

# A Study of the Acid Properties of Structurally and Compositionally Different Heteropoly Acids in Acetic Acid

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**Abstract**—The acid properties of heteropoly acids of the following three structure types were studied by conductometry in acetic acid: Keggin ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PW}_{11}\text{ThO}_{39}$ ; and  $\text{H}_5\text{PW}_{11}\text{XO}_{40}$ , where  $\text{X(IV)} = \text{Ti}$  or  $\text{Zr}$ ), Dawson ( $\alpha\text{-H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  and  $\alpha\text{-H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ ), and  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$ . These compounds are electrolytes that dissociate in only the first step of this solvent. The thermodynamic dissociation constants of the heteropoly acids were calculated by the Fuoss–Kraus method. The Hammett acidity functions  $H_0$  of the solutions of  $\text{H}_5\text{PW}_{11}\text{XO}_{40}$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ , and  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  in 85% acetic acid at 25°C were determined by the indicator method. All of the test heteropoly acids were found to be strong acids.

## INTRODUCTION

Heteropoly acids are strong Brønsted acids, and they are widely used as homogeneous and heterogeneous acid catalysts [1, 2]. Heteropoly acids with the Keggin structure have been studied in most detail. Their acidity in solutions has been quantitatively characterized and compared to the acidity of ordinary mineral acids [2–5]. In aqueous solutions, heteropoly acids are strong acids, which are fully dissociated in all steps. The acidity of these solutions expressed in terms of the Hammett acidity function  $H_0$  is at a level of the acidity of  $\text{HClO}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$  solutions [5]. Nonaqueous solvents exert a differentiating effect on the acid properties of heteropoly acids. According to Kulikov and Kozhevnikov [4], in acetic acid, Keggin structure heteropoly acids are comparatively weak electrolytes that dissociate in only the first step. The acid dissociation constants  $pK$  were determined for these compounds by conductometry, and their acidity was found to be higher than that of sulfuric acid (a conventional acid catalyst) by 2–5  $pK$  units [4].

Presently, a wide range of heteropoly acids is known, and a great body of information on their structure was accumulated [6]. However, data on the acidity of solutions of heteropoly acids that are different from Keggin structure heteropoly acids are very limited [5]. In this work, we used the indicator method and conductometry for studying acetic acid solutions of heteropoly acids of the following structure types: Keggin ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ,  $\text{H}_5\text{PW}_{11}\text{TiO}_{40}$ ,  $\text{H}_5\text{PW}_{11}\text{ZrO}_{40}$ , and  $\text{H}_3\text{PW}_{11}\text{ThO}_{39}$ ), Dawson ( $\alpha\text{-H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  and  $\alpha\text{-H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ ), and  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$ .

## EXPERIMENTAL

Heteropoly acids of the following compositions were used in this study:  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 15.4\text{H}_2\text{O}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 17.5\text{H}_2\text{O}$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 17.5\text{H}_2\text{O}$ ,  $\text{H}_5\text{PW}_{11}\text{TiO}_{40} \cdot 14.2\text{H}_2\text{O}$ ,  $\text{H}_5\text{PW}_{11}\text{ZrO}_{40} \cdot 16.5\text{H}_2\text{O}$ ,  $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62} \cdot 23.7\text{H}_2\text{O}$ ,  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 17.0\text{H}_2\text{O}$ , and  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3 \cdot 28.7\text{H}_2\text{O}$ . The above heteropoly acids were prepared according to published procedures [7–9]. The compound  $\text{H}_3\text{PW}_{11}\text{ThO}_{39} \cdot 12.7\text{H}_2\text{O}$  was synthesized electrochemically by a procedure analogous to that for other complex heteropoly acids [8]. The purity of heteropoly acids and their integrity in acetic acid solutions were monitored by  $^{31}\text{P}$  NMR spectroscopy. The compounds  $\text{CF}_3\text{SO}_3\text{H}$  (Merck, >98%) and  $\text{HClO}_4$  of chemically pure grade (concentration of 9.3 mol/l in an aqueous solution) were used without additional purification. Acetic acid (relative density  $d_4^{25} = 1.0437$  (the ratio between the density of the substance (g/ml) at 25°C to the density of water at 4°C) and specific conductivity of  $5.06 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ ) was obtained by the distillation of high-purity acid on a 0.3-m rectification column.

The Hammett acidity functions  $H_0$  of colorless heteropoly acids ( $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  and molybdenum heteropoly acids are colored) were determined by spectrophotometry at 25°C as described previously [5] with the use of *ortho*-nitroaniline and *para*-nitroaniline as indicators. The  $pK_{\text{BH}^+}$  values of the indicators for solutions in mixed solvents were determined by the Paul method as described previously [5]. These values for 85% acetic acid were equal to –0.27 and +0.99 for *ortho*-nitroaniline and *para*-nitroaniline, respectively.

**Table 1.** Hammett acidity functions  $H_0$  of heteropoly acid solutions (HOAc : H<sub>2</sub>O = 85 : 15 vol %)

H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> *		H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub> *		H <sub>4</sub> PW <sub>11</sub> TiO <sub>40</sub> **		H <sub>3</sub> PW <sub>11</sub> ThO <sub>40</sub> **		H <sub>5</sub> PW <sub>11</sub> ZrO <sub>40</sub> **		H <sub>6</sub> P <sub>2</sub> W <sub>21</sub> O <sub>71</sub> (H <sub>2</sub> O) <sub>3</sub> *	
C, mol/l	$H_0$	C, mol/l	$H_0$	C, mol/l	$H_0$	C, mol/l	$H_0$	C, mol/l	$H_0$	C, mol/l	$H_0$
0.1500	-0.45	0.1000	-0.40	0.0500	+0.19	0.075	+1.98	0.0500	+0.79	0.0500	-0.27
0.1000	-0.36	0.0667	-0.23	0.0330	+0.61	0.050	+0.70	0.0330	+1.34	0.0280	-0.09
0.0667	-0.04	0.0500	-0.07	0.0250	+0.74	0.025	+1.43	0.0250	+1.47	0.0190	-0.03
0.0500	+0.10	0.0330	+0.02	0.0125	+1.05	0.015	+1.72	0.0125	+1.97	0.0140	+0.01
0.0330	+0.27	0.0250	+0.20	—	—	—	—	—	—	0.0095	+0.19
0.0250	+0.37	0.0167	+0.27	—	—	—	—	—	—	0.0070	+0.26
0.0167	+0.62**	—	—	—	—	—	—	—	—	—	—

\* Indicator, *ortho*-nitroaniline ( $5 \times 10^{-4}$  mol/l);  $\epsilon_0 = 6597 \text{ l mol}^{-1} \text{ cm}^{-1}$ ; absorption band at 407 nm.

\*\* Indicator, *para*-nitroaniline ( $5 \times 10^{-4}$  mol/l);  $\epsilon_0 = 13724 \text{ l mol}^{-1} \text{ cm}^{-1}$ ; absorption band at 371 nm.

The conductivity of the solutions was measured at  $25 \pm 0.2^\circ\text{C}$  in a heteropoly acid concentration range of  $10^{-3}$ – $10^{-5}$  mol/l with the use of an ac bridge. A cell with platinum electrodes and a cell constant of  $0.1441 \text{ cm}^{-1}$  was used for the measurements. Because the conductivity of heteropoly acid solutions is almost independent of ac frequency, the measurements were performed at a frequency of 2000 Hz, as in a previous study [4]. We failed to measure the conductivities of a number of heteropoly acids ( $\text{H}_8\text{CeMo}_{12}\text{O}_{42} \cdot 21.2\text{H}_2\text{O}$ ,  $\text{H}_{21}\text{B}_3\text{W}_{39}\text{O}_{132} \cdot 73.7\text{H}_2\text{O}$ ,  $\text{H}_6\text{As}_2\text{W}_{21}\text{O}_{69}(\text{H}_2\text{O}) \cdot 27.4\text{H}_2\text{O}$ , and  $\text{H}_8\text{P}_2\text{W}_{20}\text{SnO}_{71}(\text{H}_2\text{O})_3 \cdot 24.2\text{H}_2\text{O}$ ) in solution because of their low solubility in anhydrous acetic acid.

## RESULTS AND DISCUSSION

Ion pairs that are formed in aqueous acetic acid solutions in a concentration range of  $90\% \leq \text{HOAc} \leq 100\%$  affect the acid–base equilibrium and the scale of

$H_0$  [11]. The effect of associates becomes insignificant at acid concentrations lower than 90%. On this basis, the values of  $H_0$  were determined in aqueous acetic acid containing 85 vol % HOAc. Table 1 summarizes the results of the measurements. The data obtained for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  are consistent with published data [3]. The acidity (on a per-proton basis) in aqueous 85% acetic acid decreases in the order listed below in Table 2:  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3 > \text{H}_4\text{SiW}_{12}\text{O}_{40} \approx \text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_5\text{PW}_{11}\text{TiO}_{40} > \text{H}_3\text{PW}_{11}\text{ThO}_{39} \approx \text{H}_5\text{PW}_{11}\text{ZrO}_{40}$ .

This order is different from the orders found for aqueous (10% H<sub>2</sub>O) acetone and acetonitrile solutions [5]. This fact is indicative of a differentiating solvent effect on the acid properties of heteropoly acids. The acidity of solutions of the first three heteropoly acids from the above series is higher than that of the solutions of strong mineral acids such as HBr and H<sub>2</sub>SO<sub>4</sub>. The solutions of heteropoly acids having a constituent ion that replaces one W ion exhibit markedly lower acidity. It is likely that the presence of potential Lewis sites (Ti<sup>4+</sup>, Zr<sup>4+</sup>, and Th<sup>4+</sup> ions, whose effects on an indicator base cannot be taken into account) is responsible for considerable interference in spectrophotometric measurements.

The acid dissociation constant, which is determined by conductometry in dilute solutions, is one of the most important characteristics of soluble acids [11]. Table 3 summarizes the molar conductivities ( $\mu$ ) of the solutions of structurally and compositionally different heteropoly acids. In almost 100% acetic acid, all of the test heteropoly acids exhibit values of  $\mu$  comparable to those of HClO<sub>4</sub> and CF<sub>3</sub>SO<sub>3</sub>H (Fig. 1). This fact indicates that heteropoly acids behave as monobasic acids in acetic acid. The low values of  $\mu$  result from the low degrees of dissociation of heteropoly acids and from the low solvent permittivity ( $D = 6.20$  [14]).

It is well known [15] that the thermodynamic dissociation constants of weak- and medium-strength electrolytes that dissociate in only the first step can be calculated by the Fuoss–Kraus method at concentrations

**Table 2.** Comparison of the Hammett acidity functions  $H_0$  for acid solutions in 85% HOAc

Acid	$H_0^*$	$H_0^{**}$
H <sub>6</sub> P <sub>2</sub> W <sub>21</sub> O <sub>71</sub> (H <sub>2</sub> O) <sub>3</sub>	-0.27	-0.20
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	+0.10	-0.17
H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	-0.07	-0.04
H <sub>5</sub> PW <sub>11</sub> TiO <sub>40</sub>	+0.19	+0.40
H <sub>5</sub> PW <sub>11</sub> ZrO <sub>40</sub>	+0.79	+1.06
H <sub>3</sub> PW <sub>11</sub> ThO <sub>39</sub>	+0.70	+1.01
HBr	—	+0.17***
H <sub>2</sub> SO <sub>4</sub>	—	+0.75****

\* Values for solutions with the same molar concentration (0.05 mol/l) of the acid.

\*\* Values for solutions with the same concentration (0.20 mol/l) of protons.

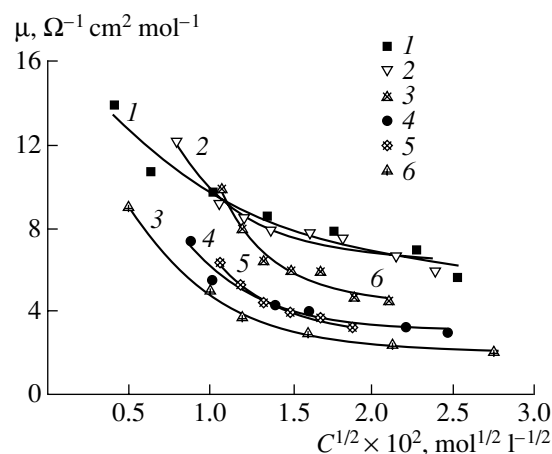
\*\*\* The value estimated from published data [12].

\*\*\*\* The value estimated from published data [13].

(C) lower than  $7 \times 10^{-5}$  mol/l in an acetic acid solution ( $C < 3 \times 10^{-7} D^3$  mol/l). Under these conditions, it is suggested that ion associates of the order higher than ion pairs are not formed. Fuoss and Kraus [15] proposed an equation for calculating thermodynamic dissociation constants. This equation relates the equivalent conductivity of solution  $\lambda$  ( $\Omega^{-1} \text{ cm}^2 \text{ g-equiv}^{-1}$ ) to the dissociation constants of ion pairs ( $K$ ) and associates that consist of three ions (triplets) ( $K'$ ):

$$\lambda\sqrt{C} = \lambda_0\sqrt{K} + \frac{\lambda'_0 C\sqrt{K}}{K'}, \quad (1)$$

where  $\lambda_0$  is the limiting conductivity (at infinite dilution) of free ions and  $\lambda'_0$  is the limiting conductivity of triplet associates. Figure 2 illustrates data obtained in accordance with Eq. (1) for heteropoly acids and  $\text{CF}_3\text{SO}_3\text{H}$  in acetic acid solutions. As can be seen in Fig. 2, at concentrations above  $2 \times 10^{-4}$  mol/l,  $\lambda\sqrt{C}$  plotted against  $C$  flattens out both in the case of heteropoly acids and  $\text{SF}_3\text{SO}_3\text{H}$ ; this fact is indicative of higher order association than ion pairs. At the same time, association in HCl was observed at acid concentrations of  $10^{-5}$ – $10^{-4}$  mol/l [4]. This estimate is rough

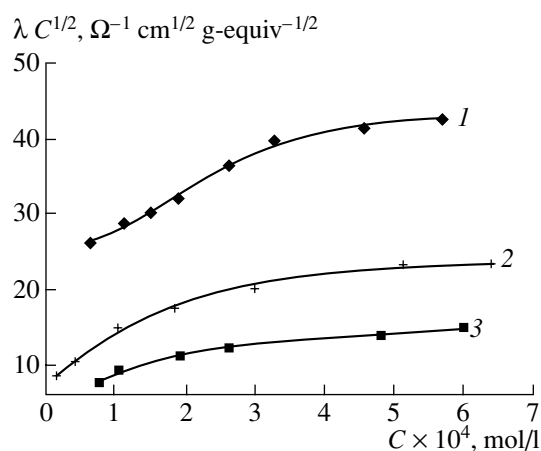


**Fig. 1.** Molar conductivity  $\mu$  as a function of  $\sqrt{C}$  for the acids: (1)  $\text{CF}_3\text{SO}_3\text{H}$ , (2)  $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ , (3)  $\text{HClO}_4$ , (4)  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , (5)  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$ , and (6)  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ .

because Eq. (1) is not strict. However, there is no question that this analysis adequately interprets the trend. Table 4 summarizes the calculated dissociation constants  $K$  and  $\lambda_0$ .

**Table 3.** Molar conductivity of heteropoly acid solutions in HOAc

$C \times 10^4, \text{ mol/l}$	$\mu, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$C \times 10^4, \text{ mol/l}$	$\mu, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$C \times 10^4, \text{ mol/l}$	$\mu, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
<b><math>\text{H}_3\text{PMo}_{12}\text{O}_{40}</math></b>		<b><math>\text{H}_4\text{SiW}_{12}\text{O}_{40}</math></b>		<b><math>\text{H}_3\text{PW}_{12}\text{O}_{40}</math></b>	
1.48	8.142	1.93	4.429	0.768	7.398
1.85	7.000	2.41	3.520	1.040	5.577
2.31	6.631	3.09	2.908	1.920	4.325
3.61	4.798	3.86	2.747	2.600	3.731
4.75	3.844	5.22	2.567	4.800	3.233
5.95	3.289	7.05	2.425	6.000	3.022
<b><math>\text{H}_5\text{PW}_{11}\text{TiO}_{40}</math></b>		<b><math>\text{H}_5\text{PW}_{11}\text{ZrO}_{40}</math></b>		<b><math>\text{H}_3\text{PW}_{11}\text{ThO}_{39}</math></b>	
0.475	8.997	2.45	10.084	0.1120	10.899
0.582	8.591	3.05	6.755	0.1596	8.772
0.792	6.187	4.08	5.196	0.2210	7.861
0.970	6.804	4.49	4.388	0.2760	5.797
1.320	4.470	5.83	3.516	—	—
—	—	6.41	3.183	—	—
<b><math>\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}</math></b>		<b><math>\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}</math></b>		<b><math>\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3</math></b>	
0.631	12.203	1.15	9.870	1.13	6.238
1.130	9.292	1.44	8.090	1.41	5.177
1.500	8.467	1.80	6.500	1.77	4.350
1.900	8.000	2.25	5.935	2.21	3.921
2.630	7.698	2.82	5.784	2.76	3.699
3.290	7.523	3.52	4.776	3.47	3.219
4.570	6.630	4.40	4.470	—	—
5.710	5.963	—	—	—	—



**Fig. 2.** Plots of  $\lambda\sqrt{C}$  against  $C$  in accordance with Eq. (1) for (1)  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ , (2)  $\text{CF}_3\text{SO}_3\text{H}$ , and (3)  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  in acetic acid solutions.

The dissociation constants can be obtained more accurately within the framework of another model proposed by Fuoss [16]. According to this model, the dissociation constant  $K$  is determined from the slope of a linear anamorphosis of the equation

$$\frac{F(Z)}{\lambda} = \frac{1}{\lambda_0} + \frac{C\lambda f^2 \lambda_0^2}{KF(Z)} = \frac{1}{\lambda_0} + \frac{\lambda_0^2}{K} Y, \quad (2)$$

where  $\lambda$  and  $\lambda_0$  are the equivalent and limiting conductivities, respectively;  $C$  is the concentration in g-equiv/l; and  $f$  is the activity coefficient. The  $F(Z)$  parameter is a function of  $Z$ ; the procedure for calculat-

ing this function and its tabulated values were published in [17]. The value of  $Z$  is determined by the equation

$$Z = \alpha(\lambda_0)^{-3/2} C^{1/2} \lambda^{1/2},$$

where  $\lambda$  is the Onsager coefficient, which is obtained by extrapolating  $\lambda/\lambda_0$  as a function of  $\sqrt{C}$  to  $C = 0$ . The activity coefficient  $f$  is calculated by the equation

$$-\log f^2 = 2\beta C^{1/2} \gamma^{1/2},$$

where  $\gamma$  is the degree of dissociation, which is equal to  $\lambda/\lambda_0 F(Z)$ ;  $\beta = 41.24Z\eta^{-1}D^{-1/2}T^{-1/2}$ ;  $\eta$  is the viscosity of the solvent;  $D$  is the permittivity; and  $T$  is the temperature. The values  $D = 6.2$  and  $\eta = 1.11$  cP for HOAc at 25°C were used in the calculations [4]. Figure 3 demonstrates a satisfactorily linear relationship between

$\frac{C\lambda f^2}{F(Z)}$  and  $\frac{F(Z)}{\lambda}$  for the solutions of structurally different heteropoly acids in acetic acid. This fact is indicative of the applicability of this method. Table 4 summarizes the values of  $K$  and  $\lambda_0$  calculated in terms of this model.

The results obtained by us for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  agree with data [4] obtained previously by conductometry, and the dissociation constant of  $\text{CF}_3\text{SO}_3\text{H}$  is also consistent with published data [14].

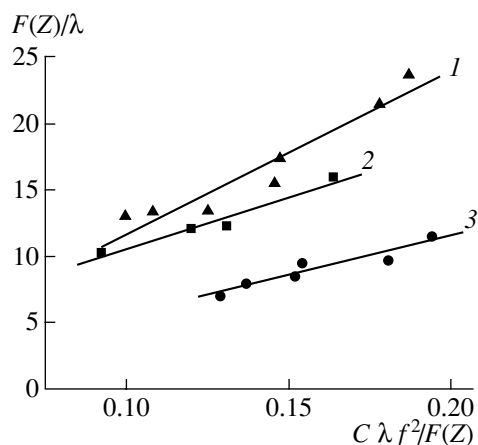
The values of  $\mu$  increased upon the addition of water to a heteropoly acid solution in acetic acid (Fig. 4). In this case, regardless of the amount of water, the follow-

**Table 4.** Dissociation constants  $K$ ,  $\text{p}K$ , and limiting conductivities  $\lambda_0$  for various heteropoly acids in acetic acid solutions

Acid	$\lambda_0$ , $\Omega^{-1} \text{ cm}^2 \text{ g-equiv}^{-1}$	$K^*$ , mol/l	$\text{p}K^*$	$\text{p}K^{**}$	$\text{p}K$ [4]
$\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$	$51.4 \pm 0.4$	$(2.18 \pm 0.2) \times 10^{-5}$	4.66	4.6	—
$\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$	$57.9 \pm 5.4$	$(4.06 \pm 0.4) \times 10^{-5}$	4.39	4.3	—
$\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$	$43.6 \pm 4.1$	$(4.31 \pm 0.4) \times 10^{-5}$	4.36	4.3	—
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$14.6 \pm 0.7$	$(2.08 \pm 0.2) \times 10^{-5}$	4.68	4.7	4.70
$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	$15.7 \pm 0.7$	$(1.35 \pm 0.1) \times 10^{-5}$	4.87	4.8	4.97
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	$14.0 \pm 0.6$	$(2.01 \pm 0.2) \times 10^{-5}$	4.70	4.7	4.77
$\text{H}_5\text{PW}_{11}\text{TiO}_{40}$	$40.8 \pm 1.3$	$(4.78 \pm 0.3) \times 10^{-6}$	5.32	5.2	—
$\text{H}_3\text{PW}_{11}\text{ThO}_{39}$	$69.7 \pm 5.1$	$(3.31 \pm 0.3) \times 10^{-6}$	5.48	5.6	—
$\text{H}_5\text{PW}_{11}\text{ZrO}_{40}$	$48.2 \pm 3.8$	$(3.55 \pm 0.3) \times 10^{-6}$	5.45	5.5	—
$\text{CF}_3\text{SO}_3\text{H}$	$27.6 \pm 0.3$	$(1.07 \pm 0.1) \times 10^{-5}$	4.97	5.0	—
$\text{HClO}_4$	44 [17]	—	—	—	4.87
$\text{HBr}$	—	—	—	—	5.6
$\text{H}_2\text{SO}_4$	—	—	—	—	7.0
$\text{HCl}$	—	—	—	—	8.4

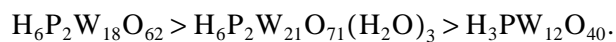
\* Calculated by Eq. (2).

\*\* Calculated by Eq. (1).



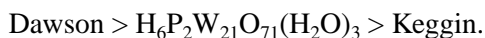
**Fig. 3.** Plots of  $\frac{F(Z)}{\lambda}$  against  $\frac{C\lambda f^2}{F(Z)}$  for the solutions of the following heteropoly acids in HOAc: (1)  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ , (2)  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , and (3)  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$ .

ing order of changes in  $\mu$  for acids remained unchanged:

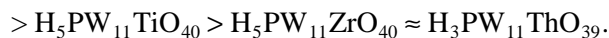
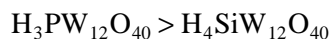


The dilution of acetic acid with water significantly increases the permittivity of the solvent ( $D = 6.2, 8.5$ , and  $15$  for  $100, 95$ , and  $85\%$  HOAc, respectively [10]). Consequently, the degrees of acid dissociation of heteropoly acids increase. A more drastic increase in the values of  $D$  for heteropoly acid solutions, as compared to that of the monobasic acid  $\text{CF}_3\text{SO}_3\text{H}$ , and a nonlinear change in these values indicate that heteropoly acids in HOAc– $\text{H}_2\text{O}$  mixtures are polyelectrolytes, and the stepwise dissociation constants intricately depend on the water content.

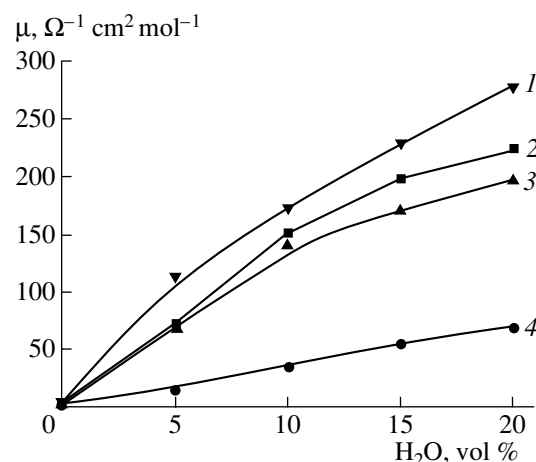
The data (Table 4, Fig. 4) suggest that the acid properties of heteropoly acids in acetic acid depend on the structure and composition of heteropoly acids. For tungsten heteropoly acids, the acidity changes in the following order according to the structure of the anions:



This is consistent with a comparative evaluation of the acidity of Dawson and Keggin structure heteropoly acids in solutions made by studying their reduced forms [18]. For heteropoly acids of the same type (Keggin structure), the dissociation constants in acetic acid decrease in the order



The catalytic activity in reactions performed in dilute solutions in acetic acid, for example, the esterification of butanol by acetic acid, changes in the same order [19]. In general, this order corresponds to the previously discovered relationship between the acidity and the anion charge of heteropoly acids [1]. The fact that



**Fig. 4.** Molar conductivity  $\mu$  as a function of the water content of HOAc solutions for the acids: (1)  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ , (2)  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}$ , (3)  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , and (4)  $\text{CF}_3\text{SO}_3\text{H}$ .

$\text{H}_3\text{PW}_{11}\text{ThO}_{39}$  drops out of this order can be associated with an unusual structure of the anion. This anion contains the bulky octacoordinated  $\text{Th}^{4+}$  ion, which cannot be placed in the internal coordination sphere of the heteropoly acid anion and, probably, is a partially aquated ion.

The replacement of  $\text{W}^{6+}$  by  $\text{Mo}^{6+}$  in the coordination sphere of the anion has no effect on the acid dissociation constants of heteropoly acids, whereas the replacement of  $\text{W}^{6+}$  by  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ , or  $\text{Th}^{4+}$  is accompanied by a decrease in the constants. This behavior is qualitatively consistent with predictions based on the simple electrostatic theory. The same behavior was observed previously using  $\text{Mo}^{5+}$  and  $\text{V}^{5+}$  substituent ions as examples [4].

For comparison, Table 4 gives the values of  $K$  for other mineral acids in acetic acid solutions. The  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  acids are similar to  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{HClO}_4$  in strength;  $\text{H}_5\text{PW}_{11}\text{TiO}_{40}$  and  $\text{H}_5\text{PW}_{11}\text{ZrO}_{40}$  are similar to  $\text{HBr}$ ; and the weakest acid  $\text{H}_3\text{PW}_{11}\text{ThO}_{39}$  is almost equal to  $\text{H}_2\text{SO}_4$  in strength. At the same time,  $\alpha\text{-H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ ,  $\alpha\text{-H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ , and  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  are somewhat stronger acids than  $\text{CF}_3\text{SO}_3\text{H}$  or  $\text{HClO}_4$ .

The results of this study and previously published data [5] demonstrate that all of the test heteropoly acids are strong acids. This is consistent with data found with the use of other techniques for studying the acidity of heteropoly acids [1, 6]. Depending on the structure of the anion, the acidity of heteropoly acids varies over only a small range. The acidity of heteropoly acids of the same type changed more markedly with changes in the anion charge and upon the introduction of substituent ions that cause local changes in the electric charge density at the surface of the heteropoly acid anion.

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## REFERENCES

- Okuhara, T., Mizuno, N., and Misono, M., *Adv. Catal.*, 1996, vol. 41, p. 113.
- Kozhevnikov, I.V., *Usp. Khim.*, 1993, vol. 62, no. 5, p. 510.
- Kozhevnikov, I.V., Khankhasaeva, S.Ts., and Kulikov, S.M., *Kinet. Katal.*, 1988, vol. 29, no. 1, p. 76.
- Kulikov, S.M. and Kozhevnikov, I.V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, no. 3, p. 498.
- Timofeeva, M.N., Maksimov, G.M., and Likholobov, V.A., *Kinet. Katal.*, 2001, vol. 42, no. 1, p. 37.
- Maksimov, G.M., *Usp. Khim.*, 1995, vol. 64, no. 5, p. 480.
- Kulikov, S.M., Maksimovskaya, R.I., and Kulikova, O.M., *Izv. Akad. Nauk, Ser. Khim.*, 1992, no. 3, p. 494.
- Maksimov, G.M., Maksimovskaya, R.I., and Kozhevnikov, I.V., *Zh. Neorg. Khim.*, 1992, vol. 37, no. 10, p. 2279.
- Maksimov, G.M., Maksimovskaya, R.I., and Kozhevnikov, I.V., *Zh. Neorg. Khim.*, 1994, vol. 39, no. 4, p. 623.
- Wiberg, K.B. and Evans, R.J., *J. Am. Chem. Soc.*, 1958, vol. 80, no. 12, p. 3019.
- King, E.J., Acid-Base Equilibria., *The International Encyclopedia of Physical Chemistry and Chemical Physics. Top. 15*, Guggenheim, E.A., Mayer, J.E., and Tompkins, F.C., Eds., Oxford: Pergamon, 1965, vol. 4.
- Zajac, W.W. and Nowicki, R.B., *J. Phys. Chem.*, 1965, vol. 69, no. 8, p. 2649.
- Torck, B., Hellin, M., and Coussement, F., *Bull. Soc. Chim. Fr.*, 1962, nos. 8–9, p. 1657.
- Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
- Fuoss, R.M. and Kraus, C.A., *J. Am. Chem. Soc.*, 1933, vol. 55, no. 7, p. 2387.
- Fuoss, R.M., *J. Am. Chem. Soc.*, 1935, vol. 57, no. 3, p. 488.
- Smith, T.L. and Elliot, J.H., *J. Am. Chem. Soc.*, 1953, vol. 75, no. 15, p. 2387.
- Papaconstantinou, E., Dimoticali, D., and Politou, A., *Inorg. Chim. Acta*, 1980, vol. 46, p. 155.
- Timofeeva, M.N., Matrosova, M.M., Maksimov, G.M., Likholobov, V.A., Golovin, A.V., Maksimovskaya, R.I., and Paukshtis, E.A., *Kinet. Katal.*, 2001, vol. 42, no. 6, p. 791.