

Factorizing of a concentration function for the mean activity coefficients of aqueous strong electrolytes into individual functions for the ionic species

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Abstract The concentration curve of mean activity coefficients to the required power was approximated by a product function. The product function parameters were optimized by experimental data for the mean activity coefficients using a nonlinear regression model. Assuming that the product function parameters can be determined, the factor functions are clearly known. The mathematical complexity and a concept solution are presented. Clear, reliable results were obtained with the help of asymptotic theory when corresponding approximations were used. The method described makes it possible to split the experimentally determinable concentration curve of the mean activity coefficients to the required power in individual factor functions of complementary ion species, $\bar{\gamma}_C(m)$ and $\bar{\gamma}_A(m)$. The results are verified by comparing them with experimentally determined quotients of single-ion activity coefficients of ternary systems. The calculated individual parts for single-ion species are plausible and show a

characteristic, typical concentration curve for cations as well as for anions. They correlate with the ion parameters.

Keywords Aqueous strong electrolytes · Activity coefficients concentration dependence · Factorization of the mean activity coefficients · Single ion activity coefficients

Introduction

In 1924, Sørensen [1] sparked interest in the individual activity of the single-ion species of dissolved electrolytes in accordance with the following definition of the pH value:

$$\text{pH} \equiv -\log a_{\text{H}^+} \quad (1)$$

a_{H^+} . . . individual activity of the hydrogen ions in the measured solution

Guggenheim [2], however, demonstrated as early as 1929 that only the mean activity a_{\pm} of an electrolyte in solution can be defined thermodynamically by means of its chemical potential μ . The conception of splitting the electrochemical potential ($\tilde{\mu}_i$) of an ion of type i into the sum of a chemical term μ_i and an electrical term $\varepsilon_i^* \psi$ (ε_i^* : charge; ψ : electrostatic potential) has no physical significance [2]. Therefore, the basis of the thermodynamic definition is missing for the single-ion activity a_i . It continues to be the subject of controversial discussion in electrochemistry as to whether the individual activity of a single-ion species has a real significance alone or not. Single ion activities a_i and individual activity coefficients γ_i of a single-ion species i do not apply in classical thermodynamics.

It must nonetheless be accepted that the mean activity coefficient to the required power of an aqueous strong

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electrolyte is purely mathematical and is the product of individual activity coefficients of the complementary ion species (2):

$$\gamma_{\pm}^{\nu_+ + \nu_-} = \gamma_C^{\nu_+} \cdot \gamma_A^{\nu_-} \quad (2a)$$

$$\gamma_{\pm} = \sqrt{\nu_+ + \nu_-} \sqrt{\gamma_C^{\nu_+} \cdot \gamma_A^{\nu_-}} \quad (2b)$$

ν_+ , Stoichiometric numbers of cation and anion from
 ν_- : one molecule $C_{\nu_+}A_{\nu_-}$

These single-ion activity coefficients γ_C and γ_A cannot be determined separately by experiments. The only factor that is experimentally accessible is the product of the individual activity coefficients of the cations γ_C and anions γ_A of an electrolyte $C_{\nu_+}A_{\nu_-}$ in the solution, a parameter known as the mean activity coefficient γ_{\pm} .

Conventions are required to eliminate the resulting “breaches” (see also [3–10]). Data, for instance about the potentials of single electrodes, liquid-junction potentials, and pH values, are available with the help of conventions. It must be realized that the use of these conventions are also regarded as quite conventional [11]. The pH (1) defined by Sørensen cannot be measured in principle; instead, the determination of a “conventional pH value” has become accepted [12]. In many cases, the users are oblivious to the fact that this “conventional pH value” allows no conclusions to be drawn about the “true acidity” of the measured solution [13, 14].

In contrast to Taylor [15], Guggenheim attempts to show in his milestone article [2] that the knowledge of individual activities of single-ion species is essentially unnecessary in the thermodynamic treatment of electrolyte solutions. It is questionable whether or not the significance of the individual efficacies of single-ion species can be neglected entirely in light of modern electrolyte research.

It is assumed in non-equilibrium thermodynamics that the relations for equilibria of classical thermodynamics remain valid when irreversible processes are treated too. The time dependence additionally is integrated in the considerations. Mathematical treatment generally yields differential equations. The dilemma is that the rigorous integration of differential equations for irreversible processes in which dissolved electrolytes are involved often requires knowledge of the individual activities of single-ion species [11, 14–19].

It is known that a one-to-one breakdown of the product (2) into factors is impossible without making additional assumptions. However, the curve of the product of the

individual activity coefficients of the single-ion species ($\gamma_C^{\nu_+} \cdot \gamma_A^{\nu_-}$) versus concentration can be determined experimentally. This additional information renders it possible to split the mean activity coefficients to the required power (2a) into individual factor functions for cations and anions. This is accomplished by using basic parametric approaches in relation to their approximation to the experimentally determinable concentration curve of the mean activity coefficients to the required power.

The individual parts that are obtained for cations and anions by mathematically splitting the mean activity coefficients are characterized by an overbar ($\bar{\gamma}_C$ and $\bar{\gamma}_A$) to differentiate it from the thermodynamically undefined single-ion activity coefficients for cations and anions (γ_C and γ_A).

It is not possible to verify the calculated values ($\bar{\gamma}_C$ and $\bar{\gamma}_A$) as individual activity coefficients in a direct experimental way. The existence of a thermodynamic state variable fails as a precondition. Its measurable change with the concentration of the electrolyte in the solution alone shows the clear function of the activity of the single-ion species. The quotients of single-ion activity coefficients in especially composed electrolyte mixtures, by contrast, can be experimentally determined by implication [14, 20, 21].

The ratio of the individual activities of two ion species with the same charge is also defined thermodynamically. Guggenheim states explicitly: “Thus, in particular, the ‘mean activity coefficient’ of a salt is defined, as is also the ratio of the activities or activity coefficients of two ionic species with the same charge” [2]. This is a criterion to prove whether the purely mathematical method of factorizing mean activity coefficients into individual parts for cations and anions as is described in the present publication produces meaningful results.

The concentration function

The square of the mean activity coefficients of a uni-univalent electrolyte CA as a function of the concentration up to high concentrations m can be approximated well using the product function (3).

$$\begin{aligned} \gamma_{\pm}^2(m) &= \bar{\gamma}_C(m) \cdot \bar{\gamma}_A(m) \\ &= \left[c_1 e^{c_7 \cdot m^{\frac{1}{2}}} + c_3 e^{c_9 \cdot m} + c_5 e^{c_{11} \cdot m^{\frac{3}{2}}} + \dots \right] \\ &\quad \times \left[c_2 e^{c_8 \cdot m^{\frac{1}{2}}} + c_4 e^{c_{10} \cdot m} + c_6 e^{c_{12} \cdot m^{\frac{3}{2}}} + \dots \right] \quad (3) \end{aligned}$$

The following Eq. (4) is valid for polyvalent electrolytes $C_{v_+}A_{v_-}$:

$$\gamma_{\pm}^{v_++v_-}(J) = \bar{\gamma}_C^{v_+}(J) \cdot \bar{\gamma}_A^{v_-}(J) \tag{4}$$

$$= \left[c_1 e^{c_7 J^{\frac{1}{2}}} + c_3 e^{c_9 J} + c_5 e^{c_{11} J^{\frac{3}{2}}} + \dots \right]^{v_+}$$

$$\left[c_2 e^{c_8 J^{\frac{1}{2}}} + c_4 e^{c_{10} J} + c_6 e^{c_{12} J^{\frac{3}{2}}} + \dots \right]^{v_-}$$

m Stoichiometric concentration of the uni-univalent electrolyte (mole per kilogram)
 J Ionic strength (mole per kilogram) in the commonly used definition as the half sum of the concentration of all ions multiplied by the square of their charge numbers [22, 23]
 $c_1, \dots, c_{12}, \dots, c_p$ Parameters

The product functions (3) and (4), respectively, fulfill all known properties for activity coefficients although they seem unusual. The basic product functions (3) and (4), respectively, result from the mathematical simulation of the concentration curve for $\gamma_{\pm}^{v_++v_-}$ and were not deduced from the calculation of the excess Gibbs energy with the help of statistical mechanics. The basis for the structure of the product functions has been presented in previous publications [14, 20, 26].

Normally, the mean activity coefficient as a function of concentration is approximated as a virial equation as follows (see, e.g., [27]):

$$\ln \gamma_{\pm}(m) = -A' \sqrt{m} + Cm + Dm^{\frac{3}{2}} + \dots \tag{5}$$

A' Debye–Hückel constant
 C, D, \dots Empirical virial coefficients

so the square of the mean activity coefficients of uni-univalent electrolytes is given by:

$$\gamma_{\pm}^2(m) = \gamma_C(m) \cdot \gamma_A(m) = e^{-2A' \sqrt{m}} \tag{6}$$

$$\cdot e^{(C_C+C_A)m} \cdot e^{(D_C+D_A)m^{\frac{3}{2}}} \cdot \dots$$

$\left(\begin{array}{l} C_C, D_C, \dots \text{ are valid for the cation;} \\ C_A, D_A, \dots \text{ are valid for the anion} \end{array} \right)$

The adaptation of $\ln \gamma_{\pm}$ to concentration m results from the treatment of the inter-ionic interaction using the statistical mechanics to calculate the excess chemical potential μ^{exc} of an electrolyte in solution. It is proportional to the logarithm of the mean activity coefficient (see, e.g., [28]):

$$\mu^{\text{exc}} = R \cdot T \cdot \ln \gamma_{\pm} \tag{7}$$

R Gas constant
 T Thermodynamic temperature
 μ^{exc} Excess chemical potential

An attempt to factorize the basic approach (6) yields infinite solutions. However, the mathematical structure of (3) and (6) is basically different. The product function (3) [and (4) too] can be clearly split in principle into its two factor functions. Nonetheless, the similarity of both Eqs. (3) and (6) is evident after their series expansions.¹

To obtain the desired individual parts $\bar{\gamma}_C$ and $\bar{\gamma}_A$ for cations and anions, the product functions (3) and (4), respectively, for the mean activity coefficients to their required power $[\gamma_{\pm}^{v_++v_-}(J)]$ were split into factor functions of predefined structure. Assuming the existence of a clear solution, estimating a product function yields the factorization of the product. The preconditions for applying this concept are (1) the correctness for the structure of the product functions (3) and (4), respectively, as well as (2) the verifiability that the factor functions of product functions (3) and (4), respectively, yield plausible values for the complementary ion species. These two prerequisites have been presented in previous publications [14, 20, 24–26].

The factor functions are the sum of several terms. Both factor functions have an identical structure. The values of the parameters in the factor functions are the only factors responsible for the gradually different concentration curves of the cations and anions resulting from the optimal approximation of product functions (3) and (4), respectively, to the existing experimental data for the concentration curve of the mean activity coefficients to the required power $[\gamma_{\pm}^{v_++v_-}(J)]$.

¹ Thus, direct equations can be established between the empirical virial coefficients of (6) and the parameters of (3), e.g., the application of the product function (20) with a definite number of parameters produces such relations.

Solution of a nonlinear regression problem

Parameters c_1, \dots, c_p of product function (3) have to be determined based on n observations $(m_i; g_i)$, whereas g_i is the measured square of mean activity coefficients $\gamma_{\pm}^2(m_i)$ for concentration m_i .

In the case of $n > p$, which is of practical importance, parameters c_1, \dots, c_p are determined by fitting the “best” model (3) to the given observations. The least squares method is an objective and efficient method for determining such a best fitting model [30, 31]. The validity of (3) is assumed on the one hand and, on the other hand, an additive random error ε_i of the measurements g_i of the product of the individual parts of complementary ion species:

$$g_i = \gamma_{\pm}^2(m_i) = \bar{\gamma}_C(m_i) \cdot \bar{\gamma}_A(m_i) + \varepsilon_i \tag{8}$$

$$= \left[c_1 e^{c_7 m_i^{\frac{1}{2}}} + c_3 e^{c_9 m_i} + c_5 e^{c_{11} m_i^{\frac{3}{2}}} + \dots \right]$$

$$\left[c_2 e^{c_8 m_i^{\frac{1}{2}}} + c_4 e^{c_{10} m_i} + c_6 e^{c_{12} m_i^{\frac{3}{2}}} + \dots \right]$$

$$+ \varepsilon_i, i = 1, \dots, n$$

The individual deviations of observations g_i from the fitted values $\bar{\gamma}_C(m_i) \cdot \bar{\gamma}_A(m_i)$ are called residuals. Parameters c_1, \dots, c_p are determined in such a way that the sum Q of squared residuals (the overall discrepancy) is minimal [29, 31, 32]:

$$Q = \sum_{i=1}^n \varepsilon_i^2 = \sum_{i=1}^n [g_i - \bar{\gamma}_C(m_i) \cdot \bar{\gamma}_A(m_i)]^2, \tag{9}$$

there is no closed form solution of the optimization problem (9). Conditions required for optimization to the desired parameters lead to a nonlinear system of equations.

Iterative methods are generally applied in solving nonlinear system of equations [29, 32]. The system of equations of the Gauss–Newton iterative procedure to be solved in each step can have a nearly singular coefficient matrix; in other words, it is ill-conditioned.

The permitted functions of the regression approach generate a highly flexible array of p parameter curves.

Suitable robust algorithms can solve ill-conditioned problems with actually unsuitable initial values and allow

the estimation of parameters. Such a method is, e.g., the Levenberg–Marquardt algorithm [29, 32]. So, at least local minima of function (9) might be found by minimizing the overall discrepancy, and the parameters are estimated simultaneously. The Levenberg–Marquardt algorithm was used preferably for the optimization problems in the present work.

Restriction of the number of summands within the factor functions of the basic product approaches

Consideration of only the first summand

If only the first summand is considered, the following equations are valid:

$$\gamma_{\pm}^2(m) = \bar{\gamma}_C(m) \cdot \bar{\gamma}_A(m) \approx \left[c_1 e^{c_7 m^{\frac{1}{2}}} \right] \left[c_2 e^{c_8 m^{\frac{1}{2}}} \right] \tag{10}$$

for polyvalent electrolytes $C_{v+}A_{v-}$, respectively,

$$\gamma_{\pm}^{v_+ + v_-}(J) = \bar{\gamma}_C^{v_+}(J) \cdot \bar{\gamma}_A^{v_-}(J) \approx \left[c_1 e^{c_7 J^{\frac{1}{2}}} \right]^{v_+} \left[c_2 e^{c_8 J^{\frac{1}{2}}} \right]^{v_-} \tag{11}$$

In this case, the validation of the basic approaches is reduced to the concentration of electrolytes nearly at zero. In the present publication, it is shown that these basic approaches containing only the first summand in the factor functions merge into the Debye–Hückel limiting law equation [33, 34] when the known limiting infinite dilution conditions are taken into consideration.

Two preconditions have to be fulfilled:

At infinite dilution, all activity coefficients will have a value of one. If $m=0$, then it follows

$$\gamma_{\pm}(0) = \bar{\gamma}_C(0) = \bar{\gamma}_A(0) = 1 \tag{12}$$

and $c_1 = c_2 = 1$. As the concentration approaches zero, the individual properties of the ions lose their influence on the activity coefficient, and it follows the same functional dependency between the activity coefficient and the concentration for all ion species with the same charge number. Debye and Hückel [33, 34] described a limiting law. This Debye–Hückel limiting law equation has the following form for univalent ions:

$$\ln \gamma_{DH}(m) = -A' \sqrt{m}. \quad \gamma_{DH} \dots \text{activity coefficients in the Debye – Hückel range } (0 \leq m < 0.01 \text{ mol/kg}) \tag{13}$$

Accordingly, the derivative of functions $\bar{\gamma}_C$ and $\bar{\gamma}_A$ with respect to m near zero is stated by the Debye–Hückel limiting law equation.

Since by equalization of the limits of the first derivatives for the border crossing $m \downarrow 0$:

$$\lim_{m \rightarrow 0} \frac{\partial \gamma_{DH}}{\partial m} = \lim_{m \rightarrow 0} \frac{\partial \bar{\gamma}_C}{\partial m} = \lim_{m \rightarrow 0} \frac{\partial \bar{\gamma}_A}{\partial m} \tag{14}$$

it follows:

$$\lim_{m \rightarrow 0} -\frac{A' \cdot e^{-A'\sqrt{m}}}{2 \cdot \sqrt{m}} = \lim_{m \rightarrow 0} \frac{c_7 \cdot e^{c_7\sqrt{m}}}{2\sqrt{m}} = \lim_{m \rightarrow 0} \frac{c_8 \cdot e^{c_8\sqrt{m}}}{2\sqrt{m}}, \tag{15}$$

and hence follows $c_7 = c_8 = -A'$ and:

$$\gamma_{\pm}^2(m) = \bar{\gamma}_C(m) \cdot \bar{\gamma}_A(m) \approx \left[e^{-A' \cdot m^{\frac{1}{2}}} \right] \left[e^{-A' \cdot m^{\frac{1}{2}}} \right] \tag{16}$$

or for the general case:

$$\gamma_{\pm}^{v_+ + v_-}(J) = \bar{\gamma}_C^{v_+}(J) \cdot \bar{\gamma}_A^{v_-}(J) \approx \left[e^{-z_C^2 \cdot A' \cdot J^{\frac{1}{2}}} \right]^{v_+} \left[e^{-z_A^2 \cdot A' \cdot J^{\frac{1}{2}}} \right]^{v_-} \tag{17}$$

z_C , Charge numbers of cation and anion in the molecule $C_{v_+}A_{v_-}$
 z_A

Relationships (16) and (17) are just the Debye–Hückel limiting law equations.

Consideration of the first two summands

If the first two summands are taken into consideration, the following equations are valid:

$$\gamma_{\pm}^2(m) = \bar{\gamma}_C(m) \cdot \bar{\gamma}_A(m) \approx \left[c_1 e^{c_7 \cdot m^{\frac{1}{2}}} + c_3 e^{c_9 \cdot m} \right] \left[c_2 e^{c_8 \cdot m^{\frac{1}{2}}} + c_4 e^{c_{10} \cdot m} \right] \tag{18}$$

and for polyvalent electrolytes $C_{v_+}A_{v_-}$, respectively:

$$\gamma_{\pm}^{v_+ + v_-}(J) = \bar{\gamma}_C^{v_+}(J) \cdot \bar{\gamma}_A^{v_-}(J) \approx \left[c_1 e^{c_7 \cdot J^{\frac{1}{2}}} + c_3 e^{c_9 \cdot J} \right]^{v_+} \left[c_2 e^{c_8 \cdot J^{\frac{1}{2}}} + c_4 e^{c_{10} \cdot J} \right]^{v_-} \tag{19}$$

With these approaches, a description of the mean activity coefficient will succeed very well for an extended range of concentration. This second partial adjustment range of concentration ranges from $m=0$ up to a maximum of 7 mol/kg generally, but the upper limit of the concentration is different for several electrolytes.

Note that the estimated parameters of the product function, which were already included for the smaller concentration range, change when an additional summand is included in both factor functions, because the system of functions is not orthogonal.

The limiting infinite dilution condition as follows from (12) is $c_1 + c_3 = 1$, respectively, $c_3 = (1 - c_1)$, and $c_2 + c_4 = 1$, respectively $c_4 = (1 - c_2)$.

The limiting infinite dilution condition (14) results in $c_1 \cdot c_7 = -A'$ respectively $c_7 = -\frac{A'}{c_1}$ and $c_2 \cdot c_8 = -A'$ respectively $c_8 = -\frac{A'}{c_2}$ [20, 26].

The product function containing two summands in the factor functions for uni-univalent electrolytes has the following form with new denotations for the parameters [14, 20, 24–26]:

$$\begin{aligned} \gamma_{\pm}^2(m) &= \bar{\gamma}_C(m) \cdot \bar{\gamma}_A(m) \\ &\approx \left[b_1 e^{-\frac{A'}{b_1} m^{\frac{1}{2}}} + (1 - b_1) e^{b_3 \cdot m} \right] \\ &\quad \times \left[b_2 e^{-\frac{A'}{b_2} m^{\frac{1}{2}}} + (1 - b_2) e^{b_4 \cdot m} \right], \end{aligned} \tag{20}$$

and for polyvalent electrolytes $C_{v_+}A_{v_-}$ as follows:

$$\begin{aligned} \gamma_{\pm}^{v_+ + v_-}(J) &= \bar{\gamma}_C^{v_+}(J) \cdot \bar{\gamma}_A^{v_-}(J) \\ &\approx \left[b_1 e^{-z_C^2 \frac{A'}{b_1} J^{\frac{1}{2}}} + (1 - b_1) e^{b_3 \cdot J} \right]^{v_+} \\ &\quad \times \left[b_2 e^{-z_A^2 \frac{A'}{b_2} J^{\frac{1}{2}}} + (1 - b_2) e^{b_4 \cdot J} \right]^{v_-} \end{aligned} \tag{21}$$

Because for all $m \geq 0$, the native conditions

$$\bar{\gamma}_C(m) > 0, \tag{22}$$

$$\bar{\gamma}_A(m) > 0 \tag{23}$$

have to be valid, the boundary conditions follow:

$$0 < b_1 < 1 \tag{24}$$

and

$$0 < b_2 < 1, \tag{25}$$

Thus, $\bar{\gamma}_C$, respectively, $\bar{\gamma}_A$ in the basic approach (20) prove to be convex linear combinations of the functions $e^{-\frac{A'\sqrt{m}}{b_1}}$ and $e^{b_3 m}$, respectively, $e^{-\frac{A'\sqrt{m}}{b_2}}$ and $e^{b_4 m}$. Of course, the analog conditions are valid for (21).

Consideration of more than two summands

Considering the large concentration ranges, the achievable approximation becomes clearly worse with the four parametric basic product approaches (20) and (21), respectively. The problems are that (1) the upper limit of the concentration, for which measured values can be used for the optimization process, is unknown without the adaptation getting markedly worse and (2) this boundary changes for different electrolytes. The “stochastic” distribution of the residuals (pure error) can be used as a decision criterion. The “stochastic” distribution of the residuals disappears in case of additional experimental data for higher concentrations are included in the optimization process. In addition, a structure of the residuals becomes more and more evident and this reflects a functional dependency of the residuals on the concentration (lack of fit error; see Figs. 1 and 2)

This phenomenon can be interpreted to the effect that the basic approaches (20) and (21), respectively, are not adequately suitable. However, the first three summands in the factor functions of the basic product approaches (3) and (4), respectively, are enough to record the concentration curve of the mean activity coefficient to the required power from zero up to the highest concentration. However, the large number of 12 parameters c_1, \dots, c_{12} cause difficulties during optimization. Using the limiting infinite dilution conditions (12) and (14) is a possible way to reduce the number of parameters. Thus, a basic approach with only eight parameters is obtained. With a new denotation for the parameters of the first three summands in the factor functions of the basic product approach (4), the product

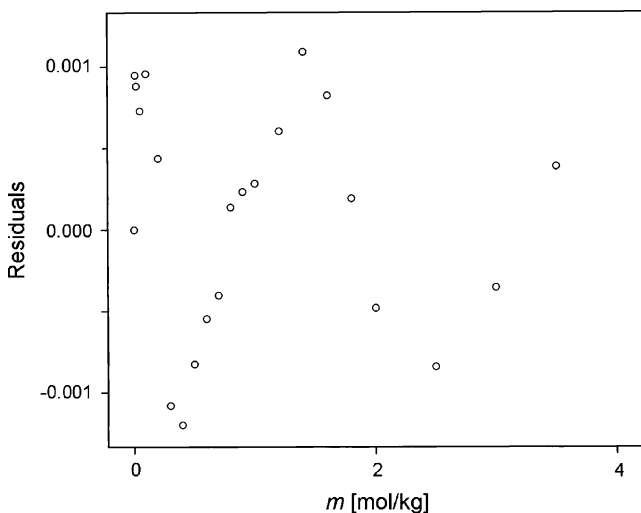


Fig. 1 Residuals for $\gamma_{\pm\text{NaCl}}^2(m)$, approximation is carried out by using the basic product approach (20), concentration range $m \leq 3.5$ mol/kg (mean activity coefficients, see [35])

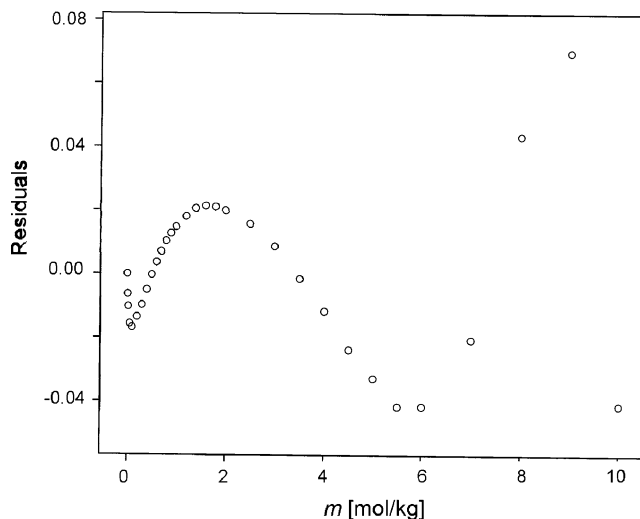


Fig. 2 Residuals for $\gamma_{\pm\text{NaCl}}^2(m)$, approximation is carried out by using the basic product approach (20), concentration range $m \leq 10$ mol/kg, (mean activity coefficients, see [35])

function for the general case of strong electrolytes $C_{v+}A_{v-}$ is formed to (26):

$$\gamma_{\pm}^{v_+ + v_-}(J) = \bar{\gamma}_C^{v_+}(J) \cdot \bar{\gamma}_A^{v_-}(J) \approx \left[d_1 e^{-\frac{z^2 d_1'}{c} J^{\frac{1}{2}}} + (1 - d_1) e^{d_3 J} + d_5 (e^{d_7 J^{\frac{3}{2}}} - e^{d_3 J}) \right]^{v_+} \cdot \left[d_2 e^{-\frac{z^2 d_2'}{d} J^{\frac{1}{2}}} + (1 - d_2) e^{d_4 J} + d_6 (e^{d_8 J^{\frac{3}{2}}} - e^{d_4 J}) \right]^{v_-} \tag{26}$$

It is not meaningful to consider more than three summands in the factor functions.

Due to the native conditions (22) and (23), and the consideration of conclusions from the Debye–Hückel theory, which in the right-hand neighborhood of zero demands, the following inequalities are valid:

$$\bar{\gamma}_C(J) < 1 \tag{27}$$

and

$$\bar{\gamma}_A(J) < 1 \tag{28}$$

and because the terms $e^J, e^{J^{\frac{3}{2}}}$ as well as the fact that the exponential functions of the higher power of J (respectively, m) at the transition $J \downarrow 0$ tend faster to 1 than $e^{-\sqrt{J}}$, the values of parameters d_1 and d_2 in (26) are limited between 0 and 1.

Choice of a limited concentration range

Using the four-parametric basic product approaches (20) and (21), respectively, only the approximation to parts of the experimental concentration curve is optimal. Selecting a

limited part of the entire slope of the experimental curve as a basis for an adaptation will imply inaccurate results because the product function beyond the limited part resulting from the estimation will continue to be unpredictable. This phenomenon, exemplified for $\gamma_{\pm\text{NaOH}}^2$ is displayed in Fig. 3. The residuals between the experimentally determined concentration curve and the slope of the calculated curves can be seen in Fig. 3. While adapting the limited part from concentration zero to point $m=3$ mol/kg of the experimental curve, for example, the determined product function, despite a good adaptation of the selected part, can deviate from the experimental curve.

The trend of the deviation is not always the same. This is visible in Fig. 3 from the residuals between the courses of the experimentally determined concentration curve and the calculated curve adapting the limited part from zero to point $m=6$ mol/kg.

The narrower selected the range of the concentration, the less stable the estimated parameters will be. This implicates incorrect factor functions. An attempt will therefore be made to maximize the concentration range for the approximation to estimate the parameters.

Test calculations have shown that the approximation to the “S”-shaped curve (see, e.g., [36]) is successful by using the product function (26) with three summands in each of the factor functions. Note that the concentration range starts at zero. The product function contains eight parameters.

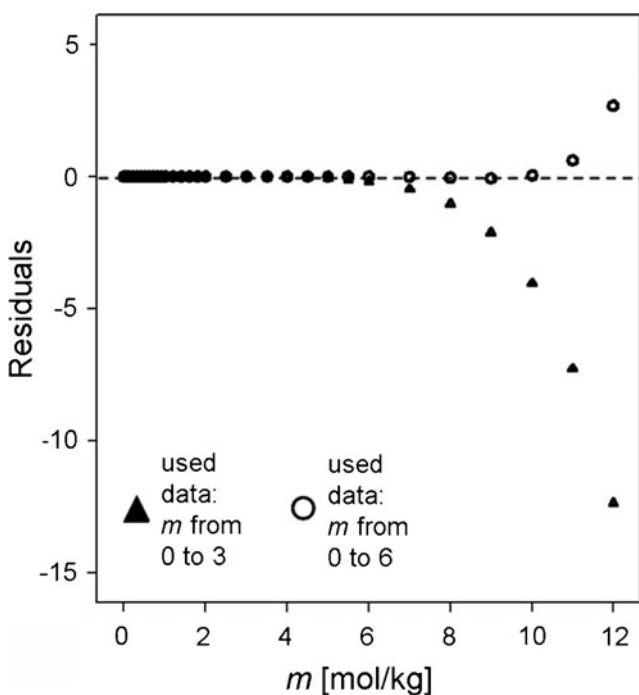


Fig. 3 Residuals ε_i corresponding to approximations using different concentration data ranges (for NaOH) on the basis of the basic product approach (20), (mean activity coefficients, see [35])

The use of higher parametric basic product approaches is generally unnecessary. The advantage gained by improved approximation is canceled out due to the problematic determination of the higher number of parameters as a result of the higher flexibility. The stability of the estimation of parameters decreases as the number of parameters increases. The parameters of the first summands are those least influenced.

The minimum sum of least squares and stochastic distribution of the residuals depending on m are the criteria for good approximation. A recognizable structure of the residues must not develop (see Figs. 1 and 2).

Mathematically correct solutions and physicochemically reasonable results

The flexibility of the basic product approaches rises with an increasing number of the considerable summands in (3) and (4), respectively. But the condition of the coefficient matrix is clearly impaired. In addition, the number of (local) minima of overall discrepancy (9) increases [37].

If an ill condition exists, the Gauss–Newton iterative method with arbitrary initial values traces a curve which is a good approximation to the collection of data. However, a lot of likewise well-approximated curves with other parameters can exist. A small change in one parameter in the approach can result in a large change in the other parameters [38]. This situation can be improved by using an extended number of measuring data with extreme accuracy. Admittedly, different minima with dependency of the initial values may possibly still result from the iteration. The solution of the optimization problem is therefore ambiguous.

With respect to optimization problem (9), all possible solutions are correct. This considerable nonlinear regression approach is not yet a basic approach without relevant background, but the nonlinear regression model describes real physicochemical facts which include concrete preconditions for the nonlinear regression approach and predetermines restrictions to the selection of practicable solutions. Only one result should be expedient from the mathematically possible solutions. In mathematics, no criterion exists to allow the choice of the physicochemically correct result from all mathematically practicable results. Such a decision must always be selected from the real background.

In the case of the single-ion activity coefficients, physicochemical knowledge is limited and mainly restricted to the concentration nearly at zero. Hence, important conclusions arise to appraise the results. Estimations, which result in a negative individual activity coefficient, are excluded a priori due to physicochemical futility. Furthermore, results have to be dismissed which do not show the requested negative slope of the single-ion activity coef-

ficients in the concentration range nearly at zero from the Debye–Hückel theory. The calculated single-ion activity coefficients of strong uni-univalent and uni-bivalent electrolytes may not be lower than the Debye–Hückel limiting law requests.² In such physicochemically absurd solutions, the parameters d_1 and d_2 , respectively, of the basic product approach (26) generally have values whose magnitude lies outside of the interval [0; 1]. In these cases, optimization has to be repeated with other initial values. However, a criterion fails for a certain specification of initial values. Another possibility is to perform the optimization under corresponding constraints. But this approach cannot work because such corresponding constraints are unknown. Although solutions can be excluded due to physicochemical futility, the information about individual activity coefficients of single-ion species does not suffice to determine the adequate physicochemical result.

It is necessary to develop and adopt a method to solve this nonlinear regression problem. The aim is to limit the result to the physicochemically practicable solution right from the outset. This aim can be reached by using the corresponding approximations. These contain known physicochemical constraints resulting from the Debye–Hückel theory.

Splitting of mean activity coefficients into individual parts for complementary ion species by using the asymptotic theory

An asymptotic theory was developed by Ferse [20, 25] and Ferse and Neumann [26] in the 1970s to estimate the parameters b_1, \dots, b_4 of the four-parametric basic product approaches (20) and (21), respectively. Clear and stable results can be attained with this method [14]. Using the asymptotic theory, the parameters b_1, \dots, b_4 were determined successively using the corresponding approximations which are derived from basic product approaches (20) and (21), respectively, for low and also high concentrations [14, 20, 25, 26].

The following relation can be applied for m or $J \geq 5$ mol/kg, respectively:

$$b_1 e^{-z_C^A \sqrt{J}} \approx b_2 e^{-z_A^A \sqrt{J}} \approx 0. \quad (29)$$

² This condition is not fulfilled by dilute solutions of high charge electrolytes, 2:2, 2:3, and 3:3, where negative deviations from Debye–Hückel limiting law occur. This occurrence does not signify that these are weak electrolytes. It is possible to prove that this effect is regularly predicted on the mere basis of the electrostatic interaction between the ions and the ion cloud [39, 40].

Thus by using the corresponding approximations (30) and (31) in the general case of high concentrations:

$$\gamma_{\pm}^{\nu_+ + \nu_-}(J) \approx (1 - b_1)^{\nu_+} (1 - b_2)^{\nu_-} \cdot e^{(\nu_+ b_3 + \nu_- b_4) J} \quad (30)$$

respectively

$$\ln \gamma_{\pm}^{\nu_+ + \nu_-}(J) \approx \ln[(1 - b_1)^{\nu_+} (1 - b_2)^{\nu_-}] + (\nu_+ b_3 + \nu_- b_4) J. \quad (31)$$

In the concentration range of m and J , respectively, between 5 and 10 mol/kg, $\ln \gamma_{\pm}$ for a strong electrolyte generally is a linear function of m respectively J ; therefore, in the first step, the sum $(\nu_+ b_3 + \nu_- b_4)$ as well as the product $[(1 - b_1)^{\nu_+} (1 - b_2)^{\nu_-}]$ are determined with the linear regression analysis as the standard mathematical method by using the corresponding approximation (31). In Fig. 4, the determination of the ordinate intercept β :

$$\beta = \ln[(1 - b_1)^{\nu_+} (1 - b_2)^{\nu_-}] \quad (32)$$

and the determination of the slope $(\nu_+ b_3 + \nu_- b_4)$ are depicted by way of example for NaClO_4 solutions. The values are $\beta_1 = -1.3142777$ and for the slope $(b_3 + b_4) = 0.0891$. The γ_{\pm} values of NaClO_4 solutions were taken from the papers by Hamer and Wu [35], Jones [42], and Rush and Johnson [43].

Parameters b_1 as well as b_2 can then be determined separately by applying an additional corresponding approxi-

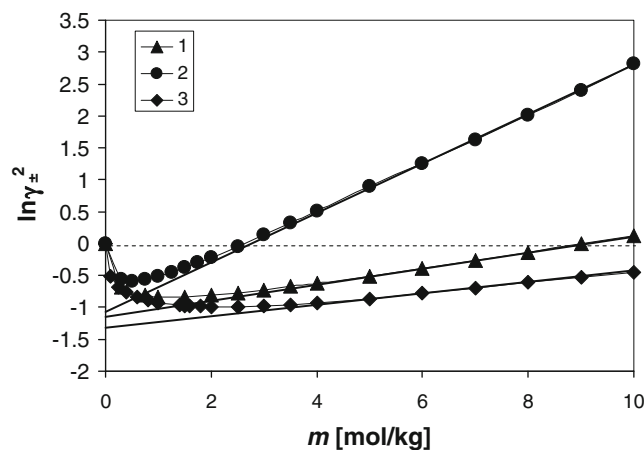


Fig. 4 Determination of the ordinate intercepts and the slopes from the concentration curves of $\ln \gamma_{\pm}^2(m)$ vs. m_{NaClO_4} for 0.01m NaCl (=1) and 0.01m HCl (=2), respectively, each with a great surplus of NaClO_4 and for pure NaClO_4 solutions (=3)

mation for very low m respectively J , e.g., $J=10^{-3}$ mol/kg (then $e^{b_3 J} \approx e^{b_4 J} \approx 1$ is valid):

$$\gamma_{\pm}^{v_+ + v_-}(0.001) = \bar{\gamma}_C^{v_+}(0.001) \cdot \bar{\gamma}_C^{v_-}(0.001) \tag{33}$$

$$\approx \left[b_1 \cdot e^{-\frac{z_C z_A}{b_1} \sqrt{10^{-3}}} + (1 - b_1) \right]^{v_+} \cdot \left[b_2 \cdot e^{-\frac{z_C z_A}{b_2} \sqrt{10^{-3}}} + (1 - b_2) \right]^{v_-}$$

The Debye–Hückel relation (13) derived from theoretical thoughts [8, 9] works well for the calculation of the mean activity coefficients during validation of the known pre-conditions. Using the extended Debye–Hückel (Eq. 34):

$$\ln \gamma_{\pm}^{v_+ + v_-} = \frac{-(v_+ + v_-) |z_C \cdot z_A| A' \sqrt{J}}{1 + B \cdot a \cdot \sqrt{J}} \tag{34}$$

$a = (\text{empirical})_{\text{ion parameter}}[A]$

the mean activity coefficients are calculated in the concentration range [22] $0 < m, J \leq 5 \cdot 10^{-2}$ mol/kg.^{3,4}

Concerning the NaClO₄ example, the value of $\gamma_{\pm}^2(0.001)$ was calculated to be 0.931228⁵ using the extended Debye–Hückel (Eq. 34). With this value in Eq. (33) and using the ordinate intercept for NaClO₄, the values b_1 and b_2 are calculated to be 0.2123 and 0.6589 [20, 26] (see Fig. 5).

Finally, the sum ($\nu_+ b_3 + \nu_- b_4$) gets separated with measured values in the area of the strongest curvature of the $\gamma_{\pm}^{v_+ + v_-} - m$ curve with the help of the Fibonacci search technique [44].

The values $b_3=0.1215$ and $b_4=-0.0324$ result for NaClO₄ solutions. For additional details, see [20, 26]. This method proved to be successful [14, 20, 24–26].

³ The following values are used after the year 1977 [41]: $A'=1.17625$ ($A=0.510839$), $B=0.32866$, previously it were used these values: $A'=1.1711$ and $B=0.3281$; all values are valid for aqueous solutions and temperature 298.15 K.

⁴ Hamer and Wu [35], for example, used the follow relation (35) for the calculation of the mean activity coefficients, but for an extended concentration range:

$$\log \gamma_{\pm} = \frac{-A |z_C \cdot z_A| \sqrt{J}}{1 + B^* \sqrt{J}} + \beta \cdot J + C \cdot J^2 + D \cdot J^3 + \dots \tag{35}$$

B^*, β, C, D, \dots : empirical constants, the values are different for all electrolytes.

Note, B^* in (35) is not identical with “ B a ” in the extended Debye–Hückel Eq. (34)!

⁵ Extremely high accuracy is certainly not really important. They afford excellent services as operands.

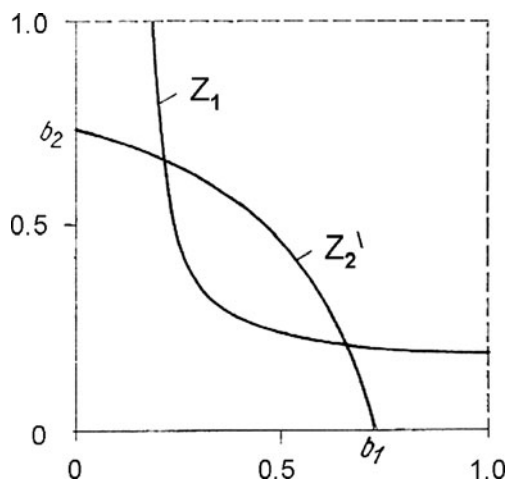


Fig. 5 Graphical separation of b_1 and b_2 with the functions z_1 and z_2 : $z_1 : \left[b_1 e^{-\frac{A'}{b_1} \sqrt{0.001}} + (1 - b_1) \right] \left[b_2 e^{-\frac{A'}{b_2} \sqrt{0.001}} + (1 - b_2) \right] = \gamma_{\pm}^2(0.001)$, $z_2 : (1 - b_1)(1 - b_2) = e^{\beta_1}$. The equations are valid for NaClO₄ with $\gamma_{\pm}^2(0.001) = 0.931228$ and $e^{\beta_1} = 0.268668$

With these values, the individual parts for the single-ion species of NaClO₄ solutions are calculated using (20) from (see footnote 3):

$$\bar{\gamma}_1(m) = 0.2123 e^{-\frac{1.1711 \sqrt{m}}{0.2123}} + 0.7877 e^{0.1215 m} [= \bar{\gamma}_{\text{Na}^+}(m)] \tag{36a}$$

$$\bar{\gamma}_2(m) = 0.6589 e^{-\frac{1.1711 \sqrt{m}}{0.6589}} + 0.3411 e^{-0.0324 m} [= \bar{\gamma}_{\text{ClO}_4^-}(m)] \tag{36b}$$

The allocation of factor functions (36a) and (36b) to the cation Na⁺ or anion ClO₄⁻ cannot be determined on a purely mathematical basis. This decision is clearly possible, however, with the help of especially composed electrolyte mixtures (see "On the allocation of the factor functions to the cation or anion" section).

In Fig. 6, the calculated individual functions for the single-ion species $\ln \bar{\gamma}_1(m)$ (= 36a) and $\ln \bar{\gamma}_2(m)$ (= 36b) versus $m^{\frac{1}{2}}$ for NaClO₄ by factorization of $\gamma_{\pm, \text{NaClO}_4}^2(m)$ are plotted together with the mean activity coefficient for NaClO₄ ($\gamma_{\pm, \text{NaClO}_4} = G$) and the Debye–Hückel limiting law equation (=DH) in the range of concentration $0 \leq m^{\frac{1}{2}} \leq 1$ mol/kg. Figure 7 shows the calculated values as a function of m up to concentration $m=5$ mol/kg for NaClO₄, together with the calculated values for especially composed electrolyte mixtures, see "On the allocation of the factor functions to the cation or anion" section.

This method of asymptotic theory only needs the knowledge of the mean activity coefficients for the concentration range m or $J > 5$ mol/kg, respectively, in the case of the corresponding approximation (31). Unfortunately, they are not known for all electrolytes.

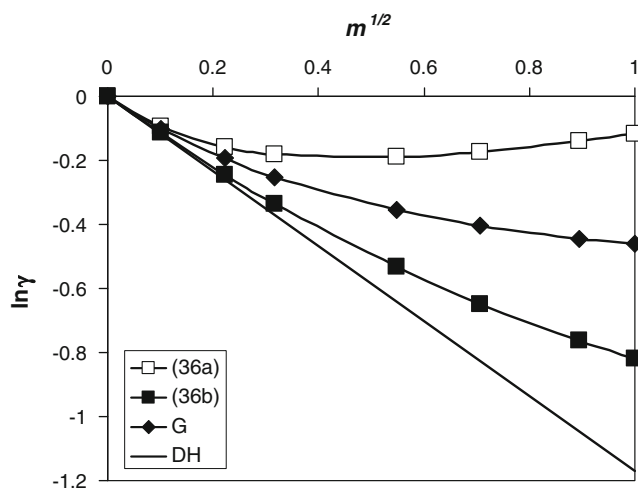


Fig. 6 Individual factor functions $\ln \bar{\gamma}_{\text{Na}^+}(m)$ (= 36a) and $\ln \bar{\gamma}_{\text{ClO}_4^-}(m)$ (= 36b) vs. $m^{1/2}$ for pure NaClO_4 solutions obtained by splitting, together with the Debye–Hückel limiting law equation (=DH) and the mean activity coefficients for NaClO_4 $\gamma_{\pm\text{NaClO}_4}$ (= G) in the concentration range $0 \leq m_{\text{NaClO}_4}^{\pm} \leq 1$

Using the asymptotic theory, the individual parts for single-ion species were calculated for the following electrolytes. These have already been published and discussed elsewhere so that a repeated description of these values and diagrams is unnecessary: alkali chlorides [14, 20], alkali bromides [24], sodium perchlorate [20, 26], alkaline earth chlorides [14, 25], alkaline earth bromides [25], magnesium iodide [25], alkaline earth perchlorates [14, 25], uranyl perchlorate [14, 25], alkali hydroxides [14, 24], hydrohalic acids [14, 24], perchloric acid [14, 24], and furthermore for

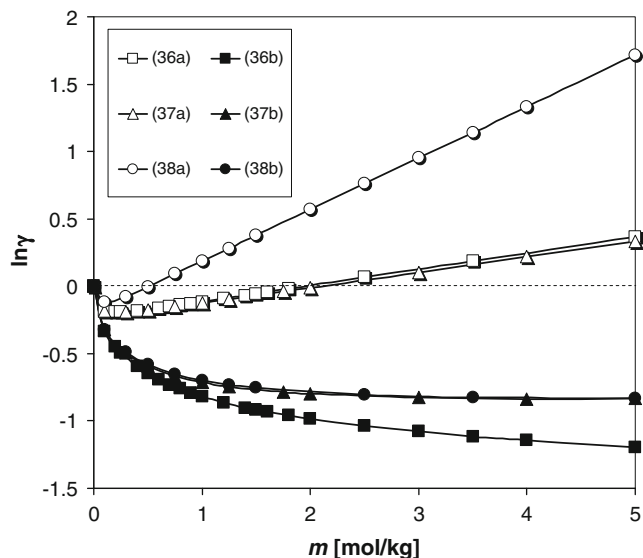


Fig. 7 Individual factor functions on a logarithmic scale obtained by splitting for pure NaClO_4 solutions $\{\ln \bar{\gamma}_{\text{Na}^+}(m)$ (= 36a) and $\ln \bar{\gamma}_{\text{ClO}_4^-}(m)$ (= 36b) $\}$ and for the mixed electrolyte solutions $0.01m$ NaCl in NaClO_4 $\{\ln \bar{\gamma}_{\text{Na}^+}(m)$ (= 37a) and $\ln \bar{\gamma}_{\text{Cl}^-}(m)$ (= 37b) $\}$ and for $0.01m$ HCl in NaClO_4 $\{\ln \bar{\gamma}_{\text{H}^+}(m)$ (= 38a) and $\ln \bar{\gamma}_{\text{Cl}^-}(m)$ (= 38b) $\}$

the mixed electrolyte solutions $0.01m$ HCl in NaClO_4 solutions [20, 26], $0.01m$ NaCl in NaClO_4 solutions [20, 26], $0.01m$ NaOH in NaClO_4 solutions [20, 26], $0.01m$ HCl in KCl solutions [14], and $0.01m$ HCl in SrCl_2 solutions [25]. The values are valid for the concentration range (ionic strength) from zero up to 5 mol/kg [14].

On the allocation of the factor functions to the cation or anion

Electrolyte solutions containing a great surplus of neutral salt additionally

The allocation of the factor functions to the cation or anion is possible in the case of the polyvalent electrolytes from the results of calculation if the exponents (ν_+ ; ν_-) of the factor functions of the basic product approach (21) have different values. With equal exponents and thus for all uni-univalent electrolytes too, it is not possible to decide on a purely mathematical basis which of the two obtained factor functions of the basic product approach (20) describes the concentration curve of the activity coefficients of the cation or anion. The factor functions can be allocated clearly to either the cation or the anion [14] with the help of specially mixed electrolyte solutions.

Mixed electrolyte solutions (such solutions contain a strong electrolyte $\kappa\alpha$ as well as a great surplus of neutral salt) are suitable for taking a decision if the general condition $m_{\kappa\alpha} \ll m_{\text{neutral salt}}$ is valid. Besides mean activity coefficients, the ratio of single-ion activity coefficients in these especially mixed electrolyte solutions can also be determined by implication [14]. In electrolyte mixtures with this special composition, the interionic interaction between the ions of the diluted electrolyte $\kappa\alpha$ one with another is negligibly small compared to the interactions with the ions of the neutral salt which are in great surplus in the electrolyte mixture [14, 20, 45]. Hence, diluted electrolytes (e.g., NaCl and HCl or HCl and HBr), each with a great surplus of the neutral salt NaClO_4 of the same concentration, have the same individual activity coefficient in consideration of the common ion species [14, 20, 21, 45]: $\gamma_{\text{Cl}^-}(\text{NaCl in NaClO}_4) = \gamma_{\text{Cl}^-}(\text{HCl in NaClO}_4)$ or $\gamma_{\text{H}^+}(\text{HCl in NaClO}_4) = \gamma_{\text{H}^+}(\text{HBr in NaClO}_4)$. The single-ion activity coefficient of the Na^+ ions of the dilute electrolyte NaCl in the mixed electrolyte solution containing a great surplus of NaClO_4 equals the single-ion activity coefficient of the Na^+ ions in the pure NaClO_4 solution of the same concentration: $\gamma_{\text{Na}^+}(\text{NaCl in NaClO}_4) = \gamma_{\text{Na}^+}(\text{pure NaClO}_4)$ [14, 20, 45]. The absolute values are still unknown. The mean activity coefficients of the diluted electrolytes $\kappa\alpha$ (NaCl and HCl or HCl and HBr , each in solutions containing a great surplus of NaClO_4 of the same concentration) are certainly different as a result of the different

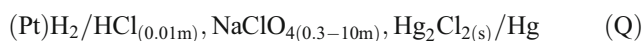
magnitude of the individual activity coefficients of the counter ions [14, 21, 45], for instance: $\gamma_{\text{Na}^+}(\text{NaCl in NaClO}_4) \neq \gamma_{\text{H}^+}(\text{HCl in NaClO}_4)$ and $\gamma_{\text{Cl}^-}(\text{HCl in NaClO}_4) \neq \gamma_{\text{Br}^-}(\text{HBr in NaClO}_4)$. The mean activity coefficient of a fourth electrolyte can be calculated from the mean activity coefficients of three other electrolytes [14], e.g., $\gamma_{\pm\text{HCl}}^2 \cdot \gamma_{\pm\text{NaBr}}^2 / \gamma_{\pm\text{NaCl}}^2 = \gamma_{\pm\text{HBr}}^2$ in the case of diluted electrolytes (each with a great surplus of the neutral salt NaClO₄ of the same concentration). Of course, in this way the quotients of single-ion activity coefficients are known in these mixed electrolyte solutions by implication [14, 21], e.g.: $\gamma_{\text{H}^+} / \gamma_{\text{Na}^+}$ and $\gamma_{\text{Br}^-} / \gamma_{\text{Cl}^-}$. This was verified by factorizing the mean activity coefficients of the diluted electrolyte $\gamma_{\pm\kappa\alpha}^2$ (by $m_{\kappa\alpha} = 0.01 = \text{const.}$) as a function of the neutral salt concentration by estimating the parameters of the basic approach (20) using the asymptotic theory like the one shown previously [14, 20, 24, 25]. The theoretically required agreement is also confirmed by a comparison with the calculated individual activity coefficients of the ions of the pure neutral salt (see also "Splitting of mean activity coefficients into individual parts for complementary ion species by using the asymptotic theory" section).

Diluted NaCl solution and diluted HCl solution:
each of these solutions with a great surplus of NaClO₄

The squares of the mean activity coefficients of diluted NaCl and diluted HCl, respectively, each with a great surplus of the neutral salt NaClO₄, were split as a function of the NaClO₄ concentration using the asymptotic theory. The concentration of the diluted electrolytes NaCl and HCl in the electrolyte mixtures was held constant at 0.01 mol/kg; the concentration of the neutral salt NaClO₄ was varied in $0.3 \leq m_{\text{NaClO}_4} \leq 10$ mol/kg. The mean activity coefficients of 0.01m NaCl as a function of the concentration of the neutral salt NaClO₄ were determined accurately thermodynamically by using e. m. f. measurements with the galvanic cell without transport (P). These results have already been published [20, 45]:



The mean activity coefficients of 0.01m HCl as a function of the concentration of the neutral salt NaClO₄ were determined accurately thermodynamically by using e. m. f. measurements with the galvanic cell without transport (Q). These results have already been published as well [20, 45]:



The functions for determining the ordinate intercept and the slope of $\ln \gamma_{\pm}^2$ vs. m_{NaClO_4} are also depicted in Fig. 4 for both of these mixed electrolyte systems. The ordinate intercept of $\ln \gamma_{\pm\text{NaCl}}^2$ vs. m_{NaClO_4} is $\beta_2 = \ln[(1 - b_{1(P)})(1 - b_{2(P)})] =$

-1.1500154 , and for $\ln \gamma_{\pm\text{HCl}}^2$ vs. m_{NaClO_4} it is $\beta_3 = \ln[(1 - b_{1(Q)})(1 - b_{2(Q)})] = -1.0696678$.

For the sole determination of $b_{1(P)}$ and $b_{2(P)}$ (valid for the system NaCl/NaClO₄), respectively, of $b_{1(Q)}$ and $b_{2(Q)}$ (valid for the system HCl/NaClO₄), the values for the mean activity coefficients of NaCl and HCl, respectively, are required in the electrolyte mixture with NaClO₄ at a concentration of $m_{\text{NaClO}_4} = 0.001\text{mol/kg}$. These values have only hypothetical character because it is difficult to prepare a corresponding electrolyte mixture with the required precondition $m_{\text{NaClorHCl}} \ll m_{\text{NaClO}_4}$. For additional details, see reference [20]. The corresponding values are $\gamma_{\pm\text{NaCl}}^2 = 0.931312$ and $\gamma_{\pm\text{HCl}}^2 = 0.931896$ [20]. With these values in Eq. (33) and by using the corresponding ordinate intercepts, the values $b_{1(P)}$ and $b_{2(P)}$ (for NaCl in NaClO₄ solutions) are calculated to be 0.2135 and 0.5974, respectively, and the values $b_{1(Q)}$ and $b_{2(Q)}$ (for HCl in NaClO₄ solutions) are calculated to be 0.1773 and 0.5829, respectively.

From the slope $(b_{3(P)} + b_{4(P)}) = 0.1259$ for 0.01m NaCl in NaClO₄ solutions the values $b_{3(P)}$ and $b_{4(P)}$ yield 0.1145 and 0.0114, respectively, and from the slope $(b_{3(Q)} + b_{4(Q)}) = 0.3875$ for 0.01m HCl in NaClO₄ solutions the values $b_{3(Q)}$ and $b_{4(Q)}$ result in 0.3823 and 0.0052, respectively, by using the Fibonacci search technique [44].

The individual parts for the single-ion species of 0.01m NaCl in NaClO₄ solutions are calculated using (20) from (see footnote 3):

$$\bar{\gamma}_{1(P)}(m) = 0.2135 e^{-\frac{1.1711\sqrt{m}}{0.2135}} + 0.7865 e^{0.1145 m} [= \bar{\gamma}_{\text{Na}^+_{(P)}}(m)] \quad (37a)$$

$$\bar{\gamma}_{2(P)}(m) = 0.5974 e^{-\frac{1.1711\sqrt{m}}{0.5974}} + 0.4026 e^{0.0114 m} [= \bar{\gamma}_{\text{Cl}^-_{(P)}}(m)] \quad (37b)$$

and the individual parts for the single-ion species of 0.01m HCl in NaClO₄ solutions from:

$$\bar{\gamma}_{1(Q)}(m) = 0.1773 e^{-\frac{1.1711\sqrt{m}}{0.1773}} + 0.8227 e^{0.3823 m} [= \bar{\gamma}_{\text{H}^+_{(Q)}}(m)] \quad (38a)$$

$$\bar{\gamma}_{2(Q)}(m) = 0.5829 e^{-\frac{1.1711\sqrt{m}}{0.5829}} + 0.4171 e^{0.0052 m} [= \bar{\gamma}_{\text{Cl}^-_{(Q)}}(m)] \quad (38b)$$

The factor functions can be allocated clearly to either the cation or the anion

The allocation to the cation or anion is not possible either for the mixed electrolyte solutions. Only comparative studies of the individual functions for the single-ion species in the three electrolyte systems (1) 0.01m NaCl in NaClO₄ solutions, (2) 0.01m HCl in NaClO₄ solutions, and (3) pure NaClO₄ solutions are able to be allocated to the cation or the anion.

In Fig. 7, the individual functions for the single-ion species for NaCl in NaClO₄ solutions $\ln \bar{\gamma}_{1(P)}(m)$ (= 37a) and $\ln \bar{\gamma}_{2(P)}(m)$ (= 37b), and for HCl in NaClO₄ solutions $\ln \bar{\gamma}_{1(Q)}(m)$ (= 38a) and $\ln \bar{\gamma}_{2(Q)}(m)$ (= 38b) are plotted together with the individual functions for the single-ion species for pure NaClO₄ solutions $\ln \bar{\gamma}_1(m)$ (= 36a) and $\ln \bar{\gamma}_2(m)$ (= 36b). It shows that the individual functions for $\ln \bar{\gamma}_{2(P)}(m)$ (= 37b) in the electrolyte mixture NaCl/NaClO₄ agree with the individual functions for $\ln \bar{\gamma}_{2(Q)}(m)$ (= 38b) in the electrolyte mixture HCl/NaClO₄. Thus, these factor functions are allocated to the Cl⁻ ion in the mixed electrolyte solutions NaCl/NaClO₄ and HCl/NaClO₄. Good agreement is shown by the individual function for $\ln \bar{\gamma}_{1(P)}(m)$ (= 37a) in the electrolyte mixture NaCl/NaClO₄ with the individual function for $\ln \bar{\gamma}_1(m)$ (= 36a) in the pure NaClO₄ solutions. These factor functions thus describe the individual concentration curves for the activity coefficients of the single-ion species Na⁺ in a pure NaClO₄ solution and in the electrolyte mixture NaCl/NaClO₄. The agreements that have been found allow the clear allocation of the obtained factor functions to the cation or anion [20, 26].

The theoretically required agreements in the individual factor functions are also found by factorizing the mean activity coefficients of other diluted electrolytes, each with a great surplus of neutral salt e.g. for the mixtures 0.01 *m* NaOH in NaClO₄ solutions [20, 26], 0.01 *m* HCl in KCl solutions [14], and 0.01 *m* HCl in SrCl₂ solutions [25].

However, it is not necessary to carry out the direct comparison for every single uni-univalent electrolyte with corresponding suitable three-component systems to decide on the allocation of the obtained factor functions to the cation or anion. A multitude of electrolytes affirm that the calculated individual activity coefficients of the cations and anions show a characteristic shape in the concentration curve [14, 24, 25], which always differs. Thus, a corresponding allocation is possible by means of analog curve shapes.

For multivalent electrolytes, whose allocation is already decided from the result of the parameter estimation due to different large exponents ($\nu_+ \neq \nu_-$) on the factor functions of the basic product approach (21), the characteristic difference was also confirmed between the concentration curves of the calculated individual activity coefficients of the cations and anions [14, 25].

Discussion of the approach and parameter determination

The mathematical approach

The classical approximation (5) or (6), respectively, regarding the concentration curve of mean activity coefficient cannot be split clearly into individual functions for the ionic species. An

attempt to factorize it yields infinite solutions. Approaches (3) and (4), by contrast, have a different mathematical structure compared to the classical approximation approach. It is possible, at least in principle, to unequivocally factorize approaches (3) and (4), respectively.

The structure of mathematical approaches (3) and (4) considers the infinitely dilute solution as one fixed point. It is possible to make accurate statements about the individual activity coefficients only to this point of reference. In addition, a special concentration range exists indirectly for those statements about individual activity coefficients. This is the range $5 \leq m \leq 10$ mol/kg, where the logarithm of the mean activity coefficient is linearly dependent on the concentration (see Fig. 4). The mathematical approach is based on this concentration range, too. If the sum of two functions results in a linear function on the concentration, it is very probable that both single functions have to be linearly dependent on the concentration as well (see (39), compare for it (31)):

$$\begin{aligned} 2 \ln \gamma_{\pm}(m) &= \Phi \cdot m + \rho = \ln \gamma_C(m) + \ln \gamma_A(m) \\ &= \phi_C \cdot m + \rho_C + \phi_A \cdot m + \rho_A \end{aligned} \quad (39)$$

(concerning the concentration range $5 \leq m \leq 10$ mol/kg) with $\Phi, \phi_C, \phi_A, \rho, \rho_C, \rho_A = \text{const.}$ where $\Phi = \phi_C + \phi_A = b_3 + b_4$ and $\rho = \rho_C + \rho_A = \ln(1 - b_1) + \ln(1 - b_2)$

There is only one exception to this rule in mathematic. The differences in the linearity of the two functions are exactly compensated for in form and size. Such a coincidence for individual activity coefficients is not thought to be plausible in view of mathematical and physical aspects. That means that the logarithms of the individual activity coefficients of complementary ion species should be linearly dependent on the concentration in this range $5 \leq m \leq 10$ mol/kg. This fact is considered by the second summands in both of the factor functions in (18).

Nonetheless, the consequence of this exception when calculating the individual activity coefficients will be discussed later (see "Impact of a hypothetical multiplicative concentration function G" section). A predefinition was not established for the concentration range between infinite dilution and 5 mol/kg. The values in this concentration range result from the sum of the first and the second summand in the factor functions in (18). Accordingly, when compared with data of the mean activity coefficients from the literature, the product of the calculated individual activity coefficients in this range demonstrates a criterion for successfully adjusting the experimentally obtained mean activity coefficients. Thus, the approach (18) is derived from mathematical considerations and differs in principle from the classical approximation of the mean activity coefficient to the concentration curve (see (5) and (6), respectively, and footnote 1).

The determination of the parameters

If only the first summand is considered in both factor functions (see (10)), the nonlinear least squared yields a great many sets of best fit independent parameters that minimize the squared deviations of $\bar{\gamma}_C \cdot \bar{\gamma}_A$ from γ_{\pm}^2 .

Fortunately, the data for the individual activity coefficients are known at concentration zero. These limiting infinite dilution conditions (12) and (14) clearly require for (10): $c_1=c_2=1$ and $c_7=c_8=-A'$. These values are strictly valid only at infinite dilution where the activity coefficients have the same size as well as the same slope. This is valid for all ionic species with the same charge number. Thus, the resulting relationship agrees with the Debye–Hückel limiting law equation. It is necessary to take into consideration the first two summands in both factor functions when factorizing the mean activity coefficient as the electrolyte concentration approaches zero, too (see "Consideration of the first two summands" section). It is important to bear in mind the fact that the product function parameters in (3) and (4), respectively, change when an additional summand is included in both factor functions because the system of functions is not orthogonal. This means for (18) compared to (10): $c_1 \neq c_2 \neq 1$ and $c_7 \neq c_8 \neq -A'$, but the limiting infinite dilution conditions (12) and (14) clearly require for the parameters in (18): $c_1 = b_1, c_2 = b_2, c_7 = -\frac{A'}{b_1}, c_8 = -\frac{A'}{b_2}$, and $c_3 = (1 - b_1), c_4 = (1 - b_2)$ as well. The nonlinear least squared yield for approach (20), just like the optimization of (10), many sets of best fit independent parameters b_1, \dots, b_4 of $\bar{\gamma}_C(m) \cdot \bar{\gamma}_A(m)$ for $\gamma_{\pm}^2(m)$ as a consequence of the ill-condition of coefficient matrix. All combinations are nearly equally suitable for fitting the concentration curve of the mean activity coefficients (see "Mathematically correct solutions and physicochemically reasonable results" section). This problem is solved with the help of the previously developed asymptotic theory [20, 26]. A successive estimation of the parameters is univocally possible (see "Splitting of mean activity coefficients into individual parts for complementary ion species by using the asymptotic theory" section). Stable and reproducible results are attained by using the asymptotic theory. The parameter combination is invariant. The basic product approach (20) is to unequivocally split into factor functions (see "Splitting of mean activity coefficients into individual parts for complementary ion species by using the asymptotic theory" section).

The parameters b_1 and b_2 and the sum $(b_3 + b_4)$ can be determined directly with the asymptotic theory (see "Splitting of mean activity coefficients into individual parts for complementary ion species by using the asymptotic theory" section). The determination of b_1 and b_2 is shown in Fig. 5 with the functions (32) and (33).

The ill-condition of (20) unfavorably influences the separation of the sum $(b_3 + b_4)$ in summands only. But the

variation width of b_3 and b_4 is limited during the separation of the sum $(b_3 + b_4)$ which is considered as a function of b_3 only because b_1, b_2 and the sum $(b_3 + b_4)$ have already been determined. The separation of the sum $(b_3 + b_4)$ is carried out using the Fibonacci search technique [44] in the range of the strongest curvature of the $\gamma_{\pm}-m$ curve ($0 \leq m \leq 5$ mol/kg).

The allocation of the determined factor functions to cation or anion is clearly decided with the help of mixed electrolyte solutions (see "On the allocation of the factor functions to the cation or anion" section).

Impact of a hypothetic multiplicative concentration function G

The impact of the exceptional case mentioned above is discussed based on the calculation of individual activity coefficients as follows.

The factorizing of $\gamma_{\pm}^2(m)$ using the asymptotic theory is univocal. Thus, it is obtained only one unique pair of factor functions. This pair represents the factor functions of the mathematical approach $\gamma_C(m)$ and $\gamma_A(m)$, and it cannot be any other pair of factor functions because the parameters of the approach are determined directly with the help of the asymptotic theory. Nevertheless, it is to consider the fact that the result could be ambiguous assuming a hypothetic concentration function G is valid. The condition is then following:

$$\gamma_C(m) \cdot G \cdot \gamma_A(m) \cdot G^{-1} = \bar{\gamma}_C^*(m) \cdot \bar{\gamma}_A^*(m) \text{ or vice - versa.} \quad (40)$$

This conforms to an 'extension' of the product function (20):

Considering the product function (20) in logarithmic form is confusing when dealing with this topic.

In the case of an "extension" of the basic product approach (20), multiplication or division of both factor functions have to be certainly valid for each separated summand in the factor functions:

$$\begin{aligned} \gamma_{\pm}^2(m) &= \bar{\gamma}_C^*(m) \cdot \bar{\gamma}_A^*(m) \\ &= \left[b_1 e^{-\frac{A'}{b_1} m^{\frac{1}{2}}} \cdot G + (1 - b_1) e^{b_3 \cdot m} \cdot G \right] \\ &\quad \cdot \left[b_2 e^{-\frac{A'}{b_2} m^{\frac{1}{2}}} \cdot G^{-1} + (1 - b_2) e^{b_4 \cdot m} \cdot G^{-1} \right] \end{aligned} \quad (41)$$

$\bar{\gamma}_C^*(m); \bar{\gamma}_A^*(m)$: "modified factor functions of cations and canions"

$$\left[\bar{\gamma}_C^*(m) = \gamma_C(m) \cdot G; \bar{\gamma}_A^*(m) = \gamma_A(m) \cdot G^{-1} \right]$$

This case has already been the subject of previous discussion [46, 47]. The question examined in this context was whether or not the individual ionic activity coefficients

calculated using the asymptotic theory are unsuitable due to the mathematical “extension” of the basic product approaches (20) and (21) with an arbitrary function G [46, 47]. It was proven that such a hypothetical function G cannot be chosen anyway, since it is constrained to the following function type [46]:

$$G = e^{K \cdot m^w} \quad (K, w = \text{constants}) \quad (42)$$

This hypothetical function G would have to have an almost universal character for all electrolytes that make the a priori existence of such a function improbable [25, 46]. The verification of the exclusion of a possible “extension” of the basic product approaches (20) and (21), respectively, whereby $G = e^{K \cdot m^w}$ can be reduced to the demonstration $K=0$.

It was shown in “Consideration of only the first summand” section that the basic product approach (3), containing only the first summand in both factor functions, has to be identical to the Debye–Hückel limiting law equation. Results for the corresponding first summands consist of the expressions $e^{-A' \cdot \sqrt{m}} \cdot e^{K \cdot m^w}$ and $e^{-A' \cdot \sqrt{m}} \cdot e^{-K \cdot m^w}$, respectively, after “extension” with the hypothetical function $G = e^{K \cdot m^w}$. Identity with the Debye–Hückel limiting law exists for $m > 0$ only at $K=0$. Moreover, an activity coefficient of a strong uni-univalent or uni-bivalent electrolyte cannot be lower than what the Debye–Hückel limiting law permits (see footnote 2). It also follows that $K=0$. Therefore, possible “extension” of the basic product approaches is excluded in principle.

Factorizing the mean activity coefficient into individual parts for a single-ion species using the asymptotic theory is actually univocal. By the exclusion of additional multiplicative terms, it is proven that the results comply in all probability with the physicochemical reality and are not a random pair of factor functions. The results are conformable with experimentally obtained quotients of single-ion activity coefficients in ternary systems. This is valid for the concentration range between 0 and 5 mol/kg [14] (see “On the allocation of the factor functions to the cation or anion” and “Validity of factor functions has to be calculated using the asymptotic theory” sections).

Discussion of results using corresponding approximations

Validity of factor functions has to be calculated using the asymptotic theory

The lack of consequences of using the corresponding approximations in the asymptotic theory can be minimized by iterative refinement [25]. The iteration converges rapidly. The question is how far the asymptotic theory

generates a systematic error in the result. The resulted linear course of $\ln \bar{\gamma}_C$ and $\ln \bar{\gamma}_A$ versus m or J , respectively, at very high concentrations ($m, J > 10$ mol/kg, see references [14, 20, 24, 25]) which is obtained from asymptotic theory does not necessarily depict reality.

The basic product approaches (20) and (21), respectively, as well as the asymptotic theory do not reflect the turning point which generally can be observed at very high concentrations if the curve of $\ln \gamma_{\pm}^{v_+ + v_-}$ versus m or J , respectively, is measured. Hence, consequences for the calculated curve of the individual activity coefficients are expected. The effects appear at high concentrations. Although the consideration of the mean activity coefficients in the concentration ranges between 5 and ca. 10 mol/kg is necessary for the use of the asymptotic theory, the scope of the calculated individual activity coefficients has to be limited to concentrations up to 5 mol/kg. This is a result of the comparisons with quotients of single-ion activity coefficients that were determined experimentally [14].

The quotients $\frac{\bar{\gamma}_{Cl^-}^{(P/Q)}}{\bar{\gamma}_{ClO_4^-}} (= A)$ and $\frac{\bar{\gamma}_{H^+}^{(Q)}}{\bar{\gamma}_{Na^+}^{(P)}} (= B)$ can be determined by factorizing with the help of the calculated individual activity coefficients for the single-ion species in the mixed electrolyte solutions. These are compared with each of the experimentally determined ratio of the single-ion activity coefficients $\frac{\gamma_{Cl^-}}{\gamma_{ClO_4^-}} (= C)$ and $\frac{\gamma_{H^+}}{\gamma_{Na^+}} (= D)$ [14, 21]. The ratio of single-ion activity coefficients is defined thermodynamically [2, 48]. The curves are shown on a logarithmic scale in Fig. 8 as a function of m_{NaClO_4} . The agreement is certainly due to the $NaClO_4$ concentration of $m=5$ mol/kg. In light of these findings, it is clear that

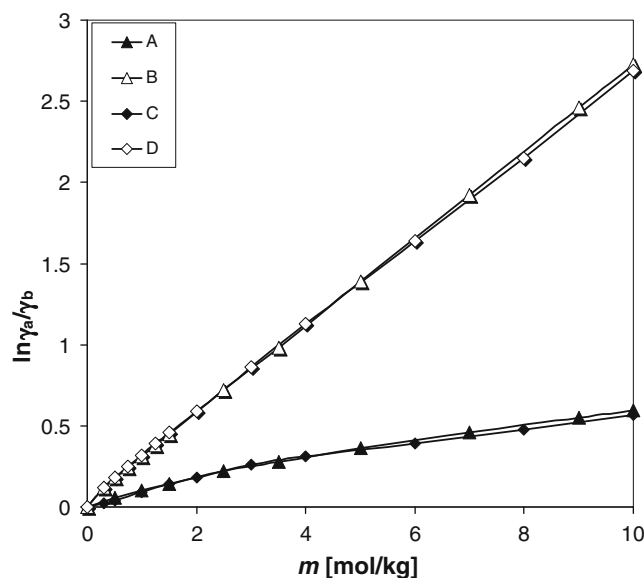


Fig. 8 The quotients $\frac{\bar{\gamma}_{Cl^-}^{(P/Q)}}{\bar{\gamma}_{ClO_4^-}} (A)$ and $\frac{\bar{\gamma}_{H^+}^{(Q)}}{\bar{\gamma}_{Na^+}^{(P)}} (B)$ obtained by splitting of mean activity coefficients compared with the experimentally determined quotients of the single-ion activity coefficients $\frac{\gamma_{Cl^-}}{\gamma_{ClO_4^-}} (= C)$ and $\frac{\gamma_{H^+}}{\gamma_{Na^+}} (= D)$ on a logarithmic scale as a function of the $NaClO_4$ concentration

plausible results are achieved with the asymptotic theory in the concentration range $0 \leq m \leq 5$ mol/kg.

As Ferse has shown for other electrolyte systems also [14], the experimentally determined quotients of individual activity coefficients of single-ion species in especially composed electrolyte mixtures agree with quotients of calculated individual activity coefficients determined using the asymptotic theory. The agreement is excellent between 0 and 5 mol/kg [14]. In all probability, the differences at higher concentrations are due to the limited validation of the basic approaches (20) respectively (21) used. It is easy to understand that the extended basic product approach (26) with eight parameters cannot be handled with the help of the asymptotic theory. In this respect, a reliable determination of the individual activity coefficients of single-ion species above the concentration of m or J , respectively, ≈ 5 mol/kg is not possible in this way. To solve this problem, it is possible to combine the results of the asymptotic theory with the factorization of the extended basic product approach (26) using the non-linear regression model. Test calculations seem to be successful.

Results obtained by applying the asymptotic theory compared with other methods for calculating single-ion activity coefficients

A comparison with results from established methods of statistical mechanics (mean spherical approximation [MSA], Monte Carlo data) does not allow exact conclusions to be drawn about the reliability of results obtained with the help of asymptotic theory. It is more difficult to detect the real conditions in an electrolyte solution quantitatively and without randomness as the distance from the Debye–Hückel range increases. All methods for estimating the excess Gibbs energy of an electrolyte in solution are based on models that are only effective for limited concentration ranges. The model concepts have to be modified if the results do not comply closely enough with the measured data.

The use of asymptotic theory is a purely mathematical method; therefore, (1) it is independent of a model for interpreting the microscopic structure of an electrolyte solution and (2) it is not limited to detecting and calculating all forming interaction forces in an electrolyte solution. The problems caused by applying the asymptotic theory are of a quite different nature. They result from the application of a purely mathematical method to a real, concrete situation. They are presented in "Choice of a limited concentration range" and "Mathematically correct solutions and physicochemically reasonable results" sections in the present publication. A practicable way of the solution is described in "Splitting of mean activity coefficients into individual parts for complementary ion species by using the asymptotic theory" and "Discussion of the approach and parameter determination"

section. The results obtained are clear and reproducible. The purely mathematical procedure is meaningful as an addition to the established methods of statistical mechanics.

The results obtained by using of asymptotic theory exhibit the same trend in ranking the individual activity coefficients of the alkali halides as the MSA [49] and Monte Carlo simulations [50]. Admittedly, these calculations are limited to the concentration range 0 up to 1 mol/l. The MSA method and Monte Carlo simulations are unsuitable at higher concentrations. The impact of the ionic parameters on the individual activity coefficients is accepted. Obviously, a mistake was made when the data of diagram 13 [49] was compared, since the differences are smaller than seen in the figure. Perhaps it is not surprising that there are differences because the activity coefficients represent all deviations from an ideal state. Besides the size of the ion, the impacts of the structure of the electrolyte solution and of a number of additional factors have to be considered. Calculations conducted with the purely mathematical procedure of asymptotic theory are independent of such influences.

The Pitzer model [27] is efficient for mean activity coefficients. Vera et al. modified the Pitzer equations for single-ion species [51]. The modified equations contain two parameters which are always valid for one ion species only. These are fitted from calculated individual activity coefficients. In this respect, they are unsuitable as a basis for confirming these single-ion activity coefficients. Vera et al. determined individual activity coefficients using ion-selective electrodes in electrochemical cells with transport. The liquid junction potential is taken into account by using approximated calculations [51, 52]. This is no way to obtain single-ion activity coefficients [14]. Malatesta [53] also doubts the correctness of this method. In principle, he excludes such a possibility of determining individual activity coefficients. That way it is not astonishing that the single-ion activity coefficients of Vera et al. [51] do not agree with the values which were calculated with the help of asymptotic theory [14, 24, 25].

A new method for measuring individual ionic activity coefficients is proposed by Zhuo, Dong, Wang, and Wanga [54]. It was used to obtain single-ion activity coefficients of sodium halides in aqueous solutions up to about 1 mol/kg. However, every experimental method to achieve individual activity coefficients of single-ion species is to be regarded as incorrect. A critical discussion of this problem is given by Malatesta in 2010 [55].

Correlations between the calculated individual activity coefficients and ionic size

The calculated single-ion activity coefficients of anions of the alkali halides and the alkaline earth halides, which are determined from the factor functions of the basic

approaches (20) and (21), respectively, using the asymptotic theory show a shallow minimum as function of the concentration [14, 20, 24, 25]. The influence of the anions on the magnitude of the cation activity coefficients is great. For instance, at the ionic strength $J=3$ mol/kg the calculated single-ion activity coefficients⁶ of magnesium halides are [14, 25]: $\bar{\gamma}_{\text{Mg}^{++}(\text{MgCl}_2)} = 2.12$; $\bar{\gamma}_{\text{Mg}^{++}(\text{MgBr}_2)} = 3.75$; $\bar{\gamma}_{\text{Mg}^{++}(\text{MgI}_2)} = 7.53$; $\bar{\gamma}_{\text{Cl}^-(\text{MgCl}_2)} = 0.28$; $\bar{\gamma}_{\text{Br}^-(\text{MgBr}_2)} = 0.29$; $\bar{\gamma}_{\text{I}^-(\text{MgI}_2)} = 0.28$. In general, with regard to the same cation, the calculated single-ion activity coefficient is greater for the anion with the greater radius. But the differences between their absolute values are small [14, 24, 25]. The complex perchloric anion is an exception [20, 25]. The calculated single-ion activity coefficients of chloride anions do not reach values higher than one in the concentration range up to 5 mol/kg (see Table 1). Such an assumption was already derived from the interpretation of the results of experimental investigations [48, 56–58]. It is affirmed by the results of asymptotic theory. The calculated single-ion activity coefficients of Cl^- ions of the alkali chlorides are summarized in Table 1. The minimum of the calculated individual activity coefficients of the Cl^- ions in the ranking from LiCl to CsCl is striking. A similar minimum may be found in the case of the activity coefficients of Cl^- ions in the homologous series of the alkaline earth chlorides [25].

The grading in the homologous series of alkali cations and alkaline earth cations in their chlorides correlates with the reciprocal ionic diameter of their non-hydrated cations [14, 24, 25] in agreement with the results by Bates, Staples and Robinson [4], who suggest this circumstance based on the hydration hypothesis by Stokes and Robinson [59]. The smallest alkali cation Li^+ exhibits the highest individual activity coefficient, whereas the large ion Cs^+ shows the lowest single-ion activity coefficient in the alkali chlorides. The values for the cations of alkali chlorides [14, 24] are shown in Table 1 also.

By contrast, the relation of the calculated individual activity coefficients of the cations of the alkali hydroxides is directly proportional to the diameter of their non-hydrated cations. They increase with increasing diameter of the non-hydrated cations [14, 24]. The values of the calculated individual activity coefficients for alkali hydroxides, e.g., at 5 mol/kg, are [14, 24]: $\bar{\gamma}_{\text{C}^+}$; $\bar{\gamma}_{\text{Cl}^-}$; $\bar{\gamma}_{\text{C}^+}$; $\bar{\gamma}_{\text{Cl}^-}$. In all probability, the contrast results from the exceptional position in the behavior of the hydroxide ions (and hydrogen ions) in the solvent water. It is known that the surplus hydroxide ions and protons as they exist in aqueous basic and acidic solutions need only very low activation energy to jump from one water molecule to another [60]. The transition frequency is on the order of magnitude 10^{12} s^{-1} [61].

Every water molecule has a very high affinity to OH^- or H^+ ions, respectively. Therefore, in temporal average, every single water molecule has a negative or positive partial charge if it is in alkaline or acidic solutions. This model allows the forming of a specific electrostatic interaction between the partial charges of the water molecules among each other and between the partial charges of the water molecules in the hydration sphere and the charges of cations of the alkali hydroxides or the anions of the acids [14, 21, 24, 60, 62]. This model explains also the unusual ranking of the calculated individual activity coefficients not only of the cations of the alkali hydroxides but also of the halide anions in hydrohalic acids [14, 24]. The small anion Cl^- of the hydrochloric acid has the largest individual activity coefficient, the anion I^- of the hydroiodic acid the lowest one. The calculated individual activity coefficients of the hydrogen ions of the hydrohalic acids increase extremely with rising concentration [14, 24] (see Table 2): Certainly, electrostatic forces cannot be responsible solely for the cause of the interaction, but in this model, the excess Gibbs energy can be estimated in good agreement with the experiments in aqueous acidic and hydroxide solutions on the basis of the electrostatic interaction [21]. A separate publication containing a detailed discussion of this topic is in preparation.

Concluding remarks

The individual activity of a single-ion species cannot be defined thermodynamically nor can it be determined experimentally. However, this does not mean that one can simply conclude that the individual activity of a single-ion species of an aqueous strong electrolyte has no real efficacy singly. On the contrary, the ratio of the individual activities of two ion species with the same charge is exactly defined in thermodynamic terms [2, 48]. Quotients of individual activities or individual activity coefficients of single-ion species can also be determined experimentally by implication using thermodynamically precise methods [14]. The quotients can differ significantly from 1 [14, 21, 63]. Hence, it is known that the thermodynamic efficacies of different ionic species with the same charge may differ from one other by more than one order of magnitude in electrolyte mixtures of the same composition [14, 21]. These important differences in values between the individual activity coefficients of different ionic species cannot be ignored. There is therefore no justification in using mean activity coefficients for the thermodynamic interpretation of equilibria and processes where dissolved electrolytes are participating. Such a procedure implies the risk of arriving at erroneous conclusions.

The search for a way out of this dilemma is legitimate and necessary.

⁶ According to IUPAC recommendation is the activity coefficient dimensionless

Table 1 Calculated individual activity coefficients of the single-ion species of alkali chlorides, alkali cations $\bar{\gamma}_{C^+}$, and chloride anions $\bar{\gamma}_{Cl^-}$, determined by the asymptotic theory, concentration range up to 5 mol/kg

Electrolyte		LiCl	NaCl	KCl	RbCl	CsCl
Parameters [14] corresponding to basic approach (20)	b_1	0.1580	0.1991	0.2117	0.2149	0.2180
	b_2	0.7861	0.7012	0.6949	0.7239	0.7555
	b_3	0.4143	0.1322	0.00288	-0.0529	-0.2462
	b_4	0.2057	0.1018	0.07321	0.1150	0.2773
Concentration m [mol/kg]						
$m=0.001$	$\bar{\gamma}_{C^+}$	0.967	0.966	0.966	0.966	0.966
	$\bar{\gamma}_{Cl^-}$	0.964	0.964	0.964	0.964	0.964
$m=0.005$	$\bar{\gamma}_{C^+}$	0.937	0.933	0.931	0.931	0.930
	$\bar{\gamma}_{Cl^-}$	0.922	0.922	0.922	0.922	0.922
$m=0.01$	$\bar{\gamma}_{C^+}$	0.921	0.913	0.910	0.909	0.907
	$\bar{\gamma}_{Cl^-}$	0.892	0.892	0.892	0.892	0.892
$m=0.02$	$\bar{\gamma}_{C^+}$	0.904	0.890	0.885	0.884	0.880
	$\bar{\gamma}_{Cl^-}$	0.852	0.853	0.853	0.853	0.853
$m=0.05$	$\bar{\gamma}_{C^+}$	0.890	0.860	0.850	0.847	0.838
	$\bar{\gamma}_{Cl^-}$	0.779	0.783	0.783	0.782	0.782
$m=0.1$	$\bar{\gamma}_{C^+}$	0.893	0.843	0.825	0.819	0.803
	$\bar{\gamma}_{Cl^-}$	0.709	0.715	0.715	0.713	0.714
$m=0.5$	$\bar{\gamma}_{C^+}$	1.04	0.859	0.794	0.769	0.696
	$\bar{\gamma}_{Cl^-}$	0.511	0.530	0.528	0.523	0.533
$m=1.0$	$\bar{\gamma}_{C^+}$	1.27	0.915	0.791	0.751	0.612
	$\bar{\gamma}_{Cl^-}$	0.440	0.463	0.457	0.453	0.483
$m=2.0$	$\bar{\gamma}_{H^+}$	1.93	1.04	0.793	0.706	0.478
	$\bar{\gamma}_{A^-}$	0.418	0.432	0.417	0.421	0.511
$m=3.0$	$\bar{\gamma}_{C^+}$	2.92	1.19	0.795	0.670	0.374
	$\bar{\gamma}_{Cl^-}$	0.456	0.444	0.418	0.434	0.613
$m=4.0$	$\bar{\gamma}_{C^+}$	4.42	1.36	0.797	0.635	0.292
	$\bar{\gamma}_{Cl^-}$	0.527	0.474	0.433	0.466	0.775
$m=5.0$	$\bar{\gamma}_{C^+}$	6.68	1.55	(0.800)	0.603	0.228
	$\bar{\gamma}_{Cl^-}$	0.626	0.514	(0.456)	0.510	1.00
References for mean activity coefficients		[36, 64]	[36, 64]	[36, 64]	[36, 64]	[36, 64]

The purely mathematical method used to calculate individual activity coefficients of single-ion species by factorizing the concentration curve of mean activity coefficients to the required power as described in this paper, is based on the following premises:

1. It is known to be impossible to determine individual activity coefficients of single-ion species of dissolved electrolytes solely by using classical thermodynamic methods. Hence, the inclusion of methods from other disciplines is necessary to obtain information about the desired individual activity coefficients of single-ion species. This approach is justified when the methods used are as completely logical in their entirety as are

classical thermodynamic methods. The mathematics then fulfills the requirements.

2. The concentration function for the mean activity coefficient to the required power must be the product of the individual concentration functions for the single-ion activity coefficients of the complementary ionic species of the dissolved strong electrolyte. The product function implicitly represents the mathematical analytical properties of the factor functions.
3. The mathematics affords the asymptotic theory as an instrument, whereby the clear factorization of the experimental available concentration curve of the mean activity coefficients of dissolved strong electrolyte, certainly to the required power $\bar{\gamma}_{H^+}$, is possible in

Table 2 Calculated individual activity coefficients of the single-ion species of hydrohalic acids, hydrogen cations $\bar{\gamma}_{\text{H}^+}$ and halide anions $\bar{\gamma}_{\text{A}^-}$, determined by the asymptotic theory, concentration range up to 5 mol/kg

Electrolyte		HCl	HBr	HI
Parameters [14] corresponding to basic approach (20)	b_1	0.1570	0.1322	0.1251
	b_2	0.6718	0.7895	0.7673
	b_3	0.2927	0.6717	0.7745
	b_4	0.3112	0.2046	0.1744
Concentration m [mol/kg]				
$m=0.001$	$\bar{\gamma}_{\text{H}^+}$	0.967	0.968	0.969
	$\bar{\gamma}_{\text{A}^-}$	0.964	0.964	0.964
$m=0.005$	$\bar{\gamma}_{\text{H}^+}$	0.937	0.941	0.943
	$\bar{\gamma}_{\text{A}^-}$	0.923	0.922	0.922
$m=0.01$	$\bar{\gamma}_{\text{H}^+}$	0.920	0.928	0.931
	$\bar{\gamma}_{\text{A}^-}$	0.893	0.892	0.892
$m=0.02$	$\bar{\gamma}_{\text{H}^+}$	0.903	0.917	0.922
	$\bar{\gamma}_{\text{A}^-}$	0.855	0.851	0.852
$m=0.05$	$\bar{\gamma}_{\text{H}^+}$	0.885	0.916	0.925
	$\bar{\gamma}_{\text{A}^-}$	0.788	0.779	0.780
$m=0.1$	$\bar{\gamma}_{\text{H}^+}$	0.883	0.936	0.952
	$\bar{\gamma}_{\text{A}^-}$	0.726	0.709	0.710
$m=0.5$	$\bar{\gamma}_{\text{H}^+}$	0.977	1.21	1.29
	$\bar{\gamma}_{\text{A}^-}$	0.579	0.510	0.515
$m=1.0$	$\bar{\gamma}_{\text{H}^+}$	1.13	1.70	1.90
	$\bar{\gamma}_{\text{A}^-}$	0.566	0.437	0.444
$m=2.0$	$\bar{\gamma}_{\text{H}^+}$	1.51	3.33	4.12
	$\bar{\gamma}_{\text{A}^-}$	0.669	0.414	0.418
$m=3.0$	$\bar{\gamma}_{\text{H}^+}$	2.03	6.51	8.93
	$\bar{\gamma}_{\text{A}^-}$	0.868	0.449	0.447
$m=4.0$	$\bar{\gamma}_{\text{H}^+}$	2.72	12.7	19.4
	$\bar{\gamma}_{\text{A}^-}$	1.16	0.518	0.504
$m=5.0$	$\bar{\gamma}_{\text{H}^+}$	3.64	24.9	42.0
	$\bar{\gamma}_{\text{A}^-}$	1.57	0.614	0.582
References for mean activity coefficients		[65]	[65]	[65]

principle in the individual functions for the cation and anion.

- Models for interpreting the microscopic structure of the electrolyte solutions and for detecting and calculating all forming interaction forces are needless.
- As the concentration approach zero, the Debye–Hückel limiting law equation becomes valid for aqueous strong electrolytes as accuracy improves.

The results obtained by purely mathematical procedure are plausible. They show the expected correlation with ion parameters such as those determined by estimating the excess Gibbs energy for model concepts using statistical mechanics.

It is possible to compare the obtained results by applying the asymptotic theory with experimental values. The ratio of

single-ion activity coefficients can be determined experimentally and also defined thermodynamically. Experimentally determined quotients of individual activity coefficients of cations and anions, respectively, prove the distinctive differences in values within the individual activity coefficients of different ionic species with the same charge in electrolyte mixtures of the same composition, especially for different cations, at higher concentrations [14, 21, 63].

Good agreement was found without exception between calculated and experimentally determined quotients of the single-ion activity coefficients for all investigated electrolyte systems in the concentration range between 0 and 5 mol/kg (see "On the allocation of the factor functions to the cation or anion" and "Validity of factor functions has to be calculated using the asymptotic theory" sections).

Certainly, agreement alone does not validate the fact that the single-ion activity coefficients can actually be calculated using the purely mathematical procedure described above. Conclusiveness, however, is given because the possible existence of additional multiplicative terms can be excluded in the light of the calculated values (see "[Discussion of the approach and parameter determination](#)" section).

Moreover, the theoretically required agreement of the corresponding factor functions in three-component systems was found in deed (see "[On the allocation of the factor functions to the cation or anion](#)" section). This finding cannot be called coincidental. On the contrary, the results are an additional confirmation that individual activity coefficients of single-ion species are achieved with the purely mathematical method as described in the present paper.

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