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Short communication

Measurement of pH by NMR spectroscopy in concentrated aqueous fluoride buffers

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ABSTRACT

An NMR spectroscopic technique has been developed to give rapid, accurate pH measurements on tenth-milliliter samples of concentrated acidic aqueous solutions buffered by fluoride ion in the pH 1.5–4.5 range. The fluoride ^{19}F chemical shift has been calibrated as a function of pH at 0.1 and 1.0 M concentration by reference to an internal 3-fluoropyridine standard. Subsequent measurements of fluoride buffer pH required no additives and only two NMR spectra in the presence of an external reference standard.

1. Introduction

Some recent experiments made us aware of the need for an accurate, convenient method to measure pH in moderately concentrated (0.1–1.0 M) fluoride buffers [1]. Briefly, the weak acidity and extreme oxidative robustness of HF were needed to form weakly coordinating, buffering electrolytes for electrochemical studies on cobalt-catalyzed water oxidation. To obtain meaningful data on the effectiveness of the cobalt oxide catalyst, the pH of the electrolysis solution must be accurately known as this determines the reversible potential for water oxidation and thus the overpotential applied during the experiment. Buffered acidic fluoride solutions are also of considerable technological importance for metal etching, electroplating, and semiconductor processing. This pH measurement is challenging, since acidic fluoride rapidly dissolves the glass membrane electrodes typically used for pH determination. Worse still, the electrode reading is inaccurate during its destruction. The Sb/Sb_2O_3 electrode is commercially available and has been used in dilute fluoride solutions, but we observed that at high fluoride concentration an equilibrium arises between antimony oxide and fluoride species that perturbs the measured potential [2,3]. Titrations were considered as well, but are time-consuming when many solutions must be prepared and generate significant amounts of waste, so we turned to spectroscopic methods.

Fluorine NMR spectroscopy is a versatile technique that can exploit the high sensitivity, broad chemical shift range, and chemical shift response to the medium of the ^{19}F nucleus [4]. Protonation of fluorine-substituted molecules will perturb the chemical shift (δ) of the fluorine nuclei and this has been used to measure the compound's pK_a by plotting δ vs. pH titration curves [5]. Conversely, the chemical shifts of fluorinated biomolecules with known pK_a have been used as pH probes of their solution environment [6]. Using these approaches simultaneously, our strategy is to measure the apparent pK_a of fluoride buffers via titration curves of the fluoride ion chemical shift in solutions of pH determined by the chemical shift of a fluorinated probe molecule [7]. With this data in hand, it is then possible to measure the pH of buffer solutions via the fluoride ion chemical shift.

NMR spectroscopic pH measurements of dilute ($\sim 10^{-3}$ M) fluoride ion solutions which exploit the ~45 ppm difference in chemical shift between F^- and HF have been reported [8]. This technique requires that one know the HF pK_a and the fully protonated and deprotonated chemical shifts (δ_{HF} and δ_F respectively) as constants in Eq. (1). We were concerned with the possibility of perturbations at higher concentrations by the fluoride–bifluoride equilibrium (2) [8a,10] leading to an apparent pK_a that differs from the accepted value as well as more general solution non-ideality and concentration-dependent hydrogen bonding and medium effects on the chemical shift [7a,9]. Thus, we decided to determine the apparent pK_a of HF under the conditions of interest and fit different functions to the δ vs. pH curve for different concentrations.

$$\mathrm{pH} = \mathrm{p}K_{HF} - \log\left(\frac{\delta_F - \delta_{obs}}{\delta_{obs} - \delta_{HF}}\right) \quad (1)$$

$$HF + F^- \rightleftarrows FHF^- \quad K \sim 4\text{–}25 \quad (2)$$

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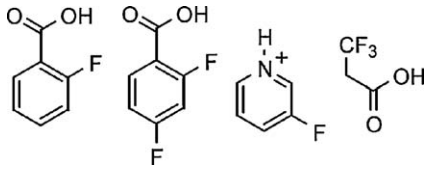

Fig. 1. Some ^{19}F chemical shift indicators with acidities similar to HF. From left to right, these are 2-fluorobenzoic acid (pK_a 3.31, $\Delta\delta_F$ 4.05), 2,4-difluorobenzoic acid (pK_a 3.29, $\Delta\delta_F$ 4.49, 5.97), 3-fluoropyridinium (3-FP) (pK_a 2.97, $\Delta\delta_F$ 9.59), and 3,3,3-trifluoropropionic acid (pK_a 3.17, $\Delta\delta_F$ −0.26).Data from [5,12,13].

Determination of an acid's pK_a by NMR spectroscopy requires an indicator of similar and known pK_a which has significant pH response, that is to say that its chemical shift or coupling constants should undergo an easily observable change across the pH range of interest [11]. In this process, solutions are made containing an indicator and the compound being studied at various inexact pH values, preferably around its expected pK_a. From the chemical shift of the indicator, the pH of each solution is determined, allowing one to plot the chemical shift response vs. pH of the analyte. Choosing among several possible indicators (Fig. 1), we used 3-fluoropyridinium (3-FP) since its reported pK_a of 2.97 is close to the accepted value for HF and its ^{19}F chemical shift changes by ~10 ppm on deprotonation [12,13].

2. Experimental methods and data

Solutions containing 0.01 M of 3-FP at known pD were prepared in 0.1 M tartrate buffer in D_2O and analyzed by NMR spectroscopy at 30 °C [14]. Fluorine chemical shifts were cross-referenced following the IUPAC recommendations for the Unified Scale [15] to the proton signal of tetramethylammonium chloride (δ = 3.180 ppm vs. TMS), which was also present in the sample. Temperature control was monitored by observation of the $\Delta\delta$ between the $(CH_3)_4N^+$ peak and residual HDO (see Supporting Information) [16]. Fitting of the data (Fig. 2) allowed us to determine a pK_a of 2.86 for 3-FP and then use the δ vs. pH equation (see Supporting Information) of 3-FP to measure pH in fluoride solutions.

NMR spectra of HF/F^- buffer solutions at 0.1 and 1.0 M total fluoride in H_2O at different pH values were obtained with 0.01 M 3-FP present in the solution. The solutions were prepared from stock solutions in a manner so that the 3-FP concentration was constant in all cases. Spectra were obtained on solutions in a fluoropolymer insert in a double-wall NMR tube, see the Supporting Information for a schematic diagram of the apparatus. Despite the small sample volume of ~100 μl, the signal/noise ratio of the 3-FP indicator was satisfactory in under 64 scans, see the Supporting Information for representative spectra. The spectrometer was locked on a solution of tetramethylammonium chloride in D_2O in the gap between the outer and inner walls of the tube with chemical shift referencing and thermometry as above using the HDO signal of the external reference where it was discernible from the sample H_2O peak and the combined peak otherwise. The solution pH of each buffer was determined from the 3-FP chemical shift and titration curves were fitted (see Supporting Information) to the resulting ^{19}F chemical shift of HF/F^- vs. pH data for 0.1 and 1.0 M buffers and gave pK_as of 3.02 and 2.94 respectively (Figs. 3 and 4).

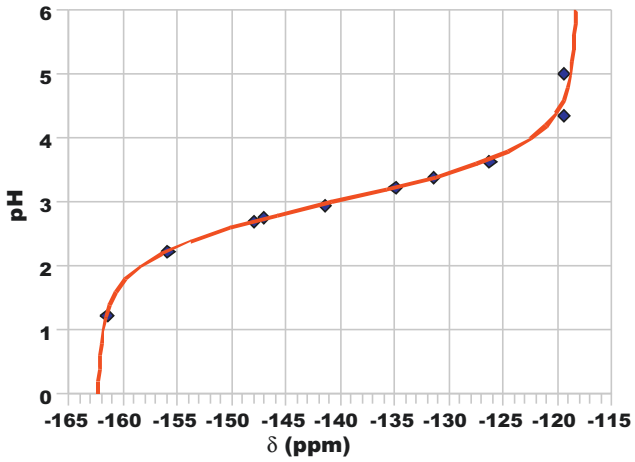

Fig. 3. ^{19}F chemical shift of 0.1 M fluoride as a function of pH, diamonds are experimental data (blue), the line is the fitted curve (red). Curve fitting gave a pK_a of 3.02. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

3. Discussion

Fitting of titration–curve equations (see Supplementary Information) to the data in Figs. 3 and 4 allowed us to determine apparent pK_as of 3.02 and 2.94 of HF at 0.1 and 1.0 M. These results differ significantly from the value of 3.17 for dilute HF and are in

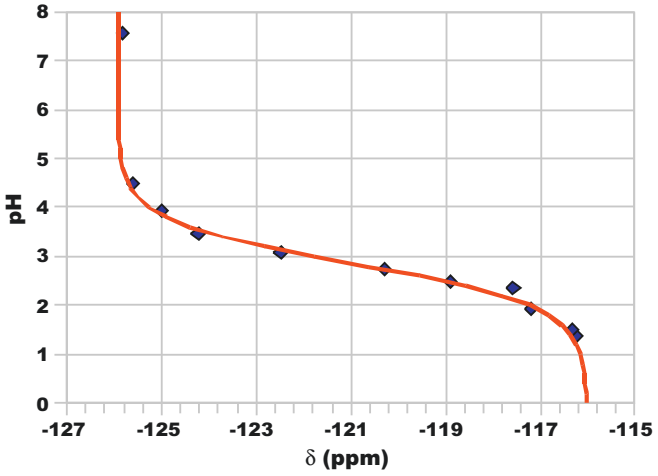

Fig. 2. ^{19}F chemical shift of 3-fluoropyridine as a function of pH, diamonds are experimental data (blue), the line is the fitted curve (red). Curve fitting gave a pK_a of 2.86. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

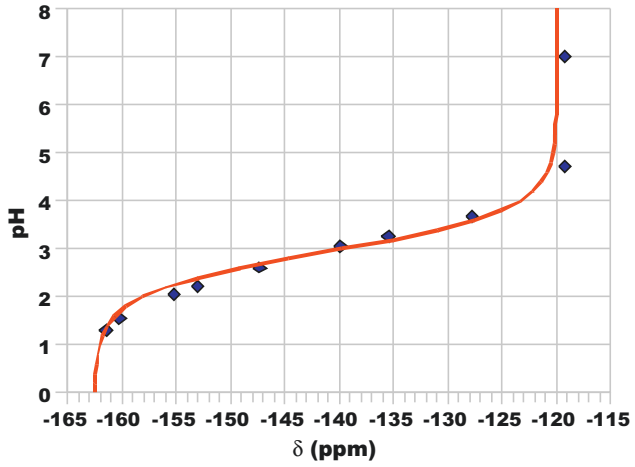

Fig. 4. ^{19}F chemical shift of 1.0 M fluoride as a function of pH, diamonds are experimental data (blue), the line is the fitted curve (red). Curve fitting gave a pK_a of 2.94. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

accord with the trend towards greater acidity of HF as the medium composition shifts from H_2O to HF [17]. With fitted equations in hand, it is possible to obtain an ^1H NMR spectrum of the external standard, a ^{19}F NMR spectrum of the sample, and cross-reference the two spectra to obtain the fluoride ion chemical shift. The pH is then solved for from the appropriate equation relating pH and chemical shift at the concentration of interest. The large difference in chemical shift between HF and F^- gives good resolution in the pH range where fluoride is a buffer, approximately pH 1.5–4.5. Since a fluoride concentration dependence is present, albeit not strong, only approximate knowledge of the total fluoride concentration is needed to select the appropriate equation.

As ^{19}F NMR chemical shifts are temperature dependent, precision is slightly improved if all measurements are made at constant temperature [18]. Use of a ^1H chemical shift reference which has a known difference in its temperature response relative to HDO allows for in situ monitoring of the spectrometer temperature regulation [16]. Conversely, the low pH sensitivity of the ^1H chemical shift of HDO minimizes the interference of pH changes in temperature measurements. However, this insensitivity also prevents the most obvious approach to NMR spectroscopic pH measurement in aqueous solutions, of correlating the solvent ^1H chemical shift with pH, from being accurate. Placing the ^1H chemical shift reference in an external reference solution avoids the need to add anything to the sample, which could potentially perturb its pH and allows for re-use of the reference. Chemical shift cross-reference reproducibility between ^1H and ^{19}F spectra is also aided by the deuterium lock signal afforded by the external reference solvent.

Any errors in determining the 3-FP δ vs. pH calibration curve will lead to an identical error in the curves for fluoride. There is also the possibility that the solution magnetic susceptibility varies with fluoride concentration or pH, but the effect of this variation can be expected to be far less than the pH-induced $\Delta\delta$ [19]. A significant assumption is that 3-FP does not interact with HF or fluoride in a concentration-dependent fashion. The most likely form of this interaction is an 3-FP–HF hydrogen bond. The effects of this hydrogen bond on chemical shift and pK_a will be opposed so that they partially cancel. Using Eq. (1) to cross-check between readings in tartrate, low fluoride, and high fluoride, there appears to be no net fluoride effect on the indicator. With the most significant source of error being the initial pH measurements, a reasonable accuracy of pH measurements by this technique would be ~0.05 pH unit based on the reproducibility of our pH meter readings. In comparison, chemical shift measurements on the same sample are reproducible over a period of weeks to 0.05 ppm, which would produce an error of 0.002 pH near pH 3 and 0.005 pH near pH 4.

4. Conclusions

Aqueous fluoride buffer solutions have existed in an NMR spectroscopy twilight between the well-studied extremes of concentrated hydrofluoric acid or anhydrous HF solvent systems and dilute or strongly complexed fluoride [7c,8,20,21]. However, due to the unique properties of fluoride as being weakly ligating to certain ions such as Co^{2+} and oxidatively robust in the extreme, these mildly acidic buffers allow one to study highly oxidizing substances such as cobalt oxide water oxidation catalysts in otherwise inaccessible pH ranges. The above technique now allows a convenient, accurate way to measure pH in these solutions, lowering one of the barriers to studying reactions in this scientifically interesting and technologically important buffer system. As the only reagents required are a reusable external standard solution and ~100 μl of the solution being tested, waste disposal is minimized.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.10.006.

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