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Molecular approach to high-temperature solvation. Formal, integral equation and experimental results*

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Abstract. The solvation of infinitely dilute CsBr in high-temperature aqueous solutions is analysed by integral equation calculations, according to the recently proposed molecular-based formalism which connects the solvent environment around individual ionic species and their macroscopic solvation behaviour. Recent experimental data for infinitely dilute CsBr aqueous solutions are interpreted via the same formalism and compared with their analogous integral equation calculations. Finally, some relevant theoretical implications regarding the modelling of high-temperature aqueous electrolyte solutions are discussed and illustrated by integral equation results.

1. Introduction

The theoretical treatment of the solvation phenomenon for simple ions in aqueous solutions has been rather difficult, despite the apparent simplicity of the system. Long-range solvent-screened electrostatic interactions, coupled to the large variation (with state conditions) of the dielectric permittivity of water, give rise to a gamut of rather complex solvation phenomena including dielectric saturation, electrostriction and ion association [1]. Notably, ion solvation in high-temperature/pressure aqueous solutions plays a leading role in hydrothermal chemistry, such as in the natural formation of ore deposits [2], scaling and corrosion in boilers and reactors [3, 4] and in high-temperature microbiology [5, 6].

Tremendous effort has been expended investigating hydrothermal solutions to determine their thermodynamic, transport and spectroscopic properties with the goal of elucidating the solute–solvent and solute–solute interactions over a wide range of state conditions [7, 8]. It is precisely at these conditions where our understanding and predictive capabilities are most precarious, in part as a result of the coexistence of processes with two rather different length scales, i.e. short-ranged (solvation) and long-ranged (compressibility-driven) phenomena [9]. The latter makes hydrothermal systems extremely challenging to model, unless we are able to

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isolate the (compressibility-driven) propagation of the density perturbation from the (solvation-related) finite-density perturbation phenomena [10].

In this paper, first we briefly review the solvation formalism for high-temperature electrolyte solutions recently proposed to tackle such problems [11], then illustrate the formalism by interpreting some recent experimental results for infinitely dilute CsBr aqueous solutions [12]. Finally, we interpret the molecular basis for the success of the underlying ideas behind the recently proposed regression approach for the solute partial molar volumes [12, 13] and discuss some issues regarding the modelling of these systems.

2. High-temperature solvation process

The solvation formalism hinges upon the discrimination of disparate length-scale phenomena, i.e. between solvation and compressibility-driven phenomena [9, 10]. This is achieved by splitting the species total correlation functions into their direct and indirect contributions according to the Ornstein–Zernike (OZ) equation [11]. Thus, the solvation of a single ionic solute (salt) $C^{\nu_+}A^{\nu_-}$ in a pure solvent at constant state conditions (constant T and either constant P or ρ) can be described by a *thought experiment* (see figure 1 of Chialvo *et al* [11]), on a system initially considered as a pure solvent in which ν solvent molecules ($\nu = \nu_+ + \nu_-$ where ν_+ and ν_- 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 [14, 15]. Then, the solvation process proceeds by the mutation of the distinguishable ν solvent molecules into the final neutral ionic solute $C^{\nu_+}A^{\nu_-}$ (e.g. through a Kirkwood coupling-parameter charging) to form the infinitely dilute *non-ideal solution*. This process, in which the original ν *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 $(\mu_U^{r\infty}(T, P) - \nu\mu_V^{r0}(T, P))$, where subscripts U and V denote solute and solvent, respectively.

The main goal of this formalism is to connect the microscopic changes of the solvent structure around the mutating species with the macroscopic (thermodynamic) properties which best characterize the solvation process. As we discussed elsewhere [16] this connection can be achieved in essentially four equivalent ways by interpreting the driving force of the solvation process, from either a microscopic or a macroscopic perspective. For the sake of clarity, we first take the neutral ionic solute as a hypothetical 'molecular' entity in order to derive the solute properties which are usually measured experimentally. Then, we go a step further by deriving the corresponding individual-ion contributions to the neutral ionic solute properties, making contact with the actual solvent environment around the individual ions.

To do so, we start from the exact thermodynamic expression,

$$\mu_U^{r\infty}(T, P) - \nu\mu_V^{r0}(T, P) = \int_0^{\rho(P)} (\bar{v}_U^\infty - \nu\bar{v}_V^0)\frac{\mathrm{d}\rho}{\kappa\rho} \tag{1}$$

which we can re-write 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. $(\partial P/\partial x_U)_{T,\rho}^\infty$ [11],

$$\mu_U^{r\infty}(T, P) - \nu\mu_V^{r0}(T, P) = \int_0^{\rho(P)} \left(\frac{\partial P}{\partial x_U}\right)_{T,\rho}^\infty \frac{\mathrm{d}\rho}{\rho^2}. \tag{2}$$

Here the superscript r denotes a residual quantity for a pure (0) or an infinitely dilute (∞) species at the indicated state conditions, respectively; T is the absolute temperature; P is the

total pressure; $\bar{v}_V^0 = v_V^0$ is the partial molar volume of the pure solvent such that $\rho = 1/\bar{v}_V^0$ is its molar density counterpart and κ is the solvent isothermal compressibility.

Equation (2) highlights the finiteness of its integrand at any state condition, and allows us to make contact with the microstructure of the system [10], i.e. (see appendix B of Chialvo *et al* [11]),

$$\left(\frac{\partial P}{\partial x_U}\right)_{T,\rho}^{\infty} = \nu\rho kT(C_{VV}^0 - C_{UV}^{\infty}) \tag{3}$$

where C_{VV}^0 and C_{UV}^{∞} are the direct correlation function integrals (DCFIs) for the solvent–solvent and solute–solvent interactions (i.e. the descriptors of the solution microstructure [17, 18]), and k is the Boltzmann constant.

An alternative way of looking at the solvation driving force is through the excess particle number [16],

$$N_{U,ex}^{\infty} = 4\pi\rho \int_0^{\infty} [g_{UV}^{\infty}(r) - g_{VV}^0(r)]r^2 \, dr \tag{4}$$

i.e. the number of solvent molecules around the solute in excess of that around any solvent molecule (the Lewis–Randall ideal solution). Because $N_{U,ex}^{\infty} = -\kappa(\partial P/\partial x_U)_{T,\rho}^{\infty}$ [10], its solvation contribution $N_{U,ex}^{\infty}$ (SR) becomes equal to $N_{U,ex}^{\infty}(\text{SR}) = (\kappa^{IG}/\kappa)N_{U,ex}^{\infty}$, and consequently,

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

where $\kappa^{IG} = (\rho kT)^{-1}$ is the isothermal compressibility of the ideal gas at the state conditions of the solvent, and SR denotes the short-range contribution (associated with the local solvent density perturbation) to the corresponding diverging $N_{U,ex}^{\infty}$. This equation highlights the connection between the pressure change (at constant T and ρ) associated with the perturbation of the solvent structure around the solute and the corresponding effective change in the number of solvent molecules. Note that, since this quantity does not involve explicitly any size for the solvation shell, $N_{U,ex}^{\infty}(\text{SR})$ can be considered as a *effective* solvation number (see Chialvo *et al* [11]), though it should not be confused with the conventional definition of hydration/solvation numbers based on the structural information of the first hydration shell.

Analogously, the pressure derivative $(\partial P/\partial x_U)_{T,\rho}^{\infty}$ can be re-written in volumetric terms as [11],

$$\left(\frac{\partial P}{\partial x_U}\right)_{T,\rho}^{\infty} = kT\rho^2(\bar{v}_U^{\infty}(\text{SR}) - \nu\bar{v}_V^0). \tag{6}$$

Therefore, the difference of chemical potentials in equation (1) can be interpreted macroscopically not only in terms of the finite pressure perturbation $(\partial P/\partial x_U)_{T,\rho}^{\infty}$ as in equation (2), but also in terms of either the finite volumetric perturbation $(\bar{v}_U^{\infty}(\text{SR}) - \nu\bar{v}_V^0)$, or the *effective* solvation number $N_{U,ex}^{\infty}(\text{SR})$ as follows,

$$\mu_U^{r\infty}(T, P) - \nu\mu_V^{r0}(T, P) = kT \int_0^{\rho(P)} (\bar{v}_U^{\infty}(\text{SR}) - \nu\bar{v}_V^0) \, d\rho \tag{7}$$

and

$$\mu_U^{r\infty}(T, P) - \nu\mu_V^{r0}(T, P) = -kT \int_0^{\rho(P)} N_{U,ex}^{\infty}(\text{SR})\frac{d\rho}{\rho}. \tag{8}$$

Even though we have introduced the properties of the neutral ionic solute in the above analysis—i.e. the properties measurable by experiment—its properties at infinite dilution are

actually linear combinations of the corresponding single-ion counterparts. In fact, the solvation process involves the perturbation of the solvent structure around the individual ions (rather than the neutral ionic solute), and, therefore, we need to connect the solvent structure around each ion with properties of the hypothetical salt species. For example, the partial molar volume of the salt $C^{\nu_+}A^{\nu_-}$ at infinite dilution becomes,

$$\bar{v}_U^\infty = \nu_- \bar{v}_-^\infty + \nu_+ \bar{v}_+^\infty \tag{9}$$

where $\bar{v}_i^\infty$ is the partial molar volume of the ion i at infinite dilution. Consequently [11],

$$\left(\frac{\partial P}{\partial x_U}\right)_{T,\rho}^\infty = \nu_+ \left(\frac{\partial P}{\partial x_+}\right)_{T,\rho}^\infty + \nu_- \left(\frac{\partial P}{\partial x_-}\right)_{T,\rho}^\infty \tag{10}$$

indicating that the experimentally determined Krichevskii parameter for electrolyte solutions [18, 19] is actually a linear combination of those corresponding to the individual ions constituting the salt, i.e.

$$\left(\frac{\partial P}{\partial x_i}\right)_{T,\rho}^\infty = kT\rho(C_{VV}^0 - C_{iV}^\infty - T_{iV}^\infty) \qquad i = +, - \tag{11}$$

or its equivalent forms [20],

$$\left(\frac{\partial P}{\partial x_i}\right)_{T,\rho}^\infty = kT\rho^2(\bar{v}_i^\infty(\text{SR}) - \bar{v}_V^0) \qquad i = +, - \tag{12}$$

and,

$$\left(\frac{\partial P}{\partial x_i}\right)_{T,\rho}^\infty = -\frac{N_{i,ex}^\infty(\text{SR})}{\kappa^{IG}} \qquad i = +, - \tag{13}$$

where $\bar{v}_i^\infty(\text{SR})$ and $N_{i,ex}^\infty(\text{SR})$ are the individual-ion counterparts of $\bar{v}_U^\infty(\text{SR})$ and $N_{U,ex}^\infty(\text{SR})$ [20], respectively, and T_{iV}^∞ is a solvent property [21],

$$T_{iV}^\infty = -\frac{4\pi\rho q_i(\varepsilon - 1)}{3\varepsilon\mu} \int_0^\infty r^3 c_{00;VV}^{101}(r)\, \mathrm{d}r. \tag{14}$$

ε is the solvent dielectric constant, q_i is the ion charge, μ is the solvent's dipole moment and $c_{00;VV}^{101}(r)$ is the r-dependent (101) coefficient of the rotational invariant expansion of the solvent–solvent direct correlation function [22]. Note that, because of the electroneutrality condition, $\nu_+ T_{+V}^\infty = -\nu_- T_{-V}^\infty$, and, consequently, T_{iU}^∞ does not contribute to $\bar{v}_U^\infty$ (equation (9)).

Equations (9)–(13) indicate that we can now define the solvation thermodynamics of the individual ions constituting the neutral ionic solute, in terms of the corresponding ion-induced effects, i.e.

$$\mu_i^{r\infty}(T, P) - \mu_V^{r0}(T, P) = \int_0^{\rho(P)} \left(\frac{\partial P}{\partial x_i}\right)_{T,\rho}^\infty \frac{\mathrm{d}\rho}{\rho^2} = kT \int_0^{\rho(P)} \left(C_{VV}^0 - C_{iV}^\infty - T_{iV}^\infty\right) \frac{\mathrm{d}\rho}{\rho}$$

$$= kT \int_0^{\rho(P)} \left(\bar{v}_i^\infty(\text{SR}) - \bar{v}_V^0\right) \mathrm{d}\rho$$

$$= -kT \int_0^{\rho(P)} \frac{N_{i,ex}^\infty(\text{SR})}{\rho} \mathrm{d}\rho = kT \ln[\hat{\phi}_i^\infty/\hat{\phi}_V^0] \qquad i = -, + \tag{15}$$

such that,

$$\mu_U^{r\infty}(T, P) - \nu\mu_V^{r0}(T, P) = \nu kT \ln(\hat{\phi}_U^\infty/\hat{\phi}_V^0) \tag{16}$$

with $(\hat{\phi}_U^\infty)^\nu = (\hat{\phi}_+^\infty)^{\nu_+}(\hat{\phi}_-^\infty)^{\nu_-}$. The corresponding entropy and enthalpy expressions for the individual ions have been derived elsewhere [11].

In summary, in the preceding analysis we have given equivalent ways to express the finite change of free energy in the solvation process that takes place when ν solvent molecules are *mutated* into ν_+ cations and ν_- anions in solution. The resulting solvation quantities exhibit well behaved state dependencies; the solvation enthalpic and entropic contributions are discussed in detail elsewhere [9, 11]. Yet, their temperature and pressure derivatives will diverge at the solvent criticality [19], a behaviour that implies an exact cancellation between the corresponding divergent portions of the enthalpic and entropic contributions to $(\mu_U^{r\infty}(T, P) - \nu\mu_V^{r0}(T, P))$. Furthermore, we have shown elsewhere [9, 11] that the diverging contributions to the partial molar enthalpy and entropy of the solute at infinite dilution are not associated with the solvation process, which is a local density perturbation. In fact, we have shown that they are associated with the propagation of the perturbation across the system; that is, they are characterized by the correlation length of the solvent. This feature suggests that the first step toward a successful modelling of high-temperature electrolyte solutions should involve the discrimination between the two contributions—i.e. solvation from compressibility-driven phenomena—to avoid working with implicity diverging quantities.

3. Integral equation calculations and interpretation of experimental results

As part of a wider investigation, we present here a few results for CsBr in an infinitely dilute aqueous-type solution, along three supercritical isotherms (643, 673 and 703 K), in the density range $0.0136 \leqslant \rho$ g cm^{-3}) $\leqslant 0.81$. A complete analysis for alkali halides is presented elsewhere [20]. In the present calculations the systems are defined as charged hard sphere ions immersed in a model aqueous-like solvent, described as a hard sphere with an embedded point polarizability and permanent electrostatic multipole moments including quadrupole and ocupoles as given in table 1. 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 [23, 24]. Details on these calculations for systems at normal conditions were presented earlier [21, 25], and some others for high temperature solutions are given elsewhere [20]. In addition, and in contrast to the normal unit charges, the ions bear only 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 contact between model predictions and experimental results, we use the above formalism to interpret the solvation behaviour of simple salts in high-temperature aqueous solutions, according to our own integral equation calculations, and the recent experimental data from Wood and co-workers [12, 13]. More specifically we are most interested in studying the quantity $D_{UV}^{\infty} = (\kappa^{IG}/\kappa)\bar{v}_U^{\infty}$ and its T–ρ dependence from a molecular viewpoint, where κ and $\bar{v}_U^{\infty}$ are the isothermal compressibility of the solvent and the partial molar volume of the ionic solute (salt) at infinite dilution, and the superscript IG denotes the ideal gas behaviour. This quantity, which was recently targeted for regression purposes by some experimentalists [12, 26] exhibits an intriguingly weak temperature dependence in the range $550 < T(\mathrm{K}) < 725$. This condition allows a rather simple and well behaved density correlation to predict (in principle) $\bar{v}_U^{\infty}$ at any other supercritical state condition [13], based solely on the thermodynamic properties of the solvent (water).

In figure 1 we show the solvent density dependence of D_{UV}^{∞} along three supercritical isotherms for infinitely dilute CsBr aqueous-like solutions as predicted by the integral equation

† The RHNC integral equation theory appears to predict a shifting upwards of the phase coexistence envelope due to the perturbing effects of bare unscreened ionic charges. These effects can be reduced by increasing the size of the ions or by decreasing the ionic charge.

Table 1. Molecular properties of the water-like solvent (v) and the ions (Cs^+, Br^-).

Property	Value
d_v	2.8 Å
d_-	3.248 Å
d_+	3.248 Å
μ	1.85×10^{-18} esu cm
α_{xx}	1.501 Å^3
α_{yy}	1.390 Å^3
α_{zz}	1.442 Å^3
Q_{xx}	2.63×10^{-26} esu cm^2
Q_{yy}	-2.50×10^{-26} esu cm^2
Q_{zz}	-0.13×10^{-26} esu cm^2
Ω_{xxz}	2.30×10^{-34} esu cm^3
Ω_{yyz}	-0.96×10^{-34} esu cm^3
Ω_{zzz}	-1.34×10^{-34} esu cm^3
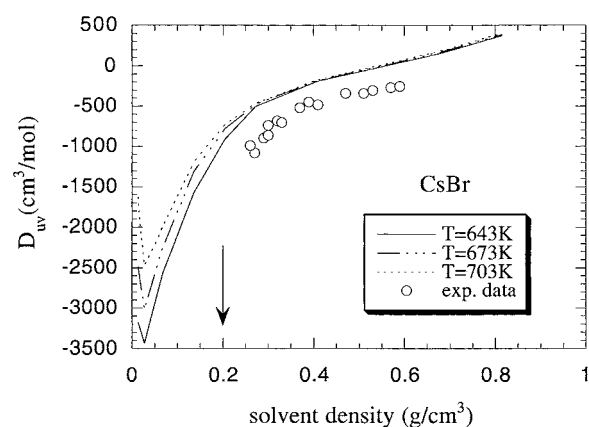
Figure 1. Behaviour of $D_{UV}^\infty = (\kappa^{IG}/\kappa)\bar{v}_U^\infty$ for an infinitely dilute CsBr aqueous solution as a function of the solvent density along three supercritical isotherms in comparison with experimental data [12]. The arrow indicates the estimated critical density of the model solvent.

calculations. Note that, according to the predicted relation between P and ρ along the isotherm $T = 643$ K, the critical point of this water-like solvent is $T_c \approx 643$ K and $\rho_c \approx 0.20$ g cm^{-3} [20], i.e. the three isotherms considered here are supercritical. We also compare these results with the corresponding experimental data of Sedlbauer *et al* [12], which were determined from measurements of solute partial molar volumes at infinite dilution within the temperature and density ranges $604 < T(\text{K}) < 717$ and $0.26 < \rho(\text{g cm}^{-3}) < 0.60$, respectively. The outstanding feature of the predicted values of D_{UV}^∞ is their lack of temperature dependence for supercritical densities, an appealing behaviour that prompts some relevant questions regarding the underlying microscopic mechanism. Incidentally, this is the same behaviour as observed previously for several types of high-temperature electrolyte and non-electrolyte aqueous solutions [12, 13, 26].

In contrast to the experimental approach, the integral equation calculations on well defined models provide all the structural information associated with the resulting macroscopic behaviour, and, consequently, allow us to interpret and to offer an explanation for the observed behaviour. For example, the weak temperature dependence exhibited by D_{UV}^∞ [10, 11] can be
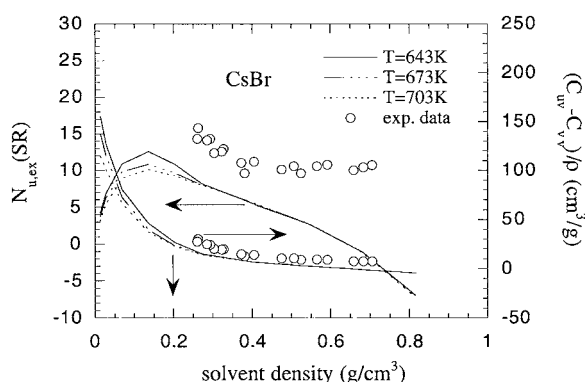
Figure 2. Behaviour of $N_{U,ex}^{\infty}$(SR) and $(C_{UV}^{\infty} - C_{VV}^{0})/\rho$ for an infinitely dilute CsBr aqueous solution as a function of the solvent density along three supercritical isotherms in comparison with experimental data [12]. The vertical arrow indicates the estimated critical density of the model solvent.

interpreted in terms of $N_{U,ex}^{\infty}$(SR) (see figure 2), a quantity that also displays a clearly negligible temperature dependence for supercritical densities. A similar behaviour can be observed for its associated quantity $(C_{UV}^{\infty} - C_{VV}^{0})/\rho$ (see equations (3) an (5)), which is another measure of the relative structural changes undergone by the solvent around the solute. By the same token, figure 2 suggests that the observed temperature dependence of D_{UV}^{∞} for subcritical densities (figure 1) arises from that of the $N_{U,ex}^{\infty}$(SR) counterpart (figure 2). This stronger temperature dependence at $\rho < \rho_c$ is not unexpected, since at low solvent densities where a second virial coefficient suffices to describe the P–ρ–T system behaviour, we have that,

$$N_{U,ex}^{\infty}(\text{SR}) \approx 2\nu\rho^3(kT)^2(B_{UV}(T) - B_{VV}(T)) + \cdots \tag{17}$$

where $B_{ij}(T)$ are the second virial coefficients for the ij-pair. Thus, $N_{U,ex}^{\infty}$(SR) and its related properties will exhibit a rather strong dependence on temperature (explicitly quadratic) and density (explicitly cubic).

Yet another way to interpret the previously mentioned weak temperature dependence is through the analysis of the two contributions to the solute partial molar volume $\bar{v}_U^{\infty}$, i.e. the solvation $\bar{v}_U^{\infty}$(SR), and the compressibility-driven $\bar{v}_U^{\infty}$(LR) contributions, respectively. From figure 3 it is clear that the solvation portion $\bar{v}_U^{\infty}$(SR) (as opposed to the compressibility-driven portion $\bar{v}_U^{\infty}$(LR)) exhibits the negligible temperature dependence found in the associated quantities (figures 1 and 2), and highlights once again the appeal of well defined solvation quantities as the target for regression purposes.

4. Discussion and conclusions

We have described the solvation process in high-temperature electrolyte solutions based on thermodynamic and statistical mechanical views, through the discrimination between the true solvation phenomena and the largely unrelated accompanying compressibility-driven phenomena. These solvation-related properties (designated as 'SR' contributions) have unambiguous microscopic meaning, in addition to their macroscopic interpretation in terms of the isothermal compressibility of the pure solvent κ and the infinite-dilution partial molar properties [11]. For the case under consideration,

$$\bar{v}_U^{\infty}(\text{SR}) = (\kappa^{IG}/\kappa)(\bar{v}_U^{\infty} - \nu v_V^0) + \nu v_V^0 \tag{18}$$
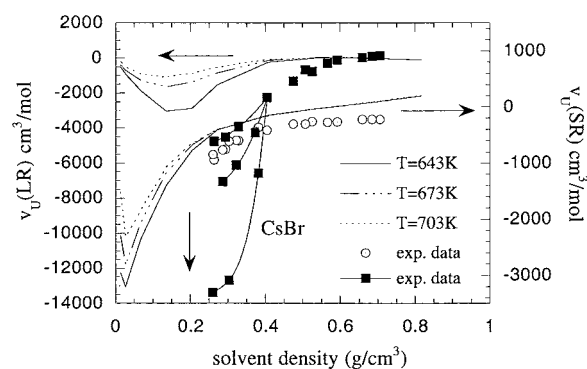
Figure 3. Behaviour of $\bar{v}_U^\infty(\mathrm{SR})$ and $\bar{v}_U^\infty(\mathrm{LR}) \equiv \bar{v}_U^\infty - \bar{v}_U^\infty(\mathrm{SR})$ for an infinitely dilute CsBr aqueous solution as a function of the solvent density along three supercritical isotherms in comparison with experimental data [12]. The vertical arrow indicates the estimated critical density of the model solvent. The three lines joining the experimental data correspond approximately to the isotherms of 669, 686 and 709 K from bottom to top, respectively.

and, consequently,

$$N_{U,ex}^\infty(\mathrm{SR}) = (1 - \nu) + (\kappa^{IG}/\kappa)(\nu - (\bar{v}_U^\infty/v_\nu^0)). \tag{19}$$

A few points are worth mentioning here. First, the excess number $N_{U,ex}^\infty(\mathrm{SR})$ and its ion counterparts should not be associated with or confused with the traditional coordination number, described as the geometric arrangement of solvent molecules around a central species. Therefore, $N_{U,ex}^\infty(\mathrm{SR})$ and its ion counterparts cannot be associated with the conventional solvation/hydration numbers obtained through NMR, EXAFS, neutron or x-ray diffraction measurements [27, 28]. In fact, $N_{U,ex}^\infty(\mathrm{SR})$ accounts for the solvent molecules *directly correlated* with the central species in excess over that in which the central molecule is also a solvent (the ideal solution in the Lewis–Randall sense). Second, while $N_{U,ex}^\infty(\mathrm{SR})$ involves unambiguous connections with all solvation properties, the more familiar concept of solvation/hydration numbers does not [11].

According to this formalism, the salt partial molar properties can be defined in terms of their individual ion counterparts, i.e. in terms of the relative structuring of the solvent environment around individual species. Consequently, the solvation properties of the individual ions can unambiguously be connected to the solvent's electrostriction around the species in solution as well as to the coefficients of the Helmholtz free energy expansion for dilute mixtures, as described elsewhere [11]. Considering that one of the primary goals of our molecular-based studies is the development of successful engineering correlations, the proposed solvation formalism becomes a powerful tool for interpreting experimental data and for choosing the best combination of properties for regression purposes.

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References

[1] Marcus Y 1985 *Ion Solvation* (Chichester: Wiley)
[2] Tödheide K 1982 *Ber. Bunsen Ges. Phys. Chem.* **86** 1005–16
[3] Mitton D B, Orzalli J C and Latanision R M 1995 *Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry* ed H J White, J V Sengers, D B Neumann and J C Bellows (New York: Begell) pp 638–43
[4] Barner H E, Huang C Y, Johnson T, Jacobs G, Martch M A and Killilea W R 1992 *J. Hazardous Mater.* **31** 1–17
[5] Cowan D A 1995 Hyperthermophilic enzymes: biochemistry and biotechnology *Hydrothermal Vents and Processes* (*Geological Society Special Publication 87*) pp 351–63
[6] Cowan D A 1995 *Hydrothermal Vents and Processes* publication 87 ed G Society (London: Geological Society) pp 351–64
[7] Barnes H L (ed) 1997 *Geochemistry of Hydrothermal Ore Deposits* (New York: Wiley)
[8] Mesmer R E, Palmer D A and Simonson J M 1991 *Activity Coefficients in Electrolyte Solutions* 2nd edn, ed K S Pitzer (Boca Raton, FL: Chemical Rubber Company) pp 491–529
[9] Chialvo A A and Cummings P T 1994 *AICHE J.* **40** 1558–73
[10] Chialvo A A and Cummings P T 1995 *Mol. Phys.* **84** 41–8
[11] Chialvo A A, Cummings P T, Simonson J M and Mesmer R E 1999 *J. Chem. Phys.* **110** 1075–86
[12] Sedlbauer J, Yezdimer E M and Wood R H 1998 *J. Chem. Thermodyn.* **30** 3–12
[13] Gruszkiewicz M S and Wood R H 1997 *J. Phys. Chem.* B **101** 6549–59
[14] Chialvo A A 1990 *J. Chem. Phys.* **92** 673–9
[15] Chialvo A A 1993 *Fluid Phase Equilibria* **83** 23–32
[16] Chialvo A A, Cummings P T, Simonson J T and Mesmer R E 1999 *J. Mol. Liquids* in press
[17] Kusalik P G and Patey G N 1987 *J. Chem. Phys.* **86** 5110–6
[18] O'Connell J P 1990 *Fluctuation Theory of Mixtures* vol 2, ed E Matteoli and G A Mansoori (New York: Taylor and Francis) pp 45–67
[19] Levelt Sengers J M H 1991 *Supercritical Fluid Technology* ed T J Bruno and J F Ely (Boca Raton, FL: Chemical Rubber Company) pp 1–56
[20] Chialvo A A, Kusalik P G, Cummings P T and Simonson J M 1999 in preparation
[21] Kusalik P G and Patey G N 1988 *J. Chem. Phys.* **89** 5845–51
[22] Fries P H and Patey G N 1985 *J. Chem. Phys.* **82** 429–40
[23] Kusalik P G and Patey G N 1988 *J. Chem. Phys.* **88** 7715–38
[24] Kusalik P G and Patey G N 1988 *J. Chem. Phys.* **89** 7478–84
[25] Kusalik P G and Patey G N 1988 *Mol. Phys.* **65** 1105–19
[26] O'Connell J P, Sharygin A V and Wood R H 1996 *Indust. Eng. Chem. Res.* **35** 2808–12
[27] Magini M, Licheri G, Paschina G, Piccaluga G and Pinna G 1988 *X-Ray Diffraction of Ions in Aqueous Solutions: Hydration and Complex Formation* (Boca Raton, FL: Chemical Rubber Company)
[28] Conway B E 1981 *Ionic Hydration in Chemistry and Biophysics* (Amsterdam: Elsevier)