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Redox potentials of molybdovanadophosphoric heteropoly acids in aqueous solutions

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Abstract

Redox potentials *E* and pH values were measured in 0.2 and 0.01 M solutions of partly reduced heteropoly acids $H_{3+x+m}PV_m^{IV}V_{x-m}^VMo_{12-x}O_{40}$ (H_mHPA-x , $1 \le x \le 4$, $0 \le m \le x$). The potentials were compared to the redox potential of a couple VO_2^+/VO^{2+} which is in equilibrium with various HPA- x_m anions. It was found that all HPA- x_m anions as VO_2^+ and VO^{2+} cations are one-electron oxidants/reductants. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Heteropoly acids $H_{3+x}PV_x^VMo_{12-x}O_{40}$ (HP-A-*x*, $1 \le x \le 4$) are reversible oxidants that are widely used as homogeneous catalysts for various substrates (Su) oxidation [1] (Su = olefins, CO, H₂S, phenols, etc.) via the overall reaction (3):

$$m/2Su + HPA-x + m/2H_2O$$

 $\rightarrow m/2SuO + H_mHPA-x$ (1)

$$H_mHPA-x + m/4O_2 \rightarrow HPA-x + m/2H_2O$$
 (2)

$$2Su + O_2 \xrightarrow{HPA-x} 2SuO$$
(3)

Their reduced forms $H_mHPA-x = H_{3+x+m}$ -PV_m^{IV}V_{x-m}^VMo_{12-x}O₄₀ (where $m = [V^{IV}]/$ [HPA-x]) are easily regenerated by dioxygen [2]. Rate and selectivity of oxidation of various Su are significantly affected by redox potentials of the H_m HPA-*x* in solution [3]. However, these potentials were often measured in strong acidic media [4] when equilibrated composition of H_m HPA-*x* solutions is very complicated due to the presence of cations VO₂⁺ and VO²⁺ (see later).

In the present work, the redox potentials of H_mHPA-x solutions at various *m* are measured in 0.2 and 0.01 M H_mHPA-x solutions without the addition of strong acids, with 0.2 M H_mHPA-x solutions mostly used as catalysts [1]. Nevertheless, 0.01 M H_mHPA-x solutions are little affected by cations VO₂⁺ and VO²⁺, and therefore they are more preferable for potentiometric study.

2. Experimental

0.2 M aqueous solutions of $H_{3+x}PV_x^V$ -Mo_{12-x}O₄₀ were synthesized using stoichiomet-

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ric quantities of V₂O₅, H₂O₂, H₃PO₄, and MoO₃ [5] and diluted with water if it was necessary. Their compositions were determined by ³¹P and ⁵¹V NMR spectroscopy [5]. Redox potentials *E* and pH values of H_mHPA-*x* solutions ($0 \le m \le x$) were measured at 293 K using a digital ionomerer I-130. The concentration of V^{IV} was determined by titration of H_mHPA-*x* solution by KMnO₄ in H₃PO₄ [6].

3. Discussion

The relationships E = f(m) and $pH = \varphi(m)$ for 0.01 M H_mHPA-x solutions are pictured in Fig. 1. Similar 0.2 M solutions (not shown) have greater E values (by ~ 0.1 V) and smaller pH ones (by ~ 0.5 unit) than the 0.01 M solutions.

$$H_{x+m-1}PV_{m}^{IV}V_{x-m}^{V}Mo_{12-x}O_{40}^{4-} + e^{-} + H^{+}$$
(HPA- x_{m})

For each *m* (i. e., each HPA- x_m /HPA- x_{m+1} pair), the redox potential E_m is given by formula (6):

$$E_{m \to m+1} = E_{m \to m+1}^{o} - 0.0591 \text{pH} + 0.0591 \log \frac{[\text{HPA-}x_m]}{[\text{HPA-}x_{m+1}]}$$
(6)

For HPA-3 and HPA-4 solutions, calculated fractions of individual HPA- x_m anions are given in Table 1.

Redox potentials of various anion pairs HPA- x_m /HPA- x_{m+1} ($E_{m \to m+1}$) are equal to the redox potential of cation pair VO₂⁺/VO²⁺ (E_V) due to equilibria (4), (5), and (7):

$$\operatorname{VO}_2^+ \cdot \operatorname{aq} + 2\operatorname{H}^+ + \operatorname{e}^- \leftrightarrow \operatorname{VO}^{2+} \cdot \operatorname{aq} + \operatorname{H}_2\operatorname{O}$$
 (7)

In aqueous solutions, HPA-x are always in equilibrium with cations VO₂⁺ due to their acidity [7]:

$$(13 - x)H_{3+x}PV_{x}Mo_{12-x}O_{40} + 12H^{+}$$

$$\stackrel{k_{ox}}{\rightleftharpoons} (12 - x)H_{2+x}PV_{x-1}Mo_{13-x}O_{40} + 12VO_{2}^{+}$$

$$+ H_{3}PO_{4} + 12H_{2}O$$
(4)

The reduced forms H_mHPA-x are in similar equilibrium with cations VO^{2+} [8]. Therefore, the more concentrated are H_mHPA-x solutions (with high H⁺ concentration), the higher are the VO_2^+ and VO_2^+ concentrations in them.

Each H_m HPA-*x* solution contains (*x* + 1) individual anions (from HPA-*x*_o to HPA-*x*_x), which are in equilibria (5).

$$\mapsto \operatorname{H}_{x+m} \operatorname{PV}_{m+1}^{\mathrm{IV}} \operatorname{V}_{x-m-1}^{\mathrm{V}} \operatorname{Mo}_{12-x} \operatorname{O}_{40}^{4-}$$

$$(\operatorname{HPA-x}_{m+1})$$

$$(5)$$



Fig. 1. *E* and pH measured for 0.01 M H_m HPA-*x* solutions as a function of the reduction degree *m*. (Digits 2, 3 and 4 are *x* values.)

Table 1

Fractions of individual partly reduced anions HPA- x_m ,	$\alpha_m,$ in 0.01 M solutions of $\mathrm{H}_m\mathrm{HPA-3}$ and $\mathrm{H}_m\mathrm{HPA-4}$
Calculation according to formula (6) following Fig. 1.	

Solution	m	$\mathrm{E}_{m \to m+1}^{+}\mathrm{a}\left(\mathrm{V}\right)$	α_m (%)					
			$HPA-x_o$	HPA- x_1	HPA- x_2	HPA- x_3	HPA- x_4	
H _m HPA-3	0		100	_	_	_	_	
	0.5	0.817						
	1		8.9	78.7	12.1	0.3	_	
	1.5	0.713					_	
	2		0.2	10.6	74.2	15.0	_	
	2.5	0.622						
	3		-	_	_	100		
H _m HPA-4	0		100					
	0.5	0.834						
	1		8.3	82.7	8.3	0.6	0.1	
	1.5	0.716						
	2		0.1	10.8	59.7	25.3	4.1	
	2.5	0.650						
	3		~ 0.02	1.6	21.4	54.6	22.3	
	3.5	0.603						
	4		-	_	-	_	100	

^a The middle-point potential for half-reduction of anion HPA- x_m to HPA- x_{m+1} .

For the last pair

$$E_{\rm V} = E_{\rm V}^{\rm o} - 0.1182 \,\mathrm{pH} + 0.0591 \log \frac{\left[\mathrm{VO}_2^+\right]}{\left[\mathrm{VO}^{2^+}\right]} \tag{8}$$

where $E_{\rm V}^{\rm o} = 1.00$ V [9].

The ratio of equilibrium concentrations $[VO_2^+]_{eq}/[VO^{2+}]_{eq}$ in the H_m HPA-*x* solution can be found from comparison between the measured potential *E* for this solution and the middle-point potential E_V^+ for cation pair VO_2^+/VO^{2+} at the same pH.

If $[VO_2^+]_{eq} = [VO^{2+}]_{eq}$, then Eq. (8) transforms to Eq. (9):

$$E_{\rm V}^+ = E_{\rm V}^{\rm o} - 0.1182 \cdot \rm pH \tag{9}$$

If $[VO_2^+]_{eq} \neq [VO^{2+}]_{eq}$, then Eq. (8) transforms to Eq. (10) considering Eq. (9) and the equality $E_V = E_{m \rightarrow m+1} = E$:

$$\log \frac{[\mathrm{VO}_{2}^{+}]_{\mathrm{eq}}}{[\mathrm{VO}^{2+}]_{\mathrm{eq}}} = \frac{E - E_{\mathrm{V}}^{\mathrm{o}} + 0.1182 \cdot \mathrm{pH}}{0.0591}$$
$$= \frac{E - E_{\mathrm{V}}^{+}}{0.0591} \tag{10}$$

Let $\beta_{\rm V}$ be a fraction of cation VO₂⁺ in all forms of V^V, and $\beta_{\rm IV}$ be a fraction of cation VO²⁺ in all forms of V^{IV}:

$$\boldsymbol{\beta}_{\mathrm{V}} = \left[\mathrm{VO}_{2}^{+}\right]_{\mathrm{eq}} / \left[\mathrm{V}_{\Sigma}^{\mathrm{V}}\right] \tag{11}$$

$$\beta_{\rm IV} = \left[\rm VO^{2+} \right]_{eq} / \left[\rm V_{\Sigma}^{\rm IV} \right]$$
(12)

If α_m is a fraction of individual anion HPA- x_m in H_mHPA-x solution, then

$$\begin{bmatrix} V_{\Sigma}^{V} \end{bmatrix} = \beta_{V} \begin{bmatrix} VO_{2}^{+} \end{bmatrix}_{eq} + (1 - \beta_{V}) \Sigma \alpha_{m} (n - m)$$
$$\times \begin{bmatrix} HPA-x_{m} \end{bmatrix} \approx \Sigma \alpha_{m} (n - m) \begin{bmatrix} HPA-x_{m} \end{bmatrix}$$
(13)

$$\begin{bmatrix} V_{\Sigma}^{IV} \end{bmatrix} = \beta_{IV} \begin{bmatrix} VO^{2+} \end{bmatrix}_{eq} + (1 - \beta_{IV}) \\ \times \Sigma \alpha_m m [HPA-x_m] \approx \Sigma \alpha_m m [HPA-x_m]$$
(14)

The values *E* and pH measured for H_m HPA-*x* solutions allow us to determine only the β_{IV}/β_V ratio, not β_{IV} and β_V separately. Taking into



Fig. 2. Ratio between fractions of VO₂⁺ in V₂^V (Eq. (11)) and VO²⁺ in V₂^{IV} (Eq. (12)) as a function of the ratio of total concentrations of V₂^V and V₂^{IV} for 0.2 M and 0.01 M H_mHPA-x solutions. (Digits 2, 3, and 4 are x values for 0.01 M solutions. Ones 2', 3', and 4' are x values for 0.2 M solutions.)

account Eqs. (11) and (12), Eq. (10) transforms to Eq. (15):

$$\log G = \log \frac{\beta_{\text{IV}}}{\beta_{\text{V}}} = \log \frac{\left[\text{V}_{\Sigma}^{\text{V}}\right]}{\left[\text{V}_{\Sigma}^{\text{IV}}\right]} - \log \frac{\left[\text{VO}_{2}^{+}\right]_{\text{eq}}}{\left[\text{VO}^{2+}\right]_{\text{eq}}}$$
(15)

Fig. 2 shows that the ratio β_{IV}/β_V depends on both x and m. It decreases if x increases, and goes through maximum if m increases. These maxima are especially clear for 0.2 M H_mHPA-x solutions. In all cases, $\beta_{IV} > \beta_V$, i.e. $[VO^{2+}]_{eq} > [VO_2^+]_{eq}$. Analogous conclusion was earlier made only for HPA-2 solutions using the very complicated computer program LAKE [10]. These results confirm that HPA- x_m and HPA- x_{m+1} anions as VO_2^+ and VO^{2+} cations in the H_mHPA-x solutions are one-electron oxidants/reductants.

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