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Thermodynamics of Vanadyl(IV)–Carboxylate Complex Formation in Aqueous Solution

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Abstract

The stability constants and the heats of formation of vanadyl(IV)–acetate, –glycolate, and –glycine complexes have been determined in aqueous solution by means of potentiometric and calorimetric measurements. In the pH range where the protolitic equilibria of VO^{2+} is certainly negligible the acetate forms two mononuclear complexes, the glycolate three whereas the glycine reacts in its zwitterionic form. The stabilities of the glycolate complexes are considerably higher than the acetate ones, in spite of its lower basicity, indicating that the complex formation involves the coordination of the hydroxyl group to the metal ion. The enthalpy changes are positive except for the glycolate where a small negative value is found. For all systems the entropy changes are positive and therefore favourable to the complex formation.

Introduction

Over the past few years a number of papers dealing with the complex formation of the vanadyl(IV) ion, VO^{2+}, with a series of monocarboxylate ligands, in aqueous solution, has been published [1–7]. The data show that a linear relationship exists between $\log \beta_1$, stability constant of the first vanadyl(IV) complex, and $-\log K^{\mathrm{H}}$, the ligand basicity constant, that is, the vanadyl complex stabilities increase with the ligand basicities. Ligands containing, in addition to the carboxylate group, other groups which may coordinate the vanadyl(IV) ion, e.g. hydroxycarboxylate, do not fall on this line.

The simplest of such ligands, the glycolate, forms with VO^{2+} much stronger complexes than does acetate, in spite of its lower basicity. The larger stability of the glycolate complexes has been ascribed to formation of a chelate complex involving coordination of both carboxylic and hydroxyl groups to the metal ion [6b].

Special attention has been devoted to the nature of the complexes formed in water by VO^{2+} with glycine, a ligand containing, beside the carboxylic group, an amino group [8, 9]. Reliable data give evidence for the formation of a monodentate complex, $VOHGly^{2+}$, at least in the pH range where the protolytic equilibria of the metal ion are surely negligible, even though the value of the stability constant found, $K_1 = 2.88$, seems to be too small taking into account the ligand basicity.

However in spite of the large number of papers concerning the complexation of VO^{2+} in aqueous solution with carboxylate ligands, very little attention has been paid to the determination of the enthalpy and entropy functions for these systems, in addition to free energy data. This paper reports the thermodynamic functions for the complex formation between VO^{2+} and the ligands acetate, glycolate and glycine.

The purpose of this investigation was first to determine the complete thermodynamic functions for the systems given above, as they are not available in the literature. Secondly, from a comparison of the thermodynamic functions of the systems investigated it should also be possible to draw some conclusion on the nature of the complexes formed in solution.

The stability constants have been re-determined potentiometrically, the enthalpy changes by direct calorimetric titrations. The investigation has been performed at 25 °C and in a medium of unit ionic strength with $NaClO_4$ as supplementary electrolyte.

Experimental

Chemicals

The chemicals used were all of analytical grade. The stock solution of vanadium(IV) perchlorate was

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prepared and standardized according to Rossotti [10]. Acetic acid (Fluka) was used without further purification. Commercially available glycine (Baker analyzed reagent) was recrystallized from water–methanol mixture, washed with methanol and ether and finally dried at 110 °C for several hours. Glycolic acid (Merck) was recrystallized from ether and dried under vacuum. $NaClO_4$ (Merck) was recrystallized from water. The concentration of the stock solution was determined by titrating the eluant from an Amberlite IR 120 ion exchange resin with standard NaOH solution.

The acetate and glycolate buffers were prepared by neutralizing exactly the appropriate amounts of acetic and glycolic acid respectively with NaOH solution, to the required $\delta = C_{HL}/C_{NaL}$. The glycine buffer was prepared by adding perchloric acid to a glycine solution to the appropriate H_2L^+/HL ratio.

Potentiometric Measurements

The galvanic cell and the experimental procedure have been described previously [6a]. A PHM 84 Radiometer was used for e.m.f. measurements. The titration vessel was equipped with a selected glass electrode Jena H 112 Thalamid and a double junction Ag/AgCl reference electrode Metrohm EA 440.

The titrations were performed by adding known volumes of ligand of $\delta = 4$ for acetate, $\delta = 2$ for glycolate and $\delta = 0.2$ for glycine, to vanadyl(IV) perchlorate solutions of known concentration C_M°. For each system at least three titration series were performed with C_M° varying from 5 to 40 mM. The pHs of the solutions during the titrations never exceeded 3 in order to prevent the hydrolysis of VO^{2+}.

The least-square programs MINIQUAD [11] and EMK [12] were used for the calculation of the stability constants, β_j, of the vanadyl(IV) complexes.

Calorimetric Measurements

For the calorimetric measurements an LKB 8721-2 Precision Calorimeter was used. The measurement technique has been described previously [13]. All the experiments were carried out at 25.000 ± 0.001 °C.

For each system investigated at least three titration series were performed and each series was repeated at least once. The heat changes for the complex formation were corrected for the heats of dilution of the ligands solutions, determined separately.

The heat of dilution of the vanadyl(IV) perchlorate solutions was found to be negligible in the metal concentration range used here. The enthalpy changes for the metal ion complexes were calculated using the least-squares program LETAGROP KALLE [14].

Results and Discussion

The thermodynamic functions for the protonation of the ligands have been determined previously [13, 15, 16]. For the VO^{2+}–acetate system, steady potentials were obtained only in the early stages of the titrations. For $\bar{n} \geqslant 1.5$, the titrations had to be interrupted, though the complex formation curve was still steeply rising, as no steady values could be obtained any longer. As the pH of the solutions at this step of the titrations was higher than 3, the e.m.f. drift was evidently due to hydrolytic reaction of the metal ion. No complexes beyond the second one could therefore be found for this system, thus confirming the results of previous investigations with acetate and other ligands of similar basicities [6, 7].

For the vanadyl(IV)–glycolate system, the experimental data are consistent with the formation of three mononuclear complexes. The equilibrium data for the VO^{2+}–glycine system were analyzed on the assumption that, in the pH range investigated, the ligand exists mainly as a zwitterionic species $H_3N^+–CH_2–COO^-$, HL [9, 16]. The data were consistent with this assumption and two mononuclear complexes, $VO(HL)^{2+}$ and $VO(HL)_2{}^{2+}$, were found. A preliminary evaluation of the stability constants, β_j, was performed by a graphical method [17]: the values thus obtained were then refined by means of the computer programs described above [11, 12]. The final values are collected in Table I. For the vanadyl(IV)–acetate and –glycolate systems our values of β_j agree quite well with those reported by other authors [16]. For the glycine complexes, on the other hand, the values of β_j reported by Tomiyasu and Gordon are lower than ours, which may be due both to the difference in ionic medium and different measurement techniques used [9].

The calorimetric data are reported as Δh_v, the total molar enthalpy changes, *versus* $\bar{n}$ in Fig. 1. The Δh_v functions are independent of C_M° which indicates that no polynuclear complexes are formed. Also the assumption that the glycine is mainly in the zwitterionic form is confirmed by the calorimetric data. From the values of ΔG_j° and ΔH_j°, the entropy changes ΔS_j° were determined. The final values of the thermodynamic parameters for the three systems investigated are listed in Table I: the errors given correspond to three standard deviations. As seen the formation of the vanadyl(IV) complexes is mainly due to a large gain in entropy. The trend observed is the one expected for interactions between typically hard acceptors and donors where the complex formation is exclusively or mainly due to a more or less huge gain in entropy whereas the enthalpy values are usually endothermic. For the VO^{2+}–acetate system the entropy term decreases smoothly from step to step, indicating a stepwise displacement of water molecules from the metal ion by the anionic ligand

TABLE I. Overall Stability Constants and Thermodynamic Functions for the Formation of Vanadyl(IV) and Uranyl(VI) Carboxylates at 25 °C in a 1 mol dm^{-3} Sodium Perchlorate Medium[a]

Ligand	Vanadyl(IV)					Uranyl(VI)[b]			
	j	log β_j	$-\Delta G_j^\circ$	ΔH_j°	ΔS_j°	log β_j	$-\Delta G_j^\circ$	ΔH_j°	ΔS_j°
$CH_3–COO^-$	1	1.97 ± 0.02	11.24 ± 0.10	10.42 ± 0.12	73 ± 1	2.46 ± 0.01	14.02 ± 0.04	11.84 ± 0.12	87 ± 1
pK_a = 4.61	2	3.46 ± 0.02	19.74 ± 0.10	19.33 ± 0.12	131 ± 1	4.38 ± 0.02	24.98 ± 0.08	17.91 ± 0.32	144 ± 1
	3	–	–	–	–	6.52 ± 0.03	37.19 ± 0.12	16.69 ± 0.40	181 ± 2
$HO–CH_2–COO^-$	1	2.56 ± 0.01	14.60 ± 0.06	−0.59 ± 0.12	47 ± 1	2.35 ± 0.01	13.43 ± 0.08	5.40 ± 0.16	63 ± 1
pK_a = 3.61	2	4.22 ± 0.02	24.07 ± 0.11	6.40 ± 0.24	102 ± 1	3.97 ± 0.04	22.68 ± 0.24	12.93 ± 0.40	119 ± 2
	3	5.19 ± 0.02	29.61 ± 0.12	4.39 ± 0.36	114 ± 2	5.17 ± 0.05	29.50 ± 0.50	12.13 ± 0.75	140 ± 4
$H_3\overset{+}{N}–CH_2–COO^-$	1	1.06 ± 0.09	6.05 ± 0.50	4.51 ± 0.25	35 ± 3	1.16 ± 0.01	6.62 ± 0.05	3.9 ± 0.2	35.3
pK_a = 2.46	2	2.25 ± 0.15	12.84 ± 0.86	3.50 ± 0.70	55 ± 5	2.20 ± 0.04	12.55 ± 0.23	4.8 ± 0.5	58.3

[a] ΔG_j° and ΔH_j° in KJ mol^{-1}; ΔS_j° in J mol^{-1} K^{-1}. [b] Refs. 15 and 16.

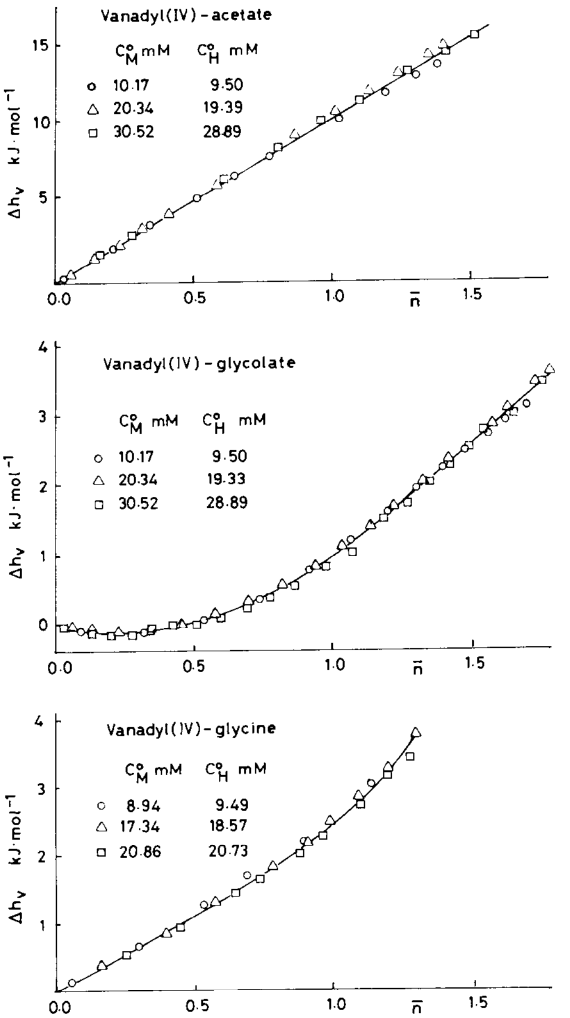

Fig. 1. The total molar enthalpy charges, Δh_v, as a function of $\bar{n}$. The fulldrawn lines have been calculated from the values of β_j and ΔH_j° reported in Table I.

with a corresponding decrease of order accompanying the lowering of the charge on the metal ion [18].

The stabilities of the complexes with glycolate are much higher than the acetate ones. The large increase in the β_1 value for the glycolate complexes is surely due to the formation of a chelate ring, as confirmed by the negative and therefore favourable value of ΔH_1° and the less favourable entropic term ΔS_1°. Also the second complex, ML_2, is likely a chelate one: the endothermic value of ΔH_2° and the slightly favourable value of ΔS_2° are consistent with a rearrangement, occurring at this step of complexation, of the ligands around the central metal ion accompanied by a contemporaneous weakening of the bonds between the cation and the hydroxyl group. Presumably also the saturated complex, ML_3^-, is a chelate one, though to a lesser extent than the first and the second one.

As for the glycine complexes, we might expect that the ΔH_j° values would become less positive on account of the lower basicity of the ligand as compared with acetate, which is the case. Yet a lower value of ΔS_1° is to be expected as no change of the charge of the metal ion occurs if we take into account that, as mentioned above, the ligand exists in the form of a zwitterion. In this case the complexes have the same charge as the free metal ion and, as a consequence, a minor solvent translational entropy is to be expected when the complexes are formed. For comparison in Table I the values of the thermodynamic functions for the actinide 'yl' ion, UO_2^{2+}, with the same ligands, in the same experimental conditions are also reported.

The acetate and glycine complexes of UO_2^{2+} are somewhat stronger than the corresponding VO^{2+} complexes. This is because for either cation the complex formation is prevalently governed by electrostatic forces and the effective charge on the uranyl(VI) ion is much higher than on the vanadyl(IV) ion. From IR measurements Larsson [19, 20] has in fact inferred that the effective charge is +4 on the uranium and +2.4 on the vanadium atom. For the glycolate complexes the opposite occurs, *i.e.* the vanadyl(IV) complexes are stronger than the uranyl(VI) ones. This likely reflects a higher inner sphere nature of the vanadyl(IV) complexes relative to the uranyl(VI) ones, where the chelation occurs via a water molecule [15].

Supplementary Material

The potentiometric data for the systems investigated are available from R.P.

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