

Modification of sorption properties of tetracyano complexes of nickel and possibility of their analytical use

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The composition of the clathrate of tetracyano complex $\text{Ni}(\text{NH}_3)_2 \cdot \text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ as well as its sorption properties changes according to the organic liquid with which this clathrate is heated. Remarkable changes in composition and sorption activity have been achieved by heating the clathrate with pyridine and 1,4-dioxan. The clathrate thus modified may be used as sorbent in gas chromatography for abstracting oxygenous substances from the analyzed sample.

Состав клатрата тетрацианидного комплекса $\text{Ni}(\text{NH}_3)_2 \cdot \text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$, а также его сорбционные свойства изменяются в зависимости от того, с какой органической жидкостью клатрат нагревают. Значительные изменения состава и сорбционной активности были достигнуты в результате нагревания упомянутого клатрата с пиридином и 1,4-диоксаном. Таким образом модифицированный клатрат можно применять в качестве сорбента в газовой хроматографии для экстракции кислородсодержащих соединений из анализируемых образцов.

Clathrates which represent a part of the great class of inclusion compounds [1] have been used as specific stationary phases for gas chromatography [2—5]. The sorption properties of tetracyano complexes of general formula $\text{M}_1(\text{L})_m \text{M}_2(\text{CN})_4 \cdot n\text{G}$ ($\text{M}_1 = \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$; $\text{M}_2 = \text{Ni}, \text{Pt}, \text{Pd}$; $\text{L} = \text{ammonia or ethylenediamine}$; $\text{G} = \text{water or organic compound}$; $m = 0—4$; $n = 0—2$) are determined by both metals, character of ligand as well as by the circumstance how the free sites in the crystal structure of clathrate are accessible for molecules of other substances. In this line, the clathrates containing the metal pairs Cu—Ni , Ni—Ni appear to be remarkable.

We have found that the original sorption properties of clathrate may be changed if the clathrate is heated with convenient organic liquid. For instance, the clathrate $\text{Cu}(\text{en})_2 \text{Ni}(\text{CN})_4 \cdot 0.14\text{C}_6\text{H}_6$ subjected to the treatment with cyclohexane so improved its sorption properties that it was able to separate all three isomers of xylene [6]. Great changes came into existence if clathrate of the composition

$\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ was exposed to the effect of organic liquids. In this paper, we present the results obtained if this clathrate was heated with such substances and subsequently used as stationary phase in gas chromatography.

Experimental

The clathrate was prepared by the method described in literature [7—9]. The composition of this clathrate was confirmed by elemental analysis performed with an instrument CHN analyser, model 185 (Hewlett—Packard, USA). The results of analysis are given in Table 1. The structure was confirmed by infrared spectroscopy. The clathrate in the form of powder was pressed into a KBr tablet. It exhibited these absorption bands: $\tilde{\nu} = 2170 \text{ cm}^{-1}$ ($\text{C}\equiv\text{N}$ group), $\tilde{\nu} = 440 \text{ cm}^{-1}$ ($\text{Ni}-\text{CN}$ bond), $\tilde{\nu} = 1230 \text{ cm}^{-1}$, 1605 cm^{-1} , and 3310 cm^{-1} (NH_3 molecule), $\tilde{\nu} = 1440 \text{ cm}^{-1}$, 3200 cm^{-1} , and 3570 cm^{-1} (OH group). The surface areas were determined by dynamic chromatographic method using liquid nitrogen [10].

Modification of sorption properties

The changes in composition as well as in sorption properties were produced as follows: We poured clathrate into excess organic liquid and evaporated this liquid on a water bath. The dry preparation obtained was analyzed by several analytical methods and its sorption properties were examined by gas chromatography.

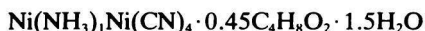
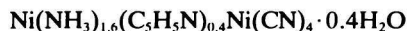
The following liquids were chosen as modifiers: n-pentane, methanol, pyridine, and 1,4-dioxan. All solvents were anal. grade chemicals and the content of water in methanol, pyridine, and dioxan was 0.12 %, 0.45 %, and 0.22 %, respectively. The change in clathrate composition after treating with a liquid was determined by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and other methods. The results of elemental analysis are given in Table 1.

Table 1

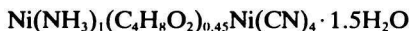
Elemental analysis of the clathrate $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ and its modified forms

Clathrate	$w_i/\%$			
	C	H	N	
Unmodified clathrate,	calc.	16.47	3.45	28.83
	found	17.1	3.1	29.1
Clathrate modified by:	n-pentane	17.2	3.0	29.2
	methanol	17.0	3.1	29.2
	pyridine	24.6	2.4	28.9
	1,4-dioxan	22.4	2.8	22.8

The data in Table 1 indicate that the change in clathrate composition is dependent on the kind of the liquid with which the clathrate was heated. This change in composition was also confirmed by infrared spectroscopy. Owing to the effect of pyridine, the absorption bands corresponding to the C—H group ($\tilde{\nu} = 1220 \text{ cm}^{-1}$, 1160 cm^{-1} , 1080 cm^{-1} , and 1045 cm^{-1}) as well as the bands corresponding to the C—N group ($\tilde{\nu} = 1660 \text{ cm}^{-1}$ and 1590 cm^{-1}) turned up in the infrared spectrum. Owing to the effect of dioxan, the bands corresponding to the C—H group ($\tilde{\nu} = 2970 \text{ cm}^{-1}$ and 2920 cm^{-1}) as well as the band corresponding to the C—O—C group ($\tilde{\nu} = 1130 \text{ cm}^{-1}$) appeared in the infrared spectrum. On the basis of these results, elemental and chemical analysis, we have determined the composition of the clathrates modified by pyridine or dioxan in our conditions as follows



resp. after heating



The infrared spectra of the clathrates modified by n-pentane and methanol were only very little different from the original spectra. We concluded from this fact that both these substances did not produce any greater change in composition of the original clathrate because they were not able to enter as ligands into the first coordination sphere of the host structure either immediately or after heating.

Thermogravimetric analysis

Clathrates change their composition in the course of heating. The variation of composition with temperature was investigated by the use of a derivatograph Q 1500 P (MOM, Budapest). Conditions of analysis: weighed amount 170 mg, temperature range 20—1000 °C, and rate of heating 10 °C min⁻¹. The curves obtained by thermal analysis of all four clathrates are represented in Fig. 1. It results from this figure that the decomposition of original clathrate proceeds in three stages. In the temperature interval 40—140 °C with the maximum at 100 °C, the mass is reduced by 10.9 %, which corresponds to a loss of 1.73 mole of water. In the temperature interval 150—350 °C with the maximum at 330 °C, two moles of NH₃ and the rest of water are liberated. The mass decreases by 13.4 %. All these changes were corroborated by infrared spectroscopy. Every mass change is referred to original clathrate.

The record obtained for the clathrate modified by n-pentane did not exhibit any change while the clathrate modified by methanol exhibited at the temperature of 100 °C a smaller loss of mass than the original clathrate. The character of changes observed at higher temperatures resembled the course of changes obtained for original clathrate.

In the course of heating, a more conspicuous change in mass with increasing temperature was exhibited by clathrates modified by pyridine and dioxan. A clathrate modified by pyridine liberates water at 70 °C while the built-in pyridine escapes in the temperature region 150—350 °C. The loss of mass up to 160 °C in a clathrate modified by dioxan reaches

13.4 %. As evidenced by infrared spectrum, the major part of clathrate water and clathrate dioxan are thus released. The decomposition of tetracyano complex takes place at the temperature of about 300 °C, which is considerably earlier than it was observed for the preceding samples.

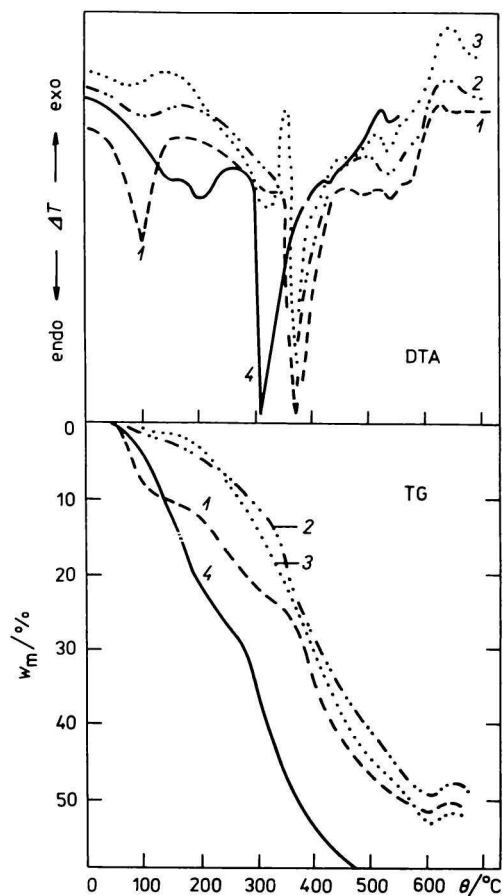


Fig. 1. Curves of thermal analysis.
 1. Original clathrate; 2. clathrate modified by methanol; 3. clathrate modified by pyridine; 4. clathrate modified by 1,4-dioxan

Study of sorption properties by gas chromatography

The measurements were performed on a chromatograph Chrom 5 (Laboratorní přístroje, Prague) equipped with a flame-ionization detector. The packing of chromatographic column was prepared by the following procedure: A weighed amount (1 g) of original clathrate is suspended in some of the above-mentioned organic liquids (50 cm³). 9 g of Chromosorb P, NAW, of 0.17—0.25 mm grain size is poured into the stirred suspension. The liquid is dry evaporated on a water bath. A column of 2.5 m length and 3 mm internal diameter is packed with this loose packing material.

For studying the sorption properties, we used the following model mixtures: C-5—C-9 n-paraffinic hydrocarbons, benzene + toluene + *o*-, *m*-, *p*-xylenes, cyclohexane + methylcyclohexane + ethylcyclohexane + propylcyclohexane, C-1—C-4 primary aliphatic alcohols, dimethyl ketone + ethyl methyl ketone + methyl propyl ketone, methyl- + ethyl- + butyl- + pentyl acetate.

The temperature of detector and injector was 200 °C while the temperature of column varied according to the applied criterion. The flow rate of carrier gas (nitrogen) was 25 cm³ min⁻¹.

Results and discussion

We confronted the sorption properties of all four clathrates modified by the above model mixtures. The chromatograms of n-paraffinic hydrocarbons obtained at 80 °C are represented in Fig. 2. The greatest retention times were measured on

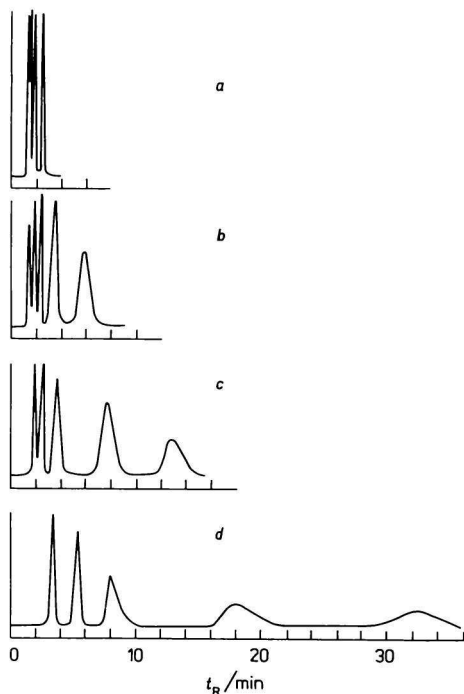


Fig. 2. Chromatograms of C-5—C-9 n-paraffinic hydrocarbons.

Temperature of column 80 °C. Clathrate modified: a) by dioxan; b) by n-pentane; c) by methanol; d) by pyridine.

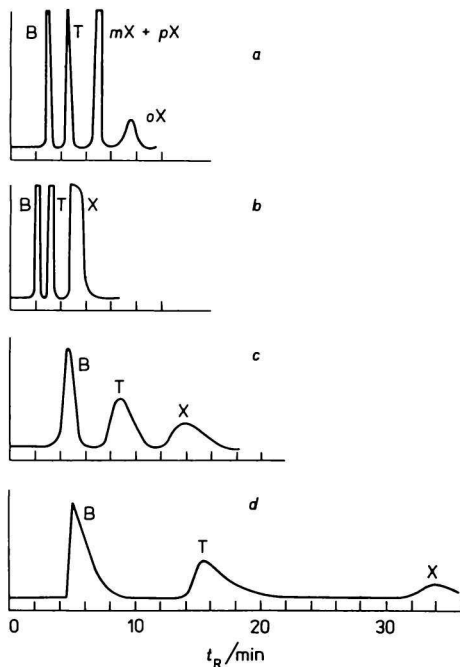


Fig. 3. Chromatograms of aromatic hydrocarbons.

Temperature of column 80 °C. Meaning of symbols a—d like in Fig. 2. B — benzene, T — toluene, X — xylene, *m*X — *meta*-xylene, *p*X — *para*-xylene, *o*X — *ortho*-xylene.

a clathrate modified by pyridine, while the shortest retention times were observed for a clathrate modified by dioxan. The cause of these differences is to be seen in variation of the surface area of clathrates. The measured results are as follows

$$A_s (\text{original clathrate}) = 19.43 \text{ m}^2 \text{ g}^{-1}$$

$$A_s (\text{clathrate modified by n-pentane}) = 19.50 \text{ m}^2 \text{ g}^{-1}$$

$$A_s (\text{clathrate modified by methanol}) = 20.21 \text{ m}^2 \text{ g}^{-1}$$

$$A_s (\text{clathrate modified by pyridine}) = 67.74 \text{ m}^2 \text{ g}^{-1}$$

$$A_s (\text{clathrate modified by dioxan}) = 5.67 \text{ m}^2 \text{ g}^{-1}$$

$$A_s (\text{clathrate modified by dioxan after heating to } 150^\circ\text{C}) = 26.44 \text{ m}^2 \text{ g}^{-1}$$

$$A_s (\text{clathrate modified by dioxan after heating to } 200^\circ\text{C}) = 27.10 \text{ m}^2 \text{ g}^{-1}$$

It is evident from these results that dioxan predominantly occupied free sites in the crystal structure of clathrate, owing to which its surface area decreased. By heating the clathrate, the liberation of dioxan or its delocalization into the first coordination sphere [11] is provoked, owing to which its surface area increases. On the other hand, pyridine enlarged the surface area of clathrate because it partially replaced the ammonia ligand and thus extended the distances between individual layers in the crystal structure of clathrate.

Equal character of sorption as observed for paraffinic hydrocarbons was also exhibited by cycloparaffinic hydrocarbons and aromates. It is interesting that

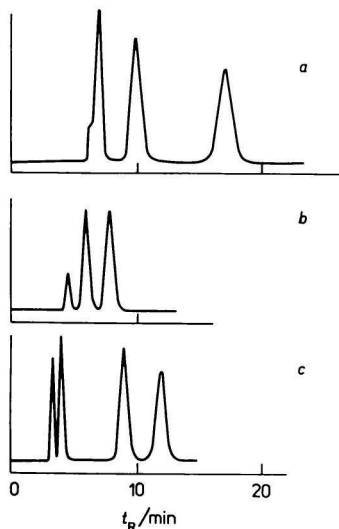


Fig. 4. Chromatograms of mixtures of oxygenous substances obtained on a clathrate modified by 1,4-dioxan.

Temperature of column 80°C . a) C-1—C-4 alcohols; b) ketones; c) acetates.

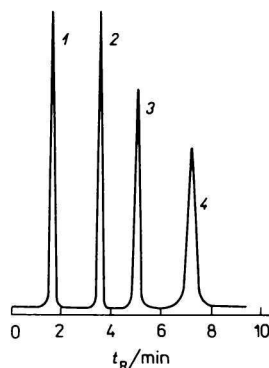


Fig. 5. Chromatogram of the Averill mixture obtained on a clathrate modified by 1,4-dioxan. Temperature of column 80°C . 1. Ethyl methyl ketone; 2. ethanol; 3. cyclohexane; 4. benzene.

aromates were quite rapidly eluted from a clathrate modified by dioxan and at the same time the best separation of the isomers of xylene was achieved (Fig. 3).

The change in sorption properties of clathrates most conspicuously manifested itself with respect to oxygenous substances. While all oxygenous substances gave symmetric waves on the clathrate modified by dioxan (Fig. 4), these substances were irreversibly sorbed on other clathrates at 80 °C. Alcohols were eluted from the column packed with the clathrate modified by pyridine only at 220 °C while they were eluted at 160–180 °C in the case of other clathrates.

The selectivity of the clathrate modified by dioxan was tested by using the model mixture according to *Averill* [12]. A chromatogram obtained with this mixture is represented in Fig. 5. It is interesting but not surprising that ethyl methyl ketone is the first substance to be eluted and other components subsequently follow in the order ethanol, cyclohexane, and benzene.

Influence of temperature on the change in sorption properties

The results of thermogravimetric analysis have shown that the heating produces changes in the composition of clathrate. Not only the included guest species but also, to a certain extent, the ligands are liberated.

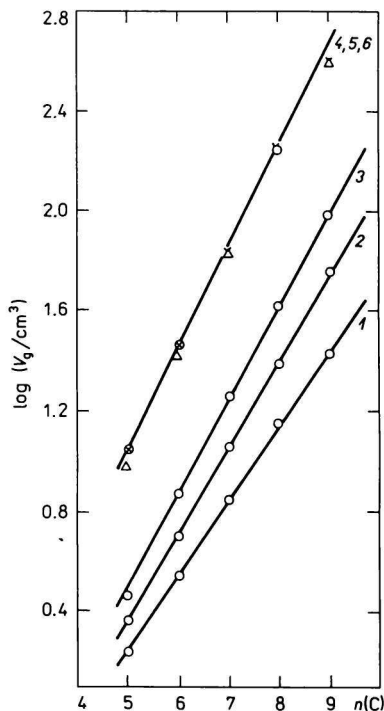


Fig. 6. Variation of $\log (V_g/\text{cm}^3)$ with the number of carbon atoms in *n*-paraffinic hydrocarbons obtained for the clathrate modified by 1,4-dioxan after its heating to the stated temperatures.

Temperature of column 80 °C. Clathrate: 1. without preceding heating; 2. heated to 140 °C; 3. heated to 160 °C; 4. heated to 180 °C; 5. heated to 200 °C; 6. heated to 220 °C.

We heated the chromatographic column with individual clathrates to higher temperature and after cooling it to 80 °C, the model mixtures were subjected again to chromatographic analysis. Fig. 6 shows how the retention volumes of n-paraffinic hydrocarbons changed with the temperature to which the clathrate modified by dioxan was heated. The heating of clathrate to 140 °C and higher resulted in liberation of the dioxan closed in free sites of crystal or its moving to the function of ligand. Thus the surface area of clathrate increased from 5.67 m² g⁻¹ to 26.44 m² g⁻¹, owing to which the retention volumes became greater. As soon as the maximum surface area of 27.10 m² g⁻¹ had been reached, the retention volumes stopped increasing.

An increase in surface area of this clathrate due to its heating to a higher temperature manifested itself not only by prolongation of the retention times of aromates but also, to a certain degree, by their irreversible adsorption (Fig. 7).

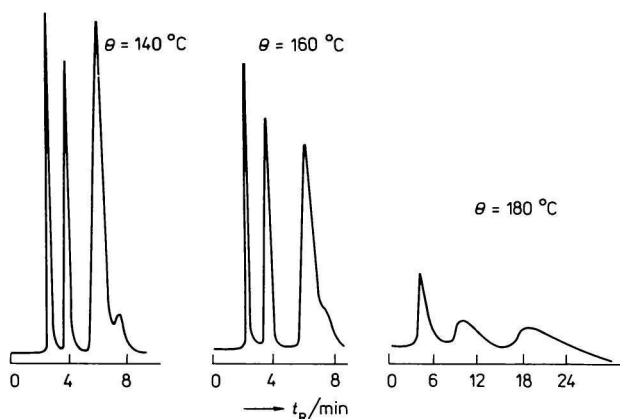


Fig. 7. Chromatograms of a mixture of aromatic hydrocarbons obtained on a clathrate modified by 1,4-dioxan after its preceding heating to the stated temperatures. Temperature of column 80 °C.

The increased accessibility of the space in the structure of clathrate still more became effective with respect to oxygenous substances. Provided this clathrate was heated to 180 °C, alcohols were sorbed irreversibly. This irreversible sorption was also observed for ketones and esters. The chromatograms of acetates after preceding heating to 140 °C, 160 °C, and 180 °C and at the column temperature of 80 °C are represented in Fig. 8.

A heating of the clathrate modified by pyridine produced an opposite change in retention of hydrocarbons. After liberation of enclathrated water and, in particular, ligand pyridine, the surface area of clathrate decreased, which manifested itself by a reduction of retention volumes of hydrocarbons. The break-down of the crystal

structure of clathrate resulted in the fact that its sorption ability decreased to the minimum. The behaviour of the clathrates modified by n-pentane and methanol was analogous.

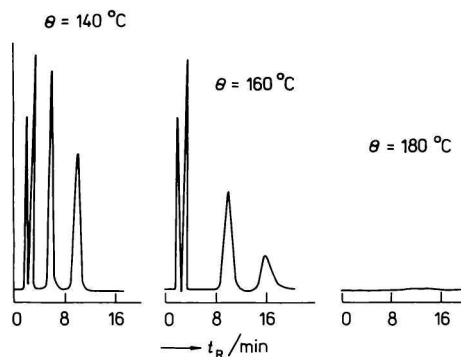


Fig. 8. Chromatograms of a mixture of acetates obtained on a clathrate modified by 1,4-dioxan after its preceding heating to the stated temperatures. Temperature of column 80 °C.

Conclusion

The clathrates modified by dioxan may be profitably used for analysis of unknown mixtures if we want to find out whether some oxygenous substances are present in the sample. The procedure is as follows: First of all, the sample is subjected to chromatographic analysis at a temperature which does not exceed 160 °C. Then the column is heated to 220 °C and after a short time of heating, it is cooled to original temperature. The sample is injected into the chromatograph under equal conditions as before and the obtained chromatograms are compared with each other. If oxygenous substances were present in the sample, the corresponding peaks must be missing in the second chromatogram.

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