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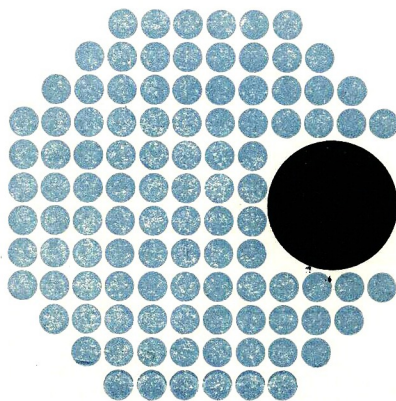
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DETERMINATION OF THERMODYNAMIC DISSOCIATION CONSTANTS AND PARAMETERS OF THE EXTENDED DEBYE-HÜCKEL EXPRESSION. APPLICATION FOR SOME SULPHONEPHTHALEIN INDICATORS*

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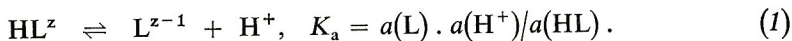
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Non-derivation algorithm for regression of a non-linear function (DH-LETAG Program) has been used for numerical analysis of a set of values expressing the dependence of mixed dissociation constant on ionic strength. Efficiency of the program has been examined with the use of sets of simulated data loaded with generated error. For six selected sulphonephthalein indicators, *i.e.* Bromocresol Green, Bromothymol Blue, Phenol Red, Bromocresol Purple, Bromophenol Red and Thymol Blue, thermodynamic dissociation constants have been determined at 25°C together with the ion-size parameters \bar{a} and the coefficients C of the extended Debye-Hückel expression, which allows calculation of a mixed dissociation constant for any value of the ionic strength within the range 0.01 to 4.

Spectrophotometric methods are preferred for determination of dissociation constants of organic acids in dilute solutions (10^{-4} to 10^{-5} M). In this way, for example, mixed dissociation constants of sulphonephthaleins were determined. The pH value of the solutions was either directly measured¹ or calculated on the basis of a known dissociation constant of the acid making the component of the buffer solution². In the latter case it is necessary to choose a buffer system with components of the same charge type as that of the studied indicator.

The dissociation equilibrium of an ion with a charge^{**} z is characterized by the thermodynamic (activity) constant K_a



As it is possible to determine experimentally the ratio of the equilibrium concentrations $[\text{L}]/[\text{HL}]$ at a given pH value (related to activity by the expression $\text{pH} = -\log a(\text{H}^+)$) when the practical pH scale is used, it is useful to define the mixed dissociation constant for a certain value of the ionic strength I (in mol l^{-1}) of the solution:

$$K_a(I) = [\text{L}] \cdot a(\text{H}^+)/[\text{HL}]. \quad (2)$$

* Part II in the series Multiparametric Curve Fitting; Part I: *Talanta* 23, 15 (1976).

** In the following equations the charges of the ions will be given only if necessary.

The dependence of the mixed dissociation constant on ionic strength can be expressed with the use of the extended Debye-Hückel expression, as follows

$$\text{p}K_a(I) = \text{p}K_a - AI^{1/2} \left[\frac{(z-1)^2}{1 + \bar{a}(L) \cdot BI^{1/2}} - \frac{z^2}{1 + \bar{a}(\text{HL}) \cdot BI^{1/2}} \right] + [C(\text{HL}) - C(L)] \cdot I, \quad (3)$$

where the constants A and B have the values $0.5115 \text{ mol}^{-1/2} \cdot \text{l}^{1/2} \text{K}^{3/2}$ and $3.291 \text{ nm}^{-1} \text{ mol}^{-1/2} \cdot \text{l}^{1/2} \text{K}^{1/2}$, respectively, for aqueous solutions and 25°C . The two parameters \bar{a} and C must be determined experimentally. On the assumption that the values of the \bar{a} (in nm) for the two ions HL^z and L^{z-1} are roughly the same, it holds that $(z-1)^2 - z^2 = 1 - 2z$. Further, an overall coefficient $C = C(\text{HL}) - C(\text{L})$ may be introduced, and so Eq. (3) simplifies to

$$\text{p}K_a(I) = \text{p}K_a - AI^{1/2}(1 - 2z)/(1 + \bar{a}BI^{1/2}) + CI. \quad (4)$$

The value of the mixed dissociation constant $\text{p}K_a(I)$ is determined usually in a medium of constant ionic strength adjusted by the addition of an indifferent electrolyte.

If a pure solvent is chosen to realize the standard state, the determination of thermodynamic dissociation constant is based on the estimation of a value referring to the zero ionic strength. A linear extrapolation of the dependence $\text{p}K_a(I) = f(I^{1/2})$ can be used only within the validity of the limiting Debye-Hückel law. It means, of course, that it is necessary to measure in solutions which have a very low ionic strength ($< 10^{-3}$) and contain a very dilute buffer ($\approx 10^{-4} \text{M}$) or no buffer. Consequently, the disturbing effects of the traces of CO_2 , the sorption and desorption on the walls of vessels *etc.* are encountered and so the dissociation constants are subject to greater errors.

The analysis of a set of $\text{p}K_a(I)$ values within a sufficiently wide range of ionic strength gives both the thermodynamic constant and the other parameters, \bar{a} and C . The expression $\text{p}K_a(I)$ in Eq. (4) represents a dependent variable which is evidently subject to random experimental error. The ionic strength, which is taken as an independent variable, can be adjusted precisely, so that its random error is less than that of the dependent variable. The three parameters of the function in Eq. (4) will be further denoted by the symbols $\beta_1, \beta_2, \beta_3$ and their iteratively improved estimations by b_1, b_2, b_3 . The influence of the parameters b_2 and b_3 on the plot $\log y^\pm = f(I^{1/2})$ was modelled with the aid of an analogue computer Meda 41B. The graph in Fig. 1 illustrates the effect of varied values of the ion-size parameter \bar{a} at a constant value of the coefficient C . Fig. 2 shows that varied values of the coefficient C have a greater effect on the shape of the curve. Thus in the non-linear function (4) the parameter b_3 is better conditioned and so it may be presumed that the parameter b_3 can be determined more precisely and accurately than the other, b_2 .

Whereas in previous papers^{2,3} the used mathematical-statistical approaches were not discussed in detail, the recent development of computer techniques evoked interest in applicability of various methods of numerical analysis. Boodts and Lison⁴ suggested a method based on linear regression of a transformed function derived

from the extended Debye-Hückel expression; in this method the most probable value of \bar{a} is estimated first, and then the thermodynamic value of pK_a is determined as an intercept of the regression straight line.

The analysis of the full function given in Eq. (4) should be based on an experimental set consisting of n pairs Y_i, I_i . The best estimation of the mentioned three parameters b_1, b_2, b_3 is obtained by such curve fitting of the given set of Y_i, I_i values, for which the sum of squares of residuals reaches minimum:

$$U = \sum_{i=1}^n w_i [Y_i - f(I_i; b_1, b_2, b_3)]^2. \quad (5)$$

The weighting factors w_i are considered to be unity in the present paper. The minimization process of the function U starts from a first guess, $b_1^{(0)}, b_2^{(0)}, b_3^{(0)}$, of the three parameters. In further steps of computation more precise values of the parameters are reached gradually. Besides other applications, a simple direct-searching algorithm has been suggested in ref.⁵ for regression of the non-linear function (4), which is suitable for a small computer. Meloun and Čermák⁶ have used two different methods to minimize the function U and have written two programs in autocode MOST F13 for a small computer Odra 1013; the program PADH based on a derivation subroutine TAYLOR⁷ works about six times faster than the program DH-LETAG; however, it does not give safely the parameter \bar{a} . The program DH-LETAG makes use of a non-derivation subroutine LETAG⁸ which was adapted from the successful

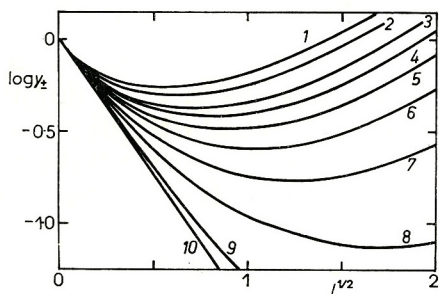


FIG. 1

Dependence of Logarithm of Mean Activity Coefficient on the Square Root of Ionic Strength ($z = -1, 25^\circ$) at Constant Value 0.20 of the Coefficient C and Varied Values of the Ion-Size Parameter (nm)

1 1.00, 2 0.80, 3 0.60, 4 0.45, 5 0.40, 6 0.30, 7 0.20, 8 0.10, 9 0.00, 10 the limiting Debye-Hückel law.

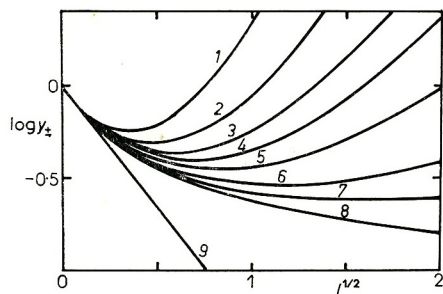


FIG. 2

Dependence of Logarithm of Mean Activity Coefficient on the Square Root of Ionic Strength ($z = -1, 25^\circ$) at a Constant Value of Ion-Size Parameter, \bar{a} 0.45, and Varied Values of the Coefficient C

1 1.00, 2 0.60, 3 0.40, 4 0.30, 5 0.20, 6 0.10, 7 0.05, 8 0.00, 9 the limiting Debye-Hückel law.

and reliable programs of the LETAGROP series by Sillén and coworkers⁹⁻¹¹. The present paper brings application of another version of the DH-LETAG program which is written in FORTRAN for computers Hewlett-Packard 2116C and Tesla 200.

Efficiency of the Program DH-LETAG

For chosen values of all the three parameters $\beta_1, \beta_2, \beta_3$ (Table I) the respective $pK_a(I)$ values were computed with the accuracy of six decimals for 20 varied values of ionic strength. The resulting function is shown in Fig. 3. The Y_i values were obtained by addition of the errors ε_i

$$Y_i = f(I_i; \beta_1, \beta_2, \beta_3) + \varepsilon_i, \quad (6)$$

which corresponded to a presumed level of the random error incurred in the determination of $pK_a(I)$ and were calculated with the use of a generator of random errors¹². Such a set of generated errors has a normal Gaussian distribution. Its standard deviation is of the same order of magnitude as the presumed value of the standard deviation $\sigma(pK_a)$ in the determination of $pK_a(I)$. Such simulated set of pairs $(I_i, pK_a(I)_i)$ was then taken for input data for the DH-LETAG program.

The termination criterion EPS determining the requested limiting value of the sum of squared residuals U (Eq. (5)) was obtained from the formula

$$\text{EPS} = (n - m) \sigma^2, \quad (7)$$

where n , m and σ is the number of pairs in the data set, the number of parameters, and a preselected value of standard deviation of the dependent variable (here $\sigma(pK_a)$), respectively. The minimization process terminates either when a U value lower than EPS is reached (the resulting parameters b_1, b_2, b_3 are then considered to be the best estimates), or when a declared maximum number of iteration is reached (here 25).

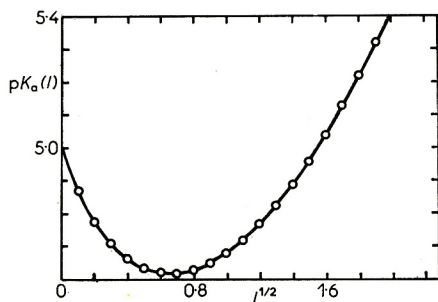


FIG. 3
Curve Representing the Function (4) for
Chosen Values of Parameters
 $z = -1$, pK_a 5.00, λ 0.45 nm, C 0.30.

Table I gives some results of test calculations of the parameters b_1, b_2, b_3 for varied standard deviation $\sigma(pK_a)$. The best estimates for the three parameters agree perfectly with the value $\beta_1, \beta_2, \beta_3$ only if the calculation is based on a precise set

TABLE I

Testing of DH-LETAG Program with Data Loaded with Simulated Error

The chosen values: $z = -1$, $\beta_1 = 5.000$, $\beta_2 = 0.450$, $\beta_3 = 0.300$; $\varepsilon' = \varepsilon \cdot 10^3$, $\Delta = 10^3$.
 . ($Y - f(I; b_1, b_2, b_3)$).

$\sigma(pK_a)$	Chosen				Found			
	0.020	0.040	0.060	0.080				
$pK_a (b_1)$	5.004	5.027	4.973	5.009				
$d, \text{nm}, (b_2)$	0.469	0.418	0.486	0.482				
$C, (b_3)$	0.290	0.304	0.288	0.268				
U_{\min}	$7.45 \cdot 10^{-3}$	$4.59 \cdot 10^{-2}$	$6.11 \cdot 10^{-2}$	$1.55 \cdot 10^{-1}$				
EPS	$6.80 \cdot 10^{-3}$	$2.72 \cdot 10^{-2}$	$6.13 \cdot 10^{-2}$	$1.09 \cdot 10^{-1}$				
$\sigma(pK_a)$	0.020	0.052	0.054	0.095				

$I^{1/2}$	$pK_a(I)$	ε'	Δ	ε'	Δ	ε'	Δ	ε'	Δ
0.1	4.8693	-11.3	16.1	77.1	-51.5	67.8	-93.9	40.3	-38.5
0.2	4.7752	15.0	-8.9	75.6	-52.6	-73.2	49.6	-61.5	64.9
0.3	4.7083	14.5	-7.1	-22.8	42.8	-51.6	30.9	47.5	-42.6
0.4	4.6625	-18.1	26.6	-76.5	93.5	-54.2	36.1	57.3	63.0
0.5	4.6342	8.1	1.3	16.2	-2.2	81.1	65.2	55.6	-49.8
0.6	4.6205	38.1	-28.2	-17.3	28.6	21.3	-35.2	48.6	-43.4
0.7	4.6196	7.8	2.4	-6.3	15.2	-91.0	78.4	-53.7	57.3
0.8	4.6301	24.0	-13.9	32.8	-26.1	36.3	-48.1	-16.7	18.0
0.9	4.6510	46.0	-36.3	22.8	-18.0	21.6	-32.9	67.1	68.9
1.0	4.6815	-8.6	17.6	40.3	-37.1	-12.3	1.0	-60.4	54.6
1.1	4.7210	16.1	-8.2	-7.9	9.8	33.2	-44.9	-96.6	85.9
1.2	4.7689	1.7	4.9	-17.2	17.9	12.7	-25.3	5.5	-21.6
1.3	4.8251	-26.7	31.7	-46.0	45.8	36.9	-50.8	168.3	-190.8
1.4	4.8890	11.0	-7.9	95.5	-96.4	-26.9	11.4	-153.2	123.6
1.5	4.9605	4.1	-3.2	35.8	-37.2	-55.1	37.5	26.8	-64.2
1.6	5.0393	-37.8	36.3	-43.0	41.3	105.4	-125.3	71.5	-117.4
1.7	5.1254	-24.0	19.8	50.0	-51.8	-3.4	-19.2	-274.4	219.2
1.8	5.2185	4.7	-11.9	-76.9	75.1	-93.1	68.0	-56.9	-8.3
1.9	5.3185	15.8	-26.2	-43.0	41.5	-42.2	13.2	-81.2	5.3
2.0	5.4254	-8.9	-4.9	37.5	-38.7	-102.5	69.9	-41.1	-46.2

of the $pK_a(I)$ values ($\sigma(pK_a)$ $1.0 \cdot 10^{-6}$). The minimum sum of squared residuals U (see Eq. (5)) was $2.9 \cdot 10^{-10}$, the termination criterion EPS for the U function being $1.7 \cdot 10^{-11}$. The $\sigma(pK_a)$ values, which are computed from the residuals $Y_i - f(I_i; b_1, b_2, b_3)$ for the best estimates of the parameters, approach the respective values in all the cases studied. The table gives also the values of the generated errors ε' and magnitude of the residual Δ for the individual pairs $I_i^{1/2}$, $pK_a(I)_i$. In the optimum case the residual should have the same magnitude but an opposite sign.

EXPERIMENTAL AND RESULTS

Reagents

1M Sodium hydroxide was prepared by dilution of 50% sodium hydroxide solution prepared according to Sørensen and standardized by potentiometric titration of oxalic acid under argon. The solution was kept in a polyethylene bottle protected with an Ascarite tube. Standard solution of 1M perchloric acid was prepared by dilution of 70% HClO_4 (analytical grader, Merck) with redistilled water. The solution was standardized by potentiometric titration using mercury(II) oxide as standard in medium of potassium iodide.

Phosphate buffer solution was prepared from a stock solution of trisodium phosphate (a commercial reagent (Lachema) was twice recrystallized) to make the final concentration $1.5 \cdot 10^{-3}\text{M}$ in the solutions to be titrated. Ionic strength was adjusted by calculated additions of sodium chloride (analytical grade, Lachema). Standard buffer solutions were prepared according to Bates¹³ from chemicals purified by repeated crystallizations. The pH values of these buffer solutions were checked by measurements with a cell with a hydrogen and a silver chloride electrode. The construction of the apparatus, the reference cell, and the potentiometric measurements, are described in detail elsewhere¹⁴.

The following acid-base indicators were chosen for the study: Bromocresol Green (3',3'',5',5''-tetrabromo-*m*-cresol sulphonephthalein); Bromothymol Blue (3',3''-dibromothymol sulphonephthalein); Phenol Red (phenol sulphonephthalein); Bromocresol Purple (5',5''-dibromo-*o*-cresol sulphonephthalein); Bromophenol Red (5',5''-dibromophenol sulphonephthalein); Thymol Blue (thymol sulphonephthalein). The commercial reagents (Lachema) were purified by preparative chromatographical separation using Whatman 3 paper in ascending arrangement and the eluent system: butanol, acetone, 26% ammonia (4 : 3 : 3) (see ref.¹⁵). An ethanolic solution containing 15 to 20 mg sulphonephthalein to be purified was brought as a strip on the start line of the chromatographical paper $200 \times 400\text{mm}$. Elution time was 14 to 16 hours. After drying, the strip corresponding to a pure form of the indicator was cut out from the chromatogram, and the indicator was eluted with ethanol. The solution gathered from a greater number of chromatograms was diluted with a small amount of water and extracted with ethyl ether. After separation of the etheric layer, the aqueous-ethanolic solution was evaporated until dry in a polyethylene vessel at 50°C . The purity of the indicators obtained was checked again chromatographically on a Whatman 2 paper using the above-mentioned eluting solvent. The original substance was chromatographed along with the samples to be checked. The chromatographically purified indicators showed only one observable spot.

Measurement of A -pH Curves and Their Interpretation

The data sets forming the A -pH curves were measured by the method of combined photometric-potentiometric titration¹⁶, the basic indicator form being transformed into the acid one by ad-

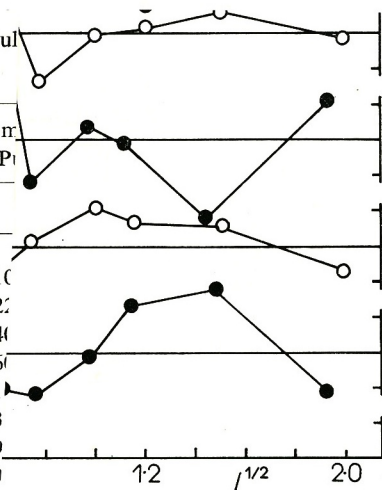
dition of 1M perchloric acid added from a plunger microburette (type E 457, Metrohm, Herisau, Switzerland). For a simultaneous monitoring of absorbance and pH the spectrophotometer Spekol (Zeiss, Jena) was equipped with a special microtitration attachment TAL^{17,18}, a phototube and an amplifier. The readings were taken either in absorbance directly on the logarithmic scale of the Spekol apparatus or in transmittance on a digital voltmeter NR 50 (Metra, Blansko). In the latter arrangement it was possible to read the third and to estimate the fourth decimal of the numerical value.

The pH cell consisted of a glass electrode type G202B (Radiometer, Copenhagen) and a silver chloride electrode which was filled with 1M sodium chloride and fitted with a glass frit junction. During measurements the temperature $25 \pm 0.1^\circ$ was maintained by means of a water thermostat U3 (Prüfgeräte-Werk, Medingen). Two types of pH-meters, PHM-4d (Radiometer) and OP 205 (Radelkis, Budapest) were used. The pH-cell was calibrated with standard buffer solutions (pH(S)) of the practical pH-scale. The measured pH(X) values were corrected both for the actual value of the calibration slope (mV/pH) of the used glass electrode and the error incurred in replacing the standard buffer solution of ionic strength $I(S)$ by the measured solution having $I(X)$, which brings about a change in the value of the liquid-junction potential E_L (in mV). The corrections E_L were determined by measuring the electromotive force of a concentration cell consisting of two silver chloride electrodes, one of them being immersed directly in a solution of known concentration of sodium chloride, the other forming the reference half-cell with 1M-NaCl (ref.¹⁴). The two corrections are involved in the following expression

$$\text{pH} = \text{pH}(S) + [\text{pH}(X) - \text{pH}(S)] \frac{59.16}{k} + [E_L(S) - E_L(X)]/59.16, \quad (8)$$

TABLE II
Mixed Dissociation Constants of Sul
Solution and at 25°C

Bromocresol Green		Bromophenol Red		Brom Pi
I	$\text{p}K_a(I)$	I	$\text{p}K_a(I)$	I
0.010	4.901	0.010	6.017	0.010
0.022	4.871	0.022	5.970	0.022
0.040	4.834	0.040	5.935	0.040
0.060	4.808	0.060	5.908	0.060
0.116	4.765	0.116	5.872	0.116
0.232	4.709	0.200	5.841	0.23
0.392	4.691	0.392	5.797	0.39
0.594	4.677	0.594	5.775	0.59
0.923	4.664	1.004	5.760	0.92
1.330	4.662	1.445	5.765	1.33
2.050	4.686	2.260	5.788	2.00
3.72	4.785	4.00	5.865	3.72



Curve $\text{p}K_a(I) = f(I)$ for the Sets of the Experimental Points
(b_1, b_2, b_3)
1. Bromocresol Purple 4. Bromocresol Blue

Determination of Thermodynamic Dissociation Constant and of the Parameters \bar{a} and C

Dissociation equilibria of the chosen sulphonephthalein indicators were studied in the pH region 4 to 9 where the second phenolic group is deprotonated. The anion formed has a symmetrical structure, and its absorption minimum is shifted to longer wavelengths. The mixed dissociation constants $pK_a(I)$ were determined for solutions containing various concentrations of sodium chloride. Each A -pH curve measurement was reproduced three times. The set of $pK_a(I)$ constants (Table II) was used as the input data of the DH-LETAG program. Table II summarizes the calculated

Survey of Thermodynamic Dissociation Constants, Ion-Size Parameters and Coefficients C for Sulphonaphthalein Indicators at 25°C

	pK_a	d	C	ref.
4·90 ^{a,b}	—	—	21	
4·985	0·49	0·59	2	
4·987	—	—	22	
—	—	—		
6·37 ^b	—	—	21	
6·33 ^c	0·70	—	23	
7·30 ^{a,b}	—	—	21	
7·341 ^c	0·45	0·26	3	
7·446 ^b	—	—	22	
7·97 ^b	—	—	21	
8·08 ^b	0·40	—	1	

Measurement of A -pH Curves and Their Interpretation

^a Measured at 15 to 30°C. The value corresponds to the use of the following scale: ^b p_sH; ^c p_cH.

values of thermodynamic dissociation constant, ion-size parameter, and salting out coefficient C for the individual indicators. A threefold standard deviation⁹ is given with each parameter. When comparing the pK_a values with those given in literature it must be taken into account that sulphonephthaleins were studied mostly in the twenties and thirties²¹ when the Sørensen p_sH scale was used. This scale differs from the practical pH scale used now by a constant deviation $+0.04$ pH. This correction must be subtracted from all results which were evidently obtained with the use of the Sørensen scale (Table III). Various definitions and methods of the measurements of pH are certainly a significant cause of deviations in the published pK_a values. On the other hand, the method of graphical extrapolation, which has been exclusively used before, can lead to somewhat lower results.

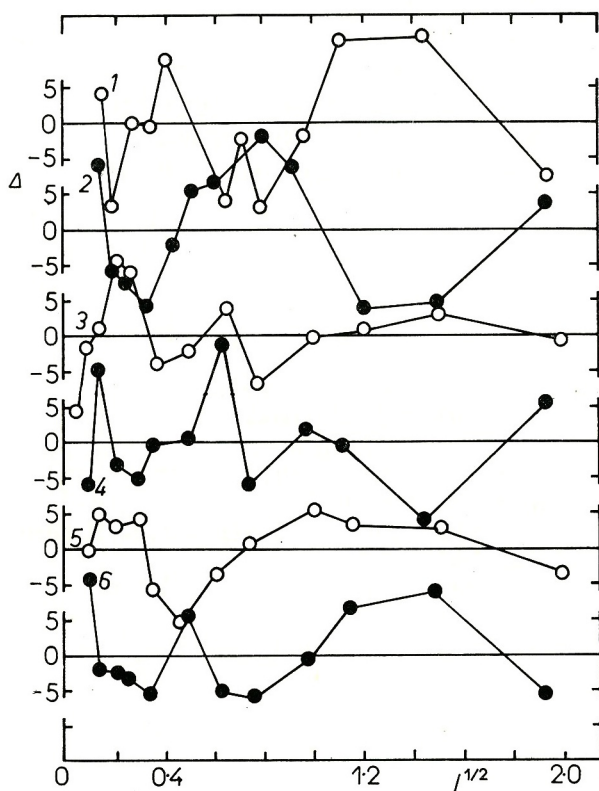


FIG. 4

Fitting of the Calculated Regression Curve $pK_a(I) = f(I)$ for the Sets of the Experimental Points Given in Table II ($\Delta = 10^3[Y - f(I; b_1, b_2, b_3)]$)

1 Bromocresol Green, 2 Bromophenol Red, 3 Bromocresol Purple, 4 Bromothymol Blue, 5 Phenol Red, 6 Thymol Blue.

In the past the parameters \bar{a} and C were scarcely determined for indicators. The five studied sulphonephthaleins have their ion-size parameters within a narrow range 0.76 to 0.88 nm. The only exception is the ion of the simplest, non-substituted sulphonephthalein, Phenol Red, for which the value 0.375 ± 0.038 nm was found in accordance with the value 0.40 published by Sendroy and Rodkey¹.

The coefficient C is within 0.055 to 0.068 for all sulphonephthaleins studied except for Phenol Red for which it is 0.018.

The sufficiently close fit of calculated regression curves with the experimental points represents a reliability criterion of the calculation of the parameters given in Table III. The agreement obtained for the studied indicators is shown in the diagram of residuals (Fig. 4).

For a given indicator the set of all three parameters defines the function (4) derived from the Debye-Hückel expression within the range of ionic strength 0.01 to 4. For any value of the ionic strength of a solution it is possible to calculate easily the corresponding value of the mixed dissociation constant of the indicator. Since the colour changes of the studied indicators cover the pH range 4 to 10, it may be expected that the data given in Table III will find application in spectrophotometric pH measurements, since they allow to eliminate practically the salt error.

The authors are indebted to Dr V. Sovišová for her assistance during development of the titration method for the determination of mixed dissociation constants of acid-base indicators.

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