

Sorption of Amides by Mixed Niobyl–Vanadyl Phosphate

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Abstract. The layered mixed niobyl-vanadyl phosphate $[(V_{0.14}Nb_{0.86})OPO_4 \cdot 2.7 H_2O]$ can intercalate different amide molecules. In all cases, the amide I bands $[v(CO)]$ of the original compound shift to lower frequencies, thereby indicating that the amide molecules interact with the layers probably *via* hydrogen bonds linking the coordinated water molecules to the metal atoms. To a lesser extent, primary amides show protonated molecules and tertiary amides show some molecules directly coordinated to the metals, as can be inferred from the bands appearing at 1732 and 1617 cm^{-1} in the IR spectrum, respectively.

Key words. Amides, mixed niobyl-vanadyl phosphate, intercalation, layered phosphates.

1. Introduction

Hydrated mixed niobyl-vanadyl phosphates occur as solid solutions of vanadyl phosphate in niobyl phosphate of generic formula $(V_x Nb_{1-x})OPO_4 \cdot 2.7 H_2O$, where x is always equal to or less than 0.21 [1]. Hydrated mixed phosphates have layered structures and are isostructural with their precursors, of formula $MO(AO_4) \cdot nH_2O$ (with $M = Nb, V$ and $A = P, As$), whose crystalline structure consists of layers where the metals, M , share edges with four PO_4^{3-} groups. Their octahedral coordination is reached by coordinating an oxygen atom – linked *via* a double bond – and a water molecule at the two remaining positions along the c axis of the crystal. The remaining water molecules (up to 2.7 mol per mole of phosphate) occupy the interlayer space and bind the layers *via* hydrogen bonds.

The mixed phosphate of formula $(V_{0.14}Nb_{0.86})OPO_4 \cdot 2.7 H_2O$, (NbVP), behaves as a solid of medium acid strength towards basic substances such as amines [2, 3]. This is also the case with its precursors; thus, α -niobyl phosphate can intercalate different amines [4], and vanadyl phosphates can intercalate pyridine, which seems to be coordinated to the metal by substitution of coordinated water molecules [5].

The peculiar nature of their functional group makes amides one of the most outstanding among the different types of organic substances liable to take part in intercalation reactions. They are well known for their ability to act as coordinating agents in a variety of systems [6, 7] and interact with other systems *via* protonation reactions [8].

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The aim of this work was to study the intercalation of different amides into NbVP in order to establish the mechanism of intercalation and to contribute new data to the scarce literature available on this subject.

2. Experimental

In order to study the different possible interactions between NbVP and amides, we chose various types of the latter, namely primary amides such as formamide (FA), acetamide (AA), butyramide (BA) and benzamide (BZ); secondary amides such as *N*-methylformamide (MFA) and *N*-methylacetamide (MAA); and tertiary amides such as *N,N*-dimethylformamide (DMFA) and *N,N*-dimethylacetamide (DMAA). For comparative purposes, some of these amides were also intercalated into mixed niobyl-vanadyl arsenate ($x = 0.07$) (NbVAs) and α -niobyl phosphate (α -NbP). Mixed niobyl-vanadyl phosphate and arsenate were prepared according to a procedure described elsewhere [1]. α -Niobyl phosphate was synthesized by the method described in the literature [9].

As contact of NbVP with the pure liquid amides for a lengthy period does not give rise to the intercalation reaction, we opted for working under reflux in every case. Occasionally, the intercalate obtained was resuspended in fresh liquid amide and refluxed. The process was continued until the X-ray diffraction pattern of the system showed a single phase. Occasionally, the patterns showed two phases, the intercalated one plus another corresponding to the dehydration of the host matrix, neither of which changed upon further refluxing. At that moment, the solids were isolated from the amides by filtration, washed with acetone and air-dried.

The solid amides (e.g. AA, BA and BZ) were intercalated by dissolving in chloroform under reflux. Once separated by filtration, the solids were dried under vacuum (0.01 mm Hg).

X-ray diffraction patterns were recorded on a Siemens D-501 automatic powder diffractometer equipped with a DACO-MP microprocessor and using monochromated CuK_α radiation from a curved graphite crystal. IR spectra were recorded on a Perkin-Elmer 883 double beam spectrophotometer using KBr pellets (2% of the products). DTG-TG curves were obtained from a Rigaku-Thermoflex high-temperature instrument using calcined alumina as the reference and a heating rate of 10 K/min. Finally, diffuse reflectance spectra were recorded on a Kontron Uvikon 810 spectrophotometer using BaSO_4 as the reference.

3. Results and Discussion

The experimental conditions and solvents in which the different intercalates were obtained are summarised in Table I. Most of the intercalates were prepared at the reflux temperature of the amide used; hence, the intercalated phase was generally accompanied by other, more or less hydrated phases, as found in the precursor phosphates [10]. Consequently, the chemical composition given in each case is referred to the unit formula of the mixed phosphate.

As can be seen from the data listed in Table I, the chemical composition of the intercalates depends on the molecular volume of the guest molecule; thus, FA was the most extensively intercalated amide, followed by MFA and DMFA. However,

Table I. Composition and basal spacing of intercalation compounds $\text{NbVOPO}_4 \cdot x \text{ Amide} \cdot y \text{ H}_2\text{O}$.

Host	Amide	Symbol	experimental conditions	Average chemical composition/ $x(\text{amide})$	y (water)	$d_{002}(\text{\AA})$
NbVP	Formamide	FA	reflux	1.3	1.2	7.61
	Acetamide	AA	chloroform (reflux)	0.4	1.6	7.16
	Butyramide	BA	chloroform (reflux)	0.2	1.9	7.03
	Benzamide	BZ	chloroform (reflux)	0.3	1.6	11.51, 6.93
	<i>N</i> -methylformamide	MFA	reflux	1.0	2.3	8.20, 6.92
	<i>N</i> -methylacetamide	MAA	reflux	0.9	1.5	8.61, 6.46
	<i>N,N</i> -dimethylformamide	DMFA	reflux	0.7	0.7	9.49, 7.99
	<i>N,N</i> -dimethylacetamide	DMAA	reflux	0.6	0.7	9.23
	Formamide	FA	reflux	1	0.6	7.68
	Formamide	FA	reflux	0.9	1.1	7.60
α -NbP						
NbVAs						

the sequence found for the acetamide series was $AA < MAA > DMAA$ as a result of AA being solid at room temperature and its intercalation being carried out in solution. This effect was checked by using pure DMFA and DMFA dissolved in acetone – the extent of intercalation was over twice as large in the former case.

The intercalates prepared had an average water content of over 1 mol per mole of phosphate, with the exception of those of the tertiary amides, which were always less than unity and smaller than those found for amine intercalates of the same phosphate [2, 3].

The diffractograms of the intercalates show more reflections than those of amines [2, 3] and allow them to be indexed in the tetragonal system. They show the (200) reflection, which is indicative of the preservation of the layered structure. As a rule, the basal spacings obtained suggest the exclusive occurrence of monolayers of amides in the intercrystal space with a molecular disposition in which the basal expansion is minimum.

The micrograph obtained for the FA intercalate (Figure 1) reveals that, despite the fact that the amide was refluxed for a lengthy period, it underwent no texture changes – there are outstanding piles of layers which confirm the laminar nature of these intercalates.

The intercalates of primary and secondary amides obtained from the liquid amides show a very similar thermal behaviour, despite their divergent water and amide contents (Figure 2). A first stage up to 200°C involves the loss of some amide

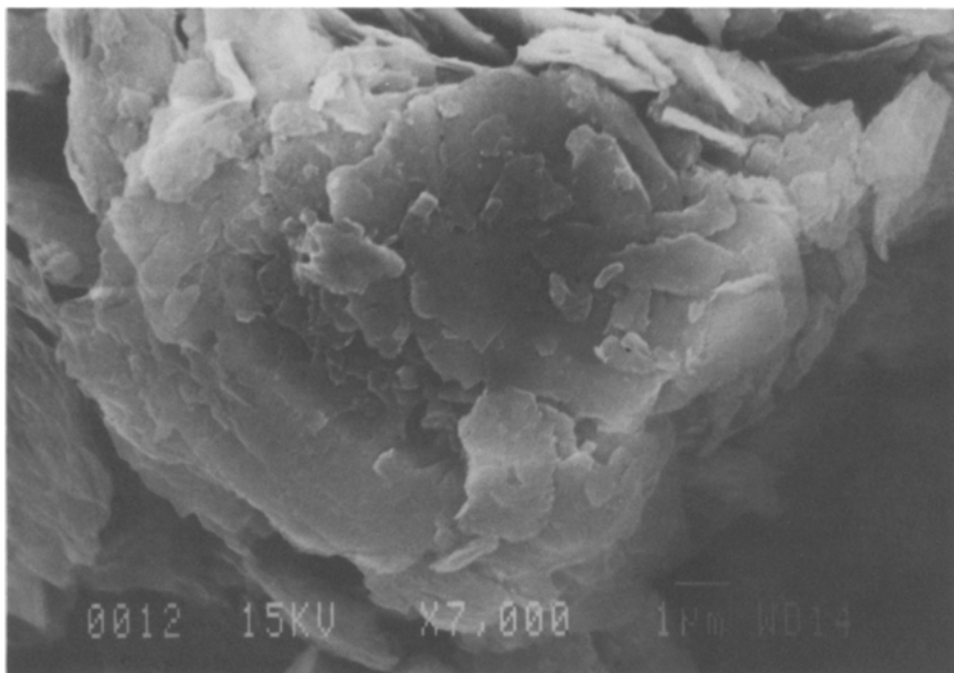


Fig. 1. SEM photomicrograph of the intercalate of formamide in $(\text{Nb}_{0.86}\text{V}_{0.14})\text{OPO}_4 \cdot 2.7 \text{H}_2\text{O}$. The bar in the lower right correspond to 1 μm .

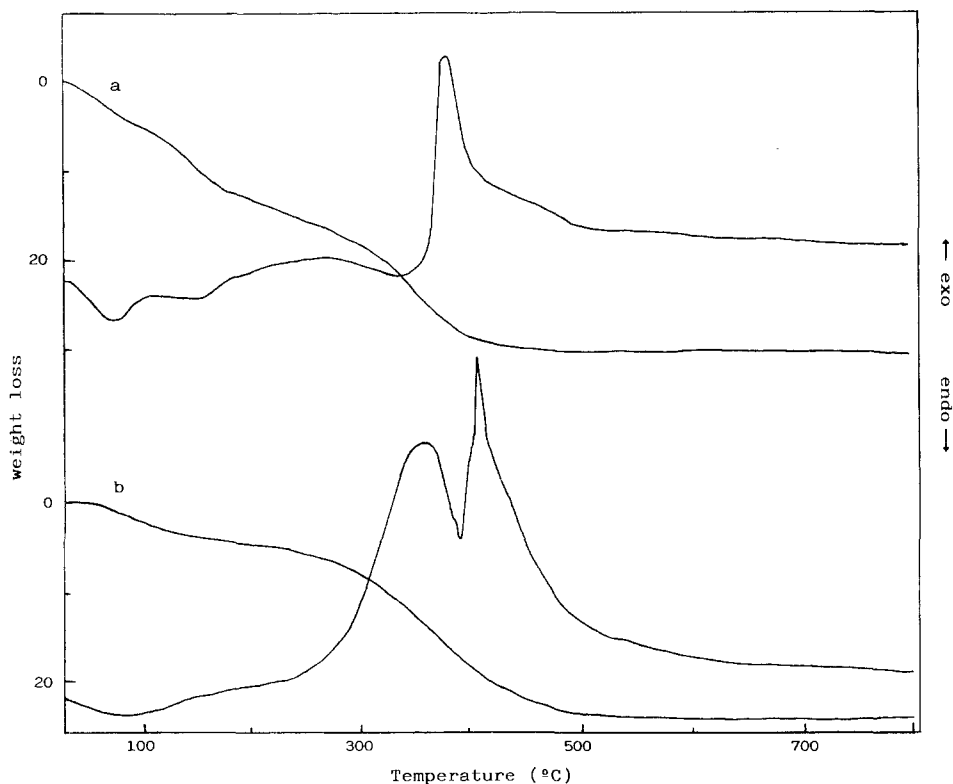


Fig. 2. DTA-TG curves of: (a) the FA-NbVP intercalate; (b) the DMFA-NbVP intercalate.

weakly retained in the interlayer space and some zeolitic water. In a second stage starting at 200°C, the water molecules coordinated to the octahedral metal atoms are lost and the amide molecules bonded to the coordinated water undergo combustion; hence the exothermal peaks in the DTA curve mask the endothermal effect corresponding to the removal of coordinated water.

With tertiary amides, the first stage only involved a small weight loss (removal of water) which results in an endothermal effect at about 80°C followed by another weight loss at about 200°C up to the full loss of the 0.7 mol of water per mole of phosphate which both intercalates contain. Above 200°C the removal and combustion of the amides occur; these temperatures are well above their boiling points, which indicates that they strongly interact with the host matrix. All these findings are consistent with the results found in the CHN analyses of the samples.

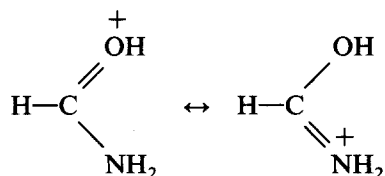
IR spectroscopy is of great use in interpreting the mechanisms *via* which host molecules such as amides intercalate into solids. Table II lists the frequencies of the most important bands in the IR spectra of intercalates, while Figures 3 and 4 show the IR spectra of the FA intercalates of NbVP, NbVAs and α -NbP, and of those of AA and BA. The interaction of primary amides with the host matrix can be diagnosed from two vibrational modes, namely the Amide I [$\nu(\text{CO})$] and Amide II

Table II. Selected vibration bands (cm^{-1}) in the IR spectra of amide intercalates and pure amides.

Host	Amide	νOH , νNH_2	νCO^*	νCO	δNH_2^*	$\delta\text{NH}_2/\delta\text{H}_2\text{O}$	$\nu_s\text{CN}$	νMO , νXO_4
NbVP	FA	3444, 3313, 3200sh	1680-90	1645, 1688sh	1618	1575	1341, 1315sh	1140, 1090, 998, 945
	AA	3600, 3361, 3280, 3232	1670-80	1655, 1687	1610	1598	1406	1140, 1080, 1004, 945
	BA	3623, 3422, 3355, 3280, 3200	1653	1649	1629	1595sh, 1617	1401	1140, 1085, 1010, 950
	BZ	3600sh, 3473, 3365, 3181	1656	1638	1574, 1616	1560, 1605, 1620	1397	1140, 1090, 1000
	MFA	3269	1689sh, 1677, 1655	1665	1543	1544, 1564sh	1390	1080sh, 995
α -NbP	MAA	3241	1650, 1640, 1635	1661, 1640sh	1562	1570	1411	1070sh, 994
	DMFA	3408, 3184	1690, 1676, 1663	1622, 1667			1497	990
	DMAA	3416, 3200	1666-70	1617, 1663			1509	995
NbVAs	FA	3447, 3316, 3240		1655, 1688		1583	1342, 1315sh	1147, 999, 941
	FA	3445, 3312, 3240		1654, 1689		1578	1339	993, 915, 814

(*)absorption bands of pure amides

$[\delta(\text{NH}_2)]$ modes. As the water molecule coordinated to octahedral metal atoms is of an acidic nature [2, 3, 11], it might protonate the amides at their oxygen atom [8], giving rise to the following resonant forms:



which would result in the appearance of two bands in the IR spectrum at 1700 cm^{-1} [$\nu(\text{C}=\text{N})$] and 1500 cm^{-1} [$\nu(\text{C}-\text{OH})$], respectively. The spectra of the FA (Figure 3) and AA and BA intercalates (Figure 4) of NbVP show a band of medium intensity at $1725\text{--}1730\text{ cm}^{-1}$ indicative of a partial protonation of the amide, consistent with the findings of other authors in other systems [8, 12]. However, no band is observed at 1500 cm^{-1} in any case. The FA intercalates of α -NbP do not present any band at 1732 cm^{-1} which might result from the weaker acidic nature of this phosphate, so that the protonation of the mixed phosphate would only occur at the octahedra containing vanadium atoms. The amide may interact with the substrate in two other ways: (a) by coordinating directly to the metal, in which case the $\nu(\text{CO})$ band would shift to considerably lower frequencies (about 1600 cm^{-1}) [10, 13]; (b) coordinating indirectly (i.e. *via* the coordinated water molecule) to the metal, which would shift the $\nu(\text{CO})$ band to only moderately lower frequencies.

As can be seen, the $\nu(\text{CO})$ band of all the intercalates of the primary amides lies at about 1650 cm^{-1} , i.e. at lower frequencies than in the pure liquid amides, thereby indicating the occurrence of a stronger interaction with the host matrix than between them through the hydrogen bonds. This suggests that the amides interact with the metal *via* their CO group, but through the coordinated water molecules.

The Amide II band in the spectrum of the FA intercalate appears at lower frequencies than in that of the liquid amide (1618 cm^{-1}), which indicates that this group is no longer involved in the hydrogen bonds.

In the spectrum of FA, the band at 1654 cm^{-1} is accompanied by a shoulder at 1688 cm^{-1} which lies very close to the $\nu(\text{CO})$ value of the liquid amide (1690 cm^{-1}) [14]. This indicates the occurrence of FA molecules interacting more weakly at the interlayer – probably with the zeolitic water – these, as stated in discussing the thermogram of this intercalate, are the first molecules to be lost in the thermal treatment.

The IR spectra of the intercalates of the secondary amides (Figure 5) show a broad band between 3600 and 2600 cm^{-1} overlapped with the N—H stretching vibrations at 3261 and 3241 cm^{-1} for MFA and MAA, respectively, i.e. at somewhat lower frequencies than in the pure amides (3330 cm^{-1}), which seems to indicate that the NH group is involved in stronger hydrogen bonds than those established in the liquid amides. Likewise, the Amide II band $[\delta(\text{NH}_2)]$ is shifted to higher frequencies with respect to the liquid amide.

Taking into account that the $\nu(\text{CO})$ band of these intercalates appears at 1660 and 1665 cm^{-1} , respectively (i.e. at frequencies similar to those of the liquid amides

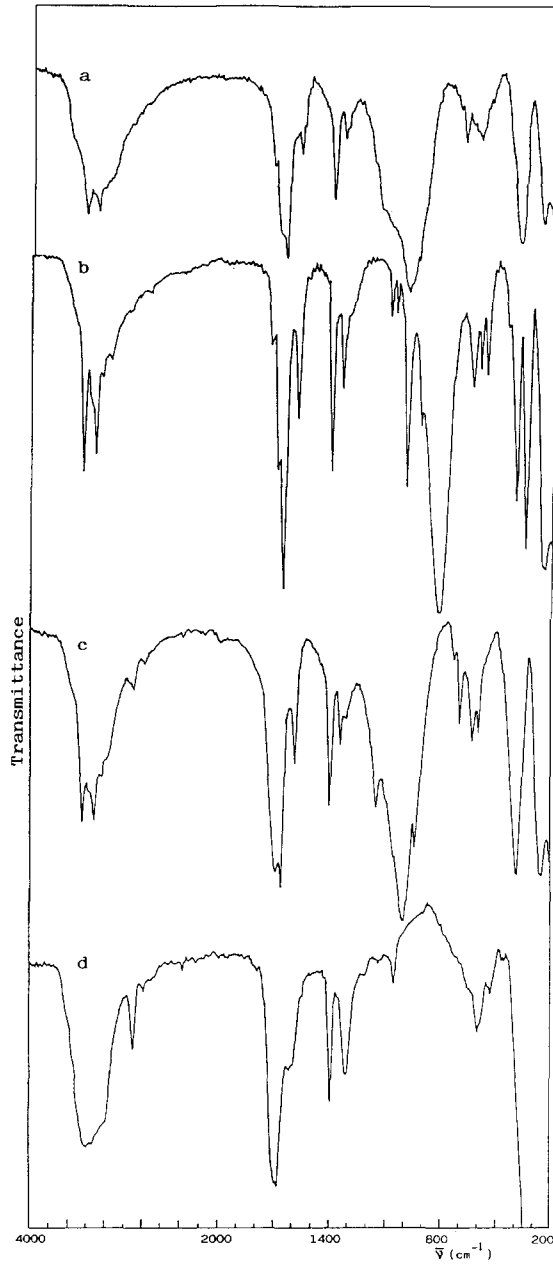


Fig. 3. IR spectra of: (a) the FA-NbVP intercalate; (b) the FA-NbVAs intercalate; (c) the FA-NbP intercalate; (d) liquid formamide.

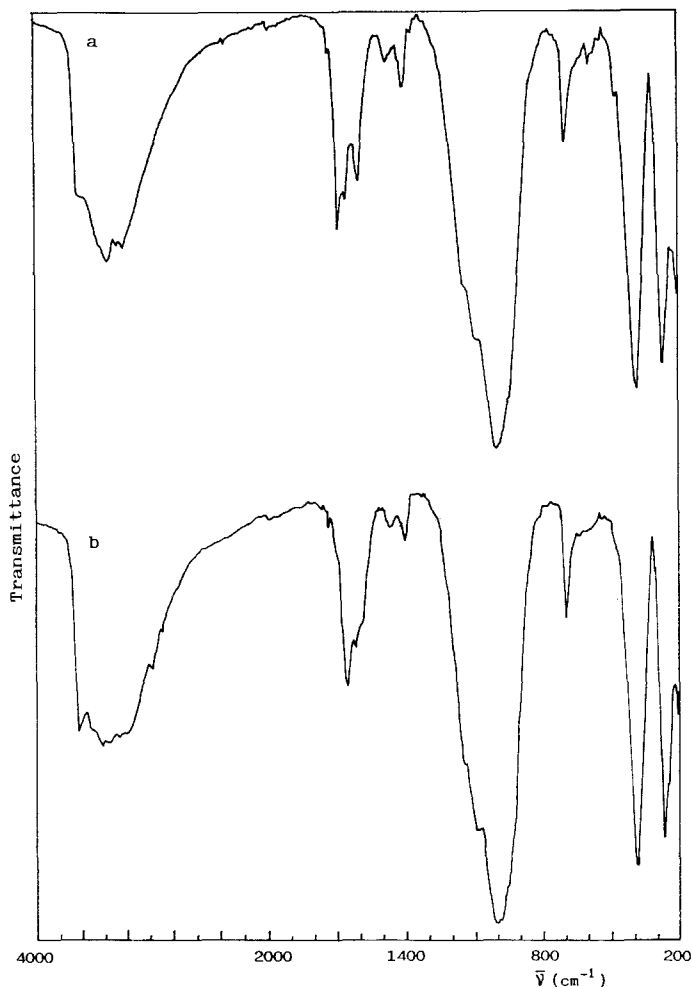


Fig. 4. IR spectra of: (a) the AA-NbVP intercalate; (b) the BA-NbVP intercalate.

but lower than those for the vapor amides or their dilute solutions [15]), we can conclude that the amides again interact through their CO group with the water molecule coordinated to the metal. However, the fact that these intercalates lose 0.3 mol of amide at low temperatures (below 200°C) indicates the occurrence of molecules weakly retained through hydrogen bonds involving NH linkages as donors towards zeolitic water [16]; hence the changes in their vibrational modes.

The IR spectra of the tertiary amides only show one diagnostic band, namely the Amide I band. Such a band appears split into two components (Figure 5) at 1667–1622 cm^{-1} in DMFA and at 1663–1617 cm^{-1} in DMAA. This splitting indicates the occurrence of two interaction modes [8, 10], although some authors go as far as ascribing it to a loss of symmetry [6]. The band at 1622 and 1617 cm^{-1} , respectively, of the two amides was assigned to the direct coordination to the metal

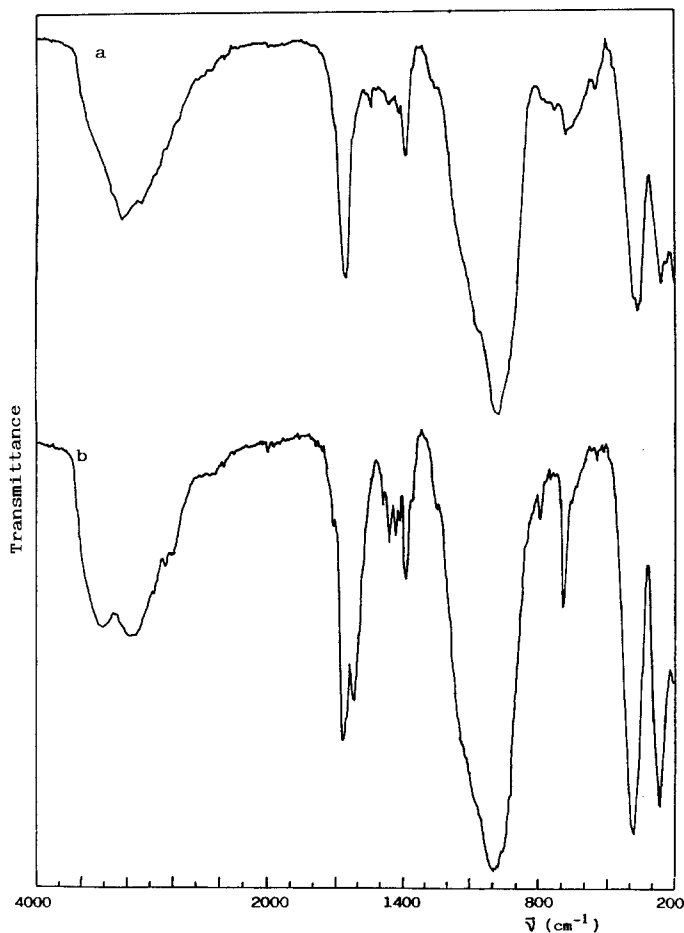


Fig. 5. IR spectra of: (a) the MFA-NbVP intercalate; (b) the DMFA-NbVP intercalate.

on account of its low frequency, which may arise from the greater basic nature and dehydrating power of these tertiary amides. This band might mask the $\delta(\text{H}_2\text{O})$ band; however, its sharp profile and its intensity, greater than that of the $\nu(\text{OH})$ band, allow it to be assigned to the $\nu(\text{CO})$ mode of the coordinated molecules. The bands at 1667 and 1633 cm^{-1} , respectively, for the two intercalates, like that for the other amides, were assigned to the $\nu(\text{CO})$ mode of the molecules coordinated to the metal through water molecules. The $\nu(\text{OH})$ bands, which appear at low frequencies (3184 and 3200 cm^{-1}), confirm the occurrence of strong hydrogen bonds with the amide molecules.

On the other hand, the $\nu(\text{M}=\text{O})$ band is shifted by changes in the other coordination positions along the c axis of the octahedron; in the spectrum of the FA intercalate of NbVAs, the band is shifted somewhat (it appears at 990 cm^{-1}) with respect to the original matrix (Figure 3). The shift is very small compared with that found in the intercalation of basic substances such as n -alkylamines (950–

970 cm^{-1}) [2]. However, it is similar to that found from the interaction of less basic substances such as pyridine (992 cm^{-1}) [5] or amides (999 cm^{-1}) [10] in vanadyl arsenate, which is consistent with the lower basicity of amides.

Finally, the diffuse reflectance spectra of the amide intercalates in the range 200–450 nm confirm the occurrence of an interaction of the amides to the water molecules coordinated to the metal (Figure 6). In fact, the charge transfer band of vanadium at 335 nm and the shoulder at 400 nm shift to the UV region, where they overlap with the bands of niobium between 245 and 255 nm [1]; this accounts for

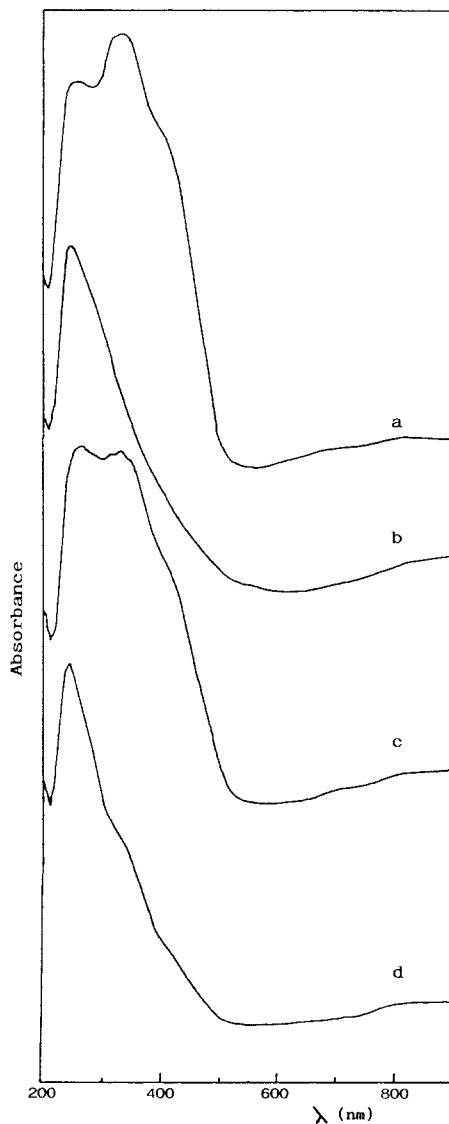


Fig. 6. Diffuse reflectance spectra of: (a) NbVP; (b) the FA-NbVP intercalate; (c) the AA-NbVP intercalate; (d) the DMFA-NbVP intercalate.

the colour change in the intercalates from the yellow of the host matrix to white.

When the intercalation takes place to a large extent (e.g. with FA, MFA and MAA, which are intercalated in a proportion of about 1 mol per mole of phosphate), the spectrum only shows the band at 245–255 nm, which indicates that all the metal atoms interact with the amide, although through the coordinated water molecule; this involves a change in the electron density of the M←L bonds. However, when the extent of intercalation is about 0.6–0.7 mol of amide per mole of phosphate (e.g. with DMFA and DMAA), there are still some vanadium atoms which do not interact, which results in the permanence of the shoulder at 330 nm. The AA, BA and BZA intercalates, which feature even lower amide contents, behave in much the same way.

4. Conclusion

We can conclude that the molecules of the different amides interact with the octahedral metal atoms through the water molecules coordinated to these by forming hydrogen bonds, although somewhat weaker than those found in amine intercalates [2]. However, primary amides show signs of protonation, although to a small extent, while in tertiary amides, probably as a result of their higher basicity and dehydrating power, a small fraction of molecules is directly coordinated to the metal.

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