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STATIONARY PHASE FOR GAS CHROMATOGRAPHY V. NITRILATION PRODUCT OF HALF EQUIVALENTLY CHLORINATED TO CARBON NUMBER OF n-ALKANES SEPARATED FROM KEROSENE. (NHECAK) PHASE

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ABSTRACT

A stationary phase was prepared by nitrilation of the chlorinated n-alkanes mixture, which were already separated from kerosene by successive urea adduction, have been chlorinated in a way that chlorine reacts with one of each two carbon atoms (NHECAK phase).

Chromatographic characteristics of the phase were investigated, separation capacity and column efficiency were demonstrated. McReynolds' constants were determined.

INTRODUCTION

In its simplest terms, retention in gas-liquid chromatography is governed primarily partition of the solute between a stationary liquid phase and mobile gas phases that is, solubility of the solute in the stationary phase. Since for solubility exact mathematical paths haven't yet found out, approach is general. In its general term "Similis Simile Dissolvantur".

We have used polychlorinated kerosene as stationary phase and observed its high degree of support deactivation property. (Obalı, 1989). This led further investigation by separating components in kerosene and by chemical reactions modifying the chromatographic character.

In this article, n-alkanes which were already separated from kerosene and then later chlorinated in a way that chlorine reacts with one of each two carbon atoms, were substituted by nitrile groups. Substitution was carried out in dimethyl sulfoxide as shown by Smiley and Arnold (1960). This nitrilated alkyl polychlorides were contained methylene groups, in the molecule because of lesser amount of chlorine substitution to carbon chain, Liquid phase with this structure gained

multidimensional character. To evaluate the chromatographic capacity of the phase McReynolds' constants were found and different functional grouped compounds were separated.

EXPERIMENTAL

Unless otherwise stated, all chemicals and solvents were general-laboratory or analytical grade. Kerosene was obtained from Orta Anadolu Rafinerisi (Kırıkkale-Ankara-Turkey) which was distilled from Kirkuk origin crudes. Specifications were B.P. range 152°–242° in which 20 % distilles in the range 152°–167°, $D_{15} = 0.7826$. Chlorine was obtained in cylinder from Koruma Tarım İlaçları A.Ş. (Dericne Kocaeli-Turkey). Chromosorb 750. A.W. Sil. Tred. 100–120 mesh was obtained from Johns-Manville İnc. (USA). Squalane was obtained from MSwil. GmbH. (Switzerland).

Infrared spectra were obtained with a Perkin Elmer Model 377 Grating Infrared Spectrophotometer Gas chromatographic work was done with a Perkin Elmer Model F11 chromatograph with temperature programmer and flame iozinzation detector connected to a Spectra Physics Autolab Minigrator in series with a 1 mv input sensitivity Perkin Elmer Model 54 linear Recorder. Chromatographic separation conditions are given in the figure captions.

n-Alkanes separated from kerosene by successive urea adduction was chlorinated as described in the previous article (Obalı, 1989) n-Alkanes mixture (Average M.W = 164.273, carbon number of hypotetic alkane is 11.5) (15 g 91.3 mmol) was chlorinated until the total weight was 34 g (5.75 chlorine atom introduced to 11.5 carbon atom). Dissolved hydrogen chloride and chlorine were removed under reduced pressure.

This chlorinated n-alkanes (15 g, 40.2 mmol) dissolved in 25 ml dimethyl sulfoxide (dried over silicagel) was added in 15 min to a rapidly stirred partially soluble mixture of sodium cyanide (13.1 g, 267.3 mmol dried at 110° overnight) in dimethyl sulfoxide (50 ml dried over silicagel) at 20°. The temperature of the mixture rose rapidly and was kept at 60 ± 5 by cooling with water when necessary for 4 hours. When the reaction was apparently completed at the end of 4 hours, reaction mixture was cooled diluted with diethyl ether (3x50 ml). The ether extract was washed with 6N hydrochloric acid (to hydrolize isocyanide that was formed) and several times with saturated sodium chloride so-

lution and dried over silicagel overnight. Main part of ether was removed by distillation under vacuum. The remained viscous liquid was poured on a watch glass and remained ether was evaporated under IR lamp. Product was brown coloured viscous liquid.

Column packing containing 7% (w/w) of nitrillated n-alkanes mixture of kerosene which was half equivalently chlorinated to carbon number. (NHECAK) on Chromosorb 750 (100–120 mesh) was prepared by using the conventional rotary evaporator technique and THF. as solvent. The air dried packing was resieved to insure proper particle size. 1/8 in, 2 m stainless steel column was cleaned by toluene, methylene chloride, acetone repeatedly dried at 120° in the oven and filled with the prepared packing, by gravity and gentle vibration by the aid of an electrical vibrator. Packed column was coiled in the appropriate shape of the instrument oven and with temperature programming conditioned overnight at 130° max.with nitrogen carrier gas flow rate 15 ml min^{-1}.

The maximum allowable temperature for the phase was established as the highest isothermal temperature at whic column could be held for 24 h without changing retention indices of McReynolds test probe series. Under constant chromatograpic condition 1 μl water was injected ten times and peak areas were determined for Hexane-Hexanol 1/1 (w/w) mixture respectively to find out any change on support stationary phase surface.

RESULTS AND DISCUSSION

Half equivalently chlorinated to carbon number of n-alkanes mixture which was separated from kerosene by four successive urea adduction, was nitril substituted with sodium cyanide in dimetil sulfoxide. The reaction mainly depends on the dryness of the reactants and solvent. The reaction was carried out according to Smiley and Arnold (1960).

IR spectra of reactant and nitrilated product are given in Figure 1. Sharp characteristic C=N stretching frequency is seen at 2260–2240 cm^{-1} while characteristic C–Cl strecthing vibrations of polychlorinated compound are appeared at low frequencies 800–700 cm^{-1}. C–H stretching vibrations of methylene groups at 2940–2840 cm^{-1} and C–H deformation vibrations of methylene groups at 1480–1440 cm^{-1} indicate the existence of unsubstituted methylene groups.

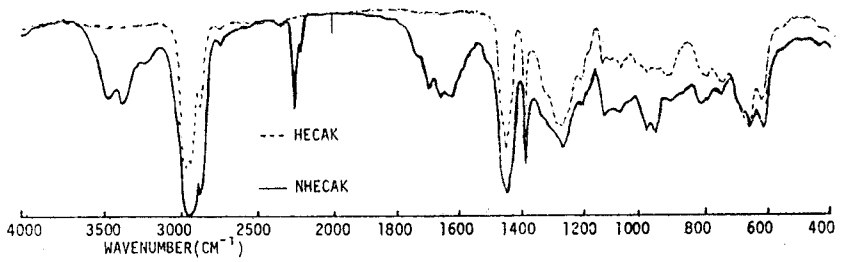

Figure 1. Infarared spectra of half equivalently chlorinated to carbon number of n-alkanes mixture which is separated from kerosene (HECAK) and nitrilated product (NHECAK), By coating on KBr pressed disc. Scan mode 5 min.

7% (w/w) NHECAK coated column has 1201 plate number per meter which is calculated for n-undecan. The test run for finding column efficiency of n-alkanes is given in Figure 2. Gas hold up times

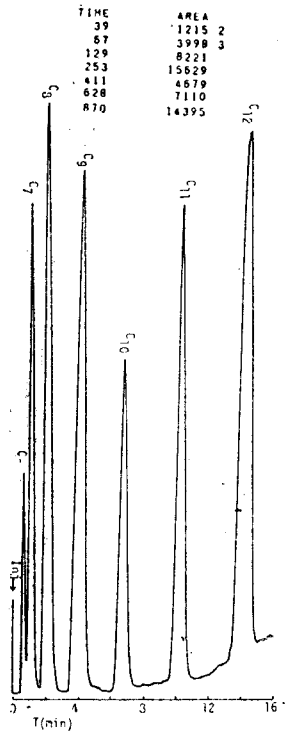

Figure 2. Test chromatogram illustrating column efficency. Test mixture C_6–C_{12} n-alkanes. Temperature program 60°–100° at 4°C min^{-1} with nitrogen carrier gas flow rate 30 ml min^{-1}.

(t_M) used in finding other retention data are calculated from three successive n-alkanes retention times by Peterson and Hirsch method. (Smith et.al. 1985).

Today to define a stationary phase McReynolds' constants (1970), the partial molar Gibbs free energy of solution for selected test probes (Golovna et.al. 1980), polarity indices (Chong et.al. 1985) and solvatochromic parameters (Brady 1984) can be used. Among these McReynolds constants still commonly are being used. For NHECAK stationary phase these constants are summarized in Table I. To make comparison constants of NPCAK (Nitrilated Polychlorine n-alkanes separated from kerosene by successive urea adduction (Obali 1989)) phase are also given. Several trends may be noted.

Table I. Summary of McReynolds' Constants Data for NHECAK and NPCAK Phases, Capacity Ratio for NHECAK Phase.

	X′	Y′	Z′	U′	S′	J
NHECAK	215	358	342	426	392	191
NPCAK	162	351	339	366	455	159
k	2.1	3.9	4.7	10.9	11.1	6.0

t_M(cal) = 23 sec.

In intermolecular interactions of NHECAK phase, higher Y′ value indicates orientation property with both proton donor and proton acceptor capabilities are important. But higher X′ and U′ values together with Y′ points out proton acceptor capability is much more effective than proton donor capability. This points out acids can be retained better than alcohols. The separation of underivatized carboxylic acids is a particulary severe test of the support deactivating properties of this phase. Under isothermal conditions some peak asymmetry is observable. Figure 3. shows the separation of carboxylic acids and Figure 4. shows the separation of pentanol isomers. Importance of orientation properties in the interactions of this phase can be seen also in the separation of aldehydes and esters. Figure 5. shows the separation of aldehydes and Figure 6. shows the separation of esters. Although McReynolds' J value which shows the separation ability of the phase to halogenated compounds, is the smallest, it is possible to separate halogenated isomers with this phase. Figure 7. shows a separation of bromobutane isomers. As it is seen from the temperature programmed separations in Figure 5 and 6. peak symetries are identical at elevated

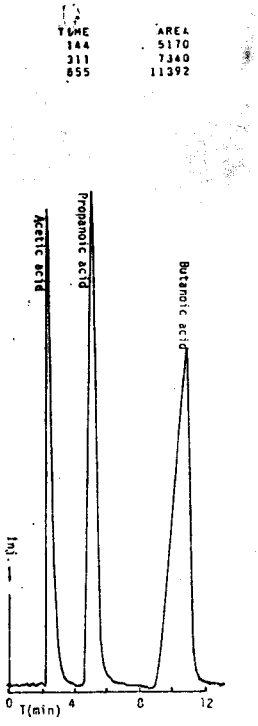

Figure 3. Separation of carboxylic acids at 89° with nitrogen carrier gas flow rate 30 ml min^{-1}.

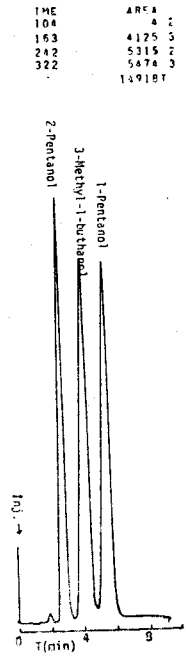

Figure 4. Separation of C_5 alcohols at 70° with nitrogen carrier gas flow rate 30 ml min^{-1}.

temperatures with the peaks at lower temperatures. This indicates strong interaction of phase, with support material. Very small changes in McReynolds' constants are observed with the repeated injection of water. This is probably because of hydrolysis of nitrile groups.

CONCLUSION

NHECAK phase is a moderately polar stationary phase, its separation properties is better than NPCAK phase and can be used in the separation of a wide variety of compounds, coating ability of the support is excellent. Chlorine atoms are seemed to take part more than NPCAK phase, in the stationary phase solute interactions. NHECAK phase is sensitive to water, so care must be taken in the separation of aquous mixtures.

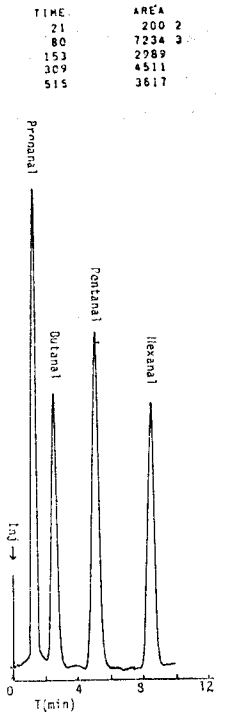

Figure 5. Separationof C_3–C_6 aldehydes, Temperature program 40°–100° at 4°C min^{-1} with nitrogen carrier gas flow rate 30 ml min^{-1}.

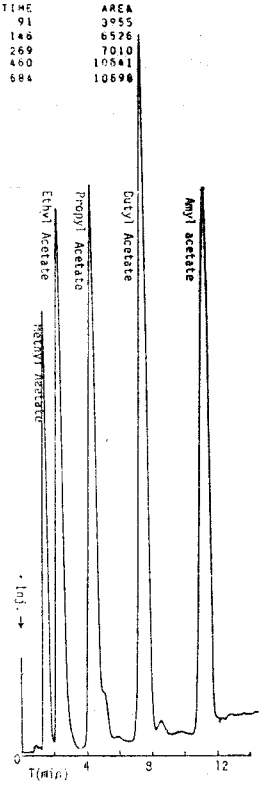

Figure 6. Separation of Alkyl acetates. Temperature program 40°–100° at 4°C min^{-1} with nitrogen carrier gas flow rate 30 ml min^{-1}.

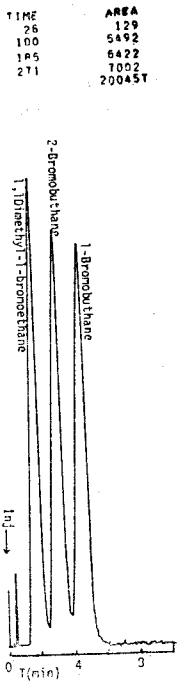

Figure 7. Sepration of bromobuthane isomers at 40°C with nitrogen carrier gas flow rate 30 ml min^{-1}.

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