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FORMATION OF CLATHRATE COMPOUNDS OF THE $Ni(NCS)_2$(4-METHYLPYRIDINE)$_4$ COMPLEX WITH METHYLNAPHTHALENES AND ITS APPLICATION TO LIQUID CHROMATOGRAPHY

JANUSZ LIPKOWSKI, KAROL LEŚNIAK, ANDRZEJ BYLINA, DANUTA SYBILSKA and KAZIMIERA DUSZCZYK

Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw (Poland)

SUMMARY

The conditions for the separation of mixtures of monomethylnaphthalenes (MeN) and naphthalene (N) were examined.

The clathrate of formula $[Ni(NCS)_2(4\text{-methylpyridine})_4] \cdot 0.7(4\text{-methylpyridine}) \cdot 0.4$(aqueous methanol) formed the stationary phase. The mobile phase was a solution which consisted of 0.43 *M* 4-methylpyridine and 0.40 *M* ammonium thiocyanate dissolved in 65% (v/v) aqueous methanol.

It was established that the monoclinic $P2_1/c$ non-clathrate forming α-modification of the complex is chromatographically inactive. Only the presence of the tetragonal clathrate of the β-form, $I4_1/a$, determines the chromatographic activity of the sorbent, and this takes place for low ranges of concentration of the analyzed compounds ($\leqslant 0.1$ *M*). Increasing the concentration of the examined MeNs ($\geqslant 0.1$ *M*) leads to the formation of the triclinic γ-form, which contains 1.3–2.0 moles of the MeN per mole of the complex. The conditions for utilizing the crystallization of these compounds for the efficient separation (with an enrichment coefficient $\geqslant 5$) of 1-MeN from mixtures with 2-MeN are suggested.

INTRODUCTION

Various methods have been used in the analysis of mixtures of methylnaphthalenes, *e.g.*, gas[1], liquid[2] and thin-layer chromatography[3] and spectrophotometry[4,5].

The use of the clathration of the molecules of various organic compounds ("guests") by some transition metal complexes of the Werner type ("hosts") for the separation of mixtures of isomers was first investigated by Schaeffer *et al.*[6] and was later utilized for many excellent separations on both the preparative and industrial scale[7]. Kemula and Sybilska[8] applied the clathrates formed from the complex compound $Ni(NCS)_2(4\text{-MePy})_4$* in the analytical liquid chromatography of mixtures of various types of compounds, mainly isomers. It was shown in later work that methylnaphthalenes can also be separated in the same way[9,10].

* MePy = methylpyridine.

In this work, we have found conditions for the chromatographic separation of mixtures of 1-methylnaphthalenes (1-MeN), 2-methylnaphthalenes (2-MeN) and naphthalene (N) on columns filled with clathrates. The clathrate formed by the complex compound $Ni(NCS)_2(4\text{-MePy})_4$, used as the column material, was submitted to physico-chemical investigations, including X-ray analysis. New intermolecular compounds of this complex compound with the methylnaphthalenes were also obtained.

The conditions for the formation of the above intermolecular compounds and the applicability of these reactions to liquid chromatography was the basic aim of this work.

EXPERIMENTAL

Reagents

The reagents and all solvents were of chemical purity grade; the 4-MePy contained 0.6% of 3-MePy.

Apparatus

The detection system consisted of a hydrogen lamp as the light source, a monochromator, a photomultiplier and a recorder. It provides a continuous single beam for the detection of the effluent at 278 nm. This wavelength was dictated by the UV cut-off of the 4-MePy that is present in the mobile phase. The photometric error was within $\pm$ 1% transmittance.

Preparation of the sorbent

The clathrate sorbent was prepared according to the procedure described previously[11], and 0.43 *M* 4-MePy and 0.4 *M* ammonium thiocyanate in 65% (v/v) aqueous methanol was used as the basic solution.

The stationary phase (0.35 or 0.15 g) of the clathrate compound was equilibrated before use for 3 days with the basic solution (50 ml). The solid phase, after separation from this mixture, was used for the preparation of the column, while the filtrate served as the mobile phase. The investigated samples were dissolved in the basic solution at concentrations $\leqslant 5 \cdot 10^{-2}$ *M*.

The flow-rate of the mobile phase was 8–16 ml/h, and in a particular experiment it was kept constant.

All determinations were carried out at a temperature of 20 $\pm$ 1°.

Analytical determinations

The procedure for the chemical and structural analysis of the substances used has been published recently[12].

The fine crystalline samples of the clathrate sorbents were analysed in the mother liquor in order to avoid the risk of changes in the crystals due to washing and drying. The error in the determination of the amount of the guest in the clathrate depends on the molecular weight of the guest and the extent of filling in the clathrate. For the typical sorbents used, the relative error in the determination of the clathrated 4-MePy was 0.1 and of the clathrated solvent (methanol–water) 0.2.

RESULTS

Chromatographic separation

The chromatographic separations were carried out using the clathrate whose analysis is described below. In Figs. 1 and 2 are shown the elution curves of the mixtures of 1-MeN, 2-MeN and N. These curves were recorded under the conditions that were found to be the most suitable. The low solubility of the $Ni(NCS)_2(4\text{-}MePy)_4$ complex in methanol and aqueous methanol solutions, and the spectral properties of methanol, led us to choose this solvent as the component of the mobile phase. The change in the methanol concentration in the mobile phase does not influence the retention of 1-MeN ($K = 0$) but we can observe a change in the retentions of 2-MeN and N. When the concentration of methanol in the mobile phase increases, the resolution constant of 2-MeN and N decreases. For concentrations $\leqslant 65\%$ (v/v) of methanol in the mobile phase, the retention volumes of 2-MeN and N increase. Concentrations of 4-MePy of 0.43 *M* and of ammonium thiocyanate of 0.4 *M* were found to be optimal, because of the stability of the sorbent, the retention of 2-MeN and N, and the conditions for the spectrophotometric detection. The recorded peaks are well shaped and symmetrical, which permits a good quantitative analysis.

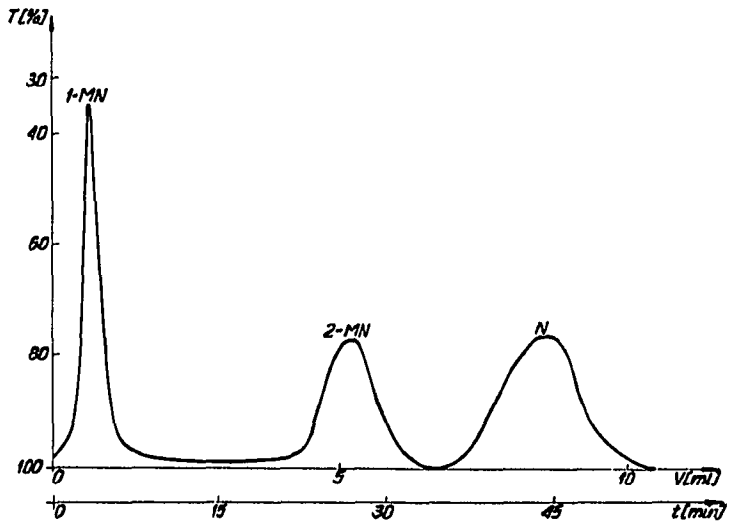

Fig. 1. Elution curve for the mixture of 1-MeN, 2-MeN and N. Column, 30 mm × 6 mm I.D.; amount of packing, 350 mg; amount of sample injected, 50 μl of a solution of concentration 0.05 *M*; elution rate, 16.0 ml/h.

The fact that the separation of a mixture of 1- and 2-MeNs can be achieved on a column of height 15 mm and I.D. 6 mm, prepared from 150 mg of the clathrate, shows that the clathrate column has a high resolving power with respect to these compounds.

X-ray and chemical analysis

From the results of the analysis, the formula of the clathrate used as the chromatographic column packing is $Ni(NCS)_2(4\text{-}MePy)_4 \cdot y(4\text{-}MePy) \cdot x(\text{solvent})$, where

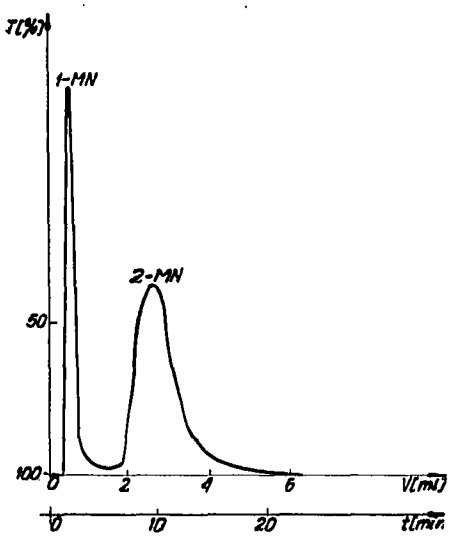

Fig. 2. Elution curve for the mixture of 1-MeN and 2-MeN. Column, 15 mm × 6 mm I.D.; amount of packing, 150 mg; amount of sample injected, 30 μl of a solution of concentration 0.02 M; elution rate, 16.0 ml/h.

$y = 0.7–0.8$ and $x \approx 0.4$. The "solvent" refers to methanol and/or water. The average particle size was 0.1–10 μ. The X-ray powder diagrams of this compound agree well with the $I4_1/a$ symmetry found by Hart and Smith[13] for similar β-clathrates. The lattice parameters of the clathrate sorbents depend upon their quantitative composition[14], which is affected by the composition of the liquid phase. For example, a variation of 4-MePy concentration in the liquid phase from 1% to 6% involves a continuous variation of the β-structure lattice parameters (at 25°) from $a = 16.97$ to 17.04 Å and $c = 22.92$ to 23.19 Å, respectively. The error in the determination of the lattice parameters at 25 ± 0.1° was 0.01 Å for the constant a, and 0.03 Å for the constant c.

The non-clathrate, monoclinic $P2_1/c$ α-form of the $Ni(NCS)_2(4\text{-MePy})_4$ complex is not chromatographically active with respect to the isomers, and is not stable in the solutions used as the liquid phase because under these conditions the α-form recrystallizes and the β-clathrate is formed. The liquid phase composition therefore seems to be of great importance in clathrate chromatography because it determines the properties of the stationary phase.

If the concentration of MeN in the solution exceeds 0.1 M, then compounds different from the β-form intermolecular compound of MeN and the $Ni(NCS)_2(4\text{-MePy})_4$ complex are formed (this was suggested earlier by Borkowska[15]). They contain 1.3–2.0 moles of MeN per mole of the host complex. These compounds are triclinic and, although they are similarly named γ-compounds after Casellato and Casu[16], the particular compounds of this group are different from each other with respect to their structure and colour.

The results of the static experiments show that 2-MeN may enter the β-structure of the clathrate as an admixture to the principal guest compound (4-MePy), but in concentrations not greater than 2–3% (in moles per mole of the host). Attempts

to increase this content in the β-clathrate by increasing the 2-MeN concentration in the mother solution result in the formation of the γ-compound. We prepared the particular compounds in a macrocrystalline form (> 0.2 cm) in order to ensure that the 2–3% admixture mentioned above does not result from surface adsorption. Analogous experiments with 1-MeN were unsuccessful; the detectable minimum content of 1-MeN in the clathrate was 0.2% (mole/mole).

The γ-compounds of 1- or 2-MeN (γ_1 and γ_2, respectively) have different solubilities in methanol, so that different concentrations of the $Ni(NCS)_2(4\text{-}MePy)_4$ complex are needed in order to precipitate these compounds. At 30°, the γ_1 form crystallizes from methanol if the concentration of the complex is not less than $3.4 \cdot 10^{-3}$ *M*, while the γ_2 form requires a concentration of the complex of $1.7 \cdot 10^{-2}$ *M* (in both instances the MeN concentration was 0.5 *M*).

From the solution containing both MeNs at a concentration of 0.5 *M* of each isomer, we obtained by crystallization the γ-compound containing 1-MeN in an amount of at least 90% of clathrated MeNs (10% was the smallest detectable content of 2-MeN in 1-MeN), and the enrichment coefficient was then $\geqslant 5$. Such a result can be obtained if the complex concentration used lies between $3.6 \cdot 10^{-3}$ and $1.4 \cdot 10^{-2}$ *M*, *i.e.* if the concentration of the complex is greater than that necessary to exceed the solubility of the γ_1 form but lower than that corresponding to the solubility of the γ_2 form.

DISCUSSION

The results of our experiments indicate that the β-form of the complex compound $Ni(NCS)_2(4\text{-}MePy)_4 \cdot 0.7(4\text{-}MePy) \cdot 0.4(aq \cdot CH_3OH)$ is responsible for the chromatographic properties of the clathrate columns.

As we found none of the α-form of the complex compound in the sorbents used, we need not consider the reaction complex-α + guest $\rightleftarrows$ clathrate-β. When the mobile phase contains 4-MePy in a high concentration in comparison with the concentration of naphthalene and its derivatives, then the stable modification is the tetragonal β-form with 4-MePy as the main guest. According to the chromatographic and preparative results, 1-MeN does not fit the cages in this structure. It also follows that, of the compounds investigated, naphthalene has the highest affinity for the β-structure.

The composition of the mobile phase is of fundamental importance in the chromatographic process for the following reasons:

(1) the 4-MePy concentration should be sufficient to ensure the stability of the chromatographically active β-form;

(2) the change of the lattice parameters of the clathrate sorbent, accompanying the change in the mobile phase, causes changes in the lattice geometry, and therefore influences the sorption properties of the clathrate.

Using these facts, we can select the most efficient system for chromatographic separations. The formation of the γ-form at concentrations greater than 0.1 *M* does not limit the chromatographic method, but one must avoid injecting into the column samples in which the concentration of the MeNs exceeds 0.1 *M*.

The results of our investigation concerning the γ-type of complex compounds lead to their practical application in the preparative separation of 1-MeN from

mixtures of methylnaphthalenes with a yield much higher than in the simple method of Schaeffer *et al.*[6].

The γ-type of complex compounds has not yet been applied in chromatography. The conditions for the stability of these compounds do not show great promise for their use in this field.

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