be portrayed by the following thought experiment (see Fig. 1 of part II) on a system initially considered as a pure solvent in which \( \nu \) solvent molecules (\( \nu = \nu_+ + \nu_- \), where \( \nu_+ \) and \( \nu_- \) are the stoichiometric coefficients of the salt) are distinguishable by their solute labels. As such, this system constitutes an ideal solution in the sense of the Lewis–Randall Rule.\textsuperscript{17,27} The experiment proceeds with the mutation of the distinguishable \( \nu \) solvent molecules into the final neutral ionic solute \( C^{\nu+}A^{\nu-} \) to form the infinitely dilute nonideal solution. This process in which the original \( \nu \) solute species in the ideal solution (where solute–solvent interactions are identical to solute–solute and solvent–solvent interactions) are converted into the neutral ionic solute, is driven by the difference of free energy \[ \mu^o_U(T,P) - \nu \mu^o_V(T,P) = \int_0^{\rho(P)} \left( \frac{\partial P}{\partial \rho} \right)_{T,P} d\rho \], where subscripts \( U \) and \( V \) denote solute and solvent species, respectively.

Our goal is the unambiguous characterization of the solvation process by drawing rigorous connections between the microscopic changes of the solvent structure around the mutating species and the relevant macroscopic (thermodynamic) properties. As we discussed elsewhere\textsuperscript{28} there are at least four equivalent ways of interpreting the driving force of the solvation process, from either a microscopic or a macroscopic perspective. For the sake of brevity, and to support our forthcoming analysis and subsequent interpretation, here we describe a few relevant expressions, considering the neutral ionic solute as a hypothetical ‘molecular’ entity in order to derive the solute properties that are usually measured experimentally. These results are then used for illustration purposes (for the individual ion counterpart the reader should consult part II) to interpret the most recent experimental data, and to suggest fundamentally-based alternatives for the regression of experimental raw data.

To display the four alternative interpretations we start from the exact thermodynamic expression for the driving force,

\[ \mu^o_U(T,P) - \nu \mu^o_V(T,P) = \int_0^{\rho(P)} \left( \frac{\partial P}{\partial \rho} \right)_{T,P} d\rho \]

where the superscript \( r \) denotes a residual quantity for a pure \( (o) \) or an infinitely dilute \( (\infty) \) species at the indicated state conditions, respectively; \( T \) is the absolute temperature; \( P \) is the total pressure; \( \bar{v}^o_U = v^o_U \) is the partial molar volume of the pure solvent such that \( \rho = 1/\bar{v}^o_U \) is its molar density counterpart; \( \kappa \) is the solvent isothermal compressibility; and \( \bar{v}^o_V \) is the solute partial molar volume. We can now rewrite Eq. (1) in terms of the rate of change of pressure (at constant temperature and solvent density) caused by the structural perturbation of the solvent around the solute, i.e., \( \left( \frac{\partial P}{\partial \rho} \right)_{T,P} \),

\[ \mu^o_U(T,P) - \nu \mu^o_V(T,P) = \int_0^{\rho(P)} \left( \frac{\partial P}{\partial \rho} \right)_{T,P} d\rho \]

Equation (2) stresses that the integrand is finite at any state condition, and allows us to make contact with the microstructure of the system,\textsuperscript{22} i.e., (see Appendix B of Chialvo et al.\textsuperscript{24}),

\[ \left( \frac{\partial P}{\partial \rho} \right)_{T,P} = -\nu \rho T (C^o_{VV} - C^o_{UV}), \quad (3) \]

where \( C^o_{VV} \) and \( C^o_{UV} \) are the direct correlation function integrals (DCFI) for the solvent–solvent and solute–solvent interactions (i.e., the descriptors of the solution microstructure),\textsuperscript{29,30} and \( k \) is the Boltzmann constant.

Another alternative expression for the driving force is obtained through the excess particle number,\textsuperscript{22}

\[ N_{U,ex}^\infty = 4\pi \rho \int_0^{\infty} \left[ g^o_{UV}(r) - g^o_{VV}(r) \right]^2 dr \]

\[ = -\kappa \left( \frac{\partial P}{\partial \rho} \right)_{T,P} N_{U,ex}^\infty \]

(4)

that represents the number of solvent molecules around the solute in excess of that around any solvent molecule, i.e., around the solute in the Lewis–Randall ideal solution. Thus, after invoking its solvation contribution \( N_{U,ex}^\infty(\text{SR}) = (\kappa^{IG}/\kappa) N_{U,ex}^\infty \) (Ref. 28) we obtain

\[ \left( \frac{\partial P}{\partial \rho} \right)_{T,P} = -\frac{N_{U,ex}^\infty(\text{SR})}{\kappa^{IG}}, \quad (5) \]

where \( \kappa^{IG} = (\rho kT)^{-1} \) is the isothermal compressibility of the ideal gas at the state conditions of the solvent, and \( \kappa \) denotes a short-ranged contribution (associated with the local solvent density perturbation) to the corresponding diverging \( N_{U,ex}^\infty \). This equation emphasizes the explicit connection between the pressure perturbation (at constant \( T \) and \( \rho \)) associated with the disruption of the solvent structure around the solute and the corresponding effective change in the number of solvating (directly correlated to the solute) solvent molecules. Note that \( N_{U,ex}^\infty(\text{SR}) \) does not involve any assumption regarding the size of the solvation shell, as opposed to the conventional definition of coordination (or solvation) numbers which relies on an ambiguous choice of a radius based on some structural information of the solvation shell. In this sense, \( N_{U,ex}^\infty(\text{SR}) \) can be described as an effective solvation number (not to be confused with a coordination number\textsuperscript{24,28}) since its knowledge allows us to reconstruct rigorously all other solvation properties.

Analogously, the pressure derivative \( \left( \frac{\partial P}{\partial \rho} \right)_{T,P} \) can be rewritten in volumetric terms as

\[ \left( \frac{\partial P}{\partial \rho} \right)_{T,P} = kT \rho^2 \left( \bar{v}^o_U(\text{SR}) - \nu \bar{v}^o_V \right) \]

(6)

so that the difference of chemical potentials in Eq. (1) can be macroscopically interpreted not only in terms of the finite pressure perturbation \( \left( \frac{\partial P}{\partial \rho} \right)_{T,P} \) as in Eq. (2), but also in terms of either the corresponding finite volumetric perturbation \( \left( \frac{\partial P}{\partial \rho} \right)_{T,P} \) or the resulting effective solvation number \( N_{U,ex}^\infty(\text{SR}) \) as follows:
\[ \mu^v_u(T, P) - \nu \mu^v_v(T, P) = kT \int_0^{\rho(P)} \left( \bar{u}^v_u(SR) - \nu \bar{u}^v_v \right) d\rho \]

As we have already discussed, the properties available from experiment are those of the hypothetical electro-neutral ionic salt. However, the salt properties at infinite dilution are actually linear combinations of the corresponding single-ion counterparts, and therefore, the solvation quantities for salts can be expressed in terms of the corresponding pressure, solvation number or density perturbation around the individual ions (the actual species in solution). This will not be addressed here since it has been discussed in much detail elsewhere.

In summary, in the preceding analysis we have given equivalent ways to express the finite change of free energy in the solvation process that creates an infinitely dilute nonideal mixture from the original ideal solution, when \( \nu \) solvent molecules are mutated into \( \nu_+ \) cations and \( \nu_- \) anions in solution. The resulting solvation properties are well-behaved state-dependent quantities; the enthalpic and entropic contributions to the free energy change on solvation are discussed in detail elsewhere. Yet, their temperature and pressure derivatives will diverge at the solvent criticality, a behavior that implies an advantageous (and not always well appreciated) exact cancellation between the corresponding divergent portions of the enthalpic and entropic contributions to \( (\mu^v_u(T, P) - \nu \mu^v_v(T, P)) \). These diverging contributions to the partial molar enthalpy and entropy of the solute at infinite dilution are not associated with the solvation process (the local perturbation) but rather with the propagation of the perturbation across the system, and are characterized by the correlation length of the solvent. This feature suggests the need for a precise sorting between the two contributions, i.e., separating solvation from compressibility-driven phenomena, to avoid working with unnecessary implicitly diverging quantities in the modeling of dilute solutions in highly-compressible media. Note that O’Connell and colleagues have developed macroscopic models, based on the regression of experimental data to determine the direct correlation function integrals as functions of state conditions and composition, and subsequently, to calculate the thermodynamic properties of a variety of systems according to the Kirkwood–Buff fluctuation theory of solutions.

III. INTEGRAL EQUATION CALCULATIONS AND INTERPRETATION OF EXPERIMENTAL RESULTS

A. Models, methodology, and state conditions

In this section we study the solvation behavior of a variety of anions and cations, covering a wide range of ionic diameters \( 1.08 < d_i / d_v < 1.96 \) (where \( d_i \) and \( d_v \) denote the diameters of the individual ions and the solvent, respectively) along three near-critical isotherms (643 K, 673 K, and 703 K), in the density range \( 0.0136 \leq \rho (g/cm^3) \leq 0.81 \). In the present calculations the systems are defined as charged hard sphere ions immersed in a model aqueouslike solvent, represented by hard spheres with embedded point polarizabilities and permanent electrostatic multipole moments including quadrupole and octupoles as given in Tables I and II. The calculations were carried out by solving the reference hypernetted-chain (RHNC) equations with solvent polarization effects treated at the self-consistent mean-field (SCMF) level as described elsewhere. Details on these calculations for systems at normal conditions were presented earlier, and some others for high temperature solutions are given elsewhere. In addition, and in contrast to the normal unit charges, the ions bear only a 66% of the full charge. The reduced charges were necessary to avoid the collapse of solvent molecules on bare ions thus ensuring the convergence of the integral equation calculations over the entire solvent density range considered.

In order to make a meaningful comparison between model predictions and experimental results, we first estimated the solvent critical conditions based on the divergence of the isothermal compressibility. According to the predicted isothermal density dependence of the isothermal compressibility, Fig. 1, the critical point of this waterlike solvent is \( T_c \approx 643 \) K and \( \rho_c \approx 0.20 \) g/cm\(^3\), i.e., the three isotherms considered in this study are supercritical. The corresponding \( P - \rho - T \) behavior of the model solvent along the isotherms 643 K, 673 K, and 703 K is presented in Fig. 2.

B. Integral equation results

We targeted the solvent properties including the dipole moment, the dielectric constant, the pressure, the isothermal compressibility, and the ion partial molar volumes at infinite dilution. Based on these properties, and according to the solvation formalism, we determined the properties of the nine resulting salts (\( U \)) at infinite dilution, i.e., CsBr, CsCl, CsI, KBr, KCl, KI, MBr, MCl, and MI, where M\(^+\) might

<table>
<thead>
<tr>
<th>Ion</th>
<th>( d^* )</th>
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<tbody>
<tr>
<td>K(^+)</td>
<td>1.08</td>
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<tr>
<td>Cl(^-)</td>
<td>1.16</td>
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<tr>
<td>Cs(^+)</td>
<td>1.28</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>1.28</td>
</tr>
<tr>
<td>I(^-)</td>
<td>1.44</td>
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<tr>
<td>M(^+)</td>
<td>1.96</td>
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<thead>
<tr>
<th>Ion</th>
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<tr>
<td>CsI</td>
<td>2.8 Å</td>
</tr>
<tr>
<td>KBr</td>
<td>1.85 \times 10^{-18} \text{ esu cm}</td>
</tr>
<tr>
<td>KCl</td>
<td>1.501 Å</td>
</tr>
<tr>
<td>KI</td>
<td>1.390 Å</td>
</tr>
<tr>
<td>MBr</td>
<td>1.442 Å</td>
</tr>
<tr>
<td>MCl</td>
<td>2.63 \times 10^{-26} \text{ esu cm}^2</td>
</tr>
<tr>
<td>MI</td>
<td>2.50 \times 10^{-26} \text{ esu cm}^2</td>
</tr>
<tr>
<td>CsI</td>
<td>1.13 \times 10^{-26} \text{ esu cm}^2</td>
</tr>
<tr>
<td>MBr</td>
<td>2.30 \times 10^{-34} \text{ esu cm}^3</td>
</tr>
<tr>
<td>MI</td>
<td>9.6 \times 10^{-34} \text{ esu cm}^3</td>
</tr>
<tr>
<td>MI</td>
<td>1.34 \times 10^{-34} \text{ esu cm}^3</td>
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represent an alkylammonium cation. In particular, we focus our attention on the isothermal density-dependence of \( \overline{v}_{U}^\prime \), \( \overline{v}_{U}^\prime(\text{SR}) \), \( (\partial P/\partial x_{U})_{T,R} \), \( N_{U,\text{ex}}^\prime(\text{SR}) \), and some related microscopic analogs.24

1. Salt partial molar volumes and their solvation counterparts

In Figs. 3(a)–11(a) we display the isothermal density dependence of the salt partial molar volumes along the three supercritical isotherms. As we might have expected, based on the strength of the ion–water interactions relative to that for the water–water interactions, these partial molar properties are negative and eventually diverge to minus infinity as the solvent approaches its critical point. In the classification scheme used in the supercritical fluid community, these salts behave as attractive40 or nonvolatile41 solutes, i.e., because the ion–water interactions are stronger than the water–water interactions, the volumetric perturbation in the process of inserting the ions in water during the solvation process translates into a volume contraction (see below the pressure and solvation number counterparts). Obviously, for this type of solute–solvent model, the volumetric perturbation on the solvent structure becomes larger with decreasing ion sizes or increasing ion charge density.

In all cases the partial molar volume exhibits a minimum at a density smaller than the solvent’s critical density. This minimum shifts to smaller densities as the temperature increases. The magnitude of \( \overline{v}_{U}^\prime \) at this minimum is approximately inversely proportional to the diameter \( d_{U} \) given by \( d_{U} = d_{+} + d_{-} \), i.e., \( d_{\text{Br}^{+}} > d_{\text{Cl}^{-}} > d_{\text{Cs}^{+}} > d_{\text{K}^{+}} > d_{\text{Cs}^{-}} > d_{\text{K}^{-}} \). Moreover, the partial molar volume increases with solvent density and eventually becomes positive for densities twice the critical value. The trend of the density dependence of \( \overline{v}_{U}^\prime \) at the crossover indicates that the larger the salt the more positive the resulting partial molar volumes. This behavior suggests that even attractive (nonvolatile) solutes at near-critical densities, such as strong electrolytes in aqueous solution, might become repulsive solutes in denser environments (see below the corresponding pressure and solvation number perturbation counterparts).

Note also that the partial molar volumes at supercritical
densities exhibit a negligibly small temperature dependence, a behavior that will take center stage in the next section. In fact, the temperature independence of $\bar{v}_U$ is noted over a wide supercritical density range in this study. See Figs. 3–11. Note that, in contrast to the behavior of the full partial molar volume $\bar{v}_U$, the solvation contribution $\bar{v}_U^{(SR)}$ displays a clear minimum around $\rho d V^3 \approx 0.02$, a density that appears to be independent of either temperature or type of solute. At this minimum, the magnitude of $\bar{v}_U^{(SR)}$ follows the same trend with $d_U$ as $\bar{v}_U$, i.e., the smaller the salt size, the larger is the solvation contribution to the salt partial molar volume.

2. Solvation numbers

In Figs. 3(c)–11(c) we present the isothermal density dependence of the solvation number $N^\infty_U(SR)$ in comparison with the corresponding $\bar{v}_U^{(SR)}$. Because of the direct connection between the two quantities [see Eqs. (5) and (6)],

$$N^\infty_U(SR) = v - \rho \bar{v}_U^{(SR)},$$

this quantity exhibits many of the same features as the corresponding $\bar{v}_U^{(SR)}$, in particular, the lack of temperature dependence for supercritical densities, and a maximum value around $\rho d V^3 \approx 0.1$ which also appears to be independent of either the temperature or the type of ions.

At subcritical densities, the solvation numbers $N^\infty_U(SR)$ are positive, reflecting the condition of attractive (nonvolatile) solutes. At the maximum ($\rho d V^3 \approx 0.1$) these solvation numbers range from $\sim 18$ for KCl to $\sim 8$ for MI. Moreover, as the solvent density increases, these solvation numbers decrease toward negative values, i.e., the solutes become repulsive (volatile) species. This crossover occurs around $\rho d V^3 \approx 0.6$ for KCl, and moves to smaller densities with increasing ion size, i.e., to $\rho d V^3 \approx 0.3$ for MI. Consequently, while KCl behaves as an attractive solute over essentially the entire range of densities studied here ($0 < \rho < 3.3 \rho_c$), the remaining eight solutes change their behavior from attractive to repulsive species, as indicated by the negative solvation numbers at $\rho d V^3 = 0.6$ which vary from $N^\infty_U(SR) = -3$ for KBr to $N^\infty_U(SR) = -34$ for MI.
3. Salt pressure perturbation parameter

In Figs. 12–14 we present the isothermal density dependence of the pressure perturbation \( \frac{\partial P}{\partial x_U} \). Because of its direct connection to the solvation number [see Eq. (5)], there is only a weak change on the density and temperature dependence of \( \frac{\partial P}{\partial x_U} \), resulting from the explicit proportionality with \( \kappa T^{-1/2} \). The pressure perturbation \( \frac{\partial P}{\partial x_U} \) becomes negative and exhibits a rather flat minimum at a supercritical density, consistent with the attractive nature of the salt. However, and as already observed in the associated solvation properties, \( \frac{\partial P}{\partial x_U} \) becomes positive with increasing density, i.e., the salts change from attractive to repulsive solutes. Obviously, this change of behavior for the neutral salt depends on the magnitude and sign of the quantities for the individual ions, since \( \frac{\partial P}{\partial x_U} \) becomes attractive to repulsive solutes. Obviously, this change of behavior for the neutral salt depends on the magnitude and sign of the quantities for the individual ions, since \( \frac{\partial P}{\partial x_U} \) becomes positive with increasing density, i.e., the salts change from attractive to repulsive solutes.

3.3. Integral equation results vs experimental data

The main challenge for an experimentalist, beyond the arduous task of performing accurate measurements, is the proper interpretation of the raw data. This is obviously not an easy task, especially when dealing with potentially divergent quantities such as the observed partial molar properties of infinitely dilute solutes. In this section we would like to illustrate how the formalism described in Sec. II, in conjunction with integral equation calculations on model systems, can facilitate the interpretation of high-temperature solvation, and guide the selection of quantities to be used in the development of engineering correlations. For example, in a series of recent publications, Wood and co-workers reported the most accurate values of partial molar properties.
for a series of ionic and nonionic species at infinite dilution in high-temperature aqueous solutions. They proposed a successful regression of the raw data in terms of the quantity

\[ D_{UV}' = \left( \frac{\kappa}{\kappa} \right) \tilde{\nu}_{UV} \]

This quantity exhibits an appealing weak temperature dependence in the range 550 ≤ T(K) ≤ 725, which allows a rather simple and well-behaved density correlation to predict \( \tilde{\nu}_{UV}' \) at any other supercritical state condition, based solely on the thermodynamic properties of pure water. While the choice of properties involved in the quantity \( D_{UV}' \) was not accidental, in that it contains all the components to cancel the potential divergence in \( \tilde{\nu}_{UV} \), it is not clear why \( D_{UV}' \) should be more advantageous than other choices, or why the temperature dependence should be negligible.

In Fig. 15 we show the solvent density-dependence of \( D_{UV}' \) along three supercritical isotherms for infinitely dilute CsCl aqueouslike solutions as predicted by the integral equation calculations (A similar comparison has already been presented for CsBr in Ref. 28). We also compare these results with the corresponding data of Sedlbauer et al., which were determined from measurements yielding solute partial molar volumes at infinite dilution within the temperature and density ranges 604 ≤ T(K) ≤ 717 and 0.26 ≤ ρ(g/cm³) ≤ 0.60, respectively. To be more precise, Sedlbauer et al. determined \( \tilde{\nu}_{UV} \), and subsequently developed a simple density correlation of \( D_{UV}' \), for NaCl, LiCl, NaBr, and CsBr. Based on this correlation, and considering that \( \tilde{\nu}_{UV} = \nu - \tilde{\nu}_{in} + \nu_{in} \tilde{\nu}_{in} \), we were able to estimate \( D_{UV}'(\text{CsCl}) = \tilde{\nu}_{UV}'(\text{NaCl}) + D_{UV}'(\text{NaBr}) + D_{UV}'(\text{CsBr}) \) as indicated in the Appendix. Subsequently, we determined \(( \partial P/\partial x_{UV} )_{T,\rho} \) and \( N_{UV}^c(SR) \) (Figs. 16 and 17) according to the calculated \( D_{UV}'(\text{CsCl}) \) and the corresponding properties of pure water.

The comparison displayed in Figs. 15–17 is only intended to show that the chosen intermolecular potential model is capable of predicting the same trends and magnitude of the solvation quantities of interest, i.e., by capturing the relevant physics underlying the solvation process.

IV. DISCUSSION AND FINAL REMARKS

We have characterized the solvation behavior of aqueous electrolytes and illustrated it with nine salts in high-temperature solutions through integral equation calculations.
of simple (nonprimitive) aqueous electrolyte models, according to thermodynamic and statistical mechanical views. The task was achieved by determining the individual properties of six infinitely dilute ions in a waterlike solvent, and through discrimination between the true solvation phenomena and the largely unrelated accompanying compressibility-driven phenomena. These solvation-related properties have unambiguous microscopic meaning and can be determined experimentally from the isothermal compressibility of the pure solvent $k$ and the infinite-dilution partial molar properties. For the case under consideration we have that the solvation contribution to $\bar{v}_U$ is given by,

$$\bar{v}_U^\infty (SR) = (\kappa^G / k)(\bar{v}^\infty_U - \nu \bar{v}_V^o) + \nu \bar{v}_V^o,$$

where $\bar{v}_U^\infty$ is the solvation number,\textsuperscript{43}

$$N_{U,ex}^\infty (SR) = (\kappa^G / k)(\nu - (\bar{v}_U^\infty / \bar{v}_V^o)),$$

and the pressure perturbation,

$$\left( \frac{\partial P}{\partial x_U} \right)^\infty_{T,\rho} = (\bar{v}_U^\infty / \bar{v}_V^o - \nu) / k.$$

Once again it is important to bear in mind that the excess number (or solvation number) $N_{U,ex}^\infty (SR)$ and its ion counterparts should not be confused with the usual coordination number, described in terms of the geometric arrangement of solvent molecules around a central species.\textsuperscript{44} Consequently, they cannot be compared with the conventional solvation/hydration numbers obtained through NMR, EXAFS, neutron or x-ray diffraction measurements.\textsuperscript{45,46} The reason is rather obvious, on the one hand $N_{U,ex}^\infty (SR)$ accounts for the solvent molecules directly correlated with the central species in excess over that for the (Lewis–Randall) ideal solution counterpart, and encompasses unambiguous connections with all solvation properties.\textsuperscript{24} On the other hand, the conventional definition considers the solute–solvent coordination within an ambiguously defined solvation shell. Beyond the obvious ambiguity in the choice of the radius of solvation, which translates into solvation numbers that depend on the method of determination, there is no clear connection between these numbers and the relevant solvation properties. The rigorous connection between structure and macroscopic properties is given by statistical mechanical expressions involving either
the total or the direct correlation function integrals over the entire volume of the system. Therefore, the use of a portion of the total correlation function, that inside the solvation shell to define the coordination number, cannot account for the remaining contributions to properties beyond the solvation radius and requires the introduction of assumptions that render the resulting approach unreliable. In summary, knowledge of $N_U^{\text{ex}}(\text{SR})$ allows us to determine $D_{UV}$ rigorously, while the more familiar concept of solvation/hydration numbers does not.

Considering that one of the primary goals of our molecular-based studies is to provide the fundamental understanding needed to develop successful engineering correlations, we use the proposed solvation formalism as a powerful tool to interpret recent experimental data, and hopefully, to guide the choice of the best combination of properties for regression purposes, and suggests some relevant questions regarding either the underlying microscopic mechanism or possible connections between $D_{UV}$ and well-defined solvation quantities. Since we have recently partially addressed the first item, here we will tackle the second one, through the interpretation of $D_{UV}$ in terms of the solvation quantities $N_U^{\text{ex}}(\text{SR})$, $(\partial P/\partial x_U)_{T,p}^\infty$, $u_V^\infty(\text{SR})$, and $v_U^0(C_{UV}^\infty-C_{VV}^\infty)$ by invoking Eqs. (3), (5), (6), and (8), i.e.,

$$D_{UV}^\infty = D_{VV}^\infty + v u_V^\infty(C_{VV}^\infty-C_{UV}^\infty)$$

$$= D_{VV}^\infty - u_V^\infty N_{U,ex}(\text{SR})$$

$$= D_{VV}^\infty + u_V^\infty \kappa^G \left( \frac{\partial P}{\partial x_U} \right)_{T,p}^\infty$$

$$= D_{VV}^\infty - v u_V^\infty + u_V^\infty(\text{SR}),$$

where for convenience we define $D_{VV}^c = u_V^\infty(\kappa^G/\kappa) = D_{UU}^{\text{IS}}$, which is a property of the pure solvent, i.e., the ideal solution counterpart of $D_{UV}^\infty$.

![FIG. 12](image1.png) Isothermal density dependence of $(\partial P/\partial x_U)_{T,p}^\infty$ for an infinitely dilute of (a) KCl, (b) KBr, and (c) KI aqueous solutions. Pressure in units of $kT$ and $d_U^\infty$.

![FIG. 13](image2.png) Isothermal density dependence of $(\partial P/\partial x_U)_{T,p}^\infty$ for an infinitely dilute of (a) CsCl, (b) CsBr, and (c) CsI aqueous solutions. Pressure in units of $kT$ and $d_U^\infty$. 

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expressions and the observed behavior for the density dependence of the solvation quantities, a more appropriate regression quantity than $D_{UV}$ would be $\Delta D_{UV}^\infty = D_{UV}^\infty - \nu D_{UV}^{(IS)}$, i.e.,

$$\Delta D_{UV}^\infty = \nu \bar{u}_V^o (C_{VV}^o - C_{UV}^o) = -\bar{u}_V^o N_{U,ex}^o (SR) = \bar{u}_V^o K^G \left( \frac{\partial P}{\partial \lambda_U} \right)_{T,P} = \bar{u}_V^o (SR) - \nu \bar{u}_V^o$$

since this quantity depends exclusively on the solute-solvent molecular asymmetries (the sources of nonidealities), and thus, it measures directly the solvation strength.

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TABLE III. Coefficients for Eq. (A1).

<table>
<thead>
<tr>
<th>Salt</th>
<th>10^4a_0 (m^3/kg)</th>
<th>10^4a_1</th>
<th>10^4a_2</th>
<th>10^6a_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBr</td>
<td>-27.747</td>
<td>14.405</td>
<td>-27.386</td>
<td>17.784</td>
</tr>
<tr>
<td>NaCl</td>
<td>-33.206</td>
<td>18.274</td>
<td>-36.306</td>
<td>24.451</td>
</tr>
</tbody>
</table>

APPENDIX

The regression proposed by Wood and co-workers for \( D_{UV}^c \) reads,

\[
D_{UV}^c = a_0 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3,
\]

where \( \rho \) is the density of pure water in units of kg/m^3, and the coefficients are given in Table III for the three salts of interest.

Based on these values the expression for the CsCl becomes

\[
D_{UV}^c = -0.3418 + 1.8831 \times 10^{-3} \rho - 3.7387 \times 10^{-6} \rho^2 \\
+ 2.5243 \times 10^{-9} \rho^3.
\]

43. Note that a misprint in the expression for \( N_{UV}^c \) (SR) has been detected in Eq. (19) of Ref. 28, and in Eq. (52) of Ref. 24. In both cases the first term, \((1 - \rho)\), should be deleted.
44. Y. Marcus, Ion Solvation (Wiley, Chichester, 1985).