Studies on Sulfinic Acids

VII.* Determination of Hammett Substituent Constants for the Ionic *meta-* and *para*-Sulfinate Groups by Potentiometric Titration of Sulfinobenzoic Acids

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The Hammett σ constants have been determined for the ionic sulfinate group in the *meta-* and *para*-sulfinobenzoic acids by means of potentiometric titration. A method of general application for deriving pK_c values for unsymmetric dibasic acids with overlapping dissociation has been derived and applied for the derivation of the σ constants. The dependence of σ constants for charged groups on ionic strength is discussed.

In a previous paper on substituent effects of various sulfur groups on the polarographic reduction of the nitro group in substituted nitrobenzenes [1] the σ constants for the anionic sulfinate group were discussed. In the present paper, the determination of the σ constants for the charged *meta-* and *para*-sulfinate groups is described. The determination was made by means of potentiometric titration of the *meta-* and *para*-sulfinobenzoic acids using an automatic titration system with a glass electrode.

The substituent effects of the ionic sulfinate groups are interesting from several different points of view, which have been discussed in various previous papers.[1-3] However, the substituent effects of charged groups present some problems, which are due to the fact that they are influenced by the ionic strength, and the dependence of the dissociation constants on ionic strength has been specially studied.

The substituent effects of another charged sulfur group, the ionic sulfonate group has previously been studied by Zollinger *et al.*[4] by means of potentiometric titration of the sulfobenzoic acids as well as by a spectrophotometric study of the dissociation. The sulfonic acid group is fully dissociated in aqueous media, whereas this is not the case with the sulfinic acid group in sulfinobenzoic acids. The potentiometric titration of these therefore involved several

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problems due to the overlapping of the dissociation steps of the two acid groups, which could only be adequately solved by the aid of a computer.

The calculation of the pK values is very sensitive to the hydrogen ion concentration, and small errors may cause inaccurate results, especially for the sulfinic acid group, which is extremely sensitive to errors in pH. This problem was solved by devising a computer program, that on the basis of theoretical considerations operated with corrected pH values and utilized the whole titration curve for determination of the pK_c values. In this way pK_c for the carboxylic group in the sulfinobenzoic acids could be determined with reasonable accuracy. The procedure is believed to be of general application for the determination of dissociation constants for unsymmetric dibasic acids with overlapping dissociation steps and this problem is therefore treated in some detail.

The σ constants were obtained by reference to benzoic acid titrated under the same conditions as the sulfinobenzoic acids. Comparison of the pK values gives by definition the σ constants. Very similar σ values were obtained for the *meta*- and *para*-substituted sulfinobenzoic acids, indicating the absence of any considerable mesomeric contribution from the *para*-sulfino group. The results are compared with those for sulfobenzoic acid.[4]

THE THEORY OF DISSOCIATION OF DIBASIC ACIDS

The theory of dissociation of a symmetric dibasic acid is well established in the literature and the dissociation constants for a large number of dibasic acids have been determined by classical methods. In early days when modern titration apparatus did not exist, a few points on the titration curve, which were determined by very exact methods, were usually employed for the calculation of the dissociation constants. With modern apparatus, the whole titration curve can easily be utilized. This has given rise to various modifications in the classical mathematical treatment of the problem. The most convenient treatment has been given by Speakman, who utilizes a linear function, the slope and intercepts of which gives the dissociation constants.[5] The same function was, however, already given by Söderbäck in a thorough treatise on the theory of the determination of dissociation constants by electrometric titration.[6]

With certain assumptions, which are permissible for most ordinary purposes, the theory for symmetric dibasic acids can be applied also to unsymmetric dibasic acids. An unsymmetric dibasic acid behaves in titration as an equimolecular mixture of two different monobasic acids, and the system can be described in terms of so called titration constants.[7]

In a dibasic unsymmetric acid with overlapping dissociation of the two acid groups four different forms of the acid are involved in the dissociation equilibrium. The sulfinobenzoic acids belong to this class and for the sake of simplicity, the dissociation scheme for an unsymmetric dibasic acid shall be given with sulfinobenzoic acid as an example, Scheme 1. The short symbols within parentheses will be used in the discussion. Other examples of equilibria of this kind treated in the literature are thioglycolic acid and cysteine.[8,9]

Scheme 1
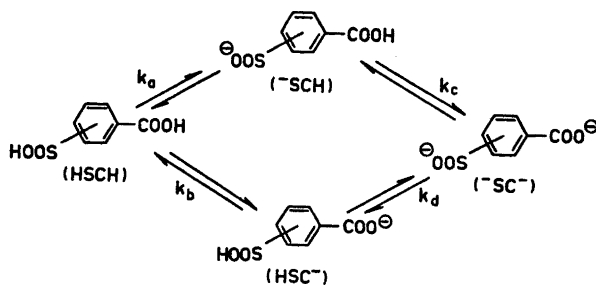
The titration constants G_1 and G_2 parallel the dissociation constants in a mixture of two monobasic acids and are used in order to deduce the theoretical form of the titration curve of an unsymmetric dibasic acid. The following relationships between the titration constants and the intrinsic dissociation constants k_a, k_b, k_c, and k_d have been deduced (Ia, b):

$$G_1 + G_2 = k_a + k_b \tag{Ia}$$

$$G_1 G_2 = k_a k_c = k_b k_d \tag{Ib}$$

The dissociation constants, K_1 and K_2 of the unsymmetric dibasic acid are defined and related to the intrinsic constants by the following relationships (IIa-c):

$$K_1 = \frac{a_{H^+}(a_{HSC^-} + a_{-SCH})}{a_{HSCH}} = k_a + k_b \tag{IIa}$$

$$K_2 = \frac{a_{H^+} \times a_{-SC^-}}{a_{HSC^-} + a_{-SCH}} \tag{IIb}$$

$$\frac{1}{K_2} = \frac{1}{k_c} + \frac{1}{k_d} \tag{IIc}$$

Finally the titration constants are related to the dissociation constants in the following manner (IIIa, b):

$$K_1 = G_1 + G_2 \tag{IIIa}$$

$$K_1 K_2 = G_1 G_2 \tag{IIIb}$$

The question naturally arises which constants should be used for the discussion of substituent effects. Since we are interested in the substituent effect of the $-SO_2^-$ group on the dissociation of the $-COOH$ group, it is most natural to consider k_c.

$$k_c = \frac{a_{H^+} a_{-SC^-}}{a_{-SCH}} \tag{IV}$$

However, the intrinsic constants cannot be determined from titration data alone. Additional information is needed, either from analytical determination of different species of ions during titration, or from estimation of one of the involved intrinsic constants from other known data. It is usually not possible to find methods, which allow the needed analytical determinations without approximations, and the estimation of intrinsic constants from other data are always subject to a measure of arbitrariness. However, if extremely high accuracy is not required, the problem can usually be solved satisfactorily from titration data alone, and this method was adopted here.

PRACTICAL APPLICATION

Important factors in the practical determination of K_1 and K_2 are the difference between them and their absolute values. If they are far apart, so that there is practically no overlap between the different dissociation stages, simple limiting cases are obtained. If, for instance, k_a is considerably greater than k_b, k_a can as a first approximation be regarded as equal to K_1 (IIa). Since $k_a/k_b = k_d/k_c$ (Ib), it follows from IIc that k_c similarly can be regarded as about equal to K_2. With this approximation, the distinction between G_1, G_2 and K_1, K_2 disappears.

The pK of the carboxylic acid group in benzoic acids is about 4 and pK of the aromatic sulfinic acid group is about 2.[10] It is assumed that they differ by the same order of magnitude in sulfinobenzoic acid, and the approximation described should be permissible.

In symmetric dibasic acids, $K_1 = G_1$ and $K_2 = G_2$. Having made an approximation, which causes the distinction between G_1, G_2 and K_1, K_2 to disappear, k_a and k_c can thus be evaluated from the titration curve in the same manner as K_1 and K_2 for symmetric dibasic acids. For this purpose the equation given by Söderbäck[6] and in the form used by Speakman[5] was employed. K_1 and K_2 are in this method related to one another by a linear function (V).

$$Y = K_1 X + K_1 K_2 \qquad\qquad (V)$$

$$Y = c_{H^+}{}^2 \left(\frac{2Cxv_0}{x_a(v_0 + x)} + c_{H^+} - c_{OH^-} \right) \frac{f_h^2 f_2}{f_0} \cdot \frac{1}{A}$$

$$X = c_{H^+} \left[\frac{Cv_0}{v_0 + x} \left(1 - \frac{2x}{x_a} \right) - c_{H^+} + c_{OH^-} \right] \frac{f_h f_2}{f_1} \cdot \frac{1}{A}$$

$$A = \left[\frac{2Cv_0}{v_0 + x} \left(1 - \frac{x}{x_a} \right) - c_{H^+} + c_{OH^-} \right]$$

C = molar concentration of acid at start of titration
v_0 = starting volume of titration solution in ml
x = added amount of NaOH in ml
x_a = consumed amount of NaOH for complete neutralization (second equivalence point)

f_h = activity factor for the hydrogen ions
f_0 = activity factor for the undissociated acid
f_1 = activity factor for the monobasic anion
f_2 = activity factor for the dibasic anion

If the activity factors for HSC^- and ^-SCH are taken as equal and $=f_1$, eqn. V becomes valid also for the unsymmetric dibasic acid, and K_1 and K_2, or with the adopted approximation k_a and k_c, are obtained from the slope and intercepts of the line described by V. In this way a great number of points taken from a titration curve can be used with equal weight for the evaluation of the dissociation constants.

If the absolute values of the dissociation constants are high, the first stage of the dissociation is almost complete, at the start of the titration. This makes the calculation of data in the early part of the titration very uncertain, and it is only possible to determine K_2 with reasonable accuracy.

Another practical difficulty is the presence of c_{H^+} and c_{OH^-} in the used form of eqn. V while a_{H^+} is measured. If the acids are not too strong, c_{H^+} is small compared with other terms, and the use of a_{H^+} obtained from the pH measurements does not cause any significant errors in the results. If Y' is defined as $Y f_0/f_2$ and X' as $X f_1/f_2$, eqn. V can in this case be used in form VI, which can be transformed to form VII, where K_1' and K_2' are the so called "incomplete" constants. Slope and intercepts thus give K_1' and K_2', which afterwards can be corrected to thermodynamic constants, if the activity factors are known.

$$Y' = K_1 X' \frac{f_0}{f_1} + K_1 K_2 \frac{f_0}{f_2} \qquad \text{(VI)}$$

$$Y' = K_1' X' + K_1' K_2' \qquad \text{(VII)}$$

With strong acids as in the present case, a_{H^+} gives curved functions and even negative K_1' values, and can accordingly not be used in the expression Y' and X', but c_{H^+} must be employed. If Y'' is defined as $Y f_0/f_2 f_h^2$ and X'' as $X f_1/f_2 f_h$, eqns. VIII and IX are obtained.

$$Y'' = K_1 X'' \frac{f_0}{f_1 \cdot f_h} + K_1 K_2 \frac{f_0}{f_h^2 f_2} \qquad \text{(VIII)}$$

$$Y'' = K_{1c} X'' + K_{1c} K_{2c} \qquad \text{(IX)}$$

Using c_{H^+}, the slope and intercept thus give the concentration constants K_{1c} and K_{2c}.

The problem is now to correct the measured pH, so as to obtain a value corresponding to c_{H^+}. This was done by means of a computer program, which calculated Y'' and X'', using the experimental pH values and correcting them by small increments stepwise. The results were plotted in a $Y''X''$ diagram, and utilizing the fact that eqn. IX is linear, the correction which gave the best fit to a straight line was chosen, and the resulting line was used for calculation of K_{1c} and K_{2c}.

RESULTS

Typical titration curves for *meta*- and *para*-sulfinobenzoic acids are shown in Fig. 1. The second titration step is only observable as a small flattening of the titration curve.
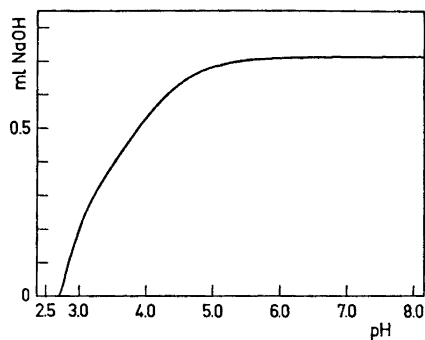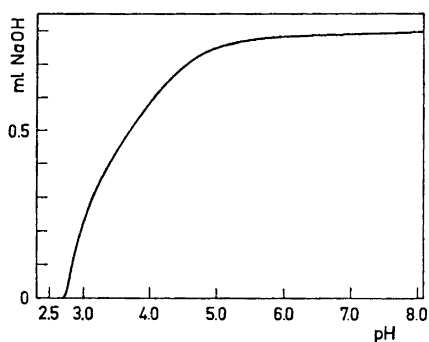

Fig. 1a. Titration curve for *meta*-sulfino-benzoic acid, $\mu=0.05$.

Fig. 1b. Titration curve for *para*-sulfino-benzoic acid, $\mu=0.025$.

Table 1. Dissociation constants for *meta*- and *para*-sulfinobenzoic acid and benzoic acid at various ionic strengths.

μ	meta-Sulfinobenzoic acid				para-Sulfinobenzoic acid				Benzoic acid	
	ΔpH	pK_{1c}	pK_{2c}	pK_{2c} mean	ΔpH	pK_{1c}	pK_{2c}	pK_{2c} mean	pK'	pK'mean
0.002	+0.06	2.2	4.09		+0.06	2.2	4.28	4.20	4.13⎫	
	+0.10	2.0	4.19	4.16	+0.10	2.3	4.12		4.11⎬	4.13
	+0.10	2.2	4.21						4.14⎭	corr. 4.21
0.004					+0.08	2.1	4.15	4.14		
					+0.10	2.2	4.12			
0.010	+0.12	2.3	4.09	4.09	+0.06	2.3	4.11	4.11		
	+0.10	2.2	4.09		+0.10	2.2	4.10			
0.025	+0.12	2.0	4.05	4.05	+0.10	2.3	4.05	4.06	4.07⎫	
	+0.04	2.1	4.04		+0.08	2.2	4.07		4.10⎪	
									4.08⎪	
0.05	+0.07	2.1	4.01	4.01	+0.07	2.1	4.02		4.06⎬	4.09
	+0.10	2.1	4.00		+0.08	2.3	3.99	4.00	4.09⎪	
					+0.10	2.2	3.98		4.12⎪	
									4.10⎭	corr. 4.18
0.10	+0.04	2.1	3.95	3.95	+0.08	2.0	3.96	3.86	4.10⎱	4.09
	0	2.0	3.94		+0.06	2.1	3.96		4.08⎰	corr. 4.17
Mean	+0.08	2.0±0.2			+0.09	2.2±0.2				

Fig. 2 shows typical plots according to eqn. IX with various corrections applied to the measured pH value and Table 1 gives the results at various ionic strengths. The uncorrected pH value usually gave a curved function, and by adding positive increments the curves gradually approach the rectilinear form predicted by theory. According to theory c_{H^+} should be greater than a_{H^+}, and accordingly negative increments should have to be applied.
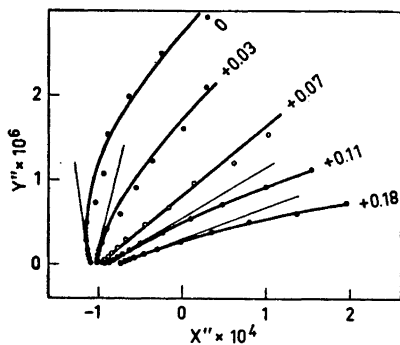

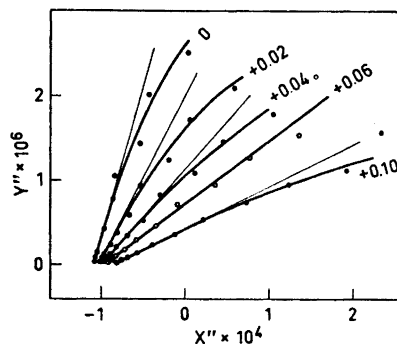*Fig. 2a.* Plots of IX for *meta*-sulfino-benzoic acid, $\mu=0.05$ with various pH corrections.

Fig. 2b. Plots of IX for *para*-sulfinobenzoic acid, $\mu=0.025$ with various pH corrections.

However, negative increments make the functions more curved and move them towards a negative slope. A comparison of a_{H^+} with the other terms in X'' shows that especially at the beginning of the titration, the value of X'' is very sensitive for errors in the pH value, and it is obvious that the experimental pH values are too low. In most cases a positive correction of about 0.09 pH units had to be applied (Table 1). A systematic error seems thus to be present in the experimental pH value. It could either be inherent in the titration system or have some other cause. A possible cause could perhaps be the presence of small traces of the very strong sulfobenzoic acid, formed by unavoidable oxidation of the sulfinobenzoic acid during handling, causing the starting pH to become too low. Experiments with sulfobenzoic acid itself and added to sulfinobenzoic acid, however, did not

Table 2. Data for *meta*-sulfobenzoic and oxalic acids.

Acid	μ	ΔpH	pK_{2c}	Lit.
m-Sulfobenzoic	0.05	+0.09	3.91	pK' 3.94 [4]
	0.05	+0.09	3.88	
Oxalic	0.05	+0.06	3.9	$pK_{\mu=0}$ 4.3 [12]
	0.05	+0.08	4.0	

give results that made this likely. Instead the same correction had to be applied for the *meta*-sulfobenzoic acid in order to obtain the correct pK value (Table 2). Furthermore, in experiments with oxalic and phthalic acid, positive corrections of the same magnitude had also to be applied in order to obtain correct results, Fig. 3 and Table 2. It seems therefore most likely that the error is due to the dynamics of the automatic titration system (electrode response).
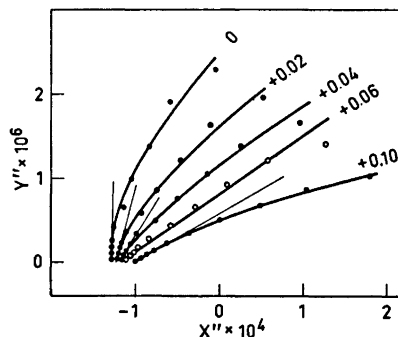

Fig. 3. Plots of IX for oxalic acid, $\mu = 0.05$ with various pH corrections.

From the figures it can be seen that it is only on the pK_{1c} value that the correction has a great influence. In the critical X'' region it has only a very small effect on the pK_{2c} value, which is used for the determination of σ. It may further be observed that the pK_{1c} values are remarkably consistent (see tables) with very little variation and have a reasonable magnitude.[10] In fact, the obtained pK_{1c} values serve as a check on the correctness of the procedure and add to the reliability of the pK_{2c} values.

For the determination of σ, benzoic acid was titrated in the same manner at various ionic strengths and the pK' value (the "incomplete" dissociation constant) was determined from the half neutralization point (Table 1). In order to obtain pK_c the same correction as used for the sulfinobenzoic acids ($+0.09$) should reasonably be applied, since the conclusion is that it is due to the titration method. Extrapolation to zero ionic strength gives a pK value very near to the literature value, which is a further proof for the correctness of the applied correction (Fig. 4, Table 3).

In the dissociation of a dibasic acid the ionization of the second acid group creates a molecule with a double negative charge, and hence the pK_c values are, as can be seen from Table 1, highly dependent on the ionic strength of the medium. The σ values were based on the pK values at infinite dilution, pK_0, which were obtained by applying the Debye-Hückel limiting law:

$$pK_0 = pK_c - 0.5\,(z_S^2 - 1 - z_B^2)\ \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \tag{X}$$

z_S = charge of acid form
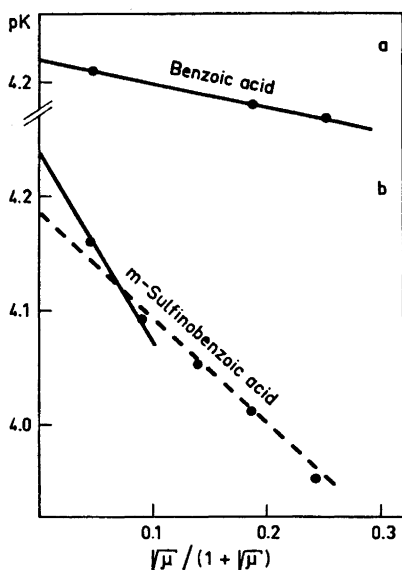z_B = charge of basic form
μ = ionic strength

Fig. 4a,b. pK_c as a function of $\sqrt{\mu}/(1+\sqrt{\mu})$ for a) benzoic acid b) *meta*-sulfinobenzoic acid.
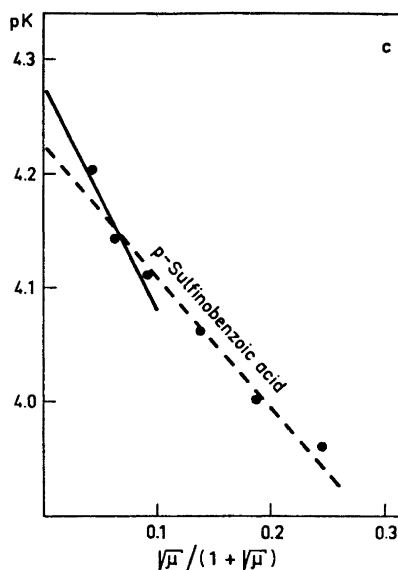
Fig. 4c. pK_c as a function of $\sqrt{\mu}/(1+\sqrt{\mu})$ for *para*-sulfinobenzoic acid.

The results are shown in Fig. 4. The function is linear over a wide range of μ-values, but with a smaller slope than theoretical, which in the region of strict validity of eqn. X, $\mu \leq 0.01$ (the so called Debye-Hückel region) should

Table 3. Extrapolated pK values and σ constants for benzoic, sulfinobenzoic, and sulfobenzoic acids.

Substituent	pK_0	σ
H	4.22 ± 0.05 (4.20) [11],[12]	0
$m\text{-SO}_2^-$	4.24 ± 0.05	-0.02
$p\text{-SO}_2^-$	4.27 ± 0.05	-0.05
$m\text{-SO}_3^-$		0.05 [13]
$p\text{-SO}_3^-$		0.09 [13]

be 2.0. The extrapolation was therefore made only using the points in this region. In Table 3 the final results are given together with the values for the ionic sulfonate group.[13]

DISCUSSION

In the discussion of σ constants for charged groups an important question is whether they are dependent on the ionic strength. For predictive purposes the σ values cannot of course be used without regard to the ionic strength. But this is not a priori due to an ionic strength effect on the σ value. If the σ values are defined on the basis of the thermodynamic equilibrium constants, they would predict any equilibrium of the present type correctly at any ionic strength within the region of validity of eqn. X, provided the slopes of the plots of pK_c against $\sqrt{\mu}/(1+\sqrt{\mu})$ are the same for the different equilibria compared. The slope of this function could therefore be applied as a test as to whether the σ constants are dependent on ionic strength. As we have seen the slopes of the sulfinobenzoic acids have about the theoretical values, only in the Debye-Hückel region. The same applies to Zollingers slopes for the sulfobenzoic acids (theoretically 1.5 for "incomplete" dissociation constant). In this region the σ constants are therefore independent of ionic strength. At higher ionic strength the pK_c values obey a linear function having the form of eqn. X but with a smaller slope, and whether the derived σ values are valid for other equilibria in which ions are involved, at ionic strengths other than zero, can only be judged from a study of the dependence of the particular equilibrium on ionic strength. It seems however, that the σ value at $\mu = 0$ represents the intrinsic polar and mesomeric effects of the charged groups, and they have therefore been used in the discussion of substituent effects in Ref. 1.

From Table 3, it is seen that there is only a small difference between the *para* and *meta* σ values of the sulfinate group. Similar to the σ values of the sulfonate group they are near to zero, suggesting that the polar effect of the oxygen-carrying sulfur is almost neutralized by the charge. They are slightly negative and in contrast to the sulfonate group the *para* value is slightly more negative than the *meta* value, suggesting a slight $+M$ mesomeric contribution to the σ value from the lone electron pair on the sulfur. Zollinger found an enhancement of the σ value for the *para*-sulfonate group in sulfanilic acid and phenolsulfonic acid, indicating a $-M$ effect.[4] This enhancement is, however, only about half that usually observed with strong $-M$ substituents. With the sulfinate group the σ_p^- value, determined polarographically, is less enhanced,[1] indicating only a weak $-M$ effect of this group. This is in accord with the reversed order of the *para* and *meta* σ values as compared with those of the sulfonate group.

EXPERIMENTAL

The titrations were made with an automatic titrator, Radiometer TTT 1c, using a 1 ml syringe burette, Radiometer type SBU 1a assembly. A 20 ml sample was titrated with 0.1 N NaOH in a thermostated jacketed titration vessel at 25.0°C, using a glass electrode, Radiometer G 202B, as indicator electrode and a saturated calomel electrode, Radiometer K 401, as a reference electrode.

The sulfinobenzoic acids were freshly prepared as described in Ref. 3. The other acids used were analytical reagents.

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