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# Anion-Specific Effects on Activity Coefficients in Aqueous Solutions of Sodium Salts: Modeling with the Extended Debye–Hückel Theory

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**Abstract**

The extended Debye–Hückel theory, which allows for concentration variation of electrolyte solution static permittivity, is employed to predict activity coefficients in aqueous solutions of sodium salts with various univalent anions (NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$ and NaSCN) at ambient conditions. Calculations without empirical adjustments reproduced the activity coefficients for NaI in the concentration range up to 6 mol·kg$^{-1}$ and for NaSCN up to 2 mol·kg$^{-1}$. In the case of other solutions, calculations underestimate water activity coefficients and overestimate mean ionic activity coefficients at concentrations beyond 0.5 mol·kg$^{-1}$. In order to improve the representations, the model was extended to include ion pairing, which resulted in a better agreement between calculated activity coefficients and experimental data, especially for $NaNO_3$. The ion pairing equilibrium constants were estimated and compared with available literature values. The extent of ion pairing was found to increase in the sequence NaI < NaSCN < NaBr < NaCl < $NaClO_4$ < $NaNO_3$, with violation of the Collins rule in the case of polyatomic oxygen-containing anions.

**Keywords** Modeling · Ion pair · Electrolyte solution · Permittivity · Solvation · Debye–Hückel theory

## 1 Introduction

Many statistical mechanical theories have been developed to describe thermodynamic properties of electrolyte solutions [1–5]. Depending on the particular definition of species considered explicitly in the theories, they can be classified as belonging to Schrödinger (nuclei and electrons), Born–Oppenheimer (ions and solvent molecules) and

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McMillan–Mayer (ions in continuous dielectric) levels [6]. The main theoretical techniques are the Poisson–Boltzmann equation, perturbation expansion, Ornstein–Zernicke equation, concentration fluctuation formalism and computer simulation methods: Monte Carlo and Molecular Dynamics [5]. There are also numerous empirical engineering models which are based on more or less heuristic combination of a long-range ionic interaction contribution with the terms describing more specific short-range ion–ion, ion–solvent and solvent–solvent interactions [7–9].

However, the application of all these models to moderately concentrated solutions is generally connected with empirical parameterization, providing, in fact, a correlation rather than a real prediction. This situation can be attributed to the difficulties associated with both the solution of statistical mechanical problems and allowance for details of the interaction potential among particles.

Therefore, the ion-specific effects in various areas of chemistry still present many unresolved anomalies and unanswered conundrums [10, 11]. In the field of solution thermodynamics, understanding of the order of activity coefficients in series of salts with different cations or anions [11, 12] has evolved not very far from empirical laws such as "like seeks like" [13] or "water matching affinity" rule [14] despite the continuing progress in statistical mechanical theory [15–18] and computer simulation methods [19–22].

The extended Debye–Hückel (EDH) theory [23] which incorporates the concentration dependence of electrolyte solution static permittivity has demonstrated an ability to predict the correct ordering of activity coefficients in the series of aqueous solutions of alkali chlorides [23] and iodides [24] without empirical adjustments. In some instances, surprisingly good predictions were obtained for concentrated solutions ranging up to 5–7 mol·kg$^{-1}$ (LiCl, NaI). This promising result can be used as a basis to unveil the ion-specific effects in activity coefficients.

In the case of aqueous solutions of alkali metal chlorides and iodides the deviations can be interpreted as resulting from the insufficient allowance for ion–ion attraction and, hence, better agreement with experiment can be achieved by taking into account an ion pairing equilibrium [24]. In the previous work [24] we put forward a hypothesis that good predictions without parameter fitting correspond to a minimal level of ion pairing and provided some arguments to support this idea based upon the results obtained in the conductivity and diffraction studies. In the present article, we focus on activity coefficients in aqueous solutions of sodium salts with various univalent anions (NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$ and NaSCN) at ambient conditions to test the validity of this hypothesis and gain insight into the anion-specific effects in solution thermodynamics.

## 2 Extended Debye–Hückel Theory

The EDH theory [23] is based on the linearized Poisson–Boltzmann equation as was the original Debye–Hückel theory [25] but takes into account the fact that the static solution permittivity is different from that of the pure solvent and varies with electrolyte concentration, which is well established by the dielectric relaxation spectroscopy [26, 27]. The concentration dependence of the relative permittivity $\varepsilon$ is represented in the theory by means of a function $f(\kappa_0)$:

$$\varepsilon = \varepsilon(c) = \varepsilon(\kappa_0) = \varepsilon_0 f(\kappa_0), \tag{1}$$

where $\varepsilon_0$ is the permittivity of pure solvent and $\kappa_0$ is the conventional inverse Debye screening length:

$$\kappa_0^2 = \frac{4\pi e_0^2}{\varepsilon_0 kTV} \sum_i N_i z_i^2. \tag{2}$$

In Eq. 2 $e_0$ is the elementary charge, $k$ is the Boltzmann constant, $T$ is the temperature, $V$ is the volume of solution, $N_i$ is the number of ions of $i$th type and $z_i$ is the valency.

The rational water activity coefficient and mean ionic activity coefficient for a solution of completely dissociated single electrolyte $\mathrm{M}_{\nu_+}^{z_+}\mathrm{X}_{\nu_-}^{z_-}$ are composed of two terms comprising contributions from ion–ion (subscript 1) and ion–water (subscript 2) interactions:

$$\ln \gamma_w = \ln \gamma_{w,1} + \ln \gamma_{w,2}, \tag{3}$$

$$\ln \gamma_\pm = \ln \gamma_{\pm,1} + \ln \gamma_{\pm,2}. \tag{4}$$

The second term corresponding to the interactions of ions with the medium will be also referred to as the solvation term.

The terms for the water activity coefficient in Eq. 3 are given by the formulae

$$\ln \gamma_{w,1} = \frac{\overline{V}_w \kappa_0^3 \sigma_1(\kappa_0, a)}{24\pi N_\mathrm{A}}, \tag{5}$$

$$\ln \gamma_{\mathrm{w},2} = -\frac{\overline{V}_\mathrm{w}\ \kappa_0^2\ \sigma_2(\kappa_0)}{16\pi\ N_\mathrm{A}\ R_\pm}. \tag{6}$$

In Eqs. 5 and 6 $\overline{V}_\mathrm{w}$ is the partial molar volume of water, $N_\mathrm{A}$ is Avogadro's number, $a$ is the distance of closest approach of ions and $R_\pm$ is the mean ionic radius. The functions $\sigma_1(\kappa_0, a)$ and $\sigma_2(\kappa_0)$ are defined by

$$\sigma_1(\kappa_0, a) = 3\int_0^1 \frac{f(\kappa_0\lambda)^{\frac{3}{2}} - \frac{3}{2}\sqrt{f(\kappa_0\lambda)}f'(\kappa_0\lambda)\ \kappa_0\lambda - af'(\kappa_0\lambda)\ \kappa_0^2\lambda^2}{f(\kappa_0\lambda)^2\left(\sqrt{f(\kappa_0\lambda)} + \kappa_0 a\lambda\right)^2}\lambda^2\ d\lambda, \tag{7}$$

$$\sigma_2(\kappa_0) = -2\kappa_0 \int_0^1 \frac{f'(\kappa_0\lambda)\ \lambda^2\ d\lambda}{f(\kappa_0\lambda)^2}\ , \tag{8}$$

where $f'(x)$ is the derivative of $f(x)$.

The contributions to the mean ionic activity coefficient $\gamma_\pm$ are as follows:

$$\ln \gamma_{\pm,1} = -\frac{\left|z_+z_-\right|e_0^2\kappa_0\ \chi_1(\kappa_0, a)}{3kT\varepsilon_0} + \frac{\overline{V}_\pm\ \kappa_0^3\ \sigma_1(\kappa_0, a)}{24\pi\ N_\mathrm{A}}, \tag{9}$$

$$\ln \gamma_{\pm,2} = \frac{\left|z_+z_-\right|e_0^2}{2R_\pm kT}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_0}\right) - \frac{\overline{V}_\pm\ \kappa_0^2\sigma_2(\kappa_0)}{16\pi\ N_\mathrm{A}\ R_\pm}. \tag{10}$$

In Eqs. 9 and 10 $\overline{V}_{\pm}$ is the mean ionic partial molar volume and the function $\chi_1(\kappa_0, a)$ is defined by

$$\chi_1(\kappa_0, a) = 3\int_0^1 \frac{\lambda^2}{f(\kappa_0\lambda)\left(\sqrt{f(\kappa_0\lambda)} + \kappa_0 a\lambda\right)}\,d\lambda + \frac{\sigma_1(\kappa_0, a)}{2}. \tag{11}$$

The rational mean ionic activity coefficients $\gamma_{\pm}^{(x)}$ given by Eqs. 4, 9 and 10 are converted to the molal scale (in which experimental data are regularly presented) using a textbook equation [2]

$$\gamma_{\pm}^{(m)} = \frac{\gamma_{\pm}^{(x)}}{1 + \nu\, m_{\mathrm{s}} M_w}, \tag{12}$$

where $m_{\mathrm{s}}$ is the molality of salt, $M_{\mathrm{w}}$ is the molar mass of water and $\nu = \nu_+ + \nu_-$. The superscript $(m)$ will be omitted henceforth.

## 3 Data Handling

The experimental activity coefficients in the aqueous solutions of the sodium salts at 298 K were taken from [28], except for $NaNO_3$ for which an updated data set was adopted [29]. They are plotted in Fig. 1 (see also Fig. 1S in the Supplementary material). The densities of solutions needed for interconversion among different concentration scales are based on Ref. [30].

The experimental static permittivities of the solutions were taken from the works [31–39]. Where possible, data from different sources for the same solution were considered and compared. The data were fitted to the polynomial form

$$\varepsilon = \varepsilon_0 + a_\varepsilon c_{\mathrm{s}} + b_\varepsilon c_{\mathrm{s}}^{3/2}, \tag{13}$$

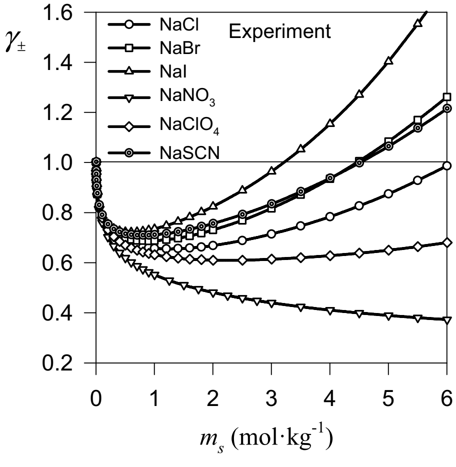


**Fig. 1** Experimental [28, 29] mean ionic activity coefficients in aqueous solutions of sodium salts at 298 K versus molality of salt $m_{\mathrm{s}}$

**Table 1** Concentration dependence of the static permittivity $\varepsilon$ of electrolyte solutions, $\varepsilon_0 = 78.36$ [40], $c_s$ is molar concentration of salt (mol·L$^{-1}$), $c_{s,\max}$ and $m_{s,\max}$ are maximum molar concentration and molality of salt in the experimental data for $\varepsilon$, $\Delta\nu$ (GHz) is the frequency range used in the dielectric spectroscopy experiment, model means equation used to fit the complex permittivity: CC (Cole–Cole) and D (Debye)

| Salt | Data set | $\varepsilon(c_s)$ | $c_{s,\max}$ | $m_{s,\max}$ | $\Delta\nu$, model | Refs. |
|---|---|---|---|---|---|---|
| NaCl | 1 | $\varepsilon = \varepsilon_0 - 15.7c_s + 3.80c_s^{3/2}$ | 4.5 | 5.0 | 0.2–20, CC | [32] |
| NaCl | 2 | $\varepsilon = \varepsilon_0 - 18.1c_s + 4.08c_s^{3/2}$ | 5.0 | 5.6 | 7–25, CC | [33] |
| NaCl | 3 | $\varepsilon = \varepsilon_0 - 16.3c_s + 3.22c_s^{3/2}$ | 4.0 | 4.4 | 2.4–12, D | [31, 34] |
| NaCl | 4 | $\varepsilon = \varepsilon_0 - 12.2c_s + 1.22c_s^{3/2}$ | 2.1 | 2.2 | 0.2–89, D+CC | [35] |
| NaBr | 1 | $\varepsilon = \varepsilon_0 - 13.2c_s + 1.54c_s^{3/2}$ | 1.4 | 1.5 | 0.2–89, CC | [36] |
| NaI | 1 | $\varepsilon = \varepsilon_0 - 14.7c_s + 2.43c_s^{3/2}$ | 1.5 | 1.6 | 0.2–89, CC | [36] |
| NaI | 2 | $\varepsilon = \varepsilon_0 - 16.7c_s + 3.57c_s^{3/2}$ | 5.5 | 7.0 | 7.5–25, CC | [37] |
| $NaNO_3$ | 1 | $\varepsilon = \varepsilon_0 - 12.2c_s + 2.57c_s^{3/2}$ | 1.5 | 1.6 | 0.2–89, CC | [36] |
| $NaNO_3$ | 2 | $\varepsilon = \varepsilon_0 - 10.6c_s + 1.78c_s^{3/2}$ | 7.4 | 10 | 7–25, CC | [38] |
| $NaNO_3$ | 3 | $\varepsilon = \varepsilon_0 - 16.4c_s + 3.99c_s^{3/2}$ | 4.0 | 4.6 | 2.4–12, D | [31, 34] |
| $NaClO_4$ | 1 | $\varepsilon = \varepsilon_0 - 13.7c_s + 2.29c_s^{3/2}$ | 1.5 | 1.6 | 0.2–89, CC | [36] |
| $NaClO_4$ | 2 | $\varepsilon = \varepsilon_0 - 18.3c_s + 4.30c_s^{3/2}$ | 5 | 6.6 | 1.6–38.5, D | [39] |
| NaSCN | 1 | $\varepsilon = \varepsilon_0 - 14.0c_s + 2.25c_s^{3/2}$ | 1.7 | 1.8 | 0.2–89, CC | [36] |

**Table 2** Ionic radii: Pauling radii ($R_P$) [41], Marcus radii ($R_M$) [42] and hydration Gibbs energies $\Delta_s G^o$ [42]

| Ion | $R_P$ (Å) | $R_M$ (Å) | $-\Delta_s G^o$ (kJ·mol$^{-1}$) |
|---|---|---|---|
| $Na^+$ | 0.95 | 1.02 | 383 |
| $Cl^-$ | 1.81 | 1.81 | 344 |
| $Br^-$ | 1.95 | 1.96 | 318 |
| $I^-$ | 2.16 | 2.20 | 280 |
| $NO_3^-$ | | 2.00 | 286 |
| $ClO_4^-$ | | 2.40 | 229 |
| $SCN^-$ | | 2.13 | 291 |

where $c_s$ is the molar concentration of salt and $\varepsilon_0 = 78.36$ [40]. Other parameters of Eq. 13 are presented in Table 1. The experimental permittivities of the solutions and those approximated and extrapolated using Eq. 13 are displayed in Figs. S2–S4.

The Pauling crystal radii [41] were used for monoatomic ions to calculate the ion size parameters $a$ and $R_\pm$; for polyatomic ions the Marcus radii were adopted [42] (Table 2). The distance of closest approach is defined as the sum of radii of cation and anion:

$$a = R_+ + R_- \tag{14}$$

and the mean ionic radius was estimated as the arithmetic mean:

$$R_\pm = \frac{R_+ + R_-}{2}. \tag{15}$$

## 4 Results and Discussion

The water activity coefficients and mean ionic activity coefficients in aqueous solutions of NaCl, NaBr, NaI, $NaClO_4$, $NaNO_3$ and NaSCN were calculated using Eqs. 3–12 with different data sets for permittivity (Table 1). The results for the mean ionic activity coefficients are displayed by solid lines in Figs. 2, 3, 4, 5, 6 and 7 in comparison with the experimental data [28, 29]. The corresponding plots for water activity coefficients are shown in Figs. S5–S10.

The nonmonotonic concentration dependence of water activity coefficient and mean ionic activity coefficient is qualitatively reproduced for solutions of NaCl, NaBr, NaI, $NaClO_4$ and NaSCN as a result of competition between effects of ion–ion and ion–water interactions. Calculations without parameter fitting reproduced the activity coefficients for NaI in the concentration range up to 6 $mol{\cdot}kg^{-1}$ and for NaSCN up to 2 $mol{\cdot}kg^{-1}$. In case of other solutions calculations underestimated water activity coefficient (accordingly, overestimated mean ionic activity coefficient) in the concentration range beyond 0.5 $mol{\cdot}kg^{-1}$. The difference between permittivities from different sources (Table 1) has a fairly small quantitative effect on the calculated activity coefficients.

The observed deviations from experimental data for solutions of NaCl, NaBr, $NaClO_4$ and $NaNO_3$ can be explained either by excessive solvation contribution due to the application of crystal radii or insufficient ion–ion attraction. The first point of view was put forward by Valiskó and Boda [43] who advocated the application of the so-called Born radii to compute the solvation contribution along with crystal radii for ion–ion interactions. In this case, the solvation contribution would be consistent with the experimental ionic hydration Gibbs energies, at least in the limit of low concentrations. In our previous work [24], we investigated this suggestion and showed that in general case it fails to successfully predict experimental data for all alkali metal iodide solutions.

Therefore, in the present study, we follow the second option and modify the EDH model by taking ion association explicitly into account through the known equation [44]

$$\gamma_{\pm} = \alpha\gamma'_{\pm}, \tag{16}$$

where $\gamma_{\pm}$ is the molal mean ionic activity coefficient, $\gamma'_{\pm}$ is that of the "free" ions and α is the dissociation degree of the electrolyte. This is a phenomenological way to go beyond

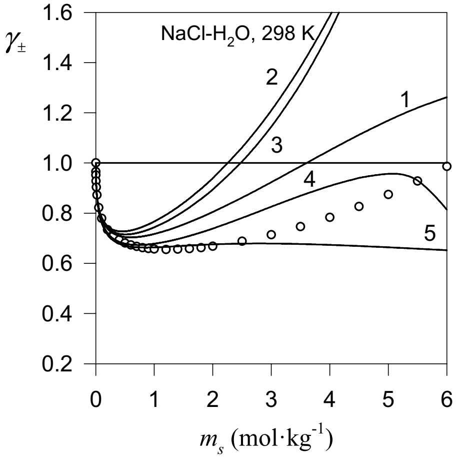


**Fig. 2** Mean ionic activity coefficient in aqueous solutions of sodium chloride at 298 K. Solid lines 1, 2, 3 and 4 are calculated using the extended Debye–Hückel theory with different data sets numbered according to Table 1, solid line 5 is calculated with data set 1 and $K_A^o = 0.16$ $L{\cdot}mol^{-1}$, open circles are experimental data [28]

the limitations of the linearized Poisson–Boltzmann equation in treating short-range electrostatic interactions. A usual way to evaluate the dissociation degree α as a function of concentration is to apply the mass action law (MAL) in the form [45]

$$K_A^o = \frac{(1-\alpha)\gamma_{IP}}{\alpha^2 {\gamma'}_{\pm}^2 c_s} = \frac{\gamma_{IP}}{{\gamma'}_{\pm}^2} K_A, \tag{17}$$

where $K_A^o$ is the thermodynamic association equilibrium constant, $K_A$ is the concentration association equilibrium constant and $\gamma_{IP}$ is the activity coefficient of ion pair, often set equal to unity because of certain difficulties with its evaluation. Various approaches to calculating $\gamma_{IP}$ have been recently reviewed [46]. For instance, two different expressions for $\gamma_{IP}$ were proposed in the framework of the Mean Spherical Approximation combined with the MAL [47, 48]. The limiting law for the activity coefficient of ion pair in different models is a linear dependence $\ln \gamma_{IP} \sim c_s$.

In our case, new theoretical expressions for $\gamma_{IP}$ with account of variable solution permittivity would be desirable for consistency with the EDH theory. However, the situation is complicated by the fact that different types of ion pairs considered as fragments of the solution structure may be responsible for the deviations from the EDH theory predictions: contact ion pairs (CIP), solvent shared ion pairs (SIP) and solvent separated ion pairs (2SIP) [45]. This requires the application of the three MAL equations for the equilibria:

$$\mathrm{M^+ + X^- \rightleftharpoons 2SIP \rightleftharpoons SIP \rightleftharpoons CIP}$$

with three equilibrium constants and the corresponding activity coefficients $\gamma_{2SIP}$, $\gamma_{SIP}$ and $\gamma_{CIP}$, all different functions of concentration due to unequal dipole moments of the ion pairs. Even such a detailed description would not resolve all problems, because the contributions of different ion pairs to the thermodynamic properties of solution may not be equal. A preliminary insight into this point can be drawn from a comparison of the cation–anion correlation function $g_{+-}(r)$, where $r$ is the distance between ions, inherent to the Debye–Hückel theory [25, 49]:

$$g_{+-}(r) = 1 - \frac{z_+ z_- e_0^2}{kT\varepsilon} \frac{e^{\kappa a}}{1+\kappa a} \frac{e^{-\kappa r}}{r}, \tag{18}$$

with the one obtained from computer simulation [50]. From the plots displayed in Fig. 8 we can deduce that CIPs give the main contribution to the mean ionic activity coefficient with the role of 2SIPs being negligible.

Considering all these difficulties, we have chosen to apply the single MAL Eq. 17 setting $\gamma_{IP}$ to one, as a first approximation. In this case, the association equilibrium constant $K_A^o$ refers to an averaged type of ion pair and the whole description is inevitably phenomenological.

The expression for the mean ionic activity coefficient of free ions $\gamma'_{\pm}$

$$\ln \gamma'_{\pm} = g(m'_s), \tag{19}$$

where $m'_s$ is the molality of dissociated salt, was obtained by fitting the activity coefficients $\gamma_{\pm}$ calculated as described above to the equation

$$\ln \gamma_{\pm} = g(m_s) = -a_0\sqrt{m_s} + b_1 m_s + b_2 m_s^{3/2} + b_3 m_s^2, \tag{20}$$

where $a_0 = 1.1766\ (\mathrm{kg{\cdot}mol^{-1}})^{1/2}$.

**Fig. 3** Mean ionic activity coefficient in aqueous solutions of sodium bromide at 298 K. Solid line 1 is calculated using the extended Debye–Hückel theory, solid line 2 is calculated with $K_A^o = 0.06\ \text{L}\cdot\text{mol}^{-1}$, open circles are experimental data [28]

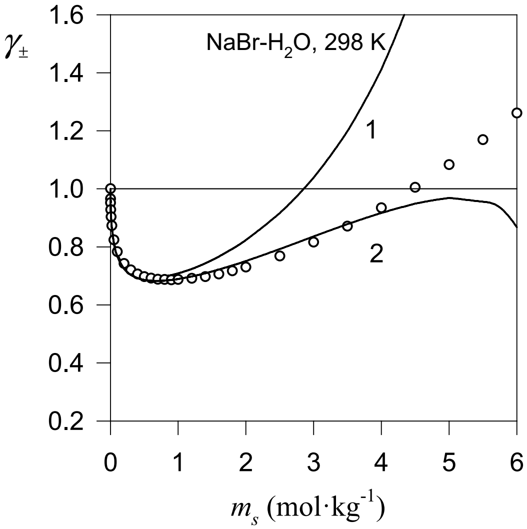
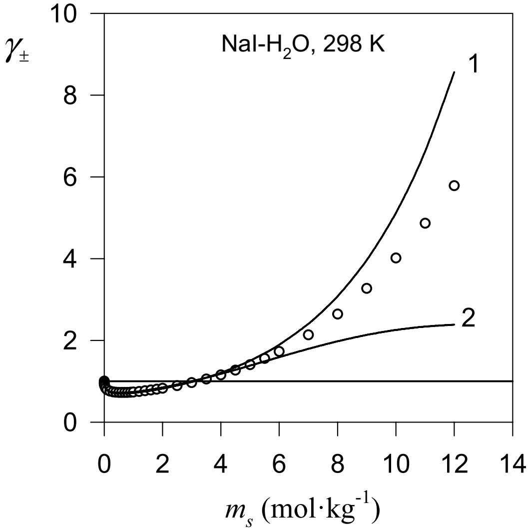


**Fig. 4** Mean ionic activity coefficient in aqueous solutions of sodium iodide at 298 K. Solid lines are calculated using the extended Debye–Hückel theory with different data sets numbered according to Table 1, open circles are experimental data [28]



Then dissociation degree α is iteratively calculated using Eq. 17 together with $\gamma'_{\pm} = \exp(g(\alpha\ m_s))$. The final mean ionic activity coefficient $\gamma_{\pm} = \alpha\gamma'_{\pm}$ was fitted to Eq. 20 and the water activity coefficient was computed according to the Gibbs–Duhem equation.

The association constants $K_A^o$ were fitted to the experimental data in the concentration range up to 2 mol·kg$^{-1}$ for solutions of NaCl, NaBr, $NaNO_3$ and $NaClO_4$. The calculated mean ionic activity coefficients are displayed by lines labeled with the greatest number for each system in Figs. 2, 3, 5 and 6. The corresponding results for water activity coefficients are shown in the same manner in Figs. S5, S6, S8 and S9. Satisfactory agreement with the experiment was achieved in the concentration range up to 2–3 mol·kg$^{-1}$

**Fig. 5** Mean ionic activity coefficient in aqueous solutions of sodium nitrate at 298 K. Solid lines 1, 2 and 3 are calculated using the extended Debye–Hückel theory with different data sets numbered according to Table 1, solid line 4 is calculated with data set 1 and $K_A^o = 0.7$ L·mol$^{-1}$, open circles are experimental data [29]

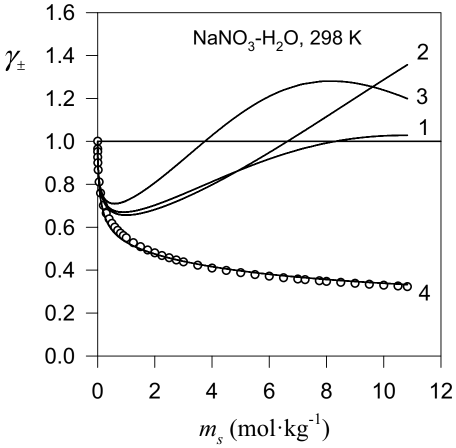


**Fig. 6** Mean ionic activity coefficient in aqueous solutions of sodium perchlorate at 298 K. Solid lines 1 and 2 are calculated using the extended Debye–Hückel theory with different data sets numbered according to Table 1, solid line 3 is calculated with data set 1 and $K_A^o = 0.25$ L·mol$^{-1}$, open circles are experimental data [28]

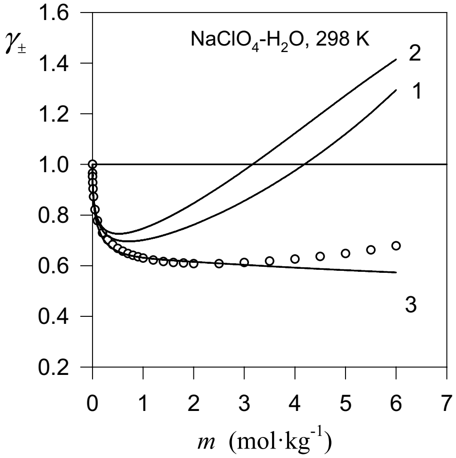
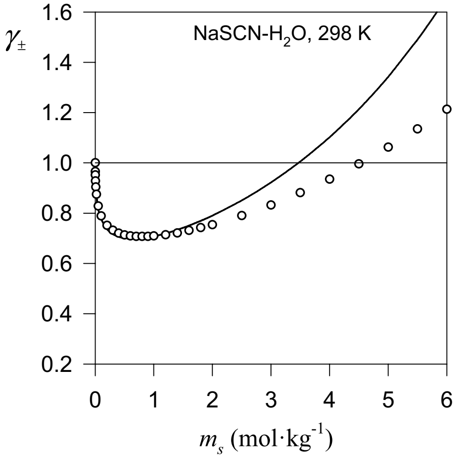


**Fig. 7** Mean ionic activity coefficient in aqueous solutions of sodium thiocyanate at 298 K. Solid line is calculated using the extended Debye–Hückel theory, open circles are experimental data [28]



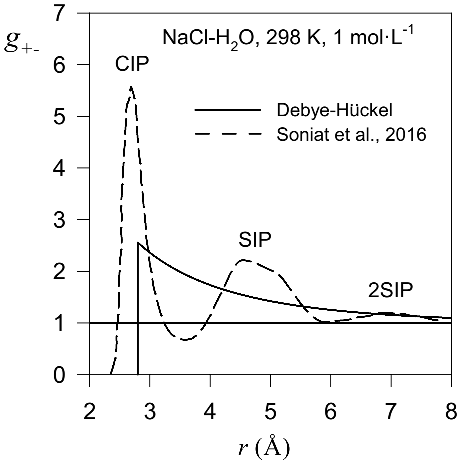


**Fig. 8** Cation–anion correlation function in aqueous solution of sodium chloride from the Debye–Hückel theory (solid line) and computer simulation [50] (dashed line), *r* is the distance between ions. The peaks of the correlation function correspond to different types of ion pairs: CIP, SIP and 2SIP

in the case of NaCl and in a broader concentration range for other salts with the best description for $NaNO_3$. The deviations at higher concentrations can be attributed to the simplified treatment of ion pairing with only one MAL equation, ignoring the variation of activity coefficient of ion pairs, neglect of higher ionic aggregates and also to extrapolation of the experimental permittivity (Table 1).

The estimated association constants $K_A^o$ are compared with literature values obtained in the dielectric relaxation studies [35, 36] and derived from the conductivity measurements [51–56] (Table 3). Although we use the same notation $K_A^o$ for the ion pairing association constants obtained in the present work and those reported in the literature, their physical meanings may not be exactly the same. The conductivity studies of ion pairing can hardly discriminate among CIP, SIP and 2SIP. Furthermore, the absolute values of association constants depend strongly on the applied conductivity equation, the choice of the distance parameter and the quality of experimental data, which can be seen from the scatter of the values for NaCl (Table 3). The association constant reported

**Table 3** Association constants $K_A^o$ (L·mol$^{-1}$) for sodium salts at 298 K

| Salt | This work | [35] | [36] | [51] | [52] | Other Refs. |
|---|---|---|---|---|---|---|
| NaCl | 0.15 | 2.1 ± 0.3 | | 0.82 | 1.58 ± 0.07 | 2.38[a] |
| NaBr | 0.06 | | 1.4 ± 1.2 | 0.73 | | |
| NaI | – | | 0.7 ± 1.1 | 0.60 | 0.34 ± 0.15 | |
| $NaNO_3$ | 0.70 | | 1.0 ± 1.2 | | | 0.26[b], 0.21[c] |
| $NaClO_4$ | 0.25 | | 0.9 ± 1.1 | | | 0.2 ± 0.14[d] |
| NaSCN | – | | 0.7 ± 1.0 | | | |

[a] Reference [53]

[b] Reference [54]

[c] Reference [55]

[d] Reference [56]

for NaCl in the dielectric relaxation study [35] is attributed to 2SIPs, while the values reported for other salts in Reference [36] correspond to SIPs.

Regarding the nature of association constants reported in the present work, the following remarks are worthwhile. First, as was mentioned above, a thermodynamic treatment of ion pairing like ours cannot properly discriminate among CIP, SIP and 2SIP and thus provides an integral measure of all three species. Second, some degree of ion association has to be already incorporated in the Debye–Hückel formalism as the cation–anion correlation function is assumed to be nonzero at distances $r \geq a$. That is why the obtained values characterize not full but excessive ion pairing and are expected to be smaller than those obtained by other methods. This is generally the case as can be seen in Table 3. Third, the ion pairing formalism used in this model does not take into account triple and higher ion aggregation which becomes more probable with increasing electrolyte concentration. However, this limitation is also applicable to the results reported in the cited works.

It follows from our analysis that the extent of ion pairing in the aqueous solutions increases in the order

$$\mathrm{NaI} < \mathrm{NaSCN} < \mathrm{NaBr} < \mathrm{NaCl} < \mathrm{NaClO_4} < \mathrm{NaNO_3}$$

and follows the order of the mean ionic activity coefficients. This series has no simple correlation either with the ionic radii of anions (Table 2) or with the famous Hofmeister series for anions [10, 11]

$$\mathrm{SO_4^{2-}} > \mathrm{HPO_4^{2-}} > \mathrm{F^-} > \mathrm{CH_3COO^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{NO_3^-} > \mathrm{I^-} > \mathrm{ClO_4^-} > \mathrm{SCN^-},$$

related to the protein precipitation, except if only the salts with halogen anions and NaSCN are considered separately. In the latter case, we get in harmony with the Collins' "law of matching water affinities" [14], which can be formulated as follows: ion pairing between oppositely charged ions is more likely if they have close hydration energies. Thus, $\mathrm{Na^+}$ is closer in hydration Gibbs energy (and size) to $\mathrm{Cl^-}$ than to $\mathrm{Br^-}$ or $\mathrm{I^-}$ (Table 2) and ion pairing in NaCl should be stronger. Note also that increasing ion pairing in NaI, NaSCN, NaBr and NaCl solutions with decreasing anion size determines the ordering of their activity coefficients despite the increasing solvation contribution, which acts in the opposite direction.

The increasing ion pairing in the order NaI < NaBr < NaCl is borne out by the conductivity studies [51, 52] (Table 3) which did not cover the polyatomic anions. The order of association constants obtained in the dielectric relaxation study [36] attributed to the solvent shared ion pairs does not lead to definite conclusions because of low precision. Therefore, an apparent violation of the Collins rule in the case of the polyatomic oxygen-containing perchlorate and nitrate ions requires further considerations. To this end, application of more elaborate statistical-mechanical models with explicit ion association [57, 58] may be of interest.

## 5 Conclusions

The extended Debye–Hückel theory, which allows for concentration variation of electrolyte solution static permittivity is employed to predict activity coefficients in aqueous solutions of sodium salts with various univalent anions (NaCl, NaBr, NaI, $\mathrm{NaNO_3}$, $\mathrm{NaClO_4}$ and NaSCN) at ambient conditions. Calculations without empirical adjustments reproduced the activity coefficients for NaI in the concentration range up to 6 $\mathrm{mol{\cdot}kg^{-1}}$ and for NaSCN up to 2 $\mathrm{mol{\cdot}kg^{-1}}$. In the case of other solutions, calculations underestimate water activity coefficients and overestimate mean ionic activity coefficients at concentrations beyond 0.5 mol·kg$^{-1}$. In order to improve the representations, the model was extended to include ion pairing, which resulted in a better agreement between calculated activity coefficients and experimental data, especially for $NaNO_3$. The ion pairing equilibrium constants were estimated and compared with available literature values. The extent of ion pairing was found to increase in the sequence NaI < NaSCN < NaBr < NaCl < $NaClO_4$ < $NaNO_3$, with violation of the Collins rule in the case of polyatomic oxygen-containing anions.

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