

ADSORPTION OF VAPOURS OF SOME ORGANIC COMPOUNDS ON SURFACE OF IRON-SUBSTITUTED LAYERED VANADYL PHOSPHATE

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Gas chromatographic measurement of specific retention volumes of vapours of selected groups of organic compounds has been used to determine differential molar enthalpy of adsorption of their molecules on the surface of layered vanadyl phosphate substituted with ferric ions having the composition of $[\text{Fe}(\text{H}_2\text{O})]_{0.20}(\text{VO})_{0.80}\text{PO}_4$. Various types of bonds of the molecules to the surface of the layered adsorbent including their probable orientation with respect to the layers have been discussed. It was observed a dependence of the specific peak elution volume and shape of chromatographic peak on the sample size in the cases of those compounds whose molecules are chemically bound to the adsorbent surface. A connection is pointed out between the adsorption strength of the organic molecules on the layered adsorbent and the tendency of the system to undergo intercalation reaction.

Key words: Adsorption; Differential molar enthalpy; Iron(III)-vanadyl phosphate; Intercalates; Phosphates; Gas chromatography; Intercalation.

Structure of tetragonal modification of anhydrous vanadyl phosphate, $\alpha_1\text{-VOPO}_4$, is formed by repeating layers of $(\text{VOPO}_4)_\infty$ in the *aaa* order^{1,2}. The structural arrangement of the $(\text{VOPO}_4)_\infty$ layer formed by a network of polar covalent bonds is depicted in Fig. 1. A similar structure has also been found in the new compounds prepared recently^{3,4}. The composition of one of them is expressed by the formula $[\text{Fe}(\text{H}_2\text{O})]_x(\text{VO})_{1-x}\text{PO}_4$ ($x \leq 0.2$). The compound is built from $\{[\text{Fe}(\text{H}_2\text{O})]_x(\text{VO})_{1-x}\text{PO}_4\}_\infty$ layers which only differ from the $(\text{VOPO}_4)_\infty$ layers by having a part (1/5 at the most) of vanadyl groups VO^{3+} replaced⁵ by $[\text{Fe}(\text{H}_2\text{O})]^{3+}$ particles.

The compound $[\text{Fe}(\text{H}_2\text{O})]_x(\text{VO})_{1-x}\text{PO}_4$ (denoted as FeVOP) is able to accept foreign molecules into its interlayer space and form intercalates⁴. In this respect it does not differ from the isostructural $\alpha_1\text{-VOPO}_4$, whose intercalation reactions have been extensively investigated, namely those giving layered hydrates⁶⁻⁹, complexes with aliphatic alcohols¹⁰⁻¹², amines¹³, alkanolic acids¹⁴ and some other compounds^{15,16}.

For the potential layered host to be able to intercalate foreign molecules, it is necessary that the guest particles may penetrate into its structure and subsequently become sufficiently firmly anchored to its layers. In the cases of FeVOP and $\alpha_1\text{-VOPO}_4$ the two conditions are probably fulfilled:

1. The layers of $(\text{VOPO}_4)_\infty$ – both substituted and nonsubstituted – are highly flexible and easily deformed as compared with other layered substances¹⁷. This facilitates penetration of guest particles into the host structure.

2. Pentacoordinated vanadium atoms V(V) of the surface of layers in 001 planes are not saturated coordinatively and can increase the coordination number to six by binding the guest molecule by means of a donor-acceptor bond. Molecules with active (acid) hydrogen atoms can also become bound to the $(\text{VOPO}_4)_\infty$ layers by means of hydrogen bridges. It was found that, *e.g.*, molecules of water¹⁸ and alcohols¹² are bound to phosphate layers by the donor-acceptor $\text{O}_{\text{guest}} \rightarrow \text{V}_{\text{host}}$ bonds and, at the same time, hydrogen bridges $\text{O}_{\text{guest}} - \text{H}_{\text{guest}} \cdots \text{O}_{\text{host}}$. The anchoring of guest molecules to the surface of layers of potential host forms the main driving force of the intercalation reactions.

We have tried to find out how firmly some selected organic molecules with various functional groups are anchored to the surface of the layered

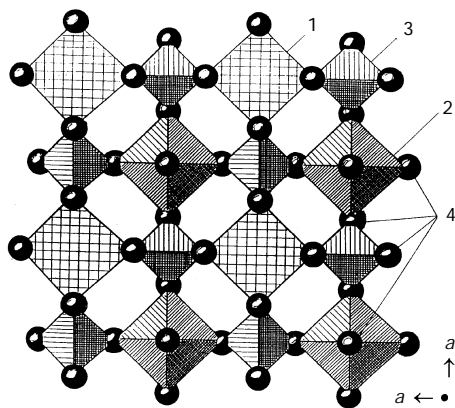


FIG. 1

Structure of $(\text{VOPO}_4)_\infty$ layer^{1,2,6,7} viewed in perpendicular direction to its plane. The layer is built by two-dimensional chains of square pyramids of VO_5 (1, 2) and tetrahedrons of PO_4 (3). The VO_5 pyramids are oriented by its apex (occupied by oxygen atom of vanadyl group) alternately to one and the other side of layer. The diagram only shows the oxygen atoms (4). The vanadium atoms are inside the VO_5 pyramids near their square base, the phosphorus atoms are in the centre of the PO_4 tetrahedrons

phosphate formed by crystallographic plane 001. A differential molar enthalpies associated with trapping of the molecules by solid adsorbent were determined by measurements of temperature dependence of the vapours retention of selected organic compounds on the powdered host placed in a gas chromatographic column. As any successful measurement necessitates an adsorbent having a sufficiently large specific surface, and α_1 -VOPO₄ does not meet this requirement, we used samples of isostructural FeVOP. The arrangement of its surface is the same⁴ as that of α_1 -VOPO₄ with the only difference that at the sites of substitutional disturbances, water molecules are very firmly bound to ferric ions which had replaced the vanadyl groups VO³⁺. This fact extends the above-mentioned host-guest binding possibilities by the capability of ionogenic acid-base interactions of FeVOP with basic particles¹⁹, e.g., ammonia $[\cdot\text{Fe}(\text{H}_2\text{O})]_{\text{host}} + (\text{NH}_3)_{\text{guest}} = [\cdot\text{Fe}(\text{OH})]^{-}(\text{NH}_4)^{+}$.

EXPERIMENTAL

Preparation of FeVOP

The compound was obtained in the following way⁵: A reaction of solid, freshly annealed (in air) V₂O₅ (24 g, 0.132 mol) with a solution containing 160 cm³ H₃PO₄ (1.710 g cm⁻³, 85 wt.%, 2.37 mol), Fe(NO₃)₃·9 H₂O (32 g, 0.079 mol) and 550 cm³ redistilled water under reflux for ca 15 h gave a precipitate of dihydrate [Fe(H₂O)]_{0.20}(VO)_{0.80}PO₄·2 H₂O (the yield 46 g, i.e. 70%), which was collected by hot filtration, washed with ca 100 cm³ of cold water and then heated in vacuum (500 Pa) at 300 °C for 5 h to give the dehydrated FeVOP of the formula [Fe(H₂O)]_{0.20}(VO)_{0.80}PO₄ quantitatively. The remaining coordinated water is liberated from it only at 500 °C, even in vacuum. The substance prepared on this way is a yellow, polycrystalline solid with the specific weight of 2.58 g cm⁻³ and specific surface about 2 m² g⁻¹. We found in preliminary experiments it has undergone intercalation reactions with aliphatic alcohols, amines, pyridine and a number of other compounds. In humid air it takes up water to give the dihydrate.

Adsorbates

For liquid adsorbates, we chose the following commercial samples (Fluka, Sigma, Aldrich) of *purum* and *purissimum* purity grades: n-hexane, cyclohexane, cyclohexene, cyclohexa-1,3-diene, cyclohexa-1,4-diene, benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, cumene, acetone, butan-2-one, butane-2,3-dione, pentan-2-one, pentan-3-one, pentane-2,3-dione, pentane-2,4-dione, alkan-1-ols (C₁-C₆), acetonitrile and nitromethane.

Measurement of Specific Retention Volumes

The specific retention volumes and their temperature dependence were measured on a CHROM 4 chromatograph (Laboratorní přístroje, Prague, Czech Republic) equipped with a flame ionisation detector. The solid adsorbent (FeVOP) of 0.16–0.20 mm grain size, specific

surface of $4.8 \text{ m}^2 \text{ g}^{-1}$ and total weight of 15.1 g was packed in a glass chromatographic column 245 cm length and 3 mm in diameter. Before use, the column was heated in vacuum at $200 \text{ }^\circ\text{C}$ for 5 h . The carrier gas was dry nitrogen with the oxygen content below 20 ppm . Its flow rate $F_c \approx 18 \text{ cm}^3 \text{ min}^{-1}$ was kept constant in the individual series of temperature measurements. The adsorbates were injected individually as liquids (the injection volume usually was $3 \cdot 10^{-4} \text{ cm}^3$, *i.e.* $0.3 \text{ }\mu\text{l}$). The temperature of injection chamber was always *ca* $30 \text{ }^\circ\text{C}$ higher than the boiling point of the adsorbate introduced.

The retention times (t_R) obtained from this measurement were recalculated to specific retention volumes V_g using the relation^{20,21}:

$$V_g = \frac{3T_0 F_c \left[\left(p_i / p_o \right)^2 - 1 \right] (t_R - t_M)}{2 T_c W_s \left[\left(p_i / p_o \right)^3 - 1 \right]}$$

where $T_0 = 273.15 \text{ K}$ and the other symbols have the following meaning: F_c ($\text{cm}^3 \text{ s}^{-1}$) is the mobile phase flow rate at column temperature, p_i and p_o are the absolute pressures at the inlet and outlet of the chromatographic column, respectively, t_R (s) is the total retention time of an adsorbate, t_M (s) stands for the retention time of a nonretained compound, T_c (K) is the column temperature and W_s (g) is the weight of the solid adsorbent.

Determination of Values of Differential Molar Enthalpy of Adsorption ΔH

The differential molar enthalpies ΔH were obtained for the adsorption of individual compounds from slopes of the linear dependence of $\ln V_g$ on $1/T_c$ (refs^{20,21}).

Electron Microscopy

The pictures of microcrystals of adsorbent were obtained with a scanning electron microscope TESLA BS 340 (Czech Republic); resolving power 7 nm , accelerating voltage of electron beam equal to 20 kV .

Adsorbent Surface

The specific surface areas of all adsorbent samples were determined from low-temperature nitrogen adsorption by the BET method using a MICROMERITICS RSAA 2200A apparatus.

RESULTS AND DISCUSSION

Macrostructure of Powdered FeVOP

The pictures obtained from the electron microscope show that the powdered FeVOP sample is obviously formed by crystal clusters of irregular shape (Fig. 2), each of them consisting of several hundreds of leafs. Individual leafs (Fig. 3) show large numbers of cracks parallel to the $\{[\text{Fe}(\text{H}_2\text{O})]_x(\text{VO})_{1-x}\text{PO}_4\}_\infty$ layers. As the original microcrystals of dihydrate, observed in an optical microscope, have a shape of compact plates, it is ob-

vious that the decomposition of microcrystals along the splitting planes takes place only during the dehydration. This phenomenon can be used well for increasing the specific surface of anhydrous samples. For instance, a repetition of three cycles "hydration + fast thermal dehydration in vacuum" increased the specific surface of FeVOP sample from *ca* 2 to *ca* 5 m² g⁻¹.

By measuring the FeVOP microcrystals (in about 100 photographs) we arrived at the estimate of 93 ± 3% of the sorbent surface being represented by crystallographic plane (001) parallel with the $\{\text{[Fe(H}_2\text{O)]}_x(\text{VO)}_{1-x}\text{PO}_4\}_\infty$ layers^{4,7}.

Adsorption of Molecules on FeVOP Surface

The dependence of specific retention volume V_g on reciprocal temperature ($1/T_c$) is linear with all the adsorbates investigated. For example, Fig. 4 presents the results of measurements of this dependence for several hydrocarbons. The experimentally found values of differential molar enthalpy ΔH and specific retention volumes V_g (recalculated to the temperature of 96 °C) are given in Table I together with the temperature intervals in which the dependence of V_g vs $1/T_c$ was measured.

Differential molar enthalpies ΔH correspond with the strength of anchoring of the molecules to the adsorbent surface. Figure 5 presents the ΔH values plotted against molecular weights of the adsorbates. The dislocation of points in this graph enables qualitative or even semiquantitative conclu-

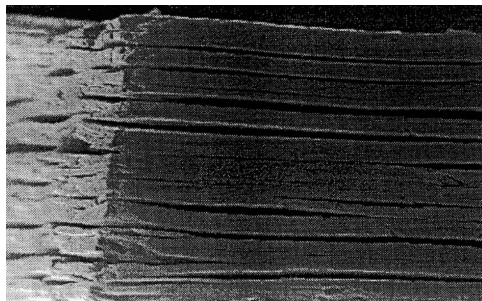
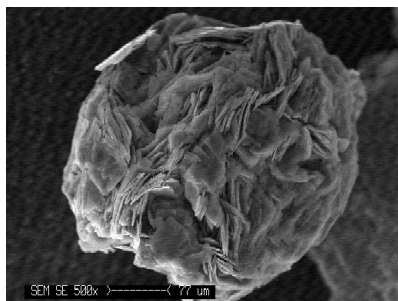


FIG. 2

Photograph of a particle of FeVOP sorbent of *ca* 0.3 mm size. The particle is a conglomerate of several hundreds of plate (or leaf) microcrystals (magnification 500×)

FIG. 3

Photograph of a single microcrystal (magnification 3 000×). Clearly visible is the disintegration of the microcrystal along the splitting planes (001) parallel to $\{\text{[Fe(H}_2\text{O)]}_x(\text{VO)}_{1-x}\text{PO}_4\}_\infty$ layers

sions to be made about the strength and probable character of the bonds and orientation of molecules with respect to the surface.

Hydrocarbons

In the group of unbranched aliphatic hydrocarbons C_5 to C_8 , the ΔH values depend on the molecular weight linearly. Also linear is the dependence of ΔH on the number of carbon atoms in the molecule (n_C), the respective

TABLE I
Values of the differential molar enthalpy, $-\Delta H$, and the specific retention volume, V_g , on various adsorbates

Adsorbate	B.p., °C	$-\Delta H$, kJ mol ⁻¹	V_g , cm ³ g ⁻¹	T_c , °C
n-Pentane	36.1	30.2	0.132	73–98
n-Hexane	68.7	37.9	0.284	73–98
n-Heptane	98.4	45.4	0.638	73–98
n-Octane	125.7	52.2	1.52	73–98
Cyclohexane	80.7	36.6	0.202	73–98
Cyclohexene	83.0	40.2	0.237	73–98
Cyclohexa-1,3-diene	80.0	47.5	0.304	73–98
Cyclohexa-1,4-diene	88.0	41.8	0.295	73–98
Benzene	80.1	41.9	0.283	73–98
Toluene	110.6	42.3	0.735	85–135
<i>o</i> -Xylene	144.4	47.1	2.03	93–150
<i>m</i> -Xylene	139.1	46.9	1.80	93–150
<i>p</i> -Xylene	138.4	47.2	1.83	93–150
Ethylbenzene	136.2	45.0	1.57	93–150
Cumene	152.4	46.2	2.38	93–150
Acetone	56.3	43.9	0.684	73–98
Butan-2-one	79.6	47.8	1.27	73–98
Butane-2,3-dione	87.5	48.2	0.546	73–98
Pentan-2-one	102.3	55.0	5.12	98–120
Pentan-3-one	102.3	52.2	2.79	98–120
Pentane-2,3-dione	107	51.9	1.44	98–120
Pentane-2,4-dione	135	50.2	8.97	98–120
Acetonitrile	81.6	43.6	0.551	75–99
Nitromethane	101.2	44.4	0.431	75–99
Methanol	64.7	49.1	2.71	75–99

equation being $-\Delta H = 7.35 n_C - 6.37$, which means that the extending of aliphatic chain by one methylene group will increase the ΔH value by only *ca* 7 kJ mol⁻¹. Such a result means that the molecules are bound by the van der Waals forces, and they adhere to the adsorbent surface by their whole lengths²⁰.

The ΔH values of n-hexane and cyclohexane are very close to each other, which means that also the cyclohexane molecules probably lie flat on the

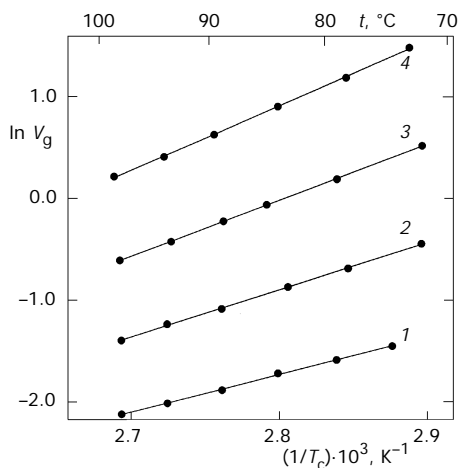


FIG. 4
Linear dependence of specific retention volumes of aliphatic nonbranched hydrocarbons on reciprocal column temperature: 1 n-pentane, 2 n-hexane, 3 n-heptane and 4 n-octane (mobile phase flow rate 18.0 ml min⁻¹, liquid sample size 0.3 μ l)

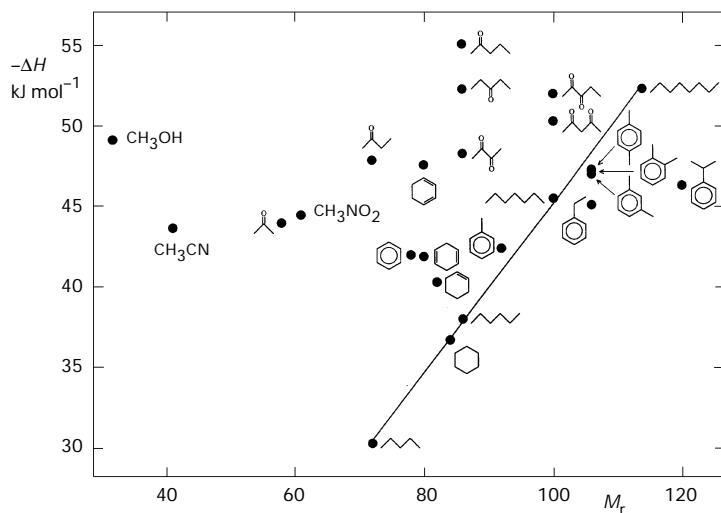


FIG. 5
Dependence of experimentally found values of differential molar enthalpy of adsorption of a group of organic compounds on their relative molecular mass

surface during adsorption, *i.e.*, in the way enabling the maximum contact with the solid phase.

The presence of one or more double bonds in a six-membered cyclic hydrocarbon structure increases the strength of adsorption of the molecule. The effect is clearly perceptible with the cyclohexa-1,3-diene molecule, whose ΔH value exceeds the van der Waals interaction red from the linear dependence $\Delta H = f(M_r)$ (*ca* 35 kJ mol⁻¹) by 12 kJ mol⁻¹. The ΔH increase similarly determined for cyclohexa-1,4-diene and benzene molecules is *ca* 6 to 7 kJ mol⁻¹, whereas for cyclohexene only 4 kJ mol⁻¹. It can be presumed that the ΔH increase in the case of unsaturated hydrocarbons is due to formation of weak donor-acceptor interactions consisting in both a shift of electron density from π orbitals of unsaturated hydrocarbons to vacant d orbitals of V(V) atoms (which are well accessible on the layer surface) and electron transfer from oxygen atoms (forming the surface of adsorbent) to vacant antibonding π^* orbitals of the adsorbed molecule.

Remarkable is the dislocation of points of all the alkyl- and dialkylbenzenes in Fig. 5. Clearly, introduction of methyl, ethyl, or isopropyl group on the benzene ring decreases the anchoring ability of the molecule to the adsorbent surface. The largest effect of this type is observed with cumene and ethylbenzene. The simplest interpretation of this phenomenon lies in the idea that the substituents deviate the molecules with benzene ring from their parallel position to the adsorbent surface, thus decreasing the extent of their interaction with the surface.

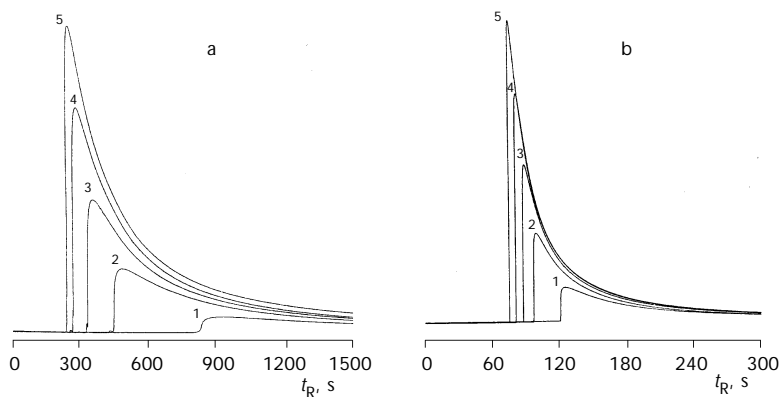


FIG. 6

Changes in the retention time and peak shape of methanol (a) and acetonitrile (b) with changing injection volume: 1 0.2, 2 0.4, 3 0.6, 4 0.8 and 5 1.0 μl (mobile phase flow rate 18.0 ml min⁻¹, column temperature 83 °C)

Aliphatic Ketones and Diketones

As compared with saturated hydrocarbons of comparable molecular weight, these compounds exhibit markedly higher ΔH values. The increase is greater with ketones than with diketones. In the series acetone, butan-2-one, pentan-2-one and pentan-3-one, the ΔH values increase with increasing number of carbon atoms, the slope of this dependence being approximately the same as that for saturated aliphatic hydrocarbons. The presence of one keto group in the molecule increases the ΔH value by 15 to 20 kJ mol⁻¹ as compared with the van der Waals interaction, the presence of two keto groups in butane-2,3-dione, pentane-2,3-dione and pentane-2,4-dione causing an increase of only ca 5 kJ mol⁻¹. It can be presumed that the chains of aliphatic ketones and diketones adhere to the adsorbent surface analogously to the saturated hydrocarbons, but, in addition, the keto group relatively firmly anchors to the surface, the V(V) atom being the only possible site on the adsorbent surface for coordination with a ketonic group. In the case of diketone molecule, the second keto group cannot be coordinated with the neighbouring vanadium atom for sterical reasons; it is pushed away from the surface by electrostatic repulsion of the negatively charged oxygen atoms forming the sorbent surface, and the anchoring strength of diketone molecules is decreased.

Alkan-1-ols, Acetonitrile and Nitromethane

According to our measurements of temperature dependence of methane retention, its molecule shows the differential molar enthalpy of adsorption equal to ca 7 kJ mol⁻¹. A substitution of one hydrogen atom in methane molecule by -OH, -CN or -NO₂ group is thus associated with an increase in the ΔH value by ca 42, 36 and 37 kJ mol⁻¹, respectively (Table I). This clearly indicates a very firm anchoring of methanol, acetonitrile, and nitromethane molecules to the adsorbent surface. Again it is most probable that these molecules are anchored to V(V) atoms by their functional groups, forming the bonds $O_{\text{guest}} \rightarrow V_{\text{host}}$ or $(C \equiv N)_{\text{guest}} \rightarrow V_{\text{host}}$. The association can of course be realised with participation of other interactions too, e.g., formation of hydrogen bridges through hydrogen atom in methanol or those in the coordinatively bound water molecule present in the substituent particle $[\text{Fe}(\text{H}_2\text{O})]^{3+}$.

Alkan-1-ols with two to six carbon atoms in their chains react with the adsorbent at temperatures above 90 °C to reduce it (V(V)→V(IV), being themselves oxidized to various alkanic acids (see refs^{22,23}). That is why

their specific retention volumes cannot be determined at these temperatures.

Asymmetry of Elution Curves of Some Sorbates

The elution curves of all the adsorbates which are bound to the adsorbent only by weak van der Waals bond are symmetrical. The elution curves of the substances bound to the host by hydrogen bond to the oxygen atoms or donor-acceptor bond to the vanadium atoms (acetonitrile and methanol on Fig. 6) are markedly asymmetrical (tailing), and, in addition, the positions of their maximum are significantly shifted with the injection volume changing. This effect is so large that it is difficultly explainable by usual way, *i.e.*, by the argument of curvature of adsorption isotherm and multilayer adsorption of molecules²⁰.

To a lesser extent is the asymmetry of peaks observed with all the substances whose figurative points are located in the top left-hand section of the graph in Fig. 5, *i.e.*, above the straight line interlacing the points belonging to aliphatic hydrocarbons, since these compounds, too, are probably bound to vanadium atoms on the adsorbent surface more firmly than to other sites.

Relation Between ΔH Values Found for Adsorption of Molecules to Adsorbent and Intercalation Reactions of These Systems

The values of differential molar enthalpy accompanying the adsorption of individual organic compounds on the layered vanadyl phosphate modified by substitution, FeVOP, correspond well with the presence of intercalation processes in the systems liquid organic compound-polycrystalline FeVOP. It can be stated that the compounds anchored to the FeVOP adsorbent surface by means of bonds substantially stronger than the van der Waals forces have considerable chance to become guests in its layered structure.

This is indicated by numerous findings coming from the chemistry of intercalates: Aliphatic alcohols (which were only represented by methanol in our studies because other alcohols are already oxidized at the temperatures used by us in the chromatographic column^{22,23}) are slowly intercalated into vanadyl phosphate or its modified version, FeVOP, at room temperature¹⁰⁻¹². Similar behaviour is exhibited by alkanediols¹² and other compounds with OH groups²⁴ possessing a donor oxygen atom as well as the ability to form hydrogen bonds. The willingness to undergo intercalation processes with vanadyl phosphate was also proved for ketones²⁴.

A certain chance of successful preparation of intercalates containing FeVOP as host is also indicated (according to the ΔH values found for acetonitrile and nitromethane) in the case of aliphatic nitriles and nitro compounds. Formation of intercalates of the host discussed with alkanes is entirely excluded.

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REFERENCES

1. Jordan B., Calvo C.: *Can. J. Chem.* **1973**, *51*, 2621.
2. Jordan B., Calvo C.: *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32*, 2899.
3. Beneš L., Richtrová K., Votinský J., Kalousová J., Zima V.: *Powder Diffr.* **1993**, *8*, 130.
4. Richtrová K., Votinský J., Kalousová J., Beneš L., Zima V.: *J. Solid State Chem.* **1995**, *116*, 400.
5. Melánová K., Votinský J., Beneš L., Zima V.: *Mater. Res. Bull.* **1995**, *30*, 1115.
6. Tietze H. R.: *Aust. J. Chem.* **1981**, *34*, 2035.
7. Tachéz M., Theobald F., Bernard J., Hewat W.: *Rev. Chim. Miner.* **1982**, *19*, 291.
8. Zima V., Beneš L., Málek J., Vlček M.: *Mater. Res. Bull.* **1994**, *29*, 687.
9. Beneš L., Zima V.: *J. Inclusion Phenom. Mol. Recogn. Chem.* **1995**, *20*, 381.
10. Beneš L., Votinský J., Kalousová J., Klikorka J.: *Inorg. Chim. Acta* **1986**, *114*, 47.
11. Votinský J., Beneš L., Kalousová J., Klikorka J.: *Inorg. Chim. Acta* **1987**, *126*, 19.
12. Beneš L., Melánová K., Zima V., Kalousová J., Votinský J.: *Inorg. Chem.* **1997**, *36*, 2854.
13. Beneš L., Hyklová R., Kalousová J., Votinský J.: *Inorg. Chim. Acta* **1990**, *177*, 71.
14. Beneš L., Votinský J., Kalousová J., Handlřík K.: *Inorg. Chim. Acta* **1990**, *176*, 255.
15. Johnson J. W., Jacobson A. J., Brody J. F., Rich S. M.: *Inorg. Chem.* **1982**, *21*, 3820.
16. Kalousová J., Votinský J., Beneš L., Melánová K., Zima V.: *Collect. Czech. Chem. Commun.* **1998**, *63*, 1.
17. Votinský J., Beneš L.: *Collect. Czech. Chem. Commun.* **1991**, *56*, 2859.
18. Čapková P., Vácha J., Votinský J.: *J. Phys. Chem. Solids* **1992**, *53*, 215.
19. Beneš L., Galli P., Massucci M. A., Melánová K., Patrono P., Zima V.: *J. Therm. Anal.* **1998**, *52*, 615.
20. Kiselev A. V., Yashin Y. I.: *Adsorption Gas and Liquid Chromatography*. Khimiya, Moscow 1984.
21. Ettore L. S. (IUPAC): *Pure Appl. Chem.* **1993**, *65*, 819.
22. Centi G., Trifiro F., Ebner J. R., Franchetti V. M.: *Chem. Rev.* **1988**, *88*, 55.
23. Centi G.: *Catal. Today* **1993**, *16*, 1.
24. Votinský J.: Unpublished results.