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Hydrate and Alcoholate Forms of Phosphomolybdic Heteropolyacid and Their Formation under Conditions of Isothermal Sorption of Water, Methanol, and Ethanol Vapors

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Abstract—Reaction of water, methanol, and ethanol vapors with a solid phosphomolybdic acid at room temperature is accompanied by formation of bulk hydrates and alcoholates. The reaction involves several stages which are readily detected by the sorption and desorption isotherms. The formation of alcoholates causes “loosening” of the acid lattice, thus favoring much more active initial sorption of alcohols, compared with water, and liquefaction once $H_3PMo_{12}O_{40} \cdot 11.5CH_3OH$ and $H_3PMo_{12}O_{40} \cdot 14.7C_2H_5OH$ compositions are attained.

Bulk crystal hydrates of row 12 solid heteropolyacids $H_m(EM_{12}O_{40}) \cdot nH_2O$ (E = R, Si; M = Mo, W) have been thoroughly studied, and their low- ($n = 6$), medium- ($n = 12$–14), and high-water forms ($n = 20$–24, 29–31) have been characterized by X-ray diffraction [1–5]. The ability of alcohols to insert into the crystal lattices of heteropolyacids have also been firmly established; thus, $H_m(EM_{12}O_{40}) \cdot 2m$ROH forms have been described, corresponding to formation of dialcoholate hydrogen ions $H^+ \cdot 2$ROH in space between heteropolyanions [6, 7]. However, the available evidence is insufficient in practical work with such acids, when one deals with both fixed, within certain ranges, and variable compositions of the vapor phase. For example, this relates in full measure to cases where heteropolyacids are exploited as solid electrolytes in fuel cells, the presence of water in which is predetermined by the very oxidation process, and the required moisture level should be maintained for stable conductance [8–12]; therewith, methanol is considered as one of the most promising fuels. Detailed information on hydration and solvation of solid acids can be obtained by adsorption gravimetry [13, 14]. Nearly continuous measurement of water (or alcohol) vapor pressure allows the most probable composition and range of existence of the resulting compounds, the character (continuous or step) of their interconversions, as well as differences in the forms arising under the solvation and desolvation modes to be assessed. To approach these problems, in the present work we used the example of reaction of phosphomolybdic acid $H_3PMo_{12}O_{40}$ with water, methanol, and ethanol vapors, aiming at revealing common and individual features of sorption of molecules capable of hydrogen bonding.

The resulting data are depicted in the figure, where the molar sorptions of water and alcohol vapors are reduced to 1 mol of the acid subjected to preliminary thermal vacuum treatment (see Experimental). In essence, this allows one to judge about the equilibrium stoichiometric compositions of the hydrates and alcoholates formed by phosphomolybdic acid over a wide range of sorbate pressures at room temperature. The acid–water system proved to have not so much in common with the acid–alcohol ones. The most important common features of the three systems are markedly unsteady sorption and desorption processes, as well as rather high hydration (solvation) numbers attainable under increasing pressure, which is generally consistent with the known mechanism of diffusion entering and distribution of molecules in the bulk of acid polycrystals. On the background of these common behavioral features, some peculiarities are observed, that merit consideration. First of all, quite a long and unusual delay in sorption of water vapors over a wide range of low and moderate pressures are noteworthy. It should be mentioned in this connection that, for instance, silicomolybdic and silicotungstic heteropolyacids began to actively absorb water immediately after it had been fed into the measurement volume, and formed hexa- and octahydrates, respectively,

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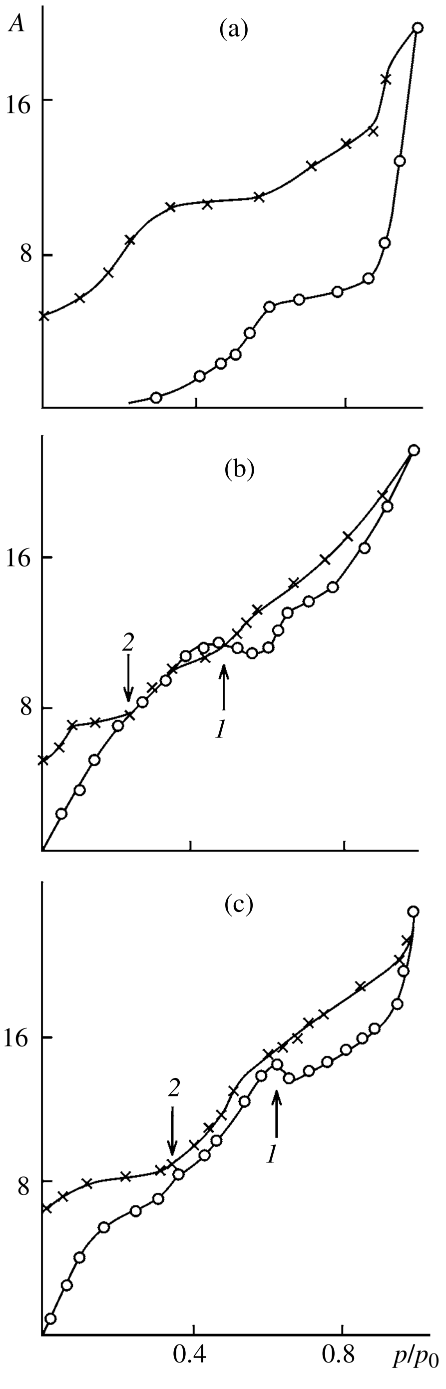


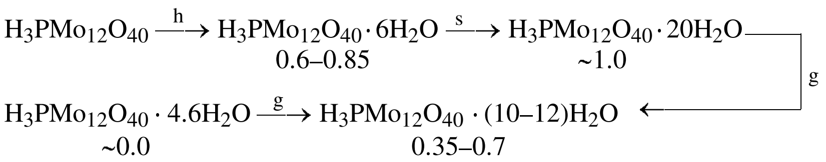
Isotherms of sorption of (a) water, (b) methanol, and (c) ethanol vapors with phosphomolybdic acid (mol/mol heteropolyacid). (Circles) Ascending and (crosses) descending branches of isotherms. (*1*) Liquefaction and (*2*) crystallization points of solvates.

at p/p_0 ~0.2 [13]. Moreover, it is hydrates which are known to be stable forms of heteropolyacids under usual conditions [1–5]. Therewith, water–proton associates hold heteropolyacids together in the crystal lattice. Note in this connection that phosphomolybdic acid markedly differs from its silicon analogs in that in anhydrous state it forms a compact structure, "closed" for water molecules over a wide pressure range. Appreciable sorption commences only when much water has been fed, and, at p/p_0 0.6, a hexahydrate is formed, as evidenced by the observation of a well-defined step in the isotherm. In the second step, phosphomolybdic acid again resists to hydration: The hexahydrate does not change up to near-saturation pressures (p/p_0 ~0.9). After that, only when such a high sorbate concentration has been attained, the lattice of the solid acid is open, and vigorous sorption develops at a short final step, resulting in formation of the high-water state $H_3PMo_{12}O_{40} \cdot 20.5H_2O$.

Having been incorporated in bulk hydrates, water is retained fairly strongly. In the course of isothermal dehydration, long hysteresis delays are observed. Therewith, gradual transition to a stable, medium-water state (n = 10–12) takes place, and then to the hydrate $H_3PMo_{12}O_{40} \cdot 4.6H_2O$ that exists to a vacuum of 0.1 Pa. The results obtained are presented by the Scheme 1, where we label "h", "s", and "g" respectively hindered, sharp, and gradual transitions to forms that reveal themselves in the sorption and desorption branches of the isotherm, and also show the relative pressures of formation and stability of the crystal hydrates.

Before proceeding to alcohol sorption, we must emphasize that phoshomolybdic acid absorbs alcohols much more actively than water. This first of all relates to low- and medium-pressure ranges (p/p_0 = 0–0.5), where water sorption is strongly hindered, whereas alcohol molecules are successfully built into the acid lattice. This result seems unexpected and contradictory in terms of the geometrical and chemical factors responsible for formation of bulk solvates. Indeed, water molecules are much smaller than alcohol molecules, and, consequently, easier to diffuse into space between heteropolyanions. No less important is that the degree of incorporation into the bulk of heteropolyacids is determined by the ability of sorbate molecules to hydrogen bonding, primarily with acid protons. In this respect, too, water much surpasses alcohols. However, the above compelling reasoning contradicts experiment. A possible explanation is that absorbed alcohol molecules effect "loosening" of the acid crystal structure. Diffusing into the surface layer of polycrystalts, they form complexes with protons, the most probable of which are dialkoholate hydrogen ions $H^+ \cdot 2ROH$ [6]. Therewith, protons prove to be screened and no longer act as binders, whereas hydrophobic alcohol "umbrellas" separate heteropolyanions, thus loosening the lattice and ensuring insertion of new molecules at the sites of developing structure

Scheme 1.



defects. As a result, solvates close in composition to $H_3PMo_{12}O_{40}\cdot 6H_2O$ are formed already at p/p_0 ~0.2. Thus the sorption process destroys the acid lattice, and further sorption ($p/p_0 > 0.2$) should inevitably result in transition of the solid solvated state to liquid. The expected transition actually occurs and is reliably detected both visually and by a characteristic peak in the isotherms (see figure). The decrease in sorption, attendant in liquefaction, seems natural in view of higher alcohol vapor pressures over solutions. The relatively small sorption drops imply that at near-transition pressures the $H_3PMo_{12}O_{40}\cdot n$ROH systems with high solvation numbers are more likely to be pseudoliquid than solid [7, 13]. It is interesting to compare characteristics of the solid–liquid transitions for methanol and ethanol (see table). Taking account of the molecular dimensions, one might expect more successful destabilization and destruction of the acid lattice with ethanol. However, with methanol, the relative pressure (p/p_0^{s-l}) of the transition and the corresponding alcohol molar fraction (A_{s-l}) proved to be much lower. The effective liquefaction volumes of solvation alcohols (V_{s-l}) for methanol are half those for ethanol. Thus, it should be admitted that steric (dimensional) features of heteropolyacid–alcohol interactions contribute little into parameters of the phase transition. A key factor in this process is likely to be the vapor pressure over the liquid solvate formed, which, under equilibrium conditions, should be close to the alcohol pressure in the measurement volume. With methanol solvates, this condition is met at the $H_3PMo_{12}O_{40}\cdot 11.5CH_3OH$ composition, whereas with the less volatile ethanol, the solid–liquid transition occurs at $n = 14.7$.

Further on active alcohol sorption with the liquid phase occurs, which is still strictly regulated by pressure. Therewith, equilibrium sorptions are attained two times faster than with solid solvates. The equilibration time is 3–4 h, which is explained by the high viscosity of the solutions. With methanol, the isotherm pattern at the $p/p_0 = 0.6–1.0$ portion is relatively steady. Ethanol, too, is absorbed steadily up to $p/p_0 = 0.95$, but further, near saturation, vigorous vapor condensation is observed. Nevertheless, the sorption branches of the isotherms end by formation of close compositions $H_3PMo_{12}O_{40}\cdot 22CH_3OH$ and $H_3Mo_{12}\cdot O_{40}\cdot 23C_2H_5OH$, implying a common chemical nature of forces responsible for ratios of interacting species in liquid solvates.

Parameters of special points in the isotherms of sorption (desorption) of alcohols and water with solid phosphomolybdic acid

Parameter[a]	CH_3OH	C_2H_5OH	H_2O
p/p_0^{s-l}	0.55	0.63	
A_{s-l}, mol/mol	11.5	14.7	
V_{s-l}, cm^3/g	0.25	0.47	
p/p_0^{l-s}	0.20	0.33	
A_{l-s}, mol/mol	7.5	8.3	
A_{max}, mol/mol	22.1	23.1	20.5
A_i, mol/mol	5.25	6.54	4.65

[a] p/p_0^{s-l}, A_{s-l}, V_{s-l}, p/p_0^{l-s}, and A_{l-s} are the relative pressure, sorption, and effective alcohol pressure in the points of lique–faction and solidification of alcoholates; A_{max} and A_i are the maximum (at $p/p_0 = 1$) and irreversible (at $p/p_0 = 0$) sorption of alcohols and water.

Appreciable irreversible sorption on the reverse run of the isotherms appears to be evidence for strongly associated viscous solutions. The extended hysteresis loops end in both cases at points where earlier (on the forward run) we observed liquefaction of solvates. However, neither the isotherm patterns nor visual observations give evidence for the expected liquid–solid transition. The acid–alcohol systems did not crystallize even when the pressure had been strongly reduced. Therewith, the forward and reverse branches of the isotherms, corresponding to a characteristic transition state, are almost coincident. Polycrystals form only at $p/p_0 = 0.20$ ($H_3PMo_{12}O_{40}\cdot CH_3OH$) and 0.33 ($H_3PMo_{12}O_{40}\cdot C_2H_5OH$), and the descending and ascending branches immediately separate (see figure and table). The resulting data allow recognition of "transition" ranges of existence of pseudoliquid solvates of phosphomolybdic heteropolyacids, that coincide when reproduced in the sorption and desorption modes and bracketed by the liquefaction and solidification points. The A_i values (see table) at the completion of measurements provide further evidence for stability of solid solvates of compositions close to $H_3PMo_{12}O_{40}\cdot 6ROH$.

EXPERIMENTAL

Polycrystalline phosphomolybdic acid of analytical grade was further purified by recrystallization from aqueous solutions. For adsorption measurements, a 10–20-μm fraction was sieved. The alcohols were dehydrated by prolonged boiling with calcined BaO, followed by treatment with metallic sodium [15]. Gravimetry was performed at 20±2°C on a vacuum sorption device equipped with a McBain balance. The isotherms were run in the forward and reverse directions. The sample weight was ~0.2 g. The uncertainty in the adsorption values was no more than 0.02 mmol/g. The acid was preliminary conditioned by heating at 120°C in a vacuum of ~0.1 Pa to constant weight. The sorption isotherms were measured at varied step frequency up to saturated water (alcohol) vapor pressures ($p/p_0 = 1$).

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