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Comparative study of dissociation constants of triheteropoly oxomolybdates and vanadates

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Abstract

A comparative study of mixed triheteropoly oxomolybdates and vanadates were studied. HPA is characterised by the Hammett acidity function. It has been established that the series of HPA strength in diluted and concentrated aqueous solution do not coincide with each other. The stock solution of acids and indicators were prepared and purified acetone is used as solvent. The data were checked by pH metrically.

Keywords: Dissociation constant, Hammett acidity function, triheteropoly oxomolybdates

1. Introduction

The existence of $[V_{12}O_{36}]^{12-}$ isopoly anions has been established by the extensive studies on the formation and structure of phospho-12-vanadic acids ^[1, 2]. An important class of 12-heteropoly molybdo tungstate with phosphorus or silicon as central atoms have been reported in the literature ^[3]. these acids thus obtain corresponds to the composition $[H_3PMO_xW_yO_{40}]$ where $x+y=12$. The catalytic application of HPA of Keggin type has been studied. This HPA significantly higher Bronsted acidity compared with the mineral acid catalyst ^[4]. The activity of HPA based catalyst has higher activity in comparison with traditional catalyst used. Huge potential is left in some new solid acid catalyst. Therefore importance is given in frame working highly active and selective site acid catalysts ^[5].

1.1 Experimental: Determination of acidity (no. of acid sites) and acid strength on a solid surface by titration with n-butyl amine, using a series of Hammett indicators has been widely used to characterise the nature of solid acid catalysts. The most convenient method to determine the acid strength by titration with Hammett indicators. The acid strength of a solid is the potential of surface to convert into its conjugate acid. Hammett acidity function H_0 is generally used to represent the acid strength of a solid acid.

$H_0 = -\log K - \log \frac{[BH^+]}{[B]} = -\log a_{H^+} \cdot f_B / f_{BH^+}$ represent proton activity, $[B]$ and $[BH^+]$ are the concentration of, f_B and f_{BH^+} represent the activity co-efficient of base and its conjugate acid respectively.

Table 1

Hammett indicators	pKa	Acid Colour	Base Colour
Crystal violet	0.8	yellow	Blue
Bromo Thymol Blue	7.2	yellow	Blue
4-Nitro aniline	18.4	yellow	Colourless
Dimethyl yellow	3.3	Red	Yellow
Methyl red	4.8	Red	Yellow
Neutral red	6.8	Red	Yellow

The heteropoly Oxometalates responded to only these Hammett indicators Dimethyl yellow and methyl red. Acidity at various strength of oxometalates was measured by titration of solid suspended in benzene with 0.1N n-Butyl amine in benzene. Basicity was measured by titrating solid suspended in benzene with 0.1N trichloro acetic acid in benzene, using same set of indicators as for acidity measurement. In this procedure we measured acid/base strengthly distribution. The acid-base strength distribution curve intersect at a point on the abscissa where acidity=basicity]. The point of intersection indicates H_0 . A solid with a large H_0 max value has strong basicities and weak acid sites. On the other hand small H_0 , max value has strong acid sites and weak basic sites.

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1.2 Principle: If acid sites of $H_0 \leq PK_{BH^+}$ exist on a solid surface, the colour of basic indicator has the PK_{BH^+} value changes to the colour of its conjugate acid. Thus the acidity and acid strength of a solid can be determined by titrating the solid suspended in benzene with n-butyl amine using the series of Hammett basic indicator. When a solid has no acid sites for which $H_0 \leq pk_{H^+}$ the colour of basic indicator does not change. If a sta. solution of Bronsted acid in benzene is added gradually, the colour of the basic indicator on the surface will change to the colour of its conjugate acid. The colour change is the end point of titration. The proton donating ability of a solid at the

endpoint of titration is either due to conjugate acids which were formed by the proton transfer from bronsted acid solution to the original solid or due to the Bronsted acid which was physically adsorbed on the surface during the titration.

2. Result and Discussion: In mixed heteropoly acids the dissociation assumed to be completed at the first three steps, the consecutive dissociation usually being unnoticeable because of leaving effect of solvent [6, 7]. According to the electro conductivity data $H_4Mo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$ are strong electrolytes respectively in aqueous solution.

Table 2

Dissociation constant	$H_4PMo_{11}VO_{40}$	$H_5PMo_{10}V_2O_{40}$	$H_7PMo_{11}CuO_{40}$	$H_8PMo_{10}VNiO_{40}$	H_3PO_4
pK ₄	1.16	1.26	3.25	3.4	-
pK ₅	-	2.14	4.62	3.83	-
pK ₆	-	-	6.00	4.01	-
pK ₇	-	-	6.9	4.28	-
pK ₈	-	-	-	5.73	-

Using a potentiometric method the dissociation constants (starting from K₄) of $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$, $H_7PMo_{11}CuO_{40}$, and $H_8PMo_{10}VNiO_{40}$ were measured. The first three proton dissociate completely and other do stepwise with increasing pH.

Determination of pK_a value is commonly performed by means of titration in a medium of high ionic strength and constant temperature. A solution of the compound in the medium is acidified with a strong acid to the point where the compound is fully protonated. The solution is then titrated with strong base

until all the protons have been removed. At each point in the titration pH is measured using glass electrode and pH meter. The dissociation constants of heteropolyoxometallates do not vary considerably, while the distinction between values of dissociation constant of inorganic acids more considerable [8, 9]. From the pK_a data it is concluded that hetero oxometalates are much stronger than H_3PO_4 . It is may be due to large size and surface density of the polyanion charge as well as by the peculiarity of the HPA proton structure.

Table 3

HPA	$(CH_3)_2CO$	C_2H_5OH
$H_4PMo_{11}VO_{40}$	pK ₄ -2.6	pK ₄ -2.6
$H_5PMo_{10}V_2O_{40}$	pK ₄ -3.2, pK ₅ -4.6	pK ₄ -3.6, pK ₅ -4.5
$H_7PMo_{11}CuO_{40}$	pK ₄ -3.6, pK ₅ -4.9, pK ₆ -5.8	pK ₄ -3.6, pK ₅ -4.9, pK ₆ -5.8

The acidic properties of HPA in ethanol and acetone was performed and don't vary significantly depending on the HPA composition and structure.

3. Conclusion: Titration method provides the qualitative determination of acid-base sites of different strength. Since the actual amount of acid-base sites in a given H_0 range is the difference between the acid-base amounts at pK_a value. All HPA are stronger acids than the usual inorganic acids. The acidity decreases by replacement of Mo^{VI} by V^V or with tetrahedral sites with Cu, Ni or Zn etc.

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