An Infrared Spectroscopic Investigation on the Complexes

formed between Boric Acid and Lactic Acid

in Aqueous Solution

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Infrared spectra of aqueous solutions of lactic acid and boric acid have been recorded in the range $1500-850$ cm^{-1}. By varying the concentrations of the two acids and by performing the measurements at pH$=2$ and pH$=6$, we have characterized the spectra of the complexes formed. At pH$=2$ one complex is formed, at pH$=6$ two complexes are formed. From the position and the splitting of the B$-$O stretching band we have concluded that the complexes formed have a distorted tetrahedral BO$_4$ center. The stability constants of the complexes have been estimated, (*cf.* eqns. (4), (5), and (6)).

On the basis of the position of the ν_{C-O} band and the absence or presence, respectively, of a δ_{OH} band we have characterized the two complexes formed at pH$=6$ as deprotonated, whereas the one formed at pH$=2$ has the OH-group of the lactic acid-boric acid complex. The dissociation constant of this acid has been estimated. Furthermore, a correlation has been found between the ν_{COO} (sym) of the carboxylate group and the splitting of the BO$_4$ stretching band.

It has long been known [1] that boric acid forms complexes with polyalcohols and α-hydroxo-carboxylic acids. Due to the intricacy of the boric acid-borate system, itself, most attempts to determine the composition of the above-mentioned complex systems have been oversimplified. Even the most adequate treatment so far, that of Roy, Laferriere and Edwards [2] on the polyol complexes of the borate ion, does not take into consideration the formation of polyborate ions and the possibility of complex formation between boric acid and the polyols in question. This situation will probably be improved in the near future by the application of potentiometric measurements combined with computer treatment of the experimental data.

It seems to be generally agreed, however, that two types of complexes can be formed: the first one with a 1:1 ratio of boron to ligand, the second one

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with a 1:2 ratio. The dedicated work of Böeseken[3] on the present problem has laid the foundation to our present knowledge of boric acid-polyalcohol complexes and many other authors (*e.g.* Refs. 4, 5) have contributed by making quantitative measurements, although in the light of present-day methods of investigating complicated equilibria, the results must be considered cautiously.

As regards the structure of these complexes, the second complex most certainly contains a tetra-coordinated boron ion,

$$\left(\begin{matrix} O \\ O \end{matrix} \! \! \! \! > B < \! \! \! \! \begin{matrix} O \\ O \end{matrix} \right)$$
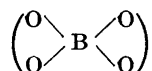
This follows, *e.g.*, from the possibility of preparing[6] solid compounds of the composition, *e.g.*,

$$M^{2+} \left[\left(\begin{matrix} O \\ O \end{matrix} \! \! \! \! > B < \! \! \! \! \begin{matrix} O \\ O \end{matrix} \right) \right]_2^{-}$$
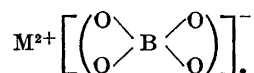
The analogy with the isoelectronic carbon atom suggest a tetrahedral arrangement of the BO_4 unit. This structure is known from X-ray analysis[7] as well as from Raman spectroscopy[8] to hold for the borate ion, $B(OH)_4^-$.
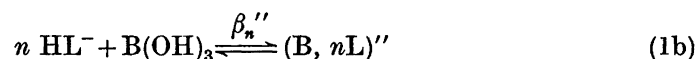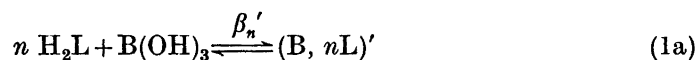
The claim has been made,[9] that resolution into optical enantiomers of such complexes of suitable ligands should prove the tetrahedral structure.

Although the structure of the second complex is relatively well established, at least in alkaline media, the problem of the structure of the first complex remains open.

As infrared spectroscopic measurements can now be performed rather easily on aqueous solutions and have been applied to many problems in the chemistry of metal complexes[10-12] we have considered it meaningful to apply such measurements to the problems of elucidating the structures of the complexes between boric acid and polyols and α-hydroxoacids. In this first communication of the results we will deal with the complexes of lactic acid.

PLAN OF INVESTIGATION

In order to avoid the difficulties related to the formation of polyborate ions we have chosen to work in such a range of pH that boric acid is the dominant boron species in solution. We have also added NaCl so that $I = 3$ M. Furthermore, we have used two separate regions of pH, namely pH $= 2$ and pH $= 6$. As the pK_a of lactic acid is 3.8 ($I = 2$ M),[13] lactic acid itself is the prevailing species in the first region whereas the lactate ion dominates in the latter one. It is then preferable to formulate the reaction schemes in terms of the prevailing species:

$$n \ H_2L + B(OH)_3 \underset{}{\overset{\beta_n'}{\rightleftharpoons}} (B, nL)' \tag{1a}$$

$$n \ HL^- + B(OH)_3 \underset{}{\overset{\beta_n''}{\rightleftharpoons}} (B, nL)'' \tag{1b}$$

Here H_2L designates lactic acid and consequently HL^- designates

$$HO \diagdown \underset{H \diagup}{C} \diagup \overset{COO^-}{\diagdown CH_3} \qquad \text{and } L^{2-} \text{ designates} \qquad {}^-O \diagdown \underset{H \diagup}{C} \diagup \overset{COO^-}{\diagdown CH_3}$$
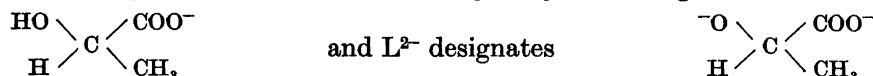
The formula (B, L_n) signifies the sum of all complexes containing n lactic acid units per boron atom; it does not specify the charge of the complex or the number of protons attached to the L entity. As long as pH is constant, the stability constants ($\beta_n{}'$ and $\beta_n{}''$) will be constant.

The aim of the spectroscopic measurements is threefold.

Pro primo, by measuring the absorbance of a suitably chosen absorption band characteristic of the free ligand only, we achieve a semi-quantitative determination of the free ligand concentration and consequently also the mean ligand number, $\bar{n}$, defined as

$$\bar{n}' = \frac{C_{H_2L} - [H_2L]}{C_B} \qquad (2a)$$

$$\bar{n}'' = \frac{C_{HL^-} - [HL^-]}{C_B} \qquad (2b)$$

From the relation between $\bar{n}$ and the free ligand concentration one can estimate the appropriate formation constants. It must be emphasized that by so doing we do not wish to compete with more accurate methods that might be applied. Our purpose is to obtain an approximate knowledge of the stoichiometric composition of the solutions, without which no meaningful analysis of the recorded spectra can be made.

Pro secundo, by observing the appearance of absorption bands corresponding to $B-O$ stretching vibrations we want to infer the coordination number of the boron atom in the complexes formed. If this is a trivial problem for complexes of the composition $(B, 2L)$ (see above), it is certainly not so for complexes of the composition (B, L). The configuration of such a complex can be either planar, tricoordinated (as in $B(OH)_3$) [14] or tetrahedral, tetracoordinated (as in $B(OH)_4{}^-$).[7] Much of the early discussion on boric acid-polyol complexes seems to have centered on this problem and a tricoordinated 1:1 complex has been prepared by Hermans.[6] Now it is known from studies [15] on aqueous solutions that boric acid has an absorption band at about 1410 cm^{-1}, whereas the borate anion absorbs at 945 cm^{-1}. These absorption bands correspond to $B-O$ stretching vibrations and the positions reflect the decrease in force constant when passing from the $B-O$ bond for tricoordinated boron compound (bond order 1 1/3) to the pure single bond in the tetracoordinated one. It is then quite reasonable to assume that a similar difference will persist also for other tri- and tetra-coordinated boron complexes. Consequently the structure of the complex (B, L) can be easily characterized.

Pro tertio, we wish to resolve the question of whether or not the proton on the α-hydroxo group is split off upon coordination. Obviously, if an absorption related to the δ_{OH} vibration can be characterized in the spectrum of the complex there must be at least a fraction of that complex in the solution that contains the alcoholic OH group intact. Also the $C-O$ stretching

absorption can be expected to be affected by the presence or absence of the proton. It may seem that this is a bogey problem as solid compounds have been prepared[6] in which at least the second complex (B, 2L) is characterized as a negatively charged one and that consequently the protons in question must have been lost from both ligands. However, there is no reason, *a priori*, to assume that this situation should prevail also in solution. Especially for the first complex a formulation like

$$
\begin{array}{c}
HO \diagdown \; OH \diagdown \\
B CH(CH_3) \\
HO \diagup \; O \diagdown \diagup \\
 O \diagdown C \\
 O
\end{array}
$$
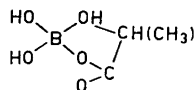
can well be made and the second complex could be formulated as an acid

$$
\begin{array}{c}
(CH_3)HC \diagdown O \diagdown \diagup OH \diagup CH(CH_3) \\
 C B C \\
O \diagup \; O \diagup O \diagdown O
\end{array}
$$
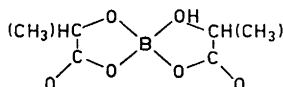
with a notable but not complete degree of protolysis to the anionic complex. In lieu of unbiased potentiometric investigations we hope spectroscopic evidence can settle this question.

EXPERIMENTAL

The spectra were recorded with a Perkin Elmer PE 521 Spectrophotometer using IRTRAN-2-windows in the cells. Teflon spacers of 25 μ thickness were used throughout the investigation. Hence we have reported all intensity data as absorbances without recalculation to absorptivity.

All chemicals were of analytical grade and solutions of boric acid and lactic acid or sodium lactate were mixed in appropriate proportions. pH was approximately adjusted to 2 and 6, respectively, with the help of sensitive indicator papers. All solutions contained sodium chloride to make the ionic strength approximately 3 M. The reference solutions, besides containing 3 M NaCl, were made to contain some boric acid in those cases when free boric acid was in excess in the sample solutions, so as to compensate as closely as possible for the absorption of this free acid.

RESULTS AND ANALYSIS OF THE SPECTRA

The system at pH = 6. Some representative spectra are reproduced in Figs. 1 and 2. Let us first consider the spectra recorded at pH = 6, corresponding to lactate solutions. A comparison between the spectrum of the free lactate ion (Fig 1, a) and that (Fig 1, b) of the lactate solutions with an excess of boric acid, which most certainly reveals the main spectral features of the first complex, presents the following major changes:

1. The band at 1035 cm^{-1} disappears.
2. A new band appears at 1063 cm^{-1}.
3. New bands are observed at 895 and 990 cm^{-1}.

4. The band at 1265 cm^{-1} decreases to unobservably low intensity. Instead a new, sharp band appears at 1293 cm^{-1}. Also, the band at 1310 cm^{-1} disappears.

5. The band at 1415 cm^{-1} disappears and a new band can be observed at 1350 cm^{-1}.
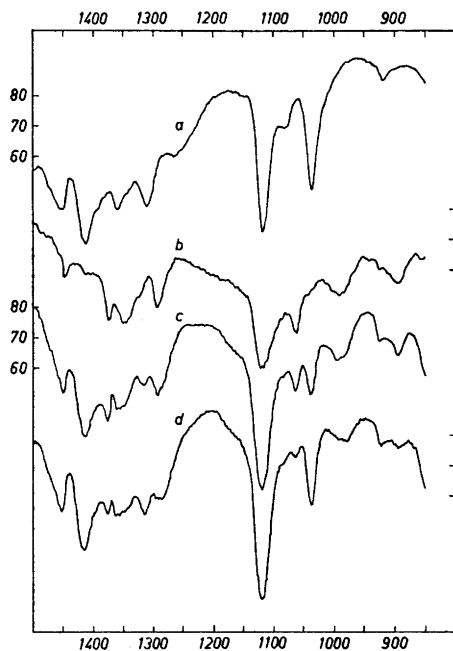
Fig. 1. Reproduction of some typical spectra at pH = 6.
a: $C_{HL^-} = 1.0$ M, $C_B = 0$.
b: $C_{HL^-} = 0.5$ M, $C_B = 1.0$ M; Ref. cell $C_B = 0.5$ M.
c: $C_{HL^-} = 1.0$ M, $C_B = 0.5$ M.
d: $C_{HL^-} = 1.0$ M, $C_B = 0.25$ M.
The ordinate scale is percent transmission.
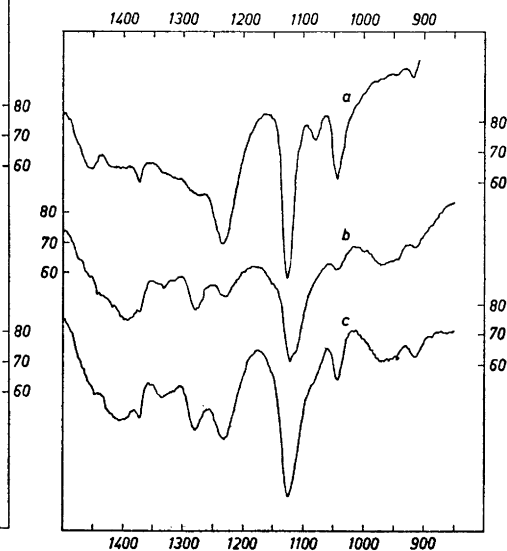
Fig. 2. Reproduction of some typical spectra at pH = 2.
a: $C_{H_2L} = 1.0$ M, $C_B = 0$.
b: $C_{H_2L} = 0.5$ M, $C_B = 1.0$ M; Ref. cell $C_B = 0.75$ M.
c: $C_{H_2L} = 1.0$ M, $C_B = 0.25$ M.
The ordinate scale is percent transmission.

6. The sharp band at 1117 cm^{-1} remains in the same position (perhaps a slight shift to 1119 cm^{-1} can be observed) but it is obviously broadened and shows what appears to be rotational wings.

7. All other bands remain in essentially the same positions. The weak band at 1080 cm^{-1} of the free lactate ion seems to disappear but could possibly be covered by the broad 1119 cm^{-1} band, cf. (6).

When the ratio C_{HL^-}/C_B is increased (Fig. 1 c-d) the following trends are observed. (The observations are numbered to stress the relation to what has been said for the case $C_B > C_{HL^-}$)

1 a. All bands characteristic of the free lactate ion are observed more or less clearly, especially the band at 1035 cm^{-1}.

2 a. The band at 1063 cm^{-1} decreases markedly in intensity (cf. Table 1).

3 a. The band at 990 cm^{-1} is slightly deformed or split, now having its absorption maximum at 980 cm^{-1} (and possibly a shoulder at 995 cm^{-1}).

5 a. The new band is less sharp and has now its maximum at about 1360 cm^{-1}.

The following rationalisations are offered for the observations reported above: The fact that new bands are observed obviously supports the idea that complex formation actually takes place. The bands under heading (3) and (3 a) must represent absorption due to B−O stretching vibrations of a principally tetrahedral BO$_4$ unit.

The virtual disappearance of the 1035 cm^{-1} band when $C_B > C_{HL^-}$ indicates that this band is one characteristic of the free lactate ions. We have utilized this situation for a calculation − albeit semiquantitative − of the free lactate concentration [HL$^-$] and the mean ligand number $\bar{n}''$ of a series of solutions differing in C_B and C_{HL^-}-values. The results of this calculation are given in Table 1 and graphically in Fig. 3. One can note that $\bar{n}''$ is tending towards

Table 1. Semi-quantitative estimations of $\bar{n}''$ from absorbance measurements at pH$=6$. A means absorbance$=^{10}\log T_0/T$ measured at the band maximum indicated. The literation of experiments are the same as in Fig. 1.

Expt. No.	C_{HL^-} (M)	C_B (M)	A_{1036}	[HL$^-$] (M)	$\bar{n}''$	A_{1063}	$\dfrac{A_{1063}}{C_B}$ (M^{-1})	A_{1293}	$\dfrac{A_{1293}}{C_B}$ (M^{-1})
1 a	1.0	—	0.23$_2$	1.0					
1 b	0.5	1.0	0.01$_6$	0.07	0.4	0.10$_1$	0.10	0.11$_0$	0.11
1 c	1.0	0.5	0.10$_5$	0.45	1.1	0.07$_0$	0.14	0.13$_1$	0.26
1 d	1.0	0.25	0.16$_6$	0.69	1.2	0.02$_7$	0.11	0.08$_6$	0.34
1 e	0.5	0.25	0.07$_5$	0.32	0.7	0.03$_2$	0.13	0.05$_3$	0.21
1 f	1.0	1.0	0.06$_8$	0.29	0.7	0.14$_5$	0.15	0.18$_1$	0.18

values >1. Consequently we estimate that two complexes are formed. Furthermore, from the values of [HL$^-$] where $\bar{n}''=0.5$ and $\bar{n}''=1.5$ (extrapolated) one can obtain approximate values of the two formation constants K_1 and K_2 defined by $K_1=\beta_1''$ and $K_2=\beta_2''/\beta_1''$ (cf. formula (1 b)).

From the formula

$$K_n = 1/[L]^-_{\bar{n}=n-0.5} \tag{3}$$

given by Bjerrum [16] we estimate from Fig. 3 the values $K_1 \approx 6$ M^{-1} and $K_2 \approx 1$ M^{-1}, i.e. $\beta_2'' \approx 6$ M^{-2}.

The fulldrawn curve representing $\bar{n}''$ of Fig. 3 is calculated from these rough values of the stability constants as is also the dotted curve representing α_1'', the fraction of the first complex. The interesting observation can now be made (Fig. 4) that the curves representing the molar absorbance of the 1293 cm^{-1} and 1063 cm^{-1} bands (cf. Table 1) versus free lactate concentration are of a form very similar to that of the $\bar{n}''$ curve and the α_1'' curve, respectively. From this fact one can conclude that the 1293 cm^{-1} band
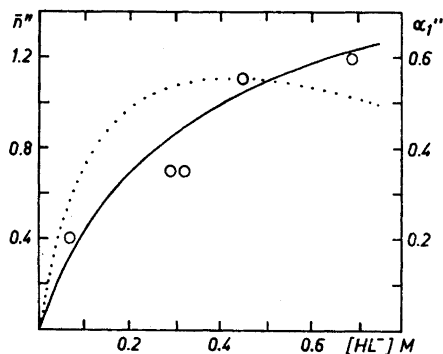
Fig. 3. Experimental values of $\bar{n}''$ (O) and calculated curves of $\bar{n}''$ (———) and α_1'' (— — —). pH = 6.
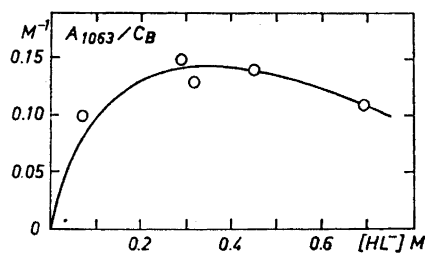
Fig. 4. Experimental values of A_{1063}/C_B (pH = 6). The curve is drawn to fit the points.

is characteristic of both the first and the second complex, whereas the 1063 cm^{-1} band is related only to the first one. It may furthermore be reasonable to assume that the above mentioned bands are the counterparts of the 1265 cm^{-1} and 1035 cm^{-1} bands, respectively, of the free lactate ion.

So much can be derived from the semi-quantitative estimation of formal molar band absorbances. We now face the difficult task of making assignments of the various bands to various vibration modes. For the free lactate ion (spectrum a, Fig. 1) the following assignments can be made rather safely by analogy from the analysis of alanine by Suzuki and coworkers:[17] The bands at 1452 cm^{-1} and 1360 cm^{-1} are δ_{CH3}, the band at 1425 cm^{-1} is CO_2^- sym. stretch, and the band at 1310 cm^{-1} corresponds to CH bending. Following Goulden [10] we further assign the broad band at about 1265 cm^{-1} to the δ_{OH} vibration. The bands between 1150 cm^{-1} and 1000 cm^{-1} are more difficult to assign as they represent vibrations that are strongly coupled, mainly the $C-CH_3$ stretch, $C-O$ stretch and CH_3 rocking, still pursuing the analogy with the alanine analysis. No band can therefore be thought to represent a pure bond vibration mode. We will, however, try to estimate the main character of the two strong bands, the one at 1117 cm^{-1} and the one at 1035 cm^{-1}, as they are so profoundly changed on coordination. The analysis by Nakamoto and coworkers [18] of glycolato complexes indicates that bands around 1060 cm^{-1} are mainly related to $C-O$ stretching vibrations, so it seems reasonable to assign the 1035 cm^{-1} band of the free lactate ion correspondingly. This is contrary to what was done by Goulden,[10] who assigned this band as $C-CH_3$ stretch. However, as already stated, the 1117 cm^{-1} band is certainly the origin of the 1119 cm^{-1} band of the first complex. As the broad band at the base of this latter band looks very much like a pair of rotational wings we tentatively suggest that the 1117 cm^{-1} (1119 cm^{-1}) band is one composed mainly of $C-CH_3$ stretch coupled with CH_3 rocking. It is the CH_3 rocking element, perpendicular to the $C-C$ bond axis that could give rise to rotational wings, considering the CH_3 group as rotating relative to the rest of the molecule. The effect thus

conceived is then rather similar to one found by Sheppard and coworkers [19] for — among other bands — the CH_3 rocking band of the complex $Au_2I_2(CH_3)_4$. Why the methyl group should rotate freely in the complex and not in the free lactate ion remains an open question.

From what has been said so far it follows that the new band at 1293 cm^{-1}, that belongs to both the first and the second complex, must be related to a vibration mode common to both complexes. It then seems reasonable that the δ_{CH} of 1310 cm^{-1} is shifted to 1293 cm^{-1} in the complexes. This means that the δ_{OH} band is not present in the spectra of the complexes. However, one cannot infer from this that the proton of the C−OH group has been expelled upon coordination, since it has been suggested by Goulden [16] that the δ_{OH} band is shifted strongly to higher frequencies on coordination. It may be noted, though, that no new band that could possibly be ascribed as $\delta_{OH(complex)}$ has been found within the investigated spectral range. The shift of the ν_{C-OH} from 1035 cm^{-1} to 1063 cm^{-1}, however, strongly suggests that the proton actually is lost upon coordination as it is known from studies [20] on metal glycolate systems (where the proton undoubtedly is not lost) that chelation lowers the frequency of this band. Indeed, Grenthe [21] has found that for the complex Er (glyc) (glyc−H), where glyc designates the glycolate ion and glyc−H designates the deprotonated glycolate ion, one actually observes a band ν_{C-O} at a higher frequency corresponding to glyc−H. So we conclude that the complex is formed with the loss of the proton in question. What is difficult to explain is the near correlation between the absorbance of the 1063 cm^{-1} band (Fig. 4) and the α_1'' curve (Fig. 3), that assigns the 1063 cm^{-1} band to the first complex only. We suggest that the corresponding band of the second complex is shifted to an even higher frequency and is consequently hidden by the strong and broad band at 1119 cm^{-1}. The increase of frequency and the corresponding increase of force constant for the C−O band must be thought to originate from the increase of negative charge on the oxygen atom and this charge is probably less compensated by the trivalent boron ion in the second complex where two such oxygen atoms are bonded to boron than is the case in the first complex.

The shift of the $\nu_{COO(sym)}$ from 1415 to 1350 cm^{-1} in the first complex and about 1360 cm^{-1} in the second one corresponds to what is usually found in carboxylate complexes.[22]

We now turn to the remaining new bands at 895 cm^{-1} and 990 cm^{-1} (point 3). It seems most reasonable to assign these as boron oxygen vibrations and the frequencies then allow us to conclude that the first complex is a tetra-coordinated one. The two peaks are situated on almost equidistant positions on both sides of the absorption band (945 cm^{-1}) of the tetrahedral $B(OH)_4^-$ ion.[15] This splitting of the three-fold degenerate, asymmetric stretching vibration of the BO_4 unit signifies a decrease in symmetry from T_d to C_{3v}. Of course, the symmetry of the total complex, formulated as

is lower than this, but regarding the oxygens of the HO- and $\diagup$C $-$ O $-$ groups as almost equivalent with respect to charge and the oxygen related to the carboxylate group as nonequivalent to the others, the effective symmetry of the BO_4 unit is actually C_{3v}. For the second complex, formulated as

the same argument gives an effective symmetry of C_{2v} to the BO_4 unit. Consequently, one should expect a complete splitting of the threefold degeneracy. We suggest that this is actually observed (point 3 b, especially with reference to Fig. 1 d). The splitting is, however, not so pronounced as for instance that of sulphato complexes of C_{2v} symmetry (cf., e.g., Ref. 12).

In this connection it must be pointed out that as all the absorption bands appearing on complex formation have been accounted for, no band can be attributed to a tricoordinated boron species. Consequently we can state that the boron complexes are present entirely as tetracoordinated species.

The system at pH = 2. Some representative spectra at pH = 2 are given in Fig. 2. As before we make a comparison between the spectrum of the free lactic acid (Fig. 2 a) and the spectrum of lactic acid with an excess of boric acid (Fig. 2 b). Drastic changes occur:

1. The band at 1045 cm^{-1} is strongly reduced in intensity.

2. No new bands are found in the vicinity, but for a very weak one at about 1000 cm^{-1}. (This may, however, have been hidden in spectrum 2 a by the low frequency tail of the 1045 cm^{-1} band).
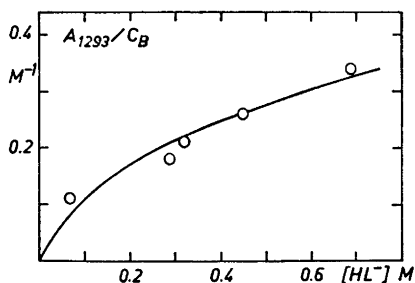
Fig. 5. Experimental values of A_{1293}/C_B (pH=6). The curve is drawn to fit the points.
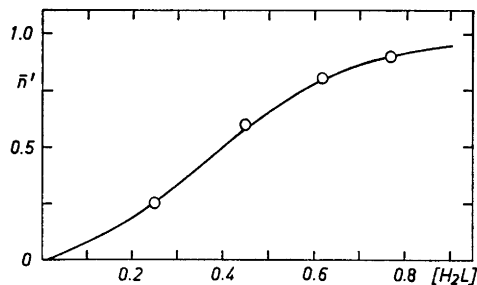
Fig. 6. Experimental values of $\bar{n}'$ (O) and $\bar{n}'$ calculated from the value of $\beta_1'=2.5$ M^{-1} (————). pH=2.

3. Two new bands appear at about 950 cm^{-1} and 970 cm^{-1}.

4. The composite structure between 1200 cm^{-1} and 1300 cm^{-1} is dissolved in a more clear pattern. Especially the strong band at 1235 cm^{-1} decreases markedly in intensity. A new band appears at 1335 cm^{-1}.

5. A new strong band at about 1395 cm^{-1} appears.

6. The sharp band at 1125 cm^{-1} is shifted slightly, broadened, and shows rotational wings, similar to those discussed above.

When the ratio C_{H_3L}/C_B is increased (Fig. 2 c) no new effects appear, but the spectrum can be regarded as a superposition of the ones in Fig. 2 a and Fig. 2 b. Thus one can conclude that only one complex species is formed at pH = 2.

In a way, analogous to that used before, we take the strong band at 1045 cm^{-1} as a measure of the free concentration of H$_2$L. For a series of C_{H_3L}/C_B ratios we have then calculated [H$_2$L] and $\bar{n}'$ (Table 2). The results are given

Table 2. Semiquantitative estimation of $\bar{n}'$ from absorbance measurements at pH = 2.

Expt. No.	C_{H_3L} (M)	C_B (M)	A_{1045}	[H$_2$L] (M)	$\bar{n}'$
2 a	1.0	—	0.16$_0$	1.0	
2 b	0.5	1.0	0.03$_9$	0.25	0.25
2 c	1.0	0.25	0.12$_4$	0.77	0.9
2 d	0.75	0.5	0.07$_2$	0.45	0.6
2 e	1.0	0.5	0.10$_0$	0.62	0.8

graphically in Fig. 6. It can be seen that $\bar{n}'$ obtained in this way never exceeds 1 but seems to approach this value for large values of [H$_2$L]. This is an independent indication of the presence of only one complex, as well as a confirmation of our assignment of the 1045 cm^{-1} band as solely related to the free lactic acid, From the value of [H$_2$L] at which $\bar{n}' = 0.5$ one obtains (cf. eqn. 3) the value of $K_1 = \beta_1' = 2.5$ M^{-1}.

In order to reach conclusions on the structure of the complex it is now necessary to make assignments of the different absorption bands described above. From the similarity in position and appearance with the bands of the lactate ion the following bands can be rather safely assigned: The 1045 cm^{-1} band as the C — OH stretch, the 950 cm^{-1} and 970 cm^{-1} bands as B — O stretch (tetrahedral BO$_4$ unit), and the 1125 cm^{-1} one as the C — CH$_3$ stretch + CH$_3$ rocking. Furthermore, the band at 1395 cm^{-1} in the complex spectrum must correspond to ν_{sym} of a coordinated COO$^-$ group. This is interesting as it implies that complex formation occurs by the loss of the carboxylic proton. The composite pattern of the free lactic acid in the range 1200 — 1300 cm^{-1} can be ascribed to the low frequency band of COO stretch in free acids and the δ_{OH} (1235 cm^{-1}) of the same carboxylic group and it is in accordance with what has just been said, that these bands disappear on complex formation. Somewhere in this range also the δ_{OH} of the alcoholic OH group must be found and we suggest that the new band appearing at 1335 cm^{-1} in the spectrum of the complex is the δ_{OH} of that group when chelated. This shift is in the same direction as that suggested by Goulden [10] but not of such great magnitude. Actually, also Nakamoto and coworkers [18] assign the δ_{OH} in metal chelated to a very high frequency (1480 cm^{-1}). However, for the

complexes investigated, the OH-group is not known to have any acidic properties which is certainly the case for the OH-group in the present complex. Thus one might expect a much lower force constant and a lower frequency.

From these observations it is then possible to formulate the complex as

$$\left[\begin{array}{c} \text{HO} \diagdown \atop \text{HO} \diagup \text{B} \diagdown \overset{O}{\underset{O}{\diagdown}} \overset{\overset{H}{|}}{\underset{\underset{C}{|}}{C}} \overset{H}{\underset{O}{\diagup}} \overset{H}{\diagdown} \text{CH}_3 \\ \end{array} \right]$$

It can then be asked: what happens with the $C-O$ stretch band, present in the acid at 1045 cm^{-1}? From the observations [20] on metal ion glycolate complexes, e.g. that of Cu(II), one knows that this band is shifted to lower frequencies when the oxycarboxylate is chelated and that its intensity decreases. As this happens to a marked extent at the formation of the not too covalent $Cu^{2+}-O$ bond it must certainly happen to a much greater extent when the quite covalent $B-O$ bond is formed. That this bond is stronger — any way — follows from the increase of acidity of the OH group.

The splitting of the BO_4 band is also observed for this complex although it is not as pronounced as before. The effective symmetry of the BO_4 units seems to be C_{3v} also in this case, the oxygen atoms of the HO− and

$$\overset{H}{\underset{\diagup}{\diagdown}} \overset{}{\underset{C}{C}} O-$$

groups appearing more nearly equivalent than that of the carboxylate group. That it is really the boron-carboxylate interaction that causes the symmetry to deviate from pure T_d is beautifully illustrated in

Fig. 7. Graphical correlation of the frequency corresponding to the carboxylate symmetric stretching vibration (ν_{COO}) and the splitting of the band corresponding to the BO_4 asymmetric vibration $(\Delta\nu_{BO})$.

Fig. 7 where the decrease of the ν_{COO} frequency, which is a measure of the central atom-carboxylate interaction,[22] has been plotted against the splitting of the BO_4 band. It is seen that an almost perfect linear relation exists.

CHEMISTRY OF THE SYSTEM

With the structural information from the analysis of the spectra we can improve the eqns. (1 a) and (1 b) and write the following reaction formulae:

$$\beta_1' = 2.5 \ M^{-1} \tag{4}$$

$$\beta_1'' = 6 \ M^{-1} \tag{5}$$

$$\beta_2'' = 6 \ M^{-2} \quad pH = 6 \tag{6}$$

One may observe that the first two β-values are independent of pH, whereas the value of β_2'' is pH-dependent.

The true expression for the equilibrium constant, β_2, can be formulated as

$$\beta_2 = \beta_2'' \ [OH^-] \tag{7}$$

β_2 should then be of the order of $10^{-7} \ M^{-1}$.

Furthermore, by combining the expressions for β_1' and β_1'' with those for the acid dissociation constants of lactic acid, $K_{a\,L}$, and that of the acidic form (I) of the lactic acid-boric acid complex $K_{a\,BL}$ one obtains

$$K_{a\,BL} = \frac{[H^+]\ [II]}{[I]} = \frac{\beta_1''}{\beta_1'} \times K_{a\,L} \tag{8}$$

Introducing numerical values of β_1'' and β_1' from above and of $K_{a\,L} = 1.6 \times 10^{-4}$ M (valid at $I = 2$ M)[12] one obtains $K_{a\,BL} = 4 \times 10^{-4}$ M. This value can be compared with the constant K_1 given by Vermaas[4] for a series of similar α-oxyacids ($K_1 = 2 - 3 \times 10^{-3}$ M). However, Vermaas gives (in our present notation) the following formulation

$$K_1 = \frac{[H^+]\ [II]}{[HB]\ [H_2L]} \tag{9}$$

which may be rewritten as

$$K_1 = K_{a\,BL} \times \beta_1' \tag{10}$$

By taking the factor β_1' into account our value of K_1 ($K_1 \approx 10^{-3}$ M) seems to be somewhat lower than those given by Vermaas.[4] One must remember, however, that the two investigations have been made at different ionic strengths.

We have hoped, with this investigation, to show the potentialities of infrared spectroscopy in aqueous media.

REFERENCES

1. Pascal, P. *Nouveau Traité de Chimie Minerale*, Part VI (1961), p. 305.
2. Roy, G. L., Laferriere, A. L. and Edwards, J. O. *J. Inorg. Nucl. Chem.* **4** (1957) 106.
3. Böeseken, J. and Vermaas, N. *J. Phys. Chem.* **35** (1931) 1477.
4. Vermaas, N. *Rec. Trav. Chim.* **51** (1932) 955.
5. Kolthoff, I. M. *Rec. Trav. Chim.* **45** (1926) 607.
6. Hermans, P. H. *Z. anorg. allgem. Chem.* **142** (1925) 83.
7. Fornaseri, M. *Ric. Sci.* **21** (1951) No. 7.
8. Edwards, J. O., Morrison, G. C., Ross, V. G. and Schultz, J. W. *J. Am. Chem. Soc.* **77** (1955) 266.
9. Böeseken, J. and Mijs, J. A. *Rec. Trav. Chim.* **44** (1925) 758.
10. Goulden, J. D. S. *Spectrochim. Acta* **16** (1960) 715.
11. Jones, L. H. and Penneman, R. A. *J. Chem. Phys.* **22** (1954) 965.
12. Larsson, R. *Acta Chem. Scand.* **18** (1964) 1923.
13. Nunziata, G. and Larsson, R. *Acta Chem. Scand. To be published.*
14. Zachariasen, W. H. *Acta Cryst.* **7** (1954) 305.
15. Goulden, J. D. S. *Spectrochim. Acta* **9** (1959) 657.
16. Bjerrum, J. *Metal Amine Formation in Aqueous Solution*, (Diss.), Copenhagen 1941.
17. Suzuki, S., Oshima, T., Tamiya, N., Fukusima, K., Shimanouchi, T. and Mizushima, S. *Spectrochim. Acta* **11** (1959) 969.
18. Nakamoto, K., McCarthy, P. J. and Miniatas, B. *Spectrochim. Acta* **21** (1065) 379.
19. Leech, R. C., Powell, D. B. and Sheppard, N. *Spectrochim. Acta* **21** (1965) 559.
20. Larsson, R. *Acta Chem. Scand.* **19** (1965) 783.
21. Grenthe, I. *Acta Chem. Scand. To be published.*
22. Nakamoto, K., Morimoto, Y. and Martell, A. E. *J. Am. Chem. Soc.* **83** (1961) 4528.

Received December 24, 1969.