frared spectra of iodosyl derivatives[25] where the iodine–oxygen bond appears to have appreciable multiple-bond character.

The Raman spectra of both tris(fluorosulfates) indicate structural similarity but are far more complex than those of the anionic species. The vibrational frequencies are listed in Table III, together with a tentative assignment. For both compounds, a total number of six vibrational modes is found in the sulfur–oxygen stretching region and two strong bands become assignable to sulfur–fluorine stretching. A similar duplication of vibrations is found in the lower range of the bending and rocking modes. Bands previously assigned to halogen–oxygen are found again with comparable intensity in the same place as the anionic species.

The obvious explanation for the multitude of bands is that two types of fluorosulfate groups are present in both compounds. One set of bands is in approximately the same place as found for the tetrafluorosulfatohalate(III) anions, even though the asymmetric S–O stretching frequency appears at a higher wave number. Again the shift is larger for the bromine compound, indicating a higher degree of covalency, as found before.

The second set of nine vibrational modes could possibly be due to a second covalently bonded monodentate SO_3F group as expected for a T-shaped molecule or for a bidentate bridging group. We clearly prefer the latter alternative for the following reasons. The halogen–oxygen frequencies would be found in a different place and a total of six Raman-active bands would be expected for the C_{2v} model with three in the stretching range. Only minor positional changes for a second terminal SO_3F group would be expected. In addition, fair agreement with the bridging fluorosulfate group in the hexacoordinated compounds $Sn(SO_3F)_4$ and $Cl_2Sn(SO_3F)_2$[11] is found.

All this points to the fact that the two halogen tris(fluorosulfates) are not monomeric in the solid state. The most likely models are a chain-type polymer or a bridged dimer, both with a square-planar configuration for the halogen. Even though the observed solubility in solvents such as $S_2O_5F_2$ and $S_2O_6F_2$ points to low molecular weight species, no clear distinction is possible at this point.

The occurrence of many doublets in the spectrum of bromine tris(fluorosulfate) is best explained by assuming different conformations of both the terminal and the bridging group. Only singlets are observed for most corresponding bands of $I(OSO_3F)_3$ present as a melt. All assignments for the two fluorosulfate groups are tentative particularly in the lower frequency range. The higher frequency S–F vibration is assigned to the bridging SO_3F group, based on the $Cl_2Sn(SO_3F)_2$[11] example. Vibrational modes at 200 cm^{-1} and lower could possibly be due to lattice modes.

Acknowledgment.—We acknowledge financial support from the National Research Council of Canada.

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CONTRIBUTION FROM THE CLIMAX MOLYBDENUM COMPANY OF MICHIGAN,
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Solution Properties of 12-Heteropoly Acids of Molybdenum

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Conductivity and pH measurements were made on the heteropoly acids $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ at 25° in mixed oxygen-containing solvents to establish the stability and electrolyte strength of the compounds. Measurements of pH were also obtained on $H_3[PMo_{12}O_{40}]$ and $H_4[SiMo_{12}O_{40}]$. The conductivity data show that the vanadium compounds exhibit typical behavior of unsymmetrical strong electrolytes in the oxygen-containing solvents. The pH data show that the heteropoly acids studied are strong, stable acids in these media. The acid $H_3[PMo_{12}O_{40}]$ is hydrolytically unstable in water, but it is stabilized by mixed oxygen-containing solvents. Diffusion coefficients were calculated for $PMo_{11}VO_{40}^{4-}$ and $PMo_{10}V_2O_{40}^{5-}$ using conductivity data.

Introduction

A previous paper[1] reported the stability and acid strength of the heteropoly acids $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ as determined by conductivity and pH measurements in aqueous solution. These data showed that $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ are strong 1:4 and 1:5 electrolytes, respectively, having conductivities that obey the Onsager–Fuoss equation.[2,3]

The present work constitutes an extension of the conductivity studies on these compounds into dioxane–water and *tert*-butyl alcohol–water solvent mixtures; the compounds are expected to find usefulness in solvents other than water alone. In addition, pH measurements of the acids $H_3[PMo_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, $H_4[PMo_{11}VO_{40}]$, and $H_5[PMo_{10}V_2O_{40}]$ were obtained in

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* To whom correspondence should be addressed.

[1] C. J. Hallada, G. A. Tsigdinos, and B. S. Hudson, *J. Phys. Chem.*, **72**, 4304 (1968).

[2] R. M. Fuoss and L. Onsager, *ibid.*, **61**, 668 (1957).

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water and mixed solvents to define better the acid strength and hydrolytic stability of these acids in various solvents.

The Onsager–Fuoss equations employed to find values for Λ^0, J, and Λ', namely, $\Lambda = \Lambda^0 - Sc^{1/2} + Ec \log c + Jc$ and $\Lambda' = \Lambda + Sc^{1/2} - Ec \log c = \Lambda^0 + Jc$, have been discussed elsewhere.[1,4]

The chemical behavior of the molybdovanadophosphoric acids has been given previously.[5]

Experimental Section

The molybdovanadophosphoric acids used in this work were prepared and analyzed as described previously.[5] *Anal.* Calcd for $H_4[PMo_{11}VO_{40}]\cdot 16H_2O$: P, 1.50; Mo, 51.00; V, 2.56. Found: P, 1.53; Mo, 50.84; V, 3.22. The molar ratios are as follows: Mo:P, 10.73:1.00; V:P, 1.20:1.00. *Anal.* Calcd for $H_5[PMo_{10}V_2O_{40}]\cdot 16H_2O$: P, 1.55; Mo, 48.10; V, 5.11. Found: P, 1.58; Mo, 48.14; V, 5.65. The molar ratios are as follows: Mo:P, 9.84:1.00; V:P, 2.17:1.00.

The 12-molybdophosphoric acid used was Mallinckrodt, Analytical Reagent. *Anal.* Calcd for $H_3[PMo_{12}O_{40}]\cdot 30H_2O$: P, 1.31; Mo, 48.67; H_2O, 22.83. Found: P, 1.33; Mo, 48.91; H_2O, 23.50 (based on ignition). The Mo:P molar ratio is 11.88:1.00. The 12-molybdosilicic acid was prepared by ion exchange from its sodium salt. *Anal.* Calcd for $H_4[SiMo_{12}O_{40}]\cdot 15H_2O$: Si, 1.34; Mo, 55.00. Found: Si, 1.35; Mo, 55.13. The molar ratio is Mo:Si, 11.95:1.00.

The conductivities were measured at 25.00 ± 0.01°, using the weight dilution technique in a flask-type cell containing shiny platinum electrodes. The cell was calibrated with standard potassium chloride solutions and found to have a constant of 0.4093 cm^{-1}. All measurements were made at 3 kc, using an Industrial Instruments Model RC-18 conductivity bridge. Results from several stock solutions of a given acid and from different preparations of a given acid show that the data were reproducible. Solvent conductivity corrections were made in all cases but this was always less than 1%.

Conductivity data for $H_4[PMo_{11}VO_{40}]$ were obtained in 20 and 60% *tert*-butyl alcohol and in 20% dioxane solution. Data for $H_5[PMo_{10}V_2O_{40}]$ were obtained in 20% *tert*-butyl alcohol and in 20 and 40% dioxane. *tert*-Butyl alcohol–water was chosen as a solvent mixture, since primary and secondary alcohols are oxidized by the molybdovanadophosphoric acids. Reproducible readings were obtained in all solutions; however, small drifts toward lower conductivity values were found when the dioxane solutions stood for several weeks.

Potentiometric measurements of the hydrogen ion activity were made with a Beckman Model 1019 Research pH meter which was calibrated with buffers accurate to ±0.01 pH unit. A glass electrode was used *vs.* the standard calomel electrode. The potentiometric titrations with base involved the acids $H_3[PMo_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, $H_4[PMo_{11}VO_{40}]$, and $H_5[PMo_{10}V_2O_{40}]$ and were conducted in water, dioxane–water, *tert*-butyl alcohol–water, and 3 *M* $NaClO_4$ solutions. The 0.100 *N* NaOH solution used for titrating contained the same solvent as that used in the heteropoly acid solution. The pH *vs.* pC_{H^+} data were obtained on the above-mentioned acids in water, 20% dioxane, and 20% dioxane containing 3 *M* $NaClO_4$. A standard curve for HCl in the three solvent mixtures was used for comparison. Unsteady values of pH were obtained in 20% dioxane containing 3 *M* $NaClO_4$, indicating adsorption on the electrodes.[6]

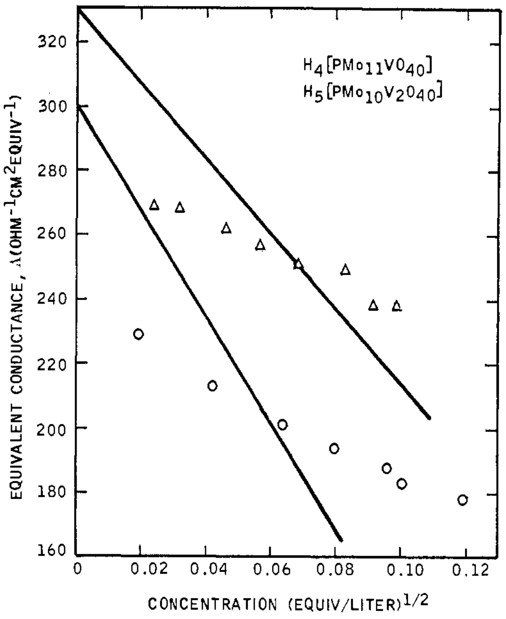

Figure 1.—Phoreograms for molybdovanadophosphoric acids in 20% dioxane. Straight lines are limiting-law slopes.

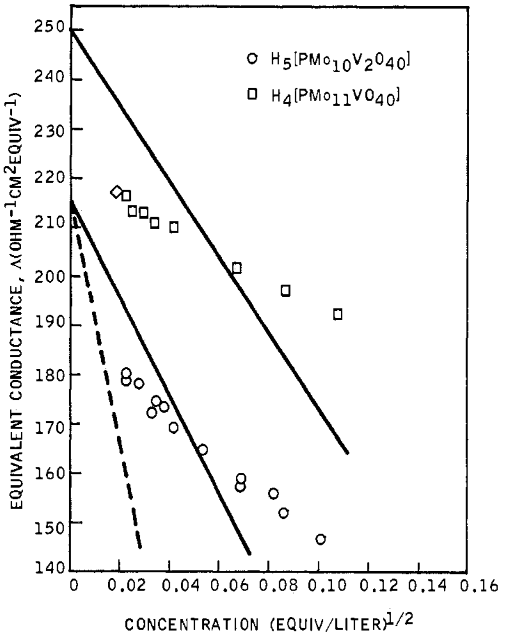

Figure 2.—Phoreograms for molybdovanadophosphoric acids in 20% *tert*-butyl alcohol. Straight lines are limiting-law slopes; the dashed line is the limiting slope based on $\lambda^0_+ = \lambda^0_-$.

Results and Discussion

Conductivity Results.—Conductivity data in water for the two molybdovanadophosphoric acids have been given in a previous paper.[1] Representative data obtained on these heteropoly acids in 20% dioxane and 20% *tert*-butyl alcohol are illustrated by the phoreograms shown in Figures 1 and 2, along with the limiting-law slopes. A typical plot of Λ' *vs.* c for $H_4[PMo_{11}VO_{40}]$ in 20% dioxane is given in Figure 3. The plots of Λ *vs.* $c^{1/2}$ obtained for all solutions and typified by those shown in Figures 1 and 2 show that if association is occurring for both acids, it is slight. The plot of Λ' *vs.* c (Figure 3) for $H_4[PMo_{11}VO_{40}]$ in 20% dioxane begins to curve downward for concentrations greater than

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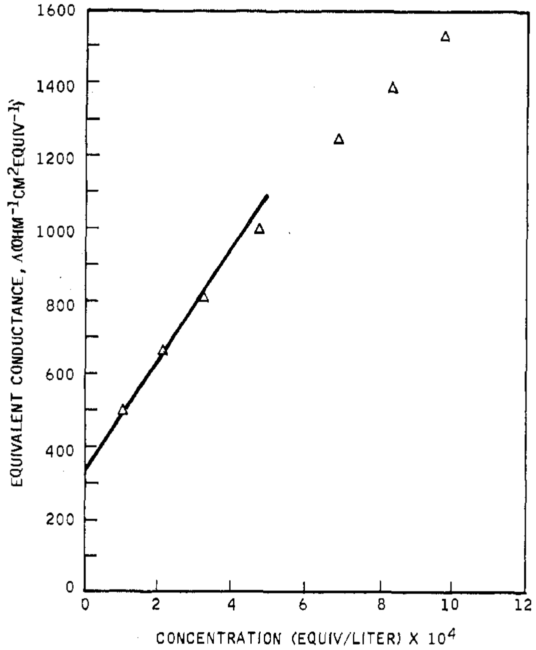

Figure 3.—Fuoss plot for $H_4[PMo_{11}VO_{40}]$ in 20% dioxane.

3×10^{-4} equiv/l. Although a similar plot for a solution of this acid in water begins to deviate from linearity at higher concentrations (an effect that may be attributed to association), conclusions about possible association in solvents of lower dielectric constant cannot be made since Λ' *vs.* c plots for unsymmetrical electrolytes in such media are not available for comparison. Consequently, the pH data yield more definitive results on the degree of association. The limiting conductivity values for the solutions were obtained by extrapolating the Λ' plots to zero concentration (Table I). In general, for the same solvent system, the values of Λ^0 for $H_4[PMo_{11}VO_{40}]$ are higher than those for $H_5[PMo_{10}V_2O_{40}]$. This difference could be the result of a difference in the anionic conductances at infinite dilution or of a small amount of hydrolysis to give protons in addition to those supplied by the acid. It was found earlier that the $PMo_{11}VO_{40}{}^{4-}$ anion is more susceptible to slight hydrolytic degradation in water than the $PMo_{10}V_2O_{40}{}^{5-}$ anion.[1]

As noted previously, *tert*-butyl alcohol–water was chosen as a solvent for conductivity studies rather than ethanol–water (in which the mobility of the H^+ ion is known) because of the attack of the heteropoly anion on primary and secondary alcohols. However, in calculating values of S, the limiting-law slope, the mobility of the hydrogen ion in ethanol–water was used, since the ion mobility values in *tert*-butyl alcohol were not available. Because the portion of Λ^0 assigned to the H^+ is quite large using this assumption (*e.g.*, in 20% *tert*-butyl alcohol, $\lambda^0{}_+ = 208$ and $\lambda^0{}_- = 7$ for $H_5[PMo_{10}V_2O_{40}]$), incorrect conclusions about acid strength might be obtained by comparison of the data to the limiting-law slope. Therefore, another system was examined in which it was assumed that the heteropoly anion and the hydrogen ion contribute equally to Λ^0; *i.e.*, $\lambda^0{}_+ = 107.5$ and $\lambda^0{}_- = 107.5$ for $H_5[PMo_{10}V_2O_{40}]$ in 20% *tert*-butyl alcohol. Limiting-law slopes calculated for each of these assumptions are shown in Figure 2. It can be seen that $H_5[PMo_{10}V_2O_{40}]$ appears to be a strong acid when either limiting slope is chosen for comparison. The actual limiting slope for $H_5[PMo_{10}V_2O_{40}]$ in 20% *tert*-butyl alcohol would probably lie between the two slopes shown in Figure 2.

TABLE I
CONDUCTIVITY DATA AT 25° FOR
MOLYBDOVANADOPHOSPHORIC ACIDS

	Dielectric constant at 25°	Viscosity at 25°,[a] mP	Limiting, conductivity, Λ^0, ohm^{-1} cm^2 equiv^{-1}	λ^0, ohm^{-1} cm^2 equiv^{-1}
	$H_4[PMo_{11}VO_{40}]$			
Water[b]	78.54	8.95	492	142
20% dioxane	60.79	12.92	330	80
20% *tert*-butyl alcohol	61.3	23.06	250	...
60% *tert*-butyl alcohol	27.9	48.16	90	...
	$H_5[PMo_{10}V_2O_{40}]$			
Water[b]	78.54	8.95	453	101
20% dioxane	60.79	12.92	300	50
40% dioxane	42.98	17.8	180	15
20% *tert*-butyl alcohol	61.3	23.06	215	...

[a] The viscosities at 25° of 20 and 60% *tert*-butyl alcohol solutions were determined with the Ostwald viscometer, using water as a standard: F. Daniels, *et al.*, "Experimental Physical Chemistry," 5th ed, McGraw-Hill, New York, N. Y., 1956, p 60.
[b] Values included for comparison; obtained from previous paper.[1]

The Walden product, $\Lambda^0\eta^0$, for $H_4[PMo_{11}VO_{40}]$ in a water–*tert*-butyl alcohol mixture and for $H_5[PMo_{10}V_2O_{40}]$ in a water–dioxane mixture was plotted *vs.* the dielectric constant, D, of the solvent along with those of hydrochloric acid in water–dioxane and in water–1-propanol mixtures[7] for comparison (Figure 4). The data for the water–alcohol mixtures exhibit maxima near the 20% alcohol–water mixtures, whereas this effect is far less pronounced in the water–dioxane mixtures. The presence of such maxima has been associated with the structure enhancement of water by the addition of small amounts of alcohol.[8] It has been reported that with HCl–ethanol mixtures, this structure enhancement appears to reach a maximum near 20–30% ethanol.[9] The sharp maximum in $\lambda^0\eta^0$ for the hydrogen ion[9] supports this conclusion since its excess mobility depends on proton transfers among associated solvent dipolar molecules. The near absence of such maxima in water–dioxane may indicate that such enhancement is not present.

Diffusion coefficients at infinite dilution, D^0, for the $PMo_{11}VO_{40}{}^{4-}$ and $PMo_{10}V_2O_{40}{}^{5-}$ anions in water and 20% dioxane were calculated from the Nernst expression,[10] $D^0 = RT\lambda^0/zF$, where λ^0 is the mobility of the ion. The $\lambda^0{}_-$ values for 20% dioxane solutions were obtained from the values of Λ^0 in that solvent and the mobility of the proton in 20% dioxane.[11] For PMo_{11}-

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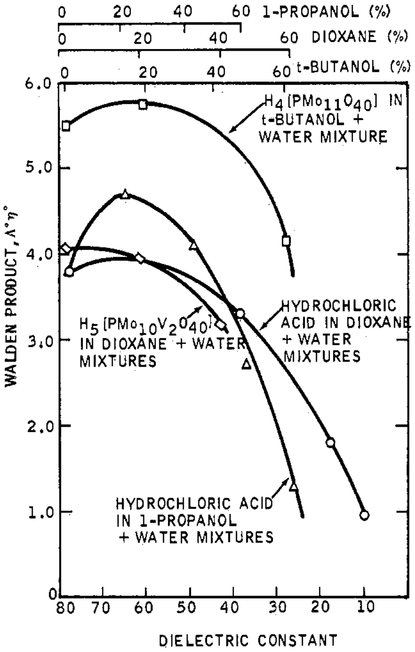

Figure 4.—Walden product *vs.* dielectric constant for hydrochloric acid and molybdovanadophosphoric acids in various solvents

VO_{40}^{4-}, the value of D^0 is 9.48×10^{-6} cm² sec⁻¹ in water and 5.34×10^{-6} cm² sec⁻¹ in 20% dioxane. For $PMo_{10}V_2O_{40}^{5-}$, D^0 is 5.51×10^{-6} cm² sec⁻¹ in water and 2.67×10^{-6} cm² sec⁻¹ in 20% dioxane. These values are in good agreement with values of diffusion coefficients obtained by others for $SiW_{12}O_{40}^{4-}$ in aqueous solutions. A value of $D = 4.51 \times 10^{-6}$ cm² sec⁻¹ was obtained by ultracentrifuge techniques[12] in acetic acid–sodium acetate (ionic strength 0.2) at 25°. Radiotracer techniques[13] in 1 *M* sodium perchlorate at 30° yielded values of 6.2×10^{-6} and 6.1×10^{-6} cm² sec⁻¹ for the $SiMo_{12}O_{40}^{4-}$ and $SiW_{12}O_{40}^{4-}$ anions, respectively. The somewhat high values of the diffusion coefficients obtained for the $PMo_{11}VO_{40}^{4-}$ anion reflect the high sensitivity of the conductivity method in ascertaining the hydrolytic stability of this anion.

Potentiometric Measurements.—It has been shown that oxygen-containing solvents such as acetone, alcohol, and dioxane stabilize heteropoly anions such as $AsMo_{12}O_{40}^{3-}$ in aqueous solutions.[14,15] Therefore, potentiometric measurements have been made on several other heteropoly acids to obtain information on the number of replaceable hydrogen ions of the acids and the hydrolytic stability of the acids in various solvent media.

The potentiometric titration of 12-molybdosilicic acid, $H_4[SiMO_{12}O_{40}]$, with sodium hydroxide shows the acid to be tetrabasic in water, as ascertained by the single point of inflection occurring at the addition of 4 mol of base per mole of acid. The same titration in 3 *M* $NaClO_4$ shows a considerable flattening of the curve, the inflection point becoming indiscernible, indicating appreciable hydrolytic degradation of the heteropoly anion in the high ionic strength medium employed. However, the same titration in 20% *tert*-butyl alcohol solution containing 3 *M* $NaClO_4$ gives a well-defined inflection point at the addition of 4 mol of base per mole of acid.

12-Molybdophosphoric acid, $H_3[PMo_{12}O_{40}]$, has long been known to undergo extensive hydrolytic degradation in water, especially in dilute solutions. This behavior has accounted for the high basicities reported for this acid in the older literature, especially by the Rosenheim school,[16] and this effect has been reported even in fairly modern literature.[17] As already indicated, 12-molybdophosphoric acid when titrated with sodium hydroxide behaves as six-to-seven basic in water or in 20% *tert*-butyl alcohol solution containing 3 *M* $NaClO_4$. However, in 20% *tert*-butyl alcohol or in 20 and 40% dioxane solution, the acid is tribasic, as formulated. It was also found that this acid still behaves as five-to-six basic in 10% dioxane and in 10% *tert*-butyl alcohol; hence, this amount of organic solvent is not sufficient to impart hydrolytic stability to the 12-molybdophosphate anion. Although 12-molybdosilicic acid is stabilized by 20% *tert*-butyl alcohol in the presence of 3 *M* $NaClO_4$, 12-molybdophosphoric acid (a hydrolytically less stable compound) is not.

Figures 5–7 represent plots of pH *vs.* pC_{H^+} for hydrochloric acid, $H_4[SiMo_{12}O_{40}]$, and $H_3[PMo_{12}O_{40}]$, respectively, where pH is the measured value and pC_{H^+} is calculated from the solution concentration. The pH data for hydrochloric acid (Figure 5) were specifically obtained both in aqueous and in 20% dioxane to show that the effect of liquid junction potentials is very small. The measured values of pH for the same concentration of hydrochloric acid in 20% dioxane are slightly below those in water as expected for these mixed

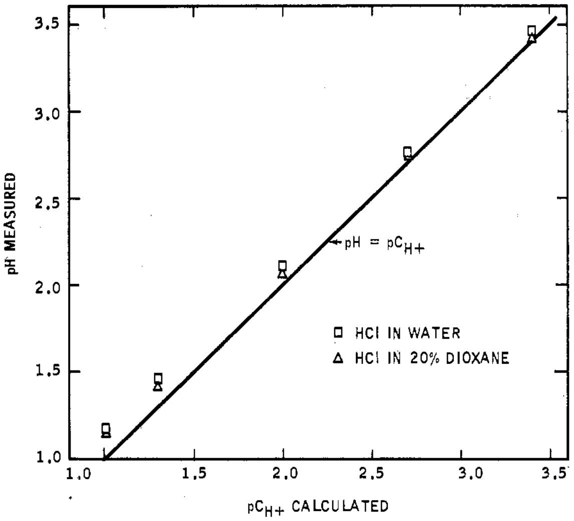

Figure 5.—pH data for HCl in water and 20% dioxane.

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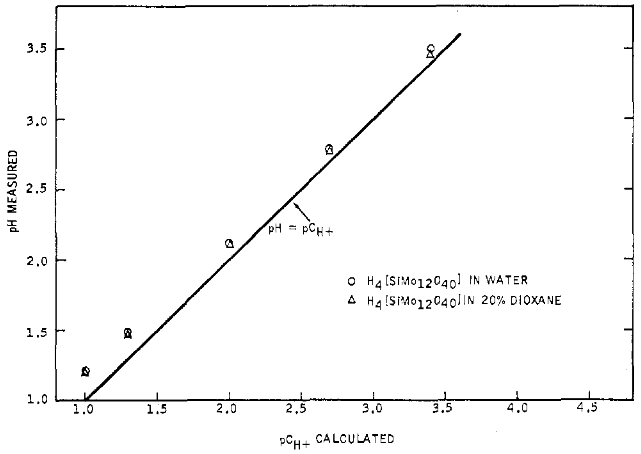

Figure 6.—pH data for $H_4[SiMo_{12}O_{40}]$ in water and 20% dioxane.

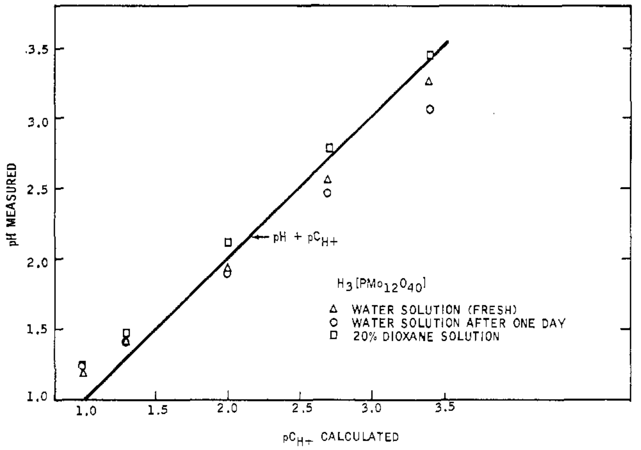

Figure 7.—pH data for $H_3[PMo_{12}O_{40}]$ in water and 20% dioxane.

solvent media[18] since the activity coefficients of hydrochloric acid are nearly identical in water and 20% dioxane.[19] The data for the heteropoly acids show that within experimental error, the pH is the same for both aqueous and 20% dioxane solutions of HCl, $H_4[SiMo_{12}O_{40}]$, and $H_3[PMo_{12}O_{40}]$; that is, Figures 5–7 are superimposable. However, in water alone, $H_3[PMo_{12}O_{40}]$ undergoes hydrolytic degradation producing hydrogen ion as shown by the fact that the pH values are *below* those calculated (shown by solid line), in the more dilute solutions. This effect is more pronounced when such solutions are allowed to stand for 1 day.

It has been shown from conductivity measurements that hydrochloric acid in water–dioxane mixtures behaves like a strong electrolyte even up to 70% dioxane.[11] Consequently, hydrochloric acid must remain unassociated at the concentrations employed in this work, both in water and dioxane–water. The upward trend of the points at low pC_{H^+}, *i.e.*, high acid concentration (Figure 5), must be due to variation of activity coefficients which are nearly identical, as already stated, in water and 20% dioxane,[19] rather than association. Such variation of activity coefficients has been established[20] in solutions less than 0.1 *m* for the heteropoly compounds $(NH_4)_3[CrMo_6O_{24}H_6]$ and $(NH_4)_3[AlMo_6O_{24}H_6]$. It has been shown in this laboratory[1] that nitric acid behaves similarly in water, but pH *vs.* pC_{H^+} plots of this acid in 3 *M* $NaClO_4$ are linear due to the high ionic strength medium employed. The similarity in behavior between $H_4[SiMo_{12}O_{40}]$ and these known strong acids in both solvents confirms that $H_4[SiMo_{12}O_{40}]$ is stable and a very strong acid in these solutions. On the other hand, $H_3[PMo_{12}O_{40}]$, a strong but unstable acid in water, retains its acid strength and is stabilized in 20% dioxane. Such stabilization may be imparted by the direct interaction of the heteropoly anion with the organic solvent. Recent infrared evidence points to the direct interaction of heteropoly anions with organic solvents containing electron-donating groups such as ketones.[21] In addition, nmr evidence has shown that the protons in heteropoly acids are present as H_3O^+ ions in the solids and in ether solutions.[22]

The acids $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ also behave like hydrochloric acid in 20% dioxane and hence are stable, strong acids in this medium. These acids have also been shown by pH measurements to be stable, strong electrolytes in water solution.[1]

Plots of pH *vs.* pC_{H^+} for HCl, $H_4[SiMo_{12}O_{40}]$, $H_4[PMo_{11}VO_{40}]$, and $H_5[PMo_{10}V_2O_{40}]$ in 20% dioxane containing 3 *M* $NaClO_4$ were also obtained. However, as already mentioned, adsorption effects on the electrodes make these pH data somewhat unreliable; hence these data are not presented.

Souchay has reported[23] that dissociation constants can be determined from partition measurements involving water and organic solvents. A p*K* value of 0.75 was reported for the acid dissociation constants of $H_4[PMo_{11}VO_{40}]$, which was measured by the distribution of this acid in water and isoamyl alcohol at varying perchloric acid concentrations. However, Souchay made the assumption that the heteropoly acid is less dissociated in higher perchloric acid concentrations and, hence, more extractable in the organic solvent. This remains only an assumption. It has been shown in this work that the heteropoly acids studied are strong electrolytes, even in mixed solvents having a low dielectric constant.

Acknowledgments.—The authors are indebted to the analytical staff of this laboratory for performing the analyses.

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