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Formation of Solvates of Phosphotungstic and Silicotungstic Heteropoly Acids in the Course of Ethanol Vapor Absorption

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Abstract—Absorption of ethanol vapor with dehydrated solid phosphotungstic and silicotungstic heteropoly acids was studied by a gravimetric adsorption procedure at room temperature. The absorption isotherms are steplike and reflect stepwise formation of proton–alcohol associates in the acid lattices.

Absorption of alcohol vapors with dehydrated solid heteropoly acids of the Keggin structure, in particular, with phosphotungstic ($H_3PW_{12}O_{40}$) and silicotungstic ($H_4SiW_{12}O_{40}$) acids involves formation of solvates in the bulk [1–4]. Monitoring of the process by ^{1}H NMR [1, 2] suggests that incorporation of molecules in lattices of heteropoly acids is mainly determined by the proton affinity of alcohols; in the space between the heteropolyanions, protonated alcohol species $H^+(2ROH)$ are formed, with the overall composition of the solvates being $H_3PW_{12}O_{40} \cdot 6ROH$ and $H_4SiW_{12}O_{40} \cdot 8ROH$. Thus, the absorption capacity of the heteropoly acids for alcohols is fairly high, and in this work we studied it quantitatively, for sorption of ethanol vapor with phosphotungstic and silicotungstic acids as example. The goal of our study was to determine the vapor pressures at which the abovementioned solvate species are stabilized and to find whether these species are limiting with respect to the alcohol content and whether they are formed monotonically or in steps.

Analytically pure grade polycrystalline samples of the heteropoly acids were purified by recrystallization from aqueous solutions. In the experiments, we used 10–20-μm fraction. Ethanol was dehydrated by prolonged refluxing over calcined BaO followed by treatment with metallic sodium [5]. Absorption was studied at 20 ± 2°C on an installation equipped with a quartz spring balance, in the course of heating and cooling. The heteropoly acid sample weight was about 0.2 g. The amount of absorbed alcohol, *a*, was determined accurate to within 0.02 $\mathrm{mmol\,g^{-1}}$. Prior to the experiment, the heteropoly acids were heat-treated in a vacuum (120°C, ~0.1 Pa).

When taking the sorption isotherms, the equilibrium vapor pressure in the systems C_2H_6O–heteropoly acid was attained within 8–10 h, which corresponds to slow diffusion of alcohol molecules into the bulk of the acid lattices [1, 2]. Indeed, the specific surface area of phosphotungstic acid after heating in a vacuum at 100°C is as small as ~1 $\mathrm{m^2\,g^{-1}}$ [3, 4]. This value is actually characteristic of surface roughness of polycrystalline nonporous substances. Thus, the sorption space in the lattices of heteropoly acids is formed in the course of alcohol absorption, which should be accompanied by changes in the unit cell parameters of the solid acids [1, 2].

The sorption isotherms measured with phosphotungstic and silicotungstic acids are generally similar (Fig. 1) but exhibit certain specific features. For example, the initial portions of the isotherms differ considerably. Noticeable absorption of alcohol with phosphotungstic acid is observed once the first portions of alcohol are admitted, and two steps of primary solvation, manifested as characteristic inflections, can be readily revealed. In the case of silicotungstic acid, the sorption is very limited up to the relative pressure $p/p_0 = 0.17$. It is known [1, 2, 6] that heteropoly acid anions exhibit a poor capability for hydrogen bonding; the driving force of alcohol absorption is its affinity for heteropoly acid protons. In terms of this concept, the delay observed in the isotherm with silicotungstic acid may be due to more rigid localization of protons in its lattice and their weaker accessibility for the alcohol molecules. This trend is, to a certain extent, consistent with the fact that silicotungstic acid is less strong than phosphotungstic acid [6].

The primary solvation step in the isotherm obtained with phosphotungstic acid is followed by the portion corresponding to active absorption of alcohol, with *a* reaching ~6.3 $\mathrm{mol\,mol^{-1}}$ acid (Fig. 1). With silicotungstic acid, the portion corresponding to active sorp-

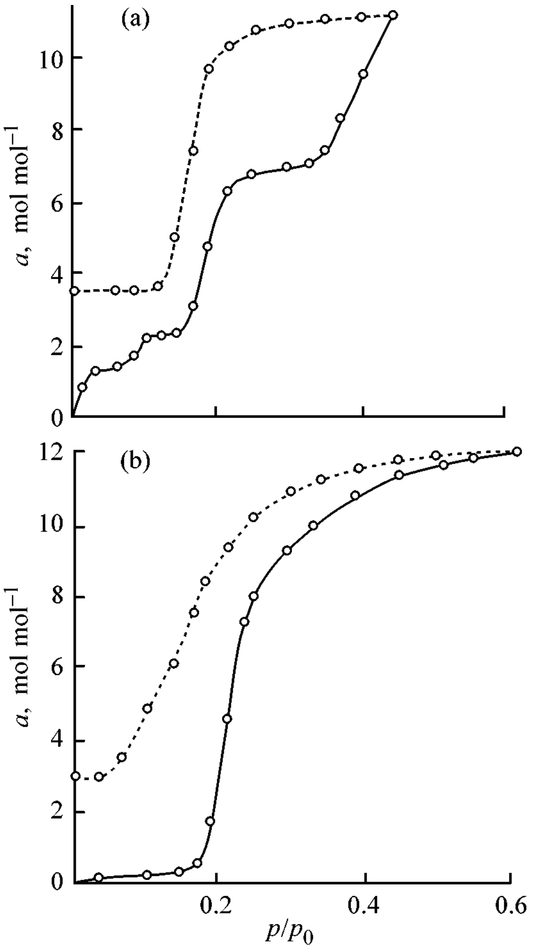

Fig. 1. (*Solid line*) Sorption and (*dashed line*) desorption isotherms of ethanol vapor on (a) phosphotungstic and (b) silicotungstic heteropoly acids. (*a*) Sorption and (*p*/*p*$_0$) relative vapor pressure of alcohol.

tion is pronounced more sharply and covers a narrower range of relative pressures; the solvate of the composition close to $H_4SiW_{12}O_{40} \cdot 8C_2H_6O$ is formed at p/p_0 = 0.25 (at higher relative pressures, the isotherm slope considerably decreases). Thus, whereas into the $H_3PW_{12}O_{40}$ lattice the alcohol molecules are incorporated relatively readily and uniformly with increasing pressure, with $H_4SiW_{12}O_{40}$ a fairly high threshold concentration of the sorbate should be attained, after which absorption occurs very actively. Apparently, solvation of the protons of the solid acids occurs up to formation of the ions $H^+(2C_2H_6O)$, which is in agreement with published data [1, 2] and is consistent with the clear manifestation in the isotherms of species with the coposition close to $H_3PW_{12}O_{40} \cdot 6C_2H_6O$ and $H_4SiW_{12}O_{40} \cdot 8C_2H_6O$. It should be noted that, despite different pathways, formation of both solvates is complete at p/p_0 = 0.22–0.25, suggesting similar structure of the solvates.

A further increase in the alcohol vapor pressure causes absorption of further amounts of alcohol, occurring in two steps with phosphotungstic acid and monotonically with silicotungstic acid (Fig. 1). Apparently, under these conditions sorption on heteropolyanions remains improbable. The process mainly involves the growth of proton–alcohol associates, with the correspondig decrease in the packing density of the solid acids. Finally, the amount of the absorbed alcohol in the lattices reaches 0.23–0.24 cm^3 g^{-1} acid. In the process, the protons become shielded with alcohol molecules and incapable of binding heteropolyanions; in turn, the alcohol molecules, tightly bound in the associates, are oriented by the hydrophobic C_2H_5 groups toward the heteropolyanions, additionally separating them and removing from each other. As a result, the anions become fully isolated, and the lattice breaks down. The final points in the isotherms correspond to the limiting compositions of the solid solvates: $H_3PW_{12}O_{40} \cdot 11.2C_2H_6O$ and $H_4SiW_{12}O_{40} \cdot 12C_2H_6O$ (Fig. 1). Admissions of further, even very small amounts of alcohol cause the solid → liquid phase transition. It should be noted that the acids become liquid at alcohol pressures far from saturation, only slightly exceeding p/p_0 = 0.45 and 0.60 for phosphotungstic and silicotungstic acids, respectively. A minor decrease in the alcohol pressure induces rapid crystallization of the substance, despite the fact that the alcohol content in the substance decreases insignificantly (Fig. 1). In this connection, it is not improbable that, in the composition range close to the phase transition point, the heteropoly acid–alcohol systems occur in the metastable “pseudo-liquid” state. In the system with water vapor, on the contrary, absorption of considerably larger amounts of water (up to the saturation pressure) does not result in liquefication of the solid acids [7]. This feature is probably due not only to the smaller molar volume of H_2O, but also, which is more important, to formation of a system of H bonds of water–proton associates with the heteropolyanions [1, 2, 6, 7].

When recording the isotherms in the desorption mode, significant hysteresis is observed (Fig. 1), indicative of high stability of the proton–alcohol groups formed in the course of absorption. The initial portions of the desorption curves have a small slope; clearly pronounced inflections at p/p_0 = 0.2 and 0.3 for phosphotungstic and silicotungstic acids correspond to the individual species $H_3PW_{12}O_{40} \cdot 10C_2H_6O$ and $H_4SiW_{12}O_{40} \cdot 11C_2H_6O$. As the pressure is decreased further, the solvates break down. The process is pronounced more sharply with phosphotungstic acid, though it does not go to completion. The compositions corresponding to irreversible sorption of approximately 3 mol of alcohol per mole of acid (with both acids) appear to be stable under the experimental conditions; they are preserved even after prolonged evacuation (0.1 Pa).

To conclude, let us consider the pathways of isothermal solvation and subsequent desolvation of heteropoly acids, distinguishing the steps of sharp (s), gradual (g), and strongly hindered (h) transitions to species manifested in the adsorption and desorption branches. The relative pressures corresponding to the transition points are given in parentheses.

$$\begin{tikzcd}
\mathrm{H_3PW_{12}O_{40}} \arrow[r, "s"] & \underset{(0.03)}{\mathrm{H_3PW_{12}O_{40}\cdot 1.3EtOH}} \arrow[r, "g"] & \underset{(0.14)}{\mathrm{H_3PW_{12}O_{40}\cdot 2.4EtOH}} \arrow[r, "s"] & \underset{(0.22)}{\mathrm{H_3PW_{12}O_{40}\cdot 6.3EtOH}} \\
\xrightarrow{g} \underset{(0.35)}{\mathrm{H_3PW_{12}O_{40}\cdot 7.4EtOH}} \arrow[r, "s"] & \underset{(0.45)}{\mathrm{H_3PW_{12}O_{40}\cdot 11.2EtOH}} \arrow[r, shift left, "s"] \arrow[dr, "h"'] & \mathrm{Liquid} \arrow[l, shift left] & \\
 & & \underset{(0.2)}{\mathrm{H_3PW_{12}O_{40}\cdot 10EtOH}} \arrow[r, "s"] & \underset{(0.12)}{\mathrm{H_3PW_{12}O_{40}\cdot 3.5EtOH}}
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{H_4SiW_{12}O_{40}} \arrow[r, "h"] & \underset{(0.17)}{\mathrm{H_4SiW_{12}O_{40}\cdot 0.5EtOH}} \arrow[r, "s"] & \underset{(0.25)}{\mathrm{H_4SiW_{12}O_{40}\cdot 8EtOH}} \\
\xrightarrow{g} \underset{(0.62)}{\mathrm{H_4SiW_{12}O_{40}\cdot 12EtOH}} \arrow[r, shift left, "s"] \arrow[dr, "h"'] & \mathrm{Liquid} \arrow[l, shift left] & \\
 & \underset{(0.3)}{\mathrm{H_4SiW_{12}O_{40}\cdot 11EtOH}} \arrow[r, "s"] & \underset{(0.04)}{\mathrm{H_4SiW_{12}O_{40}\cdot 3EtOH}}
\end{tikzcd}$$

Thus, absorption of ethanol vapor with solid phosphotungstic and silicotungstic acids at room temperature is accompanied by formation of the solvates $H_mEW_{12}O_{40} \cdot nC_2H_6O$ (E = P, $m = 3$; E = Si, $m = 4$) and occurs in several steps clearly distinguishable in the sorption isotherms. The course of absorption is, on the whole, consistent with the concept of formation of proton–alcohol associates in the heteropoly acid lattices. As these associates exceed in size the critical value corresponding to the compositions $H_3PW_{12}O_{40} \cdot 11C_2H_6O$ and $H_4SiW_{12}O_{40} \cdot 12C_2H_6O$, the acid lattices break down, and the sample becomes liquid.

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