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A complete discussion of the rationale supporting the experimental determination of individual ionic activities

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Abstract

This work discusses the reasons why the activities of ions were considered to be impossible to measure using electrochemical cells with liquid junctions. The key steps followed to overcome the experimental and conceptual barriers are outlined and an overview of the successful method for measuring ionic activities is presented. The comparison of two approaches used for reducing the experimental emf data is used to emphasize the negligible effect introduced by errors in the estimate of junction potentials. The possible effects of underlying assumptions of the method on the accuracy of the activity coefficients obtained are discussed and evaluated. Two options of handling the independent equations relating the activity of a single ion to the junction potential are presented and it is demonstrated why Malatesta's procedure cannot provide ionic activities while our method can. Additional examples are presented demonstrating that ionic activities are real quantities. The robustness of the proposed method for their measurement is tested.

Keywords: Ions; activity; Activity coefficients; Electrolytes; Junction potential; Ion selective electrodes

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1. Introduction

When our group proposed a method to measure ionic activities [1], we knew that the road would not be easy. In a recent manuscript [2], we presented a brief historical review that clearly shows how controversial the topic has been for the last 80 years. As detailed in that manuscript, most standard texts unambiguously state that the activity of individual ions cannot be measured by thermodynamic means. In practical terms, the field is divided between two schools of thought: those who, following Taylor [3] and Guggenheim [4–6], deny the mere existence of ionic activities, and those who, following Lewis and Randall [7] and Brönsted [8,9], affirm their physical existence and measurability. It is interesting to observe that at the time when this discussion started there was not even a universally accepted view on the existence of the 'ether' [10].

A deafening silence followed all the first publications of our group on the subject [1,11–15] until Malatesta [16], based on the Taylor–Guggenheim arguments, published his first manuscript against our work. There was an overlap of publications, and three of our manuscripts [17–19] were published before we became aware of Malatesta's work [16]. In all subsequent publications [20–23], we have acknowledged Malatesta's disagreement with our views on the subject. In a personal communication to the senior author, Malatesta [24] expressed his disbelief that after his publication [16] we would still be unaware that the liquid junction potentials and ion activity coefficients published by us were 'completely meaningless'. Judging that our publications damaged 'the correct progress of science', he announced that he would send papers to any journal that had published our work. We answered [2] directly the arguments presented in two of his manuscripts [16,25]. In addition, as in a recent publication [26] Malatesta exactly repeated the arguments he had already presented [25], readers of this latter manuscript were invited [27] to find our answers elsewhere [2]. This work is in response to Malatesta's most recent publication on the subject [28].

The fact that 14 publications by our group [1,2,11–15,17–23] on our method, 2 publications by other groups either following the same method or using its results [29,30], and 4 publications

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by Malatesta [16,25,26,28] against the method have all been accepted by highly qualified referees in international journals, clearly demonstrates the need for an in depth discussion of this subject.

In what follows, we clearly state the problems encountered by previous researchers trying to measure ionic activities, the ways in which our method handles these problems, a discussion of some previous queries and a rebuttal to the most recent publication by Malatesta [28]. In a previous work [20], we presented experimental evidence demonstrating that the activity of an individual ion not only has physical reality but at the same concentration and temperature has different values in the presence of different counterions. The main aim here is to prove that we indeed can measure the activity of ions, emphasize the key aspects of the method and present a few selected numerical examples. Thus, for the first time we present here an overview of the problem and the method for its solution with all detail.

2. Statement of the problem

The concept of the activity of an individual ion i, a_i, and its relation to the emf of a single electrode were introduced by Lewis [31]. In practice, we prefer to work in terms of the activity coefficient, γ_i, that has a more convenient limit at infinite dilution for a solute treated in the unsymmetrical convention. Molality is usually employed as the composition variable for the solute in the treatment of electrolyte solutions. For a solution of (dimensionless) molality $m_{i,k}$, the activity and the activity coefficient of an individual ion are related by:

$$a_{i,k} = m_{i,k}\gamma_{i,k} \tag{1}$$

Ion selective electrodes (ISE's), developed for ions other than H^+ in the 1960s [32], opened a new possibility of measuring the activity of individual ions. With these electrodes, it is possible to build an electrochemical cell formed by a single-junction Ag/AgCl reference electrode, filled with a standard solution (r), and a half-cell ISE sensitive to the selected ion i, both electrodes immersed in the sample solution (k). A figure showing the experimental setup was presented previously [22]. In the potentiometric convention [22], the schematics for this cell is written as:

Ag, AgCl|standard solution (r)|sample solution (k)|ISE (i)

The bar between the standard and the sample solutions indicates that both solutions are in contact and, thus, a junction potential, $E_{J,k}$, is present. The voltage (emf) between the reference electrode and the ISE, $E_{i,k}$, measured with a voltmeter, is related to the ionic activity and the junction potential by [33]:

$$E_{i,k} = E_{i,0} + S_i \ln a_{i,k} + E_{J,k} \tag{2}$$

where $E_{i,0}$ is constant term for a particular measurement. This constant includes the standard potential, the internal junction potential and the asymmetry potential of the ISE in addition to all fixed potentials of the reference electrode. Considering that electrodes are transient devices, mostly due to the asymmetry and the internal junction potentials, this term is not expected to be the same for measurements of the same sample composition in different runs. The constant S_i is referred to as the slope of the emf response of the ISE and there is evidence [34–37] that it may differ from the Nernstian value given by the ratio (RT/z_iF), where R is the gas constant, T the absolute temperature, F the Faraday constant and z_i is the charge of ion i. The sign of S_i is given by the sign of z_i. The expression for the junction potential between the standard and the sample solutions has the form:

$$E_{J,k} = -\frac{RT}{F}\sum_j \int_r^k \frac{t_j}{z_j}\,d\ln a_j \tag{3}$$

where the summation is over all ions present in both solutions and t_j is the transference number of species j, for which independent information is available in the literature. Eq. (3) can be obtained from physical–chemical considerations [38] or from electro-diffusion phenomena [2,22]. In addition, as we have demonstrated [2,22], it corresponds to the electric potential difference between sample solution and the standard solution.

Thus, the problem can be stated as follows: "Consider an experiment at temperature T, using a half-cell ISE for ion i and a single-junction reference electrode. Assume that the composition dependence of t_j is available from the literature for all ions present. Knowing $E_{i,k}$ from the voltmeter reading, determine the activity of ions i at a molal concentration $m_{i,k}$ of the sample solution".

As the purpose of this work is to demonstrate the measurability of ionic activities, we first concentrate the attention on the case of a concentration cell, i.e., the case in which the sample solution has the same ions as the standard solution. This type of system is sometimes referred to as homoionic. In addition, for simplicity, we consider a 1:1 electrolyte, denoting the cation and the anion by the subscripts plus and minus, respectively. At first sight, it seems that we should solve the following three equations:

$$E_{+,k} = E_{+,0} + S_+ \ln a_{+,k} + E_{J,k} \tag{2a}$$

$$E_{-,k} = E_{-,0} - |S_-| \ln a_{-,k} + E_{J,k} \tag{2b}$$

and

$$E_{J,k} = -\frac{RT}{F}\left[\int_r^k t_+\, d\ln a_+ - \int_r^k t_-\, d\ln a_-\right] \tag{3a}$$

The activity coefficients of the individual ions obtained from these equations should reproduce the known value of the mean ionic activity coefficient. This is a necessary, but not sufficient condition for acceptance of their values. For a 1:1 electrolyte this relation takes the form:

$$\gamma_\pm^2 = \gamma_+\gamma_- \tag{4}$$

The mean ionic activity coefficient is known as a function of composition for most electrolytes. On the other hand, it is perfectly possible to obtain the activity of the cation or the anion