

# Lanthanum Fluoride Electrode Response in Water and in 1M Sodium Chloride

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## ABSTRACT

Response of the fluoride-selective electrode in water and 1M NaCl solutions is accurately predicted by the Nernst equation for fluoride activities from  $10^{-1}$  to  $10^{-6}$ M when liquid junction potential changes are minimized. Useful response is available above  $10^{-1}$ M and can be obtained with difficulty down to  $10^{-7}$ M (2 parts per billion). An individual measurement of activity has relative error limits of 5.2% between  $10^{-6}$  and  $10^{-4}$ M and 2.3% between  $10^{-4}$  and  $10^{-1}$ M. Activity coefficient data for fluoride in solutions of total ionic strength between  $10^{-4}$  and  $10^{-1}$ M are validated, and a simple method for measuring fluoride impurity levels in other substances is described. There is no detectable chloride interference with electrode response in 1M NaCl for fluoride concentrations down to  $2 \times 10^{-7}$ M.

## PROBLEM STATUS

This is an interim report; work on this problem is continuing.

## AUTHORIZATION

NRL Problem G02-03  
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# LANTHANUM FLUORIDE ELECTRODE RESPONSE IN WATER AND IN 1M SODIUM CHLORIDE

## INTRODUCTION

The  $\text{LaF}_3$  electrode recently introduced (1) is a versatile and dependable indicator of fluoride ion activity in a wide range of solutions. Previous measurements of the electrode response in various media have agreed with the response theoretically expected to varying degrees, depending on the specific experimental arrangements used. Under laboratory conditions, empirical response curves can be determined and used with little loss of accuracy, but for field use, and particularly for in situ applications, it is desirable to establish conditions under which accurately predictable response can be obtained, so that the need for frequent recalibration is relaxed. One purpose of this study was to establish such conditions and to determine the probable limits of accuracy of fluoride activity measurements made in aqueous solutions of NaF.

A particular advantage of this electrode is its ability to respond selectively to fluoride ions in the presence of large excesses of other ions. For chloride ions, Frant and Ross (1) report a selectivity of at least  $10^3:1$ . Mesmer (2) recently examined the selectivity in 1m solutions of NaCl and KCl. The presence of 6 to  $15 \times 10^{-6}$ m fluoride as an impurity in the chloride solutions examined made direct measurement of chloride interference impossible. Using an indirect method in acidic solutions, he concluded that the fluoride concentration could be determined in the presence of 1m chloride down to a concentration less than  $2 \times 10^{-8}$ m. We report here direct measurements of electrode response in the presence of 1M NaCl at fluoride concentrations down to  $2 \times 10^{-7}$ M.

## EXPERIMENTAL

### Reagents

All fluoride standards were prepared 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 90-01) and the Orion Model 801 digital pH meter. Calibration verified that the meter was accurate to 0.1 mv over its entire range. The voltage was read on the meter and displayed with suppressed zero on a recorder, 5 mv full scale. Filtering reduced the noise to less than 0.05 mv.

### Procedure

Samples were pipetted into a polyethylene beaker immersed in a thermostat, were stirred magnetically using a Teflon-coated stirring bar, and were held at  $25.0 \pm 0.1^\circ\text{C}$ .

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  $\pm 0.1$  mv. The solution pH was monitored but not externally controlled and was between 5 and 6.

## RESULTS AND DISCUSSION

### Sodium Fluoride in Water

The cell potential in aqueous NaF solutions is given by the circles in Fig. 1. Two different electrodes were used, and data were obtained at both increasing and decreasing known fluoride concentrations. The line in Fig. 1 is the cell potential  $E$  predicted by the Nernst equation,

$$E = \alpha - \frac{RT}{\mathfrak{F}} \ln a_{F^-}, \quad (1)$$

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

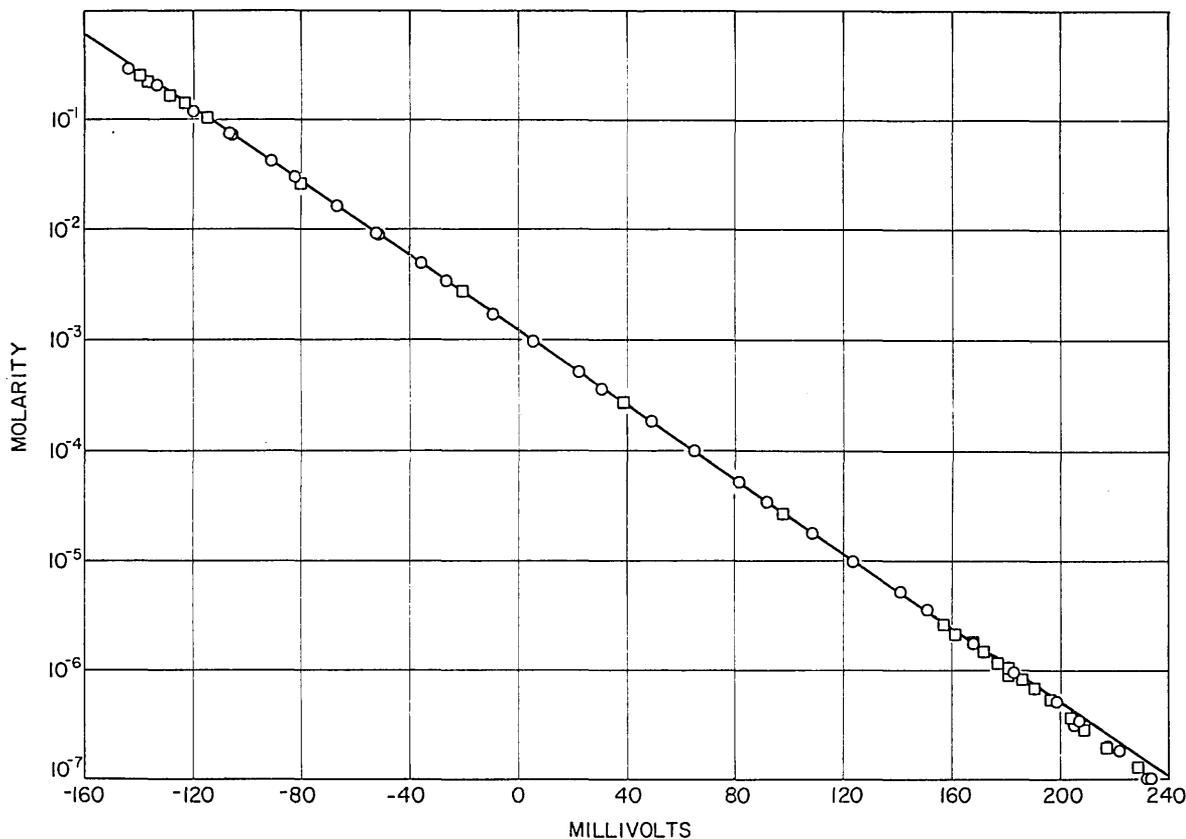


Fig. 1 - Cell potential versus NaF activity in water (circles), versus NaF activity in 1M NaCl (squares), and predicted by the Nernst equation (the line with a slope of 59.16 mv/decade)

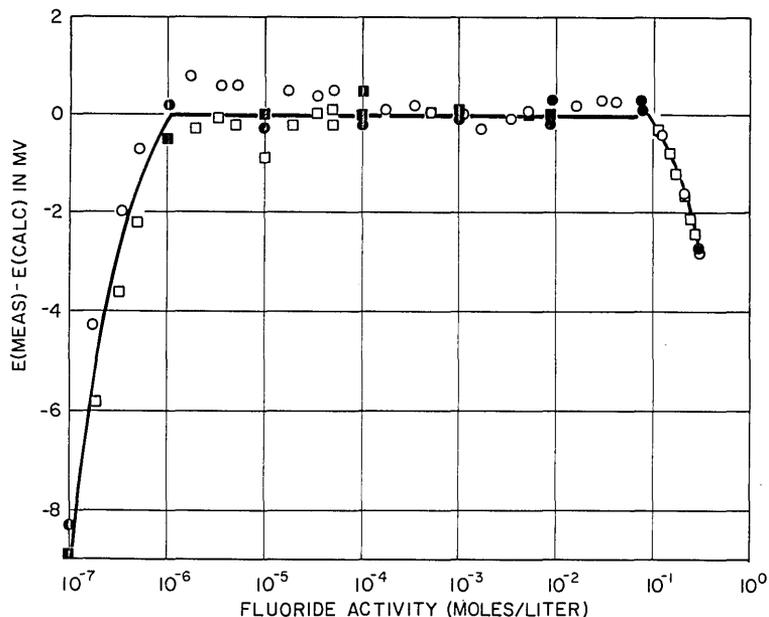


Fig. 2 - Deviations of the measured potentials from those predicted by the Nernst equation at 25°C for fluoride in water. Squares signify data taken at decreasing activities, circles at increasing activities, and solid symbols represent primary standards.

Deviations of the observed data in Fig. 1 from the predicted values are shown in Fig. 2. A single determination, typically at  $10^{-3}$  or  $10^{-4}$ M, was used each day to determine  $\alpha$ , and in treating the data it was assumed to remain constant during the measurement period. For thermally stabilized cells, changes in  $\alpha$  over an 8-hr period rarely exceeded 0.5 mv and were frequently less. No correction for drift was included in the data for Figs. 1 and 2, because these experiments were designed to evaluate the accuracy possible with infrequent standardization. Over a period of many months,  $\alpha$  varied about  $\pm 3$  mv. This appeared more due to changes in the reference than any intrinsic change in the fluoride electrode. For purposes of comparison in Fig. 1, emf data taken on different days or with different fluoride electrodes were shifted by an appropriate constant (the difference in values of  $\alpha$ ) such that they coincided at  $10^{-3}$  or  $10^{-4}$ M.

The reference electrode used is designed to have a small liquid junction potential in all but the most concentrated solutions; it is estimated by the manufacturer to be less than 0.1 mv below  $10^{-3}$ M NaCl, 0.2 mv at  $10^{-2}$ M, rising to approximately 1 mv in  $10^{-1}$ M NaCl. When this reference electrode was used, stirring did not influence the 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 the ionic activity coefficient of fluoride as a function of the total ionic strength provided by Orion Research (3) calculated from the values of Kielland (4) for ionic strengths below 0.1 and estimated from electrode measurements from 0.1 to 1.0. Since one purpose of this study was to evaluate possible errors introduced by assuming these values, the data used, which differ slightly from those of Kielland, are reproduced in Fig. 3. Representative activity coefficients at ionic strengths of  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$ , and  $5 \times 10^{-1}$ M are 1.00, 0.97, 0.91, 0.77, and 0.59, respectively.

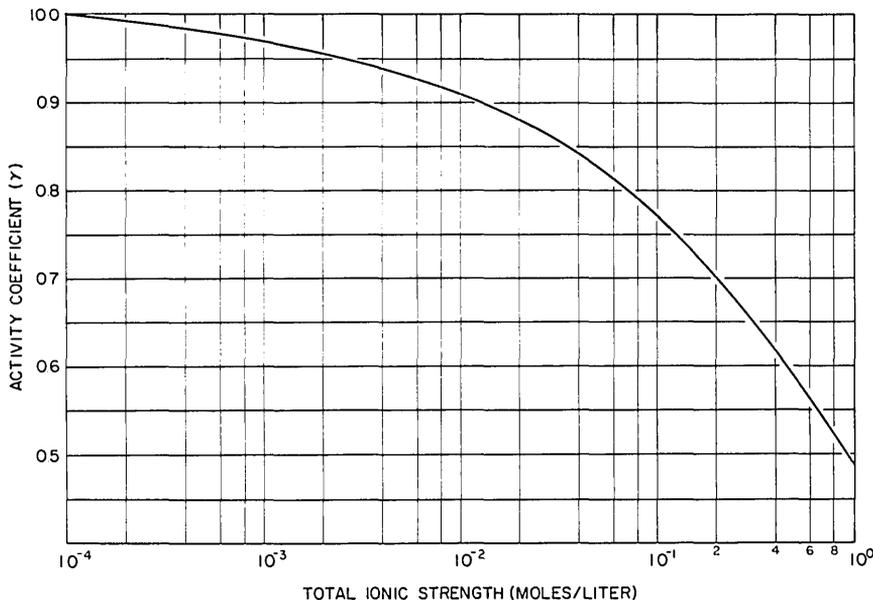


Fig. 3 - Ionic activity coefficient of fluoride as a function of the total ionic strength, taken from Ref. 3

The precision of an individual measurement in a given solution is very high. Repeated measurements in identically prepared samples at a given time generally agree to 0.1 mv. With one exception, discussed below, the variations shown in Fig. 2 may be variously considered as imprecision in a different class of measurements or inaccuracy encountered with a very precise measurement; the latter view is taken here. 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.

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  $\text{LaF}_3$  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. Note in Fig. 2 that determinations in primary standards freshly introduced into the cell were somewhat more accurate than intermediate values obtained by serial additions.

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. Response time in NaF solutions is a function of both fluoride concentration and the size of the concentration change since the previous measurement, longer times being required as the fluoride concentration decreases and as the size of the change increases. 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.

Figure 2 may also be used to express the case of more usual interest, i.e., the probable deviation from the true value of an individual estimate of activity obtained by calibrating the cell at a single point, then measuring the emf,  $E_{\text{meas}}$ , of the cell in an unknown

solution and assuming Nernstian response. Differentiating Eq. (1) gives, at 25°C where  $RT/3 = 25.7$  mv,  $d(a_{F^-})/dE = a_{F^-}/(-25.7$  mv) or, approximately a 4% change in predicted  $a_{F^-}$  per millivolt error in measurement. The relation

$$(\text{relative error in measured activity}) \approx -4(\Delta E)\% \quad (2)$$

holds correct to the nearest tenth percent relative error for  $0.1 \leq \Delta E \leq 1.7$  mv, where  $\Delta E = E_{\text{meas}} - E_{\text{true}}$ . Computed relative standard deviations of an individual measurement of activity are, therefore, 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 three times these values.

Data from  $10^{-6}$  to  $10^{-4}$ M establish that the 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 in either the electrode response or the activity coefficients used, because 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 aqueous NaF, usually  $10^{-4}$ M, and an equal volume of 2M NaCl was added. The measured emf defined the concentration calibration curve in 1M NaCl solutions, assuming theoretical response. The difference in emf between the two solutions, after allowing for a factor of two in concentration, 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. This factor will be constant in a NaCl solution of given ionic strength; hence, if all concentrations are multiplied by this factor, the resulting response curve should be superimposed on that for pure NaF standards. The factor, which, it should be stressed, is not simply an activity coefficient, was 0.54 in this case. The squares in Fig. 1 show these data in 1M NaCl so superimposed on the primary calibration curve. As before, data taken on different days were shifted by a small constant, representing the difference in values of  $\alpha$ , 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 Fig. 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 in both dilute aqueous solutions and solutions of high ionic strength over a wide range of fluoride activities. These data imply that when  $\alpha$  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. This result was expected, but it was desirable to have experimental confirmation. 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). This close agreement suggests that  $\alpha$  is not very different in the two solutions, and in view of the uncertainties in accurately determining liquid junction potentials and activity coefficients in high ionic strength solutions, it is probable that 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 encountered in the two systems. These potentials 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 (1,5) and about what response slope may be expected under various conditions has made difficult the estimation of fluoride impurity levels in other solutes (5). Mesmer (2) found fluoride impurities in NaCl and KCl 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 (6) 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 a fluoride concentration of less than  $10^{-7}$ M. On addition of enough reagent to make an approximately 0.1M solution, the indicated emf will shift rapidly in the 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 tend to 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  $CaCl_2$ . In particular, a number of samples of Baker and Adamson reagent-grade NaCl 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.

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