

# Some Aspects on the Problem of Individual Activity Coefficients of Single-ion Species of Aqueous Strong Electrolytes

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## Abstract

Individual activity coefficients of single-ion species can neither be defined in thermodynamic terms nor determined experimentally. This does not mean that the individual activity of a single-ion species of an aqueous strong electrolyte does not have a real specifically individual effectiveness. Individual ion activity coefficients are required, for instance, for data about the potentials of single electrodes and liquid junction potentials in galvanic cells with transference. A purely mathematical method is written which allows the factorizing the mean activity coefficient into individual parts of the single-ion species. The experimentally accessible concentration curve of the mean activity coefficient is fitted with a quite new mathematical approach. The parameter set of the mathematical approach can be determined univocally and invariantly with the help of the asymptotic theory using corresponding approximations.

**Keywords:** aqueous strong electrolytes, concentration dependence of activity coefficients, factorization of the mean activity coefficients, individual ion activity coefficients

## 1. Introduction

The analytical concentration “*m*” of a component within a real and homogeneous mixed phase has to be modified for the thermodynamic interpretation of equilibria, according to Eq. (1):

$$a = m \cdot \gamma \quad (1)$$

The modified concentration “*a*” is denoted as activity. The multiplicative term “*γ*” is known as activity coefficient. The activity coefficient considers all deviations from ideal behaviour of the component within the real mixed phase by forming of interaction forces.

The activity “*a*” is defined thermodynamically from the change of the chemical potential “*μ*” of a component within a mixed phase by transfer from one state into another (see Eq. (2a)):

$$d\mu = RT \cdot d \ln a \quad (2a)$$

$$\mu = \mu^\circ + RT \cdot \ln a \quad (2b)$$

*μ* ..... chemical potential

*μ*<sup>°</sup> ..... integration constant (standard chemical potential)

*R* ..... gas constant

*T* ..... absolute temperature [K]

*a* ..... activity ( $a = m \cdot \gamma$ )

The experimental determination of the activity is possible for every concentration by implication.

According to IUPAC recommendations, the activity has the dimension of the concentration, the activity coefficient is dimensionless.

By all means, it is to bear in mind the fact that strong electrolytes dissolved in water are dissociated in cations and anions in general.

## 2. Individual Activity Coefficients of Single-ion Species

The experimental determination of the activity or the activity coefficient of an aqueous strong electrolyte yields principally a product from the individual activities ( $a_C$  and  $a_A$ ) or the individual activity coefficients ( $\gamma_C$  and  $\gamma_A$ ), respectively, of the complementary ionic species of the electrolyte  $C_{v_+}A_{v_-}$ , according to Eqs. (3a) and (3b):

$$a_{\pm} = \sqrt[v_+ + v_-]{a_C^{v_+} \cdot a_A^{v_-}} \quad (3a)$$

$$\gamma_{\pm} = \sqrt[v_+ + v_-]{\gamma_C^{v_+} \cdot \gamma_A^{v_-}} \quad (3b)$$

$v_+, v_- \dots \dots$  stoichiometric number of cations and anions from one molecule  $C_{v_+}A_{v_-}$ .

This geometrical average of the individual activities or individual activity coefficients for the cations and anions are known as the mean activity " $a_{\pm}$ " and the mean activity coefficient " $\gamma_{\pm}$ ", respectively, (Stokes, 1991).

It is valid for uni-univalent electrolytes CA:

$$a_{\pm}^2 = a_C \cdot a_A \quad (4a)$$

$$\gamma_{\pm}^2 = \gamma_C \cdot \gamma_A \quad (4b)$$

$a_C, a_A \dots \dots$	individual activities of cations, of anions
$\gamma_C, \gamma_A \dots \dots$	individual activity coefficients of cations, of anions
$a_{\pm} \dots \dots$	mean activity
$\gamma_{\pm} \dots \dots$	mean activity coefficient

The separate experimental determination of the individual activity or individual activity coefficient for a single-ion species of an electrolyte is strictly impossible, because of the condition of electro-neutrality in accord with Eq. (2a) it is only possible to transfer particles without charge. This means that cations and anions could be transferred both together, but never a particle with an electrical charge like single ionic species alone.

Despite this fact, formal is a splitting of the Eq. (2b) into separated parts for cations and anions indeed thinkable:

$$\mu = \mu^{\circ} + RT \ln a_{\pm}^2 = \mu_C + \mu_A = \mu^{\circ}_C + RT \ln a_C + \mu^{\circ}_A + RT \ln a_A \quad (5)$$

$\mu_C, \mu_A \dots \dots$	formal chemical potential of the cations, anions
$\mu^{\circ}_C, \mu^{\circ}_A \dots \dots$	formal standard chemical potential of the cations, anions

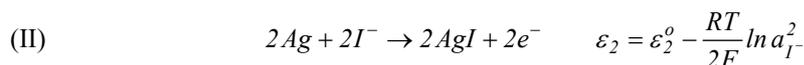
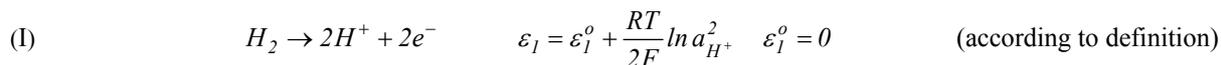
However, such a splitting is thermodynamically senseless, as has been clarified on principle by the eminent thermodynamican Guggenheim already in 1929 (Guggenheim, 1929). The conception of splitting the electrochemical potential ( $\tilde{\mu}_i$ ) of an ion of the type i into the sum of a chemical term  $\mu_i$  and an electrical term  $\varepsilon_i^* \psi$  ( $\varepsilon_i^*$ : charge;  $\psi$ : electrostatic potential) has no physical significance. Thus, the basis of the thermodynamic definition is missing for the single-ion activity  $a_i$ . Puritans of electrochemistry claim out of it, that individual activity coefficients of single-ion species are imaginary entitles without physical significance. But there is a dogma for these Puritans of electrochemistry. A part of them denies the existence of single-ion activity coefficients on principle. In contrast to it, many electrochemists (and this group increases) accept an essential importance of the individual activities of single-ion species to many a field of electrochemistry. This group of electrochemists is of opinion that the notion of single-ion activity coefficients is worthwhile and, in deed, it is necessary to tackle this problem. And this point of view are in existence very good reasons.

Guggenheim attempts to show in his milestone article (Guggenheim, 1929) that the knowledge of individual ion activities is unnecessary because the individual ion activity is not defined in thermodynamic terms. However, he had to be confessed the fact that 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" (Guggenheim, 1929). Quotients of individual activities or individual activity coefficients of single-ion species can also be determined experimentally by implication using thermodynamically precise methods. The ratio of the individual activity coefficients of the  $\Gamma^-$  ions and  $\text{OH}^-$  ions ( $\gamma_{\Gamma^-}/\gamma_{\text{OH}^-}$ ) is directly measurable with the help of a galvanic cell without transference, e. g.



A erroneous potential in the galvanic cell (A) is no fear of it because the solubility product constants (at 25 °C) of Ag(OH) ( $L_{Ag(OH)}=2.02 \cdot 10^{-8} \text{ mol}^2/\text{kg}^2$ ) (Ferse, 2005) and of AgI ( $L_{AgI}=8.52 \cdot 10^{-17} \text{ mol}^2/\text{kg}^2$ ) (Lide, 2006-2007) differ by more than eight order of magnitude.

The reactions in the cell (A) are:



with  $K_W = \frac{a_{H^+} \cdot a_{OH^-}}{\gamma_{H_2O}}$  (thermodynamic ion product of water) follows:

$$E_{(A)} = -\varepsilon_2^o + \frac{RT}{F} \ln K_W + \frac{RT}{F} \ln \gamma_{H_2O} + \frac{RT}{F} \ln(m_{I^-} \cdot \gamma_{I^-}) - \frac{RT}{F} \ln(m_{OH^-} \cdot \gamma_{OH^-})$$

$$\text{and finally: } \ln \frac{\gamma_{I^-}}{\gamma_{OH^-}} = \frac{F(E_{(A)} + \varepsilon_2^o)}{RT} - \ln K_W - \ln \gamma_{H_2O} - \ln m_{I^-} + \ln m_{OH^-}$$

(Ferse, 2008; Ferse & Müller, 2011).

Of course, it is basically always only possible the determination of the chemical potential of electrically neutral electrolytes. But in electrolyte mixtures, the individual activity coefficient of the one ionic species can disappear by the subtraction. On this way it is the ratio of the individual activity coefficients of two ionic species with the same charge accessible. The quotients can differ significantly from 1. Hence, it is known that the thermodynamic effectiveness 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 (A. Ferse & E. Ferse, 1966; Schwabe et al., 1974; Ferse, 2008). Guggenheim negates the physical significance of individual ion activity, but he confesses simultaneously that the ratios of the activities or activity coefficients of two ionic species with the same charge are defined thermodynamically (Guggenheim, 1929). As a matter of fact, this is a criterion to prove whether the purely mathematical method of factorizing mean activity coefficients into individual parts for cations and anions produces meaningful results.

It can be concluded from the interpretation of differ experimental investigations that in contrast to the individual activity coefficients of the cations the individual activity coefficients of the chlorid ions of alkali chlorides and alkaline earth chlorides are only small different and they do not reach values higher than one in the concentration range up to 5 mol/kg (Schwabe, 1967; Schwabe et al., 1968). This assumption is affirmed by the results obtained with the purely mathematical method (see Figure 5) (Ferse & Müller, 2011). The exclusive use of mean activity coefficients permanently at the thermodynamic treatment of equilibriums and processes where dissolved electrolytes take part is not justified. This implies the risk of arriving at erroneous conclusions.

### 3. Importance of Individual Activity Coefficients

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. Of course, individual activity coefficients of single-ion species can neither be defined thermodynamically nor determined experimentally. But 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 significance singly. However, it is a fact, that individual ion activities  $a_i$  and individual activity coefficients  $\gamma_i$  of a single-ion species  $i$  do not apply in classical thermodynamics. Thereby, it is arisen "breaches" in different fields of electrochemistry. The knowledge of individual ion activity coefficients is necessary to eliminate these "breaches". Precise information about the individual activity coefficients of single-ion species are the essential requirement for e.g. data of the potential of single electrodes, the calculation of the liquid junction potential in galvanic cells with transport, the answer to residual questions within the kinetics, the clarification of reaction processes in biochemical and physiologic-medicinal fields or the research

on the politically-economically important field of corrosion protection.

It was attempted a great many of ways knowledge to attain on the desired individual activity coefficients. The present paper cannot deal with the wide variety of attempted ways. Reviews with critical discussions of the used methods are given by the author in 1978 (Ferse, 1978) as well as in 2008 and 2011 (Ferse, 2008; Ferse & Müller, 2011). The discussed methods in these three articles do not claim to be complete, only basic methods on selected examples have been discussed. Experimental methods cannot be successful, on principle. 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.

Therefore, an experimental determination of individual activity coefficients is excluded (Malatesta, 2000; Malatesta, 2010), which could also be proved once more using the example of the pH measuring (Bates, 1964). The importance of pH for chemical processes and reactions in biologic-medicinal fields is beyond all question. The potentiometric pH measuring is used in scientific work e.g. in chemical laboratories or to control chemical processes as well as in biological-medicinal fields as standard method (Schwabe, 1976; Galster, 1990). But in many cases, the users are oblivious to the fact, that the pH which is measured by a galvanic cell allows no conclusions about the 'true acidity' of the measured solution (Degner, 2009) because the pH value defined by Sørensen in 1924 (Sørensen & Linderstrøm-Lang, 1924).

$$pH \equiv -\log a_{H^+} \quad (6)$$

contains the individual activity of the hydrogen ion  $a_{H^+}$ . The pH which is defined on this way cannot be measured, on principle. In the galvanic cell for pH measurements



the cell reaction is:



The individual activity of hydrogen ion in solution ( $a_{H^+}$ ) can be related to the total e.m.f. ( $E_B$ ) of the cell (B), the potential of saturated calomel reference electrode ( $E^\circ$ ), and the potential ( $E_j$ ) across the liquid junction as follows:

$$-\ln a_{H^+} = \frac{(E_B - E^\circ - E_j)F}{R \cdot T} \quad (7)$$

The liquid junction potential ( $E_j$ ) is arisen by force between the measured solution and the reference electrode in the transition layer which is marked in the galvanic cell (B) with a double line. A liquid junction potential is not preventable in cells with transport neither by a salt bridge. In addition, a calculation of the liquid junction potential without the knowledge of individual activity coefficients is impossible as well. As Harned said: "*We are thus confronted with the interesting perplexity that it is not possible to compute liquid junction potentials without knowledge of individual ion activities, and it is not possible to determine individual ion activities without an exact knowledge of liquid junction potential. For the solution of this difficult problem, it is necessary to go outside the domain of exact thermodynamics*" (Harned, 1924).

Conventions are concluded to eliminate the resulting "breaches" in different fields of electrochemistry as a consequence of absence of individual activity coefficients. Such conventions are e.g. the proposition by Nernst that the potential of the normal hydrogen electrode is zero at every temperature and also the agreement that the determination of a 'conventional pH value' has become accepted instead of the pH according to Eq. (6). The 'conventional pH value' allows no conclusions to be drawn about the 'true acidity' of the measured solution, because in the measured e.m.f. the unknown liquid junction potential is contained. The conventional pH value is eligible for comparisons beyond doubt. However, it is not identical with the negative decadal logarithm of the hydrogen ion activity in the measured solution according to Eq. (6).

#### 4. The Purely Mathematical Method of the Calculating the Individual Activity Coefficients

##### 4.1 Preliminary Remarks

On principle, it should be desirable to get information about individual activity coefficients. Certainly, it must be sought a quite new way. As Harned already said, it is necessary to use methods outside the domain of classic thermodynamics (Harned, 1924). An approach is justified when the methods used are as completely logical in their entirety as are classical thermodynamic methods. The mathematics then fulfils the requirements. The author developed a purely mathematical procedure to achieve knowledge on the desired individual ion activity coefficients in solutions up to high electrolyte concentrations (Ferse, 1977; Ferse & Neumann, 1977; Ferse, 2008;

Ferse & Müller, 2011).

#### 4.2 Principal Thoughts

An extension or modification of the *Debye-Hückel* approach where the known preconditions are restricted step by step and individual ionic parameters are used will not work. Nevertheless, the mathematical correlation between the accessible concentration dependence of the mean activity coefficient and the hypothetical concentration functions of the individual activity coefficients of the complementary ionic species allows finding a new perspective to factorize the mean activity coefficient into parts of either the cations or anions.

It must be accepted, that the mean activity coefficient to the required power of an aqueous strong electrolyte is purely mathematical. It is the product of individual activity coefficients of the complementary ion species, according to Eq. (4b) for uni-univalent electrolytes.

Of course, a one-to-one breakdown of a product into factors is impossible without making additional assumptions. But the curve of the product of the individual activity coefficients of the single-ion species ( $\gamma_C \gamma_A$ ) versus the concentration is accessible experimentally and this additional information renders it possible to split the mean activity coefficients to the required power 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. To obtain the desired individual parts  $\gamma_C$  and  $\gamma_A$  for cations and anions, respectively, a product functions for the mean activity coefficients to their required power [ $\gamma_{\pm}^2(m)$  for uni-univalent electrolytes] were split into factor functions of predefined structure. Assuming the existence of a univocal solution, estimating a product function yields the factorization of the product (Bates & Watts, 1988; Ratkowsky, 1990; Neter et al., 1996; Seber & Wild, 2003).

#### 4.3 The Mathematical Structure of the Concentration Functions

In contrast to the general point of view, it is possible to make predictions for the mathematical structure of the concentration functions for individual activity coefficients of single-ion species. When the concentration approaches to zero, the *Debye-Hückel* limiting law equation became valid for aqueous strong electrolytes as accuracy improves. For univalent ion species is valid:

$$\ln \gamma_{\pm} = \ln \gamma_C = \ln \gamma_A = -A' \sqrt{m} \quad (8)$$

$A'$  ..... *Debye-Hückel* constant

At infinite dilution all activity coefficients become the value 1:

$$\gamma_{\pm}(0) = \gamma_C(0) = \gamma_A(0) = 1 \quad (9)$$

And all ionic species with the same charge number have the same slope as well. For univalent ionic species is valid:

$$\lim_{m \rightarrow 0} \frac{\partial \gamma_{\pm}}{\partial \sqrt{m}} = \lim_{m \rightarrow 0} \frac{\partial \gamma_C}{\partial \sqrt{m}} = \lim_{m \rightarrow 0} \frac{\partial \gamma_A}{\partial \sqrt{m}} = -A' \quad (10)$$

Eqs. (9) and (10) are designated as limiting infinite dilution conditions in present paper.

In the mathematical approach by Ferse the infinitely diluted solution is considered as one fixed point for the structure of the product function. Just even with this point as reference it is possible to make accurate statements about the individual activity coefficients. This fact is considered by the first term in both factor functions of the product function (14).

In addition, a special concentration range exists indirectly for those statements about individual activity coefficients. This is the special concentration range  $5 \leq m \leq 10$  mol/kg where the logarithm of the mean activity coefficient of strong electrolytes is linearly dependent on the concentration, see Figure 1 (additional details see (Ferse & Müller, 2011)).

Concerning the concentration range  $5 \leq m \leq 10$  mol/kg the following linear equation for mean activity coefficients of uni-univalent electrolytes is valid:

$$\ln \gamma_{\pm}^2(m) = \Phi \cdot m + \rho \quad (11)$$

$\Phi, \rho = \text{constants}$

The mathematical approach (14) is based on this concentration range, as well.

In the concentration range  $5 \leq m \leq 10$  mol/kg follows from the concentration function of the mean activity coefficient for an uni-univalent electrolyte

$$\gamma_{\pm}^2(m) = \gamma_C(m) \cdot \gamma_A(m) \quad (12)$$

the logarithmic relationship (13):

$$2 \ln \gamma_{\pm}(m) = \Phi \cdot m + \rho = \ln \gamma_C(m) + \ln \gamma_A(m) = \phi_C \cdot m + \rho_C + \phi_A \cdot m + \rho_A \quad (13)$$

with  $\Phi, \phi_C, \phi_A, \rho, \rho_C, \rho_A = \text{constants}$ ; they are valid:  $\Phi = \phi_C + \phi_A$ ,  $\rho = \rho_C + \rho_A$

Without doubt, it is a fact that the concentration function of the mean activity coefficient to the required power represents implicitly the mathematical analytical properties of the concentration functions of the individual activity coefficients of the complementary ionic species.

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. There is only one exception to this rule in mathematics. 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 at all of the strong electrolytes. 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 factor functions in Eq. (14).

The experimentally accessible curve for the mean activity coefficient of a strong electrolyte to the required power as a function of the ionic strength 'J' can be well approximated up to highest concentrations using the basic product function (14) (Ferse & Müller, 2011):

$$\gamma_{\pm}^{V_+ + V_-}(J) = \gamma_C^{V_+}(J) \cdot \gamma_A^{V_-}(J) \approx \left[ \sum_{k=1}^3 \delta_k e^{\sigma_k \cdot J^{\frac{k}{2}}} \right]^{V_+} \left[ \sum_{k=1}^3 g_k e^{\tau_k \cdot J^{\frac{k}{2}}} \right]^{V_-} \quad (14)$$

$\gamma_C$  and  $\gamma_A$ : individual parts obtained for cations and anions by the mathematical splitting of the mean activity coefficients.

J: ionic strength [mol.kg<sup>-1</sup>] in the commonly used definition as the half sum of the concentration of all ions multiplied by the square of their charge numbers, e.g. (Monk, 1961)

$\delta_k, g_k, \sigma_k, \tau_k$  (index variables k = 1 up to 3): parameters

Concerning the case k = lower bound of summation 1 and upper bound of summation 3, the relationship (14) is written in the paper by (Ferse & Müller, 2011) dissolved in summands with a different designation of the parameters:

$$\gamma_{\pm}^{V_+ + V_-}(J) = \gamma_C^{V_+}(J) \cdot \gamma_A^{V_-}(J) \approx \left[ c_1 e^{c_7 \cdot J^{\frac{1}{2}}} + c_3 e^{c_9 \cdot J} + c_5 e^{c_{11} \cdot J^{\frac{3}{2}}} \right]^{V_+} \left[ c_2 e^{c_8 \cdot J^{\frac{1}{2}}} + c_4 e^{c_{10} \cdot J} + c_6 e^{c_{12} \cdot J^{\frac{3}{2}}} \right]^{V_-}$$

A predefinition was not established for the concentration range between infinite dilution and 5 mol/kg. The values in this concentration range ensue from the sum of the first and the second summand in the factor functions in relationship (14). Accordingly, the comparison of the product of the calculated individual activity coefficients in this range with data of the mean activity coefficients from the literature results a criterion for accurate adjusting. The basic product function (14) was deduced from mathematical thoughts (Ferse, 1977; Ferse & Neumann, 1977; Ferse & Müller, 2011) and is not a result from the calculation of the excess Gibbs energy using the statistical mechanics. Thus, the approach (14) differs in principle from the classical approximation of the mean activity coefficient to the concentration curve (additional details see (Ferse & Müller, 2011)).

The factor functions in the relationship (14) represent the concentration functions for the individual activity coefficients of complementary ion species of the dissolved electrolyte (Ferse & Müller, 2011). Both factor functions have the same predefined mathematical structure because all forming interaction forces in an electrolyte solution influence cations and anions as well. It is known that the result is different for the both ionic species. Concerning the mathematical approach, the values of the parameters in the factor functions of relationship (14) are the only factors responsible for the gradually different concentration curves of the individual activity coefficients of the complementary ionic species of an electrolyte.

#### 4.4 Parameter Determination of the Mathematical Approach

##### 4.4.1 The Use of the Limiting Infinite Dilution Conditions

On principle, the parameter determination of the basic product function (14) should be possible from the optimal approximation of the existing experimental data for the concentration curve of the mean activity coefficients to the required power applying the non-linear regression analysis (Bates & Watts, 1988; Ratkowsky, 1990; Neter et al., 1996; Seber & Wild, 2003).

Indeed, using relationship (14), for index variable  $k = 1, 2, 3$ , it is generally possible to fit the mean activity coefficient of a strong electrolyte in the entire concentration range, from infinite dilution up to highest concentrations of about 15 or 20 mol/kg. But applying the non-linear regression analysis, the parameter determination of the approach (14) is ambiguous in the case of  $k = 1, 2, 3$  due to the ill-conditioned coefficient matrix (Ferse & Müller, 2011). The mathematical approach (14) is univocally solvable in the cases of  $k = 1$  and  $k = 1, 2$  only. The validity of the estimated parameter set is limited to a part of the experimental concentration curve of the mean activity coefficient considering only the first summand or the first two summands in the both factor functions of Eq. (14). In these cases, the use of the limiting infinite dilution conditions (9) and (10) is requisite to solve the approach (14).

For the individual activity coefficients, the data are known at concentration zero. The limiting infinite dilution conditions (9) and (10) clearly require in the case of  $k = 1$  (consideration of only the first term of relationship (14)):  $\delta_i = \mathcal{G}_i = 1$  and  $\sigma_i = \tau_i = -z_i^2 \cdot A'$  (where  $z_i$  is the charge number of the ionic species  $i$  (cation or anion) in the molecule  $C_{v^+}A_{v^-}$ ). If only the first summand is considered, 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 (15) agrees with the *Debye-Hückel* limiting law equation:

$$\gamma_{\pm}^{v^+ + v^-}(J) = \gamma_C^{v^+}(J) \cdot \gamma_A^{v^-}(J) \approx \left[ e^{-z_C^2 \cdot A' \cdot J^{\frac{1}{2}}} \right]^{v^+} \left[ e^{-z_A^2 \cdot A' \cdot J^{\frac{1}{2}}} \right]^{v^-} \quad (15)$$

It is necessary to consider the first two summands in both factor functions in the case of the factorizing the mean activity coefficient also when the electrolyte concentration approaches zero.

It is important to bear in mind the fact that the corresponding product function parameters in (14) change when an additional summand is included in both factor functions because the system of functions is not orthogonal.

The relationship (14) in the case of index variable  $k = 1, 2$  is as follows:

$$\gamma_{\pm}^{v^+ + v^-}(J) = \gamma_C^{v^+}(J) \cdot \gamma_A^{v^-}(J) \approx \left[ \delta_1 e^{\sigma_1 J^{\frac{1}{2}}} + \delta_2 e^{\sigma_2 J} \right]^{v^+} \left[ \mathcal{G}_1 e^{\tau_1 J^{\frac{1}{2}}} + \mathcal{G}_2 e^{\tau_2 J} \right]^{v^-} \quad (16)$$

This means in the case of index variable  $k = 1, 2$  in relationship (14) (see Eqs. (16), considering the first two summands in both factor functions) compared to the case  $k = 1$ :  $\delta_i \neq \mathcal{G}_i \neq 1$ , and  $\sigma_i \neq \tau_i \neq -z_i^2 \cdot A'$ .

The relationship (17) is obtained using a new denotation of the parameters ( $\delta_i = b_i$ ,  $\mathcal{G}_i = b_i$ ,  $\sigma_i = b_3$ ,  $\tau_i = b_4$ ) and in consideration of the limiting infinite dilution conditions (9) and (10). In the case of index variable  $k = 1, 2$  in relationship (14), the limiting infinite dilution conditions (9) and (10) clearly require the parameters:

$\delta_2 = (1 - b_1)$  and  $\mathcal{G}_2 = (1 - b_2)$ ;  $\sigma_1 = -z_C^2 \frac{A'}{b_1}$  and  $\tau_1 = -z_A^2 \frac{A'}{b_2}$  (additional details see (Ferse & Müller,

2011)):

$$\gamma_{\pm}^{v^+ + v^-}(J) = \gamma_C^{v^+}(J) \cdot \gamma_A^{v^-}(J) \approx \left[ b_1 e^{-z_C^2 \frac{A'}{b_1} J^{\frac{1}{2}}} + (1 - b_1) e^{b_3 J} \right]^{v^+} \left[ b_2 e^{-z_A^2 \frac{A'}{b_2} J^{\frac{1}{2}}} + (1 - b_2) e^{b_4 J} \right]^{v^-} \quad (17)$$

Where  $b_1, \dots, b_4$  are the parameters and  $A'$  is the *Debye-Hückel* constant

(The following value is used after the year 1977 (Staples et al., 1977):  $A' = 1.17625$  ( $A = 0.51084$ ), previously it

was used this value:  $A' = 1.1711$  ( $A = 0.50860$ ); the value is valid for aqueous electrolyte solutions and the temperature 298.15 K).

Thus, the number of parameters in Eq. (17) is reduced compared to Eq. (16) from eight to four.

The non-linear least square regression method yields for approach (17) many sets of best fit independent parameters  $b_1, \dots, b_4$  of  $\gamma_{C^+}^{v_+}(J) \cdot \gamma_{A^-}^{v_-}(J)$  for  $\gamma_{\pm}^{v_+ + v_-}(J)$  in consequence of the ill-conditioned coefficient matrix. All combinations are nearly equally suitable for fitting the concentration curve of the mean activity coefficients. This problem is solved with the help of the previously developed asymptotic theory (Ferse, 1977; Ferse & Neumann, 1977).

#### 4.4.2 The Asymptotic Theory - The Use of Corresponding Approximations

A univocal parameter determination of Eq. (17) is possible using the previously developed asymptotic theory (Ferse, 1977; Ferse & Neumann, 1977; Ferse & Müller, 2011). Stable and reproducible results are attained applying the asymptotic theory. The parameter combination is invariant. The basic product approach (17) is to unequivocally split into factor functions. A successive estimation of the parameters ensues from the use of corresponding approximations which are deducible from Eq. (17) for very low and high concentrations.

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

$$b_1 e^{-z_c^2 \frac{A'}{b_1} \sqrt{J}} \approx b_2 e^{-z_A^2 \frac{A'}{b_2} \sqrt{J}} \approx 0 \quad (18)$$

Thus, the corresponding approximations (19) and (20) result from Eq. (17) for high concentrations:

$$\gamma_{\pm}^{v_+ + v_-}(J) \approx (1 - b_1)^{v_+} (1 - b_2)^{v_-} \cdot e^{(v_+ b_3 + v_- b_4) J} \quad (19)$$

$$\ln \gamma_{\pm}^{v_+ + v_-}(J) \approx \ln \left[ (1 - b_1)^{v_+} (1 - b_2)^{v_-} \right] + (v_+ b_3 + v_- b_4) J. \quad (20)$$

In the concentration range of  $J$  between 5 and 10 mol/kg,  $\ln \gamma_{\pm}$  for a strong electrolyte generally is a linear function of  $J$ , therefore, in the first step, the sum  $(v_+ b_3 + v_- b_4)$  as well as the product  $[(1 - b_1)^{v_+} (1 - b_2)^{v_-}]$  are determined with the linear regression analysis as the standard mathematical method by using the corresponding approximation (20). In Figure 1, the determination of the ordinate intercept  $\beta$  is shown:

$$\beta = \ln \left[ (1 - b_1)^{v_+} (1 - b_2)^{v_-} \right] \quad (21a)$$

or Eq. (21a) in modified form

$$(1 - b_1)^{v_+} (1 - b_2)^{v_-} = e^{\beta} \quad (21b)$$

And the determination of the slope  $(v_+ b_3 + v_- b_4)$  is depicted in the way of the examples NaOH solutions and KOH solutions. The values are  $\beta_{NaOH} = -2.2415168$ ,  $\beta_{KOH} = -1.5256335$  and the values for the slopes  $(b_3 + b_4)_{NaOH} = 0.457198$ ,  $(b_3 + b_4)_{KOH} = 0.519862$ , respectively. The  $\gamma_{\pm}$  values of NaOH solutions and KOH solutions were taken from the book by (Robinson & Stokes, 1959/65) and the paper by (Hamer & Wu 1972).

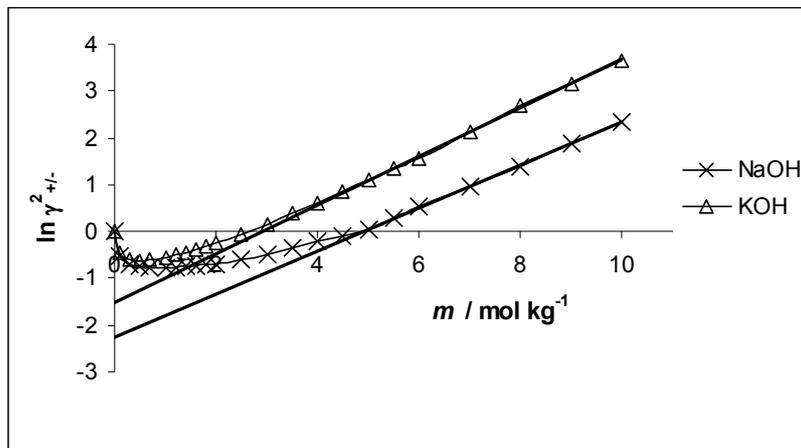


Figure 1. Determination of the ordinate intercepts  $\beta$  and the slopes  $(b_3+b_4)$  from the concentration curves of  $\ln \gamma_{NaOH}^2(m)$  vs.  $m_{NaOH}$  and  $\ln \gamma_{KOH}^2(m)$  vs.  $m_{KOH}$

Parameters  $b_1$  as well as  $b_2$  can be determined separately by applying an additional corresponding approximation for very low  $J$ , e.g.  $J = 10^{-3}$  mol/kg (then  $e^{b_3 J} \approx e^{b_4 J} \approx 1$ ). Thus, Eq. (22) is valid because the term  $e^J$  at the

$$\gamma_{\pm}^{v_+ + v_-}(0.001) \approx \left[ b_1 \cdot e^{-\frac{z_C^2 A'}{b_1} \sqrt{10^{-3}}} + (1 - b_1) \right]^{v_+} \cdot \left[ b_2 \cdot e^{-\frac{z_A^2 A'}{b_2} \sqrt{10^{-3}}} + (1 - b_2) \right]^{v_-} \quad (22)$$

The mean activity coefficients for the ionic strength  $10^{-3}$  mol/kg in Eq. (22) are calculated preferably with the help of the extended *Debye-Hückel* equation (23):

$$\ln \gamma_{\pm}^{v_+ + v_-} = \frac{-(v_+ + v_-) |z_C \cdot z_A| A' \sqrt{J}}{1 + B \cdot \tilde{a} \cdot \sqrt{J}} \quad (23)$$

$\tilde{a}$  = (empirical) ion parameter [Å]

$A'$  and  $B$  = *Debye-Hückel* constants

(The following values are used for the constants  $A'$  and  $B$  after the year 1977 (Staples et al, 1977)):  $A' = 1.17625$  ( $A = 0.51084$ ),  $B = 0.32866$ , previously it were used these values:  $A' = 1.1711$  ( $A = 0.50860$ ) and  $B = 0.3281$ ; all values are valid for aqueous electrolyte solutions and the temperature 298.15 K)

Extremely high accuracy is in reality certainly not important. Accurate values afford excellent services as operands.

Concerning the examples NaOH solutions and KOH solutions, the values of  $\gamma_{\pm}^2(0.001)$  were calculated to be 0.931561 and 0.931896, respectively, using the extended *Debye-Hückel* equation (23). With these values in equation (22) and using the ordinate intercept for NaOH  $\beta_{NaOH} = -2.2415168$ , the values  $b_{1(NaOH)}$  and  $b_{2(NaOH)}$  are calculated to be 0.1758 and 0.8710, respectively, and for KOH solutions (ordinate intercept  $\beta_{KOH} = -1.5256335$ )  $b_{1(KOH)} = 0.1654$  and  $b_{2(KOH)} = 0.7394$  (Ferse, 1978; Ferse, 2008). The graphical separation of  $b_{1(NaOH)}$  and  $b_{2(NaOH)}$  is depicted in Figure 2 and exemplifies NaOH solutions.

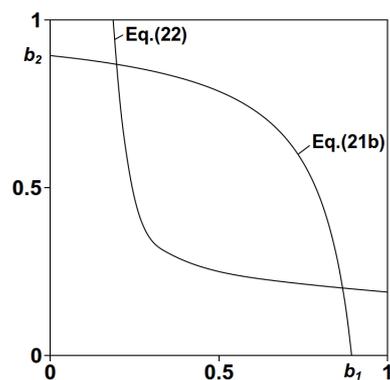


Figure 2

Graphical separation of  $b_1$  and  $b_2$  with function (21b):  $(1-b_1)(1-b_2)=e^\beta$  and function (22):

$$\gamma_{\pm}^2(0.001) = \left[ b_1 e^{-\frac{A'}{b_1} \sqrt{0.001}} + (1-b_1) \right] \cdot \left[ b_2 e^{-\frac{A'}{b_2} \sqrt{0.001}} + (1-b_2) \right].$$

The equations are valid for NaOH solutions with  $e^\beta = e^{-2.2415168} = 0.10629715$  and  $\gamma_{\pm}^2(0.001) = 0.931561$ .

Finally, the sum  $(b_3+b_4)$  gets separated with measured  $\gamma_{\pm}$  values in the area of the strongest curvature of the  $\gamma_{\pm}^2 - m$  curve ( $0 \leq m \leq 5$  mol/kg) with the help of the Fibonacci search approach (Fletcher & Powell, 1963).

Thus, the values  $b_{3(\text{NaOH})} = 0.3046$  and  $b_{4(\text{NaOH})} = 0.1526$  result for NaOH solutions, and the values  $b_{3(\text{KOH})} = 0.3725$  and  $b_{4(\text{KOH})} = 0.1474$  result for KOH solutions. For additional details, see (Ferse, 1978; Ferse, 2008). This method proved to be successful (Ferse, 1977; Ferse, 1978; Ferse, 2008; Ferse & Müller, 2011).

Applying the asymptotic theory, the ill-conditioned coefficient matrix of Eq. (17) 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 obtained set of parameters is valid for the range of an ionic strength  $0 \leq J \leq 5$  mol/kg. This limitation ensues from a comparison between experimentally determined ratios of single-ion activity coefficients to quotients formed with individual ion activity coefficients calculated with the purely mathematical procedure developed by Ferse (Ferse, 1977; Ferse, 2008; Ferse & Müller, 2011). The product function (17) is univocally solvable for electrolyte concentrations (ionic strengths) of less than 10 mol/kg only. As the electrolyte concentration (ionic strength) is increased over 5 mol/kg, the results begin to become increasing unreliable.

Of course, a purely mathematical extension of the Eq. (14) [or Eq. (17)] using a concentration function seems to be possible. This assumption would lead to ambiguous results. On principle, a possible mathematical extension of Eq. (14) [or Eq. (17)] can be excluded for the case of calculating individual ion activity coefficients. The verification is pointed out by (Ferse & Müller, 2011), Chapter: "Impact of a hypothetical multiplicative concentration function G". The results of the purely mathematical procedure by Ferse to calculate individual ion activity coefficients are univocal in any case.

With the help of the computed values  $b_1, \dots, b_4$ , and using Eq. (17), the individual ion activity coefficients of NaOH solutions are calculated with Eqs. (24a) and (24b):

$$\gamma_{\text{Na}^+}(m) = \left[ 0.1758 e^{-\frac{1.1711}{0.1758} m^{\frac{1}{2}}} + 0.8242 e^{0.3046 \cdot m} \right] \quad (24a)$$

$$\gamma_{\text{OH}^-(\text{NaOH})}(m) = \left[ 0.8719 e^{-\frac{1.1711}{0.8710} m^{\frac{1}{2}}} + 0.1281 e^{0.1526 \cdot m} \right] \quad (24b)$$

and the individual ion activity coefficients of KOH solutions are calculated with Eqs. (25a) and (25b):

$$\gamma_{K^+}(m) = \left[ 0.1654e^{-\frac{1.1711}{0.1654}m^{\frac{1}{2}}} + 0.8346e^{0.3725m} \right] \quad (25a)$$

$$\gamma_{OH^-(KOH)}(m) = \left[ 0.7394e^{-\frac{1.1711}{0.7394}m^{\frac{1}{2}}} + 0.2606e^{0.1474m} \right] \quad (25b)$$

The calculated individual activity coefficients are plotted as logarithmic values vs.  $m^{0.5}$  and  $m$ , in the Figures 3 and 4, respectively, for NaOH solutions ( $\ln\gamma_{Na^+}$  and  $\ln\gamma_{OH^-(NaOH)}$ ) as well as for KOH solutions ( $\ln\gamma_{K^+}$  and  $\ln\gamma_{OH^-(KOH)}$ ).

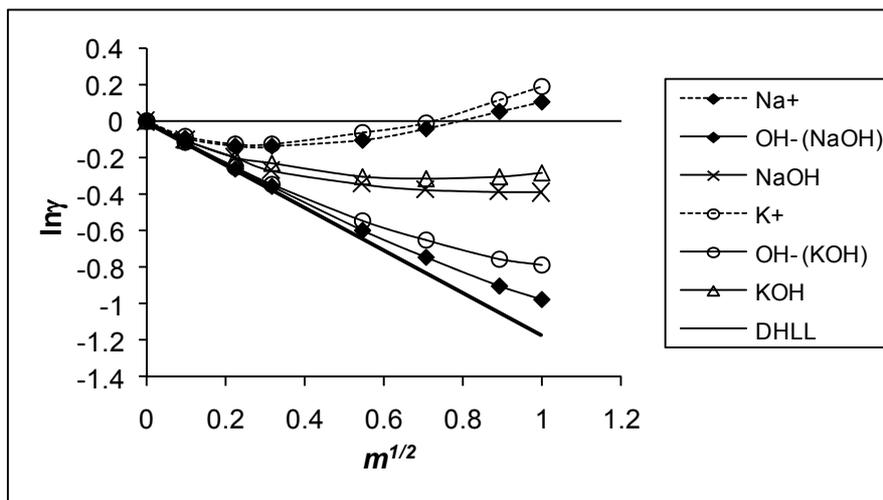


Figure 3. Individual activity coefficients as a function of  $m^{0.5}$  in the concentration range  $0 \leq m^{0.5} \leq 1$  on a logarithmic scale:  $\gamma_{Na^+}$  and  $\gamma_{OH^-(NaOH)}$  for NaOH solutions and  $\gamma_{K^+}$  and  $\gamma_{OH^-(KOH)}$  for KOH solutions, together with the mean activity coefficients  $\gamma_{\pm(NaOH)}$  and  $\gamma_{\pm(KOH)}$  and the *Debye-Hückel* limiting law equation (DHLL)

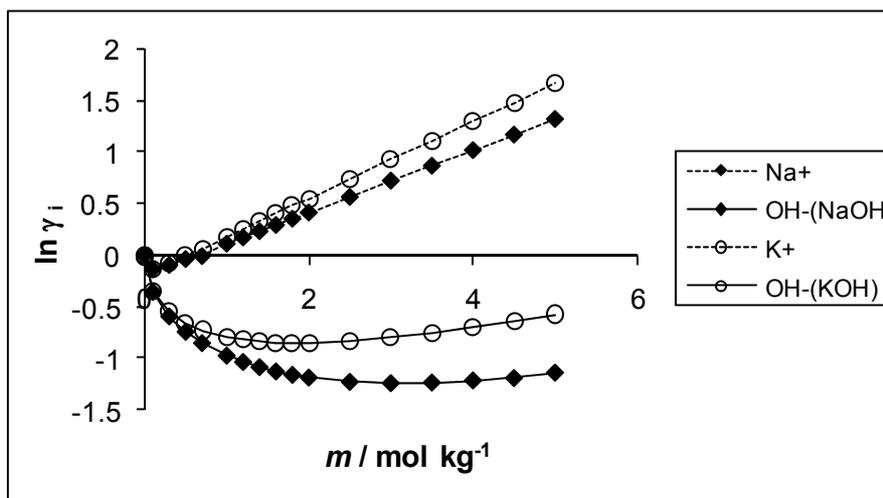


Figure 4. Individual ion activity coefficients for aqueous NaOH solutions ( $\gamma_{Na^+}$  and  $\gamma_{OH^-(NaOH)}$ ) and for aqueous KOH solutions ( $\gamma_{K^+}$  and  $\gamma_{OH^-(KOH)}$ ) on a logarithmic scale as a function of the concentrations  $m_{NaOH}$  or  $m_{KOH}$ , respectively

#### 4.4.3 Decision on the Allocation of the Factor Functions to the Cation or Anion

The allocation of the factor functions to the cation or anion is possible only in the case of the polyvalent electrolytes from the results of calculation if the exponents ( $v_+$ ;  $v_-$ ) of the factor functions of the basic product approach (17) 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 alone which of the two obtained factor functions of the basic product approach (17) 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 with the help of specially mixed electrolyte solutions (Ferse, 1977; Ferse, 2008; Ferse & Müller, 2011).

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  $m_{\kappa\alpha} \ll m_{neutral\ salt}$  is valid. Of course, the mean activity coefficients can also be measured in these especially mixed electrolyte solutions only. But, 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 (Ferse, 1977; Ferse, 2008; Ferse & Müller, 2011). Hence, diluted electrolytes (e.g. NaCl and HCl or HCl and HBr), each with a great surplus of the neutral salt NaClO<sub>4</sub> of the same concentration, have the same individual activity coefficient in consideration of the common ion species:  $\gamma_{Cl-(NaCl\ in\ NaClO_4)} = \gamma_{Cl-(HCl\ in\ NaClO_4)}$  or  $\gamma_{H+(HCl\ in\ NaClO_4)} = \gamma_{H+(HBr\ in\ NaClO_4)}$ , additional details see (Ferse, 1977; Ferse, 2008; Ferse & Müller, 2011). Of course, the absolute values of the individual activity coefficients 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<sub>4</sub> of the same concentration) are certainly different as a result of the different magnitude of the individual activity coefficients of the counter ions, for instance:  $\gamma_{Na+(NaCl\ in\ NaClO_4)} \neq \gamma_{H+(HCl\ in\ NaClO_4)}$  and  $\gamma_{Cl-(HCl\ in\ NaClO_4)} \neq \gamma_{Br-(HBr\ in\ NaClO_4)}$ . This was verified by factorizing the mean activity coefficients of the diluted electrolyte  $\gamma_{\pm\kappa\alpha}^2$  (by  $m_{\kappa\alpha} = 0.01 = const.$ ) as a function of the neutral salt concentration by estimating the parameters of the basic approach (17) using the asymptotic theory like it is shown previously. The theoretically required congruence is found in all of the investigated electrolyte systems without exception (Ferse, 1977; Ferse, 1981; Ferse, 2008; Ferse & Müller, 2011). Thus, the obtained individual factor functions by splitting the concentration function of the mean activity coefficient can be allocated to the cation or anion by implication.

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, which always differs in like manner between cation and anion (Ferse, 1978; Ferse, 1981; Ferse, 2008). Thus, a corresponding allocation is possible by means of analogue curve shapes.

For multivalent electrolytes, whose allocation is already decided from the result of the parameter estimation due to different large exponents ( $v_+ \neq v_-$ ) on the factor functions of the basic product approach (17), the characteristic difference was also confirmed between the concentration curves of the calculated individual activity coefficients of the cations and anions (Ferse, 1981; Ferse, 2008).

### 5. Verification of the Results as Concentration Functions of the Individual Activity Coefficients of Single-ion Species

A direct experimental verification of the results as concentration functions of the individual activity coefficients of single-ion species is known to be impossible. Therefore, another method has to be applied to verify that the determined factor functions are compatible with the concentration functions of the individual ion activity coefficients.

Thermodynamic conditions of the mathematical structure of the concentration functions of individual activity coefficients of single-ion species do not exist, because it is missing a thermodynamic definition of individual ion activity.

However, it must be accepted that the mean activity coefficient to the required power is purely mathematical and represents the product of the individual activity coefficients of the complementary ion species. Therefore, the concentration function of the mean activity coefficient to the required power implicitly represents the mathematically analytical properties of the hypothetical concentration functions of the individual ion activity coefficients of complementary ion species of the dissolved electrolyte. This way renders it possible to obtain information on the mathematical structure of the concentration functions of individual ion activity coefficients (see Chapter 4.3). The product of these deduced concentration functions have to be the concentration function of the

mean activity coefficient to the required power. This fact allows computing the individual ion activity coefficients by the experimentally accessible mean activity coefficients applying the non-linear regression analysis.

Mathematical monographs about non-linear regression analysis (Bates & Watts, 1988; Ratkowsky, 1990; Neter et al., 1996; Seber & Wild, 2003) point out the fact that by factorizing a product function the prerequisites are (i) the meaningful structure of the product function (ii) the univocal splitting regarding the factor functions as well as (iii) the verification that the obtained results yield plausible values.

Factorizing the concentration function of the mean activity coefficient to the required power into individual functions for the single-ion species using Eq. (17) and applying the asymptotic theory, is actually univocal. The parameter determination is invariant. Additional multiplicative terms in Eq. (17) can be excluded (Ferse & Müller, 2011). This proves that the results comply exactly with the mathematical concept of factorizing and are not a random pair of factor functions. The theoretically required congruence of the individual factor functions in three component systems is also found by independently factorizing of the mean activity coefficients of diluted electrolytes as a function of neutral salt admixtures in all of the investigated electrolyte systems. For the mixtures of 0.01 *m* NaOH in NaClO<sub>4</sub> solution and 0.01 *m* NaCl in NaClO<sub>4</sub> solution, the factor functions  $\gamma_{\text{Na}^+(\text{NaOH in NaClO}_4)}$  and  $\gamma_{\text{Na}^+(\text{NaCl in NaClO}_4)}$  in dependence on the NaClO<sub>4</sub> concentration which be obtained by independently factorizing of the mean activity coefficients of NaOH and NaCl are both coincide. Thus, both factor functions are identical with the factor function  $\gamma_{\text{Na}^+}$  of the pure NaClO<sub>4</sub> solution (Ferse, 1977; Ferse & Neumann, 1977). The factor functions  $\gamma_{\text{Cl}^-(\text{NaCl in NaClO}_4)}$  and  $\gamma_{\text{Cl}^-(\text{HCl in NaClO}_4)}$  in the mixed electrolyte solutions of 0.01 *m* NaCl in NaClO<sub>4</sub> and 0.01 *m* HCl in NaClO<sub>4</sub> (also independently calculated as a function of the NaClO<sub>4</sub> concentration from the mean activity coefficients of NaCl and HCl, respectively) are equal (Ferse, 1977; Ferse & Neumann, 1977; Ferse & Müller, 2011). Based on the independently calculated factor function of  $\gamma_{\text{Cl}^-}$  in pure KCl solution, the theoretically required congruence was found also for the factor function  $\gamma_{\text{Cl}^-(\text{HCl in KCl})}$  (factorized independently from the mean activity coefficients of 0.01 *m* HCl as a function of KCl admixture) (Ferse, 2008). In 0.01 *m* HCl in SrCl<sub>2</sub> solution, the factor function  $\gamma_{\text{Cl}^-(\text{HCl in SrCl}_2)}$  of the HCl in dependence on the SrCl<sub>2</sub> concentration is identical with the factor function  $\gamma_{\text{Cl}^-}$  of pure SrCl<sub>2</sub> solutions (factorized independently from the mean activity coefficients of pure SrCl<sub>2</sub> solutions) (Ferse, 1981).

These findings cannot be explained as coincidental results but they contain an additional conformation of the efficacy of the purely mathematical procedure as well as of the fact that the obtained results represent the concentration functions of the individual activity coefficients of single-ion species (Ferse, 2008; Ferse & Müller, 2011).

Without exception, the calculated and experimentally determined quotients of the single-ion activity coefficients for all investigated electrolyte systems also show a good congruence (Ferse, 2008; Ferse & Müller, 2011). This fact is significant, as the ratios of individual ion activity coefficients are defined thermodynamically (Guggenheim, 1929). Certainly, a good congruence alone does not validate the fact that the single-ion activity coefficients can actually be calculated using the purely mathematical procedure by Ferse. Conclusiveness however is given because the possible existence of additional multiplicative terms in the mathematical approach can be excluded in the light of its derivation and the limiting infinite dilution conditions as well as of the calculated values (Ferse & Müller, 2011).

Expressed doubts (Malatesta, 2011) about the purely mathematical conception of factorizing the mean activity coefficient to obtain individual ion activity coefficients are not substantiated. Malatesta supports the opinion of the Puritans of the electrochemists. His comment is erroneous. In the example that he declared as an argument against the purely mathematical method, mathematical laws are purposely or unintentionally ignored. In the upshot, his conclusion is wrong as well. Additional details regarding his senseless comment (Malatesta, 2011) are contained in the reply by (Ferse, 2011).

## 6. Concluding Remarks

The reasons for the variation of the activity coefficients as a function on the concentration are doubtless of a complex nature. The individual activity coefficient is the quotient of the effectiveness and analytical concentration of an ionic species. In concentrated solutions, the concentration of an ion species is without doubt not more identical with the analytical concentration. Different solvation states, formation of complex ions, ion-pairing and other effects occur in concentrated solutions and result in effective concentrations, different from the analytical values of ionic species.

With increasing deviation from *Debye-Hückel* condition of an infinitely diluted electrolyte solution, a physical meaningful interpretation of the macroscopically visible activity coefficient is becoming more and more difficult, if not impossible. For this, all interaction forces, their concentration dependences and their correlations need to

be known. Reasons, which are to search in molecular dimensions and in the structural setup, are difficultly determinable. Conclusions of the microstructure of electrolyte solutions being made from macroscopically accessible quantities are questionable, as macroscopically measurable data, being sum-effects, do not allow discrimination of the individual constituting components, thus adding to the complication to calculate the excess Gibbs energy without arbitrariness.

However, activity coefficients have as practical values their meaning. In relation to the analytical concentrations, the individual activity coefficients represent the macroscopic effectiveness of the ions in solution in easy manner.

A ranking of the individual activity coefficients of the alkaline and alkaline earth cations, and the ions of alkali hydroxides and hydrogen acids of halogens can be modeled on the basis of a specific electrostatic interaction (A. Ferse & E. Ferse, 1966; Ferse & Müller, 2011).

It is known that hydroxide ions and hydrogen ions are a special case in aqueous solution in relation to other ions. 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 (Samoilow, 1965). The transition frequency is on the order of magnitude  $10^{12} \text{ s}^{-1}$  (Eigen & De Maeyer, 1958; Wicke, Eigen, & Ackermann, 1954).

Every water molecule has a very high affinity to  $\text{OH}^-$  or  $\text{H}^+$  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 (Samoilow, 1965). 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 (Samoilow, 1965; A. Ferse & E. Ferse, 1966; Ferse, 1978; Ferse, 2008). This model explains also the unusual ranking of the calculated individual activity coefficients not only of the cations of the alkali hydroxides (see present paper) but of the halide anions in hydrohalic acids (Ferse, & Müller, 2011). 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 concordance with the experiments in aqueous acidic and hydroxide solutions (A. Ferse & E. Ferse, 1966; Ferse, 1978; Ferse, 2008). But also changes to the microstructure of the electrolyte solutions seem to play a role. Noteworthy are replacement effects (Glueckauf, 1964) as well as ionic volume induced changes to the first coordination sphere, and beyond, due to Coulomb-interactions.

Especially for anions of salts the individual activity coefficients seem to increase with increasing volume of ions. But the differences are small (Ferse, 1981). On the other hand, larger cations ( $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ), having smaller activity coefficients, induce increased activity coefficients of present anions (Ferse, 2008).

Ion pairing in concentrated solutions of alkaline earth chlorides is leading to lower individual activity coefficients of the chloride anions in comparison to the perchlorate anions in concentrated solutions of alkaline earth perchlorates. (compare Figures 5 and 6).

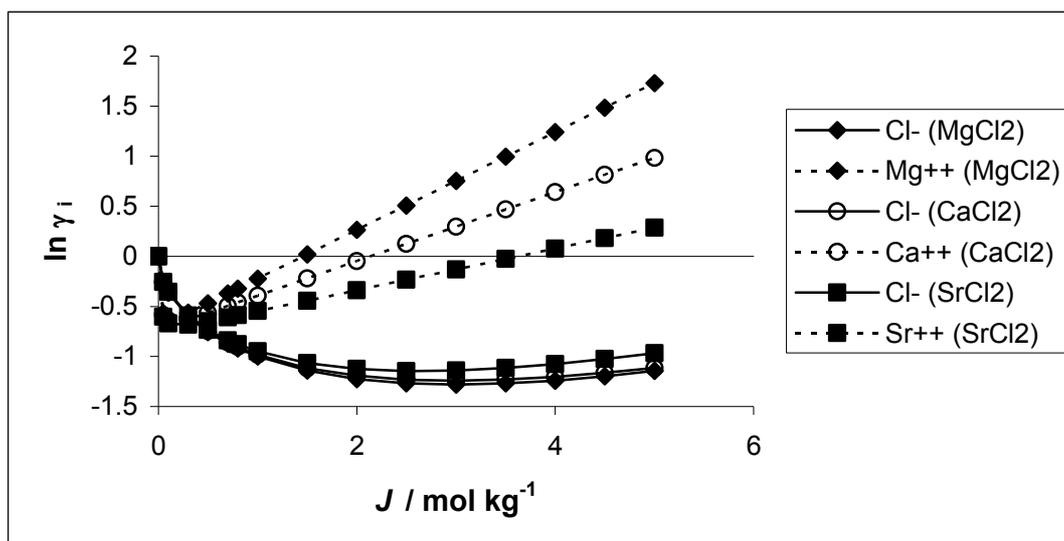


Figure 5. Individual ion activity coefficients of the alkaline earth chlorides on a logarithmic scale as a function of the ionic strength  $J$  (additional details see (Ferse, 1981))

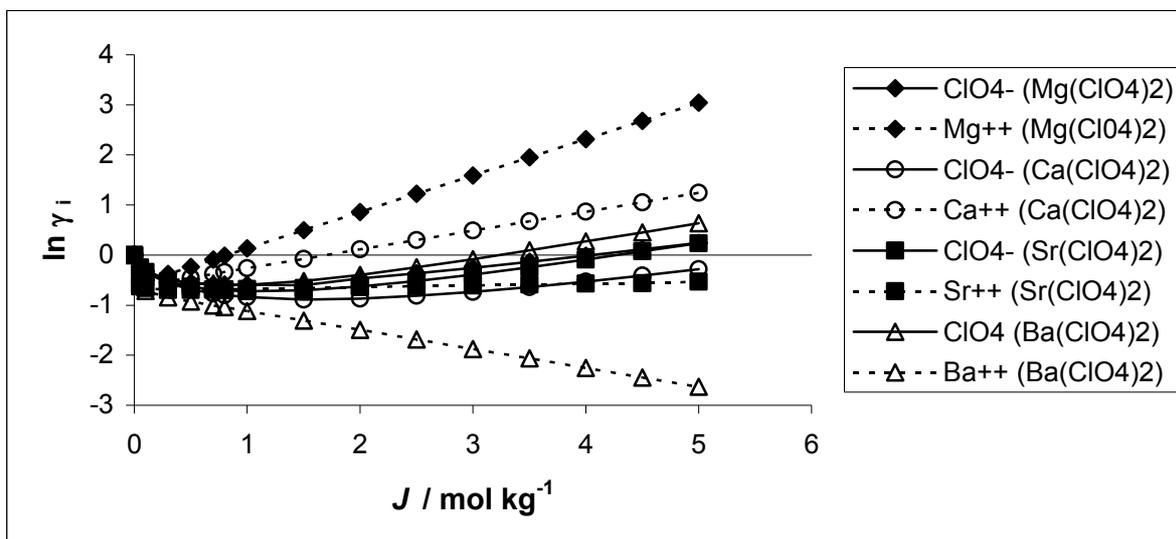


Figure 6. Individual ion activity coefficients of the alkaline earth perchlorates on a logarithmic scale as a function of the ionic strength  $J$  (additional details see (Ferse, 1981))

Knowledge of individual activity coefficients allows a determination of the diffusion potential of galvanic cells with transference without difficulties. Likewise the pH-value, as defined by Sørensen (see Eq. (6)) as well as the true acidity of a solution, can be derived.

While some phenomena, as those examples, can be readily interpreted by knowledge of individual activity coefficients, it cannot be expected that those provide answers to all electrochemical related vacant questions.

But even while the most important electrochemical equilibria and processes take place in surroundings that deviate significantly from *Debye-Hückel* conditions the knowledge of individual activity coefficients is helpful to offer new perspectives to the interpretation, e. g. also in the fields of reaction kinetics, electrode kinetics and electrochemical passivity.

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