COMMENTS

Comment on "Hofmeister Effects in pH Measurements: Role of Added Salt and Co-Ions"

Jan J. Spitzer*

IPM Emulsion Polymer Research, 6643 Lyndonville Drive, Charlotte, North Carolina 28277

A recent Letter by Boström et al.[1] suggests that the classical Nernst equation of electrochemistry is incorrect because it fails to account for the dependence of pH on background electrolyte. The authors offer their own experimental data to demonstrate "Hofmeister effects in pH measurements" and their own theoretical explanation. Mainly authors' self-references and the 1888 Hofmeister paper are cited, while the very extensive literature (about 1920−1970) of chemical thermodynamics of electrolytes is largely ignored.[2] On closer examination, the reported data appear to be dubious; the suggested interpretation contradicts classical chemical thermodynamics.[2−4]

The reported procedure of making pH measurements with glass electrodes does not follow the expected recommendations.[5] First, the unbuffered solutions appear to contain variable amounts of carbon dioxide, as shown by the acidic pH range of 5−6. Measurements of pH of solutions with low concentration of potential determining ions are not recommended. Second, glass electrodes are not "ideally" Nernstian and not suitable for precise thermodynamic work; they must be calibrated against standard buffers. These standard buffers (related to dissociation constants of weak acids and bases) were accurately established using hydrogen electrodes and by taking care of nonidealities of electrolyte solutions.[2] Third, the claim of time-invariable potentials of glass electrodes is not supported by any data; electrode potentials of glass electrodes may drift with time.[5] Hence, the reported data, supposedly discovering the "Hofmeister effect in pH measurements", are likely to be spurious.

The theoretical explanation of these "data" is also problematic. First, it is well accepted that Nernst potentials measure changes of Gibbs free energy.[3] In the case of the pH measurement, the free energy change is related to the redox equilibrium between hydrated protons and hydrogen gas. Because free energy changes are independent of properties of any interfaces, Nernstian potentials cannot be used to test theories of interfaces; clearly, an infinite number of electrostatic potential profiles (models)

can be fitted between the two values that define the Nernst (Galvani) potential difference of two bulk phases. Second, it is well accepted that ionic activities rather than concentrations are required in the Nernst equation, and the authors acknowledge that much. Notwithstanding, the authors do assume ideal ionic solutions up to 1.0 M, where ionic activities are known to be highly ion-specific.[2] Such an assumption is unwarranted and in fact unnecessary because the specific ionic activities have been measured and are available.[2] Moreover, the authors mistakenly model the glass electrode potential as an impermeable surface ionization potential rather than a membrane potential.

The explanation of the "observed results" might be as follows. The dissociation of water (or of any weak acid or base) that contributes to the proton activity is dependent on background electrolyte according to the Debye−Hückel (DH) interionic theory[4] (the background electrolyte lowers the activity of dissociating ions). Therefore, the reported data partly reflect the DH interionic effect of added electrolyte on the dissociation equilibrium of water and of small (uncontrolled) amounts of carbonic acid. At the reported high concentrations of background electrolytes, these effects are expected to be ion-specific because the bulk ionic activities are specific (e.g., see Figure 12.7, p 364 in ref 2). It is also likely that glass electrodes, given their membrane nature, malfunction somewhat at such high values of unbuffered background salt (see preceding paragraphs).

In conclusion, pH is defined by the activity of protons in aqueous solutions, and such activity can be determined by a hydrogen electrode and secondarily by a glass electrode with usual calibrations. Proper experimental precautions[5] need to be taken, however, and the nonideality of bulk electrolyte solutions must be properly accounted for in any interpretations. Equilibrium Nernstian potentials (free energies) do not depend on interfacial properties; they are thermodynamic properties of bulk phases only.

* To whom correspondence should be addressed. E-mail: ipmlatexes@ctc.net.

References and Notes

(1) Boström, M.; Craig, V. S. J.; Albion, R.; Williams, D. R. M.; Ninham, B. *J. Phys. Chem. B* **2003**, *107*, 2875.

(2) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworth & Co. Ltd.: London, 1970; Chapter 12, also see many original references cited in this book. Other books could be cited.

(3) Atkins, P. W. *Physical Chemistry*, 2nd ed.; W. H. Freeman & Co: San Francisco, 1982; Chapter 11. Many additional textbooks could be cited.

(4) Alberty, R. A.; Daniels, F. *Physical Chemistry*; John Wiley & Sons: New York, 1979; Chapter 6.

(5) Bassett, J.; Denney, R. C.; Jeffrey, G. H.; Mendham, J. *Vogel's Textbook of Quantitative Inorganic Analysis*; Longman: London, 1981; Chapter XIV.