Lanthanum Fluoride Electrode Response in Water and in Sodium Chloride

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PREVIOUS MEASUREMENTS of LaF_3 electrode response have agreed with that theoretically expected to varying degrees. Under laboratory conditions, empirical response curves can be determined and used with little loss of accuracy, but for field use accurately predictable response makes frequent recalibration unnecessary and allows *in situ* application. This study describes conditions under which accurate Nernstian response is observed down to $10^{-6}M$ fluoride, determines probable error if standardization is infrequent, and examines selectivity of response to fluoride over chloride. For chloride, Frant and Ross (*1*) found selectivity of at least 10^3 : 1. Others (*2*) report measurements at ratios up to 10^5 : 1. Mesmer (*3*) recently examined selectivity in NaCl and KCl, where presence of 6 to 15 × 10^{-6} molal fluoride as an impurity in the chloride solutions made direct measurement of chloride interference impossible. Using an indirect method in acidic solutions, he concluded that fluoride could be determined in the presence of 1 molal chloride down to <2 × 10^{-8} molal. We report here direct measurements of electrode response in the presence of $1M$ (molar) NaCl at fluoride concentrations down to 2 × $10^{-7}M$.

EXPERIMENTAL

Reagents. Fluoride standards were obtained by diluting a $0.5M$ NaF standard solution prepared by weighing Baker Analyzed Reagent Grade, as received. Sodium chloride (Baker and Adamson Reagent Grade) solutions of 2.0 and $1.0M$ were prepared by weighing, after drying. All solutions were stored in polyethylene bottles.

Apparatus. The Orion Model 94-09 fluoride electrode was used with the Orion single junction reference electrode (model

(1) M. S. Frant and J. W. Ross, Jr., *Science*, **154**, 1553 (1966).
(2) R. Bock and S. Strecker, *Z. Anal. Chem.*, **235**, 322 (1968).
(3) R. E. Mesmer, ANAL. CHEM., **40**, 443 (1968).

90-01) and the Orion Model 801 digital pH meter (calibration verified accuracy ±0.1 mV). Voltage was displayed with suppressed zero on a recorder, 5 mV full scale. Filtering reduced noise to <0.05 mV.

Procedure. Samples were pipetted into a polyethylene beaker immersed in a thermostat at 25.0 ± 0.1 °C, and were stirred magnetically using a Teflon-coated stirring bar. The bar introduced no detectable fluoride impurity over periods of many hours. Concentrations between standards were prepared by serial dilution or concentration of the existing sample. Readings were accepted only after there was no monotonic change in voltage for more than 15 min; for all but the most dilute solutions, below $10^{-6}M$, readings were stable to ±0.1 mV. Solution pH was monitored but not externally controlled and was between 5 and 6.

RESULTS AND DISCUSSION

Sodium Fluoride in Water. Cell potential in aqueous NaF solutions, using two different electrodes, is given by the circles in Figure 1. The line in Figure 1 is cell potential E predicted by the Nernst equation,

$$E = \alpha - \frac{RT}{F} \ln a_{F^-} \tag{1}$$

where a_{F^-} is the activity of fluoride ion in solution, α is the sum of contributions from internal and external reference electrodes and from liquid junction potentials, and R, T, and F are the gas constant, absolute temperature, and Faraday, respectively.

Deviations of observed data in Figure 1 from predicted values are shown in Figure 2. A single determination, typically at 10^{-3} or $10^{-4}M$, was used each day to determine α and in treating the data, α was assumed to remain constant during the measurement period. For thermally stabilized cells, changes in α over an eight-hour period rarely exceeded 0.5 mV and

Figure 1. Cell potential *vs.* NaF activity in water (○), *vs.* NaF activity in $1M$ NaCl (□), and predicted by Nernst equation (line with slope of 59.16 mV/decade)
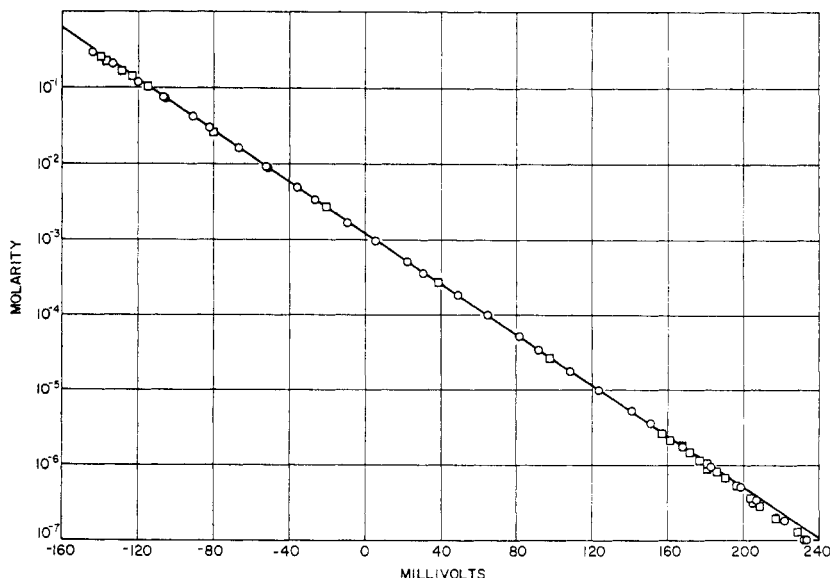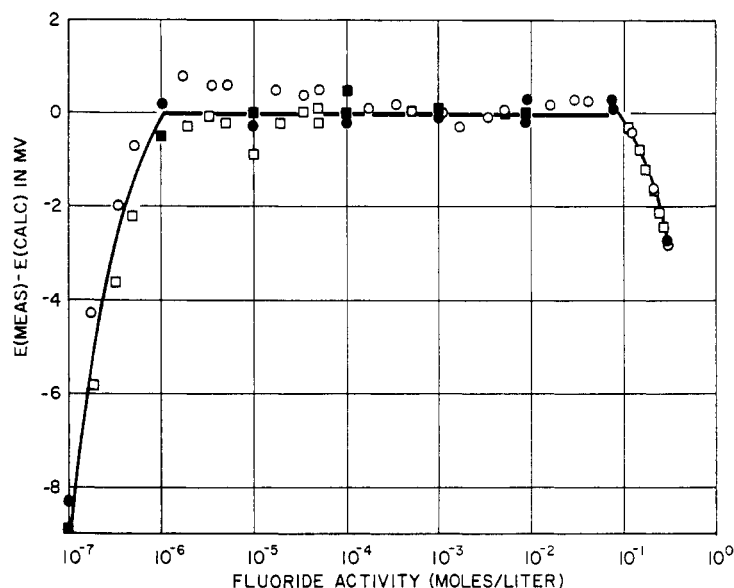
Figure 2. Deviations of measured potentials from those predicted by Nernst equation at 25 °C for fluoride in water

Squares signify data taken at decreasing activities, circles at increasing activities, and solid symbols represent primary standards

were frequently less. No correction for drift was included in the data for Figures 1 and 2, for these experiments were designed to evaluate accuracy possible with infrequent standardization. Over a period of many months, α varied about ± 3 mV. For comparison in Figure 1, emf data taken on different days or with different fluoride electrodes were shifted by an appropriate constant (the difference in α's) such that they coincided at 10^{-3} or $10^{-4}M$.

The reference electrode has a small liquid junction potential in all but the most concentrated solutions; it is estimated by the manufacturer to be <0.1 mV below $10^{-3}M$ NaCl, 0.2 mV at $10^{-2}M$, rising to ~ 1 mV in $10^{-1}M$ NaCl. Stirring did not influence cell potential except in the most dilute solutions, where a very slow drift toward higher indicated activity occurred upon interruption of stirring, probably due to solubility of the membrane.

Activities of fluoride ions for concentrations above $10^{-4}M$ were computed using the data on ionic activity coefficient of fluoride as a function of total ionic strength provided by Orion Research (4) calculated from the values of Kielland (5) for ionic strengths below 0.1 and estimated from electrode measurements from 0.1 to 1.0. One purpose of this study was to evaluate possible errors introduced by assuming these values, which differ slightly from those of Kielland. Representative activity coefficients at ionic strengths of 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, and 5×10^{-1} are 1.00, 0.97, 0.91, 0.77, and 0.59, respectively.

Precision is high; replicate measurements at a given time generally agree to 0.1 mV. Deviations in Figure 2 represent inaccuracy. Response of the fluoride electrode, in the configuration used, is predicted by the Nernst equation with a mean error of -0.06 mV and a computed standard deviation of an individual measurement about the true value over the range of 10^{-6} to $10^{-4}M$ of 0.43 mV, based on 21 measurements, and of 0.19 mV from 10^{-4} to $10^{-1}M$, based on 19 measurements. Since per cent relative error in measured activity ≈ -4 (emf error in mV), the computed relative standard deviations of an individual measurement of activity are 1.7% from 10^{-6} to $10^{-4}M$, and 0.8% from 10^{-4} to $10^{-1}M$; limits of relative error are taken as 5.2 and 2.3%, respectively.

(4) Orion Research, Inc., Instruction Manual, 2nd ed., Fluoride Ion Activity Electrode Model 94-09, 1967.
(5) J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

The larger errors observed in solutions between 10^{-6} and $10^{-4}M$ may be due to a slow redistribution of fluoride ions within the LaF_3 membrane when exposed to dilute solutions, to a net ion flux between solution and membrane, or to ion absorption or desorption from surfaces in the cell as concentrations are changed by serial additions to an existing sample. An emf approached from higher potentials tended to attain an apparent steady value just above the correct value, and that approached from lower potentials tended to be low.

Nontheoretical but useful measurements can be achieved down to $10^{-7}M$, but errors are larger and the time required to obtain a steady reading increases to several hours at the lowest concentrations. At concentrations of $10^{-5}M$ and above, readings within 0.2 mV of the final value are usually obtained in less than 15 min.

Data from 10^{-6} to $10^{-4}M$ establish that electrode response is Nernstian, and the results from 10^{-4} to $10^{-1}M$ validate the activity coefficient data used in that range. If desired, an electrode system may be standardized in more concentrated solutions, where rapid and stable response is most easily attained, with no significant loss of accuracy in converting to an activity scale. Deviations above $10^{-1}M$ do not necessarily indicate errors either in electrode response or in the activity coefficients used, for an increasingly large error due to liquid junction potentials is also included in the measured emf and its separate contribution cannot be assessed on the basis of these measurements.

Sodium Fluoride in 1M Sodium Chloride. The electrode system was first standardized in a known volume of $10^{-4}M$ aqueous NaF and an equal volume of $2M$ NaCl added. The measured emf defined the concentration calibration curve in $1M$ NaCl solutions, assuming theoretical response. The difference in emf between the two solutions yielded an "activity correction factor" which represented the sum of contributions due to change of both activity coefficient and liquid junction potential with total ionic strength. If all concentrations are multiplied by this factor, then the resulting response curve should be superimposed on that for pure NaF standards. The squares in Figure 1 show these data in $1M$ NaCl; data taken on different days were shifted by a small constant, representing the difference in α's, to make all directly comparable on the same plot. There was no significant difference in electrode response down to a concentration of $1.92 \times 10^{-7}M$ NaF in $1M$ NaCl, and deviations about the theoretical curve were

essentially the same as those in pure NaF solutions. Hence, in $1M$ NaCl accuracy equivalent to that of Figure 2 can be obtained by calibrating at a single point and assuming theoretical response, and there is no detectable chloride interference at ion ratios up to $5 \times 10^6 : 1$.

The preceding data show that the fluoride electrode behaves ideally both in dilute aqueous solutions and in solutions of high ionic strength over a wide range of fluoride activities. These data imply that when α has been determined in one solution, it does not change when transferring to solutions of very different compositions, other than the relatively small contributions assignable to changing liquid junction potentials. In the present case the "activity correction factor" of 0.54 (including a contribution from liquid junction potentials) was close to the expected activity coefficient of about 0.49 (not including this contribution) suggesting that α is not very different in the two solutions. In view of the uncertainties in accurately determining liquid junction potentials and activity coefficients in high ionic strength solutions, probably there is no difference. Hence, an electrode may be calibrated in a convenient solution, and measurements in very different environments may be interpreted on the same activity scale. Probable error depends primarily on the difference in liquid junction potentials in the two systems, which may be kept very small if all solutions are dilute.

Determination of Fluoride Impurities in Solutes. Previous uncertainty about the lower limit of theoretical response (*1*, *6*) and about what response slope may be expected under various conditions has made difficult the estimation of fluoride impurity levels in other solutes (*6*). Mesmer (*3*) found fluoride

impurities in sodium and potassium chlorides from three high-purity sources. He estimated their levels using an indirect method based on nonlinearities of response at low concentrations of added fluoride. Frant and Ross (*7*) suggested that certain of their results might be due to fluoride contamination in the reagents used to prepare their TISAB.

Reagents may be screened rapidly for fluoride contamination by conditioning an electrode in pure water until it indicates fluoride $<10^{-7}M$. Upon addition of enough reagent to make $\sim0.1M$ solution, the indicated emf will shift rapidly in presence of contamination, but will remain relatively stable if fluoride is negligible. The actual activity may be inferred from the measured emf, using calibration data obtained in a different known standard. Reagents which shift pH out of the optimum range may be screened in buffered solutions, such as TISAB. Results of screening a number of reagent grade chemicals as received indicate that most are free of detectable fluoride, two exceptions being $MgCl_2$ and $CaCl_2$. A number of samples of Baker and Adamson reagent grade sodium chloride had no detectable fluoride impurity. TISAB prepared from fluoride-free reagents may be used down to fluoride activities of $1 \times 10^{-7}M$. A sample of Orion TISAB had a fluoride impurity concentration of about $6 \times 10^{-7}M$.

(6) E. W. Baumann, *Anal. Chim. Acta.*, **42**, 127 (1968).

(7) M. S. Frant and J. W. Ross, Jr., ANAL. CHEM., **40**, 1169 (1968).

Spectrophotometric Determination of the Copper(II) Ion by N-8-Quinolyl-p-Toluenesulfonamide

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BILLMAN AND CHERNIN (*1*) reported on four sulfonamide derivatives of 8-aminoquinoline as a new class of organic reagents for analytical applications. Highly colored insoluble metal chelates were formed with silver(I), mercury(II), copper(II), lead(II), cobalt(II), and zinc(II). One of these derivatives, o-(p-toluenesulfonamide) aniline, has been described by these authors as a reagent for the spectrophotometric determination of copper(II) (*2*). Another derivative, N-8-quinolyl-p-toluenesulfonamide (QTS), has been used for the fluorimetric determination of zinc and cadmium in a chloroform solution (*3*, *4*). Work in our laboratory supports Billman's conclusion (*1*) that in basic solution the N-H proton of QTS (I) is removed and the anion (II) is a potential bidentate ligand with coordination to the metal ion taking place at the two nitrogens. The reaction is formulated as:

(I)   (II)
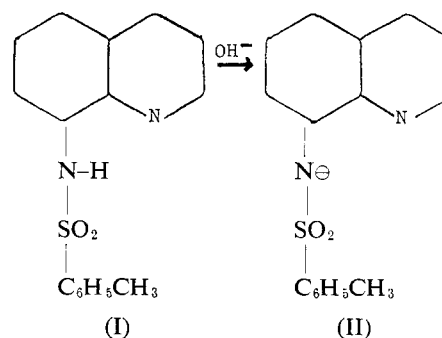
The fluorescence of the cadmium and zinc complexes of QTS was quenched by the addition of copper(II) ion. The method reported here utilizes QTS in a basic solution to form a copper chloroform soluble complex which is determined spectrophotometrically.

EXPERIMENTAL

Apparatus. Spectrophotometric measurements were made on a Beckman DK-2 and a Cary-14R.

Reagents. N-8-quinolyl-p-toluenesulfonamide (Eastman

(1) J. H. Billman and R. Chernin, ANAL. CHEM., **34**, 408 (1962).

(2) J. H. Billman and R. Chernin, *ibid.*, **36**, 552 (1964).

(3) V. M. Dziomko, *Sb. Statei, Vses, Nauchn.-Issled. Inst. Khim. Reaktivov i Osbo Chistyky Khim. Veshchestv*, **24**, 9 (1961).

(4) D. T. Haworth and R. H. Boeckeler, *Microchem. J.*, **13**, 158 (1968).