A Method for Determination of Thermodynamic Dissociation Constants from Absorption Spectra with Applications to ortho- and para-Phenylenediamines[*]

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Introduction

The dissociation constants of the mono-acidic bases or the mono-basic acids can be determined fairly well from the absorption curves of the substances in solution at different pH values[1], while with the dibasic acids and diacidic bases the spectroscopic determination of dissociation constants becomes more complicated[2]. Thamer and Voigt[2] have described a method for determining the dissociation constants in these cases. They measured the optical density of solutions of constant ionic strength at different pH values for a fixed wave length. The apparent dissociation constants are determined from these optical density data, and corrected to the true ones, using the Debye-Hückel equation.

We present here another method using the optical density data of solutions at only five different pH values. As an application of the present method, *ortho-* and *para-*phenylenediamines are chosen. There are a good many prior determinations of dissociation constants for the latter compound while the value of the second dissociation constant of the former compound is not found in the literature on the subject. The advantages and the disadvantages of the present method will also be discussed.

Method

We shall describe the method only for the diacidic bases, the application to acids or amphoteric electrolytes being obvious. The following equation can be shown to hold[2]:

$$D=\frac{Lc\left[\epsilon_1+\frac{k_{1b}}{a_{\mathrm{OH}}}\epsilon_2+\frac{k_{1b}k_{2b}}{a^2_{\mathrm{OH}}}\epsilon_3\right]}{1+\frac{k_{1b}}{a_{\mathrm{OH}}}+\frac{k_{1b}k_{2b}}{a^2_{\mathrm{OH}}}} \tag{1}$$

where ϵ_1, ϵ_2, and ϵ_3 represent the molar extinction coefficients of undissociated diacidic base B, its singly and doubly dissociated ions BH^+ and BH_2^{++}, respectively. D denotes the optical density of the solution of hydroxyl-ion activity a_{OH} and of analytical concentration c of the base in all its forms measured with an absorption cell of the length L. k_{1b} and k_{2b} are the apparent basic dissociation constants defined by

$$k_{1b}=\frac{a_{\mathrm{OH}}[BH^+]}{[B]},\qquad k_{2b}=\frac{a_{\mathrm{OH}}[BH_2^{++}]}{[BH^+]}, \tag{1a}$$

where brackets indicate concentrations. According to Thamer and Voigt "If k_1 and k_2 overlap and k_1/k_2 is therefore small, one can use optical density data and pH data with equation 4 (our equation 1) to obtain ϵ_2, k_1, and k_2 by successive approximations. However, the calculations are very laborious". It is the purpose of this paper to show that using Eq. (1) the dissociation constants can be calculated *without* successive approximations. From Eq. (1) the following equation can easily be derived:

$$D'x-y+(D'-\epsilon_3)z/a_{\mathrm{OH}}=(\epsilon_1-D')a_{\mathrm{OH}}, \tag{2}$$

where $D'=D/Lc$, $x=k_{1b}$, $y=k_{1b}\epsilon_2$, and $z=k_{1b}k_{2b}$. ϵ_1 and ϵ_3 are measurable as D' in alkaline ($p\mathrm{OH}\ll pk_{1b}$) and acidic ($p\mathrm{OH}\gg pk_{2b}$) solution, respectively. If the measurements are made of D' at three different medium pH values and constant ionic strength, Eq. (2) gives a set of linear simultaneous equations, in which x, y and z are unknowns, for a fixed wave length. No iterative process is involved in solving these equations for x, y and z, from which k_{1b}, k_{2b}, and ϵ_2 can be determined. Although what values of pH are appropriate as "three different medium pH values" depends on the substance, the following general rule may be given:

If $k_{1b}/k_{2b}\gg1$, (usually$>$10), these pH values are chosen such that $a_{\mathrm{OH}}\cong\sqrt{k_{1b}k_{2b}}$, $a_{\mathrm{OH}}\cong k_{1b}$ and $a_{\mathrm{OH}}\cong k_{2b}$.

If $k_{1b}/k_{2b}\cong1$, they are all chosen such that $p_{\mathrm{OH}}\cong pk_{1b}$ ($\cong pk_{2b}$), usually with intervals of 0.3–0.5 pH units.

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[*] Presented at the Meeting of the Kyushu Branch of the Chemical Society of Japan, Fukuoka, November 7, 1953.

[1] For example see, Hughes, Jellinek, and Ambrose, *J. Phys. Colloid Chem.*, 53, 410 (1949).

[2] B. J. Thamer and A. F. Voigt, *J. Phys. Chem.*, 56, 225 (1952).

Experimental Results

The samples of *o*- and *p*-phenylenediamines used were commercial ones. Absorption curves were determined with a Beckman DU spectrophotometer with a fixed slit-width for each substance at a given wavelength. Values of pH were determined using a pH-meter supplied by Shimadzu Seisakusho with a Beckman glass electrode. They were converted into the hydroxyl-ion activity using the ionization constant of water K_w[3]. The optical density data are listed in Tables I and II for *o*- and *p*-phenylenediamines, respectively. They are limited to those corresponding to 10–90 percent transmittance. Since it is impossible to obtain the optical density data satisfying the above criterion with one concentration value of the solution, we must use two different concentration values for each substance and for each pH value. In acidic and alkaline extremes dilution by the solvent does not bring about the change of the hydrogen-ion concentration, since in such cases the buffer action of the solvent is strong. For intermediate pH values McIlvaine's[4] Na_2HPO_4-citric acid buffer solutions with appropriate pH values were first prepared and then diluted to low ionic strength so that the Debye-Hückel equation can be applied. In this way, the buffer action was weakened and the pH value of the solution came to depend slightly upon the analytial concentration of the substance. Therefore, the optical density data of solutions with different concentrations are listed separately in the table. This supplied additional equations for the calculation of the dissociation constants and, as far as possible, two sets of equations were selected and used for calculation for a fixed wave length. The agreement between the values of the dissociation constants calculated from different sets of equations for a fixed wave length represents a measure of the experimental accuracy, particularly, of pH measurements. A preliminary investigation shows the dissociation constants of these substances to be: *o*-, $k_{1b}\cong 10^{-10}$, $k_{2b}=10^{-14}$; *p*-, $k_{1b}\cong 10^{-8}$, $k_{2b}\cong 10^{-11}$. From these figures appropriate values of pH are selected according to the criterion stated above. All measurements were made at room temperature. The control of the ionic strength was made with KCl. In the case of *o*-compound, where the relatively high ionic strength was necessary, dilution of the buffer solutions as prepared according to the indication in the literature was unnecessary. In this case the pH value does not depend on the concentration of the substance, since the buffer action of the solvent is strong. This is the reason why Table I for *o*-compound contains only one column for each intermediate pH value. The extinction coefficient ϵ_2 of singly charged ion BH^+ can in principle be calculated, but the error included will be great compared with k_{1b} and k_{2b}, because, contrary to them, ϵ_2 cannot be determined as an average value, since ϵ_2 assumes, in

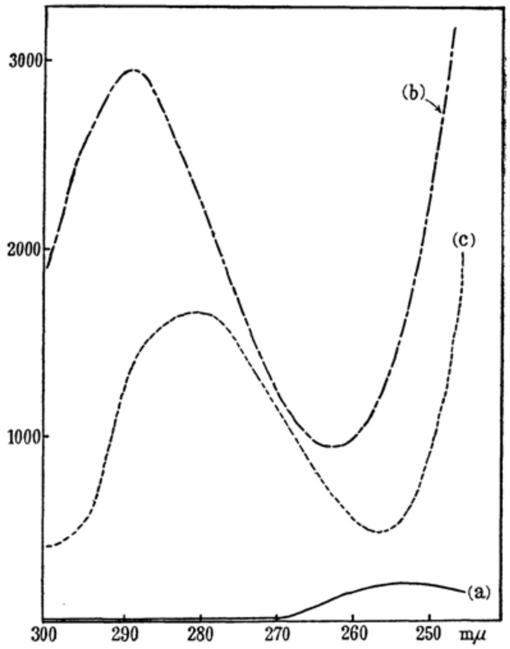

Fig. 1. Absorption curves of *o*-phenylenediamine in 6 N-HCl (a), 0.2 N-Na_2CO_3 (b), and pH 2.10 (c) solutions.

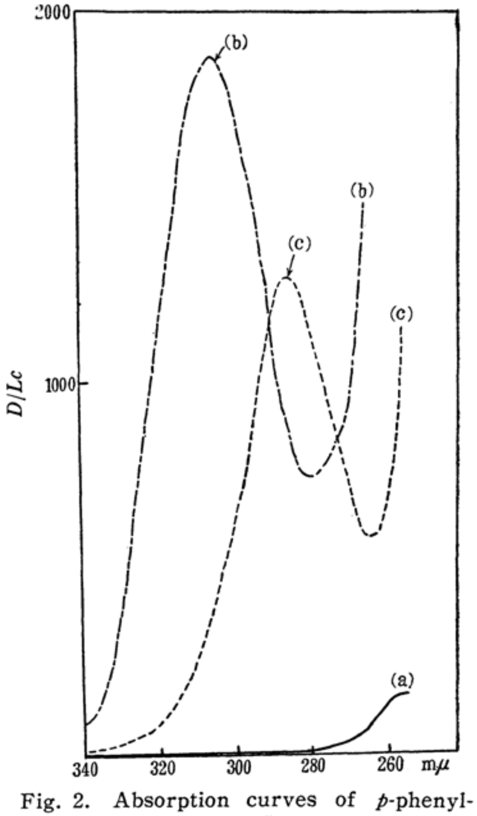

Fig. 2. Absorption curves of *p*-phenylenediamine in 1 N-HCl (a), 0.2 N-Na_2CO_3 (b), and pH 4.95 (c) solutions.

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[3] The values used for calculations are obtained by interpolation of the values reported by Harned and Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

[4] T.C. McIlvaine, *J. Biol. Chem.*, **49**, 183 (1921).

TABLE I

THE VALUES OF D', AND DISSOCIATION CONSTANTS OF o-PHENYLENEDIAMINE

Temp.: 14°C, μ: 1.0 mol./l.

Wave-length in mμ	D' Values					k_{1b} $\times 10^{10}$	k_{2b} $\times 10^{14}$
	6 N HCl	1.00 N HCl pH 0.00[a]	Na_2HPO_4-citric acid buffer solutions pH 2.10	pH 4.60	0.2 N Na_2CO_3		
290	9.5	125	1210	1640	2930	4.77	4.43
285	9.2	162	1550	1940	2800	4.11	4.21
280	12.0	175	1650	1940	2280	2.80	4.22
275	12.0	160	1490	1710	1690		5.44
270	16.0	131	1170	1340	1230		4.21
265	61.2	131	840	1000	970		4.78
260	130	166	560	710	950	2.84	5.20
255	172	192	475	700	1280	4.01	6.88
250	160	216	810	1200	2100	3.54	4.99
					Mean	3.68	4.93
						±0.32	±0.30

a) The value of the mean activity coefficient of 1.00 N-HCl is given in B. E. Conway, Electrochemical Data (Elsevier Publishing Company, Amsterdam, 1952), p. 75, to be 0.809 at 25°C which amounts to pH=0.10.

TABLE II

THE VALUES OF D', AND DISSOCIATION CONSTANTS OF p-PHENYLENEDIAMINE

Temp.: 14.5°C, μ: 0.049 mol./l.

Wave-length in mμ	D' Values								k_{1b} $\times 10^{8}$	k_{2b} $\times 10^{12}$	Columns[a] used for calc.	k_{1b} $\times 10^{8}$	k_{2b} $\times 10^{12}$	Columns[a] used for calc.
	1 N HCl	Na_2HPO_4-citric acid buffer solutions pH 3.13	pH 3.00	pH 5.20	pH 4.95	pH 6.75	pH 6.70	0.2 N Na_2CO_3						
340	3	4		7		61	60	87	1.10		3, 5, 7	1.02		3, 5, 8
335	3	4		14		127	122	180	1.08		3, 5, 7	1.09		3, 5, 8
330	3.3	6		21		248	247	355	1.07		3, 5, 7	0.97		3, 5, 8
325	3.7	7		43		447	454	645	1.06		3, 5, 7	0.93		3, 5, 8
320	4.0	16		82		721	714	1034	1.12		3, 5, 7	1.03		3, 5, 8
315	4.3	34		144	109		1000	1432	1.02		3, 5, 8	1.12		3, 6, 8
310	4.7	71		250	213		1240	1760	1.07	7.56	3, 5, 8	1.08	8.19	3, 6, 8
305	5.0	130		407	375		1390	1880	1.02	8.67	3, 5, 8	1.02	9.38	3, 6, 8
300	5.3	217	170		606		1430	1820	0.99	10.05	3, 6, 8	0.95	10.86	4, 6, 8
295	5.6	335	280		906		1395	1590	0.89	10.50	3, 6, 8	0.87	9.60	4, 6, 8
290	6.1	437	378		1177		1292	1300		10.50	3, 6, 8		10.15	4, 6, 8
285	6.6	480	408		1283		1137	1015	1.46	10.68	3, 6, 8	1.47	10.13	4, 6, 8
280	7.4	455	388		1200		961	815	1.15	10.22	3, 6, 8	1.16	10.59	4, 6, 8
275	8.3	381	316		989		827	773	0.63	10.45	3, 6, 8	0.65	10.28	4, 6, 8
270	13.5	297	237		767		814	1035		10.37	3, 6, 8		10.93	4, 6, 8
265	53	256	199		592		1058	1600	2.49	11.34	3, 6, 8	2.57	12.01	4, 6, 8
260	114	297	243		628		1738	2620	1.73	9.87	3, 6, 8	1.73	12.37	4, 6, 8
255	150	490	443		1138		3120	4400	1.46	8.95	3, 6, 8	1.45	9.56	4, 6, 8
						Mean			1.21	9.93		1.19	10.34	
									±0.11	±0.30		±0.11	±0.33	

a) The set of numbers in column 12 shows that for each wave length the set of D' values corresponding to the column indicated by these numbers is substituted in Eq. (2) and the values of k_{1b} and k_{2b} found in column 10 and 11, respectively, are calculated from the resulting set of three equations. Column 15 relates to columns 13 and 14 as column 12 does to columns 10 and 11.

general, different values at different wave lengths. For this reason, the calculated ϵ_2 values are not given in the tables. The observed D'-values of a solution whose pH value lies in the middle of pk_{1b} and pk_{2b} is a fairly good measure of the absorption by the species BH^+ only, provided pk_{1b} and pk_{2b} are separated with each other by 3 or 4 as in phenylenediamines. The influence of the other species can be neglected at this value of pH. Figs. 1 and 2 show the absorption curves of *o*- and *p*-phenylenediamines, respectively, in acidic (a), alkaline (b), and medium pH (c) solutions. As was mentioned above, the curves (a), (b) and (c) are mainly due to species BH_2^{++}, B and BH^+, respectively. If at a given wave length the extinction coefficients of species B and BH^+ are alike, the calculated value of k_{1b} at this wave length is prboably in error. In the same way, if the extinction coefficients of species BH^+ and BH_2^{++} are alike, k_{2b} calculated at this wave length is probably in error. Furthermore, the D' values corresponding to too high transmittance are likely to be in error. In fact, anomalous values are obtained from these data and these values are not given in the tables.

Thus the mean values of the apparent dissociation constants are:

o-, $k_{1b}=(3.68\pm0.32)\times10^{-10}$, $k_{2b}=(4.93\pm0.30)\times10^{-14}$:

p-, $k_{1b}=(1.20\pm0.08)\times10^{-8}$, $k_{2b}=(1.01\pm0.03)\times10^{-11}$.

For the apparent dissociation constants obtained above, activity corrections were made, using the Debye-Hückel equation of the following form[5]:

$$-\log\gamma_i=\frac{Az_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}},$$

$$A=\frac{1}{2.303}\,\frac{N^2e^3}{(DRT)^{3/2}}\left(\frac{2\pi}{1000}\right)^{1/2},$$

$$B=\left(\frac{8\pi N^2e^2}{1000DRT}\right)^{1/2},$$

where e is the electronic charge, R is the gas constants, D is the dielectric constant of water at the absolute temperasure T, N is the Avogadro's number, and μ is the ionic strength of the solution[6]. z_i and a_i are the charge and the radius of ion i. a_i is assumed to be 5 Å for both phenylenediamines in all their forms. The activity coefficients thus calculated for each experimental condition are collected in Table III.

TABLE III

ACTIVITY COEFFICIENTS OF *o*- AND *p*-PHENYLENEDIAMINES CALCULATED BY DEBYE-HÜCKEL EQUATION

Isomers	*ortho*	*para*
Temp., °C	14	14.5
μ (mol./l)	1.0	0.049
γ_B	1.00	1.00
γ_{BH^+}	0.646	0.830
$\gamma_{BH_2^{++}}$	0.174	0.474

Then the final dissociation constants are calculated to be:

o-, $K_{1b}=(2.4\pm0.3)\times10^{-10}$,
$K_{2b}=(1.3\pm0.1)\times10^{-14}$ at 14°C;

p-, $K_{1b}=(1.0\pm0.1)\times10^{-8}$,
$K_{2b}=(5.8\pm0.1)\times10^{-12}$ at 14.5°C,

where the errors due to the Debye-Hückel equation are neglected. It is interesting to compare these results with the values obtained by other methods. They are listed in Table IV taken from Landolt-Börnstein Tables[7]. It can be seen that the present method yields reasonable values of dissociation constants. Moreover, the present work adds the value of the second dissociation constants of *o*-phenylenediamine to the literature. Of course the precise value of K_{2b} of this compound is still uncertain since we were forced to make this determination at rather high ionic strength.

TABLE IV

DISSOCIATION CONSTANTS OF PHENYLENEDIAMINES[a]

Isomers	Step	Temp., °C	Constant	Method	Author
o-	1st	21	$2.3_5\times10^{-10}$	Potentiometric	Kuhn & Wassermann Kuhn & Zumstein
o-	1st	25	3.3×10^{-10}	Hydrolysis, partial extraction	Farmer & Warth
p-	1st	18	1.3×10^{-8}	Conductmetric	Walden & Ulich
p-	1st	18	1.1×10^{-8}	Potentiometric	Kolthoff & Bosch
p-	1st	ca. 20	1.0×10^{-9}	Potentiometric & colorimetric	Pring
p-	1st	21	9.5×10^{-9}	Potentiometric	Kuhn & Wassermann
p-	2nd	18	3.5×10^{-12}	Potentiometric	Kolthoff & Bosch
p-	2nd	21	1.5×10^{-11}	Potentiometric	Kuhn & Zumstein

a) Taken from ref. (7) in text.

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5) For example see, D. A. McInnes, "The Principles of the Electrochemistry", Reinhold, New York (1939), Chap. 7.

6) The values of physical constants used in the calculation are taken from DuMond and Cohen, *Revs. Modern Phys.*, 25, 691 (1953), except for the dielectric constant of water, for which the values are obtained by the interpolation of the values listed in S. Kaneko, *J. Electrochem. Soc. Japan*, 20, 273 (1952).

7) Landolt-Börnstein, "Physikalisch-Chemische Tabellen" Springer, Berlin (1931), 2te Ergänzungsband, p. 1094.

Comparison with Thamer-Voigt's Method[8,9]

As an application of the present method to the case where k_1 and k_2 are not separate from each other as for phenylenediamines, and also as a comparison of the present method with Thamer-Voigt's we have calculated the dissociation constants for isophthalic acid from the data presented by these authors[2]. The results are given in Table V. The mean values of the dissociation constants calculated by both methods agree very well.

TABLE V

OPTICAL DENSITIES[a] AND DISSOCIATION CONSTANTS OF ISOPHTHALIC ACID

Wave length in Å	Optical densities					k_1 $\times 10^4$	k_2 $\times 10^5$
	pH 1.58	3.56	4.18	5.095	8.72		
2476.0	0.987	1.134	1.152	1.036	0.982	3.21	3.62
2460.0	1.298	1.435	1.421	1.233	1.146	3.45	3.29
Wave length in Å	Optical densities					k_1 $\times 10^4$	k_2 $\times 10^5$
	pH 1.58	3.37	3.96	4.91	8.72		
2476.0	0.987	1.109	1.164	1.056	0.982	3.02	3.96
2460.0	1.298	1.410	1.446	1.256	1.146	2.71	4.52
					Mean[b]	3.10	3.85
					Mean (Thamer-Voigt)[c]	2.78	4.00

a) Optical density data are taken from ref. (2) in text.
b) Mean over four calculated values using the present method.
c) See ref. (2) in text.

In Thamer-Voigt's method it is ture that the optical density measurements of many kinds of solution of different pH values reduce the errors due to optical density or pH measurements included in the final values of k_1 and k_2, but the preparation of many kinds of solution is laborious especially for substances unstable in solution. Besides, it is necessary in their method that the optical density versus pH curve should show a decided maximum or minimum. In most cases a suitable wave length may be chosen so that the curve has a maximum or minimum. In the present method, the number of solutions to be prepared is considerably reduced. In addition, the above mentioned maximum or minimum are unnecessary. These are the advantages of the present method. While the error due to the optical density measurement becomes less by taking the mean over many values determined at different wave lengths, the error due to pH measurement cannot be reduced, which is the disadvantage of the present method.

In conclusion, the present method is experimentally easier to carry out especially for substances unstable in solution. For stable substances, the dissociation constants

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[8] It should be noted that k_1 and k_2 used in this section should be read as $k_{1\mathfrak{b}}$ and $k_{2\mathfrak{b}}$, respectively, for diacidic bases such as phenylenediamines. For dibasic acids such as isophthalic acid k_1 and k_2 should be read as k_{1a} and k_{2a}, respectively, and defined by

$$k_{1a}=\frac{a_H[AH^-]}{[AH_2]},\quad k_{2a}=\frac{a_H[A^{--}]}{[AH^-]}$$

where a_H is the H-ion activity and AH_2, AH^- and A^{--} denote undissociated, singly and doubly dissociated dibasic acid, respectively.

[9] After the preparation of this manuscript had been completed, a paper by B.J. Thamer (*J. Phys. Chem.*, 59, 450 (1955)) came to our attention. This method is essentially identical with ours excepting that ε_1 and ε_3 (in our notation) are not assumed to be the molar extinction coefficient at alkaline and acidic extremes. In diacidic bases (for example) having very small values of dissociation constants, his method may be particularly useful, since the direct determination of ε_3 necessitates the high value of ionic strength of the solution. If the optical density of the solution as acidic as possible (comforming to the requirement of low ionic strength) is practically equal to ε_3, Thamer's method has no advantages because in his method a set of five equations containing five unknowns must be solved for a fixed wave length instead of a set of three equations in our method. If the optical density of the solution as acidic as possible is considerably different from ε_3, his method may not give the precise value of the $k_{2\mathfrak{b}}$, because in such a solution rather a small fraction of the base exists in the form BH_2^{++} and even a small error in the optical density measurement results in a rather considerable error in $k_{2\mathfrak{b}}$. Therefore, for most practical purposes, our method involving the solution of a set of three equations for a fixed wave length may be sufficient.

may be determined by Thamer-Voigt's method a little more accurately.

The extension, of our method to polyelectrolytes appears possible, provided that each dissociated species has a different extinction coefficient in a proper wave-length region, although the number of simultaneous equations to be solved increases. For example, a tribasic acid requires a set of five equations.

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