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On the measurement of individual ion activities

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Abstract

This work demonstrates that the activity of individual ions is a measurable property. It reiterates that reliable values can be obtained performing continuous runs in electrochemical cells formed by a half-cell ion selective electrode (ISE) and a standard single junction reference electrode, both immersed in the sample solution. A brief historical review shows that there are no fundamental reasons to believe that the activity of individual ions cannot be measured. A proposal is then made to clarify the meaning of terms in the definition of the electrochemical potential. Malatesta's claims [F. Malatesta, J. Solution Chem. 29 (2000) 771–779; F. Malatesta, Fluid Phase Equilb. 233 (2005) 103–109] against the method for measuring the activity of ions are rebutted. It is shown that these claims, based on the analysis of Taylor's cells, are not applicable to the systems used in our studies. Measurements of the ionic activity coefficient in potassium chloride solutions, that could be thought to resemble Taylor's cells, are discussed in detail. A study of iteration between the junction potential and the activity of ions is presented for the solutions of NaCl in water. The activity of ions is incorporated in the calculation of the junction potential used to re-calculate the activity of ions. Results show that convergence is attained in less than 10 iterations. The effect of the normalization convention is examined. Future lines of research are proposed.
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1. Introduction

Values of the activity coefficients of individual ions measured using half-cell ion selective electrodes (ISE) have been reported by our group in several publications [1–11]. In addition, Lin and Lee [12], Lee et al. [13], and Schneider et al. [14,15] have performed similar measurements and confirmed our results. The theory supporting the method used for these measurements was further elaborated in the work by Rodil and Vera [10] and all values of individual ions activity coefficients measured by our group were recently revised to correct for an error in sign of the term used to estimate the junction potential [11]. These two latter publications indicate that an error in the estimation of the liquid junction potential, due

to the direct contact between the sample solution and the standard solution of the reference electrode, is largely compensated by the calibration of the ISEs. Notably, two or more runs of measurements of the electromotive force (emf) difference between a particular ISE and a single junction reference electrode, both inserted in a sample solution, will give different values of emf for the same sample molality. The data obtained from various runs, can then be reduced by at least two methods [1,4] that handle differently the effect of the estimated values for the junction potential. The surprising fact is that the values from various runs, reduced by any of the two methods quoted above, produce the same values of the activity coefficients of a single ion, reproducible to the second decimal place. When it is possible to measure independently the activity of the cation and of the anion of an electrolyte, the values of the activity of the individual ions satisfy the necessary condition of reproducing the known values of the mean ionic activity coefficient of the electrolyte. The above statements can be verified by independent measurements or using

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the values of the raw emf measurements for all single electrolyte aqueous systems measured by our group. These values are available from the CISTI Depository of Unpublished Data [16]. The measurement of the activity of individual ions goes against a firmly engrained belief that such measurements are impossible [17–26]. Thus, it is only natural that researchers, with experience in traditional electrochemical methods, may still remain unconvinced of the engineering or scientific merit of the measured activities of individual ions [27,28]. The purpose of this manuscript is to answer the repeated arguments of Malatesta [27,28] against our method to measure the activity of individual ions. We start by giving a short overview of the developments that lead to the belief that the activities of individual ions were not measurable. Based on this historical perspective, we advance a proposal harmonizing different opinions on the subject. In addition, we clearly show the difference between the method used by us to measure the activity of single ions employing ISE's and the work with standard concentration electrochemical cells discussed by Malatesta [27,28]. It has long been known that the latter procedure fails to generate physically meaningful values for individual ionic activities [17,22].

2. A brief historical perspective

The possibility of measuring the activity of individual ions was a topic that generated a heated debate at the beginning of the last century. Lewis [29–31] introduced the concepts of activity and activity coefficients of individual ions. The activity $a_{i,k}$ of a single ion i is a corrected (dimensionless) molality, $m_{i,k}$, related to the single ion activity coefficient $\gamma_{i,k}$ by:

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

This definition was introduced to satisfy the value of thermodynamic constants in systems involving ions and it was not initially related to the definition of an electrochemical potential. Lewis [32] obtained values for these activities from solubility and free energy of dilution data and also established a clear connection between them and the electromotive force of an electrochemical cell [33]. MacInnes [34] and Harned [35] did preliminary attempts to obtain the activity of single ions. Due to their limited success, the question arose whether ionic activities were experimentally accessible or not. Lewis and Randall [36], Harned [37], and Brönsted [38,39] argued in favor. Taylor [17] and Guggenheim [18–21] argued against suggesting that such concept was just a useful mathematical artifice without physical reality. To prove his point, Taylor [17] presented algebra for the case of two reversible electrodes each immersed in solutions of the same electrolyte, differing only infinitesimally in concentration, with transference across a liquid junction. Taylor [17] concluded that "indeed, with the possible exceptions of single electrode potentials and rate of reaction there appears to be no occasion

for the use of ionic free energies as experimental quantities but only as a mathematical device". Guggenheim [18] and Brönsted [38], who were both working in Copenhagen, simultaneously published work introducing the definition of the electrochemical potential of an ion, $\overline{\mu_i}$, that in modern terms can be written as:

$$\overline{\mu_i} = \mu_i + z_i F\psi \tag{2}$$

where μ_i is the chemical potential and z_i is the charge of the ion, F is the Faraday constant and ψ is a loosely defined potential of the phase. Guggenheim [18] defined ψ as 'the electrostatic potential', stating that its value is quite arbitrary. He maintained that only $\overline{\mu_i}$ had physical meaning and the chemical potential (or activity) had "no physical significance for a single ion species". Notably, when discussing various cases to prove his point, he considered only the case of ideal solutions for membrane equilibria. There is no mention to the reason why real solutions are not considered in this case. It is clear from the work of Taylor [17] and Guggenheim [18] that the treatment of single electrode potentials and membrane equilibria requires accepting the physical reality of single ion activities. Brönsted, who had adopted Lewis' definition of activity for ions [40], defined ψ in Eq. (2) as 'the electric potential' stating that, by assigning a somewhat arbitrary definition for its zero point, one could give physical meaning to the electrochemical potential and ionic activity. The exchange of views that followed between Guggenheim [19,20] and Brönsted [39] is interesting to read, not only due to the importance of the ideas discussed, but also to realize that deep disagreement and heated debate on these matters is nothing new.

The Second World War interrupted the discussion. G.N. Lewis and J.N. Brönsted died in 1946 and 1947, respectively. As the years went by and no acceptable method was found to measure the activity of ions, the idea of the impossibility of measuring them became predominant. Perhaps the most important turning point was the position taken by Harned and Owen [22] who, in their authoritative text, repeated closely the arguments of Taylor and Guggenheim. The second edition of the text of Lewis and Randall [41], revised by K.S. Pitzer and Leo Brewer, after stating that the authors were not aware of any measurements of single ion activities, still reads: "Nevertheless, single-ion properties are potentially measurable". MacInnes' text [42], although less positive, states that Guggenheim's idea that single ion activities have no physical meaning "may be an extreme position". Bates' text [43], after asking if there is any possible means still awaiting discovery of determining the activity of an individual ion, states that a cell with liquid junction "can furnish no exact information regarding the activity of single ionic species". From here on, texts definitely turned against the possibility of measuring the individual activity of ions. The texts of Bokris and Reddy [23], Pitzer [44], Skoog et al. [26] and Cogley [24], to name just a few, all convey the idea that the activity of individual ions cannot be measured. It is impressive to note that no