DECAMOLIBDODIVANADOARSENIC ACID A NEW REVERSIBLE REDOX INDICATOR FOR THE VOLUMETRIC DETERMINATION OF Sb^{3+} USING $KBrO_3$

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Abstract

$H_5[AsMo_{10}V_2O_{40}]$ can be used in Sb^{3+} $KBrO_3$ volumetric determination as a reversible redox indicator. The experimental dates were statistically compared to those obtained using classic Sb^{3+} titration method, which use organic irreversible indicators. The statistic interpretations show good results.

Introduction

The fact that heteropolyacids can be easily reduced to dark blue compounds with high speed and further easily oxidised to the initial red-orange compounds, creates the possibility to use them as irreversible redox indicators:

- Decamolibdodivanadophosphoric acid has been used as redox indicator for the bromatometry titration of some hydrazine salts and ascorbic acid.[1-3]

- Dodecamolibdosilico acid has been used for the titration of $SnCl_2$ with $K_2Cr_2O_7$ as a redox indicator.[4]

- Decamolibdodivanadophosphoric acid has been also used as an indicator for the bromatometry titration of Sb^{+3} and hydroxylamine.[5,6]

- Decamolibdodivanadosilico acid has been utilised as an indicator for the bromatometry titration of Sb^{+3}.[7]

The triheteropolyacids utilisation as indicators in the volumetric determination of Sb^{3+} is based on the Kokorin works in which the triheteropolyacids (in H_2SO_4 1-2 N medium) are reduced using Sb^{3+} to dark blue compounds. The Sb^{3+} concentration was measured with spectrofotometric methods.[8]

Mixture of triheteropolyacids with Mo and V, as compared to simple heteropolyacids, presents the advantage of a higher absorption molar coefficient in the

oxidative form. In the moment of equivalence this makes possible to observe the turning more easily and precisely.

The presence of V^{5+} in their molecule determines those heteropolyacids to be reduced or oxidised with higher speeds, changing the colour in the moment of turning more quickly and clearly.

Because $H_5[AsMo_{10}V_2O_{40}]$ presents a higher pH stability than $H_5[PMo_{10}V_2O_{40}]$, it makes it a better indicator in the volumetric determination of Sb^{3+}, which are performed in strong acidic media.

The triheteropolyacids cyclic voltammetry studies show reversible redox behaviour and a good pH stability.[9-16]

Bromatometry use irreversible indicators because the Br_2 formed from the reaction of BrO_3^- with Br^- destroys organic reversible indicators. The indicator's colour is mitigating during the titration so it is necessary to add new indicator quantities near the turning point.

$H_5[AsMo_{10}V_2O_{40}]$ being an inorganic compound is stable to the Br_2 action and may function as an reversible indicator for the bromatometry titration. And more, it functions without consumption of reactant because at the end of the titration it reappears into the same state (oxidised) as it was initially introduced.

Results and discussion

To verify the $H_5[AsMo_{10}V_2O_{40}]$ function as an reversible redox indicator in the As^{3+} titration using $KBrO_3$ the results obtained were statistically compared to the results obtained using indigo blue as redox indicator.

The results obtained with the two methods are presented in the Tables 1 and 2.

To determine the turning potential, a Sb^{3+} potentiometric determination using $H_5[AsMo_{10}V_2O_{40}]$ as colour indicator, was also performed.

In the Table 1 are presented the results obtained for the Sb^{3+} volumetric determination using $KBrO_3$ with $H_5[AsMo_{10}V_2O_{40}]$ as redox indicator and in the Table 2 those obtained for the volumetric Sb^{3+} determination using $KBrO_3$ with indigo blue as redox indicator.

Table 1. The results obtained for the Sb^{3+} volumetric determination using $KBrO_3$ with $H_5[AsMo_{10}V_2O_{40}]$ as redox indicator.

Nr. crt.	[mL] $KBrO_3$ 0.1N F=1.0103	[g] As^{3+} (X)
1	10.04	0.06875
2	10.04	0.06900
3	10.06	0.06898
4	10.02	0.06866
5	10.02	0.06878
6	10.03	0.06808
7	10.00	0.06902
8	10.05	0.06875
9	10.06	0.06899
10	10.06	0.06883

Table 2. The results obtained for the volumetric Sb^{3+} determination using $KBrO_3$ with indigo blue as redox indicator.

Nr. crt.	[mL] $KBrO_3$ 0.1N F=1.0103	[g] As^{3+} (x)
1	10.00	0.06869
2	10.02	0.06899
3	10.05	0.06898
4	10.04	0.06898
5	10.08	0.06905
6	10.04	0.06900
7	10.03	0.06890
8	10.05	0.06888
9	10.02	0.06897
10	10.08	0.06886

Results of statistical comparison

The scattering selection S^2 and the average error for the average selection S_X for both determination sets were calculated:

$S_1^2 = 0.88 \cdot 10^{-7}$; $S_{1x} = 0.88 \cdot 10^{-8}$; $x_1 = 0.06878$

$S_2^2 = 0.55 \cdot 10^{-7}$; $S_{2x} = 0.55 \cdot 10^{-8}$; $x_2 = 0.06893$

$$S_x = \frac{\sum_{i=1}^{n} (\overline{X} - X_i)^2}{n(n-1)} \quad \text{and} \quad S^2 = \frac{\sum_{i=1}^{n} (\overline{X} - X_i)^2}{n-1}$$

To verify if the results obtained for the titration using $H_5[AsMo_{10}V_2O_{40}]$ as indicator are significantly different from those obtained using indigo blue, the two sets of experimental results were statistically compared using **t** (averages comparison) and **f** (scattering comparison) criterions.

f = 1.6 < 2.26 for $k_1 = k_2 = n - 1 = 9$, liberty degrees (n is the number of experimental determinations) and the probability P = 95%.[17]

t = 0.4181 < 2.1 for $k_1 = k_2 = n - 1 = 9$, liberty degrees (n is the number of experimental determinations) and the probability P = 95%.[17]

$$\mathbf{f} = S_1^2 / S_2^2$$

$$t = \frac{|\overline{X}_1 - \overline{X}_2|}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}}$$

The results show that the difference between the two averages and scatterings are not significant, therefore the two methods have closer precision, and the difference between them are not significant.

The turning potential was calculated using Hahn method and potentiometric curve dates.[18] The obtained value is: E_1 = 768.1 mV. The experimental potential measured in the moment of the $H_5[AsMo_{10}V_2O_{40}]$ colour turning is: E *indicator* = 770 mV.

Therefore $H_5[AsMo_{10}V_2O_{40}]$ presents the turning near the equivalence point.

Conclusions

$H_5[AsMo_{10}V_2O_{40}]$ function as a reversible redox indicator without reagent consumption in the Sb^{3+} titration with $KBrO_3$ because the indicator reappears at the end of the titration in the oxidised state as it was introduced. The statistic studies, using **t** and **f** criterions, show that the results obtained using $H_5[AsMo_{10}V_2O_{40}]$ as indicator for As^{3+}

titration with $KBrO_3$ are not significantly different (average and scattering) from the results obtained with indigo blue as indicator. The $H_5[AsMo_{10}V_2O_{40}]$ colour change takes place at the equivalence potential measured by the potentiometric method.

Experimental

$H_5[AsMo_{10}V_2O_{40}]$ has been obtained using Al. Fodor and L. Ghizdavu recipe in which H_3PO_4 has been substitute with molar equivalent quantities of As_2O_5.[19,20]

When indigo blue is used as redox indicator the solution is acidified with H_2SO_4 2N and during the titration the solution colour became blue passing from green-yellow to yellow.[21] The Br_2 resulted destroy the organic indicator so at the equivalence point the indigo blue colour disappears becoming yellow.

When $H_5[AsMo_{10}V_2O_{40}]$ is used as redox indicator, the Sb^{3+} reduces the heteropolyacid to a dark blue compound which at the equivalence point is reoxidised by the Br_2 to the initial orange heteropolyacid. To proceed the solution is acidified with H_2SO_4 2N and 2 mL 2% $H_5[AsMo_{10}V_2O_{40}]$ is added. Therefore in this titration $H_5[AsMo_{10}V_2O_{40}]$ works as a reversible redox indicator without reagent consumption.

The Sb^{3+}potentiometric determination with $KBrO_3$ using $H_5[AsMo_{10}V_2O_{40}]$ as colour indicator was performed using a PM 3 Meinsberg GDR potentiometer. A conventional three electrodes cell was used: the working electrode was a Pt wire, the reference electrode was a saturated calomel electrode and the counter electrode was a Pt wire separated from the test solution by a glass frit. The measurements were performed at room temperature. To the Sb^{3+} solution it was added the same volume of H_2SO_4 (1:1) and then the volume was adjusted to 100 mL. 5 mL of $H_5[AsMo_{10}V_2O_{40}]$ 0.01 M was added and the volumetric determination with $KBrO_3$ was performed until the colour became dark blue.

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Povzetek

$H_5[AsMo_{10}V_2O_{40}]$ smo uporabili v Sb^{3+} $KBrO_3$ volumetrični določitvi kot reverzibilen redoks indikator. Eksperimentalne podatke smo statistično primerjali s tistimi, dobljenimi s klasičnimi Sb^{3+} titracijskimi metodami, ki uporabljajo organske ireverzibilne indikatorje.