AN APPROACH TO CONVENTIONAL SCALES OF IONIC ACTIVITY FOR THE STANDARDIZATION OF ION-SELECTIVE ELECTRODES

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It has long been recognized that thermodynamic methods measure only the properties of combinations of ions, especially neutral combinations, and can furnish no exact information concerning the activities of individual ionic species. Nevertheless, it is convenient and useful to consider the glass pH electrode and the newer ion-selective electrodes to respond electro-chemically to the properties of a single species of ions. This property, to which the single electrode potential is related, can be shown to be an activity rather than a concentration. Earlier reports to the IUPAC[1,2] have described a practical convention for deriving the hydrogen ion activity, and pH standards based on this convention have been recommended for international use[3].

In the short span of less than a decade, many new electrodes responding to single ion species other than hydrogen have been developed and are commercially available today. Methods for the standardization of these new sensors are, however, in an unsatisfactory state. For maximum usefulness, a single, generally accepted, mode of standardization should be employed for each type of electrode. Although conventional activity scales appear to be the only possible approach, it is essential that these scales be consistent among themselves and with the pH convention now in common use. This requirement is easily understood when one considers that the product of the single activities of the univalent cation M^+ and the univalent anion X^- determined with ion-selective electrodes must equal the square of the mean ionic activity of the electrolyte MX, a quantity that is thermodynamically defined and measurable.

The pH convention set forth by Bates and Guggenheim[1] was intended to apply to aqueous solutions of ionic strength not greater than 0.1. Mean activity coefficients display a considerable degree of uniformity in this region of low ionic strength. Differences among mean activity coefficients of uni-univalent electrolytes become pronounced, however, in concentrated solutions[4], and the pH convention cannot be expected to apply there. There is compelling reason to attribute these specific effects to selective hydration of the ions[5]. It has, in fact, been shown that the activity coefficients of many electrolytes over nearly the entire range of molality are completely described in terms of two parameters of the ions, namely a, the electrostatic ion-size parameter of the Debye–Hückel theory, and h, the sum of the hydration numbers for the ions of which the electrolyte is composed[5].

In an earlier communication[6], we have suggested that self-consistent scales of individual ionic activities might be based on this hydration theory of Stokes and Robinson and have shown that activities of the individual ions can be derived from the mean activity coefficient $\gamma_{\pm}$, the osmotic coefficient ϕ, and h values for unassociated electrolytes, provided the hydration number for a reference ionic species is either known or assigned by convention. Evidence from thermodynamic and transport measurements, pointing strongly to a hydration number of 0 for chloride ion, was presented. In the absence of proof, the acceptance of $h = 0$ for chloride ion must be regarded as a convention. With its use, it becomes possible to assign numerical values to the activities of both cation and anion in solutions of hydrochloric acid and chloride salts over the entire range of concentrations for which the mean activity coefficients have been measured. Hydration numbers of ions are considered to be constant and additive, so that h_{K^+}, for example, derived from data for potassium chloride can be combined with data for potassium fluoride to obtain h_{F^-}, etc. Furthermore, the equations are readily modified to apply with equal force when both ions are hydrated[7]. Simpler conventions, such as the convenient and widely used MacInnes convention, embody the implausible assumption that chloride ion, for example, has the same activity coefficient in different ionic environments, provided only that the ionic molality and the ionic strength are the same. In our treatment, the hydration number of the ion is an unalterable property of the ionic species, but the activity coefficient of that ion changes according to the specific natures of the other ion with which it is associated.

For uni-univalent electrolytes MX (molality m) the expressions for the activity coefficients (γ) of the individual ionic species take the forms

$$\log \gamma_{M^+} = \log \gamma_{\pm} + 0.00782 \, (h_+ - h_-) \, m\phi$$

and

$$\log \gamma_{X^-} = \log \gamma_{\pm} + 0.00782 \, (h_- - h_+) \, m\phi$$

For a bi-univalent chloride MCl_2 such as calcium chloride,

$$\log \gamma_{M^{2+}} = 2 \log \gamma_{\pm} + 0.00782 \, h_+ m\phi + \log[1 + 0.018(3 - h_+) \, m]$$

and

$$2 \log \gamma_{Cl^-} = \log \gamma_{\pm} - 0.00782 \, h_+ m\phi - \log[1 + 0.018(3 - h_+) \, m]$$

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Single ion activities (a_+ and a_-) in reference solutions useful for the standardization of chloride, sodium, calcium and fluoride ion-selective electrodes are summarized in *Table 1*. The assigned ionic hydration numbers are as follows: Cl^-, 0; Na^+, 3.5; K^+, 1.9; Ca^{2+}, 12.0; F^-, 1.9.

Table 1. Standard reference values of ionic activity in solutions of sodium chloride, potassium chloride, potassium fluoride, and calcium chloride at 25°C

molality of salt/ mol kg^{-1}	$-\log a_+$	$-\log a_-$	molality of salt/ mol kg^{-1}	$-\log a_+$	$-\log a_-$
	NaCl			KF	
0.01	2.044	2.045	0.01	2.044	2.044
0.1	1.106	1.112	0.1	1.111	1.111
0.5	0.455	0.481	0.5	0.475	0.475
1.0	0.157	0.208	1.0	0.190	0.190
2.0	−0.180	−0.072	2.0	−0.119	−0.119
	KCl			CaCl$_2$	
0·01	2.045	2.045	0.01	2.273	1.768
0.1	1.112	1.115	0.1	1.570	0.842
0.5	0.482	0.496	0.5	0.991	0.177
1.0	0.206	0.232	1.0	0.580	−0.140
2.0	−0.086	−0.032			

The lack of consistent standards for the calibration of ion-selective electrodes, if long continued, promises to lead to chaos. Although the approach outlined here is still under investigation and subject to future modification, it is already capable of bringing a semblance of order to an area whose impact on chemical research and applied chemistry is growing daily.

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