ORIGINAL PAPER

Reply to the comment by F. Malatesta on: "Factorizing of a concentration function for the mean activity coefficients of aqueous strong electrolytes into individual functions for ionic species" by A. Ferse and H.-O. Müller

Armin Ferse

Abstract The arguments of Malatesta (J Solution Chem 29:771–779, 2000; Fluid Phase Equil 295:244–248, 2010) exclude the experimental determination of individual ion activity coefficients. I agree that a measurement of single-ion activity coefficients is impossible. But the comment of Malatesta (J Solid State Electrochem (in press), 2011) in the connection with the purely mathematical procedure developed by Ferse and Müller (J Solid State Electrochem (in press), 2011) is senseless because there is no new aspect which is not also given in the paper of Ferse and Müller (J Solid State Electrochem (in press), 2011). All of the mentioned problems are already discussed and clarified in the publication by Ferse and Müller (J Solid State Electrochem (in press), 2011). The purely mathematical method is a possibility to obtain the concentration functions for the individual activity coefficients of the complementary ion species by factorizing a product function of the experimentally accessible concentration dependence of the mean activity coefficients to the required power.

A. Ferse (✉)
Leibniz-Institute of Polymer Research Dresden,
Institute of Physical Chemistry and Polymer Physics,
Hohe Str. 6,
01069 Dresden, Germany
e-mail: Armin.Ferse@googlemail.com

Present Address:
A. Ferse
Wiesenstr. 8,
01277 Dresden, Germany

The situation in general

There is a dilemma concerning the individual ion activity coefficients. The individual ion activity coefficients of dissolved electrolytes cannot be defined thermodynamically, and it is known to be impossible to measure them only by using classical thermodynamic methods.

The subject of single-ion activity coefficients splits the electrochemists in two groups: Some (even perhaps many) electrochemists meanwhile accept that the concept of single-ion activity coefficients is useful and necessary to tackle problems. The other part negates the importance of single-ion activity coefficients. Many of them claim that the individual activity coefficients of single-ion species are entities without physical significance. This is a dogma for the puritans of the electrochemists. A part of this group denies the existence of single-ion activity coefficients on principle. Malatesta is a follower of the opinion of the second category of electrochemists. Indeed, his previous communications to the impossibility of measuring of single-ion activity coefficients are justified [1, 2], but the recent paper [3] is pure polemic. His reproaches against the purely mathematical procedure to calculate individual ion activity coefficients are without any foundation.

Individual ion activity coefficients can differ significantly among each other and from the mean activity coefficient as well. This assumption is verified by the ratio of individual ion activity coefficients [4, 5]. The ratio of individual ion activity coefficients with the same charge is defined thermodynamically [6] as well as experimentally accessible [4, 5]. The important differences between the values of the individual activity coefficients of different ionic species cannot be ignored permanently. Such a procedure implies the risk of arriving at erroneous conclusions.

The knowledge of individual ion activity coefficients is important, e.g. for the interpretation of equilibriums and processes where dissolved electrolytes take part. They are a basic requirement for data about the potentials of single electrodes as well as for the calculation of the liquid-junction potential, and they are necessary for the solution of many different research fields in the electrochemistry.

I was in correspondence for a long time with Malatesta in connection with my purely mathematical procedure. Its point of view to my purely mathematical method is expressed clearly in his statement: "A mathematically-thermodynamically consistent decomposition of the mean activity coefficients into individual ion activity coefficients; which, however, is wrong (although I am not able to see any wrong statement in it!!!)" [F. Malatesta, personal communication (e-mail to Ferse A.), 2010/10/29]. Even though he was not able to find any fault in my concept and procedure, he perseveres in his point of view that nothing can be what is not allowed in his opinion. It is apparent that Malatesta recognises the efficiency of my approach, but he does not want to accept the result. With such an opinion, an objective judgement cannot be expected.

I agree with the statement that the experimental determination of individual ion activity coefficients is impossible on principle. Malatesta has logically proved this fact once more [1, 2]. But the fact that the measurement of individual ion activity coefficients is excluded does not imply that the individual ion activity is without a real efficacy. The different efficacy of various ionic species is meanwhile known [4, 5, 7]. However, it is not accepted in general because individual activity coefficients are neither defined in thermodynamic terms nor can they be determined experimentally [6]. For this reason, it is necessary to go new ways to obtain knowledge about the desired single-ion activity coefficients.

Necessity of a new way to obtain the desired single-ion activity coefficients

The purely mathematical method affords new impulses for the solution of the problem "single-ion activity". Although

the arguments by Malatesta [1, 2] exclude the experimental determination of single-ion activity coefficients, these arguments are useless for the purely mathematical procedure described by Ferse and Müller [7]. Malatesta perceives that it is possible, at least in principle, to univocally factorize my product function [3].

Of course, in contrary to the mean activity, the individual activity of single-ion species is not defined thermodynamically [6]. Nevertheless, it must also be accepted that the mean activity to the required power is purely mathematical, and it represents the product of the individual activities of the complementary ion species:

Therefore, it is a mathematically safe fact that the experimentally accessible concentration curve of the mean activity coefficient to the required power has to be the product of the concentration functions for the complementary single-ion activity coefficients of the dissolved electrolyte [7]. The mathematical approach by Ferse and Müller considers in the structure of the product function as one fixed point the infinite dilute solution. 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 special concentration range, $5 \leq J \leq 10$ mol/kg, where the logarithm of the mean activity coefficient of strong electrolytes is linearly dependent on the concentration (for additional details, see [7]). The product function was split into factor functions. Assuming the existence of a clear solution, estimating a product function yields the factorizing of the product [8–10]. Both factor functions have the same predefined structure. The values of parameters in the factor functions are the only factors responsible for the gradual different courses of the obtained factor functions. In the paper by Ferse and Müller [7], the difficulties as well as the possibility to solve these problems are described. Applying the previously developed asymptotic theory [11, 12], the parameter determination of the product function is *univocal and invariant*. The obtained set of parameters is valid in the concentration range between 0 and 5 mol/kg.

Does the comment by Malatesta contain new aspects?

The possibility to factorize univocally the product function used by Ferse and Müller is accepted by Malatesta. It is important to lay emphasis on this fact. However, Malatesta is not ready or does not want to accept that the calculated factor functions are identical with the concentration functions for the individual ion activity coefficients, and just this question is definitely relevant in the case of the purely mathematical method to calculate individual activity

coefficients. However, the arguments by Malatesta in his comment [3] are no basis to clarify this question.

Malatesta has mixed physicochemical requirements for activity coefficients and the purely mathematical considerations which are valid for products of concentration functions. He forgets that physicochemical requirements are not in existence for single-ion activity coefficients because there is no thermodynamic definition of individual ion activity [6]. In contrast to that, purely mathematical approaches are valid in any case, but it is necessary to pay attention to mathematical laws if they are used.

Obviously, Malatesta made a mistake in connection with his equation (9) [3]. In contrast to his statement, it is easy to perceive that the solution is *ambiguous regarding the* In ζ_1 and In ζ_2, respectively, in as much as the *arrangement* of the determined *parameters is variant*. Normally, the equation (9) has to be solved based on the least squares method because more measurements exist than unknown parameters. *The solution is ambiguous* as well. Therefore, his rhetorical question "Are ζ_1 and ζ_2 or $\widetilde{\xi}_1$ and $\widetilde{\xi}_2$ the better candidates for y_+ and y_- ?" [3] is vain, and it is a useless attempt of argumentation to its own disadvantage. There is nothing for it but his belief (see [F. Malatesta, personal communication (e-mail to Ferse A.), 2010/10/29]).

In mathematical monographs of nonlinear regression analysis [8–10] is noted that the prerequisites for the application of the concept of splitting of a product function are (a) the meaningful structure of the product function, (b) the splitting is univocal regarding the factor functions, and as well as (c) the verification that the obtained results yield plausible values. Therefore, these three points are discussed in detail in the publication by Ferse and Müller [7]. As is generally known, an experimental verification of the results is impossible. Ferse and Müller [7] have verified on another way that the factor functions are compatible with the concentration functions of the individual activity coefficients. The facts are given in the following sections of the paper [7]:

Discussion of the approach and parameter determination

The mathematical approach
The determination of parameters
Impact of a hypothetical multiplicative concentration function G

Discussion of results using corresponding approximations

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

Furthermore belong the exclusion of multiplicative terms in the mathematical approach used by Ferse and Müller and the theoretical required agreement of corresponding factor functions, which was found indeed if the product functions of mean activity coefficients for three-component systems are independently split (for additional details, see [7]).

It is not necessary to repeat the arguments, which are given in the sections mentioned above. These arguments verify the correctness of the purely mathematical procedure as well as that the obtained factor functions represent the desired concentration dependences of the individual ion activity coefficients.

It is not to recognise why Malatesta ignores these arguments. Malatesta's comment [3] is superfluous because it is missing in some way or other an explanation with these facts.

It is legitimate and necessary to search for a way for the solution of the problem "individual ion activity". On principle, the purely mathematical method described by Ferse and Müller [7] is a new approach to solve this problem.

References

1. Malatesta F (2000) J Solut Chem 29:771–779
2. Malatesta F (2010) Fluid Phase Equil 295:244–248
3. Malatesta F (2011) J Solid State Electrochem (in press)
4. Ferse A, Ferse E (1966) Z Chem 6:241–255
5. Ferse A (2008) Z Anorg Allg Chem 634:797–815
6. Guggenheim EA (1929) J Phys Chem 33:842–849
7. Ferse A, Müller H-O (2011) J Solid State Electrochem (in press). doi:101007/s10008-011-1413-9
8. Bates DM, Watts DG (1988) Nonlinear regression analysis and its applications. Wiley, New York
9. Neter J, Kutner MH, Nachtsheim ChJ, Wasserman W (1996) Applied nonlinear statistical models, 4th edn. McGraw-Hill, Boston
10. Seber GAF, Wild CJ (2003) Nonlinear regression. Wiley, New York
11. Ferse A (1977) Z Phys Chem Leipzig 258:257–279
12. Ferse A, Neumann P (1977) Mathem Operationsforschg und Statistik. Ser Stat 8:529–543