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Letter to the Editor

Dear Sir:

This is in regard to the paper “Preparation of a New Solid State Fluoride Ion-Selective Electrode and Application” by Somer, Kalayci, and Basak, *This Journal*, 80 (2010) 1129–1132. There was no mechanism given for how the electrode worked, and I initially tried to determine one from the data given in the paper. However, there are some serious inconsistencies in the data which I could not resolve.

For example, Fig. 3 in the paper shows the response of the fluoride electrode as a function of pH. At “various fluoride concentrations” (not specified in the paper), and in 01.M $NaNO_3$, the change in potential “from pH 1 to 8” . . .” was only 1–2 mv per pH unit”. However, the pKa for HF is 3.164 [1] at zero dilution and 2.88 [2] at 0.5 M $NaNO_3$. Assuming that the only complex between H^+ and F^- is HF (no HF^{2-} at the fluoride levels in the paper), either value of the pKa gives a calculated change in fluoride activity over the pH range 1–5 of almost 4 orders of magnitude. Even for the reported non-Nernstian slope of 26 mv, that would be a change of about 100 mv. The electrode does not seem to be responding to fluoride activity.

In the alkaline region, pH 7–13, where the fluoride activity does not change (except for ionic strength effects) the reported electrode readings *increase* by about 70 mv. Here again, the electrode does not appear to be responding to fluoride activity. (The shape of the entire curve and the increasingly negative readings on the alkaline side look very much like the pH curves obtained with divalent cations, where they precipitate or complex with hydroxide ions, but are stable in acid.)

Nonetheless, the paper reports a calibration curve for fluoride over the range of 10–1 to 10–6 M. The pH of the calibration curve is not specified. Measurements on spring and tap water, based on using standard addition are also reported. For standard addition, the problem is that two fluoride activity measurements are needed for the calculation that (for their electrode) would typically differ by about 8 mv. It is difficult to understand how an electrode that was unresponsive to orders of magnitude changes in fluoride activity due to complexation with hydrogen ion, could have the necessary precision for standard addition (or for that matter, to generate a calibration curve.)

There is nothing obvious in the electrode membrane composition that would suggest a response to fluoride ion. All of the solid state ion-selective electrodes that I am familiar with contain an ionic conductor to which the electrode responds directly or through a solubility product relationship with the ionic conductor (e.g., electrodes for $S^{=}$: Ag_2S, Cu^{++}: Ag_2S/CuS, etc.). The membrane in the Somer et al., paper contains the ionic conductor Ag_2S, but the only source of fluoride ions is CaF_2, which is not an ionic conductor and is soluble enough to yield a fluoride level of around 0.001 M F^-. Further, both AgF and CaS are soluble compounds that could not affect the dissociation of Ag_2S.

The authors have gotten some interesting data from their experiments on the membrane mixtures, but I believe that further work on the chemistry is needed to explain what it is that they are measuring.

References

[1] Hoegfeldt (Ed.), “Stability Constants of Metal Ion Complexes” IUPAC Chemical Data Series, No. 21, Pergamon Press, Oxford, 1982. Ref. 73K, p. 200.

[2] Ibid, Ref. 74S.

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