Statistical Thermodynamic Approach to the Chemical Activities in Two-Component Solutions

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It is shown how the leading terms of a semi grand canonical partition function (GCPF) can be used to develop analytic expressions relating activity to concentrations in two-component systems. The simple analytic expressions for activity coefficients can be fitted to activity coefficient versus concentration data for a wide range of aqueous solute systems. Only one or two parameters are required to accurately describe the activity coefficients of nonelectrolyte and electrolyte aqueous solute systems over their entire range of solubility. These forms derive from low-order number expressions of the GCPF that take into account the effective solvent interactions with the solute and between solute molecules for a variable amount of solvent. The GCPF leading terms and fitting parameters define apparent solute−solute oligomerization and solute packing phenomena that increase with solute concentration. Advantages using this grand canonical approach versus previous approaches are discussed.

1. Introduction

Because of the routine experimental uses of solution thermodynamics, computational methods that are able to deal with nonideal behavior over a range of concentrations and variety of solutes have had considerable utility.[1,2] A central problem is dealing with the activity coefficients of the solute and solvent in terms of their respective concentrations. This is of special interest in the highly nonideal context associated with macromolecular crowding in cells, where although species individually may have low concentrations the total concentration of all nonsolvent species may be quite high.[3] In such cases failure to take into account the nonideal nature of the system results in gross inconsistencies.

Many solution analyses have been made with reference to ideal solutions. Though most rigorous analysis for salt systems has started with extensions to the Debye−Hückel limiting law,[2] formal extensions have shown a severe sensitivity to atomic interaction potentials[4] or have been used by fitting the atomic interaction potentials.[5,6] A somewhat more successful approach has been to consider parametric fits based on an effective one-component system with mean spherical approximation correlations in the MacMillan−Mayer approach.[7]

In this paper we have taken an approach based on a semi grand canonical description of solutions due to Hill.[8] In this rigorous formal framework, chemical potentials can be written as a function of mole fractions or concentrations. This system is especially handy when it comes to asking separate questions about the solute or solvent. Though the exact coefficients from the requisite configurational integrals remains computationally unreliable, forms suitable for fitting to existing data are derived and shown to fit better with fewer parameters than previous attempts.

We begin by reviewing the semi grand ensemble Hill chose. In this ensemble the number of solvent molecules and the chemical potential of the solute are held constant, making analysis of the solute chemical potential straightforward. The resulting forms when referenced to the pure solvent system are reminiscent of Padé approximates. We then demonstrate the functional utility of the expressions on a variety of chemical systems including both ionic and nonionic solutes. Our goal is to illustrate the versatility of the approach in terms of its ability to handle many types of solutes. We intend to provide more in depth and extensive considerations of individual classes of solutes in later publications.

2. Theory

2.1. Semi Grand Canonical Partition Function. Here we sketch derivations of quantities to be used in analyses of experimental data relating chemical activity to solute concentration, beginning with the rigorous derivation of the appropriate partition function by Hill[8]

$$Z(N_w, \mu, p, T) = \exp\left(-\frac{\mu_w N_w}{kT}\right)$$

$$= \sum_N \exp\left(\frac{\mu N}{kT}\right) \sum_V \exp\left(-\frac{pV}{kT}\right) \sum_E \exp\left(-\frac{E}{kT}\right) \quad (1)$$

The defined quantities include a constant number for the solvent (N_w), a constant chemical potential for the nonvolatile solute (μ), pressure (p), temperature (T), volume (V), and energy (E), with (k) as the Boltzmann constant. We will confine our discussion to aqueous two-component systems, and for simplicity we use the subscript w to represent solvent-specific (water) quantities, whereas solute-specific quantities are represented without a subscript. In this approach, the solute and solvent of

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the two-component system can be treated separately. For now, we will focus on the rightmost side of the equation, which considers the solute molecule explicitly, attended implicitly by specified numbers of solvent molecules. Hill[8] has shown that in a two-component solution described by a semi grand canonical and isobaric ensemble, the equations effectively reduce to the same forms obtained for a real gas. This one-component construct is analogous to the treatment in the grand canonical and isochoric ensemble used by McMillan and Mayer,[9] as shown by Hill.[10] The semi grand canonical system we are dealing with contains a fixed total number of solvent molecules, but a fluctuating number of solute molecules and a variable volume. The averages of these two extensive properties, solute number and volume, are determined by the chemical potential of the solute and by the pressure, respectively.

Proceeding with the framework of Hill[8] becomes problematic at elevated activities. Thus, we use an approach that starts with Hill's choice of ensemble but makes use of the effective one-component work of Brenig.[11] From the approach, we produce a formalism with an extended accessible range of concentrations for fitting experiment by taking into account just a few low-order solute terms of the semi grand canonical partition function. From the terms that appear in the derivation, depending on the particular experimental system, some terms turn out to be inconsequential and can be eliminated, whereas others must be retained.

The treatment of two-component solutions as an effective one-component solution in a grand canonical ensemble has several advantages. The method produces formulas in which the complexity is largely reduced compared to other treatments.[11] Moreover, by employing the Gibbs−Duhem relation, it is possible to access both the chemical potential of the solute and solvent without considering the solvent explicitly during the calculations.[8,11] This can already be seen from eq 1, where the chemical potentials of both solute and solvent occur, but on different sides of the equation.

If the particle density is sufficiently low, all interactions between different particles can usually be neglected. At elevated densities this is no longer justified, because interaction between pairs of molecules take place to a significant degree. Therefore, as particle density increases, a second-order term in the partition function is needed. As the particle density is increased even more and the system comes closer to the solid state, more solute terms of the partition function are required to describe the system properly. The shape of activity vs concentration plots will be taken as a measure of the number of terms of the partition function necessary to describe the data. As will be seen, this number is unexpectedly small even for solutions as concentrated as saturated sucrose in water (approximately 70% w/w sucrose at 25°), where only two parameters are required.

The (semi) grand canonical partition function Z as given by eq 1 can be rewritten in an equivalent shortened form that is more appropriate for the current purpose of calculating activities. The partition function is composed of additive terms Z_N that are the product of the isobaric canonical partition functions Y_N of an N particle system and a weighting factor $\exp(N\mu\beta)$

$$Z = \sum_{N \geq 0} Z_N = \sum_{N \geq 0} Y_N \exp(N\mu\beta) = \sum_{N \geq 0} Y_N f^N \quad (2)$$

where $\beta = 1/kT$, k is the Boltzmann constant, μ is the chemical potential of the solute, and $\exp(\mu\beta)$ is the absolute activity f of the solute. One could choose many different states as a reference system. Infinite dilution and saturated solutions are natural extremes, so we normalize this partition function Z to the

partition function Z_0 of the solute-free pure solvent, following Hill.[8] However, in contrast to Hill, we do not expand the logarithm of the normalized partition function with respect to the activity, because this would result in serious convergence problems. This is because all coefficients of the expansion are of the order of 1.[8] Therefore, the radius of convergence of that power expansion is quite small, and Hill's approach becomes invalid for activities larger than unity. Choosing a different way of handling of the partition function will avoid such convergence problems. This is done as follows.

2.2. Relating the Semi Grand Partition Function to Quantities of Interest. For $N = 0$ the relation $Z_0 = Y_0$ holds. From the preceding equation, the average solute particle number in the system of interest can be calculated from the usual derivative with respect to the chemical potential μ[12]

$$\langle N \rangle = \left(\frac{\partial \ln Z}{\partial \mu \beta} \right)_\beta = \frac{\sum_{N \geq 1} N \dfrac{Y_N}{Y_0} \exp(N\mu\beta)}{1 + \sum_{N \geq 1} \dfrac{Y_N}{Y_0} \exp(N\mu\beta)} = \frac{\sum_{N \geq 1} N \dfrac{Y_N}{Y_0} f^N}{1 + \sum_{N \geq 1} \dfrac{Y_N}{Y_0} f^N} \quad (3)$$

where the numerator and denominator have been divided by Y_0. In the limit of infinite dilution the number of solute molecules $\langle N \rangle$ approaches zero and the chemical potential has a well-known "ideal gas" logarithmic singularity[11] (i.e., the absolute activity f is approaching zero). Under this condition only the leading terms in the numerator and denominator of eq 3 are of significance. Accordingly, the average solute particle number can be written in this limit as[11]

$$\langle N \rangle = \frac{Y_1}{Y_0} \exp(\mu\beta) = \frac{Y_1}{Y_0} f \quad (4)$$

We are dealing with the semi grand canonical ensemble (N_w, μ, p, T) discussed by Hill,[8] so per subsystem there is implicitly a fixed number of water molecules N_w. Using this number, $\langle N \rangle$ might be expressed in terms of molality m and the molecular weight of water M_w or the mass g_w (in units of kg) of the N_w water molecules

$$\langle N \rangle = mN_w M_w = mg_w \quad (5)$$

Thus, according to eq 4 the chemical potential of a system approaching infinite dilution may be written as

$$\mu = kT \ln\left(mg_w \frac{Y_0}{Y_1}\right) = \mu^{o,*} + kT \ln(mg_w) = \mu_m^{o,*} + kT \ln(m) \quad (6)$$

where we take the standard chemical potential of the solute at infinite dilution as $\mu^{o,*} = kT \ln(Y_0/Y_1)$ or $\mu_m^{o,*} = kT \ln(g_w Y_0/Y_1)$ depending on whether g_w is included or not. We will use this chemical potential as a reference chemical potential and designate it μ^* for later use. The ratio between the absolute activity f and the average particle number $\langle N \rangle$ is the absolute activity coefficient $\mathscr{G}^* = Y_0/Y_1$ of the solute in an ideal dilute system.

From eq 4 it is already obvious that Y_0 does not occur separately from other Y_N. As will be seen below in calculating the activity coefficient, the coefficient $\mathscr{G}^* = Y_0/Y_1$ also never appears in the final equation. According to eq 6, $\mathscr{G}^*$ determines the standard chemical potential $\mu_m^{o,*} = kT \ln \mathscr{G}^*$, which defines the (infinitely dilute) reference state. The standard chemical

potential is also not readily accessible by experiment. In fact, only in exceptional cases, when a volatile component in the solution of interest is in equilibrium with its (ideal) gas phase, can the absolute chemical potential be determined from the pressure using the thermal deBroglie wavelength.[11] So, in translating from theory to experiment it is more convenient to use relative activity (a) instead of absolute activity (f). The conversion from absolute to relative activity is accomplished by factoring $\mathscr{G}^*$ from the absolute activity. In effect, this amounts to splitting a standard chemical potential $\mu^{o,*}$ off of the absolute chemical potential μ giving the relative chemical potential (μ_{rel})

$$\mu_{rel} = \mu - \mu^{o,*} = kT \ln f - kT \ln \mathscr{G}^* \tag{7}$$

In terms of our statistical thermodynamic approach the relative activity a is defined by

$$a = f \frac{Y_1}{Y_0} = \frac{f}{\mathscr{G}^*} \tag{8}$$

Using this definition the partition function can be rewritten in terms of the relative activity

$$Z = \sum_{N \geq 0} Y_N f^N = Y_0 \sum_{N \geq 0} \frac{Y_N Y_0^{N-1}}{Y_1^N} a^N$$

$$= Y_0 \sum_{N \geq 0} a^N / \mathscr{G}_N = Y_0 (1 + a + a^2 / \mathscr{G}_2 + a^3 / \mathscr{G}_3 + ...) \tag{9}$$

Following eq 3, the average number of particles can then be written as

$$\langle N \rangle = \frac{a + \sum_{N \geq 2} N a^N / \mathscr{G}_N}{1 + a + \sum_{N \geq 2} a^N / \mathscr{G}_N}$$

$$= \frac{a + 2a^2 / \mathscr{G}_2 + 3a^3 / \mathscr{G}_3 + ...}{1 + a + a^2 / \mathscr{G}_2 + a^3 / \mathscr{G}_3 + ...} \tag{10}$$

where

$$\mathscr{G}_N = \frac{Y_1^N}{Y_N Y_0^{N-1}} \tag{11}$$

By this base transform, which offsets the chemical potential by the value of the standard chemical potential, the number of fitting parameters is reduced by two. The information that is usually missing experimentally, and is eliminated from the statistical physical expressions by the base transform, is the ratio of the canonical partition functions of an empty and a singly occupied system, $\mathscr{G}^* = Y_0/Y_1$. This expression corresponds to the Widom insertion free energy $kT \ln(Y_0/Y_1)$ required to add one particle to a solution,[13] where it does not interact with other solute molecules, i.e., in the dilute solution limit. The residual parameters in eq 10, $\mathscr{G}_N = Y_1^N/Y_N Y_0^{N-1}$, determine how readily the solvent accepts an uptake of N solute molecules relative to the ideal case. Equivalently, these residual parameters describe how solute particles are redistributed in the solution after being added as isolated solute molecules.[8]

Although this treatment is convenient from a theoretical point of view, it is not yet sufficient from an experimental standpoint, because it does not make the activity equal to the molality at low concentrations. This can be accomplished using the following base transformation

$$a = f \frac{Y_1}{Y_0 g_w} = \frac{f}{\mathscr{G}_m^*} \tag{12}$$

which results in

$$\langle N \rangle = \frac{a g_w + \sum_{N \geq 2} N a^N / \mathscr{G}_{N,m}}{1 + a g_w + \sum_{N \geq 2} a^N / \mathscr{G}_{N,m}}$$

$$= \frac{a g_w + 2a^2 / \mathscr{G}_{2,m} + 3a^3 / \mathscr{G}_{3,m} + ...}{1 + a g_w + a^2 / \mathscr{G}_{2,m} + a^3 / \mathscr{G}_{3,m} + ...} \tag{13}$$

The coefficients $\mathscr{G}_{N,m}$ are defined as

$$\mathscr{G}_{N,m} = \frac{\mathscr{G}_N}{g_w^N} = \frac{Y_1^N}{Y_N Y_0^{N-1} g_w^N} \tag{14}$$

which implies $\mathscr{G}_{1,m} = 1/g_w$ and $\mathscr{G}_{0,m} = 1$.

2.3. Osmotic Coefficients. Although the main purpose of this paper is to uncover the physicochemical contributions of solute and solvent to the solute chemical potential, we can also reveal the chemical potential of the solvent (component 1) by means of the Gibbs−Duhem relation. That is, the chemical potential of the water may be obtained by integration of the Gibbs−Duhem relation at constant pressure and temperature

$$N_w \left(\frac{\partial \mu_w}{\partial N} \right)_{N_w} = -N \left(\frac{\partial \mu}{\partial N} \right)_{N_w} \tag{15}$$

What results from the derivatives is the chemical potential of the water without the standard chemical potential μ_w^o contribution, which we assume to be set to that of pure water.

For the simplest case, the ideal dilute solution, the chemical potential of the solute is $kT \ln \langle N \rangle$ plus the offset $\mu^{o,*}$, and this cancels during the calculations. Using eq 15 the chemical potential of water relative to pure water is obtained in the limit of ideal behavior

$$(\mu_w - \mu_w^o)\beta = -\frac{1}{N_w} \int_0^{\langle N \rangle} N \frac{\partial \ln N}{\partial N} dN = -\frac{\langle N \rangle}{N_w} \tag{16}$$

The osmotic coefficient (ϕ) describes the deviation from ideal behavior:

$$\phi = \frac{(\mu_w - \mu_w^o)\beta}{-\langle N \rangle / N_w} \tag{17}$$

In general, we derive osmotic coefficients from the appropriate partition functions. For our purpose only the Gibbs−Duhem relation has to be integrated. If additionally the average solute particle number $\langle N \rangle$ is replaced by the derivative of the partition function with respect to the activity of the solute,

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the water activity is obtained:

$$\ln a_w = -\int \frac{N}{N_w}\frac{\partial \ln a}{\partial N}\,dN = -\int \frac{N}{N_w}d\ln a$$

$$= -\int \frac{1}{N_w}\frac{\partial \ln Z}{\partial \ln a}d\ln a$$

$$= -\frac{1}{N_w}\int d\ln Z = -\frac{1}{N_w}\ln\frac{Z}{Y_0} \qquad (18)$$

Therefore, the osmotic coefficient is

$$\phi = \frac{1}{\langle N \rangle}\ln\frac{Z}{Y_0} = \frac{1}{mg_w}\ln\!\left(\sum a^N/\mathscr{G}_N\right) \qquad (19)$$

The same result can be obtained by noting that the semi grand canonical potential is[8]

$$N_w\mu_w = -RT\ln(Z) \qquad (20)$$

From this the same expression for the osmotic coefficient as given in eq 19 follows immediately. In Appendix I osmotic coefficients are given for the examples discussed in this paper.

3. Results and Discussion

In the following sections we will investigate the expected behavior for the two simplest cases beyond ideal behavior:

(1) The case where compared to the one-particle term (fY_1/Y_0) the two-particle term (f^2Y_2/Y_0) becomes significant, whereas both still are small relative to the zeroth-order term $Y_0/Y_0 = 1$. The two-particle term is referred to as the pairwise interaction term.

(2) The case where the one-particle term is numerically close to 1, whereas all other terms are still negligible.

Case 1 will lead to an activity coefficient decay. Case 2 is related to a rapid increase of the activity coefficient due to packing. Finally, cases are considered in which pairwise interaction and packing are both significant, and a discussion is given on how to take into account N-particle systems.

In the first couple of examples we will use the absolute activity f rather than the more convenient relative activity a to render the calculations more transparent and to demonstrate that indeed $\mathscr{G}*$ does not occur in the final expressions.

3.1. Pairwise Interactions. Noninteracting solute molecules surrounded by considerable solvent can be considered as separate grand canonical systems containing, on average, zero to one solute particle each. As the activity is further increased, the second-order term of the partition function may need to be taken into account. Under these circumstances the systems under consideration contain an average of between one and two solute molecules; thus it is reasonable that the interaction between solute molecules comes into play. Such pairwise interactions could be either a direct interaction that results in the formation of a contact dimer or some indirect solvent-mediated interaction. Interactions between solute particles are occasionally modeled by excluded volume effects and attractive van der Waals forces,[7] with size, shape, and chemical character of the particles as part of the model. More exact treatments of such interactions generally include calculation of the solvent-mediated potential.[4] Here, we will not evaluate the configurational integrals over the solvent-mediated forces and the interactions between the solute molecules; rather, we will use the derived equations to
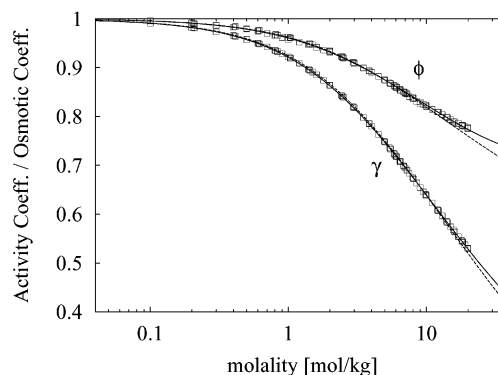

Figure 1. Osmotic coefficient ϕ and activity coefficient γ of urea up to the solubility limit at 25 °C. Shown are two sets of osmotic coefficient (ϕ) data from ref 14 as corrected by ref 15 and the data by ref 16. Using the Gibbs−Duhem relation, activity coefficients were calculated and tabulated from the parameters obtained in a polynomial fit of the osmotic coefficient data. Parameters obtained upon fitting the ϕ and γ data: (two-parameter fit) $\mathscr{G}_{2,m} = 20.32$ mol/kg $\pm$ 0.05 and $N_w = 0.270 \pm 0.005$ (solid lines) and (one-parameter fit) $\mathscr{G}_{2,m} = 22.5$ mol/kg $\pm$ 0.1 (dashed lines).

fit the experimental data. Thus, the precise nature of the interactions and molecular shapes do not have to be specified.

Having to use terms of an order greater than 1 adds some degree of complexity to the system. In the case of the sum up to $N = 2$ the denominator of eq 3 becomes unity (when the ratios Y_1f/Y_0 and Y_2f^2/Y_0 are small compared to 1) and this leaves

$$\langle N \rangle = \frac{Y_1}{Y_0}f + 2\frac{Y_2}{Y_0}f^2 \qquad (21)$$

This equation can be solved for f, and the resulting absolute activity f is then

$$f = \frac{Y_1}{4Y_2}\!\left(-1 + \sqrt{1 + \frac{8NY_2Y_0}{Y_1^{\,2}}}\right) = \frac{\mathscr{G}*\mathscr{G}_2}{4}\!\left(-1 + \sqrt{1 + \frac{8\langle N \rangle}{\mathscr{G}_2}}\right) \qquad (22)$$

where the coefficient $\mathscr{G}_2$ equals Y_1^2/Y_2Y_0 and $\mathscr{G}*$ equals Y_0/Y_1 as defined previously. The activity coefficient γ is obtained by dividing eq 22 by the absolute activity in the ideal dilute system as given by $f* = \mathscr{G}*\langle N \rangle$. This yields the activity coefficient γ_{pw} for the case of pairwise interaction

$$\gamma_{pw} = \frac{f}{f*} = \frac{\mathscr{G}_2}{4\langle N \rangle}\!\left(-1 + \sqrt{1 + \frac{8\langle N \rangle}{\mathscr{G}_2}}\right) = \frac{\mathscr{G}_{2,m}}{4m}\!\left(-1 + \sqrt{1 + \frac{8m}{\mathscr{G}_{2,m}}}\right) \qquad (23)$$

where the particle number $\langle N \rangle$ is converted into molalities m, as in eq 5 and the coefficient $\mathscr{G}_{2,m} = \mathscr{G}_2/g_w$.

As an experimental example we show in Figure 1 the combined activity and osmotic coefficient data of urea by Scatchard[14] (as corrected by Bower and Robinson[15]) and Ellerton and Dunlop.[16] Using the current statistical thermodynamic model (eq 23) to fit these data, a single parameter $\mathscr{G}_{2,m}$ is sufficient to obtain an excellent representation of the data up to 12 mol/kg and a good fit up to the solubility limit. That is, only one nonideal term (pairwise interaction) is required to fit the data with a high degree of precision over a large concentration range (lower dashed line). The root-mean-squared deviation between

the data and our model is 0.0012 up to 12 mol/kg and 0.0035 over the entire concentration range. In the case of the osmotic coefficient, a reasonably good agreement between data and fit (upper dashed line, eq 33) is obtained in the concentration range up to 12 mol/kg. For fitting the osmotic coefficient data beyond 12 mol/kg up to the solubility limit, the simple pairwise interaction model that was a good representation for the activity coefficient is no longer sufficient for describing ϕ. It therefore seems that the activity coefficient is less sensitive to the underlying model in our formalism than the osmotic coefficient is. The inclusion of packing (upper solid line, see below: eq 36), however, yields a good fit. The same parameters are equally good in representing either the osmotic coefficient or the activity coefficient (solid and dashed lines in Figure 1).

Finally, a remark on the data given by Stokes[17] should be made here. There is a deviation of the activity coefficient by up to 0.01 at the highest concentration given (12 m). This deviation is not too big, but it is avoidable. It seems to originate from the Scatchard paper,[14] where an inadequate equation used in fitting the osmotic coefficient data led to systematic residuals. Consequently, activity coefficients extracted from the fit were in error. Depending on how precise the activity coefficient data need to be, it seems prudent to check the procedure by which activity coefficients were obtained from the raw data.

3.2. Packing Effects. In the case of systems, where direct interaction between solute molecules can be neglected, the second-order term of the partition function is generally not needed to represent the data. The system still does not behave ideally, however, if the first-order term is of the same order of magnitude as the zeroth-order term. Under these circumstances, the general equation for the average particle number (eq 4) can be written as

$$\langle N \rangle = \frac{\dfrac{Y_1}{Y_0}f}{1 + \dfrac{Y_1}{Y_0}f} \tag{24}$$

This equation is easily solved for the absolute activity

$$f = \frac{\mathscr{G}*\langle N \rangle}{1 - \langle N \rangle} \tag{25}$$

where the numerator is exactly the absolute activity of the ideal dilute system. The activity coefficient is given by the ratio of the absolute activities of the real (f) and ideal ($f*$) systems:

$$\gamma_{pk} = \frac{f}{f*} = \frac{1}{1 - \langle N \rangle} = \frac{1}{1 - mg_w} \tag{26}$$

The shape of this equation is hyperbolic; i.e., close to zero concentration of the solute, the activity coefficient curve is flat and approaches unity, whereas it rapidly increases as the concentration approaches the maximum possible number of solute particles given by the condition $mg_w = 1$. This packing increase arises from the addition of molecules to the system to a degree that the amount of solvent and its ability to solvate the solute becomes limiting. We might therefore consider g_w the mass and N_w the number of solute molecules that are the minimum requirement for solvating the solute molecule, i.e., a thermodynamic solvation shell.

This interpretation of N_w as a thermodynamic hydration number is then straightforward in the present first-order case. From the point of view of the partition function there are two kinds of water molecules. Those that do not interact with the solute (zeroth-order terms) and those that do interact with the solute (first-order or higher terms). A cluster of water molecules surrounding a solute molecule and interacting with it can be considered a hydration shell. And thus we interpret hydration waters as those occurring in the first-order and higher terms. In the case of clustering solute molecules a solvation shell so defined might be shared between different solute molecules and thus the number of water molecules N_w would have to be divided by the average number of participating solute molecules to obtain the hydration number. Such an interpretation of the solution in terms of physical clusters is somewhat arbitrary, as pointed out by Hill.[18] However, the good agreement between the hydration number obtained here with numbers obtained by independent methods (see below) suggests that the current view of hydration and its relationship to physical clusters may have considerable utility.

We found no solute system where the fits exhibit pure packing behavior, but we will show an example in the next section, in which packing occurs in combination with electrostatic effects.

3.3. Response to Packing and Electrostatics: Sodium Chloride. Any system in which the solute does not form pairs or higher aggregates can apparently be fit using the zeroth- and first-order terms, where for monovalent salts we include direct interactions between solute particles via an extended Debye−Hückel approach. The most studied monovalent salt of all electrolytes, sodium chloride, is presented as an example.

Clearly, in the case of electrolyte activity coefficients, electrostatic effects have to be taken into account. The simplest and best known model for the influence of the charge distribution in the solution on the activity at low concentrations, the Debye−Hückel model, is already sufficient to account for deviations of the activity coefficient of many dilute salts from the ideal solution behavior discussed so far. The extended Debye−Hückel law for the electrostatic contribution to the activity coefficient γ_{el} has the form

$$\ln \gamma_{el} = -\frac{a\sqrt{c}}{1 + b\sqrt{c}} \tag{27}$$

with $a = 0.5108$ for a monovalent salt in water at 25 °C.[19] On a logarithmic scale the functional dependence is sigmoidal such that, at the (low and high) concentration extremes, the concentration dependence tends to flatten. The molarity scale called for in the equation can be readily transformed to molality scale using the solution density.

Archer[20] reviewed literature data up to 1991 on sodium chloride and proposed an empirical equation that describes, among other properties, the concentration dependence of the activity of sodium chloride. We used this equation to generate a set of data representative of the existing literature on NaCl. Figure 2 shows our fit to these data. The fit equation for the activity coefficient is composed of the packing-related activity coefficient given by eq 26 (upper line) and the Debye−Hückel contribution given by eq 27 (lower line) to yield

$$\ln \gamma_{el,pk} = \ln \gamma_{el} + \ln \gamma_{pk} = -\frac{a\sqrt{c}}{1 + b\sqrt{c}} - \ln(1 - mg_w) \tag{28}$$

The equation involves two parameters. That is, the number N_w = 1000 g_w/M_w of water molecules per subsystem (hydration)

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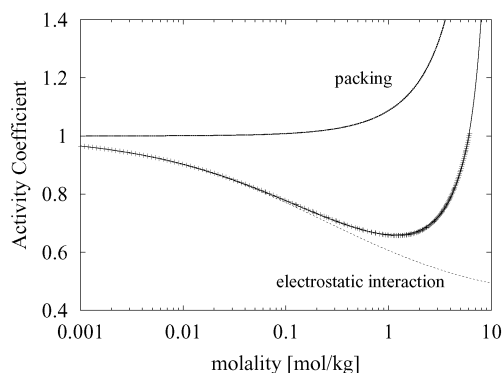*J. Phys. Chem. B, Vol. 108, No. 6, 2004* **2053**

Figure 2. Activity coefficient of NaCl in H_2O. The data[20] (crosses) were fitted to the product of the activity coefficients given by eqs 26 and 27 (solid line). The resulting fit parameters are $b = 1.36/\sqrt{mol/L} \pm 0.01$, $N_w = 4.49 \pm 0.01$ ($m_{max} = m_w/N_w = 12.41$ mol/kg ± 0.02), and root-mean-square deviation 0.0027. The parameter a is $0.5108/\sqrt{mol/L}$. Contributions from electrostatics and packing are given by the thin broken lines as labeled.

TABLE 1: Comparison of Activity Coefficient Methods Using NaCl Activity Coefficient Data of Stokes and Robinson

method	parameters	std dev	b
Bromley[a]	1	0.02454	1
Meissner[a]	1	0.10214	decay: 1.12 to 1
Pitzer[a]	3	0.00681	1.2
Chen[a]	2	0.07016	—
this work	2	0.00256	1.35
Stokes and Robinson[2b]	2	>0.002[b]	1.3
Simonin et al.[6]	3	>0.002[b]	$1.24-0.005c$

[a] Taken from ref 19, p 111. [b] Linear deviation.

and the so-called minimal ionic distance b. The fit is remarkably good with an overall standard deviation of 0.0026. At low concentrations the activity coefficient decreases according to the Debye−Hückel law. As the concentration increases, the packing effect begins to dominate, leading to the upward curvature of the activity coefficient. The absolute deviation between the data (calculated from the four-parameter equation given by Archer[20]) and the two-parameter fit is within ±0.004 up to 4 m and within ±0.01 up to the solubility limit. The bulk of the original data fitted by Archer scatter within approximately ±0.003−0.005, whereas some of the data deviate by as much as ±0.01−0.02. Two independent fits using an extended Pitzer model which requires four to five parameters[20,21] lead to mutual differences of up to 0.002 between the fitted curve and Archer's curve.

Using the data of Robinson[22] (described by a four-parameter NBS equation) several methods of expressing the activity coefficient of sodium chloride have been compared in *the Handbook of Aqueous Electrolyte Thermodynamics*.[19] The results of the comparisons are shown in Table 1 along with results from our approach. Among the four approaches in ref 19 the three-parameter Pitzer equation gave the best fit by far, with a standard deviation of 0.0068. By comparison, our two-parameter approach gives a standard deviation of 0.0026. It is clear that the current approach provides advantages over the semiempirical approach of Pitzer. More recently, Simonin et al.[6] used a mean spherical approximation approach in fitting the NaCl data of Robinson.[22] Unfortunately, neither a direct comparison between their results and that by Pitzer is given nor is a standard deviation of their fit provided. It appears from their plot that the quality of the fit by Simonin[6] is as good as that of our fit, though we use fewer parameters.
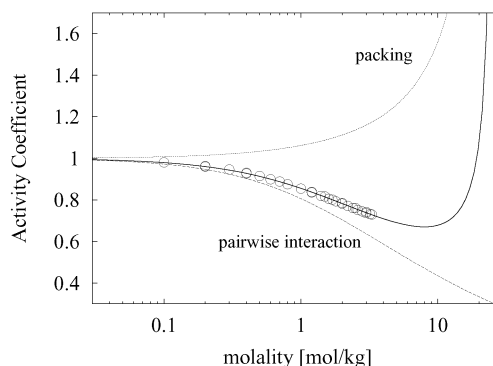

Figure 3. Activity coefficient of glycine in H_2O. The experimental data[25] (circles) were fitted to eq 29 (solid line). The resulting fit parameters are $\mathscr{G}_{2,m} = 6.68$ mol/kg ± 0.08, $N_w = 4.3 \pm 0.1$, and root-mean-square deviation 0.0018. Contributions from pairwise interaction and packing are given by the thin broken lines as labeled.

In different models the parameter b in eq 27 has quite similar values, ranging from 1 to 1.35, as shown in Table 1. The number of fitting parameters required for different models is also given. Overall, the analytic approach introduced here accounts for the data using fewer parameters and/or a lower standard deviation than the heuristic approaches used by these authors.

Of special mention is the empirical approach by Stokes and Robinson.[23] These authors assumed Debye−Hückel behavior and recognized from the previous work of others that there should be an effect of hydration on the activity coefficient as the monovalent salt solution becomes more concentrated. They assumed that water molecules bind to the salt (given as an hydration number) and that these water molecules can be subtracted from the total amount of water to yield an effectively increased molality of the salt. Their empirical nonanalytic expression is very close to that obtained from our analytic approach. A hydration number of 3.5 obtained by these authors is close to that (4.5) found using our analytic expression. This number is roughly of the size expected for the number of nearest neighbors in a liquid and is within the hydration number of 6 ± 2 obtained by independent methods.[24] This fitted hydration number is difficult to compare with explicitly structural or Hamiltonian based methods of obtaining hydration numbers.[4]

3.4. Inclusion of Both Attractive Interactions and Packing. To include both attractive pairwise (pw) interactions and packing (pk) effects, the terms of the partition function up to and including second order are required. The calculation is straightforward. Therefore, only the result is given.

$$\gamma_{pw,pk} = \frac{\mathscr{G}_{2,m}}{2m}\frac{(1-mg_w)}{(2-mg_w)}\left(-1+\sqrt{1+\frac{4m}{\mathscr{G}_{2,m}}\frac{(2-mg_w)}{(1-mg_w)^2}}\right) \quad (29)$$

In Figure 3 the molal activity coefficient of glycine is given as an example of a solution that requires attractive and packing terms, but not Debye−Hückel. At low concentrations, the experimental curve is flatter than required by the influence of pairwise interactions alone. This is apparently caused by a progressive restriction in the ability to hydrate the solute (i.e., packing effect). The packing effect is already significant within the range of solubility, although it is not strong enough to produce a positive slope within the range of experimental data.

3.5. Pairwise interaction and Electrostatics. A good example of a monovalent organic salt whose behavior can be accounted for by the inclusion of electrostatic interactions (el)
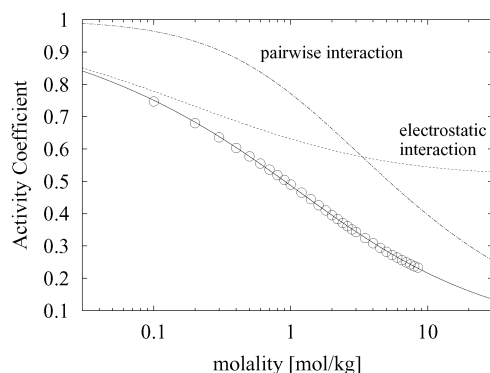
Figure 4. Activity coefficient of guanidinium chloride in H_2O according to ref 26. The experimental data (circles) were fitted to the product of the activity coefficients given by eqs 29 and 27. The resulting parameters are $\mathscr{G}_{2,m} = 5.2$ mol/kg $\pm$ 0.2, $b = 1.52/\sqrt{\text{mol/L}} \pm 0.05$, and root-mean-square deviation 0.002.

and pairwise interactions (pw) is guanidinium chloride. In Figure 4 the molal activity coefficient given by the equation

$$\ln \gamma_{\text{el,pw}} = \ln \gamma_{\text{el}} + \ln \gamma_{\text{pw}} =$$

$$-\frac{a\sqrt{c}}{1 + b\sqrt{c}} + \ln\left[\frac{\mathscr{G}_{2,m}}{4m}\left(-1 + \sqrt{1 + \frac{8m}{\mathscr{G}_{2,m}}}\right)\right] \quad (30)$$

is displayed. Due to the combination of the two negative contributions the activity coefficient reaches especially low values in fitting this particular case.

3.6. Highly Concentrated Solutions: Low Solvent Concentrations. If a solute is highly soluble, more terms of the partition function are required in accounting for the activity data than in the cases discussed above. In the case where terms of the partition function up to and including third order are of importance, eq 13 can be rearranged in terms of molality

$$m = \frac{1}{g_w} \frac{ag_w + 2a^2/\mathscr{G}_{2,m} + 3a^3/\mathscr{G}_{3,m}}{1 + ag_w + a^2/\mathscr{G}_{2,m} + a^3/\mathscr{G}_{3,m}}$$

$$= \frac{1}{g_w} \frac{ag_w + 2(ag_w/\mathscr{G}_2^{1/2})^2 + 3(ag_w/\mathscr{G}_3^{1/3})^3}{1 + ag_w + (ag_w/\mathscr{G}_2^{1/2})^2 + (ag_w/\mathscr{G}_3^{1/3})^3} \quad (31)$$

where $\langle N \rangle = mg_w$. The version of this equation using $\mathscr{G}_1^{1/i}$ separates g_w from $\mathscr{G}_N$ and is more convenient for fitting data. Solving eq 31 for a does not result in a closed expression for the activity coefficient. However, it is not necessary to solve eq 31 for the activity if the axes are exchanged and molality vs relative activity data are fitted rather than activity coefficient vs molality data. A simple division of the activity by the molality will yield the activity coefficient.

As an example for a highly concentrated solute we show the activity coefficient of sucrose in Figure 5. The three-parameter eq 31 yields a remarkable fit (solid line) over the whole range of solubility from sucrose concentration of zero up to nearly 70% by weight, giving a standard deviation of 0.003. From the fit, a number $N_w = 1000g_w/18$ of around 11 water molecules is obtained. This is higher than the hydration number of around 4−7 estimated in a recent review[28] for low concentrations of sucrose. At higher concentrations, however, our estimate converges with that given in the review because the trend of a decrease in hydration with increasing sucrose concentration reported in that review is also found in our model. This is because the average number of sucrose molecules per subsystem
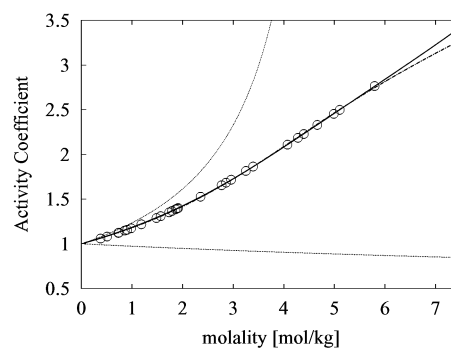

Figure 5. Activity coefficient of sucrose in H_2O. The experimental data[27] (circles) were fit to eq 31 (solid line). The resulting fitted parameters are $\mathscr{G}_2^{1/2} = 3.21 \pm 0.06$, $\mathscr{G}_3^{1/3} = 4.21 \pm 0.01$, and $N_w = 11.0 \pm 0.1$, standard deviation 0.003. The dashed line represents a fit assuming that the interaction parameters are equal. The result of the two-parameter fit gives $\mathscr{G}_2^{1/2} = \mathscr{G}_3^{1/3} = 4.11 \pm 0.02$ and $N_w = 9.8 \pm 0.1$ with standard deviation 0.007. Also plotted (as dotted lines) are the activity coefficients expected from pure pairwise interaction and pure packing if the values obtained for sucrose are plugged into eqs 23 and 26.

increases with sucrose concentration, whereas the number of water molecules remains constant.

In an early paper on sucrose hydration, Scatchard[29] also found an estimated average hydration of approximately 4 water molecules per sucrose molecule, but a high degree of uncertainty at low concentration with hydration values scattering between 1 and 10. Stokes and Robinson[30] find a hydration number of 11 for sucrose using a water binding model.

In the case of sucrose, the two interaction parameters, $\mathscr{G}_2^{1/2} = 3.21$ and $\mathscr{G}_3^{1/3} = 4.21$, are quite similar to each other. This shows that the interaction energy per particle is hardly dependent on whether the particles are interacting pairwise or in a ternary context. Indeed, if $\mathscr{G}_2^{1/2}$ and $\mathscr{G}_3^{1/3}$ are set equal, the quality of the fit (now two parameters) is nearly unchanged with a standard deviation of 0.007. The number of water molecules $N_w = 9.8$ and the interaction parameter $\mathscr{G}_2^{1/2} = 4.11$ attained from the two-parameter fit hardly differ from the parameters obtained in the three-parameter fit.

4. Conclusion

A simple and accurate model for activities should follow from a statistical thermodynamic viewpoint. Starting with Hill's isobaric semi grand partition function, we have derived simple analytic expressions that can be used to fit two-component solution activity data over the range from dilute to saturated solutions. By and large, we find that the analytic expressions require fewer parameters and yield fits with smaller standard deviations than provided by models (mostly heuristic) presented in the past. We derived forms from a low-order expansion of Hill's semi grand partition function at constant pressure. Thus our approach takes into account the effective solvent interactions with the solute and between solute molecules for a variable amount of solvent. An advantage of this approach is that it is physically based, it is applicable to a broad range of compounds having widely differing physical and chemical properties, and it provides a statistical foundation for interpreting the results.

Our purpose in this paper is to illustrate the versatility of the approach, the range of binary systems that can be studied, and the potential insight it offers in terms of the underlying physical phenomena. In future publications we will provide a more in depth analysis of the approach, expanding it to more complicated phenomena such as phase transitions.

Appendix I: Osmotic Coefficients in the Different Models

We derive here the osmotic coefficients for the different cases discussed in this paper. The calculations involve only simple mathematical operations and are therefore not given in detail. We start with the case of pairwise interaction. Application of the Gibbs−Duhem relation (eq 15) to eq 23 yields the chemical potential of the water in solution relative to that of pure water for the case of pairwise interacting solutes

$$(\mu_w - \mu_w^0)\beta = -\frac{4\langle N\rangle + (-1 + \sqrt{1 + 8\langle N\rangle/\mathscr{G}_2})\mathscr{G}_2}{8N_w} \quad (32)$$

The osmotic coefficient ϕ is then

$$\phi_{pw} = \frac{1}{2} + \frac{\mathscr{G}_2}{8\langle N\rangle}\left(-1 + \sqrt{1 + \frac{8\langle N\rangle}{\mathscr{G}_2}}\right)$$
$$= \frac{1}{2} + \frac{\mathscr{G}_{2,m}}{8m}\left(-1 + \sqrt{1 + \frac{8m}{\mathscr{G}_{2,m}}}\right) = \frac{1 + \gamma_{pw}}{2} \quad (33)$$

Expressing the osmotic coefficient in terms of the activity coefficient of the solute, as done in the last step, makes the equation especially simple.

If the same procedure is applied to the purely packing related activity coefficient (eq 26), the following simple expression is obtained:

$$\phi_{pk} = -\frac{\ln(1 - \langle N\rangle)}{\langle N\rangle} = \frac{\ln(\gamma_{pk})}{mg_w} \quad (34)$$

where γ_{pk} is given by eq 26.

For the case of the Debye−Hückel activity coefficient γ_{el} (eq 27) the same procedure yields the following osmotic coefficient:

$$\phi_{el} = -\frac{1}{b^2\langle N\rangle}\left(\frac{a\sqrt{\langle N\rangle}}{1 + b\sqrt{\langle N\rangle}} + a\sqrt{\langle N\rangle} - \frac{2a}{b}\ln(1 + b\sqrt{\langle N\rangle})\right)$$
$$= \frac{1}{b^2\langle N\rangle}\left(\ln(\gamma_{el}\gamma_{dhl}) + \frac{2a}{b}\ln\left(\frac{\ln\gamma_{dhl}}{\ln\gamma_{el}}\right)\right) \quad (35)$$

where γ_{dhl} is the Debye−Hückel limiting law activity coefficient. The conversion of $\langle N\rangle$ to different concentration scales can be included in the constants a and b.

The result for the case of pairwise interaction and packing is

$$\phi_{pk,pw} = \frac{1}{mg_w}\ln\left(\frac{1 + \gamma_{pk,pw}mg_w/2}{1 - mg_w/2}\right) \quad (36)$$

The activity coefficient $\gamma_{pk,pw}$ is given by eq 29.

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