

An Infrared Spectroscopic Investigation on the Complexes Formed Between Boric Acid and Salicylate Ions

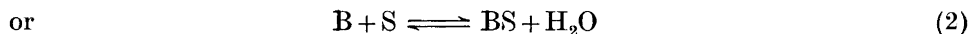
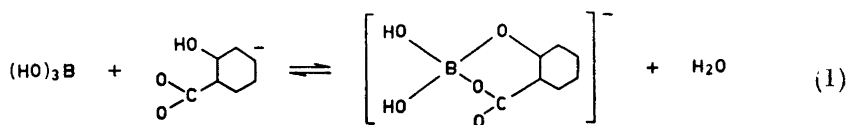
RAGNAR LARSSON and GENNARO NUNZIATA*

*Inorganic Chemistry I, Chemical Center, University of Lund,
Box 740, S-220 07 Lund 7, Sweden*

The infrared spectra of the salicylate-boric acid complexes in aqueous solution have been recorded in the range $1500-800\text{ cm}^{-1}$. The structure of the complexes is discussed and the stability constants have been determined from the spectral data ($\beta_1=17\pm 3\text{ M}^{-1}$, $\beta_2=9\pm 6\text{ M}^{-2}$ at $\text{pH}=7$).

Following an investigation by infrared spectroscopic techniques on the complexes formed in aqueous solution between boric acid and lactate ions,¹ we have endeavoured to investigate in the same manner the complexes formed between boric acid and salicylate ions. It is well known that salicylate ions form complexes with boric acid (*e.g.* Refs. 2 and 3). As in the previous investigation,¹ we have chosen to perform the measurements at such a pH – in this case $\text{pH}=7$ – that the predominating boron species is the boric acid.

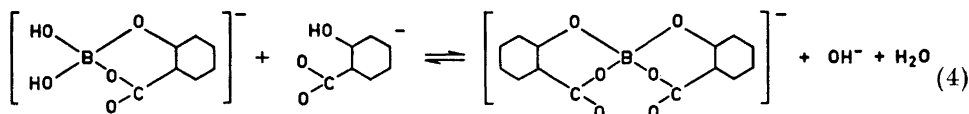
Then the reactions by which the complexes are formed can be written as



with the stability constant

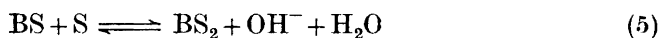
$$\beta_1 = [\text{BS}]/[\text{B}][\text{S}] \quad (3)$$

and



* Present address: Product Research Department, European Technical Center, Procter and Gamble Co., Bruxelles, Belgium.

or



with the formation constant K_2'

$$K_2' = [\text{BS}_2][\text{OH}^-]/[\text{BS}][\text{S}] \quad (6)$$

At a constant pH one can write

$$K_2 = K_2'/[\text{OH}^-] = [\text{BS}_2]/[\text{BS}][\text{S}] \quad (7)$$

and the stability constant β_2

$$\beta_2 = [\text{BS}_2]/[\text{B}][\text{S}]^2 \quad (7a)$$

EXPERIMENTAL

The experimental technique was the same as before, *i.e.*, the spectra were recorded with a Perkin Elmer 521 grating spectrophotometer, using IRTRAN 2 windows in the cells, and the cell-thickness was defined by a platinum spacer of about 20 μ . All solutions were 3 M in respect to NaCl. The reference cell also contained 3 M NaCl, except for some cases when some boric acid was added to compensate for excess boric acid in the sample solution.

As the thickness of the cells was constant during this work only absorbance data are given, not absorption coefficients.

RESULTS

Some representative spectra are given in Figs. 1 and 2. Fig. 1b represents the case when $C_B = 1.0$ M and $C_S = 0.5$ M. Hence it is to be expected that the equilibrium (1) is shifted towards the right hand side so that most of the sali-

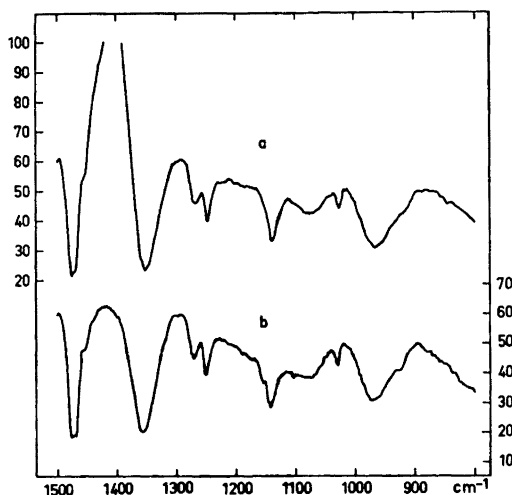


Fig 1. Spectra of sodium salicylate + boric acid. (a) $C_B = 1.0$ M, $C_S = 0.5$ M (ref. solution $C_B = 0.75$ M); (b) $C_B = 1.0$ M, $C_S = 0.5$ M (ref. solution $C_B = 0.5$ M).

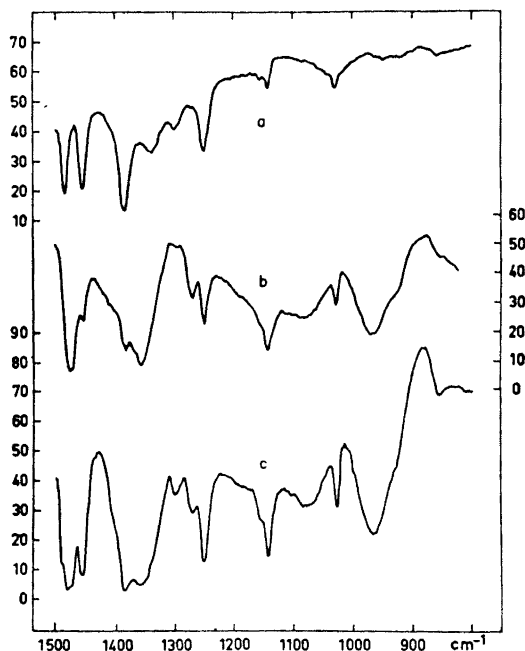


Fig. 2. Spectra of sodium salicylate + boric acid. (a) $C_S = 0.5$ M; (b) $C_S = 1.0$ M, $C_B = 1.0$ M; (c) $C_S = 2.0$ M, $C_B = 0.8$ M.

cylate is present as the first complex. As the concentration $[S]$ (the concentration of free salicylate) is then very low, the presence of BS_2 can certainly be neglected. Hence this spectrum is representative of BS. This is further borne out by a comparison with Fig. 1a. In this latter case the reference solution had $C_B = 0.75$ M whereas in the case of Fig. 1b the reference solution had $C_B = 0.5$ M. It is seen that an almost perfect compensation of the H_3BO_3 absorption band at about 1400 cm^{-1} is obtained for Fig. 1b but a strong overcompensation is found for Fig. 1a.

In Fig. 2a the spectrum of pure sodium salicylate (0.5 M) is given. A comparison between Fig. 2 and Fig. 1b then gives information on the new absorption bands that appear on formation of BS.

1. The bands at 1480 and 1455 cm^{-1} disappear and instead one, or possibly two, bands at 1470 cm^{-1} are formed.
2. The band at 1387 cm^{-1} is shifted to 1359 cm^{-1} and broadened.
3. The band at 1340 cm^{-1} disappears.
4. A new band appears at 1269 cm^{-1} .
5. Two new bands appear at 1080 and 965 cm^{-1} .
6. All other bands are almost unaffected by the complex formation.

INTERPRETATION OF THE SPECTRA

The following rationalisations can now be made:

1. The bands at 1480 and 1455 cm^{-1} are to be related ⁴ to the "19 A" and "19 B" vibration modes of the aromatic ring system ⁵, as is also probably the band system at 1470 cm^{-1} of the complex.

2. The bands at 1387 (1359) cm^{-1} are the sym. carboxylate vibrations. A shift towards lower frequencies of this is usually found ⁶ upon coordination.

3. The band at 1340 cm^{-1} most probably corresponds to a δ C-O-H mode, as this band disappears for a salicylate solution that is 3 M with respect to NaOH (Fig. 3a).

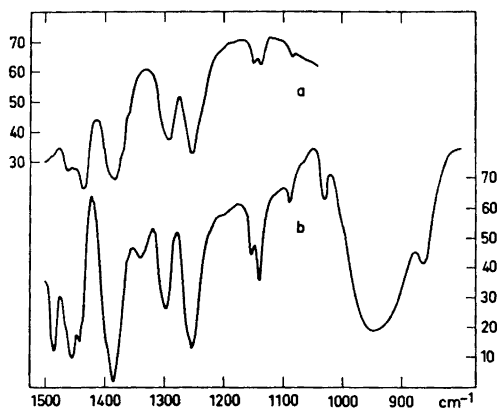


Fig. 3. (a) Spectrum of 0.7 M sodium salicylate in 3 M NaOH; (b) spectrum of sodium salicylate (1.6 M) and sodium borate (0.8 M) at $\text{pH} \approx 13$.

As no band corresponding to this can be found in the complex spectra (within the spectral range investigated) this is support for our formulation of the complex BS, *i.e.* without a proton on the C-O group.

4. The band at 1269 cm^{-1} probably corresponds to the C-O stretching mode in the complex, shifted to this position from 1250 cm^{-1} . However, it can be observed that this latter band is still found in the spectrum of the complex (*cf.* Fig. 1 b). We cannot explain this in any other way than that there is such a strong bonding to the boron atom that a splitting of the phenolic C-O stretching mode occurs, *i.e.*, the C-O group can no longer be regarded as a separate unit but is incorporated in the chelate ring and participates in the skeletal vibrations of the ring.

5. The two bands at 1080 and 965 cm^{-1} correspond to a splitting of the triply degenerate $\text{BO}_4 \nu_3$ vibration. The absorption of B(OH)_4^- occurs at 945 cm^{-1} (*cf.*, *e.g.* Ref. 7). This fact is very important ¹ as it shows that the boron atom is really tetracoordinated also in the first complex.

Actually it would be expected that the ν_3 vibration mode should give rise to three absorption bands for symmetry $C_{2v}(\text{BS}_2)$ or lower symmetry (BS). Possibly the shoulder at about 915 cm^{-1} is an indication of this (Fig. 1b).

The splitting of the ν_{BO} vibration could be related to the shift of the ν_{COO} in the case of the lactate complexes previously investigated.¹ The present pair of values $\Delta\nu_{\text{BO}}$ and ν_{COO} does not seem to fit the linear relation then¹ found. However, we have found above that the bonding between the boron atom and the phenolic oxygen is quite strong so it is reasonable to assume that it is this bonding rather than that to the carboxylate group that causes the splitting of the ν_3 band.

6. All other bands, not affected by coordination, *i.e.* the band at 1030 cm^{-1} and the doublet at 1146 and 1158 cm^{-1} , are most probably related to the aromatic ring vibrations⁵ "5" and "(9A, 9B)", respectively.

INTERPRETATION OF THE COMPLEX EQUILIBRIA

The fact that the band at 1455 cm^{-1} can be attributed solely to the free ligand makes it possible to perform a rough calculation of $[\text{S}]$ for any solution of composition $C_{\text{B}}, C_{\text{S}}$. From the spectrum of pure salicylate (Fig. 2a) the absorbance A_{1455} at $C_{\text{S}}=0.5\text{ M}$ can be calculated and $[\text{S}]$ can be obtained from A_{1455} of the other spectra. The results of these calculations are given in Table 1. The accuracy, of course, depends upon how the background line is drawn in each case.

Furthermore, the mean ligand number, \bar{n} , can now be calculated:

$$\bar{n} = (C_{\text{S}} - [\text{S}]) / C_{\text{B}} \quad (8)$$

The results of this latter calculation are given in Table 1 and Fig. 4. Now, applying the method of Bjerrum⁸ in its simplest form one obtains the formation constants

$$K_1 = \beta_1 = 1/[\text{S}]^{\bar{n}=0.5} \quad (9a)$$

$$K_2 = 1/[\text{S}]^{\bar{n}=1.5} \quad (9b)$$

Table 1. Absorbance data of some solutions ($C_{\text{B}}, C_{\text{S}}$) for the band at 1455 cm^{-1} . (pH = 7, except where otherwise stated.)

C_{S} (M)	C_{B} (M)	A_{1455}	$[\text{S}]$ (M)	$-\log[\text{S}]$	\bar{n}	
0.5	0	0.331	0.5			Fig. 2a
0.5	1.0	0.036	0.05	1.3	0.45	Fig. 1b
0.75	1.0	0.073	0.11	0.96	0.64	
1.0	1.0	0.111	0.17	0.77	0.83	Fig. 2b
2.0	0.8	0.62	0.94	0.03	1.33	Fig. 2c
0.75	0.5	0.193	0.29	0.54	0.92	
1.0	0.5	0.313	0.47	0.32	1.05	
1.5	0.5	0.615	0.93	0.25	1.14	
1.0	0.25	0.453	0.69	0.16	1.26	
1.5	0.25	0.786	1.19	-0.08	1.24	
1.8	0.9	0.65	0.97	0.01	0.91	pH = 8

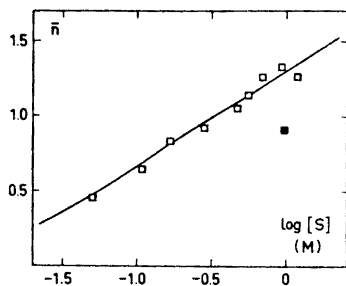


Fig. 4. Experimental values of \bar{n} at pH=7 (\square), at pH=8 (\blacksquare). The points ($\bar{n}=0.5$, $\log[S] = -1.22$) and ($\bar{n}=1.5$, $\log[S]=0.28$) have been read from a rough curve through the points (\square). The full-drawn line is calculated from the stability constants thus estimated.

Although we have only a few experimental points, and thus hardly can expect to get the two parameters with any great confidence, it is seen (Fig. 4) that the points fall rather well on a smooth curve, a fact that facilitates interpolation and extrapolation. The resulting values are

$$\beta_1 = 17 \pm 3 \text{ M}^{-1} \text{ and } K_2 = 0.5 \pm 0.3 \text{ M}^{-1}$$

If we now combine β_1 and K_2 by the relation

$$\beta_2 = \beta_1 K_2 \quad (10)$$

we obtain $\beta_2 = 9 \pm 7 \text{ M}^{-2}$ and we can consequently calculate \bar{n} at any value of [S] as a check of the formation curve. Alternatively, and with more confidence, one can estimate β_2 from the relation $\beta_2 = 1/[L]^2 \bar{n} - 1$. This yields $\beta_2 = 9 \pm 5 \text{ M}^{-2}$.

Furthermore, and more interesting, we can check the validity of formula (6) in the following way. Whereas all measurements hitherto discussed were made at pH=7, one spectrum was recorded at pH=8. The absorbance at 1455 cm^{-1} of this spectrum is included in Table 1 together with the corresponding value of \bar{n} . Now, if formulae (1) and (4) are correct, an increase of pH by one unit will not affect β_1 but as K_2' contains the factor $[\text{OH}^-]$ it must hold that

$$(K_2)_{\text{pH}=8} = 0.1(K_2)_{\text{pH}=7} \quad (11)$$

Consequently, $(\beta_1)_{\text{pH}=8} = 17 \text{ M}^{-1}$ and from the relation (10) $(\beta_2)_{\text{pH}=8} = 0.9$.

From these values we can calculate $\bar{n}_{\text{pH}=8}$ at $[S]=1.0 \text{ M}$. The result is

$$\bar{n} = \frac{17 + 2}{1 + 17 + 1} = 1.0$$

This value is in rather good agreement with the experimental one (Fig. 4), thus indicating the correctness of our general formulation of the equilibria (1) and (4).

It is also interesting to compare our value of β_1 with that given by Kolthoff³ from measurements of the solubility of silver salicylate in boric acid at a lower value of the ionic strength than we have used. He reports $\beta_1 = 22 \pm 2 \text{ M}^{-1}$ which is in reasonable agreement with our value. It must be remembered that as the formula (1) has one charged unit on each side, the variation of the activity coefficients with the ionic strength will probably cancel out to a large extent in the expression for β_1 . Thus the fact that almost the same values of β_1

are obtained at pH = 5 (Kolthoff³) and at pH = 7 (present work) indicates the correctness of the formulation of (1), *i.e.* the splitting off of the phenolic proton.

The stability constants thus estimated indicate that the salicylate-boric acid complex system is a relatively weak one. This is further borne out by our measurements at a high pH (pH \approx 13; Fig. 3b) from which it can be seen that the spectrum is a superposition of that of the salicylate and $B(OH)_4^-$ ions. This means that the equilibria (1) and (4) are completely displaced to the left hand side as the boric acid – borate ion equilibrium is itself displaced entirely in favour of the borate ion at that pH.

The financial support of the *Swedish Natural Science Research Council* and of *Fondazione F. Giordani*, Rome, Italy, is gratefully acknowledged.

REFERENCES

1. Larsson, R. and Nunziata, G. *Acta Chem. Scand.* **24** (1970) 2156.
2. Meulenhoff, J. *Rec. Trav. Chim.* **44** (1925) 161.
3. Kolthoff, I. M. *Rec. Trav. Chim.* **45** (1926) 607.
4. Spinner, E. *J. Chem. Soc. B* **1967** 874.
5. Wilson, E. B. *Phys. Rev.* **45** (1934) 706.
6. Nakamoto, K., Fujita, J., Tanaka, S. and Kobayashi, M. *J. Am. Chem. Soc.* **79** (1957) 4904.
7. Goulden, J. D. S. *Spectrochim. Acta* **9** (1959) 657.
8. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*, Diss., P. Haase and Søn, Copenhagen 1941.

Received August 19, 1971.