

Application of ATR-FTIR spectroscopy in quantitative analysis of deuterium in basic solutions

S. Heinze^{1,2}, B. Vuillemin^{1*} and P. Giroux²

¹ Laboratoire de Recherches sur la Réactivité des Solides, UMR 56-13 CNRS, BP 47 870
21078 Dijon Cedex, France

² CEA/Valduc, Service TR, 21120 Is-sur-Tille, France

Abstract. A method to measure the deuterium concentration in basic solutions, using Attenuated Total Reflection Fourier Transformed Infrared Spectroscopy (ATR-FTIR) is described. Deuterium quantification is based on the O-D bond stretching peak. A calibration curve is drawn, representing the peak intensity *versus* the deuterium percentage in a neutral solution. No calibration curve can be obtained with basic solutions, because of the strong absorbance due to hydroxide ions. Thus, an acidification is necessary prior to the analysis of a basic solution. The deuterium content of this acid solution is then measured. As we know the dilution caused by the acid addition, we can calculate the deuterium content of the initial basic solution. The relative uncertainty of this method is $\pm 2\%$.

Key words. ATR-FTIR – deuterium – heavy water.

Introduction

This paper aims to describe a routine and simple method that can be used for on-line measurements of the deuterium concentration in aqueous solution, in order to follow the electrolytic isotopic enrichment. This technique should be efficient for basic solutions with a hydroxide content up to 3 mol l⁻¹. The literature indicates that deuterium titration in water can be performed with various methods. Mass spectroscopy, which is certainly the most sensitive, can be used for quantitative analysis of deuterium percentage from 0 to 100 [1]. Other methods like density measurement of the solution [2] are also sensitive. However these methods are not sufficiently simple to be used routinely. Though its poorer sensitivity infrared spectroscopy appears to be a rapid and easy method as proposed by Lecomte to measure accurately small ($< 5\%$) and high ($> 96\%$) deuterium ratios in neutral solutions [3,4]. In this study, we use the Attenuated Total Reflection Fourier Transformed Infrared Spectroscopy (ATR-FTIR) to titrate basic solutions with deuterium content up to 50%.

Experimental procedure

Calibration mixtures, with deuterium relative ratio up to 50%, are prepared by mixing known masses of distilled water and 99.8% heavy water supplied by Eurisotop. 4 ml of each solution is poured on a horizontal ZnSe cell. The acquisition of the spectra is performed with a Perkin Elmer FT-IR 1725X spectrometer.

Deuterium quantification in H₂O+D₂O mixtures

As shown in figure 1, the infrared spectra of a H₂O+D₂O mixture displays five absorption peaks: 3360 cm⁻¹ (O-H bond stretching), 2500 cm⁻¹ (O-D bond stretching), 1650 cm⁻¹ (H₂O bending), 1450 cm⁻¹ (HDO bending), and 1210 cm⁻¹ (D₂O bending). The transmission is the ratio I/I₀, where I₀ and I are respectively the intensity of the IR radiation before and after the sample. The actual position of all peaks, as well as their intensity (minimum of transmission for the considered peak), depends on the deuterium concentration. The most reliable relation between isotopic composition and peak's intensity is obtained by considering the O-D bond stretching peak. Figure 2 shows the calibration curve representing the peak's intensity *versus* the deuterium percentage. Such a curve obviously depends on the cell used for spectra acquisition. This calibration curve allows to measure the deuterium concentration, from 0.32 to 50%, with a relative uncertainty of $\pm 2\%$.

Effect of hydroxide content on the infrared spectra

Curve b in figure 3 shows the influence of a sodium hydroxide addition in the H₂O+D₂O mixture. Hydroxide ions cause an increase of the infrared absorption. Correspondingly, the peaks intensity and the background are shifted to lower transmission values. The calibration curve obtained with neutral mixtures is therefore useless.

*Correspondence and reprints.

Received June, 18, 1999; revised July, 10, 1999; accepted July, 15, 1999.

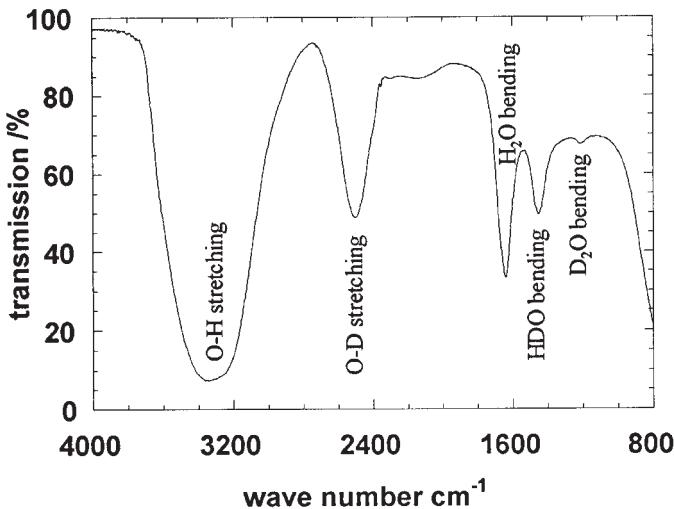


Fig. 1. Infrared spectrum of a H₂O+D₂O mixture (13.26% of deuterium) (The transmission is the ratio I/I₀, where I₀ and I are respectively the intensity of the IR radiation before and after the sample).

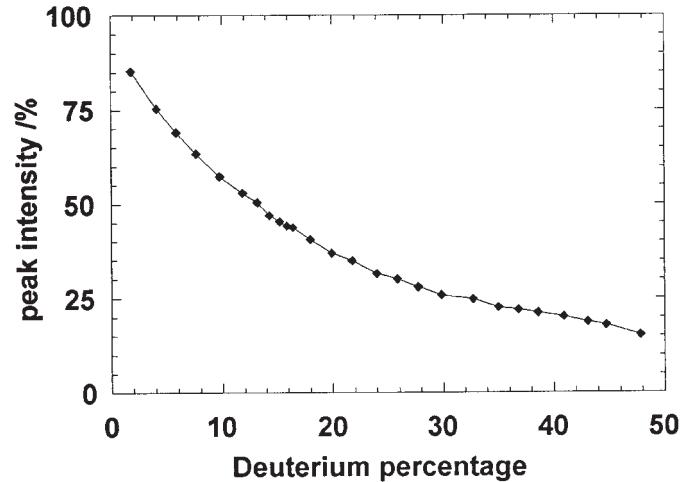


Fig. 2. Calibration curve representing the intensity (minimum of transmission for the considered peak) of the O-D bond stretching peak *versus* the deuterium content.

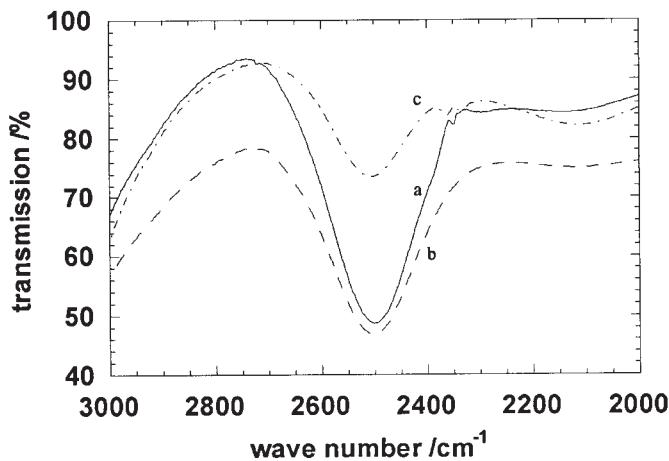


Fig. 3. a) infrared spectrum of a neutral H₂O+D₂O mixture. b) effect of a sodium hydroxide addition (about 3 mol l⁻¹). c) effect of acidification of the basic mixture.

Effect of acid addition

Molar hydrochloric acid is then added to the basic solution, until an acid value of the pH is reached. Curve c in figure 3 shows the corresponding infrared spectrum. As the hydroxide ions concentration is negligible, and as the hydronium ions cause no additional absorption, the background is identical to that obtained for neutral mixtures. Moreover, because of the hydrochloric acid addition, the deuterium per-

centage in the solution decreases. That is the reason why the peak intensity decreases in a significant way.

Experimental procedure for the determination of deuterium concentration in a basic solution

A volume of hydrochloric acid, V_a, is added to a volume, V_b, of the basic solution containing deuterium in order to obtain an acid solution. Let X be the deuterium molar ratio in the basic solution. Pure water contains 111 mol l⁻¹ of hydrogen. We consider that a basic solution contains the same concentration of hydrogen atoms. In this case, the hydrogen atoms are in water molecules as well as in hydroxide ions. So, the basic solution contains 111V_b × X moles of deuterium and 111V_b × (1-X) moles of hydrogen. On the other hand, we also consider that the hydrogen concentration in a hydrochloric acid solution is 111 mol l⁻¹. So, a volume V_a of this solution contains 111V_a moles of hydrogen. The total amount of both isotopes in the mixture is then: 111V_b × X moles of deuterium, and 111(V_a+V_b × (1-X)) moles of hydrogen, that is 111(V_a+V_b) moles of both hydrogen isotopes. The isotopic molar ratio of deuterium, Z, is then:

$$Z = \frac{V_b \times X}{V_a + V_b} \quad (1)$$

This isotopic ratio of the acid mixture, Z, is measured using the calibration curve (figure 2). Then, X is calculated using equation (1). A wide number of measurements using basic mixture of given isotopic compositions, prepared by mixing H₂O, D₂O and NaOH pellets (approximately 3 mol l⁻¹), in

the range 0.32-50% of deuterium were performed. The relative uncertainty of the method is the same for basic solutions than for neutral ones, that is $\pm 2\%$.

Conclusion

The measurement of the O-D bond stretching peak intensity by ATR infrared spectroscopy appears to be a well adapted method to measure rapidly the deuterium content, of a basic solution, in the range 0.32-50%, with a relative uncertainty of $\pm 2\%$. Moreover this technique requires only a small volume of solution (about 4 ml) and then can be used to follow the isotopic enrichment of deuterium during electrolysis.

References

1. Chenouard, J.; Gueron, J.; Roth, E. Report CEA N°87, 1951.
2. Viallard, R. In *Traité de chimie minérale, Tome 1*; Pascal, P., Ed; Masson: Paris, 1956; p 693.
3. Lecomte, J.; Ceccaldi, M., Roth, E. *J. Chim. Phys.* **1953**, *50*, 166-169.
4. Lecomte, J.; Ceccaldi, M., Roth, E. *J. Phys. Rad.* **1954**, *15*, 543-544.
5. Fuchs, Ch.; Spirig, N.; Moeller, H. *Eur. J. Clin. Chem. Clin. Biochem.* **1993**, *31*, 639-644.
6. Ceccaldi, M.; Girard, G.; Menaché, M.; Riedinger, M. Report CEA N° R-4675, 1975.
7. Gaunt, J. *Analyst*, **1954**, *79*, 580-585.