Redox Potentials of Vanadium-containing Couples. Part 3.[1] The Formal Redox Potential of the V^{3+}–V^{2+} Couple

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A method for the chemical and electrochemical preparation of mixtures of vanadium-(III) and -(II) in 1 mol dm^{-3} (H^+, Na^+) Cl^- aqueous solutions has been elaborated. The concentration of each ion can be determined under nitrogen in a completely closed system comprised essentially of a spectrophotometric cuvette and a junction-free cell containing mercury and glass electrodes. By changing the vanadium ion concentrations in 'titrations' of different kinds and by measuring the electromotive force of the galvanic cell the formal redox potential of the V^{III}–V^{II} couple has been deduced. Its value at 298 K against the normal hydrogen half cell and in 1 mol dm^{-3} (H^+, Na^+)Cl^- is −242 ± 2 mV over a large range of V^{3+}/V^{2+} ratio and of total vanadium concentration. Using the specific interaction theory (s.i.t.) approach the standard redox potential is estimated to be −196 mV. The methodology reported seems to be appropriate for studying the solution chemistry of the rather oxidizable V^{2+} ion.

In previous studies we determined the formal redox potentials of the half cells $VO_2^+ + e^- + 2H^+ \rightleftharpoons VO^{2+} + H_2O$ and $VO^{2+} + e^- + 2H^+ \rightleftharpoons V^{3+} + H_2O$ at 25 °C and in 1 mol dm^{-3} aqueous chloride solutions.[1,2] In the present paper we report an attempt to measure, along similar lines, the redox potential of the half-cell reaction $V^{3+} + e^- \rightleftharpoons V^{2+}$ under similar conditions of temperature and ionic medium.

After the pioneer investigations of Rutter,[3] Abegg *et al.*,[4] Drucker,[5] Gerke,[6] Foerster and Böttcher[7] (whose value of −0.200 V is reported by Latimer[8]), Jones and Colvin[9] carried out the most extensive investigation concerning the redox potential of this couple. They used the cell $Hg|V_2(SO_4)_3, VSO_4, H_2SO_4|H_2SO_4, Hg_2SO_4(s)|Hg$ (A) in a series of experiments at different constant concentrations of H_2SO_4, keeping the V^{3+}/V^{2+} ratio around 1 : 1 in the 5–141 mmol dm^{-3} total vanadium range. They had to take special precautions to prepare solid vanadium(II) sulfate ($VSO_4\cdot 7H_2O$) and transfer it to the measurement cell owing to its ease of oxygen absorption. The most serious difficulty was the decomposition of V^{2+} taking place in aqueous solution according to the reaction $2V^{2+} + 2H^+ \rightleftharpoons 2V^{3+} + H_2$. In the absence of any catalyst and at room temperature, this reaction does not occur at a significant speed, but it does rapidly in the presence of platinum. For this reason the authors used mercury as an electrode[10] in a form which allowed them to renew the electrode surface by dropping mercury at will.[9] Over the fresh surface, potentials were higher than over the aged one. The authors believed these values to be the nearest to the true reversible potentials. The drift of the 'best' potential values, when measurements were prolonged for several hours, could be corrected only partially by removing portions of the solution from the cell and analysing them to obtain the instantaneous contents of V^{2+} and V^{3+} in the measurement cell. From the electromotive force values of cell (A) together with Harned and Hamer's data[11] on the cell $Pt(H_2)|H_2SO_4|Hg_2SO_4, Hg$ (B), using the proper extrapolations, Colvin and Jones succeeded in determining the standard potential of the V^{3+}–V^{2+} half cell as −0.255 V at 25 °C and −0.265 V at 0 °C.

Method of Investigation

In order to minimize the changes in activity factors,[12] all the test solutions in the present investigation were made 1 mol dm^{-3} in chloride ion.[1,2] Moreover, to avoid hydrolysis effects of the rather acidic V^{3+} ion,[13,14] a concentration of 0.6–0.7 mol dm^{-3} HCl was used thoroughout;[2] under these conditions hydrolysis of V^{2+} is negligible.[15]

Experiments were carried out in a multinecked vessel, equipped with hydrogen and glass electrodes. In the vessel a solution of V^{3+} was prepared by hydrogen reduction of an aqueous suspension of a weighed amount of V_2O_5 in a NaCl–HCl mixture successively over a bright platinum net (reduction to VO^{2+}) and then a platinum black net (reduction to V^{3+}).[2] The reduction was usually carried out overnight, but for more concentrated solutions a few days were required. The resulting solution, indicated as S_3, had the accurately known composition S_3, *i.e.* $C_3V^{3+}, h_0H^+, (1 - 3C_3 - h_0)Na^+$, 1 mol dm^{-3} Cl^-. Half the volume of this solution (usually 50 cm^3) was left in the vessel and became part of the cell Pt,H_2(1 atm, *ca.* 10^5 Pa) $|S_3|$GE (C) where GE = glass electrode. The remaining part was carefully transferred to a burette and kept under nitrogen. The electromotive force E_C of cell (C) was measured and taken as equal to E°_{GE} which, at a defined temperature (25 °C) and for each experiment lasting about 12 h can be considered as the formal potential of the glass electrode. Once E°_{GE} had been determined the stream of H_2 in the vessel was switched off and the solution saturated by bubbling purified nitrogen for the remaining part of the experiment. Redistilled mercury was then introduced at the bottom of the vessel, electrically connected to a constant-current power supply together with an external counter electrode, (Na^+, H^+)Cl^-, 1 mol dm^{-3} |NaCl, 1 mol dm^{-3}| AgCl(s), Ag, setting up the electrolysis system of Fig. 1). In this way the coulometric generation of V^{2+} was started by changing solution S_3 to S_{32}, *i.e.* C_3V^{3+}, c_2V^{2+}, hH^+, $(1 - 3C_3 - 2C_2 - h)$ Na^+, 1 mol dm^{-3} Cl^-. The vessel also contained a renewable mercury electrode of the type reported in ref. 16, to get up the cell $Hg|S_{32}|$glass electrode (D) the electromotive force of which was continuously monitored. The passage of a constant current i in the electrolysis cell was allowed for a total time t, usually overnight, to a nearly constant value of E_D which depended on the total vanadium content.

Since the electrolysis yield of V^{2+} is less than 100% (gaseous H_2 being the other electrode product), C_3, C_2 and h had to be determined as follows. Switching off the current, the electromotive force of the cell (D) was carefully measured. A small portion of solution S_{32} was then sucked by means of a tight

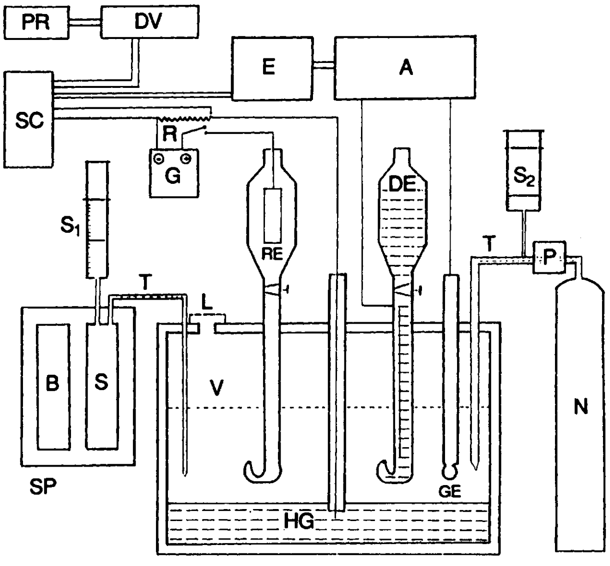

Fig. 1 The experimental set-up to generate, analyse S_{32} solutions and measure E_D values: V = vessel; HG = mercury cathode with electrical contact; GE = glass electrode; DE = dropping electrode; RE = external electrolysis anode; SP = spectrophotometer; B = blank cuvette; S = sample cuvette; S_1, S_2 plastic syringes; T = plastic tube; N = nitrogen tank; P = purification train; G = power supply; R = calibrated resistance; SC = scanner; PR = printer; DV = digital voltmeter; E = electrometer; A = amplifier; L = liquid valve

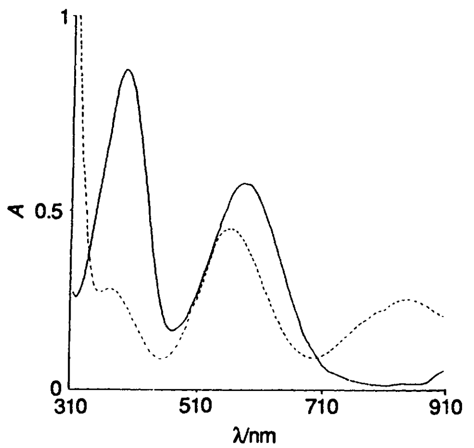

Fig. 2 The UV/VIS spectra of solutions S_3 (——, $[V^{3+}] = 20$ mmol dm^{-3}) and S_{32} (- - - -, $[V^{3+}] = 5.5$ and $[V^{2+}] = 14.5$ mmol dm^{-3}); optical path = 5 cm

plastic syringe S_1 and plastic tubes T from the vessel directly into a *d* cm long flow cuvette S located in the optical path of an UV/VIS spectrophotometer SP (Fig. 1). This allowed us to obtain the spectra of the S_{32} solutions under nitrogen. A typical example, together with the spectrum of solution S_3 ref. 2) is shown in Fig. 2. In particular the absorbance *A* of solution S_{32} was carefully measured at 400 nm where practically only V^{3+} absorbs[13] and at 845 nm[17] where only V^{2+} does. The ε value at 400 nm (8.6 ± 0.2 dm^3 mol^{-1} cm^{-1}) allowed us to measure C_3 (the concentration of V^{3+} in mol dm^{-3}) and, from the total vanadium content, the V^{2+} concentration, C_2, was obtained.

After the absorbance measurements, a small portion of solution S_{32} was pushed from the optical cell back into the vessel by syringe S_1 and the electromotive force was measured again. No difference higher than 0.1–0.2 mV was found between the two measurements and the average value was assumed as the final E_D value. From $E_D = E°_{GE} - E°_V - 59.2 \log [C_3/(C_2h)]$, the formal redox potential of the couple V^{III}–V^{II}, $E°_V$, could be calculated since all the terms including $h = h_0 - [(it/96487) - C_2]$ are known. When the first $E°_V$ value was obtained, the S_{32} composition was changed by adding to the cell measured volumes of the original solution S_3. The change in concentrations of V^{2+}, V^{3+} and H^+ following each addition resulted in a variation in E_D. After having measured E_D the concentration changes were monitored spectrophotometrically as before. Sending back the solution S_{32} from the spectrophotometer cuvette to the measurement cell and recording an additional E_D value completed the task of obtaining a new value of $E°_V$. The potential of the mercury pool was sometimes measured against the flowing mercury electrode. It never differed by more than 1 mV.

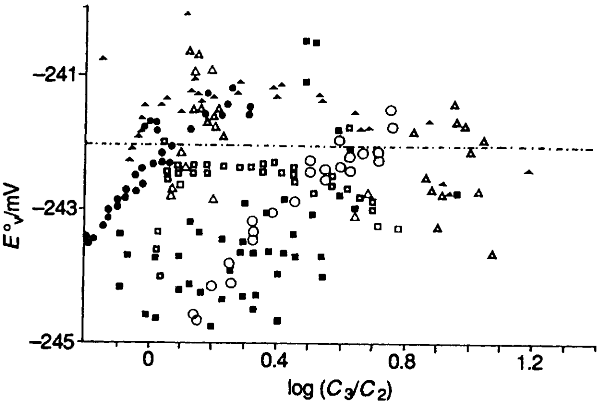

Fig. 3 Plot of $E°_V$ against log C_3/C_2 vanadium concentrations ($C_3 + C_2$) in mmol dm^{-3}: oxygen titrations, 23.6 (▲); water decomposition, 18.1 (■), 23.6 (△); volumetric titrations, 51.6 (●), 59.8 (□), 95.2 (○)

In another modification of the experiments a special type of titration was carried out by stepwise admission of oxygen into the nitrogen gas stream, from a second plastic syringe S_2, piercing the plastic tubes carrying nitrogen from the tank to the measurement vessel. The change in V^{2+}, V^{3+} and H^+ according to the reaction $2V^{2+} + \frac{1}{2}O_2 + 2H^+ \rightleftharpoons H_2O + 2V^{3+}$ resulted in a change in E_D. The concentration changes in S_{32} were monitored spectrophotometrically as before. In the most dilute vanadium solutions it was not necessary to introduce any oxygen, since the continuous slow spontaneous decomposition of V^{2+} by water was enough to give a spectrophotometrically measurable change in the concentrations of V^{3+}, V^{2+} and H^+.

Results and Discussion

The primary data and the calculated values for each step of a typical titration are in Table 1. The constancy of $A_{845}/dC_2 = \varepsilon_{845} = 3.3 \pm 0.3$ dm^3 mol^{-1} cm^{-1}, the molar absorption coefficient of V^{2+} at 845 nm, demonstrates that the approach utilized to estimate C_3, C_2 and *h* is appropriate. These data together with $E°_{GE}$ and E_D allow $E°_V$ to be calculated (see last column of Table 1). The average value of the $E°_V$ in this titration is −242 ± 1 mV. Considering the rather unstable nature of the solutions containing V^{2+}, the $E°_V$ values obtained in the present titration exhibit a quite good degree of constancy and no particular trend when the C_3/C_2 ratio changes by more than a power of ten with a corresponding change in E_D of about 60 mV. The $E°_V$ values obtained for each titration are plotted against $\log (C_3/C_2)$ in Fig. 3. The dotted line represents the grand average value −242 mV. Aside from the different ways of carrying out the final titrations (oxygen titrations, water decomposition, volumetric titrations), the points are crowded around it, with no more than a slight trend of the $E°$ values as $\log (C_3/C_2)$ is changed over about 1.5 logarithmic units, the total vanadium between 18 and 95 mmol dm^{-3}, the concentration of V^{3+} between 8 and 95 mmol dm^{-3} and the concentration of V^{2+} in the range 10–50 mmol dm^{-3}. The mean deviation of the grand average, ±2 mV, is large enough to encompass most of the 310 experimental $E°_V$ values.

Table 1 Experimental data calculated values for each step of a typical filtration

E_D/mV	A_{845}	A_{400}	$10^3\ C_3$	$10^3\ C_2$	$10^3\ h$	ε_{845}/dm^3 mol^{-1} cm^{-1}	$E°_V$/mV
			mmol dm^{-3}				
840.5	0.187	0.536	12.5	11.1	592	3.4	−242.6
839.8	0.187	0.545	12.7	10.9	592	3.4	−242.8
839.2	0.185	0.550	12.8	10.8	592	3.4	−242.7
838.7	0.181	0.553	12.9	10.7	592	3.4	−242.5
838.1	0.179	0.557	13.0	10.6	592	3.4	−242.3
837.8	0.178	0.560	13.0	10.6	592	3.4	−242.3
837.1	0.176	0.565	13.2	10.5	592	3.4	−242.2
836.9	0.175	0.569	13.3	10.4	591	3.4	−242.4
835.6	0.171	0.576	13.4	10.2	591	3.4	−241.8
834.0	0.170	0.580	13.5	10.1	591	3.4	−240.6
834.5	0.168	0.584	13.6	10.0	591	3.4	−241.5
833.9	0.166	0.587	13.7	9.9	591	3.3	−241.3
833.5	0.166	0.588	13.7	9.9	591	3.3	−241.0
832.7	0.165	0.593	13.8	9.8	591	3.4	−240.7
833.0	0.161	0.596	13.9	9.7	591	3.3	−241.3
832.8	0.161	0.600	14.0	9.6	591	3.3	−241.5
832.3	0.159	0.605	14.1	9.5	591	3.3	−241.6
832.0	0.157	0.620	14.5	9.2	590	3.4	−242.9
831.5	0.156	0.614	14.3	9.3	590	3.3	−241.7
830.4	0.154	0.617	14.4	9.2	590	3.3	−240.9
830.7	0.153	0.622	14.5	9.1	590	3.3	−241.8
830.2	0.151	0.625	14.6	9.1	590	3.3	−241.6
829.7	0.150	0.629	14.7	9.0	590	3.3	−241.5
829.3	0.148	0.633	14.8	8.9	590	3.3	−241.6
829.1	0.146	0.638	14.9	8.8	590	3.3	−241.9
802.1	0.084	0.825	19.2	4.4	585	3.8	−239.4
805.8	0.084	0.825	19.2	4.4	585	3.8	−243.1
804.3	0.080	0.832	19.4	4.2	585	3.8	−242.8
803.6	0.076	0.836	19.5	4.1	585	3.7	−242.8
794.0	0.056	0.880	20.5	3.1	584	3.6	−241.8
792.4	0.053	0.890	20.7	2.9	584	3.7	−242.5
791.6	0.051	0.894	20.8	2.8	584	3.6	−242.7
790.9	0.049	0.899	20.9	2.7	584	3.7	−243.2
789.4	0.048	0.903	21.0	2.6	584	3.7	−242.8
788.6	0.046	0.906	21.1	2.5	584	3.7	−242.8
785.9	0.045	0.911	21.2	2.4	583	3.7	−241.4
786.7	0.043	0.913	21.3	2.3	583	3.7	−242.8
785.6	0.042	0.913	21.3	2.3	583	3.6	−241.7
784.5	0.040	0.917	21.4	2.2	583	3.6	−241.7
783.7	0.039	0.921	21.5	2.2	583	3.5	−242.2
782.7	0.037	0.926	21.6	2.0	583	3.6	−242.7
781.3	0.036	0.928	21.6	2.0	583	3.6	−242.0

S_3 = 23.6 mmol dm^{-3} V^{3+}, $h°_3$ = 621 mmol dm^{-3}, [Na$^+$] = 308 mmol dm^{-3}, [Cl$^-$] = 1.0 mol dm^{-3}, $E°_{GE}$ = 614.3 mV, d = 5 cm, i = 10 mA and t = 3.8740 × 10^4 s.

Table 2 Formal redox potentials of vanadium containing couples in 1 mol dm^{-3} Co$^-$ solutions

	$E°$/mV	Ref.
$VO_2^+ + e^- + 2H^+ \rightleftharpoons VO^{2+} + H_2O$	1016 ± 2	1
$VO^{2+} + e^- + 2H^+ \rightleftharpoons V^{3+} + H_2O$	309 ± 2	2
$V^{3+} + e^- \rightleftharpoons V^{2+}$	−242 ± 2	This work

We believe that the success in achieving these results is due to the integrated method which was particularly developed for the redox equilibria studies of vanadium-containing species in acidic solution.[1,2] The completely closed system in which the preparation and analysis of all the solutions have been done and the proper set up of free junction cells to acquire potentiometric data from which one can derive the $E°_V$ values is proposed as a methodology useful for systems which, as in the series VO_2^+, VO^{2+}, V^{3+}, V^{2+}, cover a large range of redox potentials in water (Table 2).

Moreover we consider this approach particularly suited for studying solution chemistry of V^{2+}. In this connection the spectrum obtained for solution S_{32} (Fig. 2) allows one to calculate values of the molar absorption coefficient ε for V^{2+} more reliable than those reported before. In particular, at the wavelength of the maximum (λ = 845 nm) the value (3.3 dm^3 mol^{-1} cm^{-1}) reported here is higher than the highest (0.45 dm^3 mol^{-1} cm^{-1}) of the literature values[17] and in better agreement with the typical ε values of the d–d transition bands.[18]

Finally, we think it might be of interest to calculate the standard redox potential, $E°$ from the $E°_V$ measured in 1 mol dm^{-3} Cl$^-$. The two are connected through the expression $E°_V = E° + 59.16 \log f_3/(f_2 f_{H^+})$ where f_3, f_2 *and* f_{H^+} are the molar activity coefficients of V^{3+}, V^{2+} and H^+. By means of the specific interaction theory (s.i.t) approach[19] we can estimate the required f values and thus $E°$ = −196 mV. It is quite likely that the difference between our value at 1 mol dm^{-3} (H$^+$, Na$^+$)Cl$^-$, that measured by Jones and Colvin at infinite dilution in sulfate solutions and that calculated by the s.i.t. approach are determined by complex formation[13,15] stronger for V^{3+} than for V^{2+}, stronger for sulfate than for chloride, rather than by long-range electrostatic factors.

Experimental

The previous methods[1,2] were carefully followed to obtain V_2O_5, HCl, NaCl and water used as starting materials to prepare all the solutions S_3 analysed, when necessary, according to standard methods.[20]

The reaction vessel was a seven-necked flask, accommodating a glass electrode, a flowing type mercury electrode,[16] the platinum connection to the mercury pool cathode, a glass bubbler for H_2 or N_2, the bridge to the electrolytic half cell and a gas outlet to a liquid valve.

In the reduction of V^{3+} to V^{2+} direct current was delivered by an Hewlett-Packard HP6186C power supply. The current intensity never exceeded 10 mA. The number of Faradays passed was accurately determined by measuring the potential drop on a calibrated resistance R in series with the electrolytic cell. The electrolysis time, always greater than 12 h, was measured by a Danhart watchclock which was accurate to 0.3 s. The electrolysis yield was usually 60–70%.

The absorbance measurements were taken by a JASCO UV/VIS model Uvidec 610 spectrophotometer using Hellma quartz cuvettes of different (1–5 cm) length against a blank containing the ionic medium.

Gases (N_2 or H_2) were taken from cylinders and freed from oxygen by passing them through a solution train containing vanadous salt[20] VCl_2, distilled water, 1 mol dm^{-3} NaCl–HCl. In the last stage of the purification the gas stream was led through a sintered glass filter of porosity G3 to remove floating dust.

Mercury was purified by double distillation under water-pump vacuum. Dust and other impurities, gathering on storage on the surface, were eliminated by filtration through sintered glass immediately before use.

Ingold glass electrodes were used throughout this work. Their E°_{GE} values measured against the hydrogen half cell were constant (± 2 mV) over many months.

The flowing type mercury electrode was made as reported.[16] After dropping, it was necessary to wait about 1 min to read the highest potential value. Hydrogen electrodes were prepared according to ref. 21. Precautions concerning their use, hydrogen purification, humidification and pressure measurements were taken according to ref. 22.

Electromotive force measurements of the cells were carried out by means of a Cary 401 electrometer from Varian Instruments. Its output was connected to an automatic Hewlett-Packard 3421A data-acquisition system which consisted of a scanner, voltmeter, printer, model 41 CV minicomputer and an appropriate interface. The values obtained were estimated with a resolution of 0.1 mV. The accuracy was essentially of the same order of magnitude, as verified by use of standards.

A water-bath, equipped with a Julabo model VL/1 system, ensured good stirring and a temperature of 298 ± 0.1 K, as measured by a calibrated digital thermometer (Systemteknik AB 1320 Series).

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