The Absorption Spectra of Naphthalene Sulfonic Acid Derivatives*

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The purpose of the present investigation is to explain the electronic spectra of some naphthalene sulfonic acid derivatives which have the amino and/or the hydroxyl groups as the functional. The samples used here show a marked spectral change with the pH variation of the solution. In view of the fact that an intense effect as a proton acceptor or donor of the groups must be responsible for the spectral change, we attempted to explain this by considering the relative position between the functional and the sulfonic group, the intramolecular hydrogen bonding effect, and, moreover, the resonance effect of the functional groups. Further, the assignment of the electronic bands of the derivatives could be made experimentally from the band shift, taking into account the band assignment of naphthalene, which is already known.

Experimental

The chemical structures of the samples used here are shown in Table I. Naphthionic acid (Sample No. 2), γ-acid (No. 5), J-acid (No. 6) and H-acid (No. 9) were purified by repeated precipitations by hydrochloric acid, and the rest, by repeated recrystallizations from water.

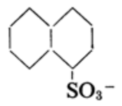
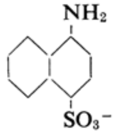
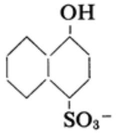
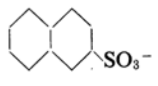
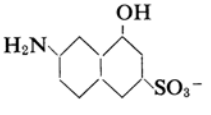
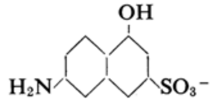
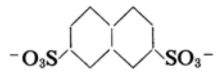
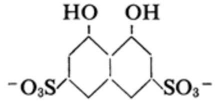
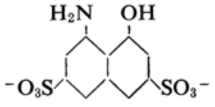
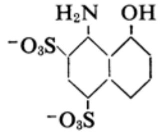
The concentrations of the sample solutions were about 10^{-5} mol./l. The pH value of the solution was adjusted by hydrochloric acid or sodium hydroxide. The absorption measurement was made immediately after the determination of pH. When the pH of a solution becomes higher than 10, the absorption of the solvent can not be neglected. In such cases, a sodium hydroxide solution with the same pH value is used as the reference.

The absorption measurement was carried out by a Shimadzu QR-50 spectrophotometer and also by a Hitachi EPSO22 spectrophotometer. The pH value was determined by a Tōa Denpa Kōgyo pH meter HM-5A.

Results

Figure 1 illustrates the absorption spectra of the naphthalene sulfonic acid ions (Nos. 1, 4 and 7 in Table I). None of them shows any appreciable spectral change within the limits of pH 2 to 11.

TABLE I. NAMES AND STRUCTURES OF SAMPLES

No.	Name	Structure
1	α-Naphthalene sulfonic acid	
2	Naphthionic acid	
3	NW-acid	
4	β-Naphthalene sulfonic acid	
5	γ-acid	
6	J-acid	
7	2, 7-Naphthalene disulfonic acid	
8	Chromotropic acid	
9	H-acid	
10	SS-acid	

The spectra of the naphthionic acid ion (No. 2) are illustrated in Fig. 2. In this case, the spectral change was not observed above pH 4.4, and the spectra were in accord with curve I, while for pH values below 4.4 the spectra changed, while, however, keeping the isosbestic points. The absorption curve (V) for the smallest pH value closely resembles that of α-naphthalene sulfonic acid, which is shown in Fig. 1.

The absorption spectra of NW-acid (No. 3) are shown in Fig. 3. The isosbestic points appeared in the 6.3—10.8 pH range, and the curve did not change in shape below pH 6.3.

According to the above data, naphthionic acid and NW-acid show the two isosbestic

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* Presented at the Local Meeting of the Chemical Society of Japan, Kōriyama, October, 1963.

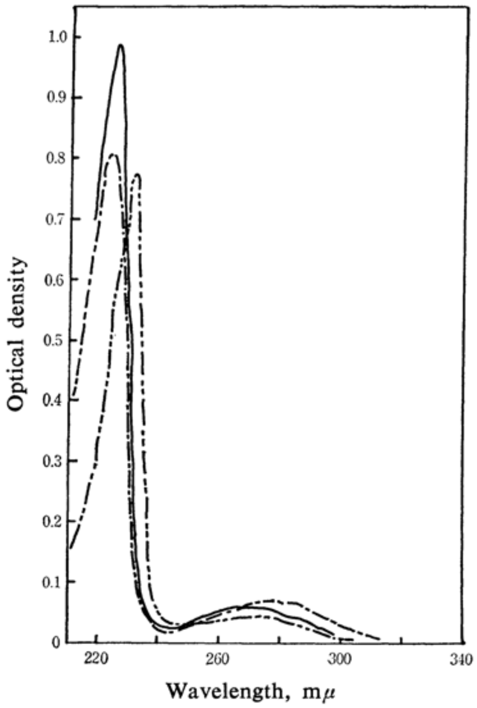


Fig. 1. Absorption spectra of naphthalene sulfonic acids, pH 2—11.

— — — α-Naphthalene sulfonic acid
——— β-Naphthalene sulfonic acid
—·—·— 2,7-Naphthalene disulfonic acid

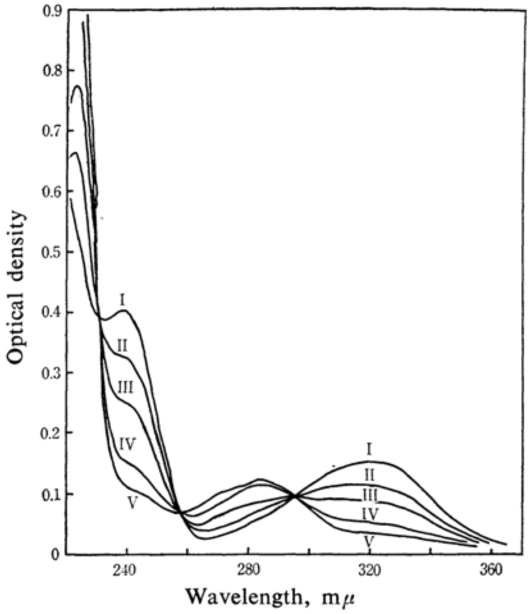


Fig. 2. Spectral change of naphthionic acid with pH.

I	pH	11.1
II		3.2
III		2.7
IV		2.0
V		1.5

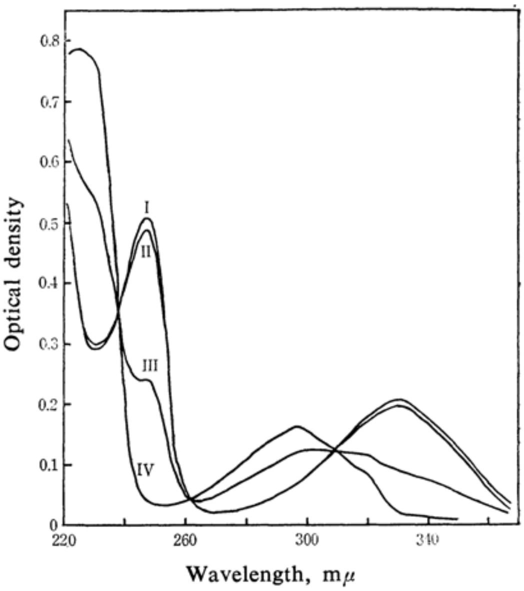


Fig. 3. Spectral change of NW-acid with pH.

I	pH	10.8
II		10.0
III		9.2
IV		6.3

points in different pH regions, namely the acid and alkali regions respectively. Because this is apparently due to the different properties of the amino and the hydroxyl groups, samples with two such kinds of groups are expected to show the isosbestic points in the two corresponding pH ranges. In truth γ-acid (No. 5), J-acid (No. 6) and H-acid (No. 9) behaved as expected. The case of γ-acid is shown as an example in Figs. 4a and 4b; there are well defined isosbestic points in the respective pH regions of 2.55—6.5 and of 9.2—10.6. In the pH range of about 5—8, of course, the absorption spectra did not change.

The pH regions in which the isosbestic points appear are illustrated schematically in Fig. 5 for all samples. In the figure, the shadings indicate the pH range with the isosbestic points, and the blank spaces, that with no spectral change. According to Fig. 5, the shading of naphthionic acid (with only one amino group) and that of NW-acid (one hydroxyl group) exist in quite separated pH regions. The two shaded regions of J-acid (with amino and hydroxyl group) nearly correspond in situation to those of naphthionic acid and NW-acid, whereas, in the case of γ-acid or H-acid, the two shaded regions do not coincide with those of naphthionic acid and NW-acid, and shift together toward the higher pH side. Further, the following facts are noticed: SS-acid indicates no spectral change in the acid region

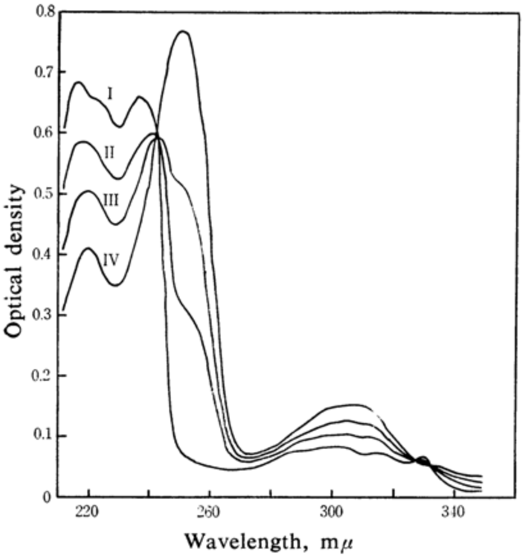


Fig. 4a. Spectral change of γ-acid with pH in acidic solution.

I	pH	2.6
II		3.6
III		4.1
IV		6.5

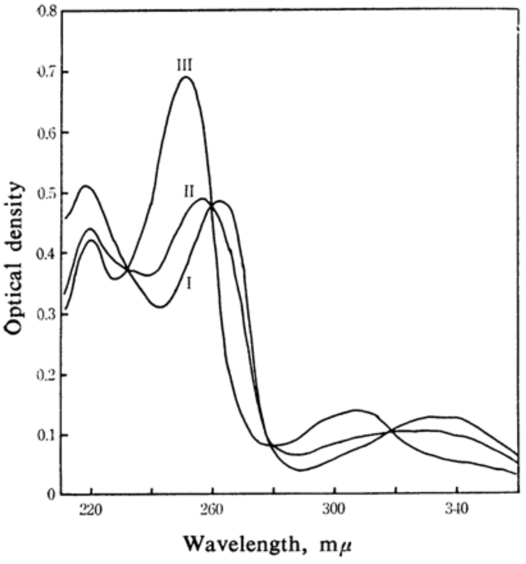


Fig. 4b. Spectral change of γ-acid with pH in basic solution.

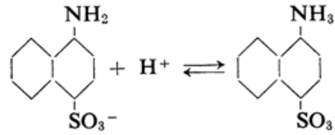
I	pH	10.6
II		9.8
III		9.2

despite the presence of an amino group, the shading region of chromotropic acid corresponding to that of NW-acid shifts to a much lower pH side, and so on. In the following section these problems will be discussed.

Discussion

The existence of the isosbestic points implies that there are two kinds of molecular species with different characters in absorption, with an equilibrium kept between them. The equilibrium depends on the change in pH. There will be, therefore, an equilibrium in the addition and dissociation of the hydrogen ion. Since the naphthalene sulfonic acid ion did not show any spectral change in the pH range measured here, the amino and hydroxyl groups must be responsible for the spectral change in connection with the hydrogen ion.*

For that reason, the following equilibrium can be considered for the case of naphthionic acid;



If we use the notation, for instance, of $(\text{-NH}_2)_\text{N}$, etc. standing for naphthionic acid, etc., the above equilibrium can be written as follows;

$$(\text{-NH}_2)_\text{N}+\text{H}^+ \rightleftarrows (\text{-NH}_3{}^+)_\text{N} \qquad (1)$$

The lone pair electrons on the nitrogen atom (2pπ type) can not conjugate with the naphthalene link when a proton is attached to the amino group. Thus, the above-mentioned fact that the absorption spectrum of naphthionic acid in the solution of pH 1.45 (Fig. 2) is almost identical with that of α-naphthalene sulfonic acid (Fig. 1) can be explained as the result of the complete shift of the equilibrium 1 to the right side.

For NW-acid, similarly, the following equation may be considered as the dissociation equilibrium of the hydroxyl groups;

$$(\text{-OH})_\text{NW} \rightleftarrows (\text{-O}^-)_\text{NW}+\text{H}^+ \qquad (2)$$

This equilibrium should move toward the right side with a lowering of the concentration of the hydrogen ion. Therefore, it can be said that curves I and IV in Fig. 3 indicate the electronic spectra of $(\text{-O}^-)_\text{NW}$ and $(\text{-OH})_\text{NW}$ respectively.

Similarly, all the spectral changes of the other samples should be explained by a proton addition or dissociation process like that of Eq. 1 or 2. According to Fig. 5, however, the

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* From a different standpoint from that of the present discussion, an equilibrium may be plausibly considered between the monomer and the dimer (e. g., an ion pair). This would, however, be unreasonable for the following reason: the spectrum of naphthionic acid in the acid solution, for instance, did not reveal the Davydov splitting, even in the most concentrated hydrogen ion employed here, but, on the contrary, approached the simple spectrum of α-naphthalene sulfonic acid.

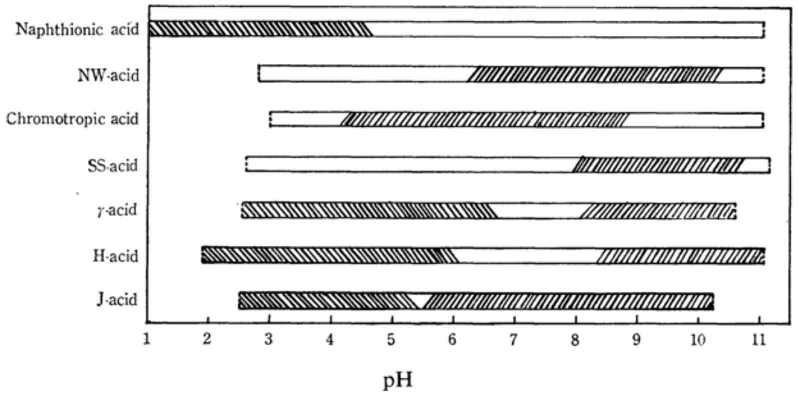

Fig. 5. Schematical diagram of the pH ranges with the spectral change; The shading indicates the pH ranges with the isosbestic points and the blank space that with no spectral change.

TABLE II. THE ORDER OF THE STARTING pH VALUES OF THE ADDITION AND THE DISSOCIATION PROCESS

Sample[1]	Effects by[2] (A) sulfonic group and (B) hydrogen bond	The order of the starting pH values of the process of addition or dissociation: To be estimated by factor A and B[2]	Taking account of factor C	Observed
N-acid	$\overset{\sigma_p}{(\text{-NH}_2)}$			
NW-acid	$\overset{\sigma_p}{(\text{-OH})}$	Addition	Addition	Addition
Ch-acid	$(\overset{\sigma_m-\delta}{\text{-OH}}, \overset{\sigma_m+\delta}{\text{-OH}})$	$N<\begin{pmatrix}\gamma\\J\end{pmatrix}<H$	$\begin{cases}N<J<H\\J<\gamma\end{cases}$	$N<J<H<\gamma$
SS-acid	$(\overset{\sigma_{o,p}+\delta}{\text{-NH}_2}, \overset{-\delta}{\text{-OH}})$			
γ-acid	$(\text{-NH}_2, \overset{\sigma_m}{\text{-OH}})$	Dissociation	Dissociation	Dissociation
H-acid	$(\overset{\sigma_m-\delta}{\text{-NH}_2}, \overset{\sigma_m+\delta}{\text{-OH}})$			
J-acid	$(\text{-NH}_2, \overset{\sigma_m}{\text{-OH}})$	$\begin{pmatrix}Ch\\H\end{pmatrix}<\begin{pmatrix}\gamma\\J\end{pmatrix}<NW<SS$	$\begin{cases}Ch<J<NW<SS\\Ch<H\\J<\gamma\end{cases}$	$Ch<J<NW<\begin{pmatrix}SS\\\gamma\\H\end{pmatrix}$

Note. 1) N-acid and Ch-acid mean naphthionic acid and chromotropic acid, respectively.
2) The electric charge induced by the sulfonic group or by the hydrogen bond formation is indicated by σ or δ, respectively, and is assumed that $\delta>\sigma$.

starting values of the pH of the corresponding processes do not always coincide with one another; the orders of the pH value are $N<J<H<\gamma$ for the addition process and $Ch<J<NW<SS\leq\gamma\leq H$ for the dissociation (see Table II). The possible reasons for this may be a change in the electron density of the functional group as a result of (A) the displacement of the σ electron by the sulfonic group as the electron-accepting group, (B) the formation of an intramolecular hydrogen bond between the functional groups, and (C) the resonance effect of the functional group.

First let us consider the A factor. The electron density on a substituent will be reduced by the inductive effect of the sulfonic group. If the effect from the sulfonic group in the other link is disregarded, the positive charge on each functional group will be represented by the notation σ, as is shown in the second column of Table II, where the suffix of σ used with, for example, *o*, *m* or *p* indicates the position of the sulfonic group with respect to the functional group. Since the magnitude of σ will be in the order $\sigma_o>\sigma_m>\sigma_p$, the amino and the hydroxyl groups of H-acid, for instance, become more positive than the corresponding groups of naphthionic acid and NW-acid. Therefore, the following processes, 3 and 4, for H-acid

$$(\text{-NH}_2,\ \text{-OH})_\text{H} + \text{H}^+ \rightleftarrows (\text{-NH}_3{}^+,\ \text{-OH})_\text{H} \qquad (3)$$

$$(\text{-NH}_2,\ \text{-OH})_\text{H} \rightleftarrows \text{-}(\text{NH}_2,\ \text{-O}^-)_\text{H} + \text{H}^+ \qquad (4)$$

will take place at a lower pH than Eqs. 1 and 2 respectively. Thus the orders of the pH values starting the processes of addition and dissociation because of only the A factor will become SS<H<N<γ=J and Ch=γ=H=J<NW<SS respectively.

Next let us consider the B factor. The formation of the intramolecular hydrogen bond between the two functional groups will occur in chromotropic acid, SS-acid and H-acid. The relative displacement of charge due to this effect will be described by the notation $-\delta$ or $+\delta$, as is shown in Table II. Here, as for H-acid, the hydrogen atom of the amino group is employed in the hydrogen bond in order to make both of the groups conjugate to the naphthalene link.* On the other hand, in the case of SS-acid, hydrogen of the hydroxyl group may be used, because the N–C bond is largely twisted from the plane of the link due to the steric hindrance of the sulfonic group adjacent to the amino group1) (see Table I). Therefore, the spectral change corresponding to the proton addition to the amino group of SS-acid should not appear. This is indeed true, as is indicated in Fig. 5. For only the B factor, therefore, the starting points in the pH value of the addition or the dissociation process to be estimated will become the order N=γ=J<H or Ch=H<NW=γ=J<SS respectively.

As for the A and B factors in connection with the σ-electron, if we assume that the effect of A is smaller than that of B, the correlations of the starting pH values of the proton addition and the dissociation process will be obtained as shown in the third column of Table II.

Finally, let us take into consideration the effect of the C factor; the resonance effect of the functional groups in connection with the π-electron system. In only γ-acid is the direct conjugation through the link between the functional groups allowed. In such a particular case, the positive charge on the groups to be produced by the migration of π-electron to the link should be much decreased compared to the case without such direct conjugation or lacking in either functional groups. For that reason, the negative net charge on the two groups of γ-acid may be the largest. According to the experimental results (the last column of Table II), γ-acid is ranked in the highest orders of the pH values of the addition and the dissociation process. This indicates that the resonance effect by the direct conjugation is quite large.

For the other samples, the two functional groups will indirectly affect each other by means of repulsive interaction between the negative charges on the link induced by the resonance effect of the individual group. As will be seen later, the order of the magnitude of the resonance effect of the groups on the naphthalene link is $\text{-NH}_3{}^+ < \text{-OH} < \text{-NH}_2 < \text{-O}^-$. From this relation, it may be accepted that $\text{-OH}^{-\delta} < \text{-NH}_2{}^{-\delta}$. The $\text{-OH}^{+\delta}$ group of H-acid to be dissociated, therefore, should become more negative than that of chromotropic acid as a result of the resonance effect of $\text{-NH}_2{}^{-\delta}$ being larger than that of $\text{-OH}^{-\delta}$. For that reason, the dissociation process of H-acid becomes more difficult than that of chromotropic acid, namely, Ch<H. Unfortunately, at present the relative position of H-acid in the order can not be decided.

At any rate, most of the experimental results have been explained, as is shown in the fourth column of Table II, though the order in each case does not always coincide in detail with that observed; for example, the expected and the observed order of NW-acid and J-acid are just the converse of one another.

The Direction of the Transition Moment of the Absorption Bands.—With the introduction of the amino and/or the hydroxyl group, the absorption spectra of the original naphthalene sulfonic acid ion are changed markedly by the resonance effect of the group. According to the clarified findings concerning such a substitution effect,2,3) in α-substitution the band with the transition vector in the a direction (short axis) is subjected to a larger effect than when the vector is in the b direction (long axis). Here, in order to obtain some information about the transition direction of each band, the spectral change will be discussed from this standpoint.

Figure 6 illustrates the substitution effect on the absorption spectra of α-naphthalene sulfonic acid. The intense band in the higher wave number region (to be called the second band) of α-naphthalene sulfonic acid is shifted

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* Though it is generally accepted that the proton-donating power is stronger in the hydroxyl group than in the amino group, in the case of H-acid the hydrogen bond of the N-H···O type must be considered, because H-acid shows the typical spectral change for the proton addition process. This indicates that the lone-pair electrons on the amino group can migrate to the naphthalene link in the neutral state.

1) T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, 33, 913 (1960).

2) N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

3) S. Suzuki and H. Baba, This Bulletin, **37**, 519 (1964).

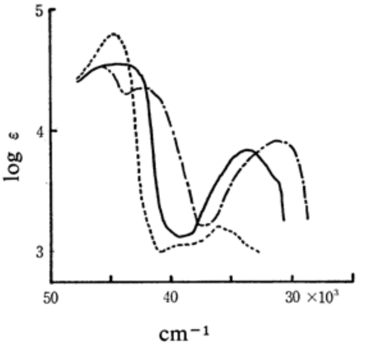

Fig. 6. Substitution effect on the absorption spectra of α-naphthalene sulfonic acid.
- - - - α-Naphthalene sulfonic acid
——— NW acid ; [−OH]
— - — Naphthionic acid ; [$-NH_2$]

merely 350 cm⁻¹ lower when the hydroxyl group is introduced to the α-position (NW-acid), while the weak band in the lower region (the first band) is shifted lower by as much as 2190 cm⁻¹. Moreover, the ε_{max} of the first band increases from 5340 to 7050, whereas that of the second band decreased nearly one half, from 61600 to 35100. In the case of naphthionic acid, nearly the same relation as that above may be seen. Figure 7 also indicates that a similar tendency appears for the cases of chromotropic acid and H-acid with two substituents at α-positions. This time, however, in the first band there appeared a fine structure which was not obvious for 2,7-naphthalene disulfonic acid, the parent molecule of the samples (cf. Fig. 1). Such a fine structure appears at about 285 mμ of the naphthalene spectrum; according to Platt,[4] this can be assigned to the ^1L_a transition. Therefore, it seems plausible that the transition vector of the first band of the naphthalene sulfonic acid derivatives is in the a direction on the naphthalene skeleton as a result of the shifting of the ^1L_a transition. On the other hand, the second band is in the b direction. It is not possible, however, to assign the intense second band to the ^1L_b transition, because the ^1L_b of naphthalene appears at about 310 mμ and is very weak. The second band under consideration, therefore, must be the ^1B_b transition, which is the next b direction. In this case, the bands shift to the longer wavelength side without changing the order.

As γ-acid has the hydroxyl group at the α-position and the amino group at the β, it is interesting to compare the band position in the acidic, the neutral and the basic solutions (Fig. 8). When we compare the spectra in the neutral solution of γ-acid with that of β-naphthalene sulfonic acid, which is the parent molecule, it is found that both the first and the second band shift to the lower wave number in the same order (about 4000 cm⁻¹). Since the hydroxyl group at the α-position shifts the band with the transition moment of the a direction (the first band), the displacement of the second band must be brought about mainly by the amino group at the β-position. However, it may be noticed that the first band of γ-acid shifts by 4080 cm⁻¹ in contrast with the shift of 2190 cm⁻¹ of NW-acid. This means that the effect of the amino group at the β-position is largely responsible for the first band, too. On the other hand, in the acidic solution, only the hydroxyl group at the α-position is left as a group able to resonate with the link, since the substitution effect of the amino group is very much reduced. In such a situation, the first band is

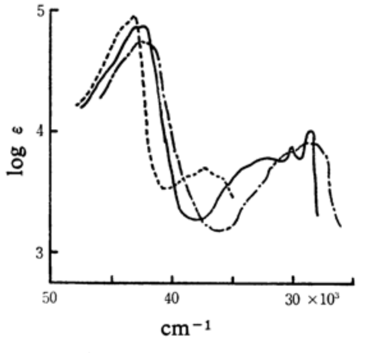

Fig. 7. Substitution effect on the absorption spectra of 2,7-naphthalene disulfonic acid.
- - - - 2,7-Naphthalene disulfonic acid
——— Chromotropic acid ; [−OH, −OH]
— - — H-acid ; [$-NH_2$, −OH]

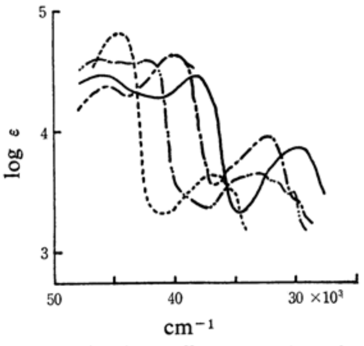

Fig. 8. Substitution effect on the absorption spectra of β-naphthalene sulfonic acid.
- - - - β-Naphthalene sulfonic acid
——— γ-Acid in alkaline solution ; [$-NH_2$, $-O^-$]
— - — γ-Acid in neutral solution ; [$-NH_2$, −OH]
— - - — γ-Acid in acidic solution ; [$-NH_3^+$, −OH]

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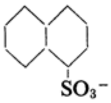
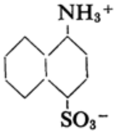
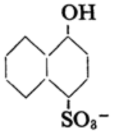
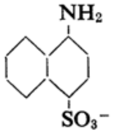
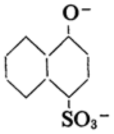
[4] J. R. Platt, *J. Chem. Phys.*, **17**, 487 (1949).

expected to be affected more largely than the second band; this expectation is in agreement with the results of NW-acid and others described above. In the basic solution, the shifts of both bands become the same order again, because the $-O^-$ group is at the α- and the $-NH_2$ group at the β-position. As may be seen from Fig. 8, the shifts are, even though very slight, relatively large for the second band in the neutral solution and for the first band in the basic solution. This must be due to the magnitude of the resonance effect of the substituent groups; judging from the present deta, it seems that $-NH_2 < -O^-$.

Taking into account the band shifts of γ-acid in the neutral and the acid solutions, the order of the effect of the amino group at the β-position on the a and b directions can be estimated approximately.* Because the amino group of γ-acid loses its resonance effect in the acid solution, the contribution by the amino group must be estimated by subtracting the change of the wave number in the acid solution from that in the neutral one. The results indicate that the contribution is 420 cm^{-1} for the first band (a direction) and 2350 cm^{-1} for the second (b direction). Consequently, it is established that the substituent at the β-position is more effective in the b direction (five to sixfold) not in the same order in both the directions, a and b.

TABLE III. SUBSTITUTION EFFECT ON THE FIRST BAND

Sample (nature of solution)	Structure	First band mμ
α-Naphthalene sulfonic acid		280
Naphthionic acid (acidic)		285
NW-acid (acidic)		295
Naphthionic acid (alkaline)		318
NW-acid (alkaline)		330

In order to decide the order of magnitude of the substitution effect, the positions of the first bands for the α-substituent were compared. The results are shown in Table III. It is apparent from the table that the order of the substitution effect is as follows;

$$-NH_3^+ < -OH < -NH_2 < -O^-$$

Summary

1) The absorption spectra of some naphthalene sulfonic acid derivatives have been determined in various pH solutions.

2) The remarkable spectral change revealed by the variation in pH value can be interpreted in terms of the process of the proton association and dissociation of the functional groups.

3) The pH region in which the process takes place is characteristic of the kinds, $-NH_2$, $-OH$, and the number of the functional groups and their locations on the naphthalene skeleton.

4) The relative pH regions have been explained in outline by taking into account the effects of the sulfonic group, the intramolecular hydrogen bond formed between the functional groups, and the resonance of the functional group to the link.

5) The band assignment concerning the transition direction of the derivatives has been decided; the first and the second band correspond, respectively, to the ^1L_a and ^1B_b of naphthalene.

6) The order of the magnitude of the substitution effect has been clarified as $-NH_3^+ < -OH < -NH_2 < -O^-$.

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* When the amino and the hydroxyl group coexist, the respective resonance effects will have an influence upon each other. However, the order of the magnitude will roughly be obtained.