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Estimation of activity coefficients of ionic species of aqueous strong electrolytes within the extended Debye–Hückel concentration range

Armin Ferse

Abstract The concentration curve of mean activity coefficient to the required power was fitted by a product function. The product function can be factorized in factor functions which represent the concentration dependence of the single-ion species (J Solid State Electrochem, in press, [1]). With a simplified procedure of this method, it is possible to split the mean activity coefficients into the individual parts for the ionic species within the extended Debye–Hückel concentration range. This method is applicable to all strong electrolytes because it is not necessary to have further data or additional assumptions.

Keywords Aqueous strong electrolytes · Activity concentration dependence · Factorizing of the mean activity coefficient · Single-ion activity coefficients · Debye–Hückel concentration range

Introduction

The analytical concentration "m" has to be modified with a multiplicative term "γ" for the thermodynamic interpretation of equilibriums within real mixed phases. This considers all forming interaction forces within the solution. The denotation activity "a" is used in physical chemistry

A. Ferse
Institute of Physical Chemistry and Polymer Physics,
Leibniz-Institute of Polymer Research Dresden,
Hohe Str. 6,
01069 Dresden, Germany

Present Address:
A. Ferse (✉)
Wiesenstr. 8,
01277 Dresden, Germany
e-mail: Armin.Ferse@googlemail.com

for the "modified concentration." The factor "γ" is designated to activity coefficient.

$$a = m \cdot \gamma \tag{1}$$

Equation 1 is valid for every solution component. The experimental determination of the activity coefficient "γ" is possible by implication. By all means, it is to bear in mind the fact that dissolved electrolytes in water in general are dissociated in cations and anions. The experimental determination of the activity or activity coefficient for a dissolved electrolyte basically yields the products of the values for the cations and anions $a_C \cdot a_A$ or $\gamma_C \cdot \gamma_A$, respectively. These products of the individual activities and the individual activity coefficients of the complementary ionic species are known as the mean activity "$a_\pm$" or mean activity coefficient "$\gamma_\pm$," respectively. For uni-univalent electrolytes, CA is valid:

$$a_C \cdot a_A = a_\pm^2 \tag{2a}$$

$$\gamma_C \cdot \gamma_A = \gamma_\pm^2 \tag{2b}$$

and for polyvalent electrolytes $C_{v_+}A_{v_-}$ it is valid as well:

$$a_C^{v_+} \cdot a_A^{v_-} = a_\pm^{v_+ + v_-} \tag{2c}$$

$$\gamma_C^{v_+} \cdot \gamma_A^{v_-} = \gamma_\pm^{v_+ + v_-} \tag{2d}$$

v_+, v_-: stoichiometric numbers of cation and anion from one molecule $C_{v_+}A_{v_-}$

In contrast to the mean activity, the individual activity of a single-ion species is not defined thermodynamically [2]. In principle, it is impossible to measure the individual ion activities or the individual activity coefficients of the

single-ion species [3, 4]. It must nonetheless be accepted that the mean activity coefficient to the required power of an aqueous strong electrolyte is purely mathematical and is the product of individual activity coefficients of the complementary ion species according to (2b) and (2d), respectively.

However, the ratios of individual activities and individual activity coefficients of two ion species with the same charge are defined thermodynamically [2], and these ratios are also determinable experimentally [5–7].

It was deduced from different investigations that the individual activity coefficients within mixed electrolyte solutions of the same composition can be differ significantly, especially the hydrogen ions of acids can reach extremely high values [5–10]. The important differences in values between the individual activity coefficients of different ionic species cannot be ignored permanently. There is therefore no justification in using mean activity coefficients for the thermodynamic interpretation of equilibriums and processes where dissolved electrolytes take part. Such a procedure implies the risk of arriving at erroneous conclusions. The search for a way to obtain knowledge of individual activity coefficients is legitimate and necessary.

However, precise information about the individual activity coefficients of single-ion species are the essential requirement for, e.g., the determination of the potential of single electrodes, the calculation of the liquid junction potential, 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.

To calculate single-ion activity coefficients, a purely mathematical method was developed by Ferse using the factorizing of a concentration function for mean activity coefficients of strong electrolytes in aqueous solution [1, 7, 11–13].

The generic mathematical approach

The experimentally accessible concentration curve for the mean activity coefficient to the required power has to be the product of the concentration functions for the individual activity coefficients of the complementary ion species of the dissolved electrolyte. For a uni-univalent electrolyte has to be valid:

$$\gamma_{\pm}^2(m) = \gamma_C(m) \cdot \gamma_A(m) \tag{3}$$

The concentration function of the mean activity coefficient $\gamma_{\pm}^2(m)$ represents implicitly the mathematically analytical properties of the factor functions. The mean activity

coefficient to the required power as function of the ionic strength "J" can be approximated well up to high concentrations using the basic product function (4) [1][1]:

$$\gamma_{\pm}^{\nu_+ + \nu_-}(J) = \overline{\gamma}_C^{\nu_+}(J) \cdot \overline{\gamma}_A^{\nu_-}(J) \approx \left[\sum_{k=1}^3 \delta_k e^{\sigma_k \cdot J^{\frac{k}{2}}}\right]^{\nu_+} \left[\sum_{k=1}^3 \vartheta_k e^{\tau_k \cdot J^{\frac{k}{2}}}\right]^{\nu_-} \tag{4}$$

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

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 [14]

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

The basic product function (4) was deduced from mathematical thoughts [1] and is not a result from the calculation of the excess Gibbs energy using the statistical mechanics. The factor functions in the relationship (4) represent the concentration functions for the individual activity coefficients of complementary ion species of the dissolved electrolyte [1]. 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 both ionic species. Concerning the mathematical approach, the values of the parameters in the factor functions of (4) are the only factors responsible for the gradually different concentration curves of the individual activity coefficients of the cations and anions [1].

The parameter determination of the basic product function (4) results from the optimal approximation of product function (4) to the existing experimental data for the concentration curve of the mean activity coefficients to the required power applying the nonlinear regression analysis [15–17]. Assuming the existence of a clear solution, estimating the product function yields the factorization of the product [15–17].

Generally, it is possible to fit the mean activity coefficient for the concentration range on the whole (from

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[1] Concerning the case $k=$lower bound of summation 1 and upper bound of summation 3, the relationship (4) is written in the paper by Ferse and Müller [1] dissolved in summands with a different designation of the parameters:

$$\gamma_{\pm}^{\nu_+ + \nu_-}(J) = \overline{\gamma}_C^{\nu_+}(J) \cdot \overline{\gamma}_A^{\nu_-}(J) \approx \left[c_1 e^{c'_7 \cdot J^{\frac{1}{2}}} + c_3 e^{c_9 \cdot J} + c_5 e^{c_{11} \cdot J^{\frac{3}{2}}}\right]^{\nu_+}$$
$$\left[c_2 e^{c'_8 \cdot J^{\frac{1}{2}}} + c_4 e^{c_{10} \cdot J} + c_6 e^{c_{12} \cdot J^{\frac{3}{2}}}\right]^{\nu_-}$$

zero up to highest concentrations of about 15 or 20 mol/kg) with the relationship (4) for the case of the index variable $k=1$, 2, 3, but applying the nonlinear regression analysis, the solution of the approach (4) is in the case $k=1$, 2, 3 ambiguous as a consequence of the ill-conditioned coefficient matrix [1]. The mathematical approach (4) is univocally soluble for the cases $k=1$ and $k=1$, 2 only. In these cases, the use of the limiting infinite dilution conditions (5) and (6) is requisite to the solute approach (4).

At infinite dilution have all activity coefficients the value 1:

$$\gamma_{\pm}(0) = \overline{\gamma}_C(0) = \overline{\gamma}_A(0) = 1 \qquad (5)$$

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

$$\lim_{m \to 0} \frac{\partial \gamma_{\pm}}{\partial \sqrt{m}} = \lim_{m \to 0} \frac{\partial \overline{\gamma}_C}{\partial \sqrt{m}} = \lim_{m \to 0} \frac{\partial \overline{\gamma}_A}{\partial \sqrt{m}} = -A' \qquad (6)$$

The solution of approach (4) for the case $k=1$ is limited to an electrolyte concentration zero (or nearly at zero), and the result is identical with the Debye–Hückel limiting law equation [18, 19] (for additional details see [1]). It is necessary to take in consideration the case $k=1$, 2 when the concentration $m>0$. The relationship (4) for the case $k=1$, 2 had the following form:

$$\gamma_{\pm}^{\nu_+ + \nu_-}(J) = \overline{\gamma}_C^{\nu_+}(J) \cdot \overline{\gamma}_A^{\nu_-}(J)$$
$$\approx \left[\delta_1 e^{\sigma_1 \cdot J^{\frac{1}{2}}} + \delta_2 e^{\sigma_2 \cdot J} \right]^{\nu_+} \left[\vartheta_1 e^{\tau_1 \cdot J^{\frac{1}{2}}} + \vartheta_2 e^{\tau_2 \cdot J} \right]^{\nu_-} \qquad (7)$$

In consideration of the limiting infinite dilution conditions (5) and (6), the relationship (8) is obtained using a new denotation of the parameters (for additional details see [1]):

$$\gamma_{\pm}^{\nu_+ + \nu_-}(J) = \overline{\gamma}_C^{\nu_+}(J) \cdot \overline{\gamma}_A^{\nu_-}(J) \approx \left[b_1 e^{-z_C^2 \cdot \frac{A'}{b_1} \cdot J^{\frac{1}{2}}} + (1-b_1) e^{b_3 \cdot J} \right]^{\nu_+}$$
$$\left[b_2 e^{-z_A^2 \cdot \frac{A'}{b_2} \cdot J^{\frac{1}{2}}} + (1-b_2) e^{b_4 \cdot J} \right]^{\nu_-} \qquad (8)$$

where $b_1, \ldots, b_4$ are the parameters A′: Debye–Hückel constant z_C, z_A: charge numbers of cation and anion in the molecule $C_{\nu_+} A_{\nu_-}$

It is to mind the fact that the values for the corresponding parameters change when an additional summand is considered in both factor functions became the system of functions is not orthogonal [1].

The parameters of the relationship (8) are univocally determinable only with the help of the previously developed asymptotic theory [1, 7, 11, 13]. The obtained set of parameters is valid for the concentration range $0 \leq m$; $J \leq 5$ mol/kg. This limitation results 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 [1, 7, 11, 12].

The present paper describes a simplified procedure deduced from this purely mathematical method using a "reduced approach." With the help of this "reduced approach" can be estimated the individual activity coefficients of single-ion species of aqueous strong electrolytes within the extended Debye–Hückel concentration range.

Splitting of mean activity coefficients into individual parts for complementary ion species within the extended Debye–Hückel concentration range using the "reduced approach"

The experimentally determined concentration curve for the mean activity coefficient to the required power is fitted with the relationship (8), and it is split in the factor functions for the individual activity coefficients of the complementary ion species using the asymptotic theory [1, 7, 13]. This method yields univocal and

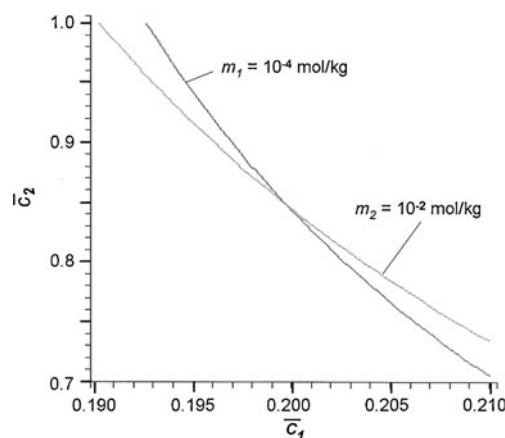**Fig. 1** Determination of the basic parameters $\overline{c}_1$ and $\overline{c}_2$ exemplified for an electrolyte of the empirical ion parameter $\tilde{a}=3.75$ Å with relationship (9) using the concentrations $m_1 = 10^{-4}$ mol/kg and $m_2 = 10^{-2}$ mol/kg and the corresponding mean activity coefficients (calculated with (10)) $\gamma_{\pm 1}^2 = 0.977029346$ and $\gamma_{\pm 2}^2 = 0.811040436$

Table 1 Calculated individual activity coefficients of the single-ion species of alkali chlorides, alkali cations $\overline{\gamma}_{C^+}$, and chloride anions $\overline{\gamma}_{Cl^-}$ determined by the "reduced approach" (9) using basic parameters $\overline{c}_1$ and $\overline{c}_2$, concentration range up to 0.05 mol/kg

Electrolyte		LiCl	NaCl	KCl	RbCl	CsCl
Ion parameter [Å]	$\widetilde{a}$	5.2	4.7	4.0	3.5	2.9
Basic parameters	$\overline{c}_1$	0.166	0.179	0.201	0.220	0.250
	$\overline{c}_2$	0.595	0.637	0.706	0.764	0.846
Concentration m [mol/kg]						
$m=0.001$	$\overline{\gamma}_{C^+}$	0.967	0.966	0.966	0.966	0.965
	$\overline{\gamma}_{Cl^-}$	0.964	0.964	0.964	0.964	0.964
$m=0.005$	$\overline{\gamma}_{C^+}$	0.935	0.933	0.932	0.931	0.929
	$\overline{\gamma}_{Cl^-}$	0.923	0.922	0.922	0.921	0.921
$m=0.01$	$\overline{\gamma}_{C^+}$	0.916	0.914	0.911	0.909	0.906
	$\overline{\gamma}_{Cl^-}$	0.893	0.893	0.892	0.890	0.890
$m=0.02$	$\overline{\gamma}_{C^+}$	0.895	0.892	0.887	0.883	0.879
	$\overline{\gamma}_{Cl^-}$	0.855	0.854	0.852	0.851	0.849
$m=0.05$	$\overline{\gamma}_{C^+}$	0.868	0.862	0.853	0.847	0.837
	$\overline{\gamma}_{Cl^-}$	0.787	0.785	0.780	0.777	0.774

reproducible results in the range of electrolyte concentrations between 0 and 5 mol/kg [1]. The set of parameters is invariant [1].

As the concentration approaches zero, the four-parametric basic approach (8) (and higher parametric basic approaches as well) [1, 7, 11, 12] leads to the relationship (9) with improved accuracy:

$$
\begin{aligned}
\gamma_{\pm}^{\nu_+ + \nu_-}(J) &= \overline{\gamma}_C^{\nu_+}(J) \cdot \overline{\gamma}_A^{\nu_-}(J) \\
&\approx \left[\overline{c}_1 e^{-z_C^2 \frac{A'}{\overline{c}_1}\sqrt{J}} + (1 - \overline{c}_1)\right]^{\nu_+} \\
&\quad \cdot \left[\overline{c}_2 e^{-z_A^2 \frac{A'}{\overline{c}_2}\sqrt{J}} + (1 - \overline{c}_2)\right]^{\nu_-},
\end{aligned}
\tag{9}
$$

where $\overline{c}_1$ and $\overline{c}_2$ are basic parameters because of the term e^J (and the fact that the exponential functions of the higher power of J as well) tends to approximate faster to 1 than $e^{\sqrt{J}}$ under this condition.

The Debye–Hückel relationship derived from theoretical thoughts [18, 19] works well for the calculation of the mean activity coefficients during the validation of the known preconditions. The extended Debye–Hückel Eq. 10:

$$
\ln \gamma_{\pm}^{\nu_+ + \nu_-} = \frac{-(\nu_+ + \nu_-)|z_C \cdot z_A|A'\sqrt{J}}{1 + B \cdot \widetilde{a} \cdot \sqrt{J}}
\tag{10}
$$

contains the empirical ion parameter $\widetilde{a}$. This factor $\widetilde{a}$ depends on both the cation and the anion of the dissolved electrolyte. With the help of Eq. 10, the mean activity coefficients are

calculable in the concentration range [14] $0 < m$, $J \leq 5 \times 10^{-2}$ mol/kg.[2] Equations can be established using relationship (9) for different ionic strengths, and hence the values $\gamma_{\pm}^{\nu_+ + \nu_-}(J)$ are preferably calculated by the extended Debye–Hückel relationship (10)[3, 4]. Thus, the parameters $\overline{c}_1$ and $\overline{c}_2$ can be determined as basic values for each strong electrolyte. The determination of the basic parameters $\overline{c}_1$ and $\overline{c}_2$ is exemplified for a uni-univalent electrolyte with the empirical ion parameter $\widetilde{a}=3.75$ Å in Fig. 1 applying both Eqs. 12 and 13. They are valid for the concentrations $m_1 = 10^{-4}$ mol/kg and $m_2 = 10^{-2}$ mol/kg, respectively.

$$
\begin{aligned}
\gamma_{\pm}^2(0.0001) = 0.977029346 &\approx \left[\overline{c}_1 e^{-\frac{A'}{\overline{c}_1}\sqrt{0.0001}} + (1 - \overline{c}_1)\right] \cdot \\
&\left[\overline{c}_2 e^{-\frac{A'}{\overline{c}_2}\sqrt{0.0001}} + (1 - \overline{c}_2)\right]
\end{aligned}
\tag{12}
$$

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[2] The following values [20] are used after the year 1977: $A' = 1.17625$ ($A = 0.510839$), $B = 0.32866$; all values are valid for aqueous solutions and a temperature of 298.15 K.

[3] Hamer and Wu [21], for example, used the following relationship (11) for the calculation of the mean activity coefficients but for an extended concentration range:

$$
\log \gamma_{\pm} = \frac{-A|z_C \cdot z_A|\sqrt{J}}{1 + B^*\sqrt{J}} + \beta \cdot J + C \cdot J^2 + D \cdot J^3 + \ldots
\tag{11}
$$

$B^*, \beta, C, D\ldots$: empirical constants, the values are different for all electrolytes.

Note: B^* in (11) is not identical with "$B \widetilde{a}$" in the extended Debye–Hückel Eq. 10!

[4] Extremely high accuracy is certainly not really important. They afford excellent services as operands.

Table 2 Calculated individual activity coefficients of the single-ion species of alkali hydroxides, alkali cations $\overline{\gamma}_{C^+}$, and hydroxide anions $\overline{\gamma}_{OH^-}$ determined by the "reduced approach" (9) using basic parameters $\overline{c}_1$ and $\overline{c}_2$, concentration range up to 0.05 mol/kg

Electrolyte		LiOH	NaOH	KOH	CsOH
Ion parameter [Å]	$\widetilde{a}$	2.1	4.3	4.5	6.1
Basic	$\overline{c}_1\overline{c}_2$	0.304	0.191	0.185	0.147
parameters		0.978	0.675	0.655	0.531
Concentration m [mol/kg]					
$m=0.001$	$\overline{\gamma}_{C^+}$	0.965	0.966	0.966	0.967
	$\overline{\gamma}_{OH^-}$	0.964	0.964	0.964	0.964
$m=0.005$	$\overline{\gamma}_{C^+}$	0.927	0.933	0.933	0.936
	$\overline{\gamma}_{OH^-}$	0.920	0.922	0.922	0.923
$m=0.01$	$\overline{\gamma}_{C^+}$	0.902	0.912	0.913	0.919
	$\overline{\gamma}_{OH^-}$	0.889	0.892	0.892	0.894
$m=0.02$	$\overline{\gamma}_{C^+}$	0.872	0.889	0.890	0.900
	$\overline{\gamma}_{OH^-}$	0.847	0.853	0.853	0.857
$m=0.05$	$\overline{\gamma}_{C^+}$	0.824	0.857	0.860	0.878
	$\overline{\gamma}_{OH^-}$	0.769	0.782	0.783	0.793

$$\gamma_{\pm}^2(0.01) = 0.811040436 \approx \left[\overline{c}_1 e^{-\frac{A'}{\overline{c}_1}\sqrt{0.01}} + (1 - \overline{c}_1)\right] \cdot$$
$$\left[\overline{c}_2 e^{-\frac{A'}{\overline{c}_2}\sqrt{0.01}} + (1 - \overline{c}_2)\right]$$

(13)

The parameters $\overline{c}_1$ and $\overline{c}_2$ used for calculating the individual ion activity coefficients are the average values obtained from the determinations in the concentration range between 10^{-5} and 5×10^{-2} mol/kg. The individual parts for complementary ion species are calculable by the "reduced approach" (9) with the basic parameters $\overline{c}_1$ and $\overline{c}_2$ determined in that way. The validity of the relation of approximation (9) limits the concentration range where it

can be applied. This range is identical to the extended Debye–Hückel concentration range in many cases.

The individual parts for single-ion species of alkali chlorides, alkali hydroxides, and alkaline earth chlorides of the concentration range $0<m$; $J\leq0.05$ mol/kg calculated by the "reduced approach" (9) are summarized in Tables 1, 2, and 3. These values are compared with values calculated with Eq. 8 using the asymptotic theory; these values are shown in Tables 4, 5, and 6 (for additional details see [1, 7]).

The agreements of values of the individual parts for single-ion species calculated with both methods are on average better than 0.5% in the concentration range of m and J between 0 and 0.02 mol/kg. Many uni-univalent electrolytes show good agreement at even higher concen-

Table 3 Calculated individual activity coefficients of the single-ion species of alkaline earth chlorides, alkaline earth cations $\overline{\gamma}_{C^{++}}$, and chloride anions $\overline{\gamma}_{Cl^-}$ determined by the "reduced approach" (9) using basic parameters $\overline{c}_1$ and $\overline{c}_2$, ionic strength up to 0.05 mol/kg

Electrolyte		$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
Ion parameter [Å]	$\widetilde{a}$	5.82	5.20	4.75	4.42
Basic parameters	$\overline{c}_1$	0.459	0.481	0.499	0.513
	$\overline{c}_2$	2.560	3.834	5.975	10.051
Ionic strength J^a [mol/kg]					
$J=0.001$	$\overline{\gamma}_{C^{++}}$	0.873	0.872	0.871	0.871
($m=0.000333$)	$\overline{\gamma}_{Cl^-}$	0.963	0.963	0.963	0.963
$J=0.005$	$\overline{\gamma}_{C^{++}}$	0.763	0.760	0.757	0.755
($m=0.001667$)	$\overline{\gamma}_{Cl^-}$	0.918	0.918	0.917	0.917
$J=0.01$	$\overline{\gamma}_{C^{++}}$	0.706	0.700	0.695	0.692
($m=0.003333$)	$\overline{\gamma}_{Cl^-}$	0.885	0.884	0.884	0.883
$J=0.02$	$\overline{\gamma}_{C^{++}}$	0.649	0.640	0.633	0.627
($m=0.006667$)	$\overline{\gamma}_{Cl^-}$	0.839	0.837	0.836	0.835
$J=0.05$	$\overline{\gamma}_{C^{++}}$	0.587	0.573	0.562	0.553
($m=0.016667$)	$\overline{\gamma}_{Cl^-}$	0.750	0.746	0.743	0.740

[a] The specified ionic strengths correspond to fractional concentrations. Thus, they were chosen to render a direct comparison with corresponding values at uni-univalent electrolytes

Table 4 Calculated individual activity coefficients of the single-ion species of alkali chlorides, alkali cations $\overline{\gamma}_{C^+}$, and chloride anions $\overline{\gamma}_{Cl^-}$ determined by the asymptotic theory [11, 13], concentration range up to 0.05 mol/kg

Electrolyte		LiCl	NaCl	KCl	RbCl	CsCl
Parameters [1, 7]	b$_1$	0.158	0.199	0.212	0.215	0.218
Corresponding to	b$_2$	0.786	0.701	0.695	0.724	0.756
basic approach (8)	b$_3$	0.414	0.132	0.00288	−0.0529	−0.246
	b$_4$	0.206	0.102	0.0732	0.115	0.277
Concentration m [mol/kg]						
$m=0.001$	$\overline{\gamma}_{C^+}$	0.967	0.966	0.966	0.966	0.966
	$\overline{\gamma}_{Cl^-}$	0.964	0.964	0.964	0.964	0.964
$m=0.005$	$\overline{\gamma}_{C^+}$	0.937	0.933	0.931	0.931	0.930
	$\overline{\gamma}_{Cl^-}$	0.922	0.922	0.922	0.922	0.922
$m=0.01$	$\overline{\gamma}_{C^+}$	0.921	0.913	0.910	0.909	0.907
	$\overline{\gamma}_{Cl^-}$	0.892	0.892	0.892	0.892	0.892
$m=0.02$	$\overline{\gamma}_{C^+}$	0.904	0.890	0.885	0.884	0.880
	$\overline{\gamma}_{Cl^-}$	0.852	0.853	0.853	0.853	0.853
$m=0.05$	$\overline{\gamma}_{C^+}$	0.890	0.860	0.850	0.847	0.838
	$\overline{\gamma}_{Cl^-}$	0.779	0.783	0.783	0.782	0.782

trations. The considerable increase in the deviations of a few electrolytes above 0.02 mol/kg are plausible because the mean activity coefficients of these electrolytes calculated by the extended Debye–Hückel relationship (10) differ clearly from the experimental data. Experimental data from the mean activity coefficients have to be used to calculate the individual parts for single-ion species with the help of (8) using the asymptotic theory. The result is that there cannot be an agreement in the calculated values when both methods are used. For polyvalent electrolytes, the approximations in (9) lose their validity step by step at ionic strengths $J>0.01$ mol/kg due to the enhanced complexity.

Discussion of results

The calculation of the single-ion activity coefficients with the "reduced approach" (9) is successful within the extended Debye–Hückel region. For this purpose, it is necessary to calculate the basic parameters $\overline{c}_1$ and $\overline{c}_2$. These basic parameters were obtained from mean activity coefficients which were advantageously determined with the help of the extended Debye–Hückel Eq. 10.

This method is applicable to every strong electrolyte within the extended Debye–Hückel region because it is not necessary to have further data or additional assumptions.

Table 5 Calculated individual activity coefficients of the single-ion species of alkali hydroxides, alkali cations $\overline{\gamma}_{C^+}$, and hydroxide anions $\overline{\gamma}_{OH^-}$ determined by the asymptotic theory [11, 13], concentration range up to 0.05 mol/kg

Electrolyte		LiOH	NaOH	KOH	CsOH
Parameters [7] corresponding	b$_1$	[a]	0.176	0.165	[a]
to basic approach (8)	b$_2$		0.871	0.739	
	b$_3$		0.305	0.372	
	b$_4$		0.153	0.147	
Concentration m [mol/kg]					
$m=0.001$	$\overline{\gamma}_{C^+}$		0.967	0.967	
	$\overline{\gamma}_{OH^-}$		0.964	0.964	
$m=0.005$	$\overline{\gamma}_{C^+}$		0.935	0.936	
	$\overline{\gamma}_{OH^-}$		0.921	0.922	
$m=0.01$	$\overline{\gamma}_{C^+}$		0.917	0.919	
	$\overline{\gamma}_{OH^-}$		0.890	0.892	
$m=0.02$	$\overline{\gamma}_{C^+}$		0.897	0.901	
	$\overline{\gamma}_{OH^-}$		0.849	0.852	
$m=0.05$	$\overline{\gamma}_{C^+}$		0.876	0.884	
	$\overline{\gamma}_{OH^-}$		0.774	0.781	

[a] It is not possible to determine because of missing mean activity coefficients in the concentration range >5 mol/kg

Table 6 Calculated individual activity coefficients of the single-ion species of alkaline earth chlorides, alkaline earth cations $\overline{\gamma}_{C^{++}}$, and chloride anions $\overline{\gamma}_{Cl^-}$ determined by the asymptotic theory [11, 13], ionic strength up to 0.05 mol/kg

Electrolyte		MgCl$_2$	CaCl$_2$	SrCl$_2$	BaCl$_2$
Parameters [7] corresponding to basic approach (8)	b$_1$	0.5102	0.5215	0.5300	a
	b$_2$	0.8930	0.8774	0.8580	
	b$_3$	0.4885	0.3442	0.2083	
	b$_4$	0.1862	0.1684	0.1749	
Ionic strength J[b] [mol/kg]					
$J=0.001$	$\overline{\gamma}_{C^{++}}$	0.871	0.871	0.870	
($m=0.000333$)	$\overline{\gamma}_{Cl^-}$	0.964	0.964	0.964	
$J=0.005$	$\overline{\gamma}_{C^{++}}$	0.757	0.755	0.753	
($m=0.001667$)	$\overline{\gamma}_{Cl^-}$	0.921	0.921	0.921	
$J=0.01$	$\overline{\gamma}_{C^{++}}$	0.695	0.691	0.689	
($m=0.003333$)	$\overline{\gamma}_{Cl^-}$	0.890	0.890	0.890	
$J=0.02$	$\overline{\gamma}_{C^{++}}$	0.633	0.627	0.623	
($m=0.006667$)	$\overline{\gamma}_{Cl^-}$	0.849	0.849	0.849	
$J=0.05$	$\overline{\gamma}_{C^{++}}$	0.567	0.556	0.548	
($m=0.016667$)	$\overline{\gamma}_{Cl^-}$	0.773	0.774	0.775	

[a] It is not possible to determine because of the missing mean activity coefficients in the concentration range >5 mol/kg

[b] The specified ionic strengths correspond to fractional concentrations. Thus, they were chosen to render a direct comparison with corresponding values at uni-univalent electrolytes

The impracticality of the "reduced approach" (9) for higher ionic strengths is obvious because one of the basic parameters is larger than 1 at polyvalent electrolytes (see Table 3). Hence, "negative single-ion activity coefficients" are obtained at high ionic strengths. This is a direct consequence of the approximations used in the derivation of (9). These approximations caused major differences in polyvalent electrolytes due to the enhanced complexity. This effect only occurs insignificant at lower concentrations.

For concentrations outside the extended Debye–Hückel region, the factorizing of mean activity coefficients into individual parts for single-ion species have to be calculated with the help of the asymptotic theory using the relationship (8) (for additional details see [1, 7]).

Kielland [22, 23] took advantage of the modified Debye–Hückel Eq. 14 to calculate individual ion activity coefficients γ_i within the extended Debye–Hückel concentration range:

$$-\log \gamma_i = \frac{A \cdot z_i^2 \sqrt{J}}{1+\rho\sqrt{J}} \qquad (14)$$

where $\rho = B \cdot \tilde{a}_i'$

$\tilde{a}_i'$ is the individual ionic parameter. In contrast to $\tilde{a}$ in Eq. 10, the individual ionic parameter $\tilde{a}_i'$ is always valid for one ionic species only, either the cation or the anion. Kielland received the values of $\tilde{a}_i'$ from data for the ionic mobilities, radii in the crystalline solid, deformability, and hydration numbers. The individual ion activity coefficients γ_i for different ions calculated with the help of these $\tilde{a}_i'$ and Eq. 14 are shown in Table 7.

Table 7 Individual activity coefficients of single-ion species by Kielland [22] calculated with the modified Debye–Hückel Eq. 14

Ion	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Cl$^-$	OH$^-$
$\tilde{a}_i'$ [Å]	6	4.5	3	2.5	2.5	8	6	5	5	3	3.5

Calculated values of the individual activity coefficients by Kielland are independent on the complementary ion species

Ionic strength

J [mol/kg]											
$J=0.001$	0.966	0.965	0.965	0.964	0.964	0.871	0.869	0.868	0.868	0.965	0.965
$J=0.005$	0.929	0.928	0.925	0.924	0.924	0.755	0.749	0.744	0.744	0.925	0.926
$J=0.01$	0.907	0.902	0.899	0.898	0.898	0.69	0.675	0.67	0.67	0.899	0.900
$J=0.02$	0.878	0.871	0.864	0.862	0.862	0.616	0.594	0.583	0.583	0.864	0.867
$J=0.05$	0.835	0.82	0.805	0.80	0.80	0.52	0.485	0.465	0.465	0.805	0.81

Excerpt from Tables 3–2: "Activity Coefficients of Ions in Water" [23] completed partially

The individual ion activity coefficients in the present paper exhibit the same trend in the dependence on the concentration as well as the ionic species as the value by Kielland. Admittedly, the agreement is not perfect. The differences increase with increasing concentration. At rising concentration, the calculated mean activity coefficients using the individual activity coefficients by Kielland are smaller than the measured values for real salt solutions in many cases. Perhaps it is not surprising that there are differences. The greatest disadvantage of the individual activity coefficients calculated by Kielland is the fact that the values are independent of the complementary ionic species. This result does not reflect the reality. Electrolyte solutions always contain cations and anions in combination. The interionic interaction is caused from all ionic species in the solution. Consequently, the individual activity coefficients of a single-ion species must depend on the complementary ion species as well. This fact is realized using the purely mathematical method [1] as well as the "reduced approach" described above.

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