Studies of Oxovanadium(IV) Complexes

I. The Formation of Complexes of R-Lactate Ions in Solution

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The stepwise formation constants for the R-lactate oxovanadium(IV) system have been determined using circular dichroism measurements and spectrophotometry. The results obtained by the two independent techniques are in exellent agreement, giving the values $K_1 = 4.77 \times 10^2$ l mole^{-1} and $\beta_2 = 6.73 \times 10^4$ l^2 mole^{-2} in 1 M $Na(ClO_4 + CH_3CHOHCOO)$.

Very little quantative work has been reported concerning the complexing ability of vanadium(IV) in aqueous solution. Rossotti and Rossotti [1] have shown that oxovanadium(IV) exists as a monomeric aqua ion in the acid region 3 M > [H$^+$] > 0.002 M. In more basic solutions hydrolysis was found to occur and the potentiometric data obtained were explained by assuming the formation of only the two simple species $VO(OH)^+$ and $(VO)_2(OH)_2^{2+}$. From some of the results quoted in the literature dipositive oxovanadium(IV) ion resembles copper(II) in its coordination.[2-4] In this study of the oxovanadium(IV) lactate system, it was hoped not only to elucidate the equilibrium system, but also to demonstrate the usefulness of the circular dichroism measurements for such studies.

EXPERIMENTAL

"Fluka" purum grade R-lactic acid (33 % R, 7 % S isomer) solutions were used without further purification. A stock solution of the acid was prepared by dilution and standardized by titration with standard alkali.

A stock solution of approximately 0.1 M oxovanadium(IV) perchlorate in 0.1 M perchloric acid was prepared from reagent grade oxovanadium(IV) sulfate ("Fluka") by reducing any vanadium(V) with pure SO_2 gas, the excess SO_2 being removed by boiling the solution under nitrogen, and the sulfate precipitated with the stoichiometric amount of barium perchlorate ("Fluka" guaranteed pure grade). After filtration, the solution was shown to be free of both barium and sulfate ions by standard qualitative tests. The concentration of vanadium(IV) in the stock solution was found by

permanganate titrations, whilst the free acid was determined by potentiometric titra-
tions as described by Gran [5] ($\Delta V_{\text{NaOH}}/\Delta\text{pH} \to 0$ at equivalence point).

A stock solution of sodium perchlorate (5 M) was prepared from "Fluka" (guaranteed
pure reagent) crystalline reagent, and analysed by cation exchange.

The pH was measured with a Radiometer *PHM* 4, using a selected glass electrode
(Radiometer type *G* 202 *B*) in conjunction with a saturated KCl calomel electrode (con-
tact being obtained through a 1 M NH_4NO_3 salt bridge). The system was standardized
to measure hydrogen ion concentration by performing a standard acid-base titration
in 1 M NaClO_4.

In order to minimize errors due to hydrolysis and ionization of the complexed hy-
droxide group the absorption and circular dichroism measurements were performed at
a constant acid pH. Solutions of the appropriate concentrations of oxovanadium(IV)
perchlorate and lactic acid were adjusted to pH 3.0 with 1 M NaOH. The calculated
volume of 5 M NaClO_4 was then added (giving $C_{\text{NaClO}_4} + C_{\text{Nalact}} = 1.00$ M in the
final solution), and the solution was diluted to 50 ml. The final pH was adjusted to
3.320 with 1 M NaOH by means of a micro-syringe (volume of added alkali was always
less than 0.05 ml).

The pK_a of lactic acid was determined by glass electrode measurements on buffer
solutions fulfilling the condition $C_{\text{NaClO}_4} + C_{\text{Nalact}} = 1.00$ M.

Absorption spectra were recorded on a Cary 14 spectrophotometer, thermostated
at 20°. The circular dichroism spectra were measured on a Roussel-Jouan dichrograph
with extended wavelength scale. The accuracy and reproducibility of the dichrograph
was tested thoroughly beforehand. A "Lambert-Beer's" law was found to be valid
under conditions similar to those used in the present study.

RESULTS

The pK_a of lactic acid at 20° ($I = 1.00$) was found by glass electrode
measurements to be 3.626 ± 0.002 (root mean square error).

Stability constants for the lactato oxovanadium(IV) complexes were
determined by the method of corresponding solutions.[6] By definition, solutions
containing different total metal concentrations are corresponding when their
free ligand concentrations, and therefore their $\bar{n}$-values and the distributions
of the metal over the various complexes, are the same. This implies that the
value of any intensive property (*e.g.* absorption or circular dichroism) will
be the same per unit metal concentration. In this study, the compositions
of corresponding solutions for three total oxovanadium(IV) concentrations
($C_{\text{VO}}{}^a$, $C_{\text{VO}}{}^b$, $C_{\text{VO}}{}^c$) have been found from the plots of formal molar cir-
cular dichroism (and of formal molar absorption) *versus* total lactate con-
centration (C_{lact}) (see Fig. 1) by interpolations to $C_{lact}{}^a$, $C_{lact}{}^b$, and $C_{lact}{}^c$ for
various values of the intensive property. Values of $\bar{n}$ and [lact] were cal-
culated from the expressions

$$\bar{n} = (C_{lact}{}^a - ([\text{H}lact] + [lact]))/C_{\text{VO}}{}^a = (C_{lact}{}^b - ([\text{H}lact] + [lact]))/C_{lact}{}^b =$$
$$(C_{lact}{}^c - ([\text{H}lact] + [lact]))/C_{\text{VO}}{}^c$$

K_1 and β_2 were evaluated by a graphical method [7] based on the equation

$$\bar{n} = K_1(1 - \bar{n})\,[lact] + \beta_2\,(2 - \bar{n})\,[lact]^2 + ..$$

Preliminary experiments showed that the wavelength 580 nm was the most
sensitive, and hence was used throughout the work. However, absorption
and circular dichroism curves were recorded for the whole range 800—400 nm
and the results were checked at other wavelengths.

Table 1. The compositions of the measured solutions, the formal absorption coefficient, ε_f, and formal molar circular dichroism, $\Delta\varepsilon_f$.

C_{lact}(M)	C_{VO}(M)	ε_f	$\Delta\varepsilon_f \times 10^2$
0.00000	0.01144	3.94	—
0.01000	0.01144	5.68	4.41
0.01500	0.01144	6.32	6.34
0.02000	0.01144	7.06	7.74
0.02500	0.01144	7.54	8.80
0.03000	0.01144	8.00	9.70
0.03674	0.01144	8.39	10.64
0.04500	0.01144	8.80	11.49
0.05000	0.01144	8.92	11.75
0.05674	0.01144	9.13	12.06
0.07348	0.01144	9.56	12.64
0.09224	0.01144	9.91	13.24
0.1837	0.01144	10.72	14.16
0.01000	0.02288	4.96	2.94
0.02000	0.02288	6.00	5.57
0.02500	0.02288	6.54	6.50
0.03000	0.02288	6.93	7.40
0.03674	0.02288	7.53	8.69
0.04500	0.02288	8.08	10.00
0.05674	0.02288	8.59	11.10
0.07348	0.02288	9.14	12.00
0.09224	0.02288	9.61	12.72
0.1837	0.02288	10.64	13.93
0.01000	0.03432	4.69	2.05
0.02000	0.03432	5.43	3.89
0.03000	0.03432	6.18	5.94
0.04000	0.03432	6.90	7.64
0.06000	0.03432	8.07	9.95
0.0223	0.03432	9.18	12.24
0.1837	0.03432	10.46	13.53

The compositions of the measured solutions and the measured formal molar absorption and circular dichroism at 580 nm are given in Table 1 ($\varepsilon_f = D/(C_{VO} \times l)$ and $\Delta\varepsilon_f = \Delta D/(C_{VO} \times l)$), where D is the optical density, ΔD the circular dichroism in logarithmic units and l the cell lenght in cm).

In Fig. 1 the plot of $\Delta\varepsilon_f$ *versus* C_{lact} is shown in order to demonstrate the insignificant scattering in the experiments. In Fig. 2 the experimental points for the formation curve obtained by the two techniques are given as well as the curve calculated from the constants $K_1 = 4.77 \times 10^2$ and $\beta_2 = 6.73 \times 10^4$.

DISCUSSION

This work shows that the Roussel-Jouan dichrograph can be employed for accurate measurements of broad circular dichroism bands. In the above experiments the dichrograph has been used to determine the stepwise formation constants for the R-lactato oxovanadium(IV) complexes. The accuracy in the determination of the formation curve from circular dichroism measurements is comparable to that obtained from spectrophotometry over a large
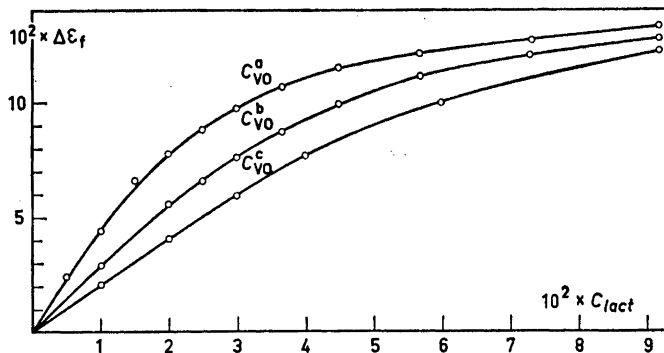
Fig. 1. Graphs of formal molar circular dichroism, $\Delta\varepsilon_f$, against total ligand concentration, C_{lact}, at three different total metal concentrations, $C_{VO}{}^a = 0.01144$ M, $C_{VO}{}^b = 0.02288$ M and $C_{VO}{}^c = 0.03432$ M.

range of $\bar{n}$ values as can be seen from Fig. 2. However, at low $\bar{n}$ values only the circular dichroism is sensitive to changes in the total ligand concentration, and therefore, this method gives better results in the range below $\bar{n} \simeq 0.2$.

The formation curve (Fig. 2) seems to tend towards $n = 2$. In contrast to the behaviour of the lactato copper(II) system [8] no decrease in circular dichroism with increase of [lact] has been observed, even up to [lact] = 0.5 M. If it is assumed that only chelated optical active ligands can transmit measurable Cotton effects to the d-d transitions in a 1:1 and planar 1:2 complex, then the decrease in the magnitude of a Cotton effect in the copper(II) case can be interpreted as a further uptake of ligands causing the concentration of chelated species to diminish. That this does not happen in the oxovanadium(IV) system may be due to higher values of the equilibrium constants of the type $K = [\text{M chel}]/[\text{M chel*}]$ (where [M chel*] denotes the concentration of the monodentate species) relative to the copper(II) system. The much higher circular dichroism of the oxovanadium(IV) complexes is in agreement with this.
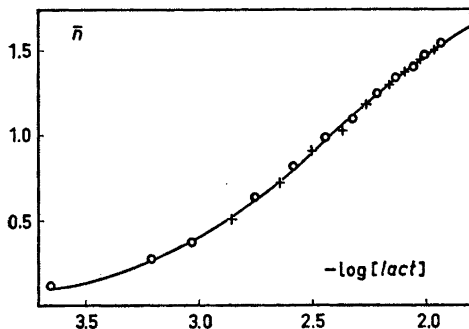

Fig. 2. The complex formation curve of the oxovanadium(IV) lactate system. Experimental points from circular dichroism measurements: O. Experimental points from absorption measurements: +. The full curve is calculated from the constants $K_1 = 4.77 \times 10^2$ l mole^{-1} and $\beta_2 = 6.73 \times 10^4$ l^2 mole^{-2}.

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