

The Properties of Tetracyanocomplexes After Contact with Ethyl Alcohol

VIERA SZMERĚKOVÁ

Department of Physical and Analytical Chemistry, Faculty of Sciences, P. J. Šafarik's University, Moyzesova 11, 041 54 Košice, Czechoslovakia

and

ANNA SOPKOVÁ*

Department of Inorganic Chemistry, Faculty of Sciences, P. J. Šafarik's University, Moyzesova 11, 041 54 Košice, Czechoslovakia

(Received: 25 September 1986; in final form: 17 March 1987)

Abstract. The clathrates $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_6\text{H}_6$ (**1**) and $\text{Cd}(\text{en})\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_6\text{H}_6$ (**2**) have been studied as separative materials for the separation of mixtures of alkanes, of benzene and its derivatives, and of the chloroderivatives of methane and pyridine.

By identifying the chromatographically active solid form we could observe on the basis of the IR spectra and the thermal analysis that the ethylalcohol after contact with clathrate (**1**) substituted one mole of benzene. Clathrate (**2**) was not affected by the action of ethylalcohol. The facts agree with the interactions existing between the tetracyanocomplexes and the sorbates.

Key words. Tetracyanonickelate clathrates, gel permeation chromatography.

1. Introduction

In the last few years the possibilities of using new types of stationary phases based on clathrate compounds have been studied. Some of them have already been used as stationary phases in gas and liquid chromatography. In previous studies we succeeded in the separation of aromatic compounds, and of aniline and its derivatives by the use of the $\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 0.14 \text{C}_6\text{H}_6$ and $\text{Zn}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 0.14 \text{C}_6\text{H}_6$ compounds as stationary phases [1]. The clathrates were deposited (10% w/w) onto silanized Chromaton such that they served as the stationary phases in gas chromatography. In references [2–5] *n*-alkanes and aliphatic alcohols were separated. We found that if the clathrates lost all their guest component (e.g. by heating to temperatures where the loss of the guest component was complete) then the sorptive capabilities of the appropriate clathrate were also lost. In other cases after their recovery from auxiliary solvents, the tetracyanocomplexes exhibited good separative capabilities when used as stationary phases [6]. The most striking properties were achieved in the case of the clathrate $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n \text{H}_2\text{O}$ after such modification (recovery) with pyridine or with 1,4-dioxane, when a very good separation of oxygen containing compounds was achieved [7].

* Author for correspondence.

Bhattacharayya *et al.* [8, 9] separated aromatic and aliphatic compounds by filling the Werner type clathrates (Fe, Co) Ni (NCS)₂(4-Mepy)₄ into CG columns.

The best results in liquid chromatography with stationary phases represented by clathrates were achieved in the Polish school, led by W. Kemula, D. Sybilska and J. Lipkowski. They separated different derivatives of nitrotoluene [10], methyl-naphthalenes [11], nitronaphthalene [12] and some isomers [13–15] using columns filled with Ni(4-Mepy)₄(NCS)₂0.7(4-Mepy) and Co(4-Mepy)₄(NCS)₂0.8(4-Mepy).

The aim of the present study is to examine the possibilities of using clathrates of tetracyanocomplexes as separative materials in gel permeation chromatography, where the lattice of the clathrate could serve as the gel and the dimensions of the lattice could allow only some molecules to enter into the clathrate.

2. Experimental

2.1. INSTRUMENTATION

A liquid chromatograph (Knauer, Germany) with a high pressure pump, high pressure sample valve, refractometer (RI), UV detector ($\lambda = 254$ nm), double line recorder (Kutész, Hungary) and a drop counter (Lab. přístroje, Prague) was used. Other instrumentation used were Universal Polarograph OH-105 (Radelkis, Hungary), IR spectrometer Specord 75 (Carl Zeiss Jena, GDR) and Derivatograph (Paulik-Paulik, Erdey, MOM Budapest, Hungary).

2.2. MATERIALS

The tetracyanonickelate clathrates



were prepared in our Department [4, 5].

Other chemicals used were: ethyl alcohol – 96% (Lachema, Brno) as eluent; the samples of dichloromethane, trichloromethane, tetrachloromethane, benzene, toluene, xylene (Lachema Brno), pyridine (Banbury Exon), hexane (Reachim USSR), octane (Lachema Brno), decane and undecane (Fluka Switzerland).

The tetracyanonickelate clathrate (1) was filled in a column of dimensions 300 × 8 mm, and the compound (2) in a longer column (600 × 8 mm). Both the columns and the capillaries were made of stainless steel.

2.3. IDENTIFICATION

The original samples of clathrates were studied by thermal analysis (Figures 1 and 2) and by measuring their IR spectra (Figures 3 and 4) before their modification.

The tetracyanonickelates were used in a microcrystalline powder form after screening on sieves. The columns were then separately filled with both samples (1) and (2) after a 24 hours long contact with ethyl alcohol. Only in this manner were they used as fillings in the chromatographic system.

After their use and after the elution with about 1000 ml of ethyl alcohol the samples of the eluates were tested for the presence of NH₃, Cd²⁺, Ni²⁺ and CN⁻ ions.

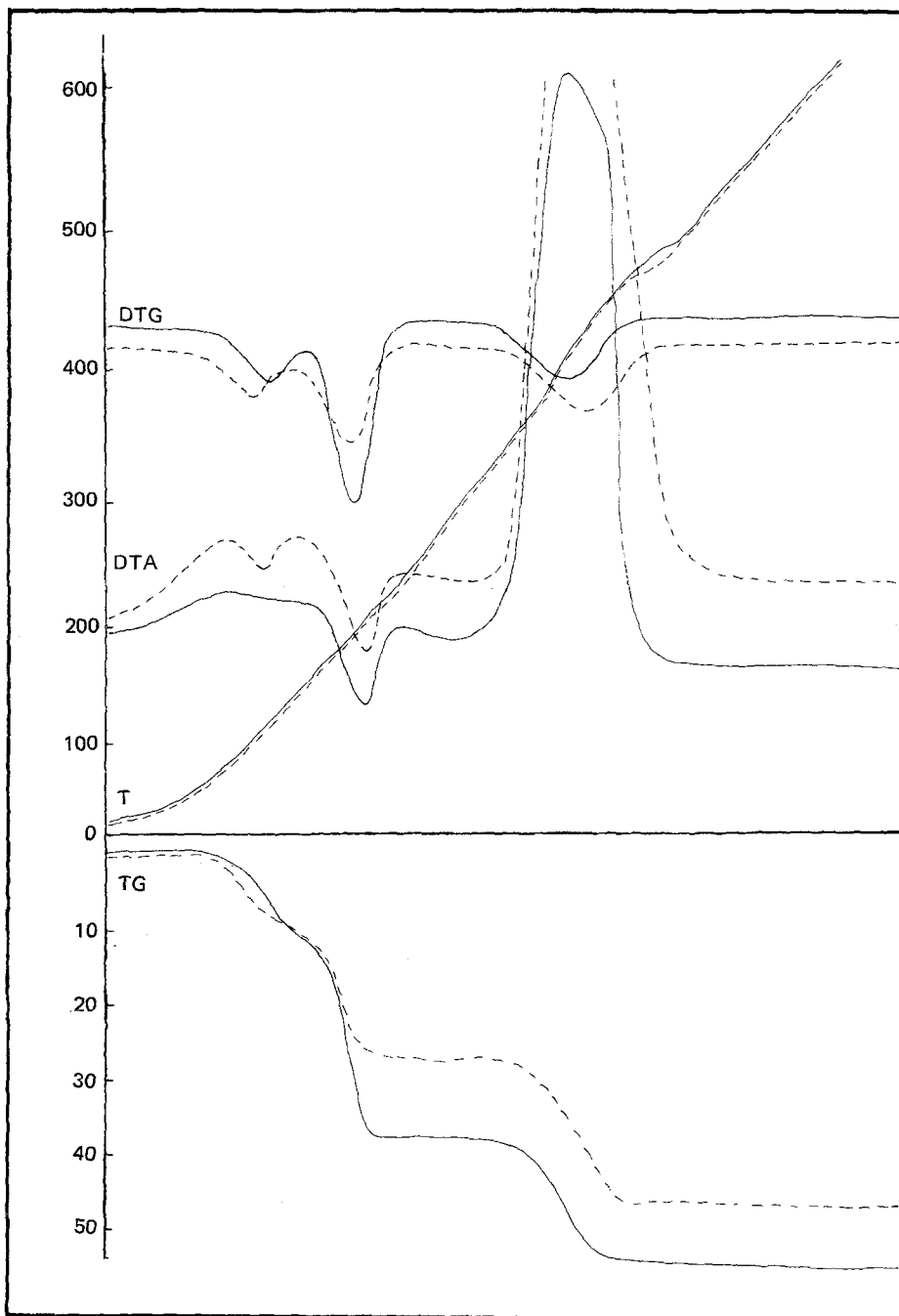


Fig. 1. The thermogravimetric curves of the compound $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (I) in the original form (—) and after contact with ethyl alcohol (-----).

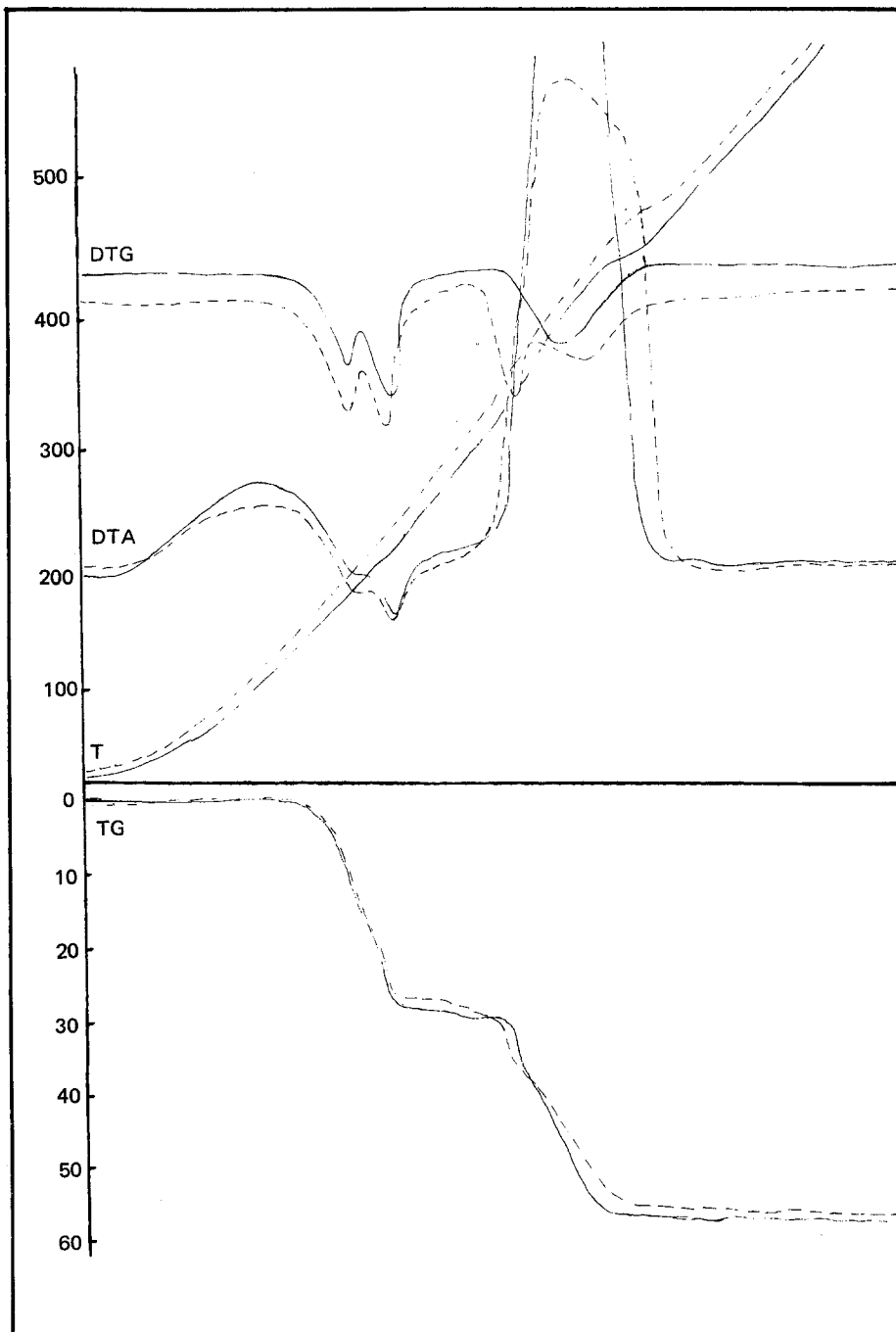


Fig. 2. The thermogravimetric curves of the compound $\text{Cd(en)Ni(CN)}_4 \cdot 2 \text{C}_6\text{H}_6$ (2) in the original form (—) and after contact with ethyl alcohol (-----).

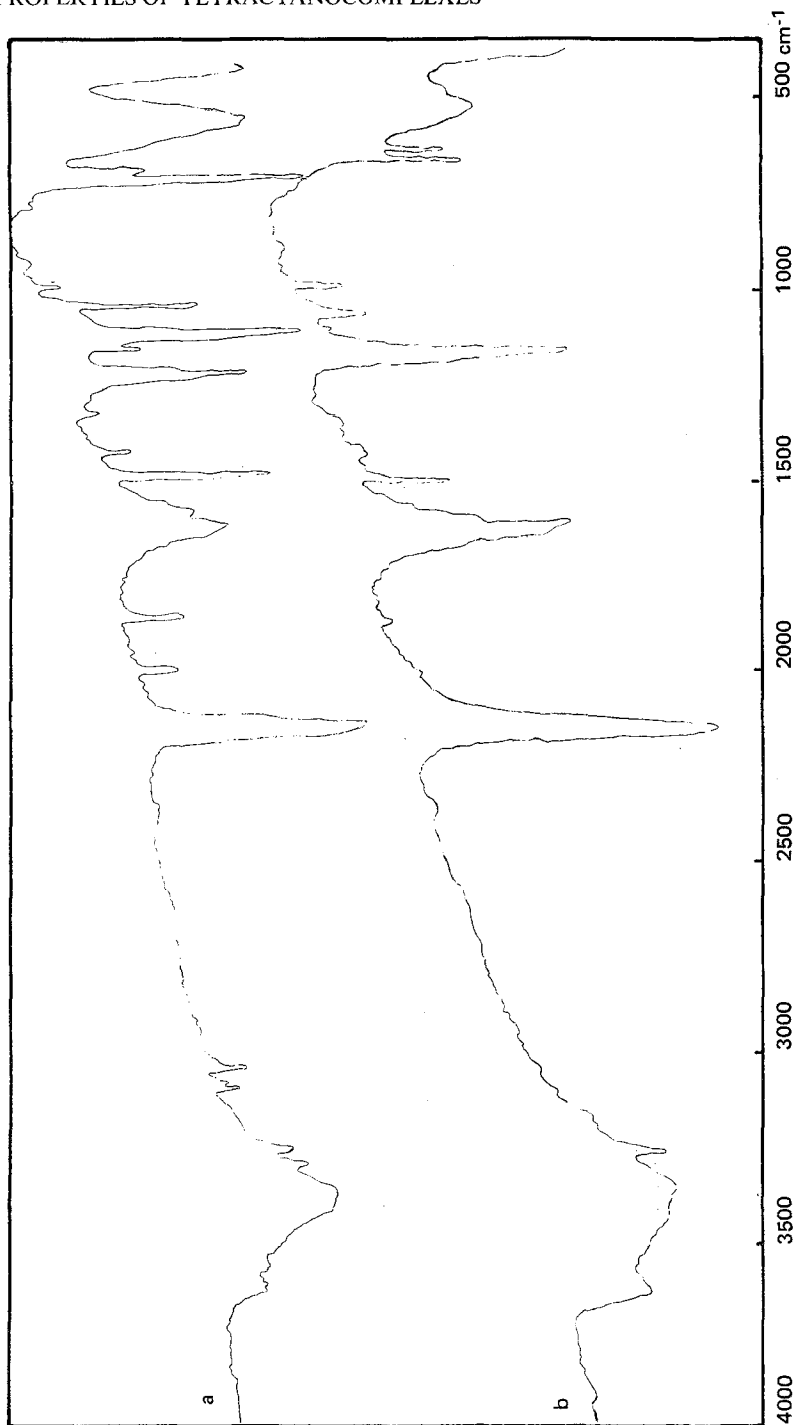


Fig. 3. The IR spectra of the compound $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_6\text{H}_6$ (1) in the original form (a) and after contact with ethyl alcohol (b).

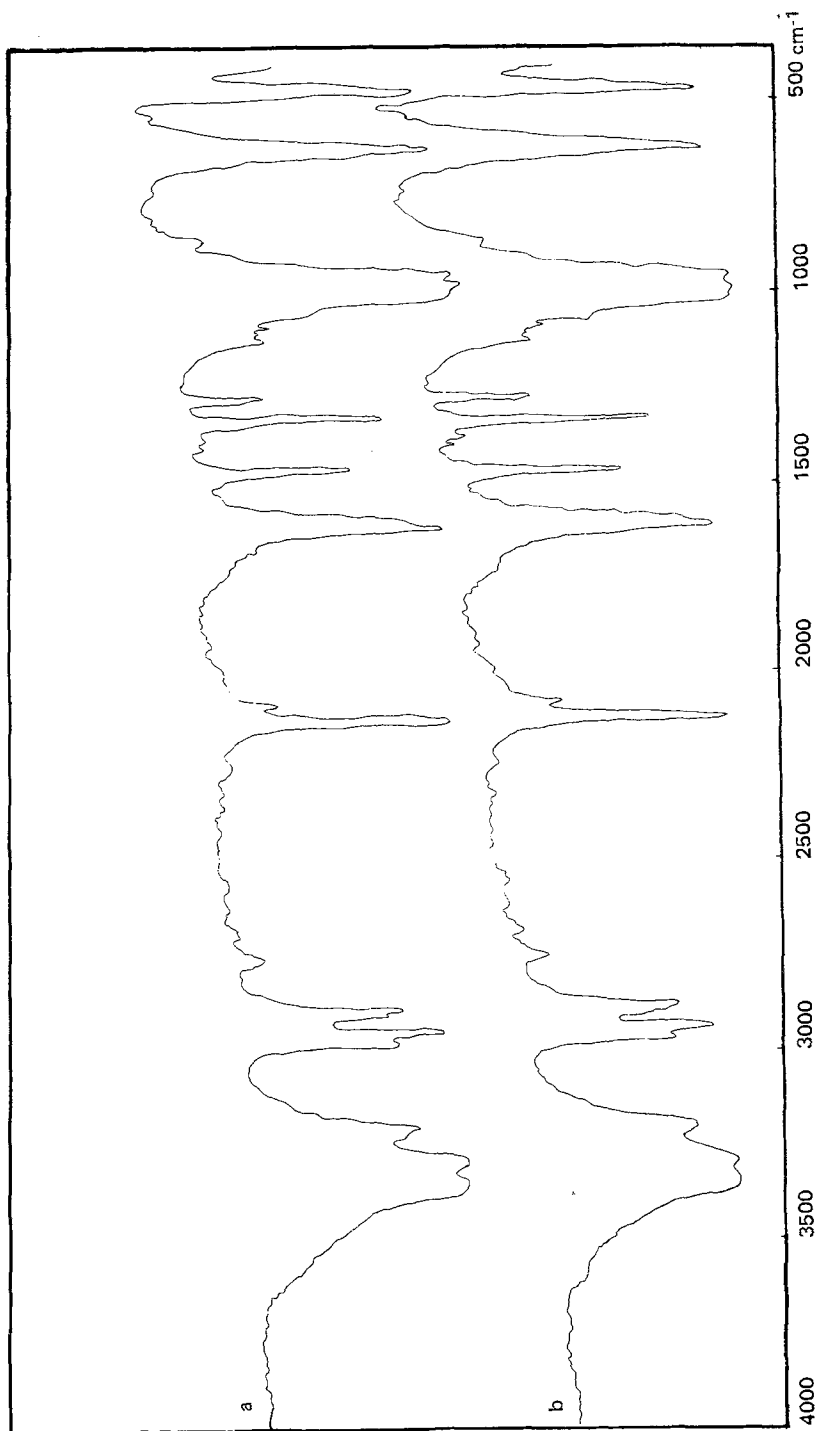


Fig. 4. The IR spectra of the compound $\text{Cd(en)Ni(CN)}_4 \cdot 2 \text{C}_6\text{H}_6$ (2) in the original form (a) and after contact with ethyl alcohol (b).

Using the classical methods of the chemical analysis (the dimethylglyoxime test for Ni^{2+} , the ammonium sulphide test for Cd^{2+} , Nessler's reagent for NH_3 and the AgNO_3 reaction for the CN^- ion) we could detect some dissolution of the clathrates (according to the presence of the above indicated ions and groups).

Using pulse polarography we controlled the presence of Cd^{2+} and Ni^{2+} ions in the solutions. Nickel could not be estimated by this method, but we found cadmium present in the eluates of both tested samples in the concentration of $5.7 \cdot 10^{-5}$ mol/dm³. This value shows a slight dissolution and liberation of the cadmium present as the cation in the host component lattice after the reaction with ethyl alcohol.

Before the use of the column in the chromatographic experiments (but after a 24 hour-long interaction of both samples with ethylalcohol and after its evaporation) the compounds were again examined by thermogravimetric and IR spectral measurements.

3. Results and Discussion

3.1. IR SPECTRA

The IR spectra and the thermal analysis curves (Figs. 2 and 4) indicated no change had occurred with $\text{Cd(en)Ni(CN)}_4 \cdot 2 \text{C}_6\text{H}_6$ (**2**) during contact with ethyl alcohol.

However the IR spectra of $\text{Cd(NH}_3)_2\text{Ni(CN)}_4 \cdot 2 \text{C}_6\text{H}_6$ (Fig. 3) indicated that some changes had occurred during contact with ethyl alcohol.

The absorption intensities of the bands due to the C—H bonds of the benzene (at 1980, 1840, 1480, 1030 and 705 cm⁻¹) decreased and some weak bands of the benzene (at 3085 and 3030 cm⁻¹) are lost (Fig. 3b) after the interaction with ethyl alcohol. The intensity of the band due to the O—H bond (3620 cm⁻¹) increased after contact with $\text{C}_2\text{H}_5\text{OH}$. Equally, after contact with $\text{C}_2\text{H}_5\text{OH}$, the intensities of bands due to N—H (3340, 3250, 1600, 1200 cm⁻¹) are stronger. The bands at 3340 and 3250 cm⁻¹ are also broadened and shifted in the direction of the O—H bands. The intensity of the band for the metal—nitrogen bond (at 570 cm⁻¹) is decreased.

The decrease in the intensity of the benzene bands and the higher intensities of the band for the O—H bond after contact of clathrate (**1**) with ethylalcohol can be explained by the inclusion of the alcohol in the host instead of the benzene guest species and to some extent by ethyl alcohol substituting only partly the benzene guest. The inclusion of the ethyl alcohol (as a polar species) in many kinds of host components is often used in the literature [16] for the separation of alcohols from some wastes.

In this connection we have to add that in a previous study [17] the tetracyanocomplexes were recovered from methylalcohol as an auxiliary solvent. In the case of $\text{Cd(en)Pd(CN)}_4 \cdot 2 \text{C}_6\text{H}_6$ we could find a small change of the absorption intensity in the 1000 and 700 cm⁻¹ region of the IR spectrum [18, 19]. The presence of two guests (the polar methanol and benzene) could be deduced, since both benzene and methylalcohol bands could be seen.

In the present study we can explain the stronger intensities of the bands assigned to the N—H bonds and the weaker bands of the M—N bond as a strong interaction of the alcohol, most likely with the nitrogen of these bonds – and mainly because of the stronger polarity of the ethyl alcohol molecule compared to benzene.

3.2. THERMAL ANALYSIS

The quantitative evaluation of the derivatograms of clathrate (1) after its contact with ethylalcohol (Fig. 1a and 1b) supports the conclusion reached from the IR spectrum about the partial replacement of benzene by ethyl alcohol. The first step of the thermal degradation (up to 150 °C) corresponds to a weight loss of 11% in the clathrate; this agrees with the theoretical value for the loss of the ethyl alcohol in the compound of stoichiometry $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \text{C}_6\text{H}_6 \cdot \text{C}_2\text{H}_5\text{OH}$ (1a).

The second step of the thermal degradation (up to 200 °C) corresponds to a 17% weight loss (1 mole of benzene theoretically equals 18%).

The product has two kinds of guests G_1 and G_2 applying the following stoichiometry in its formula: $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot a \text{C}_6\text{H}_6 \cdot b \text{C}_2\text{H}_5\text{OH}$ (1a). The sum ($a + b$) is governed by the spatial disposition of the host structure in the Hofmann type clathrate.

3.3. SEPARATIVE ABILITIES

With the aim of studying this kind of property of the tetracyanocomplex, we injected into the columns filled with the clathrate $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_6\text{H}_6$ (1) the liquid mixtures of organic compounds. The mixture of benzene and its derivatives, the chloroderivatives of methane and pyridine were not evidently separated. The differences in the elution columns of these samples were statistically not significant. They were eluted from the columns at their external volume ($V_0 = 8$ ml), one is therefore tempted to think that the samples were not able to pull out from the lattice of the clathrate the included benzene or ethyl alcohol respectively. This shows a rather

Table I. Chromatographic parameters obtained in the present study using $\text{Cd}(\text{en})\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_6\text{H}_6$ eluted with ethanol

Sample	V_e (cm^3)	k_1	V_e (cm^3)	k_2	R
C_{11} alkane + benzene	19.8	1.48	10.8	0.35	0.74
C_{11} alkane + toluene	19.8	1.48	11.0	0.38	0.71
C_{11} alkane + xylene	19.8	1.48	10.4	0.30	0.78
C_{11} alkane + pyridine	19.8	1.48	11.7	0.46	0.61
C_8 alkane + benzene	18.0	1.25	10.8	0.35	0.62
C_8 alkane + toluene	18.0	1.25	11.0	0.38	0.60
C_8 alkane + xylene	18.0	1.25	10.4	0.30	0.67
C_8 alkane + pyridine	18.0	1.25	11.7	0.46	0.53
C_6 alkane + benzene	14.8	0.85	10.8	0.35	0.39
C_6 alkane + toluene	14.8	0.85	11.0	0.38	0.37
C_6 alkane + xylene	14.8	0.85	10.4	0.30	0.44
C_6 alkane + C_{11} alkane	14.8	0.85	19.8	1.48	0.36

Note: The following relations are used:

$$k = \frac{V_e - V_0}{V_0} \quad R = \frac{k_2 - k_1}{k_2 + k_1 + 2} \cdot \frac{\sqrt{n}}{2}$$

$$n = 16 \left(\frac{V_e}{w} \right)^2$$

w = width of the peak.

strong interaction existing between the molecules of benzene, or ethyl alcohol and the individual groups or ions of the host. In contrast the results of the gas chromatographic experiments [6, 7], gained with the same clathrate after modification with different auxiliary solvents, showed some increase of the active sites in the clathrate.

The clathrate $\text{Cd(en)Ni(CN)}_4 \cdot 2 \text{C}_6\text{H}_6$ (**2**) containing the ethylenediamine ligand instead of the ammonia ligands in the Hofmann type clathrates [2, 4] is thermally more stable than clathrate (**1**), as can be seen from Figures 1 and 2. This fact contributes to some degree to the inertness of clathrate (**2**) against the interaction with a polar compound. Thus the ethyl alcohol could not occupy the sites in the host of

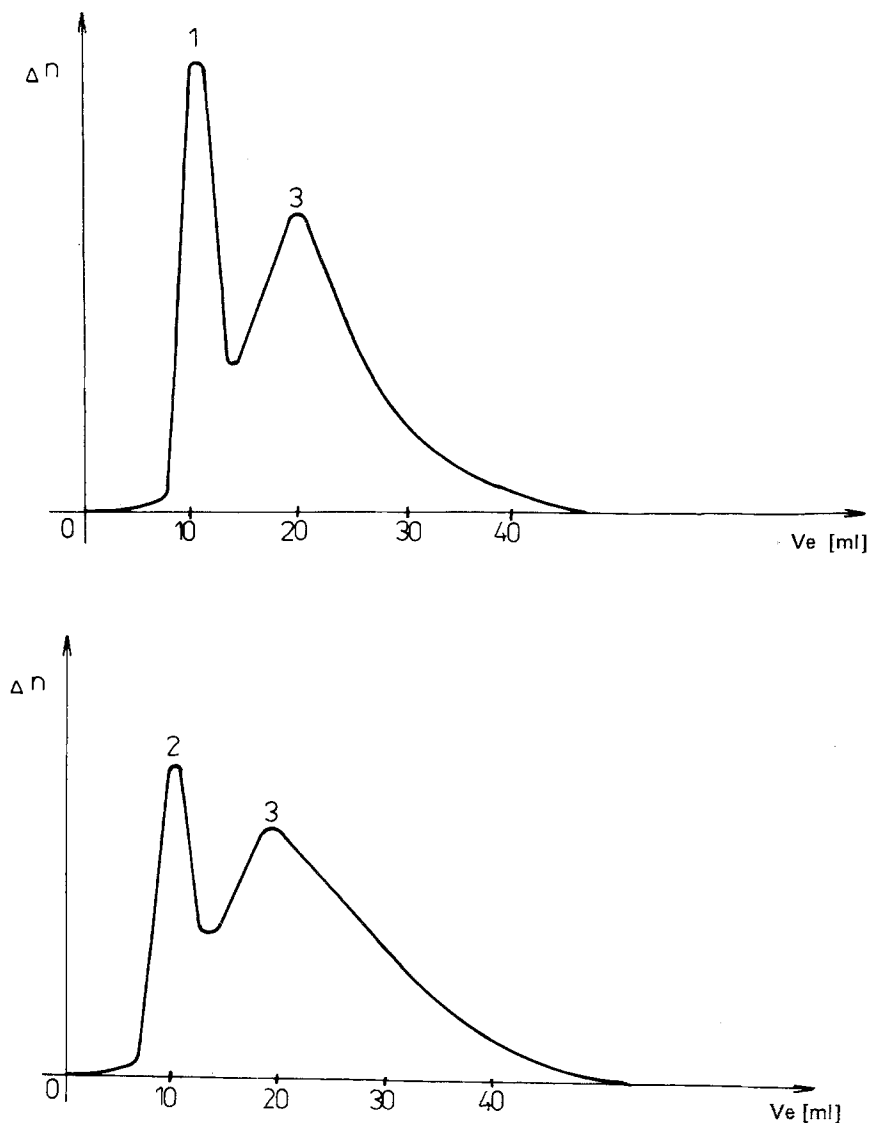


Fig. 5. $\text{Cd(en)Ni(CN)}_4 \cdot 2 \text{C}_6\text{H}_6$ (**2**) as a stationary phase in LC. Samples (1 - toluene, 2 - benzene, 3 - C_{11} alkane) eluted with ethyl alcohol.

the clathrate, which serve to retain the injected sample. In agreement with this hypothesis some separative abilities of compound (2) could be observed, as summarized in Table I. From the data one can state that the sorption in the column increased with the chain length in the alkanes. The differences of the elution volumes decreased with increasing number of atoms in the chain.

We could separate the alkanes from the pyridine, the chloroderivatives from methane, benzene and its derivatives, with the column packed with clathrate (2). (Figure 5).

From the identification and from the preliminary separative properties of clathrates (1) and (2) we can propose the following. The inability of clathrate (1) to separate the alkanes, and benzene and its derivatives after elution with ethyl alcohol is affected by the stronger interaction of the polar ethyl alcohol as guest with the NH_3 groups in the host and by the interaction of the less polar samples with the NH_3 groups.

In contrast the ethylenediammine ligand present in clathrate (2) being less polar prefers the interaction with less polar samples.

Thus one can expect that the tested material as a stationary phase in liquid chromatography could utilize the competitive exchange of the guest component present in the host lattice and equally the interactions between some component of the used systems.

References

1. M. Šingliar and A. Sopková: *Proc. Intern. Microsymp. Clathrate and Molecular Inclusion Compounds*, Stará Lesná, p. 223 (1981).
2. A. Sopková: *J. Mol. Struct.* **75**, 81 (1981).
3. A. Sopková, M. Šingliar, J. Bubanec, T. Görnerová and P. Králik: *Czech. Patent*, 222 610 (9 March 1983).
4. A. Sopková, M. Šingliar, J. Chomič, J. Skoršepa and E. Matejčíková: *Czech. Patent* 186 492 (7 July 1978).
5. M. Šingliar, A. Sopková, J. Chomič, J. Skoršepa, and E. Matejčíková: *Czech. Patent* 185 986 (6 June 1978).
6. A. Sopková, M. Šingliar, J. Skoršepa, J. Matanin, and E. Terpáková: *J. Incl. Phenom.* **3**, 297 (1985).
7. M. Šingliar, A. Sopková and J. Matanin: *Petrochémiá* **24**, 153 (1984).
8. A. C. Bhattacharyya: *J. Chromatogr.* **41**, 446 (1969).
9. A. C. Bhattacharyya and A. Bhattacharjee: *Anal. Chem.* **41**, 2055 (1969).
10. W. Kemula, A. Kwiecińska, and D. Sybilska: *Proc. III. Czechoslovakia - Poland Symposium on Petro- and Carbochemistry*, Nováky, ICHO Warsaw, pp. 95-103 (1967).
11. D. Sybilska: *Proc. VI. Intern. Symposium on Chromatography and Electrophoresis*, Presses Académiques Européennes, Brussels, pp. 212-221 (1971).
12. W. Kemula, A. Kurjan, and A. Kwiecińska: *Chem. Anal. (Warsaw)* **12**, 869 (1967).
13. W. Kemula, Z. Borowska, and D. Sybilska: *Monatsh. Chem.* **103**, 860 (1972).
14. W. Kemula, D. Sybilska, and K. Chlebicka: *Roczniki Chem.* **39**, 1499 (1965).
15. J. Lipkowski, K. Suwinska, J. Hatt, A. Zielenkiewicz, and W. Zielenkiewicz: *J. Incl. Phenom.* **2**, 317 (1984).
16. K. Tanaka, F. Toda, and T. C.W. Mak: *J. Incl. Phenom.* **2**, 99 (1984).
17. A. Sopková, and P. Králik: *Proc. Intern. Microsymp. Clathrate and Molecular Inclusion Compounds*, Stará Lesná, p. 87 (1981).
18. A. Sopková and M. Šingliar: *Collection Czechoslovak Chem. Commun.* **51**, 526 (1986).
19. A. Sopková, M. Šingliar, and P. Králik: *J. Incl. Phenom.* **1**, 263 (1984).