

Redox potentials of molybdovanadophosphoric heteropoly acids in aqueous solutions

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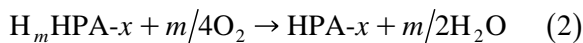
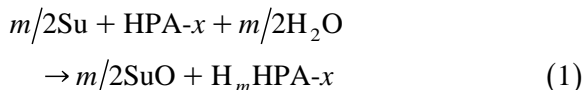
Abstract

Redox potentials E and pH values were measured in 0.2 and 0.01 M solutions of partly reduced heteropoly acids $H_{3+x+m}PV_m^{IV}V_{x-m}^V Mo_{12-x}O_{40}$ (H_m HPA- x , $1 \leq x \leq 4$, $0 \leq m \leq x$). 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.

Keywords: Heteropoly acids; Molybdovanadophosphates; Redox potentials; Solutions

1. Introduction

Heteropoly acids $H_{3+x}PV_x^V Mo_{12-x}O_{40}$ (HPA- x , $1 \leq x \leq 4$) 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):



Their reduced forms $H_mHPA-x = H_{3+x+m}PV_m^{IV}V_{x-m}^V Mo_{12-x}O_{40}$ (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_mHPA-x in solution [3]. However, these potentials were often measured in strong acidic media [4] when equilibrated composition of H_mHPA-x solutions is very complicated due to the presence of cations VO_2^+ and VO^{2+} (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 VO_2^+ and VO^{2+} , and therefore they are more preferable for potentiometric study.

2. Experimental

0.2 M aqueous solutions of $H_{3+x}PV_x^V Mo_{12-x}O_{40}$ were synthesized using stoichiomet-

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Table 1

Fractions of individual partly reduced anions HPA- x_m , α_m , in 0.01 M solutions of H_mHPA-3 and H_mHPA-4
Calculation according to formula (6) following Fig. 1.

Solution	m	$E_{m \rightarrow m+1}^+$ (V) ^a	α_m (%)				
			HPA- x_0	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					
H _m HPA-4	3		–	–	–	100	
	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	

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

For the last pair

$$E_V = E_V^0 - 0.1182 \text{ pH} + 0.0591 \log \frac{[\text{VO}_2^+]}{[\text{VO}^{2+}]} \quad (8)$$

where $E_V^0 = 1.00 \text{ V}$ [9].

The ratio of equilibrium concentrations $[\text{VO}_2^+]_{\text{eq}}/[\text{VO}^{2+}]_{\text{eq}}$ in the H_mHPA- 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 $\text{VO}_2^+/\text{VO}^{2+}$ at the same pH.

If $[\text{VO}_2^+]_{\text{eq}} = [\text{VO}^{2+}]_{\text{eq}}$, then Eq. (8) transforms to Eq. (9):

$$E_V^+ = E_V^0 - 0.1182 \cdot \text{pH} \quad (9)$$

If $[\text{VO}_2^+]_{\text{eq}} \neq [\text{VO}^{2+}]_{\text{eq}}$, then Eq. (8) transforms to Eq. (10) considering Eq. (9) and the equality $E_V = E_{m \rightarrow m+1} = E$:

$$\begin{aligned} \log \frac{[\text{VO}_2^+]_{\text{eq}}}{[\text{VO}^{2+}]_{\text{eq}}} &= \frac{E - E_V^0 + 0.1182 \cdot \text{pH}}{0.0591} \\ &= \frac{E - E_V^+}{0.0591} \end{aligned} \quad (10)$$

Let β_V be a fraction of cation VO_2^+ in all forms of V^V , and β_{IV} be a fraction of cation VO^{2+} in all forms of V^{IV} :

$$\beta_V = [\text{VO}_2^+]_{\text{eq}} / [\text{V}_\Sigma^V] \quad (11)$$

$$\beta_{\text{IV}} = [\text{VO}^{2+}]_{\text{eq}} / [\text{V}_\Sigma^{\text{IV}}] \quad (12)$$

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

$$\begin{aligned} [\text{V}_\Sigma^V] &= \beta_V [\text{VO}_2^+]_{\text{eq}} + (1 - \beta_V) \Sigma \alpha_m (n - m) \\ &\times [\text{HPA-}x_m] \approx \Sigma \alpha_m (n - m) [\text{HPA-}x_m] \end{aligned} \quad (13)$$

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

The values E and pH measured for H_mHPA- x solutions allow us to determine only the $\beta_{\text{IV}}/\beta_V$ ratio, not β_{IV} and β_V separately. Taking into

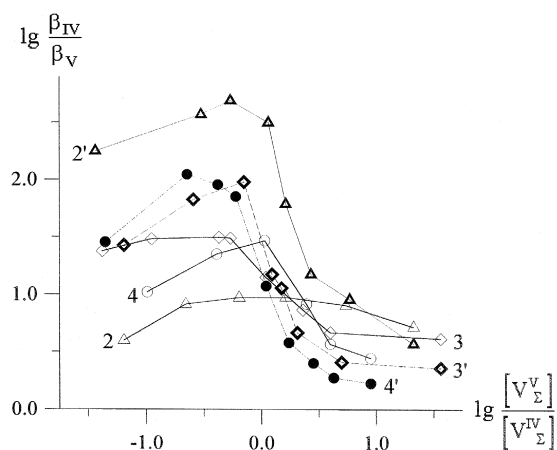


Fig. 2. Ratio between fractions of VO_2^+ in $\text{V}_\Sigma^{\text{V}}$ (Eq. (11)) and VO^{2+} in $\text{V}_\Sigma^{\text{IV}}$ (Eq. (12)) as a function of the ratio of total concentrations of $\text{V}_\Sigma^{\text{V}}$ and $\text{V}_\Sigma^{\text{IV}}$ for 0.2 M and 0.01 M $\text{H}_m\text{HPA}-x$ 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):

$$\log G = \log \frac{\beta_{\text{IV}}}{\beta_{\text{V}}} = \log \frac{[\text{V}_\Sigma^{\text{V}}]}{[\text{V}_\Sigma^{\text{IV}}]} - \log \frac{[\text{VO}_2^+]_{\text{eq}}}{[\text{VO}^{2+}]_{\text{eq}}} \quad (15)$$

Fig. 2 shows that the ratio $\beta_{\text{IV}}/\beta_{\text{V}}$ 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

$\text{H}_m\text{HPA}-x$ solutions. In all cases, $\beta_{\text{IV}} > \beta_{\text{V}}$, i.e. $[\text{VO}_2^+]_{\text{eq}} > [\text{VO}^{2+}]_{\text{eq}}$. Analogous conclusion was earlier made only for $\text{HPA}-2$ solutions using the very complicated computer program LAKE [10]. These results confirm that $\text{HPA}-x_m$ and $\text{HPA}-x_{m+1}$ anions as VO_2^+ and VO^{2+} cations in the $\text{H}_m\text{HPA}-x$ solutions are one-electron oxidants/reductants.

References

- [1] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
- [2] K.I. Matveev, in: Study of Properties and Application of Heteropolyacids in Catalysis, 1978, p. 3, Novosibirsk (in Russian).
- [3] K.I. Matveev, V.F. Odyakov, E.G. Zhizhina, J. Mol. Catal. A: Chem. 114 (1996) 151.
- [4] E.G. Zhizhina, L.I. Kuznetsova, E.N. Yurchenko, K.I. Matveev, Koord. Khim. 6 (1980) 1846.
- [5] V.F. Odyakov, E.G. Zhizhina, R.I. Maksimovskaya, K.I. Matveev, Kinet. Catal. 36 (1995) 733.
- [6] L.S.A. Dikshitulu, G. Gopala Rao, Fresenius' Z. Anal. Chem. 189 (1962) 421.
- [7] P. Souchay, F. Chauveau, P. Courtin, Bull. Soc. Chim. Fr. (1968) 2384.
- [8] L.I. Kuznetsova, E.N. Yurchenko, R.I. Maksimovskaya, N.P. Kirik, K.I. Matveev, Koord. Khim. 3 (1977) 51.
- [9] J. Israel, L. Meites, in: Standard Potentials in Aqueous Solution (IUPAC), Marcer Dekker, New York, 1985, p. 520.
- [10] L. Pettersson, in: Polyoxometalates. From Platonic Solids to Anti-Retroviral Activity, Kluwer Academic Publishing, Dordrecht, 1994, p. 26.