TÜBİTAK

Turkish Journal of Physics

http://journals.tubitak.gov.tr/physics/

Research Article

Turk J Phys
(2013) 37: 208 – 211

doi:10.3906/fiz-1203-1

A different point of view: a continuous tracing of acid–base titration with fiber-optic sensor

Şerafettin YALTKAYA,[1,*] **Esra KENDİR**[2]

[1]Department of Physics, Faculty of Science, Akdeniz University, 07058 Antalya, Turkey

[2]Department of Physics, Graduate School of Natural Sciences, Akdeniz University, 07058 Antalya, Turkey

Received: 02.03.2012 • **Accepted:** 18.10.2012 • **Published Online:** 19.06.2013 • **Printed:** 12.07.2013

Abstract: Our main aim was to investigate variations in the refractive index of a solution during chemical reaction. The variation of refractive index was measured through the entire acid–base titration process, especially near the equivalence point. To determine the equivalence point, the conductivity of the solution and the refractive index were measured simultaneously. In this preliminary study, sodium hydroxide and hydrochloric acid were used as the base and the acid solution, respectively. To measure the refractive index variation, a fiber-optic refractive index sensor was designed. The fiber-optic probe was dipped into the solution and acted as a refractive index sensor according to Fresnel's fundamental reflection law. A conductometer, a lab-made fiber-optic refractive index sensor ensemble, and a lab-made optical drop counter were each connected to a computer via an analog digital converter and the data acquisition was performed with the LabVIEW program. The equivalence point was derived easily from the refractive index data for the sodium hydroxide solution with different molarities of hydrochloric acid. In our opinion, the measurement of the variation of the refractive index during this kind of chemical reaction is more sensitive than the conductometric measurement.

Key words: Acid base titration, refractive index, optical fiber sensor

1. Introduction

The contribution of different measurement techniques to the development of science is undeniable. Many new kinds of sensors are being produced based on contemporary technologies. In addition, some existing sensors are being applied to different areas. In recent decades, the development of optoelectronics has led to the production of new types of optochemical sensors [1–4]. Titration is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of a known reactant among the other spectrophotometric, spectrofluorimetric, phosphorescent, scattering, chemiluminescent, chromatography, and nuclear magnetic resonance spectroscopy techniques, etc.

In this study, a fiber-optic refractive index sensor was designed and the refractive index variations during acid–base titration were measured continuously in our laboratory. To our knowledge, this kind of continuous measurement, over short time intervals, is the first work of its type conducted on acid–base titration. However, similar work was carried out at particular concentration points by Zhenjian et al. [5].

The variations in the refractive index of the solution can be monitored easily by immersing the optical fiber probe. During the acid–base titration, the equivalence point can be determined easily and the reaction between the titrant and the analyte can be monitored from the refractive index data.

*Correspondence: yaltkaya@akdeniz.edu.tr

The intersection of the solution and the core of the optical fiber constitutes the boundary surface. The intensity of light reflected from the boundary surface was measured at 660 nm, and by utilizing Fresnel's fundamental reflection law, the refractive index of the solution was calculated. The Fresnel equation and the refractive index calculations were described in [6]. The calculations and the data acquisition were performed using the LabVIEW program. The optical fiber collects all the reflected light, which also meets the small angle criteria, from the boundary surface. At small angles ($<10^\circ$), the reflection coefficients for both parallel and perpendicular polarization states are the same, and so the Fresnel reflection amplitude (r) coefficients reduce to

$$r = \frac{n_f - n_s}{n_f + n_s}, \tag{1}$$

where n_f and n_s are the refractive indices of the fiber's core and the solution, respectively [7].

2. Experimental

The sensor arrangement is shown in Figure 1 and is designed to capture the intensity of the reflecting light that emits from the almost intensity-stable, single-mode, fiber-coupled diode laser at 660 nm (full width at half maximum, FWHM) wavelength (Melles Griot, 10 mW). During the experiment, the intensity of the laser diode was recorded with silicon detector-II by computer via an analog digital converter (ADC; National Instruments 6070E). The data acquisition was performed instantaneously for all the ADC inputs, and data points were collected at 250-μs time intervals. The root mean square (RMS) value was calculated for each input (detector-I, detector-II, drop counter, and conductometer) every 200 data points, and this was also used as a data point for the graphics. Therefore, the points in the graphics are located at 50-ms time intervals. The lab-made drop counter, consisting of a Schmidt trigger circuit with a photogate, an AT90S1200 integrated circuit, and a counter, sends a pulse to one of the ADC's analog inputs for each drop of the titrant. Thus, the number of drops of titrant added during the titration is recorded.

The added titrant volume is calculated from the drop volume of the titrant and the number of drops added. One of the pigtailed arms of the 2 $\times$ 2-coupler (3-dB fiber coupler) was used as an optical probe where the boundary surface was located, and the reflected light was detected by a power meter (Melles Griot, Universal Power Meter) via silicon detector-I. In addition, as the response time of conductometric measurements is faster than pH measurements, the conductance of the analyte was measured with a conductometer (WPA, Linton, Cambridge, UK) via a low-pass filter, as depicted in Figure 1.

3. Results and discussion

A titration curve is the graph of the conductivity and the refractive index of a solution versus the volume of titrant added. In the simple titration of 0.5 M hydrochloric acid with 40 mL of $\sim$0.5 M sodium hydroxide, the titration curve has a single very steep section at the equivalence point, as shown in Figure 2, which has 16,400 RMS values. In addition to this, the refractive index data indicate the incline close to the equivalence point when the conductivity of the solution is almost constant. In Figure 3, the variation of the first derivative of the refractive index is shown for each added drop of titrant. The maximum point on the curve corresponds to a titrant volume of 39.460 mL, according to the OriginLab graphing and data analysis software.

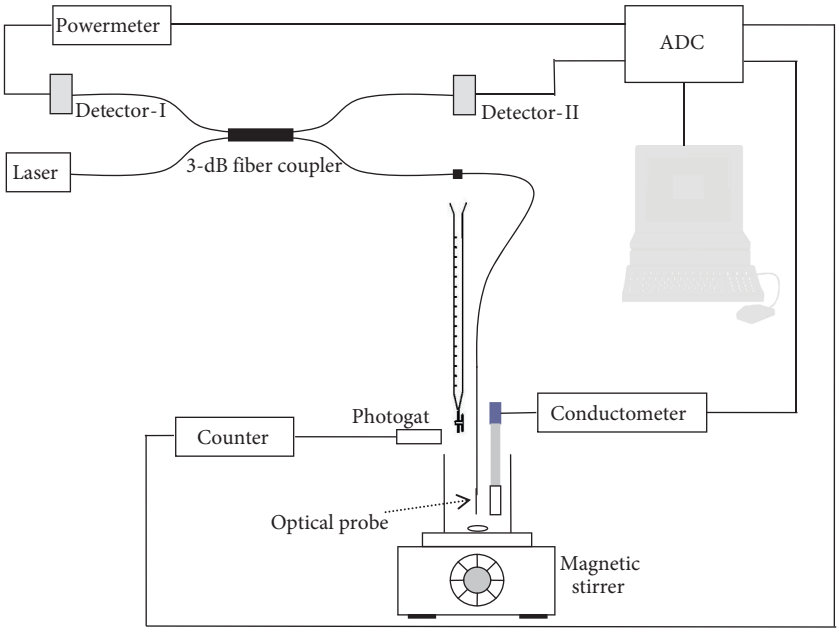

Figure 1. Scheme of the experimental setup. See the text for details.

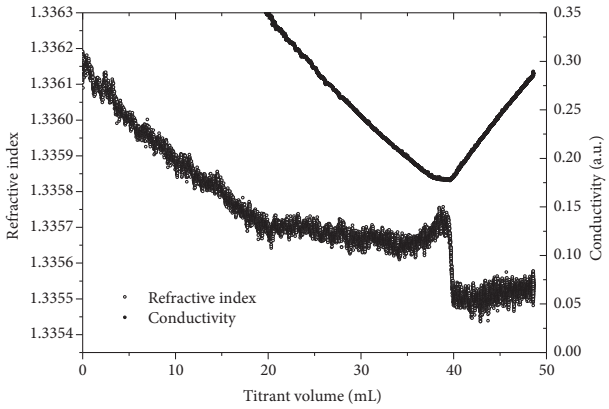

Figure 2. The conductivity and the refractive index of a solution versus the volume of titrant added.

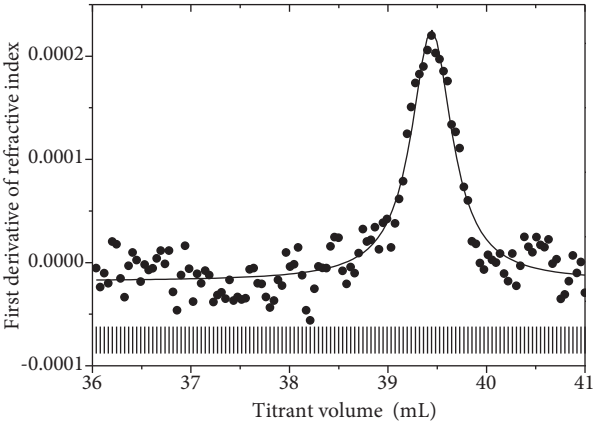

Figure 3. The variation of the first derivative of the refractive index. The bars indicate the drop localization.

The refractive index of the 0.5 M NaOH was measured at NTP before the titration. The refractive index values of $(1.33614 \pm 1.25) \times 10^{-5}$ with the standard error of 4.44×10^{-7} were obtained. Since the sampling rate was high, the standard error and also the width of the confidence interval were greatly reduced. The equation of the linear fit was calculated in the linear region of the variation of refractive index values with the titrant volume (Figure 2). By using the equation of the linear fit, a graph (as shown in Figure 4) was drawn for the data points of the refractive index values versus the molarities of the NaOH for each drop of the titrant. Only one error bar is shown in Figure 4. Therefore, during the titration, the minimum resolvable molarity of NaOH was determined as 15.32 ± 0.63 mM.

The method of calculating the end-point values from refractive index data was also applied to conductometric data analysis and a titrant volume of 39.40 mL was obtained. This result is in close agreement with the result of the refractive index end-point calculation and the equivalence-point titrant volume calculation.

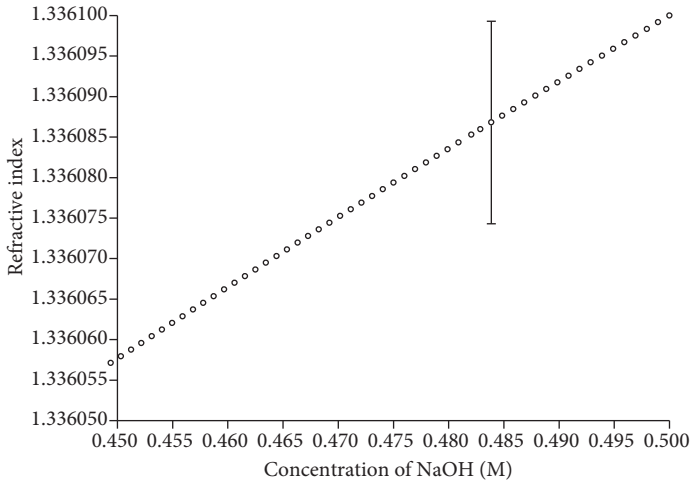

Figure 4. The variation of the refractive index with the concentration of NaOH.

Acknowledgment

The authors thank the Scientific Research Projects Unit of Akdeniz University for their support of this study.

References

[1] G. Gauglitz, *Anal. Bioanal. Chem.*, **381**, (2005), 141.

[2] Fiber Optic Sensors, eds. S. Yin, F. T. S. Yu and P. B. Ruffin (CRC Press Taylor & Francis Group, Boca Raton, 2008) p. 435.

[3] A. Dér, S. Valkai, A. Mathesz, I. Andó, E. K. Wolff and P. Ormo, *Sensor Actuat. B-Chem.*, **151**, (2010), 26.

[4] J. Dakin and B. Culshaw, eds., Optical Fiber Sensors, Applications, Analysis, and Future Trends, Vol. 4 (Artech House, Boston, London, 1997) p. 478.

[5] H. Zhenjian, T. Chunhua and H. Xuguang, *Acta Chim. Sin.*, **68**, (2010), 1098.

[6] S. Yaltkaya and R. Aydın, *Turk. J. Phys.*, **26**, (2002), 41.

[7] E. Hecht, Optics (International Edition, Addison Wesley, Boston, 2002) p. 689.