Determining Acid Equilibrium Constants by Means of Chromatic Parameters*

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A method has been developed for the determination of acid-base equilibrium constants, which is applicable to compounds that absorb in the visible. The tristimulus (X, Y, Z) and the colorimetric coordinate values (L^*, a^*, b^*) of the chromatic space CIELAB 1976 are calculated by means of the transmittances of the entire spectral range. The curves, in the *a,b* plane, of chromatic differences vs. pH intersect at a pH value agreeing with the pK_a; this configuration occurs because a chromatic equilibrium of both species takes place at this point, which corresponds to the chemical equilibrium. With this method, the acidity constants are found easily and quickly, and they yield very good results. The validity of the method has been tested with the acid-base indicator bromophenol blue, obtaining pK_a = 3.943 at 25 °C; this result is compared with those obtained through the usual spectrophotometric methods. Also, thermodynamic magnitudes obtained from pK_a values at different temperatures from 20 to 70 °C have been determined, resulting in $\Delta H^0 = -(13.93 \pm 0.88)$ kJ mol^{-1}, $\Delta S^0 = -(122.6 \pm 2.8)$ J K^{-1} mol^{-1}.

Index Headings: **pK_a by chromatic coordinates method; Bromophenol blue; Chromatic parameters of the CIE L^*, a^*, b^* system; Thermodynamic values.**

INTRODUCTION

Colorimetric systems based on the Commission Internationale de l'Eclairage (CIE) recommendations for the color determination of a substance, measuring reflected or transmitted light, are increasingly important. The CIE recommends the use of two approximately uniform color spaces and associated color-difference formulae, the CIE 1976 ($L^*u^*v^*$) space and the CIE 1976 ($L^*a^*b^*$) space (CIELAB). Either of these two systems can be used to define the components of color differences in terms of appropriate correlations of the lightness, chroma, and hue; but the CIELAB system offers better results for the color of substances in solution.[1–3]

From a chemical point of view both the search for relationships between the chromatic parameters and physico-chemical constants of a substance and the changes in the chromatic parameters of a substance (such as an indicator) with the variation of its physico-chemical constants is of great interest. One of these constants is the acidity of substances in solution, such as the indicators of pH, which produce an important change in the color of a solution and, therefore, a change in the profile of the visible spectrum when the pH is varied.

Although there exist several methods[4,5] for the evaluation of acid-base equilibrium constants of substances in solution, based on the change in band profiles of some zones of the electromagnetic spectrum, we have developed an alternative. The method is applicable to compounds that absorb in the visible region, reading absorbances every 1 nm through the range 380–770 nm, to calculate the tristimulus values X, Y, and Z and subsequently the chromatic coordinates L^*, a^*, and b^* of the chromatic space CIELAB 1976. The acidity constants are evaluated easily and quickly, yielding good results.

This work is based on a pH scale of free hydrogen ion molality, since the difference with respect to the negative logarithm of the hydrogen ion activity is very small and is less than the experimental error, because the compound solutions are very diluted and a constant moderated value of the ionic strength was maintained.[6–14]

To verify the validity of the proposed method, we have applied it to tetrabromophenol sulfonphthalein (bromophenol blue). Its acidity constant has also been obtained spectrometrically for comparison with results by other authors.[15–17]

EXPERIMENTAL

Reagents. The tetrabromophenol sulfonphthalein was from the Sigma Co. and did not need any subsequent purification. Buffers and other products were from Merck (standard solutions according to DIN 19266 and NBS primary standards).

The initial solutions were prepared and weighed with a precision of more than ±0.05 mg, from which stock solutions with concentrations of around 10^{-3} M with ionic strength of 0.01 M in KCl with the use of buffer solutions were prepared. The working solutions were prepared from the previous solutions, by using buffer solutions of different pH as dilutants, to cover a wide pH range for the determination of the pK_a of the substance. Final compound concentration was 2.18 10^{-5} M with a total estimated ionic strength of 0.01 M. After the solutions were prepared, they were stored in darkness, so that their spectra did not vary over time.

Instrumentation. The UV-visible spectra were recorded at a rate of 60 nm/min in a Perkin–Elmer spectrometer, Lambda 5, controlled through an interface by a compatible PC. The slit width was 1 nm, which is the appropriate width for the absorption bands studied and thus provides a favorable signal-to-noise ratio. The spectrometer was calibrated on the absorbance and wavelength scales by using a holmium oxide glass and solutions of potassium dichromate, as recommended by the NBS.[18]

For the spectrometer, a relative spectral radiant power distribution of CIE standard illuminant *C* with a visual field of less than 4° is assumed.

Cells of 1 cm of Suprasil® quartz were used, which

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were cleaned periodically with the detergent Mucasol™ from Brand. The same buffer solution was used for the reference beam as for the sample. To determine the pH, we used a CRISON MicropH 2002 with a reproducibility of 0.001 pH units, and it was calibrated with commercial buffers.

Determination of the pK_a. This determination is based on the variation with the pH of the chromatic parameters a^* and b^* with respect to their values when the acid-base equilibrium is strongly displaced in either direction and one species predominates.

The method simultaneously uses 391 transmittance values measured every 1 nm in the visible spectral interval (380–770 nm), resulting in more reliable tristimulus X, Y, Z in comparison with other methods. With X, Y, and Z the coordinates L^*, a^*, and b^* are calculated. However, it was necessary to calculate beforehand the coefficients of the appropriate color-matching function to obtain the tristimulus, because the table with coefficients found in the bibliography has an interval of 5 nm. The method of calculating the tristimulus and the coordinates L^*, a^*, and b^* is described elsewhere.[3,19]

The total color difference ΔE^*_{ab} between two color stimuli is usually calculated from $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{½}$. Two aspects are formulated in this expression: first, the chromatic aspects included by the coordinate a^* and b^*, and, second, the contribution of the lightness (L^*), related to the transparency or opacity of the sample. From this, the magnitude of chromatic difference can be defined as $\Delta c^* = [(\Delta a^*)^2 + (\Delta b^*)^2]^{½}$, which results in better predictions than are acquired from using ΔE^*_{ab}, because of its emphasis on the chromatic aspects. In our case, $\Delta a^* = a^*_{A(max)} - a^*_A$ and $\Delta b^* = b^*_{A(max)} - b^*_A$, where a^* and b^* are chromatic coordinates of solutions with their pH near the expected pK_a, while $a^*_{A(max)}$ and $b^*_{A(max)}$ are a^* and b^* values of a solution with a pH more distant from the acid-base equilibrium; there are two $a^*_{A(max)}$ and $b^*_{A(max)}$ values, depending on whether the equilibrium is displaced towards the acid or the basic, and therefore two series of chromatic differences—termed Δc^* and $(\Delta c^*)'$—are obtained.

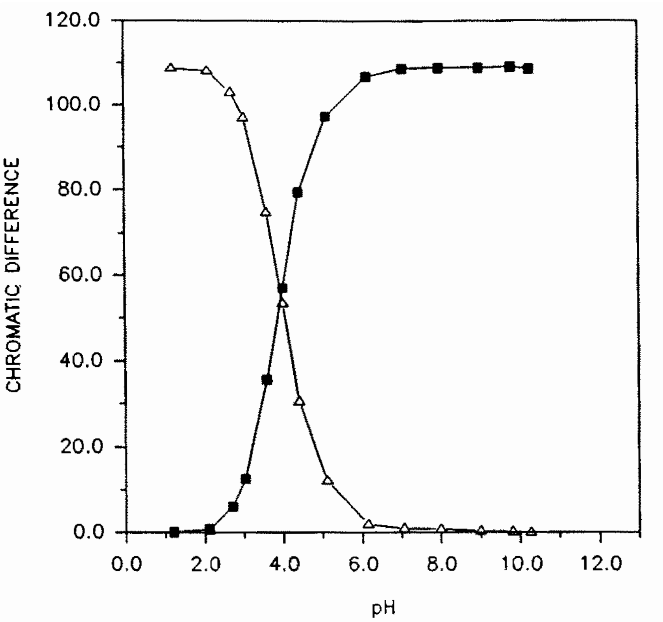

FIG. 1. Diagram of chromatic differences vs. pH, for the bromophenol blue solutions. (■) Δc^*; (△) $(\Delta c^*)'$.

The graph of these chromatic differences vs. pH shows S-shaped curves as shown in Fig. 1; the Δc^* increases with pH, while $(\Delta c^*)'$ decreases. Both curves intersect at a point whose abscissa yields the value of the pK_a, since at this point there is a chromatic equilibrium that corresponds to the chemical equilibrium when the acid and basic species have the same concentration. Similarly, other chromatic parameters related to the coordinates a^* and b^*, such as chroma and hue, can be used to obtain the pK_a.

An alternative to the graphical representation is the following calculation procedure based on data around the intersection point where the Δc^* – pH curves are almost straight lines. The equation of the straight line that passes through the points [pH$_1$, $(\Delta c^*)_1$] and [pH$_2$, $(\Delta c^*)_2$] is

$$\frac{\mathrm{pH} - \mathrm{pH}_1}{\mathrm{pH}_2 - \mathrm{pH}_1} = \frac{(\Delta c^*) - (\Delta c^*)_1}{(\Delta c^*)_2 - (\Delta c^*)_1}$$

and the line that passes through the points [pH$_1$, $(\Delta c^*)_1'$] and [pH$_2$, $(\Delta c^*)_2'$] is

$$\frac{\mathrm{pH} - \mathrm{pH}_1}{\mathrm{pH}_2 - \mathrm{pH}_1} = \frac{(\Delta c^*)' - (\Delta c^*)_1'}{(\Delta c^*)_2' - (\Delta c^*)_1'}.$$

Both pH$_1$ and pH$_2$ are near the expected pK_a value. The abscissa of the intersection point [pH, $\Delta c^* = (\Delta c^*)'$] is

$$\mathrm{p}K_a \simeq \mathrm{pH}_1 + \frac{(\mathrm{pH}_2 - \mathrm{pH}_1)\cdot[(\Delta c^*)_1' - (\Delta c^*)_1]}{[(\Delta c^*)_2 - (\Delta c^*)_2'] + [(\Delta c^*)_1' - (\Delta c^*)_1]}. \qquad (1)$$

This relation is an approximate shortcut to obtain the pK_a and only needs measurements in four spectra at different pH. Two of these spectra correspond to solutions at pH$_1$ and pH$_2$ and the other two to the case where the acid-base equilibrium is strongly displaced towards either acid or basic, respectively; by combining the four a^*, b^* pairs of chromatic coordinates, one obtains the four chromatic differences necessary in Eq. 1.

The pK_a error is due mainly to the pH error of the solutions; in comparison, the chromatic parameter errors are smaller since they are due to errors in the determination of the absorbance. Also, the moderate ionic strength and the low concentration of the compound make the difference between the thermodynamic pK_a and the practical pK_a—which uses concentrations—lower than the experimental pH error.

RESULTS AND DISCUSSION

To study the acid-base equilibrium, we recorded spectra of bromophenol blue in several buffered solutions of identical concentration and ionic strength (2.18×10^{-5}) and 1×10^{-2} M, respectively). The solutions, at 25 °C, change their color from yellow at pH < 3 to blue at pH > 6, as described in the literature.[14,15,20] In Fig. 2 some of these spectra are shown. The 430-nm band gives rise to the yellow coloring of the solution at a very low pH. This band diminishes its intensity as the pH increases, with a new band appearing around pH = 2.123 whose

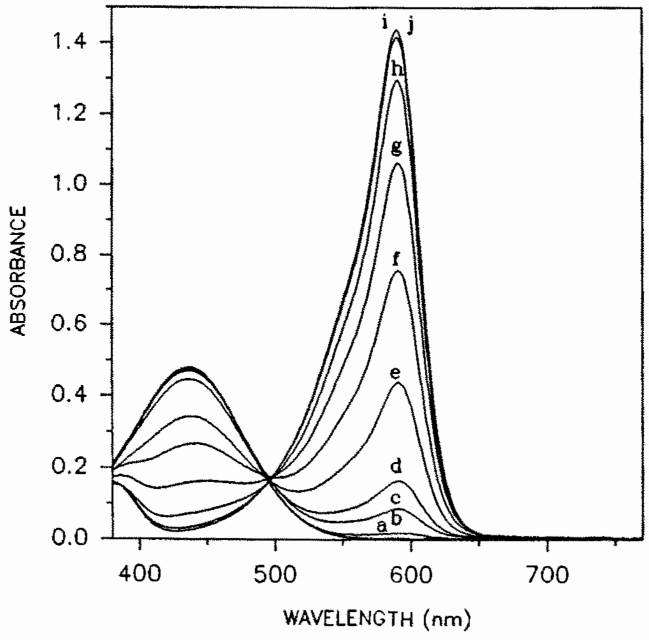

FIG. 2. Spectra of bromophenol blue (2.18×10^{-5} M) in buffer solutions at 25 °C and ionic strength 1×10^{-2} M at different pH values. Spectra ***a*** and ***j*** are acidic and basic forms. Spectra ***b–i*** are different ratios of acidic and basic forms. The pH values of the solutions are: ***a*** = 1.210; ***b*** = 2.123; ***c*** = 2.711; ***d*** = 3.032; ***e*** = 3.598; ***f*** = 4.003; ***g*** = 4.407; ***h*** = 5.111; ***i*** = 6.146; ***j*** = 7.063.

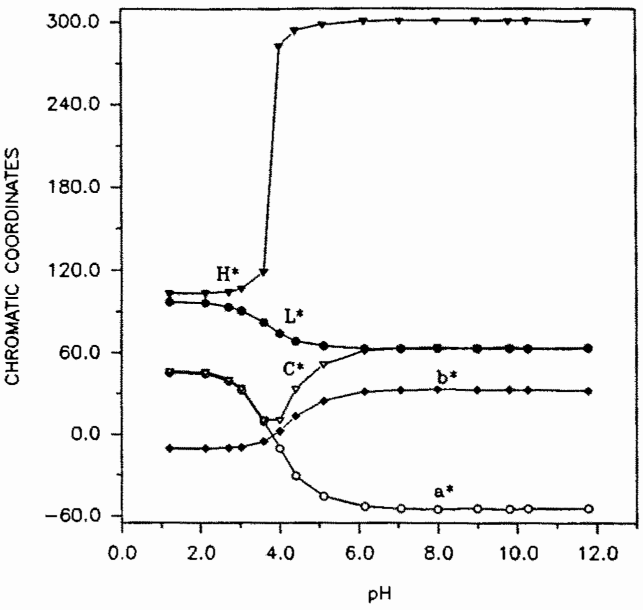

FIG. 3. Plot of the chromatic coordinates of tetrabromophenol sulfonphthalein vs. pH.

maximum is at 588 nm, its intensity increasing up to the value of pH = 7.063, where it stabilizes. There is an isosbestic point near 500 nm, suggesting the existence of an acid-base equilibrium. It was observed that over time the alkaline solutions with pH ≥ 12 diminish their color intensity until becoming transparent, with the absorption band at 588 nm simultaneously diminishing in intensity.

The tristimulus X, Y, and Z values and the chromatic coordinates L^*, a^*, and b^* were calculated by using a computer program developed in our laboratory on the basis of transmittance values from the entire visible spectrum.[21] This calculation was done with the spectrum of all the buffered solutions of the compound; some of the results are shown graphically in Fig. 3. Coordinates a^* and b^* vary with the pH, following a curve with a shape similar to a potentiometric titration curve, and their maximum rates of change are at a pH proximate to the corresponding pK_a; they vary slowly near the upper and lower limits of pH because, in these two zones, one or the other of the two forms of the compound predominate. In contrast, the graphs of the coordinate L^* and the parameters C^* and H^* vs. pH pass through minima near the pK_a (see Fig. 3). Therefore, it is often useful to examine the variation of the chromatic parameters with the pH, to determine the equilibria and qualitative pK_a values.

With the coordinates a^* and b^*, the chromatic differences, Δc^* and $(\Delta c^*)'$, were calculated, which are represented with respect to pH in Fig. 1. Both curves intersect at a point between pH = 3.60 and pH = 4.41. The linear part of both curves shows a good least-squares fit to the straight lines: $(\Delta c^*) = (-137.1 \pm 9.8) + (48.76 \pm 2.55) \cdot \text{pH}$, with the correlation coefficient $r = 0.997$ and $(\Delta c^*)' = (245.3 \pm 11.5) - (48.3 \pm 3.0) \cdot \text{pH}$, with $r = 0.996$. The projection of the intersection of both straight lines on the X-axis yields a value of $pK_a = 3.94$; this is affected by the experimental error, estimated at ±0.02.

Furthermore, with the use of the approximate method described in Eq. 1, the data $\Delta c^*_1 = 35.78$ and $(\Delta c^*_1)' = 74.77$, corresponding to pH = 3.60, and $\Delta c^*_2 = 97.06$ and $(\Delta c^*_2)' = 30.72$, corresponding to pH = 4.41, yield $pK_a = 3.96 \pm 0.02$; this value is fairly similar to the above result.

In order to compare the results of this colorimetric method, the pK_a of bromophenol blue was calculated by using (1) absorbances at the maximum of the acidic and basic forms of the compound obtained from solutions with $\text{pH} < pK_a - 2$ and $\text{pH} > pK_a + 2$, respectively; and (2) the absorbance of a solution with its $\text{pH} \simeq pK_a$ and midway between those of earlier ones or an absorbance as intermediate as possible between the upper and lower limits. Thus, calculation rounding-off errors were reduced because the absorbance differences were of a similar size. This calculation was repeated with the use of other solutions with absorbances also near the intermediate of the acidic and basic forms, the average of the results of each calculation being a good approximation to the pK_a.

The results are shown in the third column on the right in Table I; the mean value is $pK_a = 3.950$ and the standard error ±0.013. Other columns in this table show the

TABLE I. Variation of the pK_a of tetrabromophenol sulfonphthalein with the pH and the wavelength of the band maximum.

	λ (nm)						
pH	430	437	450	580	591	600	Mean
3.032	4.196	4.197	4.209	3.946	3.928	3.906	4.064
3.598	3.978	3.984	3.988	3.975	3.958	3.940	3.971
4.003	4.066	4.063	4.094	3.983	3.958	3.929	4.016
4.407	4.039	4.041	4.055	3.993	3.955	3.910	3.999
Mean	4.070	4.071	4.087	3.974	3.950	3.922	4.012

TABLE II. **pK_a values of tetrabromphenol sulfonphthalein obtained by different methods.**

	Ionic strength	T (°C)	pK_a
Stenström-Goldsmith method[4]	0.01	25.0 ± 0.1	3.88 ± 0.04
Sommer method[5]	0.01	25.0 ± 0.1	3.90 ± 0.03
Mean of several measurements	0.01	25.0 ± 0.1	4.01 ± 0.02
New colorimetric method	0.01	25.0 ± 0.1	3.94 ± 0.02
Ibid., Eq. 1	0.01	25.0 ± 0.1	3.96 ± 0.02
Kolthoff and Laitinen[15]	0.01	20	4.06
Pearson[16]	—	—	4.00
King and Kester[17]	0.7	25.0 ± 0.1	3.695 ± 0.007

pK_a obtained by measuring the absorbance at other wavelengths. The values do not differ much if the wavelengths are very different and distant from the band maximum. The variations of the pK_a with the wavelength are due to the use of quotients of the differences between increasingly similar absorbances with increasingly larger errors as the wavelength moves away from the band maximum. The arithmetic mean of all the values in the table yields pK_a = 4.01 ± 0.09, which is somewhat higher than the result from the colorimetric method proposed here. Although both methods are based on absorbance measurements at various wavelengths along the entire spectral range, the colorimetric method uses many more absorbance values, and not all of them contribute in the same degree to the result, because the coefficients to obtain the tristimulus X, Y, and Z depend on the wavelength. The colorimetric method may be understood as the calculation of the area under the spectral profile.

Likewise, the pK_a has been calculated by the spectrometric methods of Stenström and Goldsmith[4] and Sommer.[5] In the Stenström and Goldsmith method, the data are fitted to a straight line; a least-squares regression gives pK_a = 3.877 with $r = 0.999$ and a standard error of ±0.043.

For application of the Sommer method, $[(A_A - C_i\epsilon_{AH})/A_A][H^+]$ values were represented vs. C_i/A_i values, where A_i is the absorbance at the maximum of solutions with compound concentration C_i and acid concentration $[H^+]$, and A_A is the absorbance of the most acid solution with molar absorptivity ϵ_{AH}. The decimal logarithm of the intercept of the line fitted by least-squares regression—$r = 0.999$—gives pK_a = 3.896 ± 0.029. The original method, in which ordinates and abscissas are the opposite of those used here and the pK_a is the decimal logarithm of the ratio of the intercept to the slope, has been changed.

Table II shows the results obtained by the different methods, together with the bibliographic values;[15,16,17] that of King and Kester[17] was obtained in seawater with an ionic strength of 0.7 and significant concentrations of Mg^{2+}, Ca^{2+}, Na^+, Cl^-, and SO_4^{2-}, which affect the activity coefficients of acid-base equilibria. The arithmetical mean of results at 25 °C with an ionic strength of 0.01 is 3.938 ± 0.051, assuming the experiments were independent. Unlike the colorimetric method proposed here, the spectrometric methods have the drawback of using only one absorbance value for each solution and not the whole visible spectrum. Besides, they require that the equilibrium be totally displaced to the acid or to the base forms by means of the stability of the spectra at extreme pH. In spite of this consideration, the methods of Stenström–Goldsmith and Sommer give acceptable results, although the arithmetic mean in Table I yields a better value. The method of King and Kester also used full spectral data to derive pK_a.

The proposed colorimetric method gives a result with a small deviation with respect to the mean, compared with the other methods used. With it the certainty that the equilibrium will be displaced towards the acid and/or base form is not so crucial. This method can be used routinely to get the pK_a of colored substances using commercial colorimeters, some of which directly give a^* and b^*; hence the value of pK_a can be obtained simultaneously. Nevertheless, we suggest using many more absorbance values than are proposed in the bibliography for certain types of substances.[22,23] The only limitation of the proposed method is the need for the solutions to be colored (i.e., to absorb in the visible zone).

Temperature Dependence. The colorimetric method has also been used to obtain the pK_a of tetrabromophenol sulfonphthalein at other temperatures; the results can be found in Table III. The application of the van't Hoff equation $\ln K_a = -(\Delta H^0/RT) + \Delta S^0/R$ makes it possible to estimate thermodynamic parameters if ΔH^0 *y* ΔS^0 are independent of the temperature or vary very little with it. The linear fit of data in Table III to the equation of van't Hoff yields $\log K_a = -(6.40 \pm 0.14) + (728 \pm 46)\cdot(1/T)$ with $r = 0.996$. From this, $\Delta S^0 = -(122.6 \pm 2.8)$ J K^{-1} mol^{-1}, and $\Delta H^0 = -(13.93 \pm 0.88)$ kJ mol^{-1}. These values show that the process is exothermic—the equilibrium constant decreases with increasing temperature—with a negative entropy. $\Delta G^0 > 0$, at any temperature in the range 20–70 °C; i.e., the ionization process is not spontaneous (it would only be so at temperatures lower than 114 K). The variations in enthalpy and entropy are similar to those of other aromatic organic compounds.

CONCLUSION

The method proposed for the calculation of acid equilibrium constants of compounds which absorb in the visible region has the advantage that it uses information from the entire absorbing region (380–770 nm). The pK_a is determined easily and quickly from chromatic coordinates at different pH values and yields very good results. Data from four spectra are enough to compute a reasonable approximation of the pK_a—two at pH values near the expected pK_a, and the other two at pH values more distant from the equilibrium conditions. The pK_a can be obtained with a colorimeter by using a simple computer program that complements the commercial

TABLE III. **pK_a and ΔG^0 of tetrabromphenol sulfonphthalein at different temperatures.**

$T \pm 0.1$ °C	25.0	35.0	40.0	50.0	60.0	70.0
pK_a ± 0.02	3.94	4.06	4.09	4.14	4.21	4.28
ΔG^0(kJ mol^{-1})	22.60 ± 0.11	23.94 ± 0.12	24.54 ± 0.12	25.64 ± 0.12	26.87 ± 0.13	28.12 ± 0.13

software for the calculation of the chromatic coordinates—L^*, a^*, and b^*.

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