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Vanadyl(IV) Monocarboxylate Complexes in Aqueous Solution

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The complex formation of vanadyl(IV) with monochloroacetate, β-chloropropionate and glycolate ions has been studied by potentiometric $[H^+]$ *measurements in 1* M *$NaClO_4$ solution at 25 °C. On the basis of the data obtained, in a wide range of concentration of the ligands, it is concluded that the* VO^{++} *ion forms mononuclear successive complexes with a coordination number higher than 2. The relationship between the stability of the vanadyl complexes and the ligand basicity is discussed.*

Introduction

The literature data concerning the interaction of the VO^{++} ion with various simple monocarboxylic ligands in aqueous solution are few and disagreeing [1–5].

In a recent work [5] a possible correlation between the ligand basicity and the stability constant of the complexes was suggested.

As a further study on the complex formation equilibria between the VO^{++} ion and monocarboxylate ligands, in this paper we report the results of a potentiometric investigation on the vanadyl(IV) monochloroacetate,–β-chloropropionate, and –glycolate systems. The first two systems were studied in order to obtain a quantitative estimate of the complex-forming power of the VO^{++} ion as the ligand basicity is varied. The VO^{++}–glycolate system was instead studied in order to verify if the α-hydroxy group takes part in the formation of a chelate ring.

This investigation was carried out by potentiometric method in aqueous 1 *M* $NaClO_4$ solution at 25 °C.

Experimental

Chemicals

Solutions containing known $VO(ClO_4)_2$, $HClO_4$ and $NaClO_4$ amounts were prepared as described in ref. 6. Buffer solutions of the ligands were prepared with analytical grade reagents, purified by published methods [7].

Apparatus and Procedure

A glass electrode was employed for the determination of the hydrogen ion concentration in solutions obtained by adding known volumes of a solution S_1 to known volumes of solution S_2 where

$$S_1 = C^o_{NaL}\ M;\ C^o_{HL}\ M;\ 1.000\ M\ Na^+;\ \delta = C^o_{HL}/C^o_{NaL}$$

$$S_2 = C^o_M\ mM\ VO(ClO_4)_2;\ C^o_H\ mM\ HClO_4;\ 1.000 M\ Na^+$$

The buffer solutions, S_1, were prepared by partial neutralization of the acids with standard NaOH so that the sodium salt concentration was 0.500 *M* in the glycolate and β-chloropropionate buffers, 1.000 *M* in the monochloroacetate one.

The solutions S_1 containing β-chloropropionic or monochloroacetic acid were prepared immediately before use to avoid the presence of Cl^- that might be formed by hydrolysis.

In order to determine the protonation constants, K_H, of the acids, some titrations were carried out by adding the solution S_1 to a solution S_2 in which $C^o_M = C^o_H = 0$.

The experimental procedure for the determination of the H^+ ion concentration and the data treatment were as previously adopted [5].

Results and Discussion

The experimental results concerning the systems studied are reported in Fig. 1 as values of $\bar{n}$ *vs.* –log

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TABLE I. The log β_n Values of the Vanadyl(IV) Monocarboxylate Complexes.

Ligand	log K_H	log β_1	log β_2	log β_3
Acetate	4.61	1.86 ± 0.01	2.96 ± 0.02	
β-Chloropionate	3.89	1.54 ± 0.02	2.63 ± 0.07	3.20 ± 0.15
Glycolate	3.60	2.56 ± 0.01	4.22 ± 0.05	5.19 ± 0.07
Monochloroacetate	2.66	1.04 ± 0.04	1.60 ± 0.09	2.15 ± 0.15

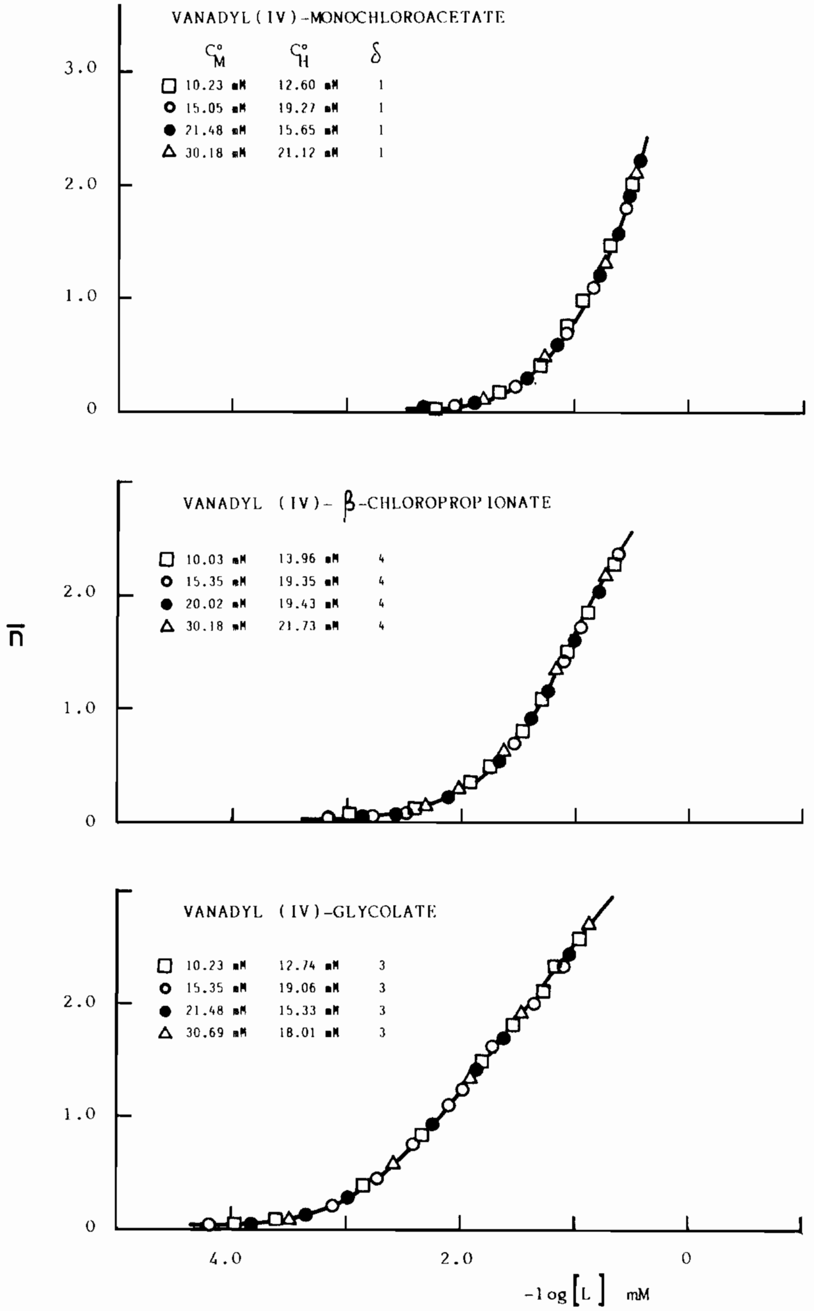

Fig. 1. The complex formation curves of the vanadyl(IV)– monocarboxylate systems. Full-drawn curve obtained from refined complexity constants.

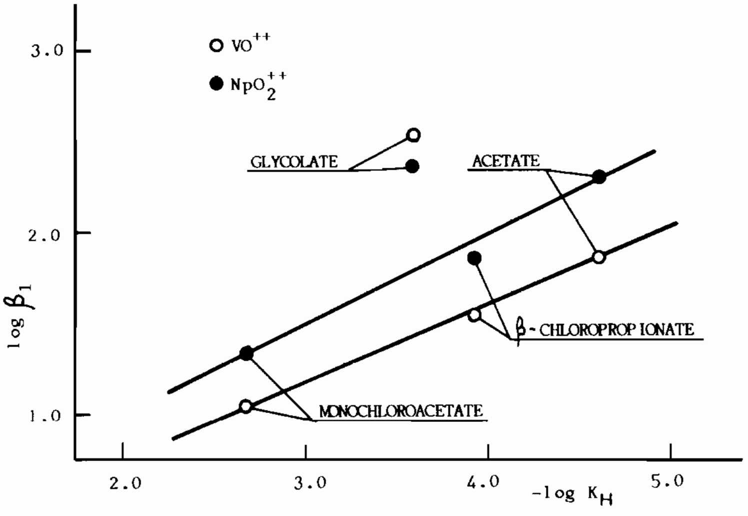

Fig. 2. Relationship between log β_1 for the vanadyl and the neptunyl complexes and log K_H for the monocarboxylic acid corresponding to the anionic ligand.

[L]. The various symbols relate to different C_M^o values in the range 10–30 m*M*. For a given [L] value, $\bar{n}$ is not dependent upon C_M^o and/or C_H^o; this indicates the formation of only mononuclear complexes. For all the systems values of $\bar{n} > 2$ are reached, so complexes with at least three ligands per metal ion are to be considered. In our previous paper concerning the vanadyl(IV)–acetate system, we have reported the formation constants for only two successive acetato complexes.

By applying Fronaeus' extrapolation method [8] to the related values of $\bar{n}$ and [L], the overall formation constants, β_n, for the successive equilibria:

$$VO^{++} + nL^- \rightleftharpoons [VOL]^{2-n}$$

(n = 1, 2, and 3; $L^- = CH_2ClCOO^-$, $CH_2ClCH_2COO^-$, CH_2OHCOO^-) were calculated. The stability constants obtained by this way were then refined by the least squares program Letagrop Vrid [9].

The refined stability constants are reported in Table I together with the values of log K_H of the corresponding carboxylic acids assessed at the same experimental conditions. The quoted errors correspond to three standard deviations. In Table I the known log β_n values for the vanadyl acetate complexes are also reported.

Our data for the vanadyl monochloroacetate system fairly agree well with those obtained by Dartiguenave *et al.* [2] under the same experimental conditions. This author reports the following values: log β_1 = 1.15; log β_2 = 1.78; log β_3 = 2.14. Moreover, also the K_H values are in good agreement with those previously determined [10].

From the results in Table I two main features may be pointed out:

a) the stability of monocarboxylate complexes increases with increasing donor ability of the carboxylate group;

b) the log β_n values for the formation of the vanadyl–glycolate complexes, which are much higher than expected considering the ligand basicity, indicate the formation of chelate species *via* the α-hydroxy group of the ligand.

As far as the first point is concerned, Fig. 2 shows plots of log β_1 of the vanadyl complexes *vs.* log K_H of the ligands. For the sake of comparison, in Fig. 2 are also reported the corresponding values for the formation of the analogous complexes of the NpO_2^{++} ion [11]. For both vanadyl- and neptunyl-monocarboxylato complexes a linear correlation is observed between log β_1 and log K_H in accordance with the 'a' character of the interacting ions [12]. Further, as a consequence of the lower effective charge on the metal atom in the VO^{++} ion [13], the stability constants of the unchelated complexes of neptunyl ion are higher than those of the vanadyl ones. On the contrary, the log β_n values for the formation of vanadyl-glycolate complexes are significantly higher than those for the neptunyl ones. In this connection, it may be of interest to note that also the UO_2^{++} [14] and PuO_2^{++} [15] ions form monocarboxylate complexes (their log β_1 increase linearly with log K_H) stronger than the vanadyl ones. But, while in the actinyl-glycolate complexes the differences (Δ log β_1) between the experimental log β_1 values and those expected from the linear relationship range between 0.5 and 0.6 log units, a greater difference is observed for the vanadyl complexes (Δ log β_1 = 1.14). A similar trend may be observed also for the formation of uranyl [14] and vanadyl [16] lactato complexes. These results clearly point out that the α-hydroxy group of these ligands play a greater role in the formation of the vanadyl chelate complexes. The lack of thermodynamic data about the formation of vanadyl carboxylato complexes does not allow to decide if this extra stabilization is entropic or enthalpic in character. We hope to elucidate this point in the next investigations.

Finally, the results in Fig. 2 indicate that the literature value for the stability constant of the vanadyl-formato complex [3], log β_1 = 1.98, seems to be too high considering the ligand basicity, log $K_H = 3.53$.

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