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Potentiometric and Spectroscopic Determinaton of Acid Dissociation Constants of Some Phenols and Salicylic Acids

Rahmiye AYDIN, Ulviye ÖZER
Department of Chemistry,
Faculty of Arts and Sciences, Uludağ University,
16059, Bursa-TURKEY
Naciye TÜRKEL
Department of Chemistry,
Faculty of Arts and Sciences, Abant-İzzet Baysal University,
14280, Bolu-TURKEY

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The dissociation constant of the catechol derivatives 4-nitrocatechol (NCAT), 2,3-dihydroxybenzoic acid (2,3-DHBA), 3,4-dihydroxybenzoic acid (3,4-DBHA), 3,4-dihydroxyhenylacetic acid (3,4-DPHA) and 3,4-dihydroxycinnamic acid (3,4-DHCA) were identified in 0.1M $NaClO_4$ ionic medium, at t=25 °C, by potentiometry. In addition, the first and second dissociation constants of the salicylic acid derivatives 5-nitrosalicylic acid (5-NSA), 4-hydroxysalicylic acid (4-HSA) 5-nitrosalicylic acid (5-HSA) were also determined by potentiometry. Furthermore, the second acid dissociation constants of these ligands were evaluated in I=0.1M $NaClO_4$ ionic medium, at a temperature of 25 °C by computer analysis of spectroscopic data.

Key words: Acid dissociation constants, catechol derivatives, salicylic acid derivatives.

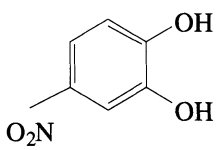
Introduction

Phenolate oxygens have been shown to be very effective donors, especially for metal ions which have a strong tendency to form hydroxo species in aqueous solutions[1,4]. Furthermore, the modelling of the interactons of metal ions with soil organic matter, as well as the study on the bioavailability to plants of metal ions, have aroused interest in the elucidation of the behaviour of phenolic ligands[1]. Catechol and salcylic acid derivatives are of widespread biological occurence and importance[2].

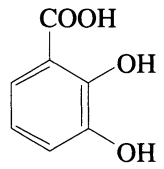
In our study, the stability constants of various coordination compounds formed between metal ions and ligands, catechol and salicylic acid derivatives, were determined. Potentiometry, conductiometry and colorimetry are the most commonly used methods of determining the acid dissociation constants of weak acids[1,3-9]. However, these methods are not useful for determining the second dissociation constants of very weak acids such as catechol and salicylic acid derivatives[10,11]. Although the ionization steps of catechol and salicylic acid dericatives have been studied by potentionmetry[1,4,6-9], they have been determined for different

ionic mediums and spectroscopy has not been used with all of these ligands[5–7,9,12,13]. The present paper deals with the acid dissociation constants of the ligands chosen: 4-nitrocatechol, 4-NCAT, **I;** 2,3 dihydroxybenzoic acid, 2,3-DHBA, **II;** 3,4-dihydroxybenzoic acid, 3,4-DHBA, **III;** 3,4-dihydroxyphenylacetic acid, 3,4-DHPA, **IV;** 3,4-dihydroxycinnamic acid, 3,4-DHCA, **V;** 5-nitrosalicylic acid, 5-NSA, **VI;** 4-hydroxysalicylic acid, 4-HSA, **VII;** and 5-hydroxysalicylic acid, 5-HSA, **VIII**.

We used potentiometry and spectroscopy to obtain the acid dissociation constants of the above-mentioned ligands, in 0.1M $NaClO_4$ ionic medium in all cases at a temperature of 25 °C. But the first acid dissociation constant of 5-NSA was determined in 0.1M/or 0.2M ionic medium at 25 °C by spectroscopy and the second acid dissociation constant of this ligand was evaluated by extrapolation[11]. However, Ernst et al. have determined only the second acid dissociation constant of 5-NSA by spectroscopy[13].



I. 4-NCAT



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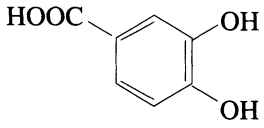
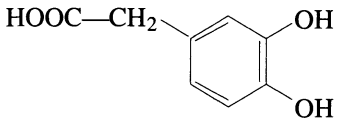
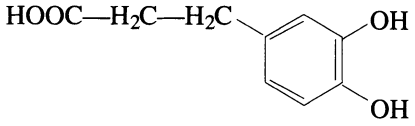


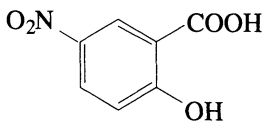
III. 3,4-DHBA



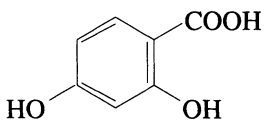
IV. 3,4-DHPA



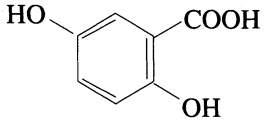
V. 3,4-DHCA



VI. 5-NSA



VII. 4-HSA



VIII. 5-HSA

Experimental

Reagent and Other Chemicals

All ligands used in this study are of analytical-grade purity. They were used as received, since Gran Plots[14] of the ligand potentiometric data indicated high purity. The purity of 4-NCAT is 97%, 2,3-DHBA is 99%, 3,4-DHBA is 97% 3,4-DHPA is 98% 3,4-DHCA is 98%, 5-NSA is 99%, 4-HSA is 99%, and 5-HSA is 99%.

Distilled and deionized water was redistilled in an all-glass apparatus. Carbon dioxide-free 0.1M NaOH stock solution was prepared with NaOH purchased from Merck Co. and was standardized with potassium hydrogen phthalate, $HKC_8H_4O_4$(Merck Co., analytical grade, dried at 120 °C prior to use). Standardizatons of NaOH solutions were repeated at least three times.

All measurements were performed in an oxygen-free nitrogen atmosphere at 25 ∓ 0.1 °C in a water-jacketed titration cell.

Potentiometric Measurements

Potentiometric titrations were carried out in a water-jacketed cell maintained at $25 \mp 0.1\,^{\circ}$C by means of an external constant-temperature circulating bath. A digital Schott CG 805 model pH-meter equipped with an combined pH-electrode was calibrated with the two standard buffer solutions in nearest pH range of interest. Volumes of solutions were dispensed with calibrated class A pipets. All of these ligands are solid. They were introduced into the titration cell and volumes were completed to a definite amount by supporting electrolyte; that is, 0.1M $NaClO_4$, so 0.1-0.4 mmol/ml. Solutions of catechol and salicylic acid dericatives were prepared in a jacketed titraton cell.

A standard NaOH solution was achieved with an ultraprecise Schott digital micrometer buret. Readings of pH were taken with the stirring motor off. Once solutions reached thermal equilibrium, changes in pH values after the addition of small amounts of standard 0.1M NaOH solution were read from the pH-meter.

Spectroscopic Measurements

The absorption spectra of aqueous solutions were recorded in the ultraviolet and visible regions on a UNICAM UV2 recording spectrophotometer with a quartz flow cell (light-path, 10mm) in an atmosphere of oxygen-free nitrogen and the temperature of the solution was maintained at $25 \mp 0.1\,^{\circ}$C. The spectra were recorded for each ligand with definite concentration in the closed system, by adding varying amounts of base titrant to the aqueous solution of these weak acids. Absorbance and pH readings were taken in order to plot them at definite wavelengths for each weak acid.

Computational Methods

a. Potentiometric Method

The computer program RANA[16] was written for the computation and refinement of the dissociation constants of catechol and salicylic acid derivatives. The dissociation contants are refined by Gauss-Newton least squares. RANA consists of several parts in order to analyse the data of potentiometric titrations.

Acid dissociation constants of very weak acids with two and three protons are calculated using mathematical method directly[16].

Catechol and salicylic acid derivatives are all regarded as dibasic acids (H_2L) and the fully deprotonated ligand is represented as L^{-2}. However, 2,3-DHBA, 3,4-DHBA, 3,4-DHPA, 3,4-DHCA, 4-HSA and 5-HSA acids are considered to be tribasic acids and the fully deprotonated form is represented as L^{-3}.

The dissociation equilibria involved in the dissociation process of catechol and salicylic acid derivatives, H_nL, are

$$H_nL \rightleftharpoons H^-_{n-1} + H^+ \tag{1}$$

$$K_{H_nL} = \frac{[H_{n-1}L^-][H^+]}{[H_nL]} \tag{2}$$

$$H_{n-1}L^- \rightleftharpoons H_{n-2}L^{-2} + H^+ \tag{3}$$

$$K_{H_{n-1}L} = \frac{[H_{n-2}L^{-2}][H^+]}{[H_{n-1}L^+]} \tag{4}$$

where $[H^+]$ is hydrogen ion concentration, $[H_{n-1}L]$ and $[H_{n-2}L]$ are concentrations of phenol or phenolate ions and $[H_nL]$ is a concentration of catechol or salicylic acid derivatives.

Total concentrations of related ligand species and protons that are the data of potentiometric titration, were expressed by equations (5) and (6), respectively:

$$T_L = [H_nL] + [H_{n-1}L^-] \tag{5}$$

$$a.T_L + [H^+] - [OH^-] = [H_{n-1}L^-] \tag{6}$$

where "a" is mmole of base added to the titration medium. K_{H_nL} and $K_{H_{n-1}L}$ values for equilibria (1) and (3) were calculated from equations (9) and (10) which derived from equation (2) and (4).

Similarly, total ligand concentration (equation 7) and proton concentration (equation 8) can be expressed for the second buffer region f potentiometric titration as follows:

$$T_L = [H_{n-1}L^-] + [H_{n-2}L^{-2}] \tag{7}$$

$$(a-1).T_L + [H^+] - [OH^-] = [H_{n-2}L^{-2}] \tag{8}$$

$$K_{H_nL} = \frac{(a.T_L + [H^+] - [OH^-]) = [H^+]}{(T_L = (1-a) - [H^+] + [OH^-])} \tag{9}$$

$$K_{H_{n-1}L} = \frac{((a-1)T_L + [H^+] - [OH^-]) = [H^+]}{(T_L(2-a) - [H^+] + [OH^-])} \tag{10}$$

b. Spectroscopic Method

The acidity constants $K_{H_{n-1}L}$ of the catechol and salicylic acid derivatives were evaluated from the effect of pH on the absorbance values.

The Varielle method[17], as described by Mc Bryde[18], was used to determine the acid dissociation constants of eight ligands. This technique can be applied to cases where the absorbtion spectra of the various species present in the solution are sufficiently different and where no more than two species are present at any particular pH. When these conditions are satisfied, plots of absorbance values as a function of pH will show isosbestic points corresponding to interconversions between species[6]. By identifying the individual absorption coefficients one can calculate the equilibrium constants associated with the dissociation equilibria of weak acids.

The second acid dissociation constants of weak acid can be expressed by equation (11):

$$K_{H_{n-1}L} = \frac{[H_{n-2}L^{-2}][H^+]}{[H_{n-1}L^+]} \tag{11}$$

The total concentration of ions at the second buffer region of potentionmetric data, here the dissociation of very weak acid occurs, is represented by equation (12):

$$T_L = [H_{n-2}L^{-2}] + [H_{n-1}L^-] \tag{12}$$

If an ion formed in the second buffer region of weak acid absorbs a certaion wavelength of light, according to Beer's Lambert Law, the absorbance values that were measured are equal to

$$A = \epsilon_{H_{n-2}L^-}[H_{n-2}L^{-2}] + \epsilon_{H_{n-1}L^-}[H_{n-1}L^-] \tag{13}$$

Throught equations (11)-(13), the following equation (14) has been derived:

$$\frac{T_L}{A} = \frac{1}{\epsilon_{H_{n-2}L}} + \left([H^+]\frac{(A - \epsilon_{H_{n-1}L}T_L)}{A}\right)\frac{1}{K_{H_{n-2}L}.\epsilon_{H_{n-2}L}} \tag{14}$$

If T_L/A is plotted graphically against the expression within the brackets, a straight line should be obtained[10] with an intercept of $1/\epsilon_{H_{n-1}L}$ a slope of $1/K_{H_{n-2}L}\epsilon_{H_{n-1}L}$. by identifying the individual absorption coefficients, one can calculate the dissociation constants of weak acids.

Result and Discussion

Potentiometric Data

The potentiometric titrations were carried out at low ligand concentration (0.1-0.4 mmol/ml) up to high pH ($\sim$11.5). It was found that the phenolic groups do not undergo dissociation in the measurable pH range. Figurs 1 and 2 and Tables 1 and 2 summarize the results of the potentiometric titration studies.

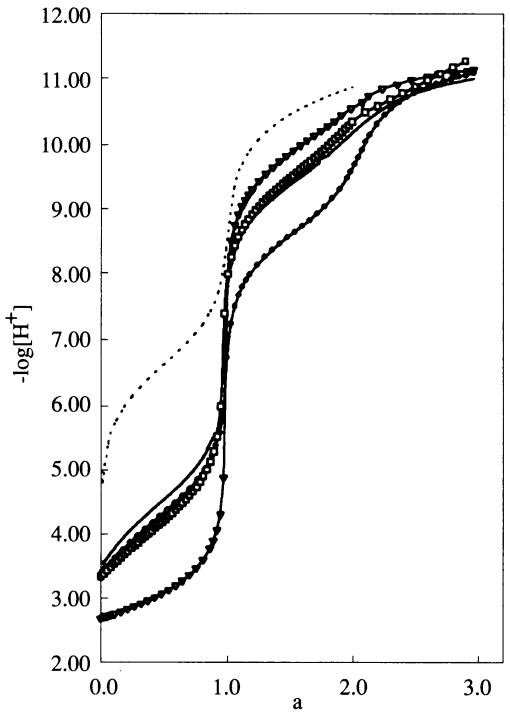


Figure 1. Potentiometric titration curves of catechol derivatives (I=0.1M $NaClO_4$ and t=25 ° C).

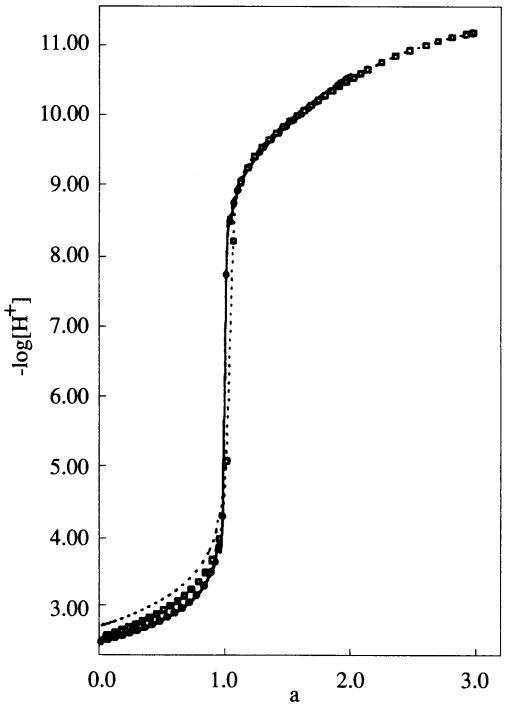


Figure 2. Potentiometric titration curves of salicylic acid derivatives (I=0.1M $NaClO_4$ and t=25 ° C).

4-NCAT — 3,4-DHCA —♦— 3,4-DHBA —○— 3,4-DHPA —▽— 2,3-DHBA

4-HSA —□— 5-HSA —♦— 5-NSA

Of the eight ligands used in this study, we observed that 4-NCAT and 5-NSA have two dissociable protons, while the others have three. These results were also clearly seen in potentiometric titration curves of 4-NCAT containing two hydroxyl group in addition to the nitro group. But 5-NSA contains one carboxyl

and also nitro groups; carboxyl proton is more acidic than the hydroxyl proton. The other six ligands contain three dissociable protons; in 2,3-DHBA, there is a carboxyl and neighboring hydroxy, and next to this hydroxyl group, antoher hydroxyl group that resides in the molecule; in 3,4-DHBA, the carboxyl group is located in an ortho-position relative to neighbouring hydroxyl groups 3,4-DHBA and 3,4-DHCA, stachiometrically similar to 3,4-DHBA, but in 3,4-DHPA, but in 3,4-DHPA, there is a -CH_2COOH group instead of hydroxyl. Similarly, there is a -CH_2- -CH_2COO^- group instead of hydroxyl in 3,4-DHCA. On the other hand, 4-HSA and 5-HSA contain three dissociable protons; there are neigbouring carboxyl and hydroxyl groups in both ligands. In addition to these groups, there is an additional hydroxyl group at the 4-position in 4-HSA and 5-position in 5-HSA.

Spectroscopic Data

In order to determine only the second acid dissociation constants of the ligands by spectroscopic method, pH values of the buffer regions in which protons dissociate were read from potentiometric titration curves, and then absorbance values of each weak acid, at selected pH values from potentiometric titration curves, were recorded against wavelengths in the near-U.V and visible regions (Figure 3-10). These selected wavelengths were 540, 355, 320nm for the 4-NCAT, 2,3-DHBA and 3,4-DHBA, respectively. 310nm is the selected wavelength for both 3,4-DHPA and 3,4-DHCA. 5-NSA, 4-HSA and 5-HSA were studied at 430, 310 and 360nm, respectively. Thus the pH values, where no more than two species are present, were defined from the absorption spectra of each weak acid. Then isobestic points corresponding to interconversions between species were determined and related. $K_{H_{n-2}}$ values were found by introducing related values into equation (14). The results of the second dissociation constants are given in Table 2.

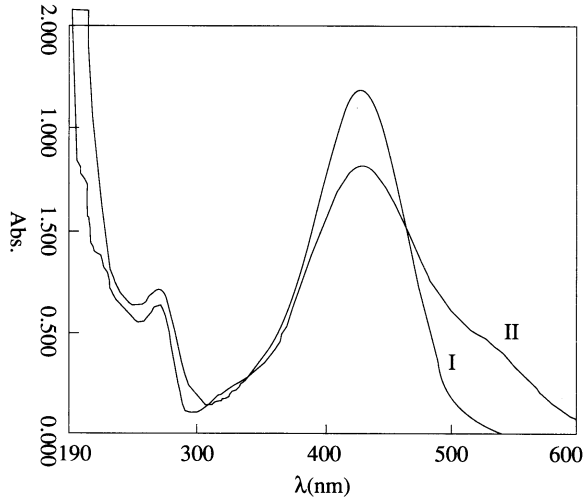


Figure 3. 4-nitrocatechol (Abs. vs. λ in nm)
Curve I. $NO_2.C_6H_3(OH)(O^-)$, pH=8.20
Curve II. $NO_2.C_6H_3(O^-)(O^-)$, pH=10.54

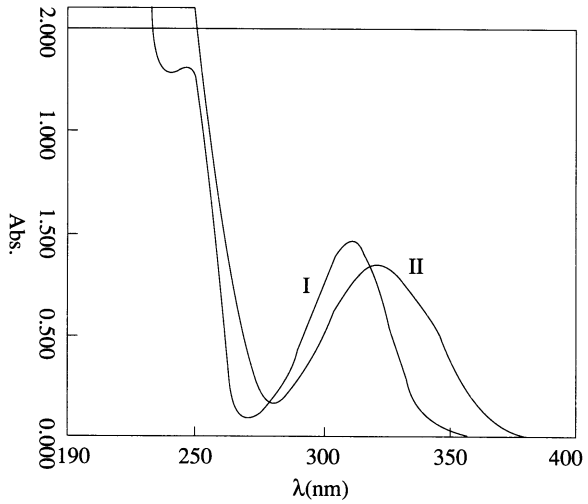


Figure 4. 2,3-dihydroxybenzoic acid (Abs. vs. λ in nm)
Curve I. $C_6H_3(COO^-)(OH)(OH), pH = 4.97$
Curve II. $C_6H_3(COO^-)(OH)(O^-)$, ph=10.17

Acid Dissociation Constants

Seven of the eight ligands, exluding 4-NCAT, contained acid carboxylate protons. Carboxylate protons were found to be more acidic than hydroxyl protons (Table 1), since carboxyl protons can dissociate easily. The

first acid dissociation constant of 5-NSA is the smallest one, since there is an electron-withdrawing nitro group in 5-NSA that facilitates the dissociation of the proton by withdrawing an electron on the ring. But the first acid dissociation constant of 3,4-DHCA is the biggest one in this group. The dissociation of the carboxylate proton of 3,4-DHCA is more difficult than that of the protons of 3,4-DHBA because of the effect of hydroxyl groups on the ring, and the carboxylate group of 3,4-DHCA is at the end of the longest chain, if compared with the chain of carboxyl groups on 3,4-DHCA and 2,3-DHBA.

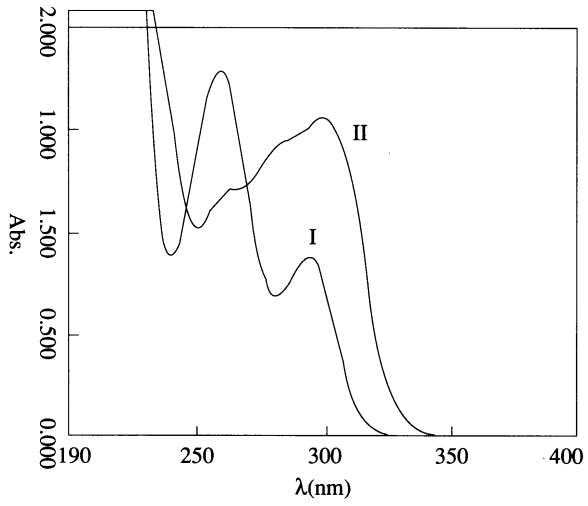


Figure 5. 3,4-dihydroxybenzoic acid (Abs. vs. λ in nm)
Curve I. $C_6H_3(COO^-)(OH)(OH)$, ph=4.24
Curve II. $C_6H_3(COO^-)(OH)(O^-)$, ph=9.02

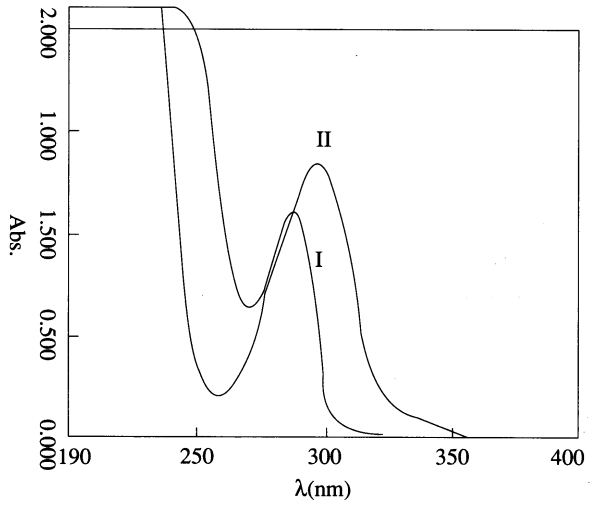


Figure 6. 3,4-dihydroxyphenylacetic acid (Abs. vs.λ in nm)
Curve I. $C_6H_3(COO^-)(OH)(OH)$, pH=5.16
Curve II. $C_6H_3(COO^-)(OH)(O^-)$, ph=9.85

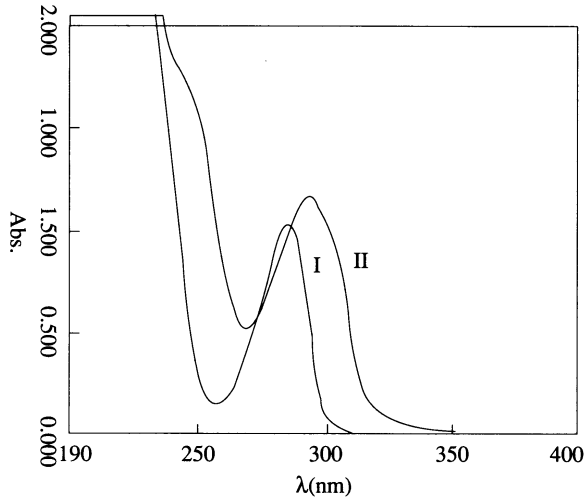


Figure 7. 3,4-dihydroxycinnamic acid (Abs. vs.λ in nm)
Curve I. $C_6H_3(COO^-)(OH)(OH)$, pH=5.60
Curve II. $C_6H_3(COO^-)(OH)(O^-)$, pH=9.92

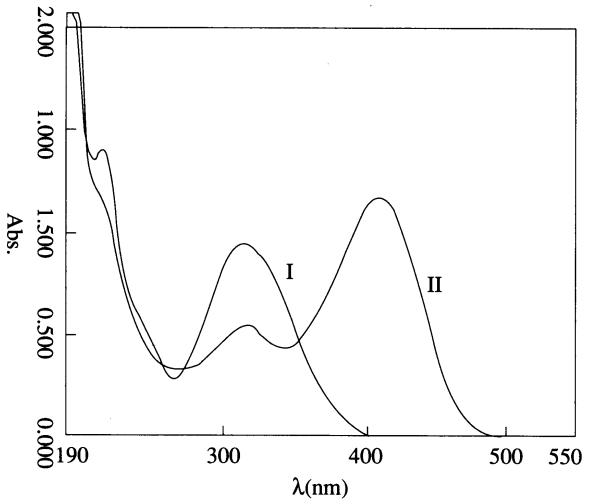


Figure 8. 5-nitrosalicylic acid (Abs. vs.λ in nm)
Curve I. $NO_2.C_6H_3(COO^-)(OH)$, pH=5.15
Curve II. $NO_2.C_6H_3(COO^-)(O^-)$, pH=10.14

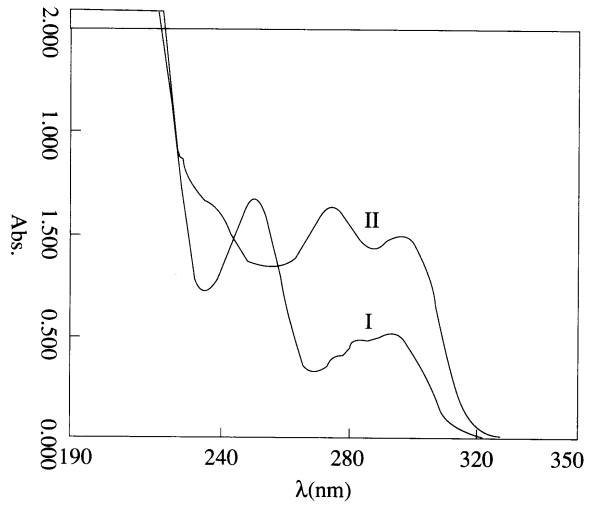


Figure 9. 4-hydroxysalicylic acid (Abs. vs. λ in nm)
Curve I. $C_6H_3(COO^-)(OH)(OH)$, pH=4.16
Curve II. $C_6H_3(COO^-)(OH)(O^-)$, pH=8.83

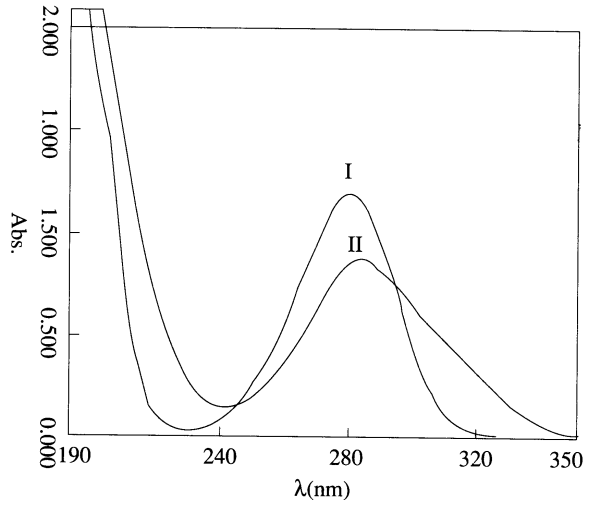


Figure 10. 5-hydroxysalicylic acid (Abs. vs. λ in nm)
Curve I. $C_6H_3(COO^-)(OH)(OH)$, pH=3.93
Curve II. $C_6H_3(COO^-)(OH)(O^-)$, pH=10.03

The first proton of the phenolic groups in 4-NCAT is more acidic than the other catechol derivatives such as 2,3-DHBA, 3,4-DHBA, 3,4-DHPA, 3,4-DHCA.

Table 1. The acid dissociation constants obtained by potentiometric method (0.1M $NaClO_4$ ve t=25 °C)

Ligand	pK_{H_3L}	pK_{H_2L}	pK_{HL}
4-NCAT	-	6.62∓0.01	10.75∓0.01
2,3-DHBA	2.74∓0.01	9.91∓0.01	
3,4-DHBA	4.26∓0.01	8.66∓0.01	
3,4-DHPA	4.24∓0.01	9.52∓0.01	
3,4-DHCA	4.36∓0.01	9.30∓0.01	
5-NSA	-	1.95∓0.01	9.87∓0.01
4-HSA	2.62∓0.01	8.46∓0.01	
5-HSA	2.13∓0.02	9.84∓0.01	

The pK_{H_2L} value was determined to be 6.62 for 4-NCAT; but the pK_{H_2L} value was found to be 9.91 for 2,3-DHBA. The reason for the higher 4-NCAT value is that electron-withdrawing nitro group located on the same ring weakens the O-H bond by withdrawing electrons and facilitates the dissociation of protons. But 2,3-DHBA contains a carboxylate group in ortho position. This group is not a strong electron-withdrowing group, hence the acidity of 2,3-DHBA is low.

Salicylic acid derivative 5-NSA contains carboxylate group next to the hydroxyl group; 4-HSA contains a hydroxyl group in ortho and para position, while 5-HSA has hydroxyl in ortho and meta position on the ring. Dissociation of hydroxyl groups located in ortho position on 4-HSA and 5-HSA is highly difficult because of the hydrogen bond formed with the carboxylate group on the same ring. Therefore, the acidity constants of this ligands are greater than those of others. Therefore, the only protons that are investigated in this study were those located in para position on 4-HSA and meta position on 5-HSA.

The second acid dissociation constants of 4-HSA and 5-HSA were identified to be pK_{H_2L}=8.48 and pK_{HL}=10.00, respectively. In 5-HSA, there may be an increase in the electron density of the hydroxyl group in meta position relative to the carboxylate group, thus making dissociation of protons rather difficult;

hence, 5-HSA has relatively small acidity value. Due to the existence of the nitro group, it was expected that dissociation of the hydroxyl group of 5-NSA would be more easier than the dissociation of the first hydroxyl groups of 4-HSA and 5-HSA. The second dissociation constant of 5-HSA is very close to the pK_{H_2L} value of 5-HSA, the reason being that there is a strong electron withdrawing nitro group on 5-NSA; but the carboxylate group forms a hydrogen bond with the hydroxyl group which, in turn, makes proton dissociation difficult.

When the acid dissociation constans of ligands determined by potentiometry are compared, it can be seen that the acid dissociation constant obtained by spectrometry is greater than that obtained by potentiometry.

Table 2. Acid dissociation constants obtained by spectroscopy (0.1M $NaClO_4$ ve t=25 ° C)

Ligand	pK_{H_2L}	pK_{HL}
4-NCAT		10.79∓0.02
2,3-DHBA	10.16∓0.01	
3,4-DHBA	9.06∓0.02	
3,4-DHPA	9.57∓0.01	
3,4-DHCA	9.62∓0.03	
5-NSA		10.10∓0.02
4-HSA	8.80∓0.01	
5-HSA	10.18∓0.02	

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