

Differential Pulse Polarographic Determination of Vanadium(V) using Catalytic current in the Presence of Bromate

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A method for the determination of trace levels of vanadium(V) using differential pulse polarography (DPP) is described. The method is based on the catalytic current of vanadium(V) obtained in the presence of sodium bromate. Experimental conditions such as pH and the composition of supporting electrolyte were optimized to get a linear calibration graph. The effect of several cations and anions on the catalytic current was investigated. The relative standard deviation (from 6 replications) at 0.50 $\mu\text{g/ml}$ vanadium(V) was 2.5%.

The conventional polarographic methods for vanadium [1,2] are of poor sensitivity. Catalytic currents have been observed for the reduction of vanadium ions in the presence of oxidants like hydrogen peroxide [3,4], nitrate [5], nitrite [6] and bromate [7,8]; but the catalytic effect depends on the nature and oxidation state of vanadium ions, type of the oxidant and its concentration and also pH of the medium. The catalytic current of vanadium in the presence of hydrogen peroxide showed a pronounced maximum [3]. The catalytic rate constants obtained in the presence of nitrate and nitrite were very low and hence these were not analytically useful. Perchlorate has no catalytic effect on vanadium(V). The reduction of vanadium(V) has not been known to be catalyzed by chlorate, iodate or periodate ions.

Rao and Rao [7] have reported vanadium catalyzed reduction of bromate in acetate buffer at pH 4.95. However, the relationship between peak current and concentration of neither vanadium nor bromate was linear under the experimental conditions used by them. In this paper, the experimental conditions were modified so that good linearity between the catalytic current and vanadium(V) concentration could be obtained. The effect of pH,

temperature and bromate concentration on the catalytic current was studied and the mechanism of electrode process was investigated using Birke et al's DPP diagnostic criteria.

EXPERIMENTAL

The polarograph with the cell assembly was described earlier [9]. For DPP measurements, the pulse duration was 0.04 s and the pulse amplitude (ΔE) was 50 mV. All the polarograms were recorded at a constant temperature of 25°C.

All reagents were of analytical reagent grade. A stock solution of 1000 ppm V(V) was prepared from ammonium vanadate and diluted as required. Solutions of sodium acetate (1 M) and sodium bromate (1 M) were also prepared. The polarographic solutions were deaerated by bubbling pure nitrogen for 10 min.

RESULTS AND DISCUSSION

Differential Pulse Polarograms of Vanadium(V)

In 0.2 M sodium acetate medium of pH 5.7 V(V) gives two peaks at about -0.13

and -1.2 V. The peak potentials were dependent on pH and shifted in the negative direction with increase in pH. The two peaks correspond to the stepwise reductions of V(V) to V(IV) and V(IV) to V(III) respectively. It was found that the height of peak 1 was enhanced in the presence of bromate (Fig.1). The enhancement in sensitivity was about 11 in the presence of 0.12 M sodium bromate.

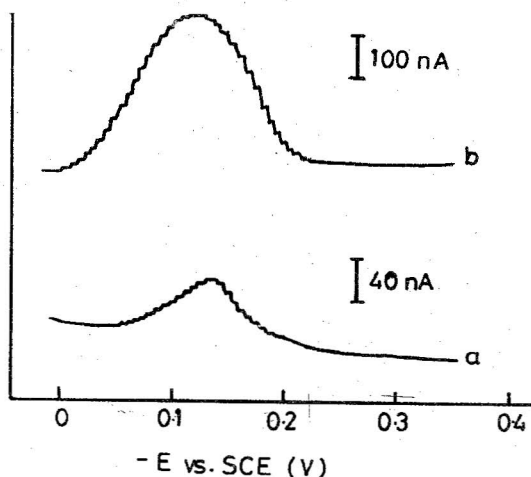


Fig 1. DP polarograms of vanadium(V)

Medium: 0.2 sodium acetate at pH 5.7 ± 0.1 ;
(a) in the absence and (b) in the presence of 0.1 M sodium bromate.

[V(V)] = 0.6 ppm; $t = 0.5$ s;

$\Delta E = 50$ mV; scan rate = 12 mV/s.

The effect of the change in V(V) concentrations on the first peak of V(V) in the presence of sodium bromate was studied and the results are shown in Fig.2. It was found that the peak current steadily increased with increase in vanadium concentrations from 0.1 up to 1.5 ppm. Above this concentration, the peak broadened and there was a tendency to split into two peaks. This may be due to the formation of some poly-vanadate species in solution at higher vanadium concentrations.

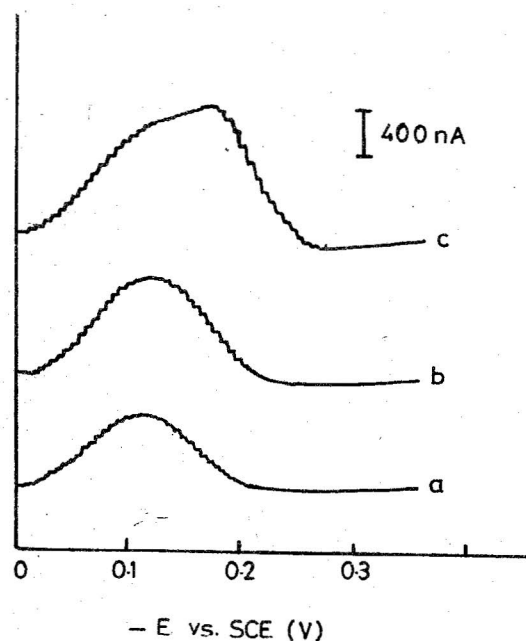


Fig 2. Dependence of the peak current on vanadium(V) concentration

S.E. = 0.2 M sodium acetate + 0.1 M sodium bromate at pH 5.7 ± 0.1 ;

V(V) (a) 0.8 ppm; (b) 1.5 ppm; (c) 2.3 ppm;
DPP conditions same as in Fig 1.

Effect of pH and the concentration of bromate on the catalytic current

The effect of pH on peak 1 of V(V) in a supporting electrolyte of 0.2 M sodium acetate and 0.1 M sodium bromate was examined in the pH range of 5-7. It was found that the peak potential shifted to more negative values with increase in pH. The slope $\Delta E_p / \Delta pH$ was about 116.7 mV. This shows that two hydrogen ions are involved in the reduction of V(V) to V(IV) as shown in equation 1. The peak current was maximum at pH 5.7 ± 0.1 .

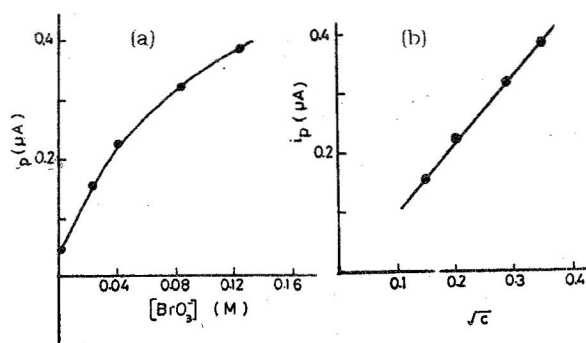


Fig 3. Effect of variation of bromate concentration on the catalytic peak of V(V)

- (a) peak current vs c ;
 (b) peak current vs \sqrt{c} .

The dependence of the current of peak 1 on bromate concentration are shown in Fig.3. The peak current (i_p) increased with increase in bromate concentration in a nonlinear fashion. A plot of i_p vs square root of bromate concentration gave a straight line. This is typical of electrode processes of EC (catalytic) mechanism [11].

Effect of temperature on the catalytic current

The peak currents were measured at various temperature in the range of 25 to 50° C (Fig.4). It was seen that i_p initially increased with temperature from 25° -43°C in a nonlinear manner and decreased after 43° C and increased again. The half peak width ($W_{1/2}$) increased and the peak potential (E_p) shifted in the negative direction with increase in temperature as shown in Table 1.

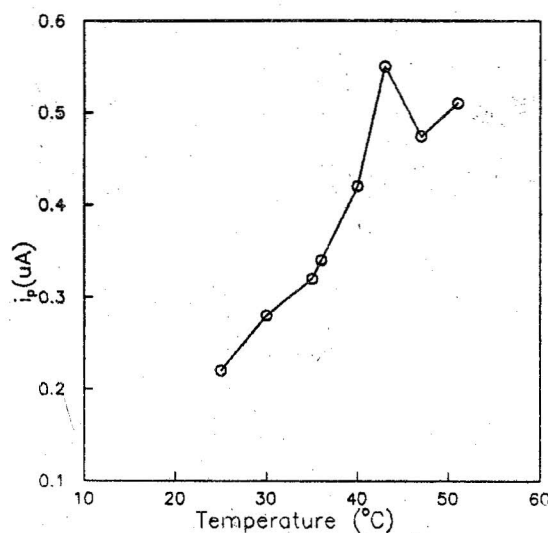


Fig 4. Effect of temperature on the peak current of V(V)

[V(V)] = 0.4 ppm; S.E. and DPP conditions same as in Fig 2.

Table 1.

Effect of temperature on the half peak width ($W_{1/2}$) and the peak potential (E_p)

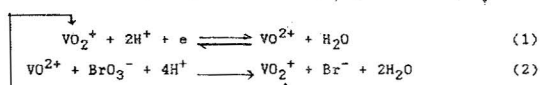
Temperature °C	$W_{1/2}$ mV	E_p (V)
25	100	-0.115
30	110	-0.115
34.5	120	-0.120
36	124	-0.125
40	128	-0.135
43	144	-0.135
48	156	-0.145
51.5	152	-0.155

Both these observations indicate that the rate constant of the electron transfer reaction decreases with increase in temperature. The catalytic chemical reaction step is accelerated by increase in temperature and this results in the increase of peak current. The temperature coefficient at 25° C was about 4% / °C.

Mechanism of the electrode process

DPP diagnostic criteria of Birke et al. [10, 11] was used for the characterization of the electrode process. It was found that the ratio of anodic to cathodic peak current was 0.78 and the difference in peak potentials was less than the pulse amplitude. This indicates that the electron transfer step is not reversible. The half peak width value (at $\Delta E = 50$ mV) varied from 90 to 110 mV depending on the vanadium concentration and other experimental variables. A logarithmic analysis of the DC polarogram of vanadium(V) in this medium gave a slope value of 1/84. This shows that the electrode process is quasi-reversible in the time scale of DC polarography. The enhancement of the current in the presence of bromate confirmed the catalytic nature. Hence the electrode process is considered to be an EC (catalytic) mechanism.

The catalytic rate constant (k) was calculated using the equation, $i_c/i_d = (\pi \delta k C_z)^{1/2}$ where i_c is catalytic current and i_d is the diffusion current in the absence of oxidant in DPP, k is the second order rate constant, δ is the pulse duration and C_z is the concentration of oxidant in moles/l. Substituting the experimental values, the second order rate constant, k was found to be $8.028 \times 10^3 \text{ s}^{-1} \text{ M}^{-1}$. The probable mechanism for the catalytic reaction is given below:



A comparison of the sensitivities of the catalytic current of V(V) by DPP and charging current compensated DC polarography (CCDCP) was carried out. It was found that CCDCP was 2.4 times more sensitive than DPP. This result is in agreement with our earlier results for the catalytic currents of Mo(VI) and Ti(IV) [12-13].

Linearity of Calibration Graph

The catalytic current was found to be a linear function of V(V) concentration in the range of 0.1 - 1.5 ppm. The medium was 0.2 M sodium acetate and 0.1 M sodium bromate at pH 5.7 ± 0.1 . The DPP conditions were $t = 0.5$ s; $\Delta E = 50$ mV. The least square fit of the catalytic current vs V(V) concentration data was done by y-residual minimization. The regression parameters were: slope = 600 nA/ppm; intercept = 20 nA; correlation coefficient = 0.9997. The sensitivity increased with increase in drop time. Thus 3 - 3.5 times higher sensitivity could be obtained by increasing the drop time from 0.5 s to 2 s. The regression parameters at $t = 2$ s were: slope = 1768 nA/ppm; intercept = 130 nA and correlation coefficient = 0.9994.

At vanadium concentrations higher than $2 \times 10^{-5} \text{ M}$, the peak broadens and peak potential shifts in the negative direction (Fig.2). This was due to the formation of polyvanadate species at higher concentrations of V(V). Rao and Rao [7] had studied the catalytic current of vanadium(V) in the presence of bromate in the concentration range $1.0 - 5.0 \times 10^{-4} \text{ M}$ and found that there was no linear relationship between the peak current and either vanadium or bromate concentration. This nonlinearity was due to the presence of polyvanadate species at the higher vanadium concentrations.

Study of interferences

The effect of various cations and anions on the catalytic peak current of V(V) was examined. It was found that cations like Pb(II), Cd(II), Ni(II), Co(II), Zn(II) and Mn(II) did not interfere when present in 10-fold weight ratio to vanadium. Fe(III) interfered seriously by forming ferric vanadate and

hence the vanadium catalytic peak disappeared in the presence of Fe(III). More than 3-fold amounts of W(VI) interfered with the determination because of the formation of heteropoly acid ions with vanadium. There was no interference from 100-fold amounts of phosphate but a mixture of phosphate and tungstate interfered by suppressing vanadium peak. This may be due to the formation of phospho-vanado-tungstate. A mixture of phosphate and molybdate was found not to interfere. Al(III) can be tolerated up to 100 ppm levels. At higher Al(III) concentrations, aluminium hydroxide precipitated.

The effect of anionic surfactants [like sodium lauryl sulphate (SLS) and sodium oleate (SO)] on the catalytic current of vanadium was studied. It was found that the catalytic current decreased with increase in SLS concentration, whereas the peak current increased in the presence of SO.

Procedure

Transfer an aliquot of the sample solution into a beaker, add 4 ml sodium acetate and 2 ml sodium bromate and adjust the pH to 5.7 ± 0.1 with dilute acetic acid or sodium hydroxide. Dilute to 20 ml with water and transfer the solution to a polarographic cell. Deaerate and record the polarogram from 0 to -0.40 V vs SCE. The vanadium concentration in the aliquot is determined by standard addition method.

Synthetic solutions were prepared by adding known amounts of V(V) to distilled water and these were analyzed using the procedure described here. The relative standard deviation for 6 replicate measurements at $0.5 \mu\text{g ml}^{-1}$ V(V) was found to be 2.5%.

REFERENCES

1. I.M. Kolthoff and J.J. Lingane, *Polarography, Volume II*, Second Edition, **Interscience** (1952) p.447.
2. G.W.C. Milner, *The Principles and Applications of Polarography and other Electroanalytical Processes*, **Longmans, London** (1957) p.257.
3. A.J. Bard, *Encyclopedia of Electrochemistry of the Elements*, Vol. VII, **Marcel Dekker, Inc. New York** (1973) p.337.
4. I.M. Kolthoff and E.P. Parry, *J. Am. Chem. Soc.*, **73** (1951) 5315.
5. N. Kato and K. Aoki, *J. Electroanal. Chem.*, **262** (1989) 309.
6. F. Baumann, *J. Electroanal. Chem.* **6** (1963) 245.
7. V. Suryanarayana Rao and S. Brahmaji Rao, *J. Electroanal. Chem.*, **108** (1980) 373.
8. V.S.N. Rao and S.B. Rao, *Talanta*, **26** (1979) 502.
9. Bharathibai J. Basu and S.R. Rajagopalan, *Analyst*, **117** (1992) 1623.
10. R.L. Birke, M.H. Kim and M. Strassfeld, *Anal. Chem.*, **53** (1981) 852.
11. M.H. Kim and R.L. Birke, *Anal. Chem.*, **55** (1983) 522.
12. Bharathibai J. Basu, D.K. Padma and S.R. Rajagopalan, *Talanta*, **38** (1991) 1431.
13. Bharathibai J. Basu and S.R. Rajagopalan, *Bull. Electrochem.*, **9** (1993) 35.