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Studies of Layered Uranium (VI) Compounds. VI. Ionic Conductivities and Thermal Stabilities of $MUO_2PO_4 \cdot nH_2O$, Where *M* = H, Li,Na,K,NH_4 or ½ Ca, and Where *n* Is between 0 and 4

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We have measured the ionic conductivities of pressed pellets of the layered compounds $MUO_2PO_4 \cdot nH_2O$, and correlated the results with TGA data. The conductivities (in ohm^{-1} m^{-1}), at temperatures increasing with decreasing water content over the range 20 to 200°C, were approximately as follows: Li^+-$4H_2O$, 10^{-4}; Li^+–, Na^+–, K^+–, and NH_4^+–$3H_2O$, 10^{-4}, 10^{-2}, 10^{-4}, and 10^{-4}; H^+–, Li^+–, and Na^+–$1.5H_2O$, 10^{-2}, 10^{-4}, and 10^{-4}; Na^+–$1H_2O$, 10^{-5}; H^+–, K^+–, and NH_4^+–$0.5H_2O$, all 10^{-5}; and H^+–, Li^+–, Na^+–, K^+–, NH_4^+–, and $\frac{1}{2}Ca^{2+}$–$0H_2O$, 10^{-5}, 10^{-5}, 10^{-4}, 10^{-5}, 10^{-5}, and 10^{-6}. A ring mechanism is proposed to account for the high conductivity found in $NaUO_2PO_4 \cdot 3.1H_2O$. The accurate TGA data showed that most of the hydrates had water vacancies of the Schottky type, and should be represented as $MUO_2PO_4(A - x)H_2O$, where x can be between 0 and 0.3.

Introduction

The observation of high proton conductivity in hydrogen uranyl phosphate tetrahydrate, $HUO_2PO_4 \cdot 4H_2O$ (HUP) (*1*) has prompted studies of the mechanism of conduction (*2, 3*), the NMR behavior (*4, 5*), the antiferroelectric behavior (*6*), the structure (*7*), the thermal stability (*8*), and the fabrication properties (*9, 10*) of the material, and its use in hydride batteries (*11*), fuel cells (*12*), and electrochromic displays (*9*). In addition to possessing properties favorable to H^+ conduction, the structure has features which suggest that other cations, substituted for H^+, may also be mobile. We wish to report here our study of the conductivity of other cations in selected analogs of HUP, and also of H^+ conductivity in the lower hydrates of HUP.

The normal hydrates ($n = 3$ or 4) of the compounds $MUO_2PO_4 \cdot nH_2O$ adopt the *meta*-autunite structure when *M* is a monovalent cation (*7, 13, 14*). The negatively charged $(UO_2PO_4)_n^{n-}$ layers are stacked one above the other, and are interspaced with layers containing water molecules and the counterbalancing cations, arranged, in the case of HUP (*7*) and a mixed H^+/K^+ compound (*14*), in the form of linked squares, as shown in Fig. 1. In the latter case the K^+ ions were not separately identified, and were assumed to substitute on the water sites, in concurrence with the totally substituted K^+ form being a trihydrate (*15*) rather than a tetrahydrate. Although the cell dimensions of a large range of substituted

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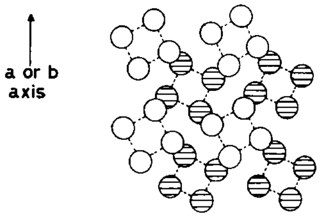

FIG. 1. Plan of the interlayer sites between the $(UO_2PO_4)_n^{n-}$ layers (after Ross and Evans (*14*)). The unshaded sites are elevated with respect to the shaded ones. The sites can be occupied by either water molecules or monovalent cations.

analogs have been determined (*15*), the cation positions are not yet known for any other compounds. (The Li^+ form is presently being studied by neutron diffraction (*16*).)

Evidence regarding the structures of the lower hydrates ($n \leq 3$), and in particular the interlayer site positions, is scanty. HUP can be reversibly dehydrated down to the monohydrate (*17, 18*), with retention of the layer structure, which remains even in the anhydrous compound HUO_2PO_4 (*18*). Similarly the lower hydrates of the Ca^{2+} form are known to retain the layer structure (*meta*-autunite I) (*13*), which is still retained in a distorted form in the anhydrous compound (*meta*-autunite II) (*13*). (The normal hydrates of the divalent metal salts such as $Ca(UO_2PO_4)_2 \cdot 10.5H_2O$ adopt the autunite structure, which in contrast to the *meta*-autunite structure, contains a mirror plane between the layers (*13*).)

The retention of the layer structure in the lower hydrates provided us with the opportunity to study the effect of the concentration of water vacancies on the conductivity behavior, both of HUP and of the metal-substituted compounds. These studies have been valuable in identifying and elucidating the various mechanisms of conduction which we have found to be present in these compounds. Of particular interest was the possibility of high proton conductivity in anhydrous HUO_2PO_4, which is stable over the range 200 to 500°C (*19*). In this case the protons must reside on some of the oxygens belonging to either the uranyl or the phosphate groups, and such acidic environments should aid proton transfer within the partially protonated closely spaced oxygen network.

Experimental

HUP was prepared by precipitation from solution, as previously described (*2, 10*). Following Weigel and Hoffmann (*15*), other cations were substituted for H^+ by stirring HUP with a large excess of a 4 *M* solution of the appropriate chloride or nitrate for 1 day. The substituted compounds are all formed preferentially to HUP, and are also more insoluble than HUP (*20*). The extent of substitution was checked in the case of the Na^+ analog by performing a second exchange, which did not result in any change in the measured conductivity, as will be discussed later. X-Ray powder diffraction indicated only the desired compound in each case. Samples for the conductivity and TGA measurements were washed with distilled water several times until the conductivity of the filtrate solution was less than 10^{-2} ohm^{-1} m^{-1}. The precipitate was pressed between filter papers, then spread out and left to dry to constant weight in air before being lightly ground and loaded into the sample holders. This procedure minimized the contribution of any salt residue to the conductivity of the pressed pellets.

Alternate-current conductivities were measured using a Wayne–Kerr B221 bridge with an external source and an oscilloscope as detector (500 Hz to 50 kHz), a Wayne–Kerr B224 automatic bridge (1592 Hz), and Wayne–Kerr B601 bridge (50 kHz to 1 MHz). The heated rig used for some of the conductivity measurements was controlled to approximately 0.2°C with a Eurotherm

091 PID controller in conjunction with a standardized Pt/Pt 13% Rh thermocouple. TGA measurements were performed on approximately 10-mg samples using a Stanton Redcroft TG770 microbalance instrument. A small thermal flow correction was applied to the results.

Results

Degree of Hydration

In order to be able to correlate the conductivity results with the degree of hydration of the samples, we first needed to accurately establish the water contents of the various stable hydrates in the atmospheric water vapor pressure conditions under which the conductivity measurements were to be made. Such data are only available for the H^+ (*8*) and Na^+ (*21*) forms.

Figure 2 shows the thermograms obtained for a range of analogs. As far as the conductivity studies are concerned, the data first establish the existence of many subhydrates under our conditions. The results show that the general pattern of behavior, as reported earlier by Weigel and Hoffman (*15*) for a water vapor pressure of 12.3 kN m^{-2} (92.5 mm Hg), extends essentially unchanged down to the normal water vapor pressures of 0.5 to 0.7 kN m^{-2} used in our study, at which, however, the transition temperatures, as obtained from the data in Fig. 2, are all about 30°C lower.

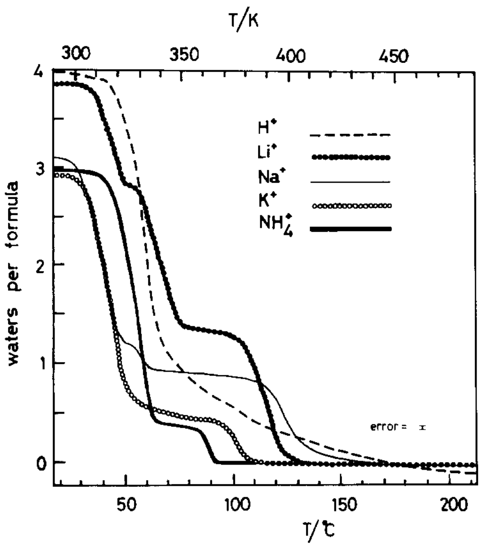

FIG. 2. TGA thermograms for selected compounds $MUO_2PO_4 \cdot (A - x)H_2O$, where x is the number of Schottky water vacancies per formula. The samples were heated at 2°C min^{-1} in laboratory air, having a water vapor pressure of 0.5 to 0.7 kN m^{-2} (ca 4–5 mm Hg) and flowing at 30 ml min^{-1}.

Second, the data, because of the greatly improved accuracy, clearly confirm previous indications (*15*) that many of the hydrates have a nonstoichioimetric number of water molecules per formula. This we attribute to the formation of Schottky defects in the form of water vacancies within the water network. The effect can be clearly seen in Fig. 2 as a reduction in the water contents from the nominal 4-, 3-, 1.5-, 1.0-, and 0.5-water forms. (The exception to this in the case of the Na^+ trihydrate will be discussed later.) The presence of Schottky defects in HUP was clearly demonstrated by very accurate TGA runs (*8*). The formulas of the hydrates are thus more accurately represented as $MUO_2PO_4(A - x)H_2O$, where A is given by the numbers above, and x is, for example close to 0 for $NH_4UO_2PO_4 \cdot 3H_2O$, 0.1 for $HUO_2PO_4 \cdot 4H_2O$ at 40°C (*8*), and 0.3 for $NaUO_2PO_4 \cdot 1.5H_2O$ at 55°C.

It will be seen from Fig. 2 that the behavior of HUP is rather anomalous. The gradual weight loss, which continues up to 400°C, is attributed to loss of H_3PO_4 as well as water (*8*, *22*). Thus for HUP, unlike all the other compounds, the weight of the totally anhydrous phase was not precisely known, thus preventing the calculation of the initial water content. In view of this the initial composition, at 17°C, has been taken as $HUO_2PO_4 \cdot 3.97H_2O$, as estimated from our earlier study (*8*).

Conductivities of the Normal Hydrates

Since the plate-like crystallites were expected to show highly anisotropic conductivity, the pellet press shown in Fig. 3 was designed to measure the conductivity in the direction perpendicular to the applied pressure and thus in the easy conduction direction. Previous measurements on HUP have shown that, after a period of time, the crystallites align to within about 10° from being flat against the base of the press (*2*, *10*). The parallel conductivity thus measured on dense pellets was essentially the same as that measured for single crystals of HUP (*3*).

The parallel conductivities of the normal hydrates of the analogs measured at 22°C are given in Table I (italicized values). It will be seen that in addition to HUP, the Na^+ form also exhibits a high conductivity, whereas for the other compounds the conductivities are much lower. Several features of the measurements call for comment.

First, the conductivities, which were normally measured while the hydraulic pressure of 12 MN m^{-2} was applied to the samples, did not show any significant changes compared to the values obtained in the absence of pressure, showing that water was not being squeezed out of the layers by the pressure.

Second, values which varied by less than 10% between 1 and 20 kHz could normally be obtained for the samples with low conductivities, but for the H^+ and Na^+ compounds it was found to be necessary to Pt-black the hemicylindrical electrodes to achieve frequency invariant values. Admittance plots, constructed from data taken over the range 200 Hz to 1 MHz, did not reveal any unusual features, and confirmed that the more accurate data taken in the central frequency range would be equivalent to the dc conductivities.

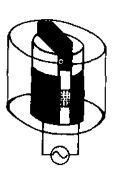

FIG. 3. Pressure die for measuring parallel conductivities. Shaded areas—stainless steel; clear areas—Perspex; dashed area—sample.

Third, although the conductivities of the H^+ and Na^+ compounds showed only a few percent change with time after initial pressing in the press, the conductivities of the other compounds kept dropping over several days at constant applied pressure. For the Li^+, K^+, NH_4^+, and Ca^{2+} compounds the final steady values as given in Table I were factors of 18, 2, 4, and 11 times, respectively, lower than the values recorded initially. This effect is most likely caused by the gradual expulsion of adsorbed surface water. The data presented in Fig. 5, to be discussed below, show that heating in the absence of high pressures also causes an initial conductivity drop for these compounds consistent with loss of surface water. For the samples with the low conductivities, the values were not affected either by conduction through the Perspex, as shown by a blank measurement, or by edge effects, since the conductivities were independent of the height of the pellets.

Conductivities of the Lower Hydrates and Anhydrous Compounds

The conductivity of selected samples was monitored continuously for 2 weeks while the temperature was raised at a rate of 0.3°C hr^{-1}, determined so as to allow virtually complete equilibration of the water contents at all temperatures. The apparatus is illustrated in Fig. 4. The samples were loaded as finely ground, dry powders and compressed under tough spring pressure.

The results are shown in Fig. 5, and

TABLE I

CONDUCTIVITIES OF $MUO_2PO_4 \cdot (A - x)H_2O$ (ohm^{-1} m^{-1}) AT VARIOUS TEMPERATURES[a]

	M					
$A - x$	H	Li	Na	K	NH_4	½Ca
$4 - x$	*3×10^{-1}* (22)	*1×10^{-4}* (22)				*2×10^{-5}* (22)
$3 - x$		1×10^{-4} (50)	*1×10^{-2}* (22)	*5×10^{-4}* (22)	*2×10^{-4}* (22)	
$1.5 - x$	5×10^{-2} (45)	2×10^{-4} (75)	8×10^{-5} (50)			
$1.0 - x$			2×10^{-5} (75)			
$0.5 - x$	3×10^{-5} (110)			1×10^{-5} (75)	2×10^{-5} (75)	
0	7×10^{-6} (150)	1×10^{-5} (150)	8×10^{-5} (150)	2×10^{-5} (150)	1×10^{-5} (150)	2×10^{-6} (150)

[a] Temperatures (°C) are given in parens. Italicized values were measured in the direction parallel to the lie of the platelets in the pellet. The remaining values have been converted from the perpendicular values indicated in Fig. 5 to estimated parallel values by multiplying the former values by 7, the experimental anisotropy factor for the pellets.

reveal a drop in conductivity with water loss for each sample, with the exception that the Na^+ and K^+ compounds showed an increase in conductivity upon final dehydration to the anhydrous state. Careful inspection shows that every plateau evident in the TGA thermograms is reflected in the conductivities. Indeed in the case of HUP, the conductivity indicates an 0.5-hydrate more clearly than the barely perceptible inflection in the thermogram (between 130 and 160°C).

The initial conductivities obtained using the high-temperature rig were consistently lower than the parallel values by a value of approximately 7 for all but the NH_4^+-form, for which the value was anomolously lower by a factor of 30. Since only the parallel values represent the bulk property of in-plane conduction, we have

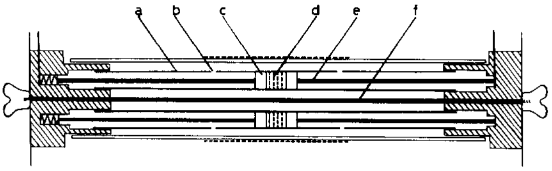

FIG. 4. Heated conductivity rig showing two of the five sample positions around the central tightening rod. (a) Glass tube; (b) water vapor escape hole; (c) Pt-blacked Ag electrode; (d) sample; (e) steel rod; (f) tightening rod.

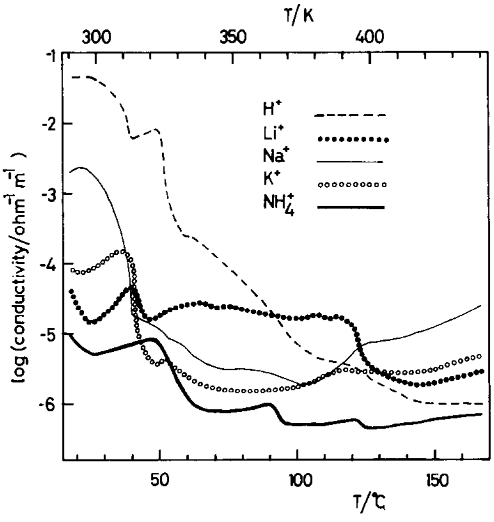

FIG. 5. Log conductivity (perpendicular) as a function of temperature.

estimated the parallel conductivities from the perpendicular conductivities shown in Fig. 5 by multiplying by these factors. The values, as obtained from the midpoints of the respective plateaus in Fig. 5, are present in Table I.

Discussion

Concerning first the normal hydrates, it is clear that the conductivities of the metal-substituted compounds are significantly lower than that of HUP. In HUP (*6*), and almost certainly in the other analogs, the interlayer water network is essentially solid-like, and the water molecules and most cations would be expected to be comparatively immobile. However, H^+ ions can still move through such a lattice by the Grotthus mechanism, which requires only water rotation coupled with intermolecular H-hopping (*2, 3*), thus naturally accounting for the anomalously high proton conductivity. This situation contrasts with the presence of liquid-like water layers in the montmorillonite hydrates, in which both H^+ (*23*) and metal cations (*24*) exhibit appreciable conductivities.

Upon dehydration to the lower hydrates, the marginal drop in the conductivity of the H^+ form might be expected since there are fewer H bonds for the protons to pass along. For the other compounds, the drop in the conductivities implies that the remaining water molecules and cations are not randomly distributed among the sites, but adopt an ordered arrangement. Finally, the low conductivity of the completely anhydrous forms is probably the result of structural distortions which have destroyed the equivalence of the interlayer sites.

Returning to the normal hydrates, the order of the conductivities at room temperature is $H^+ > Na^+ > K^+ > NH_4^+ > Li^+ > Ca^{2+}$. The comparatively high conductivity of the Na^+ form undoubtedly reflects the attainment of an optimum ionic radius for mobility. However, the following evidence suggests that this condition is achieved in a rather subtle way. We base our discussion on the evidence, supplied by NMR studies, that the conductivity of Na^+ is of a bulk nature, and not due to possible grain boundary effects. Sugitani *et al.* (*25*) have shown that the proton NMR line from $NaUO_2PO_4 \cdot 3.15H_2O$ is sharp at room temperature, compared to the broad line obtained from $Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$, and their conclusion of mobile species has been conformed by pulsed NMR experiments (*26*).

The general pattern of water contents of the hydrates strongly suggests that Li^+ and Na^+ can occupy two types of site: first the site in the center of the water squares as in the tetrahydrates, of which the Na^+ form is only stable at elevated water vapor pressures (*27, 28*), and second, a normal water site, as in the trihydrates, as is also the case for K^+ (*14*) and probably NH_4^+. A further observation is that at elevated water vapor pressures Li^+ can form a 4.2-hydrate (*15*), and Na^+ can form a 4.8-hydrate (*15*). The extra water molecules probably occupy the comparatively large interstices which lie between the normal water network and the phosphate oxygens.

The multiplicity of possible sites for both Na^+ and water molecules would favor high conductivity, especially by a ring mechanism in which, for instance, a Na^+ ion and a water molecule each on the square-type site interchange by the Na^+ ion passing through the central site. This mechanism could operate even in the absence of water vacancies. A vacancy mechanism is certainly not obviously suggested by the data in general, since many of the hydrates have appreciable proportions of water vancancies which do not appear to result in correspondingly enhanced conductivites.

The value of the conductivity of $NaUO_2PO_4 \cdot 3.1H_2O$ of 1×10^{-2} ohm^{-1} m^{-1} at 22°C is among the highest known for Na^+

conductivity in an inorganic crystalline hydrate. In Na-montmorillonite hydrate the conductivity is approximately 10^{-2} ohm^{-1} m^{-1} for the bilayer hydrate and approximately 10^{-3} ohm^{-1} m^{-1} for the monolayer hydrate at 20°C (*24*). Among the hydrated zeolites, chabazite exhibits by far the highest Na$^+$ diffusion coefficient, of 5×10^{-13} m^2 sec^{-1} at 21°C (*29*), indicating an ionic conductivity of 10^{-1} to 10^{-2} ohm^{-1} m^{-1}.

In comparison with anhydrous Na$^+$ ion conductors, the Na$^+$ conductivity in $NaUO_2PO_4 \cdot 3.1H_2O$ is at the top end of the range, but below that found in the β- and β''-alumina family (1 to 0.01 ohm^{-1} m^{-1} at 20°C) (*30*), $Na_3Zr_2PSiO_{12}$ (0.08 ohm^{-1} m^{-1} at 20°C) (*31*), and $Na_5YSi_4O_{12}$ (0.1 ohm^{-1} m^{-1} at 20°C) (*32*).

Acknowledgments

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