Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 141 (2015) 161–168

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Photometric method for determination of acidity constants through integral spectra analysis

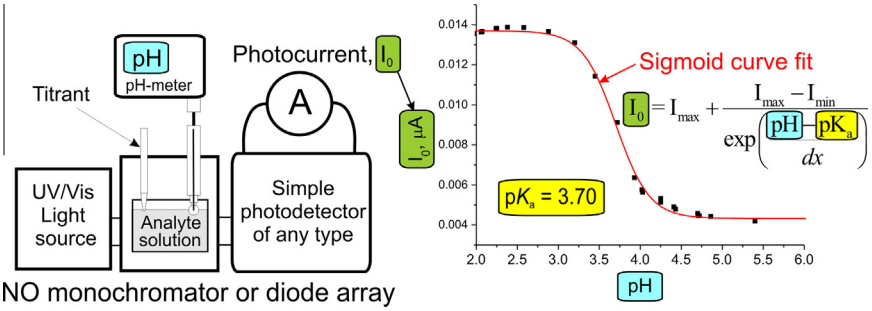
Yuriy Eduardovich Zevatskiy [a], Daniil Olegovich Ruzanov [b], Denis Vladimirovich Samoylov [c,*]

[a] Saint-Petersburg State University of Technology & Design, Bolshaya Morskaya str. 18, Saint-Petersburg, 191186, Russia
[b] Saint-Petersburg State Institute of Technology (Technical University), Moskovskiy ave., 26, Saint-Petersburg, 190013, Russia
[c] NovBytKhim corp, V.O. Kosaya line. 15b, Saint-Petersburg, 199026, Russia

HIGHLIGHTS

- The method allows to obtain reliable values of acidity constants in 10–20 min.
- Only photocurrent of detector device at each pH needs to be registered to obtain pK_a.
- Experimental equipment has lower cost because of exclusion of monochromator device and diode array.
- Method is suitable for determination pK_a values for substances with low spectral change.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 August 2014
Received in revised form 1 January 2015
Accepted 15 January 2015
Available online 30 January 2015

Keywords:
Acidity constant
Spectrometry
Photometry
Integral spectra

ABSTRACT

An express method for determination of acidity constants of organic acids, based on the analysis of the integral transmittance *vs.* pH dependence is developed. The integral value is registered as a photocurrent of photometric device simultaneously with potentiometric titration. The proposed method allows to obtain pK_a using only simple and low-cost instrumentation. The optical part of the experimental setup has been optimized through the exclusion of the monochromator device. Thus it only takes 10–15 min to obtain one pK_a value with the absolute error of less than 0.15 pH units. Application limitations and reliability of the method have been tested for a series of organic acids of various nature.

Introduction

The studies of ionic equilibria in a solution always confront certain challenges imposed by the area of application of each experimental method. Since the acidity constant is a most significant quantitative parameter of an equilibrium [1,2], it is essential to develop a simple, reliable, and high-throughput approach to obtaining this value.

For practical purposes (life science, pharmaceutical chemistry and related fields), it is essential to keep in mind that the possibility, the direction and the intensity of transport phenomena depend on pK_a value. This value defines the concentration ratio of charged and uncharged prototropic forms in a selected medium, that have drastically different transport properties due to the different types of electrostatic interactions [3].

Though considerable advances have been made in the calculation techniques for the estimation of acidity constants in aqueous solution [4–8], there also are major developments in the experimental express methods based on HPLC [9,10], capillary zone electrophoresis [11–13], ^{13}C- and ^{15}N-NMR [14,15], spectrophotometric

* Corresponding author.
E-mail addresses: daniilruzanov@mail.ru (D.O. Ruzanov), samoylov@newchem.ru (D.V. Samoylov).

http://dx.doi.org/10.1016/j.saa.2015.01.045
1386-1425/

titration [16–19] and also in the combination of the above approaches [19–22]. Besides, new original methods that use various types of spectroscopy are being introduced [23–25].

Standard spectrophotometric method (SSM) has so far been one of the most popular traditional methods for obtaining pK_a. Since it allows to study complex prototropic equilibria complicated by tautomeric equilibria, this method is widely used both in its classical form [26–30] and in its more advanced modifications [31–33].

It is common knowledge that the method in its classical form is based on measuring the UV–Vis absorption spectra of prototropic form mixtures at several pH values in the vicinity of the assumed pK_a value. As the result, the dependence of absorbance (D) on one or several analytical wavelengths (λ_{analyt}) *vs.* pH is obtained. The numerical analysis of this dependence allows to obtain the desired pK_a value.

The following are responsible for the principal limitations of SSM:

(1) Resolution of absorption spectra of protonated and deprotonated forms. For the simple alkyl- and arylcarboxylic acids, the difference in spectra of anionic and neutral forms is considered to be insufficient for the application of SSM for obtaining pK_a [34]. But for carboxylic acids with complex substituents that include chromophore fragments and functional groups (*e.g.* Phenolphatelein or xanthene dyes) the spectra of the forms with protonated and deprotonated carboxygroups are sufficiently different to obtain the pK_a by SSM [35].
(2) The dependence of absorbance D at analytical wavelength *vs.* pH must be informative, *i.e.* it must have at least one maximum of the first or second derivative by pH in the pH area corresponding to the pK_a value. Therefore in the case of poorly resolved spectra and of a complex system of equilibria, the use of several analytical wavelengths is necessary. Low resolution of spectra of prototropic forms also hampers the selection of analytical wavelengths that ensure sufficient difference in the absorbance and the informativity or experimental dependences [30].
(3) Preparation of a series of working solutions with the constant concentration of analyte and ionic strength in the entire pH range is very time-consuming.

Numerous efforts have been directed recently towards the elimination of some of the abovementioned limitations of the spectrophotometric method. The main trends are: (a) expressness *i.e.* reducing the time required for the sample preparation and (b) automation of the registration and collection of experimental data and (c) the determination of acidity constants for polybasic acids (polyacid bases) with different types of ionizing groups. Therefore currently it is more common to register the complete absorption spectra of an analyte at various pH, as well as to apply modern methods of numerical and statistical analysis to the processing of D–λ–pH experimental data for calculation of pK_a [19,26,30,36].

Thus, the "spectrophotometric titration" method implies express registration of complete absorption spectra by a photodiode array matrix with the use of fiber-optic probes [17,37,38]. In automated systems the probe is placed into a vessel where potentiometric titration is performed, and thus the registration of spectra and the pH measurement are preformed "one-pot" and simultaneously.

The other successful express modification of SSM is the "linear pH-gradient method" [31]. Registration of spectra is performed in a transparent glass tube filled with analyte solution in the mixed buffer by a linear photodiode array positioned along the tube. The pH value in the tube changes linearly with position because of the system of two multicomponent buffer mixing and pumping systems. It takes *ca.* 10 min to obtain one pK_a value using this method.

However, the precision and the reliability of modern approaches are seriously affected by inclusion of non-informative wavelengths data into the calculation procedures and the accumulating error that occurs when pH values are obtained indirectly or calculated [39].

Pursuing the goal of simplification of procedure and equipment we have developed a photometric method for determination acidity constants for organic acids based on the analysis of integral transmittance spectra *vs.* pH.

Materials and methods

The experimental setup for the registration of the photocurrent, voltage–current (V–I) curves, pH and for automatic titration is shown in Fig. 1. It contains: (1) A UV/Vis light source with switchable deuterium (DDS-30, Russia) and halogen lamps and a light collimator, (2) a digital electrometer (Keithley 6514), (3) a photometric chamber (designed and assembled by «Spectron-Analyt», Russia) that includes: (a) a vacuum Sb–K–Cs phototube F-26 with sensitivity range 220–650 nm («MELZ», Russia), (b) a cell holder, (c) an electrometric amplifier (gain factor 10^9–10^{11}, «Spectron-Analyt»), (d) an electric circuit commutation board, (e) a metal casing for screening the low-current circuit against electromagnetic interference and the phototube against stray light, (4) a digital pH-meter («Aquilon» I-500, Russia) with a combination glass/Ag/AgCl electrode «pH-com» («Econics», Russia), (5) a magnetic stirrer, (6) a metal casing with a lid, inlets for a titrant and an electrode, a thermostated holder for the optical cell, (7) a burette with an electromagnetic valve, (8) a PC for data collection and processing and for the control of automatic titration. The valve operation was controlled through a Keithley 6514 digital output *via* a relay coil.

The light from the source passes through the solution «as is» *i.e.* without monochromatization or optical filtering. The titrant was added directly into the optical cell using a burette with a computer controlled electromagnetic valve. Titrant solution in burette was protected from exposure of air by standard absorption system [34]. A quartz optical cell (l = 5 cm) with a magnetic stirrer was tightly fixed inside the light path, in between the light source and the photometric chamber. The electrode, the stirrer and the titrant tube were placed outside the light aperture. pH values of

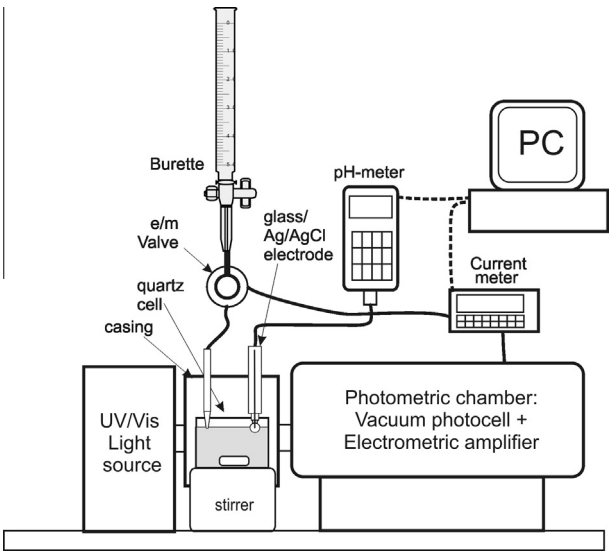


Fig. 1. Experimental setup layout.