A C T A U N I V E R S I T A T I S L O D Z I E N S I S
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NICKEL (II) SCHIFF BASE COMPLEXES AS STATIONARY PHASES IN GAS CHROMATOGRAPHY**

The possibility of separating some alkanes or alcohols mixture by gas chromatography in a packed columns with tetradentate Schiff base nickel (II) complexes has been studied. The effects of modification in the chelate structure on the column selectivity are presented comparing the appropriate heats of adsorption.

It is now well established that the Schiff base complexes of the number transition metal ions could be successfully employed as liquid [1, 2] or solid [3] phases for the gas chromatographic (GC) separation of a wide range of solutes. However, in these reports the nickel (II) complexes with bidentate [1, 2] or tetradentate [3] substituted salicylaldiminates were only used. In the preliminary studies [4] we noted that the neutral nickel (II) chelates of the tetradentate Schiff bases, derived from ß-diketones and appropriate diamines, could be applied as the components of intimately mixed GC stationary phases. It was reported [5] that the coordination geometry, thermal stability and volality of such chelates had many superior features than those of the previously used in GC. Therefore, in present paper, a range of nickel (II) chelates containing certain modifications to the ligand structure are being compared in terms of separation efficiency towards aliphatic hydrocarbons and alcohols. On the basis of some thermodynamic data it was interesting to investigate the distinction in such GC columns selectivity what can be applied for the optimization of the sorbents composition in GC.

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Experimental

Materials

All complexes see (Table 1) were synthetized, purified and characterized according to methods described previously [6, 7]. As the sorbates the alkanes and alcohols were used, all in analytical reagent grade.

Table 1

Schiff base nickel (II) chelates studied

No	Systematic name	Abbreviation	Mol. wt.
1	N,N'-ethylenebis(acetylacetoneimine)Ni (II)	Ni(en)AA	282.28
2	N,N'-trimetylenebis(acetylacetoneimine)Ni (II)	Ni(tm)AA	296.30
3	N,N'-orto-phenylenebis(acetylacetoneimine)Ni (II)	Ni(ph)AA	334.68
4	N,N'-ethylenebis(benzoyloacetoneimine)Ni (II)	Ni(en)BA	405.10
5	N,N'-trimetylenebis(benzoyloacetoneimine)Ni (II)	Ni(tm)BA	419.12
6	N,N'-orto-phenylenebis(benzoyloacetoneimine)Ni (II)	Ni(ph)BA	457.50

Gas Chromatography

A model 504 gas chromatograph (Mera-Elwro, Wrocław, Poland) equipped with a flame ionization detector and a model KB5503 digital integrator (Kabidez, Warsaw, Poland) was used. The stainless steel columns, 1.3 m x 0.4 cm i.d., packed with 18% of the appropriate nickel (II) chelate on Chromosorb W NAW, 80/100 mesh, were used in all instances. The amounts of chelate deposited on the support were checked thermogravimetrically by using the derivatograph of Paulik-Paulik-Erdey system (MOM, Budapest, Hungary). The adsorbents were heated in the nitrogen atmosphere with the heating rate 5 ^{o}C/min.

The GC measurements were made isothermally at 100, 120 and 135 ± 0.1 ^{o}C. Helium was used as the carrier gas and the constant flow rate, 40 ml/min, was mantained. The solutes were injected as diluted vapours by use a 10 µl gas-tight syringe, what caused that symetric and sample size (1 : 20) independent peaks were obtained. At such low coverage of the adsorbents surface the heats of adsorption were determined from the slopes of $\ln t'_R$ versus 1/T (column temperature) plots [8]. Adjusted retention times t'_R of the solutes studied were determined by Ettre method [9].

Results and Discussion

The nickel (II) complexes studied differ in the hydrocarbon bridge connecting the two nitrogen donor atoms and in the phenyl substituent on the carbonyl groups in the ligand moiety (see Figure 1). Both of these substitution produce the changes in polarity, magnetic and Lewis acid-base properties of these planar, coordinatively unsaturated chelates [10].

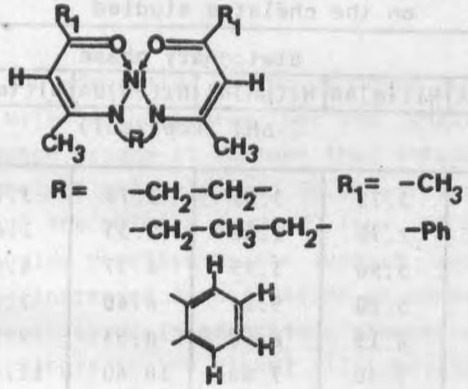

Fig. 1. Structure of the chelates studied

The heats of adsorption determined for non-specifically interacting alkanes and for specific adsorbates are listed in Table 2 and 3. Under the conditions employed the linear relationships between heats of adsorption and the total number of carbon atoms in the molecule of homologous series of the sorbates were observed. In Table 4 the best fit regression data for these functions are given. The results demonstrate that heats of adsorption increased with respect to the hydrocarbon bridge in the nickel (II)

Table 2

Heats of adsorption $(-\Delta H)$ of n-alkanes on the chelates studied

Solute	Stationary phase					
	Ni(en)AA	Ni(tm)AA	Ni(ph)AA	Ni(en)BA	Ni(tm)BA	Ni(ph)BA
	$(-\Delta H)$(kcal/mol)					
Pentane	2.42	2.51	3.20	3.75	3.96	4.03
Hexane	2.73	2.89	3.55	4.50	4.88	5.10
Heptane	3.10	3.35	3.90	5.24	5.79	6.18
Octane	3.40	3.81	4.30	6.01	6.70	7.31
Nonane	3.73	4.26	4.68	6.76	7.60	8.52
Decane	4.09	4.73	5.01	7.53	8.50	9.56

Table 3

Heats of adsorption $(-\Delta H)$ of alcohols on the chelates studied

Soulte	Stationary phase					
	Ni(en)AA	Ni(tm)AA	Ni(ph)AA	Ni(en)BA	Ni(tm)BA	Ni(ph)BA
	$(-\Delta H)$ (kcal/mol)					
Methanol	3.61	3.72	3.75	3.74	3.70	3.69
Ethanol	2.62	2.70	2.62	2.33	2.65	3.26
Propanol	3.50	3.90	3.95	4.37	4.81	5.53
Butanol	4.40	5.10	5.21	6.40	7.18	7.92
Pentanol	5.35	6.15	6.50	8.53	9.35	10.20
Hexanol	6.22	7.30	7.80	10.60	11.65	12.48
iso-Propanol	1.78	2.05	2.25	2.60	2.70	3.10
iso-Butanol	2.12	2.60	2.93	3.64	3.83	4.40
iso-Pentanol	2.60	3.10	3.58	4.60	5.10	5.70
sec-Butanol	1.33	1.78	1.83	1.95	2.10	2.36
sec-iso-Pentanol	1.87	1.95	2.20	2.38	2.56	2.78
tert-Butanol	0.53	0.65	0.72	0.78	0.85	0.98

Table 4

Results of regression analysis for the function $(-\Delta H) = f(C_N)$

Stationary phase	Solutes							
	n-Alcohols $(C_2 - C_6)^x$				n-Alkanes $(C_5 - C_{10})^x$			
	a	s_b	b	R	a	s_b	b	R
Ni(en)AA	0.91	0.035	0.78	0.9988	0.33	0.073	0.81	0.9987
Ni(tm)AA	1.14	0.063	0.44	0.9995	0.45	0.065	0.25	0.9983
Ni(ph)AA	1.29	0.075	0.08	0.9986	0.37	0.087	1.39	0.9982
Ni(en)BA	2.08	0.056	-1.80	0.9981	0.75	0.043	0.05	0.9989
Ni(tm)BA	2.24	0.065	-1.83	0.9975	0.91	0.033	-0.55	0.9991
Ni(ph)BA	2.32	0.087	-1.38	0.9986	1.11	0.091	-1.54	0.9993

Note: a = slope, s_b = standard error of the slope, b = intercept, R = correlation coefficient, x = number of carbon atoms in the solutes.

chelates, e.g. the adsorption on the Ni(ph)AA is stronger than those on Ni(tm)AA or Ni(en)AA complexes. For the chelates with the same kind of hydrocarbon bridge it is seen that introduction of phenylene groups in the chelate molecule lead to an increase in the heats of adsorption of the solutes studied. Thus, it can be assumed that the chelates studied deactivates the support surface in different way and that the increased stabilization of these chelates planar structure may be involved in adsorption phenomena [10].

Structural changes in the nickel (II) chelates produce a variation in the GC columns selectivity which can be expressed by measuring differences of the thermodynamic quantities involved in the processes of adsorption for some selected pairs of isomeric solutes [11]. Mentioned values can be calculated from equation:

$$\frac{\Delta(\Delta H)}{T} = \frac{\Delta H_1 - \Delta H_2}{T} \tag{1}$$

where ΔH_1 and ΔH_2 denotes the heats of adsorption of the solute 1 and 2 respectively, considered as constant in the narrow temperature range studied, T the column temperature. This relation was evaluated for the isometric pairs of alcohols in the column temperature equal 120 ^{o}C and is presented in Figure 2 as the function of molecular weight of the chelates studied.

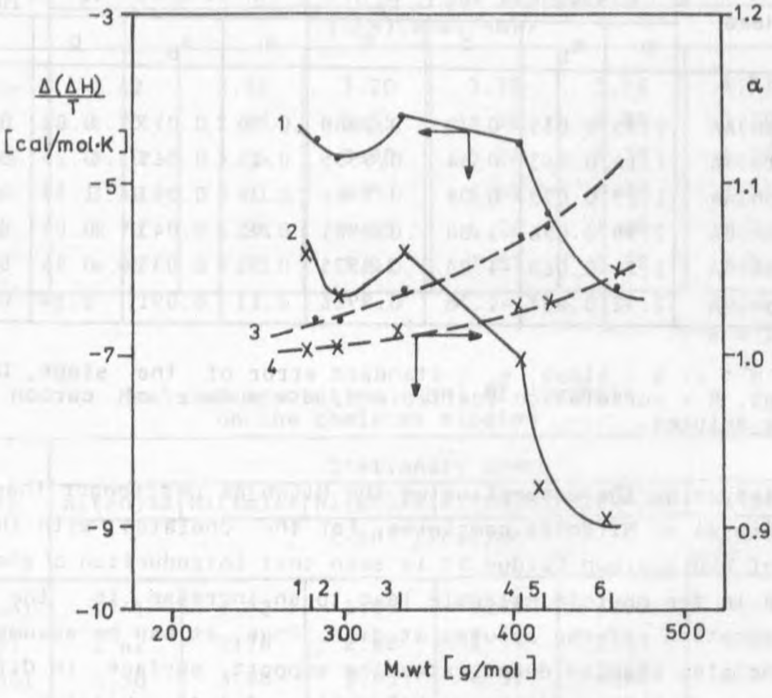

Fig. 2. Differences in heats of adsorption H/T and relative retention upon separation at 120°C of the alcohol mixture: propanol and iso-propanol curves 1 and 3 or butanol and iso-butanol curves 2 and 4, as the function of molecular weight changes in the chelates studied

This figure shows that the separation of the linear molecules with very slight difference in their electron density distribution is possible by a properly modified structure of stationary phase. Replacing a methylene groups with a phenyl substituent in the chelates studied considerably increased the column selectivity. The changes in the relative retention α of alcohol pairs as the structure of chelates is varied (see Figure 2) are meaningfull in ilustrating some features of the working mechanism of such GC columns. For example we assume that specific adsorption of alcohols is strongly influenced by steric effects. Thus, the effectiveness of the separation of the branched alcohols mixture can be optimized by use Ni(ph)BA chelate as the stationary phase. Another important factor affecting the adsorption properties of the nickel (II) chelates studied involves the polymerization equillibria in the solid state [12]. Distortion in the nickel (II) chelate molecule can influence homomolecular interaction and hence their GC separation ability of different class of polar compounds. These considerations will be extended in the future communications.

Acknowledgements

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WYKORZYSTANIE KOMPLEKSÓW Ni (II) Z ZASADAMI SCHIFFA JAKO FAZ STACJONARNYCH W CHROMATOGRAFII GAZOWEJ

Badania nad zastosowaniem różnych kompleksów metali przejściowych z dwu- i czterokleszczowymi zasadami Schiffa wykazały, że związki te spełniają wymagania stawiane fazom stacjonarnym stosowanym w chromatografii gazowej.

W przedstawionej pracy zbadano wpływ modyfikacji struktury ligandu w symetrycznych kompleksach Ni (II) na zdolność rozdzielczą i wartość ciepeł adsorpcji alkanów i alkoholi. W tym celu nośnik diatomitowy pokrywano w jednakowej ilości (18%) kolejno różnymi sześcioma chelatami Ni (II), uzyskanymi na drodze kondensacji acetyloacetonu lub benzoiloacetonu i etyleno-, propyleno- lub fenylenodiaminy.

Stwierdzono, że wielkość oddziaływań specyficznych mierzona zmianami ciepeł adsorpcji badanych sorbatów uzależniona jest od długości mostka azot-azot w cząsteczce czterokleszczowego chelatu Ni (II). Wprowadzenie grupy fenylowej do cząsteczki kompleksu powoduje wzrost selektywności uzyskanych nośników chromatograficznych na skutek wzrostu energii oddziaływań specyficznych kompleks metalu-sorbat.

Umożliwiło to otrzymanie selektywnego rozdziału par izomerycznych alkoholi, porównywalnego z rozdziałami uzyskanymi w klasycznej chromatografii gaz-ciecz.

Na selektywność uzyskiwanego rozdziału alkoholi może mieć także wpływ różny stopień polimeryzacji cząsteczek badanych kompleksów Ni (II) oraz tworzenie adduktów molekularnych o różnej trwałości.

Uzyskane wyniki pozwalają na przypuszczenie, że wypełnienia z opisanymi kompleksami chelatowymi Ni (II) oprócz zastosowań analitycznych mogą być wykorzystane do badania oddziaływań adsorbent-adsorbat.