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Ion exchange of intercalation compounds from WOP_2O_7 and intercalation of *n*-alkylamines

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Ion exchange of $Na_xWOP_2O_7 \cdot nH_2O$ ($x \sim 1.4$) prepared from WOP_2O_7 was attempted, using alkaline and alkaline earth ions. The degree of exchange was observed to be >50% at 90° C except for Mg^{2+}. The basal spacing of ion-exchanged materials for the hydrated phase were dependent on the number of water molecules in the interlayer spaces, while those for the dehydrated phase increased with the size of ions in the interlayer spaces. The network of water molecules linked by the hydrogen bond in the interlayer spaces seems to determine the basal spacing. By the ion-exchange reaction, *n*-alkylammonium ions were intercalated into the interlayer spaces of $Na_xWOP_2O_7 \cdot nH_2O$ ($x \sim 1.4$) and $Sn_xH_yWOP_2O_7 \cdot nH_2O$ ($2x + y \sim 0.5$). In spite of the difference in the charge density of the host layer, a similar arrangement of alkyl chains in the interlayer spaces resulted, and neutral amines were considered to be intercalated as well as ammonium ions. Direct reaction of *n*-alkylamine with WOP_2O_7 produced an intercalation compound without reduction of tungsten. The arrangement of the amines in the interlayer spaces is similar to that supposed to the ion-exchanged derivatives when heated at 140° C *in vacuo*.

1. Introduction

Some compounds composed of neutrally charged layers have been known to take up cations on reduction of the host layer by chemical or electrochemical methods [1-5]. Then, the cations intercalated were found to be exchanged with other cations as ordinary layered compounds including cations in their interlayer spaces [6, 7]. Therefore, the intercalation technique can provide new members of an ion-exchange substance. Furthermore, the combination of intercalation and ion-exchange techniques allows production of new compounds which cannot be obtained by ordinary preparative methods.

Diphosphato oxotungsten (VI), WOP_2O_7, has been reported to have a layered structure composed of electrically neutral layers stacked along the *a*-axis [8]. We found it possible to produce intercalation compounds by reducing WOP_2O_7 with aqueous solutions of $Na_2S_2O_4$ and $SnCl_2$, and the solvated cations were taken up [9]. The intercalation compound is unique in respect of the wide adjustable range of cation concentration in the interlayer spaces (the charge density on the host layer). The most reduced composition was $Na_{1.4}WOP_2O_7 \cdot nH_2O$ and the least reduced product was $Sn_xH_yWOP_2O_7 \cdot nH_2O$ ($2x + y \sim 0.5$). Their ion-exchange properties and direct reaction of WOP_2O_7 with *n*-alkylamines will be described here.

2. Experimental techniques

The starting materials were prepared as described elsewhere [9]: $Na_xWOP_2O_7 \cdot nH_2O$ ($x \sim 1.4$) by reducing WOP_2O_7 with 1 mol dm^{-3} $Na_2S_2O_4$ solution at 60° C and $Sn_xH_yWOP_2O_7 \cdot nH_2O$ ($2x + y \sim 0.5$) with 0.1 mol dm^{-3} acidified solution of $SnCl_2$ at room temperature. The ion-exchange reaction with metal ions was carried out in the 1 mol dm^{-3} chloride solutions of alkaline and alkaline earth elements at room temperature and 90° C for 1 week. In the case of ion exchange with *n*-alkylammonium ions with carbon numbers from 1 to 18, 0.2 and 0.5 mol dm^{-3} chloride solution were used. When the alkylammonium chloride was not available commercially, the chloride solution was prepared from the corresponding amine as described by Lagaly [10]. The product was washed with distilled water several times and dried in air. The degree of exchange was determined by analysing Na^+ ion released in the solution by the atomic absorption method. For the product exchanged with Mg^{2+} ions, which did not show a change of the basal spacing on exchange, the amount of magnesium in the product was analysed. To achieve the dehydrated state, the products were heated at 150° C *in vacuo*.

X-ray powder patterns of products were recorded with Cu$K\alpha$ radiation and a scanning speed of 1° min^{-1}, consisting nearly of reflections with the $h00$ indices. Deformation of the host layer on intercalation and ion exchange was examined by electron diffraction. The $0kl$ diffraction patterns were very similar to one another and indicated that the host layer was deformed only to a limited extent on reaction. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out at a heating rate of 10° C min^{-1}. The

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amount of alkylammonium ion and amine in the interlayer spacing was estimated from a weight loss observed in the TG curve. As the TG curves for the starting materials indicated that the weight loss caused by removal of water was completed at 200° C and decomposition of the ammonium ions was observed at $> 200°$ C [11], the weight loss observed above 200° C for alkyl ammonium derivatives was thought to correspond to decomposition and removal of the ammonium ions.

The direct intercalation of alkylamines into the van der Waals gap of WOP_2O_7 was attempted, using liquid *n*-alkylamines the carbon number of which ranged from 3 to 10 at room temperature, resulting in swelling of the starting material. The basal spacing was measured for the products in the presence of the amines reacting, and dried in air and *in vacuo* at 140° C. The TG and DTA measurements were carried out on the sample washed with ethanol, and samples dried in air and *in vacuo*.

3. Results and discussion

3.1. Ion exchange with metal cations

The maximum degrees of exchange are listed in Table I, as well as the basal spacings for the exchanged derivatives. The basal spacings for each derivative in the table indicate the maximum and minimum observed values which corresponded to the highly hydrated state and the almost dehydrated state. The exchange ratio with alkaline ions is generally higher than that with alkaline earth ions, and showed a small temperature dependence. An attempt to exchange for Na^+ with Mg^{2+} resulted in no change of the basal spacing, and chemical analysis of the product indicated that Mg^{2+} ions were not substituted for Na^+ ions to any detectable extent. The other alkaline earth ions are exchanged for Na^+ ions, but the exchange rate was small, especially at low temperature, 22.1% for Ca^{2+}, 53.3% for Sr^{2+} and 71.7% for Ba^{2+} at room temperature, respectively. At 90° C, a ratio $> 50\%$ was observed for all alkaline earth ions except Mg^{2+}. From this fact, the reduced diphosphato oxotungsten is considered to take up alkaline ions in the interlayer spaces more preferentially than alkaline earth ions.

The weight losses for the potassium, rubidium and caesium derivatives were $< 2.0\%$ and they also showed little change in the basal spacings on dehydration. Therefore, the weight loss is considered to be caused by water adsorbed on the surface of the product. On the other hand, the ions which have stronger polarizing power, such as Li^+, Ca^{2+}, Sr^{2+} and Ba^{2+}, were greatly hydrated in the interlayer spaces and the derivatives gave large weight losses and long basal spacings. This dependence of hydration on ions was generally observed for layered compounds [12, 13]. The lithium-derivative showed a weight loss at a temperature $> 200°$ C. So the minimum basal spacing for this compound in Table I is not the basal spacing for the dehydrated phase.

TABLE I Results of ion exchange with alkaline and alkaline earth ions. The maximum and minimum basal spacings correspond to the basal spacing for the hydrated and dehydrated phases, respectively

Ions	Exchange ratio (%)	Maximum basal spacing (nm)	Minimum basal spacing (nm)	Weight loss (%)
Na^+	–	1.082	0.954	4.3
Li^+	98	1.27	1.01*	7.2
K^+	100	1.01	1.00	0.3
Rb^+	74	1.02	1.02	1.0
Cs^+	98	1.05	1.04	1.7
Ca^{2+}	75	1.13	0.951	6.8
Sr^{2+}	73	1.20	0.953	8.5
Ba^{2+}	96	1.24	1.01	8.7

*The value is not the basal spacing of completely dehydrated compounds.

Several hydration states seem to exist for the exchanged derivatives, because the basal spacings decreased from the maximum value to the minimum one for the dehydrated phase via some discrete basal spacings. As seen in Fig. 1, the basal spacings for the dehydrated phase depended on the size of ions in the interlayer spacing, but those for the hydrated phases did not. As pointed out previously [9], the basal spacing of the intercalation compounds from WOP_2O_7 seems to be determined by the framework of water molecules in the interlayer spaces linked by hydrogen bonds, depending on the number of water molecules. The basal spacings for the hydrated derivatives are similar to one another at a certain hydrated state and almost correspond to that observed for a hydrated phase of $Na_xWOP_2O_7 \cdot nH_2O$. This fact indicates that the framework of water molecules combined by hydrogen bonds in the interlayer spaces is little affected by the charge and size of ions in the interlayer spaces.

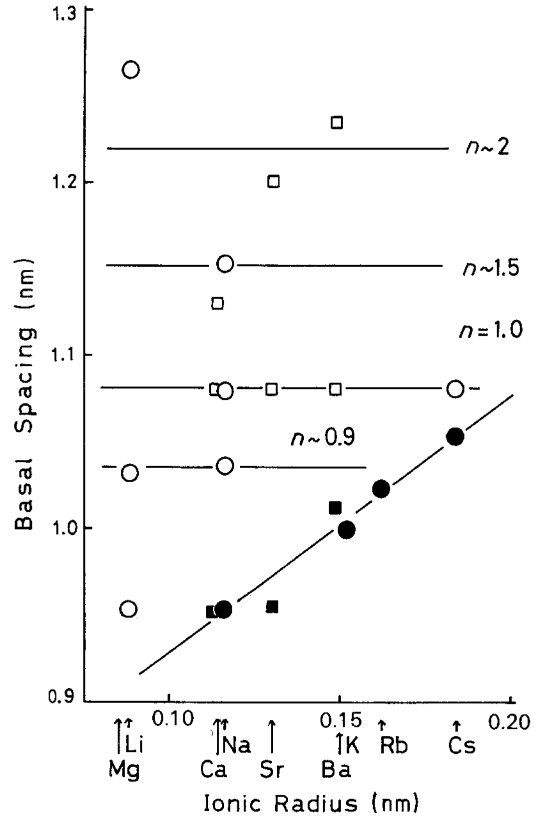

Figure 1 Basal spacing plotted against ionic radius: (●) dehydrated alkali derivatives; (○) hydrated alkali derivatives; (■) dehydrated alkali earth derivatives; (□) hydrated alkali earth derivatives. The numbers of water molecules, *n*, given in this figure are the numbers observed for $Na_xWOP_2O_7 \cdot nH_2O$. The ionic radii are after Shannon and Prewitt [19] for six-fold coordination.

3.2. Insertion of *n*-alkylammonium ions and *n*-alkylamines

As indicated by the fact that the starting material swells in liquid amines, amine molecules intercalate into the van der Waals gap of WOP_2O_7. Thus the colour of the starting materials was virtually unchanged or changed to pale blue, but the amount of reduction of tungsten in the host layer was so small as not to be detected by redox titration with $Ce(SO_4)_2$. Therfore amines were taken up as neutral molecules. The maximum and minimum basal spacings observed for the intercalation compounds and the basal spacings for the ion exchanged derivatives dried at 140° C *in vacuo* are listed in Table II as well as the degree of exchange for the products from $Na_xWOP_2O_7 \cdot nH_2O$.

Fig. 2 shows TG curves for compounds obtained by ion exchange with alkylammonium ions and by intercalation of amine for the case where the number of carbons (NC) in the alkyl chain was 5. The number of water molecules in the interlayer spaces was found to be less than the derivatives obtained by ion exchange with metal ions. The compounds including alkylammonium ions showed weight losses continuing up to high temperatures, while the intercalation compounds of alkylamines exhibited fairly sharp weight losses, and the weight losses were completed at lower temperatures than for the ion-exchanged derivatives containing the corresponding alkylammonium ions. It is also interesting to mention that the ion-exchanged derivatives showed exothermic peaks in the DTA curves, while the intercalation compounds showed endothermic peaks. These facts are reasonable if the bonding between amine molecules and the host layers is taken into account. In the case of the intercalation compounds, only the hydrogen bonding and/or the van der Waals bonding should be considered, because the amines in the interlayer spaces are neutral molecules. The weight losses expected from the degree of exchange for the derivatives from $Na_xWOP_2O_7 \cdot nH_2O$ were larger by several per cent than those observed, but the number of alkylammonium ions in the interlayer spaces was thought almost to correspond to the number of released Na^+ ions. As the product after TG-DTA measurement was glassy, the removal of hydrocarbon was not complete.

TABLE II Basal spacings of alkylammonium derivatives of $Na_xWOP_2O_7 \cdot nH_2O$ (basal spacing I) and of $Sn_xH_yWOP_2O_7 \cdot nH_2O$ (basal spacing II), and of the intercalation compounds. NC denotes the number of carbons in the alkyl chain. The basal spacings III and IV indicate those for the intercalation compounds as prepared and dried at 140° C *in vacuo*. The degrees of exchange are those observed for $Na_xWOP_2O_7 \cdot nH_2O$

NC	Basal spacing I (nm)	Basal spacing II (nm)	Basal spacing III (nm)	Basal spacing IV (nm)	Exchange ratio (%)
1	1.11	1.15	–	–	97
2	1.27	1.28	–	–	72
3	1.32	1.33	1.39	1.36	74
4	1.51	1.56	1.56	1.50	90
5	1.66	1.67	1.82	1.65	–
6	1.75	1.74	2.00	1.76	90
7	1.92	1.94	2.19	1.87	88
8	2.01	2.02	2.54	2.07	82
9	2.17	2.19	2.89	2.14	85
10	2.25	2.28	3.22	2.23	–
12	2.70	2.50	–	–	–
14	2.85	2.97	–	–	–
16	3.18	3.20	–	–	–
18	3.41	3.46	–	–	–

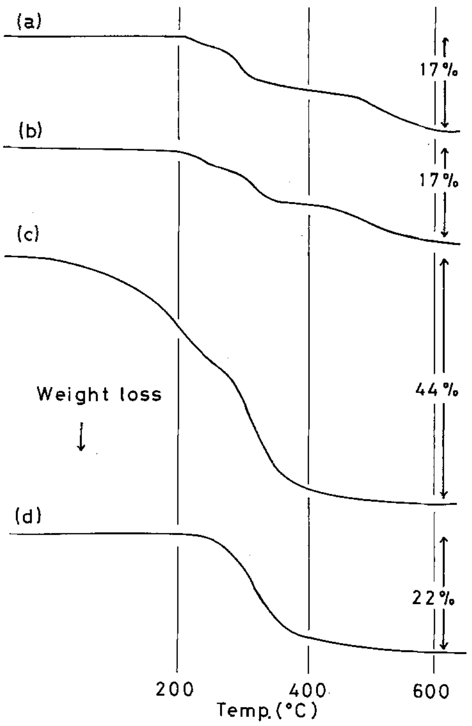

Figure 2 TG curves for the compounds including amylammonium ions and/or amylamine: ion-exchanged derivative from (a) $Na_xWOP_2O_7 \cdot nH_2O$, (b) $Sn_xH_yWOP_2O_7 \cdot nH_2O$; intercalation compound of the amine (c) as-prepared and (d) after heating at 140° C *in vacuo.*

When NC > 10, the basal spacing of exchanged derivatives from $Na_xWOP_2O_7 \cdot nH_2O$ decreased on drying more than that for smaller NC, where a negligible shrinkage of the basal spacing was observed, for example from 3.72 to 3.41 nm for NC = 18. The derivative from $Sn_xH_yWOP_2O_7 \cdot nH_2O$ showed larger shrinkage and more weight loss at < 200° C than the former case over the whole range of NC on drying. The maximum basal spacing observed for the derivative from $Sn_xH_yWOP_2O_7 \cdot nH_2O$ is similar to the value for the intercalation compound with corresponding amines rather than to the derivatives from $Na_xWOP_2O_7 \cdot nH_2O$.

The dependence of basal spacings on NC is shown in Fig. 3. The odd/even alternating basal spacings which should be observed with a highly ordered interlayer structure [10, 14] are seen for the basal spacings of ion-exchanged derivatives from $Na_xWOP_2O_7 \cdot nH_2O$ and $Sn_xH_yWOP_2O_7 \cdot nH_2O$, when dried. The basal spacings of ion-exchanged derivatives almost coincided with each other for corresponding alkylammonium ions, in spite of the difference in the electric charge on the host layers of the starting materials. Furthermore, the weight losses for the derivatives from $Sn_xH_yWOP_2O_7 \cdot nH_2O$ were found to be as much as those from $Na_xWOP_2O_7 \cdot nH_2O$. Therefore, alkyl chains are arranged similarly in the interlayer spaces of both kinds of product. This means that the neutral alkylamines were taken up as well as the alkylammonium ions in the derivatives from $Sn_xH_yWOP_2O_7 \cdot nH_2O$. As seen in Fig. 3, the spacing

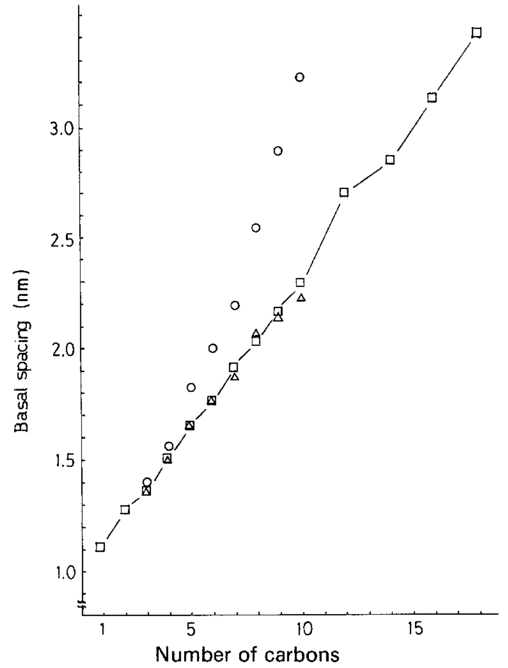

Figure 3 Basal spacing plotted against number of carbons in the alkyl chain: (○) intercalation compound of amine as-prepared; (△) intercalation compound of amine after heating at 140° C *in vacuo*; (□) ion-exchanged derivative from $Na_xWOP_2O_7 \cdot nH_2O$ after heating at 140° C *in vacuo*. The basal spacing for the ion-exchanged derivative from $Sn_xH_yWOP_2O_7 \cdot nH_2O$ is omitted for clarity.

increases by 0.126 nm per carbon in the alkyl chain. The chains in the interlayer spaces were considered to be in contact with each other with a tilt angle of about 83° to the host layer, forming monolayers.

As the above fact indicates the possibility of intercalation of alkylamines into the interlayer spaces of WOP_2O_7, direct intercalation was attempted. The relation between NC and basal spacing for the intercalation compounds was not simple, as seen in the case of ion-exchanged derivatives and the odd/even alternative basal spacings were not observed. At $NC = 3$ and 4, the basal spacings of the intercalation compounds coincided with those of the ion-exchanged derivatives. When $NC > 4$, the basal spacings deviated upwards from the line observed for the ion-exchanged derivatives, especially in the region of $NC > 7$. A much greater number of amines was taken up into the interlayer spaces over $NC > 4$ than in the case of ion exchange.

The arrangement of alkylamines in the interlayer spaces might be divided three regions by NC: up to $NC = 4$, from $NC = 5$ to 7 and from $NC = 8$ to 10. In the first region, the arrangement of alkylamines is considered to be similar to that for the ion-exchanged derivatives. The increase of the spacing per carbon was found to be 0.20 nm in the second region and 0.34 nm in the third region. In these regions, the alkylamines seem to form multilayers with tilt angles less than for the case of ion exchange. However the odd/even alternating basal spacings were not seen in these regions, and this indicates a less ordered arrangement of alkylamines in the interlayer spaces.

The products in the second and third regions showed decreases of the basal spacing on leaving them in air, and finally on heating at 140° C *in vacuo* the basal spacings fell on the line, indicating a linear relationship between basal spacing and NC observed for the ion-exchange derivatives. The weight losses observed for these samples heated at 140° C *in vacuo* almost coincided with the values of ion-exchanged derivatives with corresponding alkylammonium ions, too. Therefore the alkylamines were packed as monolayers similar to the arrangement supposed for the ion-exchange derivatives in the interlayer spaces of WOP_2O_7. Polar organic molecules such as amines and alcohols have been reported to be taken up into the interlayer spaces of layered compounds [15, 16]. When the host layer is a phosphate, only phosphate having protons in the structure has been known to form the intercalation compound with neutral organic molecules [17, 18].

The arrangement of alkylammonium ions in the interlayer spaces was often observed to depend on the charge density on the host layer [10]. The charge density presented as the area per monovalence of the host layers studied here was about 0.13 nm^2 for $Na_xWOP_2O_7 \cdot nH_2O$ and 0.39 nm^2 for $Sn_xH_yWOP_2O_7 \cdot nH_2O$, but the arrangement of alkyl chains was similar. The precursor of these phosphates, WOP_2O_7, was found to form the intercalation compounds with alkylamines directly, and the compound with low charge density takes up neutral amine molecules as well as ammonium ions. Therefore, the charge density did not affect the arrangement of alkyl chains in the interlayer spacings.

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