Overlapping Dissociation Constants of 4,4'-Diaminobenzophenone from Spectral-Absorbancy Measurements[1]

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Dissociation constants and related thermodynamic quantities can be calculated directly from spectral-absorbancy measurements and known hydrogen-ion concentrations, when the compound, whether base or acid, has only one group capable of accepting or donating a proton. When two groups are present, one may also calculate the constants of the reaction directly if the ratio of the two constants is large, that is, if the pK values are separated by several units. If the two reactions closely overlap, the ratio is small, and a complicated series of approximations is necessary.

An example of the latter type of reaction is the overlapping dissociation of the ions of 4,4'-diaminobenzophenone. The spectral-absorbancy curves of the undissociated and of the completely dissociated species can be obtained experimentally. The spectral curve representing the one-group dissociated species cannot be measured. The bands of the three species are superimposed upon one another and, during the overlapping reactions, each of the three species contributes to the observed absorbancy values. Using a series of solutions with very small differences in hydrogen-ion concentrations, the two constants were first calculated from measurements at the very beginning and at the very end of the reactions. Equations were developed, using the constants, activity-coefficient terms following the simple Debye-Hückel relationships for the first constant, and the hydrogen-ion concentrations, to determine the relative amounts of each species at any stage during the dissociation. The validity of the method was proved by its application to all intermediate data where the two reactions overlap. The agreement of the calculated sums of absorbancy with the observed values is well within experimental error. The method will be useful for many substances where electromotive-force methods cannot be applied.

1. Introduction

The diphenylketones are important intermediates in the synthesis of many organic compounds. They are so slightly soluble in water, that several physicochemical methods of approach in studying their behavior are precluded. However, in most cases, small quantities of the order of 2 to 20 mg can be dissolved in 1 liter of water at room termperatures. The solutions are then 10^{-5} or 10^{-4} molar, which are ideal for spectrophotometric measurements. Aromatic compounds of this type show absorption in the ultraviolet range of the spectrum, and their equilibrium constants and other related thermodynamic quantities can be calculated from spectrophotometric measurements made under carefully controlled conditions.

The spectrophotometric method is straightforward and precise for a substance, whether base or acid, in which only one group is capable of accepting or donating a proton. Representative of this single-group dissociation is the reaction of 4-aminobenzophenone with hydrochloric acid, a subject of recent study by the authors [1].[2]

If two groups are present, and their dissociation constants are separated by several units, as in the case of p-hydroxybenzoic acid, the procedure is still straightforward [2]. This acid has a carboxyl group ionizing between pH 3 and 5, and a hydroxyl group ionizing between pH 8 and 10. The three limiting spectral-absorbancy curves representing the un-ionized, one-group ionized, and the completely ionized compound can be obtained experimentally.[3] The two constants can be calculated from separate series of absorbancy curves and hydrogen-ion concentrations in the usual manner.

A more complicated picture is presented when an amino compound, such as 4,4'-diaminobenzophenone, reacts with a strong acid, such as hydrochloric acid in two stages, and the two cations formed by addition of hydrogen ion dissociate according to the reaction, as follows:
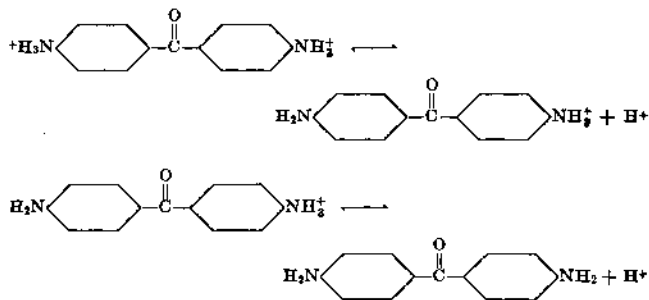
For simplicity in writing all equations that follow, the above reactions may be expressed thus:

$$R^{++} \longrightarrow R^{+} + H^{+} \tag{1}$$

$$R^{+} \longrightarrow R + H^{+}. \tag{2}$$

The constants for the equilibria (1) and (2) are the first and second acidic dissociation constants, respectively, for the doubly charged ion.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] When the carboxyl group is ionized, the band of maximum absorbancy occurs at lower wavelengths than that of the un-ionized acid. With ionization of the hydroxyl group, a much greater shift of maximum absorbancy in the opposite direction is found.

The spectral-absorbancy curves representing R^{++} and R can be obtained experimentally, but the curve for R^+ cannot be obtained. Extensive data in which very small differences in hydrogen-ion concentration are used, which result in very small differences in absorbancy, enable one, however, to calculate a theoretical curve for R^+. Upon close examination of the series of curves at the very beginning, and at the very end of the reactions, it is evident that several curves share common isosbestic points. Assuming that in each case only two species are involved in one reaction, provisional values of each constant may be calculated, using the absorbancy values at the beginning and known hydrogen-ion concentrations at the beginning and at the end of the series. It will be shown later that use of the simple Debye-Hückel limiting law to express the activity-coefficient terms for the first constant is adequate.

2. Experimental Details

2.1 Materials

4,4′-Diaminobenzophenone was obtained from Eastman Kodak Co. It was twice recrystallized from ethyl alcohol and water. The yellow crystals melted at 244.1° to 244.4° C.

Conductivity water was used to dissolve the compound and to prepare all solutions. Hydrochloric acid of reagent grade was used to make stock solutions, from which the lower concentrations were prepared.

2.2 Equipment

A model DU Beckman spectrophotometer was modified with a constant-temperature cell compartment of the authors' design made in the Instrument Shop of the Bureau. The cell assemblies consisted of Pyrex cylinders, 38 mm in diameter, with removable crystalline-quartz end plates, which were held together in metal containers with screw caps, metal inner sleeves, and rubber and Bakelite gaskets. Temperature within the cell compartment was controlled to within ±0.1° C, and all measurements reported in this paper were made at 25° C.

A commercial glass-electrode assembly was used to measure the pH of all solutions as a check on the hydrogen-ion concentrations.

3. Method of Calculation

Some of the absorbancy curves calculated from spectrophotometric measurements of a series of solutions of 4,4′-diaminobenzophenone at various hydrogen-ion concentrations are shown in figure 1. Thirty-six solutions were measured throughout the ultraviolet, but all curves are not shown in the figure, as mechanical difficulties were encountered in reproducing them in one drawing. Curve 1 represents the neutral base and curve 36, the doubly charged ion.

The constants for the first and second dissociations, as expressed in eq 1 and 2, are calculated as follows:

$$K_1 = \frac{a_{R^+} a_{H^+}}{a_{R^{++}}} = K_{1c} \frac{f_{R^+} f_{H^+}}{f_{R^{++}}} = \frac{[R^+][H^+] f_{R^+} f_{H^+}}{[R^{++}] f_{R^{++}}} \quad (3)$$

and

$$K_2 = \frac{a_R a_{H^+}}{a_{R^+}} = K_{2c} \frac{f_R f_{H^+}}{f_{R^+}} = \frac{[R][H^+] f_R f_{H^+}}{[R^+] f_{R^+}}, \quad (4)$$

in which a denotes activity and f denotes activity coefficient with the appropriate subscripts, concentrations are denoted by brackets, and K_{1c} and K_{2c} represent the concentration constants for the first and second reactions.

The relative amounts of R^{++}, R^+, and R at any stage during the overlapping dissociations may be calculated from the following equations developed in a manner similar to a method described by Clark [3]. He applied it to an acid of the type HAH dissociating stepwise to HA^- and A^{--}, using electromotive-force measurements. However, the calculation of the ratios of R^+ to R^{++} and of R to R^+ from spectrophotometric measurements is more involved than approximations from emf measurements.

Let [S] represent the original concentration of the diaminobenzophenone, which does not change during the dissociation, but is the sum of all species present at any stage of the reaction. Then

$$[S] = [R^{++}] + [R^+] + [R], \quad (5)$$

Let

$$\alpha_1 = [R^{++}]/[S], \quad (6)$$

$$\alpha_2 = [R^+]/[S], \quad (7)$$

$$\alpha_3 = [R]/[S]. \quad (8)$$

The sum of α_1, α_2, and α_3 is 1.

It is reasonable to assume that the combined activity-coefficient term, $f_R f_{H^+}/f_{R^+}$, in eq 4 is very small, especially in such dilute solutions, and may be taken as unity. It thereby cancels out, and K_2 is equal to K_{2c}. The evaluation of the combined terms, $f_{R^+} f_{H^+}/f_{R^{++}}$, in eq 3 will be considered later, and for simplicity will henceforth be represented
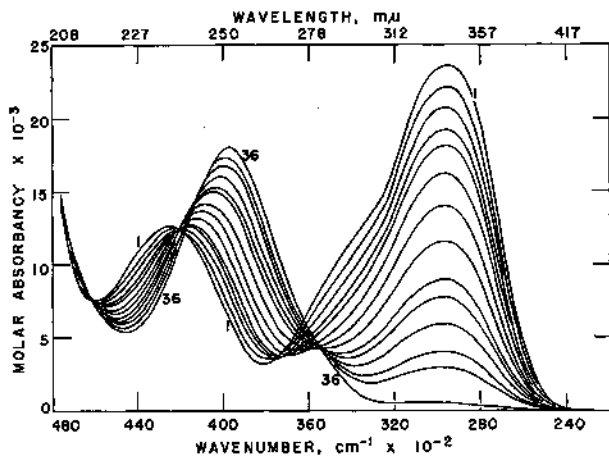

FIGURE 1. *Spectral absorbancy curves representing the overlapping dissociation of the ions of 4,4′-Diaminobenzophenone.*

Curve 1 is for the neutral base and curve 36, the doubly-charged species.

as f. The concentration constant, K_{1c}, will change with change in ionic strength, and is equal to K_1/f.

By rearrangement of eq 3 and 4, and the above considerations, the concentrations of the three species may now be expressed as follows:

$$[R^{++}] = \frac{[R^+][H^+]}{K_1/f} = \frac{[R][H^+]^2}{(K_1/f)K_2}, \tag{9}$$

$$[R^+] = \frac{[R][H^+]}{K_2} = \frac{(K_1/f)[R^{++}]}{[H^+]}, \tag{10}$$

$$[R] = \frac{K_2[R^+]}{[H^+]} = \frac{(K_1/f)K_2[R^{++}]}{[H^+]^2}. \tag{11}$$

Combining the above relationships with eq 5, 6, 7, and 8, the following expressions are obtained.

$$\alpha_1 = \frac{[R^{++}]}{[R^{++}] + \frac{[R^{++}](K_1/f)}{[H^+]} + \frac{(K_1/f)K_2[R^{++}]}{[H^+]^2}}, \tag{12}$$

$$\alpha_2 = \frac{[R^+]}{\frac{[R^+][H^+]}{K_1/f} + [R^+] + \frac{K_2[R^+]}{[H^+]}}, \tag{13}$$

$$\alpha_3 = \frac{[R]}{\frac{[R][H^+]^2}{(K_1/f)K_2} + \frac{[R][H^+]}{K_2} + [R]}. \tag{14}$$

By dividing the right-hand side of eq 12, 13, and 14 by $[R^{++}]$, $[R^+]$, and $[R]$, respectively, and simplifying, we have

$$\alpha_1 = \frac{[H^+]^2}{[H^+]^2 + (K_1/f)[H^+] + (K_1/f)K_2}, \tag{15}$$

$$\alpha_2 = \frac{(K_1/f)[H^+]}{[H^+]^2 + (K_1/f)[H^+] + (K_1/f)K_2}, \tag{16}$$

$$\alpha_3 = \frac{(K_1/f)K_2}{[H^+]^2 + (K_1/f)[H^+] + (K_1/f)K_2}. \tag{17}$$

The law of absorption states that, at any given wavelength,

$$a_M = A/bM, \tag{18}$$

where a_M is the molar absorbancy index of a pure compound or species (frequently called molecular extinction coefficient, ϵ), A is the specific absorbancy ($-\log_{10}$ transmittancy) of the compound in solution, b is the depth in centimeters through which the radiant energy passes, and M is the concentration of the absorbing compound in moles per liter. Let $a_{M(R^{++})}$, $a_{M(R^+)}$, and $a_{M(R)}$ represent the molar-absorbancy index of the doubly charged ion, the one-group dissociated species, and the neutral base, respectively. Let $a_{M(obs)}$ be the molar-absorbancy index at any known hydrogen-ion concentration at any observed stage during the dissociations. If only two species are present, the ratio of their concentra-tions may be calculated at any given wavelength if the molar absorbancy index of each species is known at that wavelength, and if the observed absorbancy is the sum of the absorbancies of each component species. As $a_{M(R^+)}$ is unknown, a means must be found to determine it before the ratio of $[R^+]$ to $[R^{++}]$, or of $[R]$ to $[R^+]$ can be calculated. Close examination of the absorbancy curves for the 36 solutions shows that practically identical isosbestic points are obtained for solutions 1 to 11, inclusive, and for 29 to 36, inclusive. This is demonstrated in figure 2. It may therefore be assumed that in each case only two species are involved, thus the second constant may be calculated from the absorbancy data of solutions 1 to 11, and the first constant may be calculated from the data of solutions 29 to 36. Inasmuch as activity-coefficient terms must be considered in determining K_1, it is more convenient to first calculate K_2.

According to the law of absorption, the concentration of a particular species is proportional to its molar-absorbancy index. It follows, then, that if only R^+ and R are present, the ratio, $[R]/[R^+]$, can be calculated as in eq 19:

$$\frac{[R]}{[R^+]} = \frac{a_{M(obs)} - a_{M(R^+)}}{a_{M(R)} - a_{M(obs)}}. \tag{19}$$

Equation 19 combined with eq 3 results in the following:

$$K_2 = [H^+] \frac{a_{M(obs)} - a_{M(R^+)}}{a_{M(R)} - a_{M(obs)}}. \tag{20}$$

As stated previously, $a_{M(R^+)}$ cannot be obtained experimentally. It can be determined, however, by an extrapolation procedure similar to that used by Weil and Morris [4]. If $a_{M(obs)}$ is plotted on the X-axis and $[a_{M(R)} - a_{M(obs)}]/[H^+]$ on the Y-axis, the intercept on the X-axis should be $a_{M(R^+)}$. The calculation of values for $a_{M(R^+)}$ may also be made at any wavelength, by simply equating the absorbancy relation-
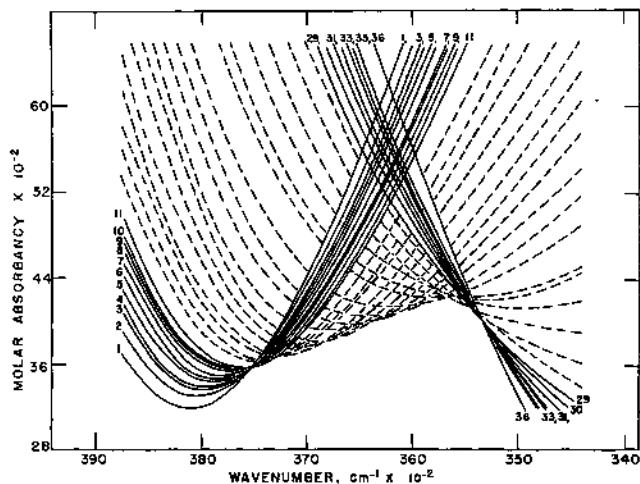

FIGURE 2. *Absorbancy values showing isosbestic points for solutions 1 to 11, and for solutions 29 to 36.*

Dotted lines represent values for solutions 12 to 28, inclusive, the intermediate data where the two dissociations overlap.
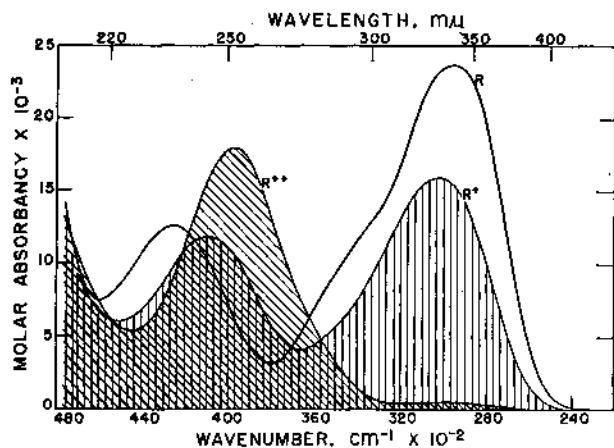
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FIGURE 3. *Molar absorbancy values obtained experimentally for the neutral base, R, and for the doubly-charged species, R^{++}, and calculated values for the singly-charged species, R^+.*

ships and hydrogen-ion concentrations of any pair of curves, using solutions 1 to 11, inclusive. From values at many wavelengths a molar-absorbancy curve for the species R^+ is obtained, as shown in figure 3. The curves for R^{++} and R are also given in the figure for comparison.

The average of several calculated values of $a_{M(R^+)}$ at wavelength 338 (the wavelength of maximum absorption for the neutral base) is 15600, whereas from experimental observations, $a_{M(R)}$ is 23600.

Before K_2 can be calculated, the relative amount of R^+ at each hydrogen-ion concentration is determined (see table 1). This amount multiplied by the molar concentration of the base used, namely, 2.506×10^{-5}, in this case, gives an equivalent to be subtracted from the hydrogen-ion concentration of the hydrochloric acid, thus giving a corrected hydrogen-ion concentration. This figure, multiplied by the ratio $[R]/[R^+]$, gives the second dissociation constant. It is readily seen that the values in the last column are practically constant, and therefore the assumption that the activity-coefficient term $f_R f_{H^+}/f_{R^+}$ is unity appears to be valid. At 25° C, K_2 is 0.0012 mole per liter, in round numbers, and $-\log K_2$, or pK_2, is then 2.92.

The concentration constants for the first dissociation may now be calculated, using the absorbancy values and hydrogen-ion concentrations of solutions 28 to 36, inclusive.[4] The isosbestic points shared by these solutions indicate that only two species are involved, namely, $[R^+]$ and $[R^{++}]$. The ratios $[R^+]/[R^{++}]$ may be calculated according to eq 21, in which,

$$\frac{[R^+]}{[R^{++}]} = \frac{a_{M(obs)} - a_{M(R^{++})}}{a_{M(R^+)} - a_{M(obs)}}. \quad (21)$$

The results are shown in table 2. In this case the hydrogen-ion concentration of the hydrochloric

[4] Although the spectral-absorbancy curve for solution 28 did not pass through the isosbestic point shared by solutions 29 to 36, it was used to calculate the K_2 values.

TABLE 1. *Calculation of K_{2c} from absorbancies at wavelength 338 and known hydrogen-ion concentrations*

$a_{M(obs)} = 15600[R^+] + 23600[R]; [R^+] + [R] = 1$

Solution	$a_{M(obs)}$	$a_{M(R)} - a_{M(obs)}$	$[R^+]$	Hydrochloric acid concentration	$[H^+]$	$[R]/[R^+]$	K_{2c}
1	23,600	0	0.0000	---------	---------	---------	-------
2	22,980	620	.0775	10.03×10^{-5}	9.84×10^{-5}	11.90	0.00117
3	22,660	940	.1175	16.05	15.76	7.51	.00118
4	22,440	1,160	.1450	20.06	19.70	5.90	.00116
5	22,150	1,450	.1813	26.18	25.73	4.52	.00116
6	21,880	1,720	.2150	33.10	32.56	3.65	.00119
7	21,510	2,090	.2612	42.13	41.48	2.83	.00117
8	21,360	2,240	.2800	46.14	45.44	2.57	.00117
9	21,210	2,390	.2988	51.15	50.40	2.35	.00118
10	21,010	2,590	.3238	57.17	56.36	2.09	.00118
11	20,740	2,860	.3575	66.20	65.30	1.80	.00117

TABLE 2. *Calculation of K_{1c} from absorbancies at wavelength 338 and known hydrogen-ion concentrations*

$a_{M(obs)} = 460[R^{++}] + 15600[R^+]; [R^{++}] + [R^+] = 1$

Solution	$a_{M(obs)}$	$a_{M(obs)} - a_{M(R^{++})}$	$[R^+]$	Hydrochloric acid concentration	$[H^+]$	$[R^+]/[R^{++}]$	K_{1c}	pK_{1c}
28	6,640	6,180	0.408	$4,082 \times 10^{-5}$	$4,078 \times 10^{-5}$	0.689	0.0281	1.551
29	5,900	5,440	.359	4,840	4,836	.560	.0271	1.567
30	5,160	4,700	.310	5,760	5,756	.449	.0258	1.589
31	4,570	4,110	.271	6,760	6,756	.372	.0251	1.600
32	4,020	3,560	.235	7,839	7,835	.307	.0240	1.620
33	3,610	3,150	.208	8,995	8,990	.263	.0236	1.627
34	3,190	2,730	.180	10,240	10,235	.220	.0225	1.648
35	2,900	2,440	.161	11,560	11,555	.192	.0222	1.654
36	460	0	.000	---------	---------	---------	------	------

acid is corrected by the amount necessary to convert R^{++} to R^+ and R^+ to R. The ratio $[R^+]/[R^{++}]$ is multiplied by the hydrogen-ion concentration to give the concentration constant, K_{1c}. It is readily seen that as the ionic strength increases, the concentration constants decrease in an orderly manner. The values of $-\log K_{1c}$, or pK_{1c}, are also given in the table.

pK_{1c} is now plotted as a function of ionic strength, as shown in figure 4, to determine whether an extrapolation to infinite dilution can be made. Inasmuch as there are no values for the low ionic strengths, it is impossible to make such an extrapolation without some consideration of the activity-coefficient terms, $f_R f_{H^+}/f_{R^{++}}$. As a first estimate of the terms, the Debye-Hückel law may be applied. It becomes in this case

$$-\log f = -2A\sqrt{\mu}, \qquad (22)$$

where A is the constant 0.5092 at 25° C [5], and μ is the ionic strength. The constant K_1 is equal to $K_{1c}f$; therefore,

$$pK_1 = pK_{1c} - 1.018\sqrt{\mu}. \qquad (23)$$

When the values for the different ionic strengths are plotted, they lie on a practically straight line, which may be extrapolated to infinite dilution. It is reasonable to assume that use of the extended Debye equation

$$-\log f = -\frac{2A\sqrt{\mu}}{1 - Ba^*\sqrt{\mu}}, \qquad (24)$$

in which B is the constant with a value of 0.3281 at 25° C [5] and a^* is an adjustable parameter, might give a better extrapolation. However, the same value for pK_1 is found when 1, 2, or 4 is assigned
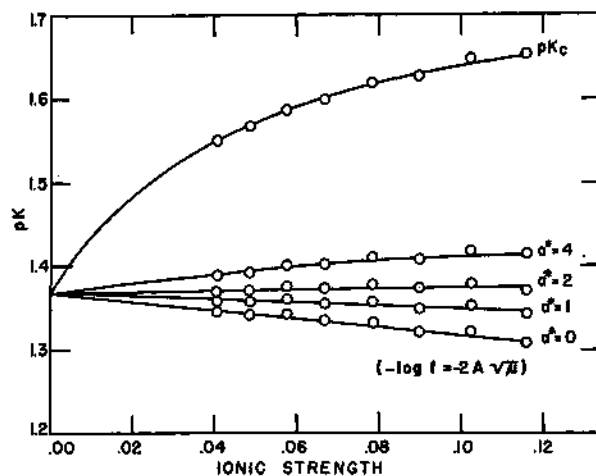

FIGURE 4. pK_{1c} plotted as a function of ionic strength, and extrapolation to pK_1 using the Debye-Hückel equation.

empirically to a^*. pK_1 is 1.367 at 25° C, and K_1 is therefore 0.043 mole per liter.

The validity of the calculated constants and activity-coefficient terms may next be subjected to test in the intermediate data where the dissociations overlap, and where both constants are involved. A first approximation of the relative amounts of the three species R^{++}, R^+, and R, is given in table 3. The original concentration of hydrochloric acid is used as the ionic strength, and f is calculated according to eq 22, for each solution. The values K_1/f, $[H^+]^2$, $[H^+](K_1/f)$, and $[H^+](K_1/f)K_2$ are then calculated and are given in columns 3, 4, 5, and 6. The amounts of the three species are calculated according to eq 15, 16, and 17, and are shown in columns 8, 9, and 10 as α_1, α_2, and α_3.

A second approximation is given in table 4. The ionic strength now includes all ions and is very slightly changed. A recalculation of f is made for

TABLE 3. *First approximation of relative amounts of R^{++}, R^+, and R from intermediate data*

Solution	Original concentration of hydrochloric acid	ᵃK_1/f	ᵇ$[H^+]^2$	$[H^+](K_1/f)$	$[H^+](K_1/f)K_2$	Sum of columns 4, 5, 6	α_1 $[R^{++}]/[S]$	α_2 $[R^+]/[S]$	α_3 $[R]/[S]$
1	2	3	4	5	6	7	8	9	10
9	51.2×10⁻⁵	0.04077	0.026×10⁻⁵	2.087×10⁻⁵	4.892×10⁻⁵	7.005×10⁻⁵	0.004	0.296	0.698
10	57.2	.04066	.033	2.326	4.879	7.238	.004	.321	.674
11	66.2	.04049	.044	2.680	4.859	7.583	.006	.353	.641
12	100.3	.03992	.101	4.004	4.790	8.895	.011	.450	.539
13	130	.03951	.169	5.136	4.741	10.046	.017	.511	.472
14	161	.03914	.259	6.301	4.697	11.257	.023	.560	.417
15	200	.03872	.400	7.744	4.646	12.790	.031	.605	.363
16	256	.03819	.655	9.777	4.583	15.015	.044	.651	.305
17	331	.03758	1.096	12.439	4.510	18.045	.061	.689	.250
18	406	.03704	1.648	15.038	4.444	21.130	.078	.712	.210
19	510	.03637	2.601	18.549	4.364	25.514	.102	.727	.171
20	644	.03564	4.147	22.952	4.277	31.376	.132	.732	.136
21	802	.03485	6.432	27.950	4.182	38.564	.167	.725	.108
22	1,000	.03402	10.000	34.020	4.092	48.102	.208	.707	.085
23	1,440	.03247	20.736	46.757	3.896	71.389	.290	.655	.055
24	1,600	.03198	25.600	51.168	3.838	80.606	.318	.635	.048
25	2,001	.03087	40.040	61.771	3.704	105.515	.379	.585	.035
26	2,560	.02956	65.536	75.674	3.547	144.757	.453	.523	.024
27	3,240	.02821	104.976	91.400	3.385	199.761	.525	.457	.017

ᵃ f is provisionally calculated using the concentration of HCl as the ionic strength.
ᵇ Hydrogen-ion concentration is provisionally calculated from the concentration of HCl.

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TABLE 4. *Second approximation of relative amounts of* R^{++}, R^+, *and* R, *and calculated molar absorbancies compared with observed values*

Solution	μ^a	f^b	$[H^+]^2$	$[H^+](K_1/f)$	$(K_1/f)K_2c$	Sum of columns 4, 5, 6	α_1	α_2	α_3	$460\alpha_1$ a_M	$15,600\alpha_2$ a_M	$23,600\alpha_3$ a_M	Calculated sum a_M	Observed a_M
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
9	51×10^{-5}	1.054	0.025×10^{-5}	2.055×10^{-5}	4.892×10^{-5}	6.972×10^{-5}	0.003	0.295	0.702	0	4,600	16,570	21,170	21,180
10	57	1.058	.032	2.293	4.878	7.202	.004	.318	.677	0	4,960	15,980	20,940	21,010
11	66	1.062	.043	2.643	4.857	7.543	.006	.350	.644	0	5,460	15,200	20,660	20,720
12	100	1.077	.098	3.956	4.790	8.844	.011	.447	.542	0	6,970	12,790	19,760	19,800
13	130	1.088	.166	5.097	4.741	10.004	.016	.510	.474	10	7,960	11,190	19,160	19,200
14	161	1.098	.253	6.223	4.697	11.173	.023	.557	.420	10	8,690	9,910	18,610	18,700
15	200	1.110	.392	7.670	4.648	12.710	.031	.603	.366	10	9,410	8,640	18,060	18,130
16	256	1.126	.645	9.698	4.581	14.924	.043	.650	.307	20	10,140	7,240	17,400	17,490
17	331	1.144	1.082	12.361	4.508	17.951	.060	.689	.251	30	10,750	5,920	16,700	16,830
18	406	1.161	1.632	14.960	4.443	21.035	.078	.711	.211	40	11,090	4,980	16,110	16,180
19	510	1.182	2.581	18.476	4.364	25.421	.101	.727	.172	50	11,340	4,060	15,450	15,480
20	644	1.207	4.122	22.868	4.274	31.264	.132	.731	.137	60	11,400	3,230	14,690	14,790
21	802	1.234	6.384	27.845	4.182	38.411	.166	.725	.109	80	11,310	2,570	13,960	13,950
22	1,000	1.264	9.940	33.908	4.081	47.929	.207	.708	.085	100	11,040	2,010	13,150	13,140
23	1,441	1.325	20.650	46.631	3.894	71.174	.290	.655	.055	130	10,220	1,300	11,650	11,570
24	1,601	1.345	25.504	51.040	3.835	80.379	.317	.635	.048	140	9,910	1,130	11,180	11,080
25	2,002	1.393	39.920	61.638	3.702	105.260	.379	.586	.035	170	9,140	830	10,140	10,080
26	2,561	1.455	65.331	75.504	3.544	144.379	.452	.523	.025	210	8,160	590	8,960	8,940
27	3,241	1.525	104.717	91.223	3.382	199.322	.525	.458	.017	240	7,140	400	7,780	7,760

^{a} $\mu = ([H^+]+[Cl^-]+[R^+]+4[R^{++}])/2$. ^{b} $f = f_R+f_{H^+}/f_{R^{++}}$; $-\log f = -2A\sqrt{\mu} = -1.0184\sqrt{\mu}$. ^{c} $K_1 = 0.043$; $K_2 = 0.0012$.

each stage in the overlapping dissociation, and the values are given in column 3. Slightly different values for α_1, α_2, and α_3 are now obtained, as shown in columns 8, 9, and 10. The absorbancy contributed by each species may now be calculated, by multiplying the relative amounts of each species by its respective molar-absorbancy index. These values are given in columns 11, 12, and 13. The sum of the absorbancies of the three species should be the total absorbancy, which should agree with the observed value. For example, at wavelength 338:

$$a_{M(obs)} = 460\alpha_1 + 15600\alpha_2 + 23600\alpha_3. \qquad (25)$$

The agreement of the calculated sums of absorbancies with the observed values is satisfactory. When one considers that the molar absorbancies are calculated from observed transmittancy or absorbancy readings, which can easily be in error ±1 in the third figure from error in setting the dials and reading the scales, aside from any additional errors in prepara-tion of the solutions, the fourth significant figure should probably not be reported. However, if the values are rounded off to the third figure, there would be perfect agreement in 8 of the 19 cases. Because the agreement is well within experimental error, the validity of the constants is substantiated, and the relationships employed throughout are essentially correct.

4. References

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