Modeling of activity coefficients of aqueous solutions of quaternary ammonium salts with the electrolyte-NRTL equation

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Abstract

Ionic liquids (ILs) have been studied recently as potential “green” solvents due to their negligible vapor pressure. Modeling their phase behavior with water and organic solvents and their partitioning between aqueous and organic phases is vital for evaluating their many potential uses. Unfortunately, phase behavior data for the popular imidazolium and pyridinium salts are still somewhat limited. However, there exists a wealth of data for aqueous solutions of quaternary ammonium salts, a class of compounds that includes potentially interesting ILs. Therefore, as a first step towards modeling the phase behavior of IL solutions, we will show how a conventional electrolyte model, the electrolyte nonrandom two-liquid (NRTL) model proposed by Chen *et al.*,[1] can be applied to model activity coefficients of quaternary ammonium salts in water. This model requires two parameters per salt that must be fit to the experimental data. Particular attention has been paid to computing these binary parameters using a reliable parameter estimation technique, which is based on interval analysis. Indeed, this technique allows us to find deterministically the global minimum and, if desired, all the local minima in the parameter estimation problem within a given interval. Results indicate that this model is able to capture the nonideal phase behavior of these salts in aqueous solutions up to relatively high concentrations. Limitations of this simple model appear at higher concentrations and for highly branched compounds, most likely due to effects of incomplete dissociation and micelle formation that are not taken into account in the model.

Introduction

Low melting organic salts or ionic liquids (ILs) have been vigorously investigated in the past decade. Since they are salts, they exhibit negligible vapor pressure and, therefore, cannot contribute to air pollution. Much work has focused on their ability to serve as solvents for reactions and their potential as phase-transfer catalysts. In addition, they are known for their good heat transfer properties and high conductivities. Their stability, large liquidus range and good solvation properties for both polar and nonpolar compounds[2] make them interesting as solvents for chemical reactions and separations. Their physical properties are tunable by wise selection of cation, anion and substituents. Some recent reviews giving an overview of the potential of these salts for synthesis, catalysis, and separations are available.[3-6]

To be able to use ILs efficiently as solvents, it is important to characterize their fundamental thermodynamic properties and phase behavior with water and organic solvents, as well as their partitioning between aqueous and organic phases. Because ILs (in particular the popular imidazolium and pyridinium salts) are relatively new, experimental measurements of phase behavior and activity coefficients, with which to evaluate thermodynamic models, are relatively limited. The only phase behavior data that are currently available include some infinite dilution activity coefficients of chemicals in ILs,[7-10] some gas, liquid and solid solubilities in ILs,[2,11-31] and some liquid-liquid equilibrium data between ILs and alcohols.[32,33] On the other hand, there is a significant body of data on activity coefficients of aqueous solutions of quaternary ammonium salts, a class of compounds that includes potentially interesting ILs. Thus, this paper will focus on quaternary ammonium salts. These salts have been used widely in industry as phase-transfer catalysts, in hair care and cosmetics products, as disinfectants and preservatives, and as additives in animal feed (choline salts). Moreover, they can be biodegradable, nontoxic and nonirritant, which may confer them with a major advantage over other classes of ILs.[34,35] The only problem with these types of salts, including the ones analyzed in this present work, is that they tend to have somewhat higher melting points than many other classes of ILs. It is likely that this disadvantage can be resolved by changing cation substituents and using more complex anions to lower the melting point.[36]

The objective of this work is to test the ability of a conventional electrolyte model to describe activity coefficients of quaternary ammonium salts at low concentration in water. In future work we will be concerned with higher salt concentrations in water and the phase behavior of organic salt mixtures with organic solvents. These are cases where we anticipate that the salts will not be fully dissociated, which is an assumption of the model used here. In the long term, we hope that this approach will provide us with some predictive power for new species, so that we can estimate phase behavior and partitioning of these salts between aqueous and organic solutions. An especially important quantity is the octanol/water partition coefficient, since it is a key parameter for understanding the environmental fate of any compound.

The earliest theoretical model for estimation of activity coefficients in electrolyte solutions is the Debye-Hückel model,[37] which takes into account the long-range electrostatic interactions between ions. This model provides good results only at very dilute concentrations, so a variety of improvements have been made for more concentrated systems. Several of these models, which contain varying numbers of adjustable parameters, have shown significant success in modeling activity coefficients of conventional electrolyte systems (e.g., inorganic salts). We have chosen one of these, the electrolyte-NRTL model of Chen *et al.*,[1] and Chen and Evans,[38] for this study.

For a binary salt-solvent system, this simple model involves only two parameters to completely describe the system: the "molecule/salt parameter" and the "salt/molecule parameter," where "molecule" is the solvent, water in this case. Depending on the solute studied, the parameter estimation can lead to an optimization problem with multiple local minima. This situation raises the issue of the reliability of the parameter estimation technique used. For this reason the interval-Newton technique, which provides us with the capability of finding the *globally* optimal parameter set, as well as, if desired, all the locally optimal parameter sets, has been applied in this work.

To summarize, this work begins with a description of Chen *et al.*'s electrolyte-NRTL model,[1] followed by a summary of the reliable parameter estimation technique used. Next, results for fifty-seven quaternary ammonium salts in water at 25 °C are presented. The results are discussed and the limitations of the model are explored.

Model

As mentioned above, there have been many improved models of electrolyte solutions since the Debye-Hückel model[37] was introduced. Among the main models developed, the Pitzer model has been widely used in the chemical industry. It is based on a modified Debye-Hückel term representing the long-range interactions added to a virial expansion in electrolyte concentration to account for the short-range ionic interactions. The three adjustable parameters used in the virial expansion are specific for each salt and have been obtained from least-squares fits to experimental osmotic and activity coefficient data.[39-41] Later, Cruz and Renon[42] and Chen *et al.*[1] used the NRTL model for short-range interactions to account for differences between bulk and local compositions. They both used a modified Debye-Hückel term to take long-range interactions into account, the one in Chen *et al.*'s model[1] being directly inspired by Pitzer. Cruz and Renon[42] used four adjustable parameters to get good results on fitting osmotic coefficients of partially or completely dissociated electrolytes, whereas Chen *et al.*,[1] by using new assumptions about the local composition, developed a two adjustable parameter model, where the parameters are salt specific. Others models using the Wilson equation[43] or an extended UNIFAC model[44,45] to account for local compositions and short-range forces have been developed also. In this case, the number of parameters needed is dependent on the system studied because they are ion specific.

Here we choose to use the electrolyte-NRTL model of Chen *et al.*[1] because it works very well for a large variety of simple salts. The original authors successfully correlated a wide variety of single-solvent, single-electrolyte systems over wide ranges of concentration and temperature, assuming complete dissociation of the electrolyte.[1] Later Chen and Evans generalized the model to multicomponent electrolyte systems.[38]

This approach is very well adapted to electrolyte solutions and allows one to take into account a variety of interactions, in addition to coulombic forces. Also, it does not require any specific area or volume data and retains an easy to use algebraic form for the single-solvent, single-electrolyte, completely-dissociated system model. This model is applied in this work to quaternary ammonium salts at relatively low concentrations in water using only two adjustable parameters. One would anticipate that the assumption of complete dissociation of the salt would be a good one for low concentrations in water.

An overview of Chen *et al.*'s model is presented here; more details can be found in the original paper.[1] The model can be described as a sum of two terms. First, there is a Debye-Hückel term, as modified by Pitzer, which accounts for long-range forces. It represents the electrostatic forces between ions and is given by:

$$\frac{g^{\mathrm{ex*}}}{RT} = -\sqrt{\frac{1000}{M_{\mathrm{S}}}}\, A_{\varphi}\, \frac{4\,I}{\rho}\ln\left(1+\rho\, I^{0.5}\right), \tag{1}$$

where $g^{\mathrm{ex*}}$ is the molar excess Gibbs energy relative to an unsymmetric reference state (indicated by the asterisk superscript) in which the activity coefficient of the solvent goes to one for pure solvent and the activity coefficients of the ionic species go to one at infinite dilution. Here M_{S} is the molecular weight of the solvent, x_k is the mole fraction of each species in the solution, and ρ is the closest approach parameter, which is fixed at 14.9 for all the components.[1] The ionic strength I, which depends on the charge of each ion (Z_i) and their concentration in terms of mole fraction, is given by:

$$I = \frac{1}{2}\sum_i Z_i^2 x_i\ . \tag{2}$$

A_{φ} is the Debye-Hückel parameter, which we calculate here using the expression obtained by Chen *et al.*,[1] which includes temperature dependence but is valid only for solutes in water.

Since $RT\ln(\gamma_i^*)$ is the partial molar excess Gibbs free energy, the Pitzer-modified Debye-Hückel expression, Eq. (1), leads to the following expression for the activity coefficient (due to coulombic forces) of species *i* in the solution:

$$\ln\gamma_i^{\mathrm{*PDH}} = -\sqrt{\frac{1000}{M_{\mathrm{S}}}} A_{\varphi}\left(\frac{2\,Z_i^2}{\rho}\ln\left(1+\rho\, I^{0.5}\right)+\frac{Z_i^2\, I^{0.5}-2\,I^{1.5}}{1+\rho\, I^{0.5}}\right) \tag{3}$$

The second part of the model is an NRTL term corresponding to the short-range forces. Like the regular NRTL model from Renon and Prausnitz,[46] the electrolyte-NRTL model assumes that the local mole fractions of species around a central molecule are different than the bulk mole fractions. Here the species can be anions (a), cations (c) or solvent molecules (m). The model accounts for ion/molecule electrostatic forces if the molecule has a permanent dipole and various molecule/molecule interactions, such as dipole/dipole, induced dipole and van der Waals forces. Two assumptions are made in deriving this part of the model. First, like-ion repulsion due to the large repulsive forces between ions of the same charge is assumed. This means that the area immediately surrounding a cation will not contain other cations and the area immediately surrounding an anion will not contain other anions. Second, local electroneutrality is assumed, so that around a central molecule the net ionic charge is zero.

For the electrolyte case with the local electroneutrality assumption, the NRTL parameters G can be expressed in terms of $\tau_{\mathrm{ca,m}}$, the salt/molecule parameter, and $\tau_{\mathrm{m,ca}}$, the molecule/salt parameter:

$$G_{\mathrm{am}} = G_{\mathrm{cm}} = \exp\left(-\alpha\ \tau_{\mathrm{ca,m}}\right) \equiv G_{\mathrm{ca,m}} \tag{4}$$

$$G_{\mathrm{mc,ac}} = G_{\mathrm{ma,ca}} = \exp\left(-\alpha\ \tau_{\mathrm{m,ca}}\right) \equiv G_{\mathrm{m,ca}}\ . \tag{5}$$

The nonrandomness factor, α, is fixed at a value of 0.2 in this study, as it has been done previously for electrolyte solutions.[1] Physically, the τ values can be interpreted in terms of the differences in interaction energies between a cation and a solvent molecule (g_{cm}), between an anion and a solvent molecule (g_{am}), between a solvent molecule and another solvent molecule (g_{mm}), and between a cation and an anion (g_{ca}).

$$\tau_{\mathrm{ca,m}} = \tau_{\mathrm{cm}} = \frac{g_{\mathrm{cm}} - g_{\mathrm{mm}}}{RT} = \tau_{\mathrm{am}} = \frac{g_{\mathrm{am}} - g_{\mathrm{mm}}}{RT} \tag{6}$$

$$\tau_{\mathrm{m,ca}} = \tau_{\mathrm{ma,ca}} = \frac{g_{\mathrm{ma}} - g_{\mathrm{ca}}}{RT} = \tau_{\mathrm{mc,ac}} = \frac{g_{\mathrm{mc}} - g_{\mathrm{ac}}}{RT} \tag{7}$$

Note also that $g_{ij} = g_{ji}$. The two adjustable parameters, $\tau_{\mathrm{ca,m}}$ and $\tau_{\mathrm{m,ca}}$, are empirical since they are determined by fit to experimental data, but do have some physical significance since they represent the differences in interaction energies shown in Eqs. (6) and (7). The cation/anion interaction should be strongest, followed by the anion/molecule and cation/molecule interactions. The molecule/molecule interactions should be weakest. Remembering that all of these interaction energies are negative (i.e., attraction), this means that we would expect $g_{\mathrm{ac}} << g_{\mathrm{mc}}$ and $g_{\mathrm{am}} < g_{\mathrm{mm}} < 0$. This leads to the expectation that:

$$\tau_{\mathrm{ca,m}} \le 0 \ ; \qquad \tau_{\mathrm{m,ca}} \ge 0 \ ; \qquad \left|\tau_{\mathrm{ca,m}}\right| << \left|\tau_{\mathrm{m,ca}}\right| \ . \tag{8}$$

The NRTL excess Gibbs energy contribution is derived by applying electroneutrality on a local scale and by normalizing to the infinite dilution reference state for the ions. Then, by taking the partial molar excess Gibbs free energy, the NRTL contribution to the activity coefficient for each ion is:

$$\begin{aligned}\ln\left(\gamma_{\mathrm{c}}^{*\mathrm{NRTL}}\right) = {} & \frac{\tau_{\mathrm{ca,m}} x_{\mathrm{m}}^{2} G_{\mathrm{ca,m}}}{\left(x_{\mathrm{a}} G_{\mathrm{ca,m}} + x_{\mathrm{c}} G_{\mathrm{ca,m}} + x_{\mathrm{m}}\right)^{2}} + \frac{\tau_{\mathrm{m,ca}} Z_{\mathrm{c}} x_{\mathrm{m}} G_{\mathrm{m,ca}}}{x_{\mathrm{a}} + x_{\mathrm{m}} G_{\mathrm{m,ca}}} - \frac{\tau_{\mathrm{m,ca}} Z_{\mathrm{a}} x_{\mathrm{a}} x_{\mathrm{m}} G_{\mathrm{m,ca}}}{\left(x_{\mathrm{m}} G_{\mathrm{m,ca}} + x_{\mathrm{c}}\right)^{2}} \\ & - \tau_{\mathrm{ca,m}} G_{\mathrm{ca,m}} - \tau_{\mathrm{m,ca}} Z_{\mathrm{c}}\end{aligned} \tag{9}$$

$$\begin{aligned}\ln\left(\gamma_{\mathrm{a}}^{*\mathrm{NRTL}}\right) = {} & \frac{\tau_{\mathrm{ca,m}} x_{\mathrm{m}}^{2} G_{\mathrm{ca,m}}}{\left(x_{\mathrm{a}} G_{\mathrm{ca,m}} + x_{\mathrm{c}} G_{\mathrm{ca,m}} + x_{\mathrm{m}}\right)^{2}} + \frac{\tau_{\mathrm{m,ca}} Z_{\mathrm{a}} x_{\mathrm{m}} G_{\mathrm{m,ac}}}{x_{\mathrm{c}} + x_{\mathrm{m}} G_{\mathrm{m,ca}}} - \frac{\tau_{\mathrm{m,ca}} Z_{\mathrm{c}} x_{\mathrm{c}} x_{\mathrm{m}} G_{\mathrm{m,ca}}}{\left(x_{\mathrm{m}} G_{\mathrm{m,ca}} + x_{\mathrm{a}}\right)^{2}} \\ & - \tau_{\mathrm{ca,m}} G_{\mathrm{ca,m}} - \tau_{\mathrm{m,ca}} Z_{\mathrm{a}}\end{aligned} \tag{10}$$

It is interesting to note that these equations are symmetric for the two ionic species and involve only ion charges (Z_i), the NRTL parameters, $\tau_{\mathrm{ca,m}}$ and $\tau_{\mathrm{m,ca}}$, and the mole fractions of each species (note that the G's depend on $\tau_{\mathrm{ca,m}}$ and $\tau_{\mathrm{m,ca}}$).

For each species, the activity coefficient is the sum of the Pitzer-Debye-Hückel contribution and the NRTL contribution.

$$\ln\left(\gamma_i^*\right) = \ln\left(\gamma_i^{*\mathrm{PDH}}\right) + \ln\left(\gamma_i^{*\mathrm{NRTL}}\right). \tag{11}$$

However, in order to compare the model with experimental values, one must relate the ionic activity coefficients to the *mean activity coefficient* of the salt in the solution, which is the quantity actually measured. The mean activity coefficient (molality scale) is a function of molality (m), solvent molecular weight (M_{s}), the stoichiometric coefficients (υ_+, υ_-) written in the chemical equilibrium $M_{\upsilon+} X_{\upsilon-} \leftrightarrow \upsilon_+ M^{Z+} + \upsilon_- X^{Z-}$ and the sum of these stoichiometric coefficients $\upsilon = \upsilon_+ + \upsilon_-$. The mean activity coefficient is related to the ionic activity coefficients by:

$$\ln\left(\gamma_{\pm\mathrm{m}}^*\right) = \frac{1}{\upsilon}\left[\upsilon_+ \ln\left(\gamma_{\mathrm{c}}^*\right) + \upsilon_- \ln\left(\gamma_{\mathrm{a}}^*\right)\right] - \ln\left(1 + 0.001 M_{\mathrm{S}}\, m\, \upsilon\right) \tag{12}$$

It is necessary to emphasize that this model is for a single electrolyte in a single solvent (water in this case), where we assume that the salt is completely dissociated. We anticipate that this should work well for relatively low concentrations of salts in water. At higher concentrations, or even for low concentration in a non polar organic solvent, the assumption of complete dissociation is not likely to be valid. In future work, we anticipate applying a more sophisticated version of the model that includes a partially dissociated constraint[38] or a more recent version that may even be able to account for micelle formation.[47]

Reliable parameter estimation

There are two model parameters, $\tau_{\mathrm{ca,m}}$ (the salt/molecule parameter) and $\tau_{\mathrm{m,ca}}$ (the molecule/salt parameter), that must be estimated using measured mean activity coefficient data from the literature. For this purpose we use the simple least squares objective function given by:

$$\phi(\tau_{\mathrm{ca,m}}, \tau_{\mathrm{m,ca}}) = \sum_i \left[\ln\left(\gamma_{\pm\mathrm{m}}^{*\exp} \right)_i - \ln\left(\gamma_{\pm\mathrm{m}}^{*\mathrm{calc}} \right)_i \right]^2 \tag{13}$$

This is the same objective function used by Chen *et al.*[1] and several others.

The objective function ϕ to be minimized is nonconvex in the parameters and thus may have multiple local minima. Indeed, initial efforts to minimize ϕ using a simplex pattern search routine (fminsearch in Matlab 6) gave results that were highly initialization dependent, confirming there to be multiple local minima for many of the compounds considered. Failure to find the globally optimal parameters in an activity coefficient model can have significant consequences in subsequent phase equilibrium computations using the model, as demonstrated by Gau *et al.*[48] In order to avoid time-consuming initialization issues, and to provide a *guarantee* that the *global* minimum of ϕ is found (or, if desired, that *all* local minima of ϕ are found), we adopted the methodology of Gau *et al.*[48] This involves a *deterministic* global optimization procedure based on the use of interval computing, in particular an interval-Newton methodology combined with generalized bisection.[49] This technique is summarized very briefly here. Additional details are provided by Gau *et al.*[48] and Schnepper and Stadtherr.[50]

For minimizing a function $\phi(\boldsymbol{\theta})$, where $\boldsymbol{\theta} = (\theta_1, \theta_2, \ldots, \theta_q)^{\mathrm{T}}$ denotes a vector of parameters to be estimated, a common approach is to determine the gradient of $\phi(\boldsymbol{\theta})$ and to then solve the nonlinear equation system $\boldsymbol{g}(\boldsymbol{\theta}) \equiv \nabla\phi(\boldsymbol{\theta}) = \mathbf{0}$. The interval-Newton/generalized bisection (IN/GB) approach is of interest here because, given a system of nonlinear equations with a finite number of real roots, it provides the capability to find (or more precisely, narrowly enclose within a very narrow interval) *all* the roots of the equation system that lie within some given initial interval. In this case, the initial parameter interval $\boldsymbol{\Theta}^{(0)}$ can be chosen large enough to include all reasonable parameter values. A discussion of how this was selected for the problems considered here is given below.

Given the initial interval $\boldsymbol{\Theta}^{(0)}$, the interval-Newton algorithm is applied to a sequence of subintervals. For a subinterval $\boldsymbol{\Theta}^{(k)}$ in the sequence, the first step is the *function range test*. An interval extension $\boldsymbol{G}(\boldsymbol{\Theta}^{(k)})$ of the function $\boldsymbol{g}(\boldsymbol{\theta})$ is calculated, which provides upper and lower bounds on the range of values of $\boldsymbol{g}(\boldsymbol{\theta})$ in $\boldsymbol{\Theta}^{(k)}$. If there is any component of the interval extension $\boldsymbol{G}(\boldsymbol{\Theta}^{(k)})$ that does not include zero, then the interval can be discarded, since no solution of $\boldsymbol{g}(\boldsymbol{\theta}) = \mathbf{0}$ can exist in this interval. The next subinterval in the sequence may then be considered. Otherwise, testing of $\boldsymbol{\Theta}^{(k)}$ continues.

For a global minimization problem, the next step is the *objective range test*. The interval extension $\Phi(\boldsymbol{\Theta}^{(k)})$, containing the range of $\phi(\boldsymbol{\theta})$ over $\boldsymbol{\Theta}^{(k)}$ is computed. If the lower bound of $\Phi(\boldsymbol{\Theta}^{(k)})$ is greater than a known upper bound on the global minimum, then $\boldsymbol{\Theta}^{(k)}$ can be discarded since it cannot contain the global minimum and need not be further tested. In cases that all the stationary points of $\phi(\boldsymbol{\theta})$ (solutions of $\boldsymbol{g}(\boldsymbol{\theta}) = \mathbf{0}$**)** are desired rather than just the global minimum, this test step can be turned off.

The next step is the *interval-Newton test*. The linear interval equation system

$$G'(\boldsymbol{\Theta}^{(k)})(\boldsymbol{N}^{(k)} - \boldsymbol{\theta}^{(k)}) = -\boldsymbol{g}(\boldsymbol{\theta}^{(k)}) \tag{14}$$

is solved for a new interval $\boldsymbol{N}^{(k)}$, where $G'(\boldsymbol{\Theta}^{(k)})$ is an interval extension of the Jacobian of $\boldsymbol{g}(\boldsymbol{\theta})$, and $\boldsymbol{\theta}^{(k)}$ is an arbitrary point in $\boldsymbol{\Theta}^{(k)}$. It has been shown that any root contained in $\boldsymbol{\Theta}^{(k)}$ is also contained in the image $\boldsymbol{N}^{(k)}$. This implies that when $\boldsymbol{\Theta}^{(k)} \cap \boldsymbol{N}^{(k)}$ is empty, then no root exists in $\boldsymbol{\Theta}^{(k)}$, and also suggests the iteration scheme $\boldsymbol{\Theta}^{(k+1)} = \boldsymbol{\Theta}^{(k)} \cap \boldsymbol{N}^{(k)}$. In addition, if $\boldsymbol{N}^{(k)} \subset \boldsymbol{\Theta}^{(k)}$, there is a *unique* root contained in $\boldsymbol{\Theta}^{(k)}$ and thus in $\boldsymbol{N}^{(k)}$. Thus, after computation of $\boldsymbol{N}^{(k)}$, there are three possibilities: 1. $\boldsymbol{\Theta}^{(k)} \cap \boldsymbol{N}^{(k)} = \varnothing$, meaning there is no root in the current interval $\boldsymbol{\Theta}^{(k)}$ and it can be discarded; 2. $\boldsymbol{N}^{(k)} \subset \boldsymbol{\Theta}^{(k)}$, meaning that there is exactly one root in the current interval $\boldsymbol{\Theta}^{(k)}$; 3. Neither of the above, meaning that no conclusion can be drawn. In the last case, if $\boldsymbol{\Theta}^{(k)} \cap \boldsymbol{N}^{(k)}$ is sufficiently smaller than $\boldsymbol{\Theta}^{(k)}$, then the interval-Newton test can be reapplied to the resulting intersection. Otherwise, the intersection is bisected, and the resulting two subintervals are added to the sequence of subintervals to be tested. This approach is referred to as an interval-Newton/generalized-bisection (IN/GB) method. At termination, when the subintervals in the sequence have all been tested, the *global* minimum of $\phi(\boldsymbol{\theta})$ will have been enclosed, or, if the objective range test has been turned off, *all* the stationary points of $\phi(\boldsymbol{\theta})$ will have been enclosed.

This is a *deterministic* method that is mathematically guaranteed to enclose the global minimum. Also, because it is implemented using interval arithmetic, which deals automatically with rounding error issues, this method provides a computational guarantee of reliability. For the parameter estimation problems solved here, we used the C++ implementation of IN/GB provided by Liang.[51]

The initial intervals used for the parameters in the search for the global minimum were $\tau_{\mathrm{ca,m}} \in [-50, 10]$ and $\tau_{\mathrm{m,ca}} \in [-10, 50]$. These are very wide intervals around the expected parameter values. Note that, although physically we should expect $\tau_{\mathrm{ca,m}} < 0$ and $\tau_{\mathrm{m,ca}} > 0$, we have extended the search space beyond these bounds. This is useful, since if the globally optimal parameters values are consistently outside the physically expected range, it suggests inadequacies in the model.

Results and Discussion

We have used the electrolyte-NRTL model to correlate mean activity coefficient data for aqueous solutions of fifty-seven different ammonium salts (see Tables 1 and 4-10). The data available in the literature[52-68] was at 25 °C and the majority of the values were obtained using the gravimetric isopiestic vapor pressure comparison method of Robinson and Sinclair.[69,70] The substituents on the central nitrogen atom of the quaternary ammonium cations range from simple hydrogen atoms to butyl, ethoxy, and benzyl groups. The anions are primarily halides, nitrates, sulfates, perchlorates and alkylsulfonates. As mentioned earlier, these pure salts all have relatively high melting points, greater than 100 °C in most cases. However, they all have significant solubility in water.

For each compound, the deviation between experimental and calculated values of the mean activity coefficients is expressed in term of both the residual standard deviation (σ) and the absolute average relative deviation (%AARD):

$$\sigma = \sqrt{\frac{\phi}{N-p}} = \sqrt{\frac{\sum_{i=1}^{N}\left[\ln\left(\gamma_{\pm\mathrm{m}}^{*\mathrm{exp}}\right)_i - \ln\left(\gamma_{\pm\mathrm{m}}^{*\mathrm{calc}}\right)_i\right]^2}{N-p}} \tag{15}$$

$$\%\mathrm{AARD} = \frac{100}{N}\sum_{i}\frac{\left|\left(\gamma_{\pm\mathrm{m}}^{*\exp}\right)_i - \left(\gamma_{\pm\mathrm{m}}^{*\mathrm{calc}}\right)_i\right|}{\left(\gamma_{\pm\mathrm{m}}^{*\exp}\right)}, \tag{16}$$

where N is the number of experimental data points, and $p = 2$ is the number of parameters in the model. The standard deviation, which is traditionally done for ln γ_i, tends to mask errors in small values of the activity coefficients, whereas these errors are more faithfully represented by the %AARD calculated for γ_i.

In order to put the results for the electrolyte-NRTL model in perspective, we also show in the Tables the residual standard deviation and %AARD for the popular Pitzer model,[71] which has been used previously to model almost all of the systems investigated. Note that the Pitzer model is a three-parameter model; these parameters were determined here using the same data sets, objective function, and methodology as were used for the electrolyte-NRTL model. There are also parameter values for the Pitzer model available in the literature[71], fit to much of the same data, but using a different objective function (weighted least squares) over a smaller range of molality. In general, the results shown in the Tables for the Pitzer model are better than those obtained using the literature parameters. The improvement is especially significantly in cases for which the range of molalities considered here exceeds the range to which the literature parameters were fit, and for which the model with literature parameters must thus be extrapolated.

Results are shown in Table 1 and Figure 1 for simple ammonium salts. The electrolyte-NRTL model does an excellent job of correlating the data. This two-parameter model provides a fit almost as good as the three-parameter Pitzer model, even though it requires one fewer parameter. The model is able to represent the negative deviations from ideality (i.e., γ_i values less than 1.0) for these simple salts. The data is available at concentrations as high as 26 molal (this is a mole fraction of 0.48) and the electrolyte-NRTL model is able to correlate the data over the entire composition range. The values found for $\tau_{\mathrm{ca,m}}$ are negative and the values found for $\tau_{\mathrm{m,ca}}$ are positive, with $|\tau_{\mathrm{ca,m}}| << |\tau_{\mathrm{m,ca}}|$, which is consistent with the physical arguments discussed in the Model section. For all the simple salts except $[NH_4^+][I^-]$ and $[NH_4^+][C_2H_5SO_3^-]$, these parameters also represent the globally optimal parameter values found by using the IN/GB methodology. In the case of $[NH_4^+][I^-]$, the globally optimally parameter values found were $\tau_{ca,m} = -1.2616$ and $\tau_{m,ca} = 0.5641$ with $\phi = 0.000995$. Since these values did not meet the physical expectations, we then used IN/GB to search for *all* the stationary points of ϕ in the search interval, and thus identify other local minima. The results of this search are shown in Table 2, which indicates a local minima at $\tau_{ca,m} = -3.9608$ and $\tau_{m,ca} = 7.6287$ with $\phi = 0.001108$. Since these parameter values do meet the physical expectations and with a goodness of fit just slightly worse than the global minimum, we chose to use these parameter values, and this is what is reported in Table 1. A similar procedure was followed for the case of $[NH_4^+][C_2H_5SO_3^-]$, with results shown in Table 2. In the other results below (Tables 4-10), there is only one other case, namely $[NH_4^+]_2[B_{10}H_{10}^{2-}]$, in which the global optimal did not meet physical expectations and all stationary points were sought in order to identify a good local minimum. These results are also shown in Table 2. As in the case of $[NH_4^+][I^-]$, the $[NH_4^+][C_2H_5SO_3^-]$ and $[NH_4^+]_2[B_{10}H_{10}^{2-}]$ salts exhibit a local minimum meeting physical expectation with a goodness of fit only slightly worse than the global minimum.

In all other cases (54 of the 57 salts considered) the globally optimal parameters did in fact meet the physical expectations, suggesting that this is indeed a very good model for the systems of interest in this range of molalities. Even in these cases, however, we noted that it was not uncommon for there to be multiple local minima in the parameter estimation problem. For example, we used IN/GB to search for all stationary points for three additional compounds, shown in Table 3. In two cases there is one local (but not global) minimum and in one case there are two. The situation is similar for several other compounds. This indicates the importance of using the reliable parameter estimation procedure (IN/GB) outlined above. This guarantees that the globally optimal parameter values will be determined, and can be done easily and automatically, without need for time-consuming user intervention to deal with initialization issues.

Tables 4-6 and Figures 2-4 show the results for tetramethyl, tetraethyl and tetrapropyl ammonium salts, respectively. The highest concentration for which data is available for each salt is listed in the Tables. As with the simple ammonium salts, the mean ionic activity coefficients of these compounds in water are represented quite well by the electrolyte-NRTL model. The model is able to capture both positive and negative deviations from ideality remarkably well. However, in the cases of tetramethyl ammonium fluoride ($[(CH_3)_4N^+][F^-]$) and tetraethyl ammonium fluoride ($[(C_2H_5)_4N^+][F^-]$), which have activity coefficients much greater than unity, one can identify a significant difference between the data and the model at the higher molalities. The same remark can be made for tetramethyl ammonium chloride ($[(CH_3)_4N^+][Cl^-]$). The model does not work very well for this compound at higher concentrations, which extend to 19 molal (which corresponds to a mole fraction of 0.4). Nonetheless, for these groups of compounds, the globally optimal parameters always corresponded to a physically reasonable set of model parameters.

Methylammonium salts are shown in Figure 5 and Table 7. These salts have one or more methyl substituents on the central nitrogen, with the remaining substituents being hydrogen atoms. Figure 6 and Table 8 shows a number of quaternary ammonium salts with ethoxy and benzyl substituents. Clearly, the electrolyte-NRTL model is equally as successful in modeling these systems as in the case of the simpler quaternary ammonium salts.

A limitation of the electrolyte-NRTL model in correlating the mean ionic activity coefficients for quaternary ammonium salts in water can be seen in Figure 7 and Table 9. Here we show tetrabutyl ammonium salts. From Figure 7, it is clear that the activity coefficient behavior for some compounds is quite different, showing both minima and maxima, than those shown previously. Moreover, the electrolyte-NRTL model is not able to successfully capture this behavior. The unusual behavior has been attributed to micelle formation in solutions.[58] Obviously, there is nothing in the simple electrolyte-NRTL model that could account for this type of behavior. A solution to this problem may be to adopt Chen *et al.*'s[47] more recent (2001) model for organic salts, which adds a third term, derived from Flory-Huggins theory, into the sum of the excess Gibbs energies.

Finally, in Figure 8 and Table 10, we show the results for some ammonium salts with divalent anions and divalent cations. Many of these divalent cations are effectively dimers, where two singly charged quaternary ammonium cations share an alkyl chain. While the electrolyte-NRTL model performs very well for the simple ammonium salts with divalent anions ($[NH_4^+]_2[SO_4^{2-}]$ and $[NH_4^+]_2[B_{10}H_{10}^{2-}]$), it is not able to reproduce the thermodynamic behavior for all of the salts with divalent cations, performing particularly poorly in the case of the benzyldisulfonate anion. These data are the solid squares in Figure 8, but the poorly fit model is the solid line exhibiting a sharp minimum and terminating at molality of 1.2. One reason for this may be that the divalent cation, $(CH_3)_3\text{-}N^+\text{-}CH_2\text{-}CH_2\text{-}N^+\text{-}(CH_3)_3$, could form micelles in solution, a phenomenon that is not accounted for in the model. Also, the aromatic sulfonate anions might exhibit an unusual behavior because the two negative charges are significantly separated compared to a smaller divalent anion like SO_4^{2-}. Finally, the extremely fast decrease of the mean activity coefficient for the bibenzyldisulfonate anion, which is captured by the model, at least for the low concentrations studied, has been attributed to the formation of a chain of several monomer units in length.[63]

As pointed out earlier with the tetraalkyl ammonium fluorides and chloride, we expect the model to fail at higher salt concentrations. This is because one would expect the assumption of complete dissociation of the salt to break down at higher salt concentrations. The complete dissociation assumption is also expected to break down for salts in organic solvents. For solvents that are not highly polar, this could be a problem even at very low concentrations of the salt. We plan to address this problem in future work by investigating the application of the multicomponent electrolyte-NRTL model[38] and using an adjustable equilibrium constant to describe the degree of dissociation of the salt.

Concluding Remarks

The electrolyte nonrandom two-liquid (NRTL) model proposed by Chen *et al.*[1] works very well in modeling activity coefficients of quaternary ammonium salts in water at 25 °C, providing a fit almost as good as the three-parameter Pitzer model, despite requiring only two parameters. However some limitations are apparent from our results.

This simple model is not able to treat micelle formation in the solution, and we expect the fundamental hypothesis of complete dissociation of the salt to break down at higher concentrations or in an organic solvent. Future work will treat the problem of incomplete dissociation with a multicomponent version[38] of Chen *et al.*'s model, including the equilibrium constant of dissociation of the salt as an adjustable parameter.

Based on our experience in solving these parameter estimation problems, the use of a reliable parameter estimation technique, capable of finding the *globally* optimal parameter values, is highly recommended when using this model, to ensure that the best fit has been achieved. Indeed, for many compounds there were multiple local minima in the least squares function, so using a technique capable of finding the global minimum, or even all of the local minima, is important in guaranteeing the success of the parameter estimation.

Acknowledgments

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Notation

A_φ = Debye-Hückel parameter

I = ionic strength based on mole fraction concentrations, Eq. (2)

M_s = solvent molecular weight (g/mol)

R = gas constant

T = temperature (K)

Z_i = absolute value of charge of ionic species i

m = molality (mole/kg of solvent)

x_i = liquid phase mole fraction of species i

g^{ex} = molar excess Gibbs free energy

Greek letters

v = electrolyte stoichiometric coefficients

γ = activity coefficient

ϕ = objective function in parameter estimation

ρ = closest approach parameter (= 14.9)

τ = NRTL binary interaction energy parameter

α = NRTL nonrandomness factor (= 0.2)

Superscripts

* = unsymmetric convention for reference state

PDH = long-range contribution represented by the Pitzer modification of the Debye-Hückel equation

NRTL = short-range contribution represented by the NRTL equation

calc = calculated value

exp = experimental value

Subscripts

a = anion

c = cation

ca = salt

i, = any species

m = any molecular species

±m = mean ionic, molality scale

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Figure Captions

Figure 1: Comparison of experimental and modeled activity coefficients for simple ammonium salts in water at 25 ºC.

Figure 2: Comparison of experimental and modeled activity coefficients for tetramethylammonium salts in water at 25 ºC.

Figure 3: Comparison of experimental and modeled activity coefficients for tetraethylammonium salts in water at 25 ºC.

Figure 4: Comparison of experimental and modeled activity coefficients for tetrapropylammonium salts in water at 25 ºC.

Figure 5: Comparison of experimental and modeled activity coefficients for methylammonium salts in water at 25 ºC.

Figure 6: Comparison of experimental and modeled activity coefficients for ammonium salts with ethoxy, tetraethoxy, and benzyl substituents in water at 25 ºC.

Figure 7: Comparison of experimental and modeled activity coefficients for tetrabutylammonium salts in water at 25 ºC.

Figure 8: Comparison of experimental and modeled activity coefficients for dimeric and divalent ammonium salts in water at 25 ºC.

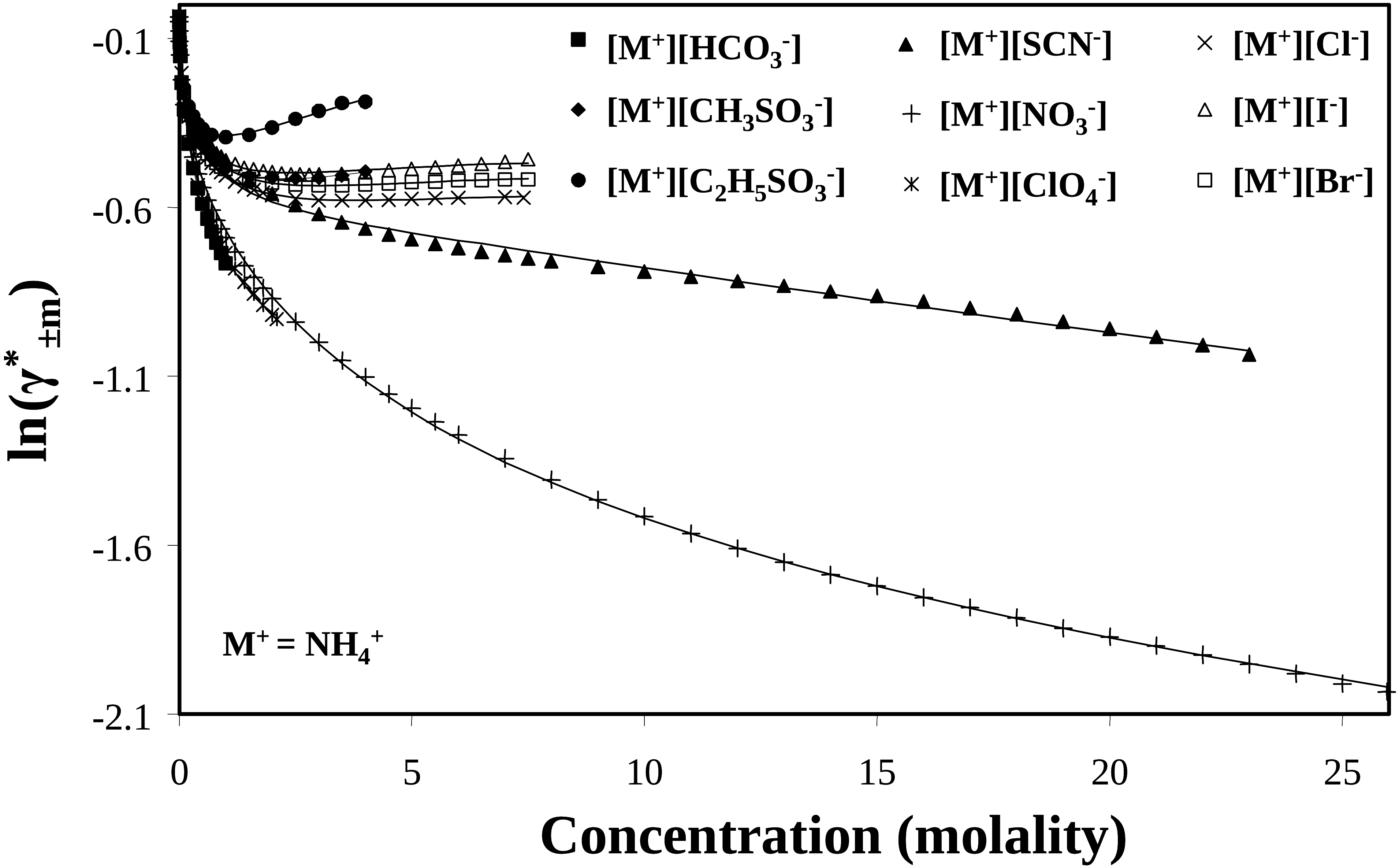

Figure 1: Comparison of experimental and modeled activity coefficients for simple ammonium salts in water at 25 ºC.

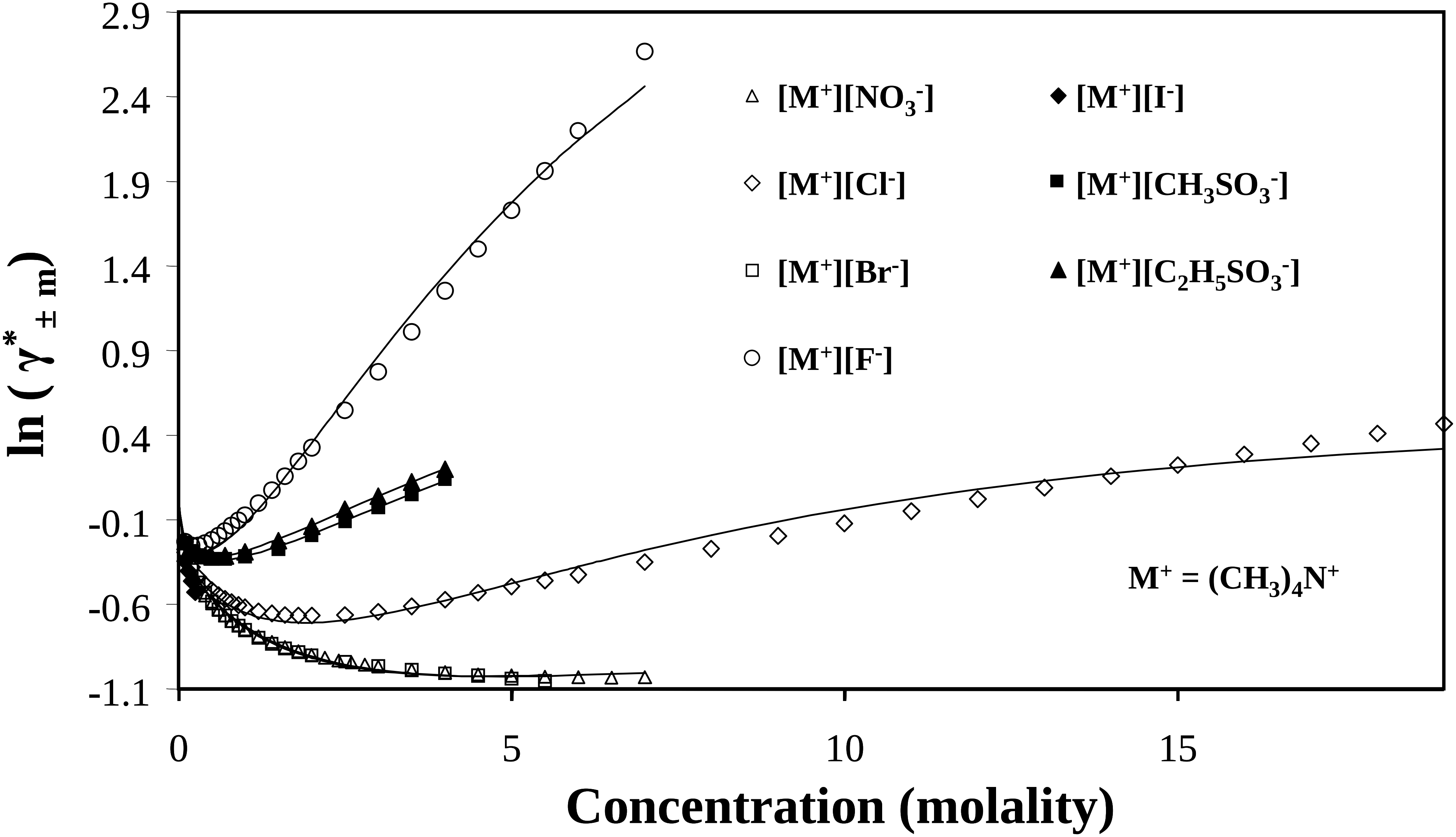

Figure 2: Comparison of experimental and modeled activity coefficients for tetramethylammonium salts in water at 25 ºC.

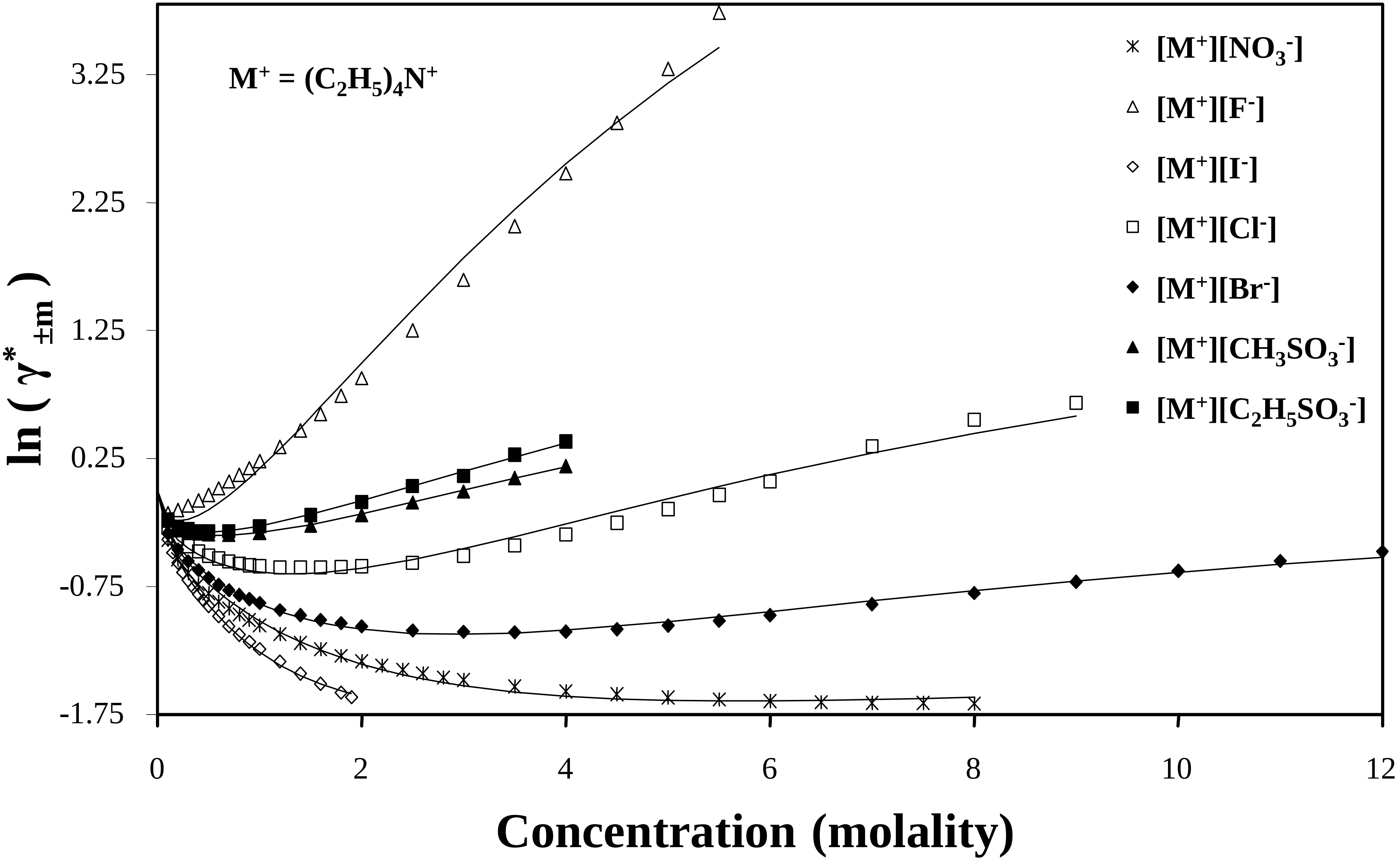

Figure 3: Comparison of experimental and modeled activity coefficients for tetraethylammonium salts in water at 25 °C.

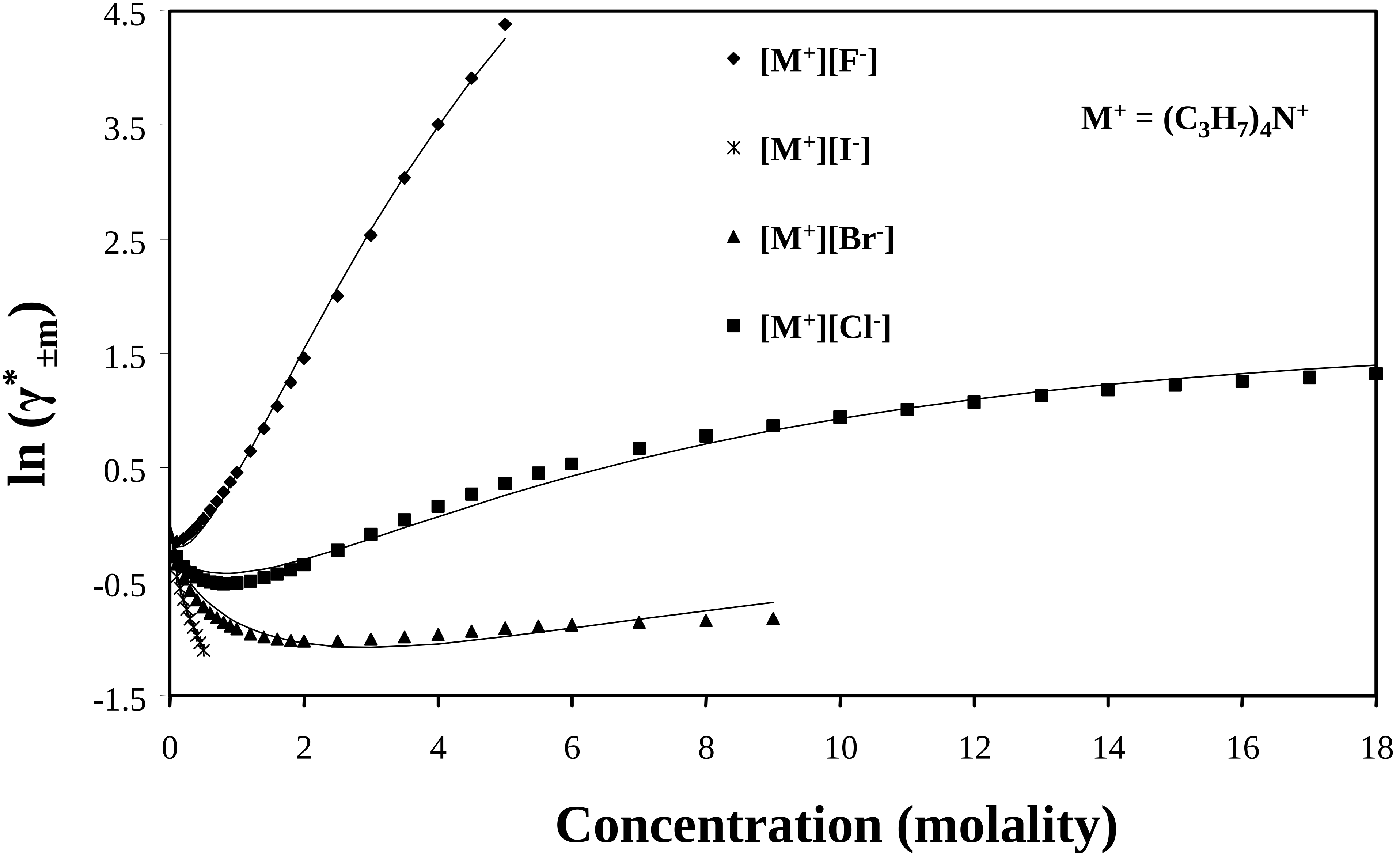

Figure 4: Comparison of experimental and modeled activity coefficients for tetrapropylammonium salts in water at 25 ºC.

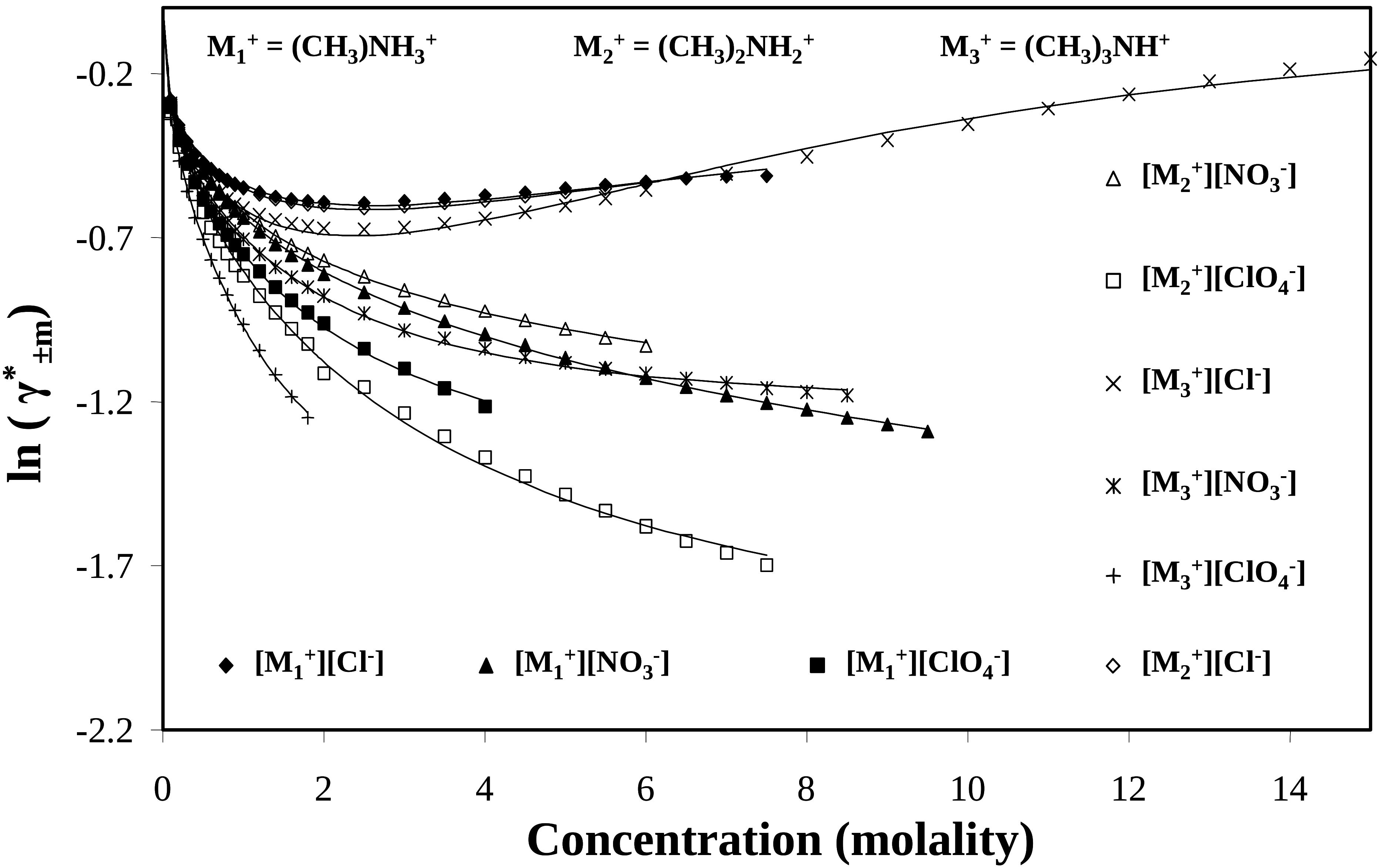

Figure 5: Comparison of experimental and modeled activity coefficients for methylammonium salts in water at 25 ºC.

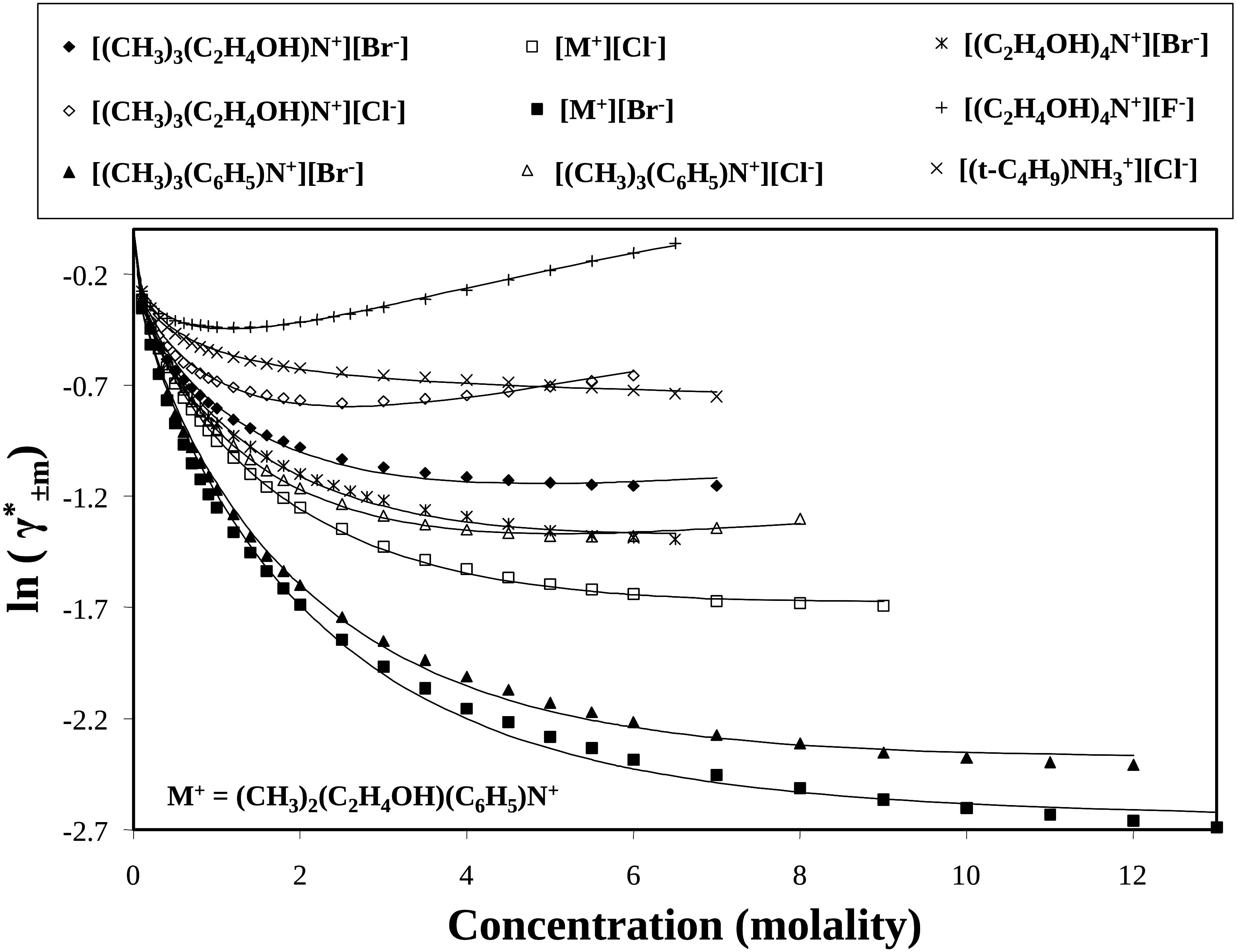

Figure 6: Comparison of experimental and modeled activity coefficients for ammonium salts with ethoxy, tetraethoxy, and benzyl substituents in water at 25 ºC.

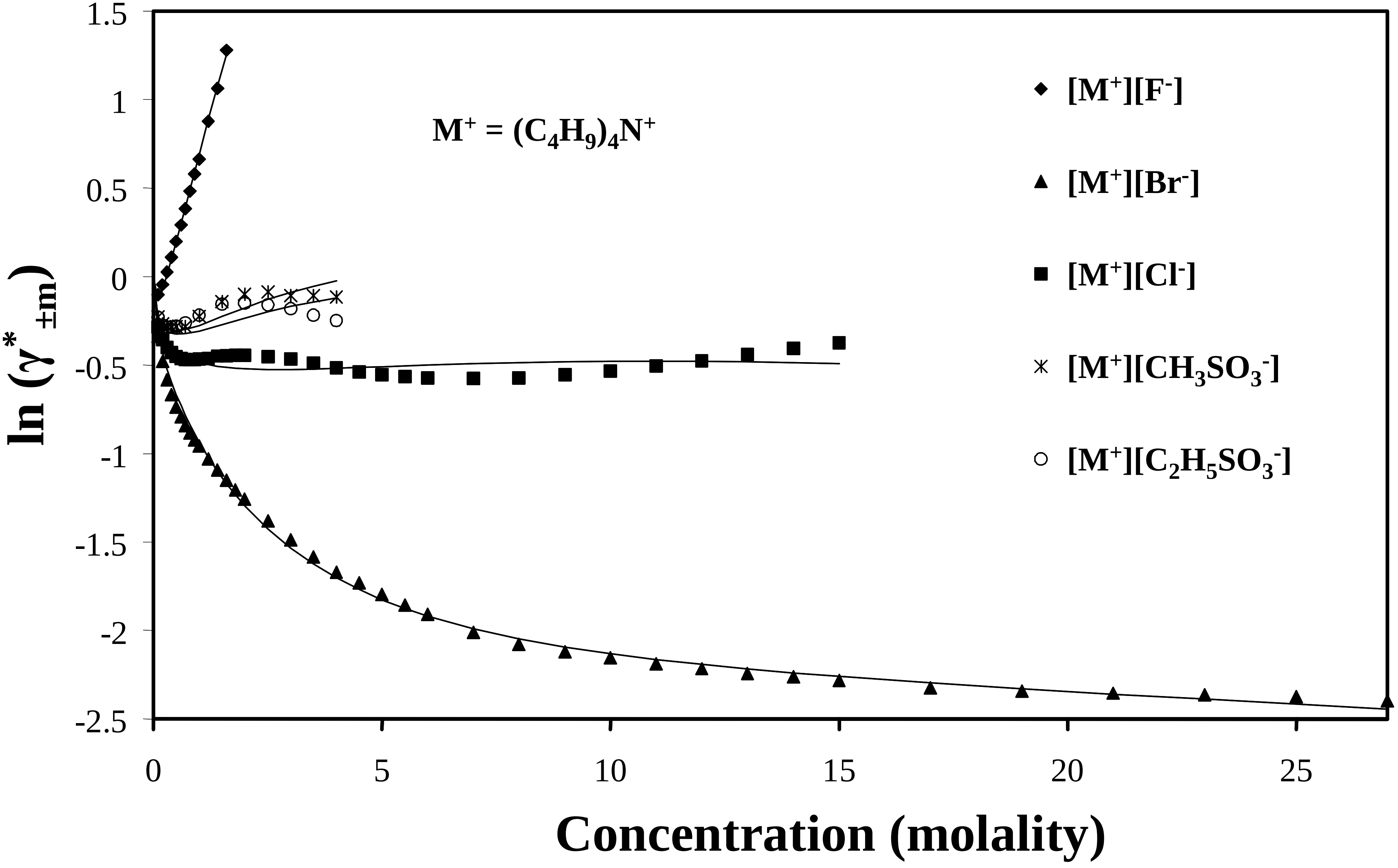

Figure 7: Comparison of experimental and modeled activity coefficients for tetrabutylammonium salts in water at 25 ºC.

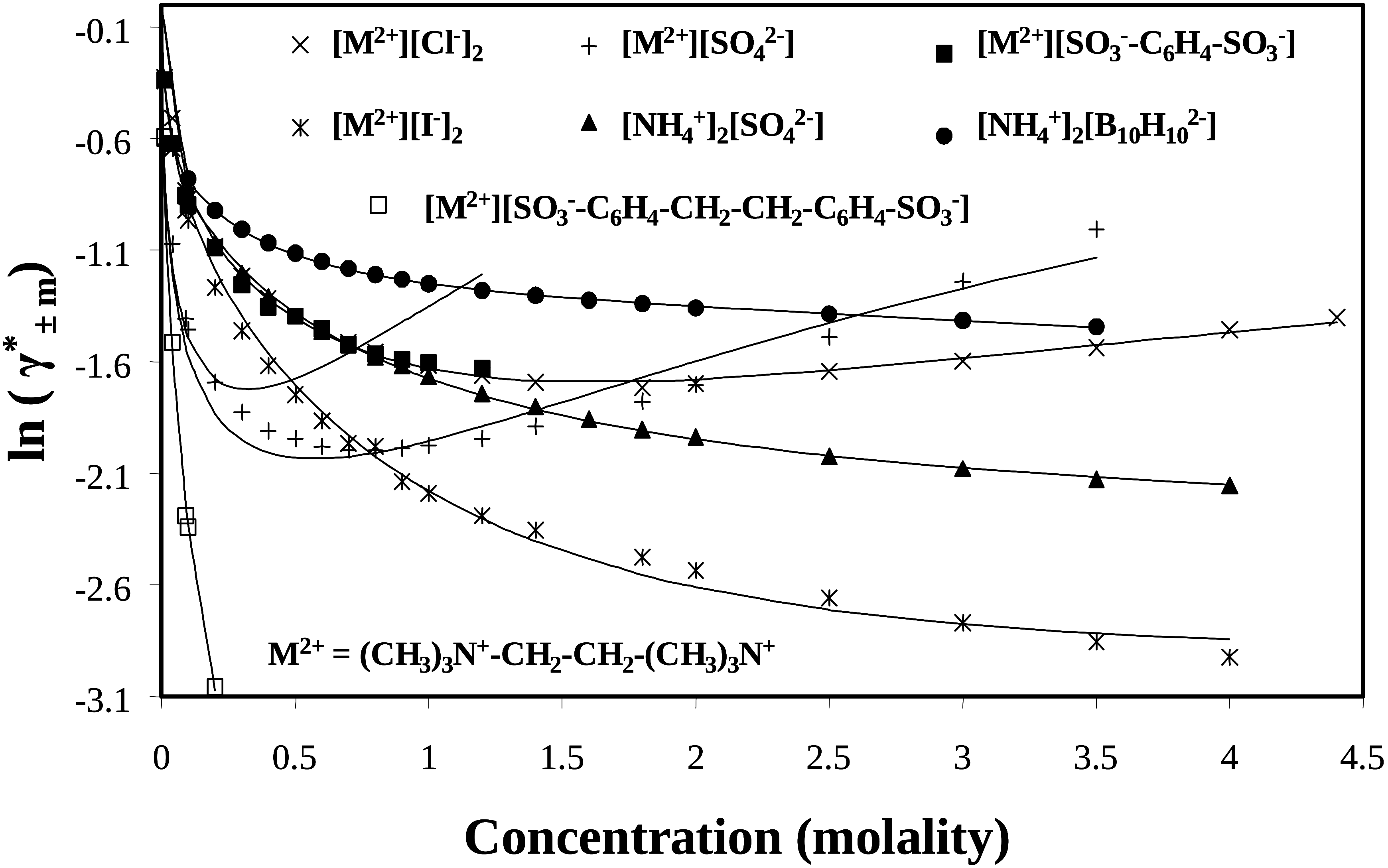

Figure 8: Comparison of experimental and modeled activity coefficients for dimeric and divalent ammonium salts in water at 25 °C.

Table 1: Results for the mean activity coefficients of simple ammonium salts in water at 25 ºC.

	Maximum	Pitzer		NRTL				
Simple salts	**molality**	**σ (lnγ)**	**%AARD (γ)**	$\tau_{ca,m}$	$\tau_{m,ca}$	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[NH_4^+][Cl^-]$	7.4	0.002	0.13	-4.0061	7.8442	0.002	0.12	[65]
$[NH_4^+][NO_3^-]$	26	0.006	0.43	-3.3267	6.9385	0.013	0.94	[65]
$[NH_4^+][ClO_4^-]$	2.1	0.001	0.04	-4.3840	9.1833	0.009	0.70	[65]
$[NH_4^+][HCO_3^-]$	1	0.001	0.06	-4.7595	9.9636	0.005	0.37	[68]
$[NH_4^+][I^-]$	7.5	0.002	0.12	-3.9608	7.6287	0.006	0.54	[59]
$[NH_4^+][Br^-]$	7.5	0.002	0.14	-3.9897	7.7506	0.001	0.10	[67]
$[NH_4^+][SCN^-]$	23	0.001	0.05	-3.7017	7.1891	0.026	2.10	[66]
$[NH_4^+][CH_3SO_3^-]$	4	0.002	0.13	-4.1044	7.9970	0.002	0.13	[52]
$[NH_4^+][C_2H_5SO_3^-]$	4	0.004	0.36	-4.0416	7.5919	0.005	0.40	[52]

Table 2: Compounds for which the globally optimal parameters did not meet physical expectations. All stationary points of the least squares function ϕ in the search interval are listed.

Compound	$\tau_{ca,m}$	$\tau_{m,ca}$	Φ	Status
$[NH_4^+][I^-]$	2.6911	-5.2482	2.359001	Saddle point
	-0.4329	-6.2443	0.016649	Saddle point
	-3.0223	5.2905	0.041553	Saddle point
	-3.9608	7.6287	0.001108	Local minimum
	-1.2616	0.5641	0.000995	Global Minimum
$[NH_4^+][C_2H_5SO_3^-]$	2.6174	-5.1479	1.295283	Saddle point
	-1.0768	-5.9343	0.003248	Saddle point
	-4.0416	7.5919	0.000266	Local minimum
	-3.2847	5.6647	0.002200	Saddle point
	-2.0573	2.1699	0.000258	Global Minimum
$[NH_4^+]_2[B_{10}H_{10}^{2-}]$	2.6284	-5.1805	0.991637	Saddle point
	-0.5518	-6.2355	0.034600	Saddle point
	-4.0994	6.9108	0.000909	Local minimum
	-3.5284	5.6065	0.002231	Saddle point
	-2.7419	3.8018	0.000890	Global Minimum

Table 3: Selected compounds for which there are multiple local minima in the least squares function ϕ. All the stationary points of ϕ in the search are listed.

Compound	$\tau_{ca,m}$	$\tau_{m,ca}$	Φ	Status
$[(t\text{-}C_4H_9)NH_3^+][Cl^-]$	2.6901	-5.2451	0.396560	Saddle point
	0.0670	-2.3462	0.005567	Local minimum
	0.3173	-6.7403	0.006177	Saddle point
	-2.7964	5.1199	0.045622	Saddle point
	-3.9061	7.7280	0.003940	Global Minimum
$[(CH_3)_3(C_2H_4OH)N^+][Cl^-]$	7.1557	-7.7710	0.241480	Local minimum
	2.7422	-5.3013	0.333657	Saddle point
	0.7071	-6.8000	0.226948	Local minimum
	-2.6724	5.0231	0.380336	Saddle point
	-4.5456	9.3783	0.007146	Global Minimum
$[(C_2H_4OH)_4N^+][Br^-]$	4.8930	1.4209	0.537361	Saddle point
	2.6483	-5.1914	3.247395	Saddle point
	-0.4745	2.6983	0.499805	Local minimum
	-0.8304	3.1149	0.499895	Saddle point
	-4.1846	9.0250	0.014529	Global Minimum

Table 4: Results for the mean activity coefficients of tetramethylammonium salts in water at 25 ºC.

	Maximum	Pitzer		NRTL				
Tetramethylammonium salts	**molality**	**σ (lnγ)**	**%AARD (γ)**	**$\tau_{ca,m}$**	**$\tau_{m,ca}$**	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[(CH_3)_4N^+][Cl^-]$	19	0.010	0.80	-4.7370	9.7227	0.053	5.39	[58]
$[(CH_3)_4N^+][Br^-]$	5.5	0.013	1.05	-4.2846	8.9780	0.018	1.45	[58]
$[(CH_3)_4N^+][I^-]$	0.25	0.001	0.03	-5.2654	11.2253	0.010	0.68	[58]
$[(CH_3)_4N^+][F^-]$	7	0.006	0.47	-5.7093	11.1634	0.071	5.38	[55]
$[(CH_3)_4N^+][NO_3^-]$	7	0.004	0.37	-4.2473	8.8870	0.021	1.80	[59]
$[(CH_3)_4N^+][CH_3SO_3^-]$	4	0.006	0.47	-4.7458	9.1036	0.010	0.81	[52]
$[(CH_3)_4N^+][C_2H_5SO_3^-]$	4	0.007	0.58	-4.7435	9.0298	0.007	0.55	[52]

Table 5: Results for the mean activity coefficients of tetraethylammonium salts in water at 25 ºC.

	Maximum	**Pitzer**		**NRTL**				
Tetraethylammonium salts	**molality**	**σ (lnγ)**	**%AARD (γ)**	$\tau_{ca,m}$	$\tau_{m,ca}$	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[(C_2H_5)_4N^+][Cl^-]$	9	0.030	2.05	-5.1011	10.4780	0.058	4.83	[58]
$[(C_2H_5)_4N^+][Br^-]$	12	0.031	2.64	-4.6898	10.0455	0.022	1.91	[58]
$[(C_2H_5)_4N^+][I^-]$	1.9	0.006	0.43	-4.8567	10.9294	0.020	1.69	[58]
$[(C_2H_5)_4N^+][F^-]$	5.5	0.017	1.42	-6.1729	12.0187	0.119	9.64	[55]
$[(C_2H_5)_4N^+][NO_3^-]$	8	0.009	0.75	-4.3083	9.5757	0.047	4.00	[59]
$[(C_2H_5)_4N^+][CH_3SO_3^-]$	4	0.008	0.60	-4.8961	9.4929	0.009	0.72	[52]
$[(C_2H_5)_4N^+][C_2H_5SO_3^-]$	4	0.012	0.82	-5.0163	9.6874	0.015	0.99	[52]

Table 6: Results for the mean activity coefficients of tetrapropylammonium salts in water at 25 ºC.

	Maximum	Pitzer		NRTL				
Tetrapropylammonium salts	**molality**	**σ (lnγ)**	**%AARD (γ)**	**$\tau_{ca,m}$**	**$\tau_{m,ca}$**	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[(C_3H_7)_4N^+][Cl^-]$	18	0.065	5.29	-4.9997	9.8999	0.073	6.53	[58]
$[(C_3H_7)_4N^+][F^-]$	5	0.033	2.84	-6.4365	12.4485	0.063	5.22	[55]
$[(C_3H_7)_4N^+][I^-]$	0.5	0.003	0.25	-5.6715	12.6573	0.009	0.57	[58]
$[(C_3H_7)_4N^+][Br^-]$	9	0.023	1.85	-4.6633	9.9374	0.068	5.99	[58]

Table 7: Results for the mean activity coefficients of methylammonium salts in water at 25 ºC.

		Pitzer		NRTL				
Methylammonium salts	**Maximum molality**	**σ (lnγ)**	**%AARD (γ)**	**$\tau_{ca,m}$**	**$\tau_{m,ca}$**	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[(CH_3)NH_3^+][Cl^-]$	7.5	0.002	0.12	-4.2478	8.4528	0.011	0.94	[60]
$[(CH_3)NH_3^+][ClO_4^-]$	4	0.002	0.16	-3.8946	8.2530	0.011	0.88	[62]
$[(CH_3)NH_3^+][NO_3^-]$	9.5	0.005	0.34	-3.5364	7.2445	0.005	0.37	[61]

		Pitzer		NRTL				
Dimethylammonium salts	**Maximum molality**	**σ (lnγ)**	**%AARD (γ)**	**$\tau_{ca,m}$**	**$\tau_{m,ca}$**	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[(CH_3)_2NH_2^+][Cl^-]$	6.5	0.001	0.11	-4.2895	8.5674	0.008	0.62	[60]
$[(CH_3)_2NH_2^+][ClO_4^-]$	7.5	0.011	0.52	-3.6304	7.9053	0.023	2.00	[62]
$[(CH_3)_2NH_2^+][NO_3^-]$	6	0.004	0.31	-3.7311	7.5915	0.004	0.35	[61]

		Pitzer		NRTL				
Trimethylammonium salts	**Maximum molality**	**σ (lnγ)**	**%AARD (γ)**	**$\tau_{ca,m}$**	**$\tau_{m,ca}$**	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[(CH_3)_3NH^+][Cl^-]$	15	0.004	0.30	-4.4925	9.1405	0.017	1.46	[64]
$[(CH_3)_3NH^+][ClO_4^-]$	1.8	0.001	0.11	-4.3379	9.5431	0.010	0.78	[62]
$[(CH_3)_3NH^+][NO_3^-]$	8.5	0.007	0.61	-3.9542	8.2334	0.011	0.93	[61]

Table 8: Results for the mean activity coefficients of ammonium salts with ethoxy and benzyl substituents in water at 25 ºC.

Ammonium salts with ethoxy and benzyl substituents	**Maximum molality**	**Pitzer**		**NRTL**				
		σ (lnγ)	**%AARD (γ)**	$\tau_{ca,m}$	$\tau_{m,ca}$	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[(CH_3)_3(C_2H_4OH)N^+][Br^-]$	7	0.004	0.33	-4.2909	9.1011	0.027	2.28	[54]
$[(CH_3)_3(C_2H_4OH)N^+][Cl^-]$	6	0.003	0.20	-4.5456	9.3783	0.018	1.57	[54]
$[(CH_3)_2(C_2H_4OH)(C_6H_5)N^+][Br^-]$	13	0.050	4.10	-3.8735	9.2040	0.046	3.98	[54]
$[(CH_3)_2(C_2H_4OH)(C_6H_5)N^+][Cl^-]$	9	0.024	2.07	-4.0962	9.0462	0.013	1.15	[54]
$[(CH_3)_3(C_6H_5)N^+][Br^-]$	12	0.044	3.81	-3.9587	9.2347	0.032	2.86	[54]
$[(CH_3)_3(C_6H_5)N^+][Cl^-]$	8	0.018	1.57	-4.3242	9.3819	0.009	0.62	[54]
$[(C_2H_4OH)_4N^+][Br^-]$	6.5	0.009	0.69	-4.1846	9.0250	0.024	2.10	[57]
$[(C_2H_4OH)_4N^+][F^-]$	6.5	0.006	0.37	-4.5171	8.8387	0.008	0.58	[57]
$[(t\text{-}C_4H_9)NH_3^+][Cl^-]$	7	0.001	0.08	-3.9061	7.7280	0.013	1.14	[53]

Table 9: Results for the mean activity coefficients of tetrabutylammonium salts in water at 25 ºC.

	Maximum	Pitzer		NRTL				
Tetrabutylammonium salts	**molality**	**σ (lnγ)**	**%AARD (γ)**	$\tau_{ca,m}$	$\tau_{m,ca}$	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[(C_4H_9)_4N^+][Br^-]$	27	0.056	4.84	-3.6717	8.3169	0.038	3.29	[58]
$[(C_4H_9)_4N^+][Cl^-]$	15	0.047	4.03	-4.0247	7.8229	0.056	4.57	[58]
$[(C_4H_9)_4N^+][F^-]$	1.6	0.006	0.49	-5.8619	10.4185	0.019	1.40	[55]
$[(C_4H_9)_4N^+][CH_3SO_3^-]$	4	0.016	1.08	-3.5331	5.8863	0.053	3.91	[52]
$[(C_4H_9)_4N^+][C_2H_5SO_3^-]$	4	0.016	1.24	-3.4531	5.8168	0.075	5.59	[52]

Table 10: Results for the mean activity coefficients of dimeric and divalent ammonium salts in water at 25 ºC.

Dimeric and divalent salts	**Maximum**	**Pitzer**		**NRTL**				
$M^{2+} = (CH_3)_3N^+\text{-}CH_2\text{-}CH_2\text{-}(CH_3)_3N^+$	**molality**	**σ (lnγ)**	**%AARD (γ)**	**$\tau_{ca,m}$**	**$\tau_{m,ca}$**	**σ (lnγ)**	**%AARD (γ)**	**Ref.**
$[M^{2+}][Cl^-]_2$	4.4	0.086	5.34	-5.2974	9.9984	0.026	1.81	[63]
$[M^{2+}][I^-]_2$	4	0.127	8.45	-4.8585	9.7021	0.054	4.55	[63]
$[M^{2+}][SO_4^{2-}]$	3.5	0.029	2.13	-6.7370	10.2714	0.096	7.82	[63]
$[M^{2+}][SO_3^-\text{-}C_6H_4\text{-}SO_3^-]$	1.2	0.100	6.21	-6.3895	8.7924	0.434	30.53	[63]
$[M^{2+}][SO_3^-\text{-}C_6H_4\text{-}CH_2\text{-}CH_2\text{-}C_6H_4\text{-}SO_3^-]$	0.2	0.098	6.03	-9.2143	16.7305	0.142	6.72	[63]
$[NH_4^+]_2[SO_4^{2-}]$	4	0.024	1.43	-4.6019	8.6232	0.017	1.17	[70]
$[NH_4^+]_2[B_{10}H_{10}^{2-}]$	3.5	0.2159	10.6829	-4.0994	6.9108	0.008	0.48	[56]