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SEPARATION OF AMINOALCOHOLS BY HPLC WITH BINARY MOBILE PHASE CONTAINING NICKEL (II) CHELATE ADDITIVE

A system of coordinatively unsaturated metal complexes is introduced as a mobile phase modifier for high performance liquid chromatography HPLC. Unlike previous ionic metal additives Ni(saed) is a neutral, square planar complex capable of producing highly selective and effective separations of polar compounds. Interaction with the metal complex and the subsequent increase in a solute retention is shown to be dependent on steric, dipole and solvatation effects.

INTRODUCTION

Metal chelate addition to the mobile phase is an equivalent to the addition of a counterion since the ratio of metal chelate is mantained constant [1]. However it was shown that functional group selectivity and steric or isomeric resolution was much more pronounced with coordinatively unsaturated metal chelates relative to the usual counterions employed in reversed phase ion-pair liquid chromatography. In this paper we will describe the use of Ni(II) chelate as the mobile phase constituents in normal phase liquid chromatography of aliphatic aminoalcohols mixture.

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EXPERIMENTAL

Chromatographic measurements were performed on a Liquochrom 2010 (Labor MIM, Budapest, Hungary) model apparatus consisting of a pump, 20 µl valve injector and multiwavelenght UV detector. The separation of aminoalcohols mixture was performed using the stainless steel columns (25 x 0.46 cm I.D.) packed with Chromsil type silica gel (d_p = 10 µm) (Labor MIM, Budapest, Hungary) operating at 1.4 ml/min with dichloromethane + methanol (80 + 20) with and without Ni(II) chelate additive as the mobile phase.

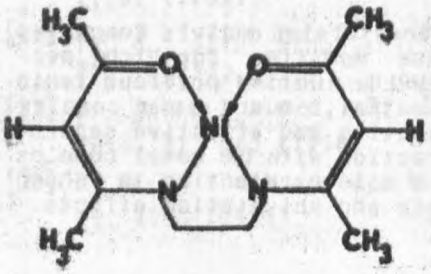

Fig. 1. Structure of Ni(aaed) chelate

For chromatography 1×10^{-3} M stock solutions of twelve aminoalcohols in methanol were prepared. All measurements were made at 25 ± 0.1°C and recordered at 270 nm in triplicate and subjected to regression analysis on the microcomputer. The measurements were made with concentration of Ni(II) chelate in mobile phase from 1×10^{-1} to 1×10^{-5}M. The [4,4-(ethane-1,2-diyldiimino)bis(pent-3-en-2-onato)(2-)]nickel(II) chelate obbreviated as Ni(aaed) synthetized according to the method mentioned earlier [2] was used in this study. The chemical structure of this chelate is presented in Fig. 1. All solvents were of high purity and were obtained from E. Merck, Darmstadt, FRG. The aminoalcohols were supplied by Fluka AG (Switzerland), Riedel-de-Haen FRG, Bayer AG (FRG) and P.O.Ch. (Poland).

RESULTS AND DISCUSSION

Table 1 shows the retention, i.e. capacity ratios k', of the investigated aminoalcohols by the normal phase chromatography with and without Ni(aaed) in the mobile phase. We measured also the effect of Ni(aaed) concentration in the mobile phase on the retention order of aminoalcohols and the results are shown in Fig. 2. Up to 1×10^{-3} M Ni(II) chelate the retention generally increases

Table 1

Retention increase of aminoalcohols obtained by HPLC method with different mobile phase composition

Compound	Code	Capacity ratio k'	
		Phase 1[a]	Phase 2[b]
2-Aminoethanol	MEA	0.88	1.20
Diethanoloamine	DEA	0.71	1.00
N-Methyl-diethanoloamine	MDEA	0.66	1.50
N-Buthyl-diethanoloamine	BDEA	0.85	2.15
N-t-Buthyl-diethanolamine	tBDEA	0.78	2.87
N-Phenyl-diethanolamine	PDEA	2.27	4.25
N-o-Toluidine-diethanolamine	oTDEA	1.72	8.30
N-p-Toluidine-diethanolamine	pTDEA	1.85	14.00
Triethanolamine	TEA	2.18	9.10
Diisopropanolamine	DIP	0.58	1.80
2-Amino-2-hydroxymethyl-1,3--propanodiol	APD	1.90	10.70
N-(2-Aminoethyl)ethanolamine	NAE	3.90	11.40

[a] Phase 1: CH_2Cl_2 + MeOH (80 : 20).
[b] Phase 2: CH_2Cl_2 + MeOH (80 : 20) + 1 x 10^{-3} M Ni(aaed).

after which a dramatic decrease in retention is observed particularly for the most strongly retained species. As it is shown in Fig. 3 a baseline resolution of some aminoalcohols could be achieved using adsorption HPLC with modified mobile phase. As it is presented in Table 1 the order of retention is changed with use of the mobile phase containing Ni(aaed) chelate compare to the reference eluent. This change in the elution order can be explained in terms of the steric selectivity affected by the Ni(II) chelate system. For example this phenomenon can be observed in the separation of oTDEA and PDEA. We can see that a methyl group attached to aromatic ring leads to lower retention due to the weaker outher--sphere complexation caused by steric hindrance. Similar effect was reported [3] during separation of aminoacids by complexation HPLC. It is supposed that nickel(II) ion does not effectively chelate

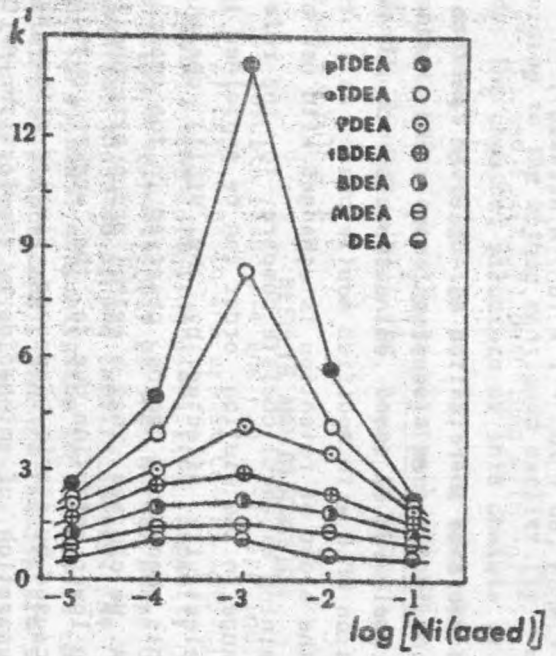

Fig. 2. Influence of Ni(aaed) concentration on the retention of some diethanolamines. Mobile phase: dichloromethane + + methanol (80 + 20)

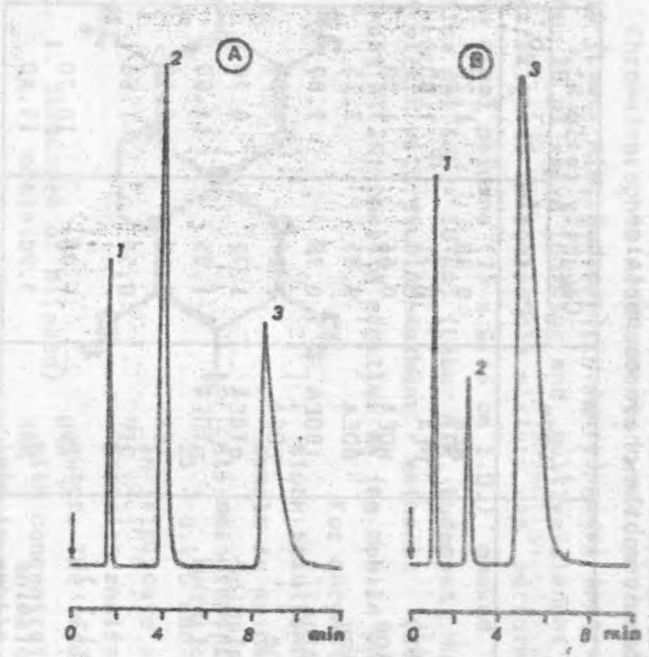

Fig. 3. Separation of some aminoalcohols on silica gel column with mobile phase CH_2Cl_2 + MeOH (80 : 20) containing Ni(aaed) chelate (1×10^{-2} M) additive. Peaks: (A) 1. BDE, 2. PDEA, 3. pTDEA. (B) 1. MDEA, 2. tBDEA, 3. oTDEA. Flow rate: 1.4 ml/min. Chart speed 0.5 cm/min. Detector sensitivity 0.05 Aufs.

with N-hydroxyloamines [4]. However, stable adducts are formed between the molecules of different Ni(II) chelates and amines [5]. We assumed that the stability of the adducts formed in the mobile phase leads to increase of the retention times t'_R and capacity rations k' of investigated aminoalcohols. The stability of these adducts can be enhanced by addition of a small amount of pH modifier like ammonia to the mobile phase. The influence of ammonia addition to the mobile phase on retention of some aminoalcohols on silica gel supports was observed in our previous work [6]. However, in this time, mixed chelates can be formed because the change in pH of the mobile phase shifts the equilibrium distribution of the various metal species in solution. The elution behaviour and selectivity at neutral reaction is caused in differences in the stability of adducts formed on one hand and the adsorption of these adducts on the surface of silica support on the other. Thus large molecular volume of adducts like Ni(saed)-oTDEA, causes probably longer retention of larger aminoalcohols and the aromatic molecules over the straight chain or branched isomers. In summary we have seen that some association effects in the mobile phase can be effectively used to enhance the separation ability of strongly polar substances such as the aminoalcohols by HPLC.

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ROZDZIELANIE AMINOALKOHOLI ALIFATYCZNYCH METODĄ WYSOKO SPRAWNEJ CHROMATOGRAFII CIECZOWEJ Z DWUSKŁADNIKOWĄ FAZĄ RUCHOMĄ ZAWIERAJĄCĄ KOMPLEKSY CHELATOWE Ni(II)

W pracy przedstawiono wyniki wykorzystania koordynacyjnie nienasyconych kompleksów chelatowych Ni(II) jako modyfikatorów fazy ruchomej dichlorometan-woda (80 + 20), stosowanej w wysoko sprawnej chromatografii cieczowej (HPLC). Przebadano wpływ zmiany stężenia dodawanego chelatu do fazy ruchomej na uzyskiwaną zdolność rozdzielczą kilkunastu dietanoloamin alifatycznych. Stwierdzono, że powstawanie asocjatów typu chelat Ni(II)-aminoalkohol w fazie ruchomej prowadzi do zwiększenia selektywności rozdziału mieszaniny badanych związków. W zastosowanej fazie ruchomej występujący proces tworzenia asocjatów typu chelat Ni(II)-aminoalkohol jest prawdopodobnie zjawiskiem konkurencyjnym w stosunku do samoasocjacji cząsteczek aminoalkoholi oraz powstawania asocjatów typu rozpuszczalnik polarny - aminoalkohol.