

Activity coefficients of ions in sodium halide solutions: Critical remarks

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ABSTRACT

The fundamentals of an experimental method proposed by Zhuo et al. [1], to determine activity coefficients of sodium and halide ions in sodium halide solutions, are critically examined. It is shown that this method relies on a key hypothesis, which proves to be incorrect, about the liquid junction potential, whose value is assumed not to change when the concentration of the sample solution is changed. The direct consequence of this assumption is that results that are interpreted as the activity coefficients of sodium and halide ions are, instead, conventional values, which only depend on the mean activity coefficients and transport numbers, and have no connection with the activity coefficients of the respective ions.

Considerations valid for all papers dealing with the experimental determination of ionic activity coefficients are derived. Such papers are to be regarded as incorrect.

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1. Introduction

A paper was recently published in this Journal, “Activity coefficients of individual ions in aqueous solutions of sodium halides at 298.15 K”, by Zhuo et al. [1], in which conventional values of ionic activity coefficients are taken for the activity coefficients of the corresponding ionic species. This confusion is potentially negative for scholars working with electrolyte solutions, owing to the risk that findings that are a mere artifact of arbitrary assumptions (e.g., the activity coefficients of Na^+ found to be lower than those of F^- and higher than those of Cl^- and Br^- in [1]) may be mistaken for experimental evidence. The purported ionic activity coefficients of [1] rely on an arbitrary assumption regarding the liquid junction potential (E_j), a quantity that, like the ionic activity coefficients, can be defined only in conventional terms. Conventions for ionic activity coefficients (γ_i) and liquid junction potentials are interrelated, and infinite self-consistent combinations exist, which are perfectly equivalent and interchangeable.

The question of the determination of ionic activities dates back to last century. In late 1921, Lewis and Randall emphasized that ‘it would be of much theoretical interest if we could determine the actual activity of an ion in a solution of any concentration. This indeed might be accomplished if we had any general method of calculating the potential at a liquid junction’ [2]. As regards the possibility of calculating the potential at a liquid junction, however, severe reservations were expressed a few years later by Taylor [3] and Guggenheim [4,5] who proved, respectively, that (i) also in cells

with liquid junctions, the electromotive force depends on the activity of complete electrolytes, and not on the individual activities of the ions that compose these electrolytes, exactly as in the case of cells without liquid junctions [3]; and, (ii) the calculation of the liquid junction potential is impossible without the prior knowledge of the same ion activities that one would like to derive from the knowledge of the liquid junction potential [4], thus yielding infinite equivalent possibilities. Even more important, Guggenheim (and to some extent Taylor) demonstrated that the very concept of a difference of electrical potential between two different phases has no physical significance; by consequence, also the individual electrode potentials, chemical potentials of charged constituents of a solution, liquid junction potentials, and activities and activity coefficients of individual ionic species, are entities with no physical significance and can only be defined in merely conventional terms [3–5].

A quantity that cannot be defined uniquely cannot be measured *a fortiori*; therefore, it was to be expected that after 1930, no scientist would insist on attempting to determine the actual values of ion activity coefficients. Things evolved otherwise, however. Papers [6–8] may give an idea of the debate between supporters of the opinion that experimental determinations of ion activity coefficients are in some way possible, and those who exclude this possibility.

In reality, the discussion had no reason to exist: Guggenheim’s arguments that exclude any possible determination of these quantities have never been invalidated. Yet, ignoring the conceptual impossibility, Zhuo et al. [1] published their experimental values of ionic activity coefficients.

To show that their results are not valid, we will not appeal once again to the general principle that ionic activity coefficients and

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E_j are concepts with no physical significance; we will act instead (like the authors of [1]) as if the γ_i and E_j functions were univocally definable and potentially knowable, and we will examine in depth the effects of the basic assumption paper [1] relies on, i.e., that the variation of E_j with the concentration of the solution examined “*can be safely neglected*” [1]. We will prove in the next sections that, because of this assumption, the quantities taken for γ_i in [1] are, instead, other functions which only depend on the mean activity coefficients (γ_{\pm}) and transport numbers (t_i) and are unrelated to γ_i .

2. Fundamentals

For any isothermal Voltaic cell, a general equation exists [9],

$$E = E_{\omega}^{\circ} - E_{\alpha}^{\circ} - S \sum_s v_{s,\alpha} \ln a_{s,\alpha} + v_{s,\omega} \ln a_{s,\omega} + \int_{\alpha}^{\omega} \tau_s d(\ln a_s) \quad (1)$$

in which S is the Nernstian slope RT/F ; E_{α}° and E_{ω}° are the standard potentials of the terminal electrodes; $v_{s,\alpha}$ and $v_{s,\omega}$ are the virtual numbers of moles of any species s (ions or molecules) formed at the respective electrodes when one virtual faraday of electricity goes through the cell from left to right in the cell; τ_s (the “*transferance*” number of s using the Scatchard definition [9]) are the moles of species s which would be virtually transferred in the direction of the cations for any virtual faraday, at constant composition (the product $\tau_s \times z_s$, where z_s is the charge of s with its sign, is the usual transport number of s , t_s , null for molecules); and a_s is the activity of s . The term $-S \sum_s \int_{\alpha}^{\omega} \tau_s d(\ln a_s)$ represents the overall potential introduced by liquid junctions and membranes encountered along the path which, starting from the metal–solution interface (α) of the left electrode (e.g., the internal metallic electrode of an ISE), arrives at the metal/solution interface (ω) of the right electrode (e.g., the internal metallic electrode of another ISE). Eq. (1) of Ref. [1] is a corollary of the present Eq. (1). Although the ionic activity coefficients are apparently involved in Eq. (1) through the a_s terms, it has been well known since Taylor’s paper [3] that these quantities are connected to one another in such a way that only the activities of neutral sets of ions (e.g., $\text{Na}^+ + \text{Cl}^-$) and molecular species (e.g., H_2O) survive. Therefore, the electromotive force of any cell – the only quantity that the experiments provide – contains no information about the γ_i values [3,6]; any set of possible γ_i functions that are consistent with the E values is perfectly equivalent to, and replaceable by, infinite other sets of alternative γ_i functions able to compose the same γ_{\pm} values, with no physical possibility of distinction.

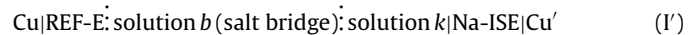
If one divides a cell into arbitrary sections, then the individual potentials of these sections conserve, unlike E , a net dependence on individual ionic activities that do not simplify off (e.g., the individual potential of a section consisting of a silver chloride–silver electrode immersed in a KCl solution is a function of a_{Cl^-}). Unfortunately, the potentials of the individual sections are quantities that cannot be measured, or even defined except in a conventional form. To draw from E the potential E_X of a section X (e.g., an ISE; a liquid junction; a membrane; etc.), which contains in theory the desired information about one or more γ_i , it would be necessary to know the complementary quantity $E_Y = E - E_X$ pertaining to the residual sections, which however depends on other unknown γ_i ; and vice-versa. If we use an approximate estimation for E_Y (which is the same as assigning conventional γ_i values inside all cell sections but X), then we obtain conventional values also for E_X and the γ_i involved in E_X . That is exactly the procedure adopted in Ref. [1], where the convention concerns the connection between the inner solution of the reference electrode and the sample solution. In Ref. [1], indeed, it is assumed arbitrarily that the double junction connection allows the liquid junction potential to remain constant when the concentra-

tion of the sample solution varies, ‘*as the major internal component [i.e., the filling solution of the salt bridge] stays constant*’. This arbitrary assumption (or in other words, this *convention*) leads us to determine experimental values of something (we shall name it Ξ_i for short) which is supposed, in Ref. [1], to coincide with $\gamma_i/\gamma_{i,R}$ ($\gamma_{i,R}$, the value of γ_i in a solution k indicated as R , selected as a reference point). Starting from this supposition, the Ξ_i values are used in connection with an expanded form of the Debye–Hückel equation in order to identify, by least squares, the value of the quantity that is assumed to be $\gamma_{i,R}$ in Ξ_i (and would really be $\gamma_{i,R}$ if Ξ_i were $\gamma_i/\gamma_{i,R}$, which is not the case). The supposed $\gamma_{i,R}$ and Ξ_i values used as if these were $\gamma_i/\gamma_{i,R}$, provide *conventional* γ_i , which Zhuo et al. [1] take for γ_i . Furthermore, as any error ε_j in E_j introduces opposite errors ε_j/S and $-\varepsilon_j/S$ in $\ln \gamma_+$ and $\ln \gamma_-$, these conventional γ_i obey the correct relationship $\ln \gamma_+ + \ln \gamma_- = 2 \ln \gamma_{\pm}$ as if these were the ion activity coefficients, but this occurrence, of course, has no value to demonstrate that these are the “correct” γ_i .

A closer examination of the methods used by Zhuo et al. [1] (next section) allows us to better understand the consequences of the key assumption that the dependence of E_j on the concentration of sodium halide “*can be safely neglected*” [1].

3. The quantities that the method of Zhuo et al. [1] identifies

Let us examine what really happens in a cell very similar to cell (I) of Zhuo et al. [1],



For E to represent the difference between the potential of the right side metal Cu' and the left side metal Cu of the cell, in (I') we have exchanged left and right electrodes, compared with cell (I) of Ref. [1]. As in cell (I) of [1], the ISE is Nernstian. The only difference between cell (I) of [1] and this cell (I') is the salt bridge b , which in cell (I) is filled by a different electrolyte (10% sodium nitrate, [1]), while in cell (I') it contains NaX (concentration m_b) like k (concentration m). This condition is required for exact mathematical development to be feasible (with a heteroionic salt bridge as in cell (I), E_j depends on the individual profiles of ion concentrations in the transition zone between b and k , which are time-dependent until they reach some no better identified stationary equilibrium). By indicating as n_{w+} and n_{w-} the hydration numbers of the cation and anion, the transference number of water holds $\tau_w = n_{w+}t_+ - n_{w-}t_-$. The electromotive force of cell (I') has the same conventional form reported in [1] for cell (I):

$$E = E^{\circ} + S \ln a_i + E_j \quad (2)$$

($i = \text{Na}^+$; E_j , the liquid junction potential between b and k ; $E^{\circ} = E^{\circ}_{\text{ISE}} - E_{\text{REF-E}} + E'_j$, where E'_j is the liquid junction potential on the left side of b , constant). Following Zhuo et al. [1], we select one particular solution k , named R , as our reference point, and define ΔE as the difference between the E values measured in each solution k and in R ,

$$\Delta E = S \ln \left(\frac{a_i}{a_{i,R}} \right) + \Delta E_j \quad (3)$$

with $\Delta E_j = E_j - E_{j(R)}$

According to the general equation of voltaic cells, we have

$$E_j = -S \sum_s \int_b^k \tau_s d(\ln a_s) \quad (4)$$

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