Short Communication

Salting-out thin-layer chromatography of transition metal complexes

II. Mixed aminocarboxylatocobalt(III) complexes on a polyacrylonitrile sorbent

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ABSTRACT

Fourteen mixed aminocarboxylatocobalt(III) complexes, belonging to three homologous series, were investigated by salting-out thin-layer chromatography on a polyacrylonitrile sorbent using six aqueous ammonium sulphate solutions. An increase in the salt concentration of the solvent system was found to result in a decrease in the R_F values of the complexes, giving rise to a reversed-phase order. It was established that the members of a homologous series containing aminocarboxylato ligands with a straight carbon chain exhibit lower R_F values than the isomeric members with branched chains. A linear dependence was found between the R_M values of the investigated complexes and the concentration of the salt in the solvent system applied, and also between the R_M values of complexes belonging to the same homologous series and the number of carbon atoms in their hydrophobic parts. An increase in the salt content of the solvent system causes an increase in the separation factor (α) between two adjacent members of a homologous series, and a linear dependence between log α and the concentration of ammonium sulphate was established. The separation processes described are consistent with a mechanism of non-specific hydrophobic interactions.

INTRODUCTION

As far as we know, salting-out thin-layer chromatography (SOTLC) has so far been investigated on cellulose by Lederer and co-workers [1–5], who separated many classes of organic compounds, and on silica gel by Vučković *et al.* [6], who effected the separation of some mixed aminocarboxylatocobalt

(III) complexes. Continuing these investigations, in this work we applied this method on thin layers of a polyacrylonitrile sorbent (PANS), the characteristics of which [7] differ considerably from those of the two previously mentioned sorbents [8]. This sorbent, owing to its moderate polarity, is suitable for both normal-phase [7,9,10] and reversed-phase [9–11] chromatography. For, this purpose we applied, as in Part I [6], mixed aminocarboxylatocobalt(III) complexes.

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EXPERIMENTAL

The investigated complexes were synthesized according to the procedures described in the literature given in Table I.

The chromatograms were developed with aqueous ammonium sulphate solutions. Ammonium sulphate used was of analytical-reagent grade from Kemika (Zagreb, Croatia).

The chromatographic separations were performed as in a previous paper [7], using aliquots of 0.5 μl of freshly prepared aqueous solutions of the investigated complexes of concentration 8 mg/cm^3.

Detection was performed by keeping the plates for 10 min above 2 M ammonium sulphide solution.

All investigations were performed at 25 ± 2°C.

RESULTS AND DISCUSSION

As can be seen from Table I, investigations were carried out with fourteen mixed aminocarboxylato-cobalt(III) complexes of anionic and neutral type, which could be assigned to three homologous series of complexes, i.e., 1–7, 8–11 and 12–14; the first series contains members with aminocarboxylato ligands having straight (1–3) or branched (4–7) carbon chains. In addition to aminocarboxylato ligands, all the complexes also contain nitro groups, and in some instances ammonia. As solvent systems aqueous ammonium sulphate solutions of various concentrations were used, as this salt is most often used in salting-out chromatography, owing to its high solubility and great salting-out effect [1–6,16].

TABLE I

hR_F VALUES OF THE INVESTIGATED COMPLEXES

No.	Complex[a]	n^b	Ref.[c]	Content of ammonium sulphate in solvent[d]					
				0.92	1.88	2.89	3.97	5.12	6.36 mol%
				0.50	1.00	1.50	2.00	2.50	3.00 mol/dm^3
1	(+)$_{589}$-cis(NO$_2$),trans(N)-[Co(S-Ala)$_2$(NO$_2$)$_2$]$^-$	4	12	82	73	56	42	31	20
2	(S-Nval)$_2$	8	13	41	27	15	7	4	2
3	(S-Nleu)$_2$	10	13	20	11	5	2	1	0.5
4	(Aibu)$_2$	6	13	75	67	49	30	21	13
5	(S-Val)$_2$	8	13	47	36	22	11	6	3
6	(S-Leu)$_2$	10	13	27	14	8	4	2	1
7	(S-Ilc)$_2$	10	13	28	17	9	4	2	1
8	mer-[CoGly(NO$_2$)$_3$NH$_3$]$^-$	1	14	68	61	53	47	42	34
9	(−)$_{589}$-mer-[Co(S-Ala)(NO$_2$)$_3$NH$_3$]$^-$	2	14	68	58	47	37	29	20
10	(S-Abu)	3	14	57	43	33	22	16	10
11	(S-Nval)	4	14	43	31	20	13	8	5
12	cis(NO$_2$),trans(NH$_2$,NH$_3$)-[CoGly(NO$_2$)$_2$(NH$_3$)$_2$]	1	15	88	86	84	81	78	76
13	(+)$_{589}$-cis(NO$_2$),trans(NH$_2$,NH$_3$)-[Co(S-Ala)(NO$_2$)$_2$(NH$_3$)$_2$]	2	15	83	80	76	71	62	57
14	(S-Abu)	3	15	76	72	65	58	52	44

[a] GlyH = glycine; S-AlaH = (S)-alanine; S-AbuH = (S)-aminobutyric acid; S-NvalH = (S)-norvaline; S-NleuH = (S)-norleucine; AibuH = aminoisobutyric acid; S-ValH = (S)-valine; S-LeuH = (S)-leucine; S-IleH = (S)-isoleucine.

[b] n = Number of carbon atoms in the hydrophobic (hydrocarbon) part of a complex.

[c] Syntheses used.

[d] The developing times in minutes for solutions of different ammonium sulphate concentrations (mol/dm^3, in parentheses) were 35 (0.50 and 1.00), 40 (1.50), 45 (2.00), 50 (2.50) and 75 (3.00).

The R_F values obtained are given in Table I. They show that in all instances an increase in the salt concentration in the solvent applied results in a decrease in the R_F values of the corresponding complexes in their reversed-phase order. This is consistent with the results obtained by Lederer and co-workers [1–5] in the SOTLC of numerous organic compounds on cellulose, and also with the results obtained by Vučković et al. [6] for the SOTLC of mixed aminocarboxylatocobalt(III) complexes on

silica gel. These findings might be explained by an increase in surface tension of a solvent with increasing salt concentration [17].

In addition, from Table I it can be seen that the R_F values of complexes belonging to the same homologous series (complexes 1–3, 8–11 and 12–14) are the smaller the larger is the number of carbon atoms in the hydrophobic part of the complex, which might be ascribed to an increase in their hydrocarbonaceous surface areas [17,18].
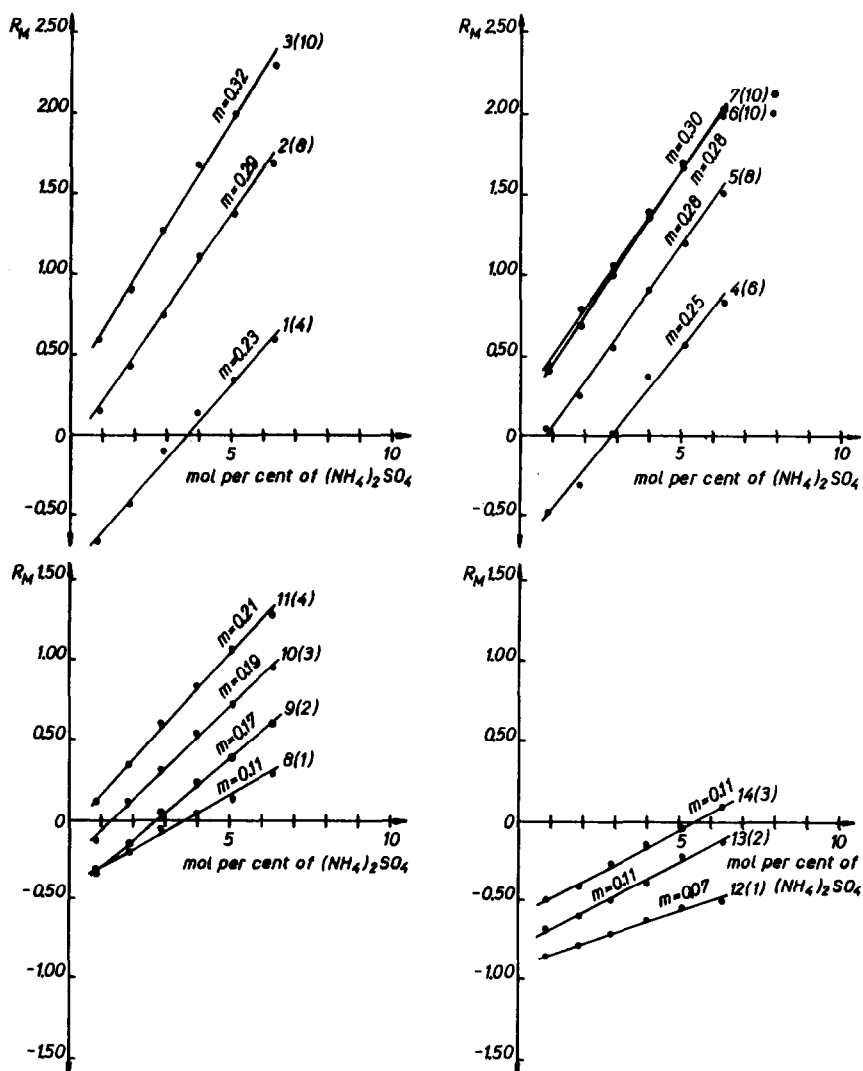

Fig. 1. Dependence of the R_M values of the investigated complexes on mol% of ammonium sulphate in the solvent systems used. Numbers on the right of lines denote the numbers of the complexes in Table I, the values in parentheses being the number of carbon atoms in hydrocrbon part of a complex; m is the slope of the straight lines.

It was established also that the complexes of the same composition containing branched-chain aminocarboxylato ligands exhibit higher R_F values than the corresponding complexes containing aminocarboxylato ligands with straight carbon chains (complexes 2 and 5 and complexes 3, 6 and 7, respectively). This phenomenon is in accord with the results obtained by other workers [19] in investigations on dialkyldithiocarbamatocopper(II) complexes.

A linear dependence between the R_M values of the investigated complexes and the mol% of ammonium sulphate in the solvent was established (Fig. 1). This dependence can be described by the equation

$$R_M = R_{M_0} + m \,[\text{mol}\% \text{ of } (\text{NH}_4)_2\text{SO}_4] \qquad (1)$$

where R_{M_0} denotes the intercept and m the slope. As the magnitude of m represents an increase in the R_M value resulting from an increase of the mol% of the salt in the solvent by one unit, it could be taken as a criterion for the salting-out efficiency, as was shown in Part I [6]. The slopes of the straight lines within one homologous series increase gradually with in-

crease in the hydrophobic part of the complexes, which is in accord with the results obtained previously [6].

The dependence of the R_M values of the members of a homologous series on the number of carbon atoms in their hydrocarbon part is linear with a reversed-phase order for the complexes containing either straight or branched side-chains (Fig. 2). A deviation from linearity occurred with complex 8, which contains only one coordinated glycinato ligand, i.e., whose hydrophobic part is the smallest. This deviation occurred with the three lowest salt concentrations, where the weakest non-specific hydrophobic interactions could be expected. Hence it may be assumed that this deviation is the result of a greater effect of specific interactions of the sorbend with the sorbent, as in these instances R_F values lower than expected were obtained. The slopes of the straight lines obtained for different groups of complexes do not differ much, which indicates that the increase in the R_M values of the complexes depends mainly on the increase in the number of carbon atoms in the hydrophobic part of the complexes, and less on other constituents or structure.
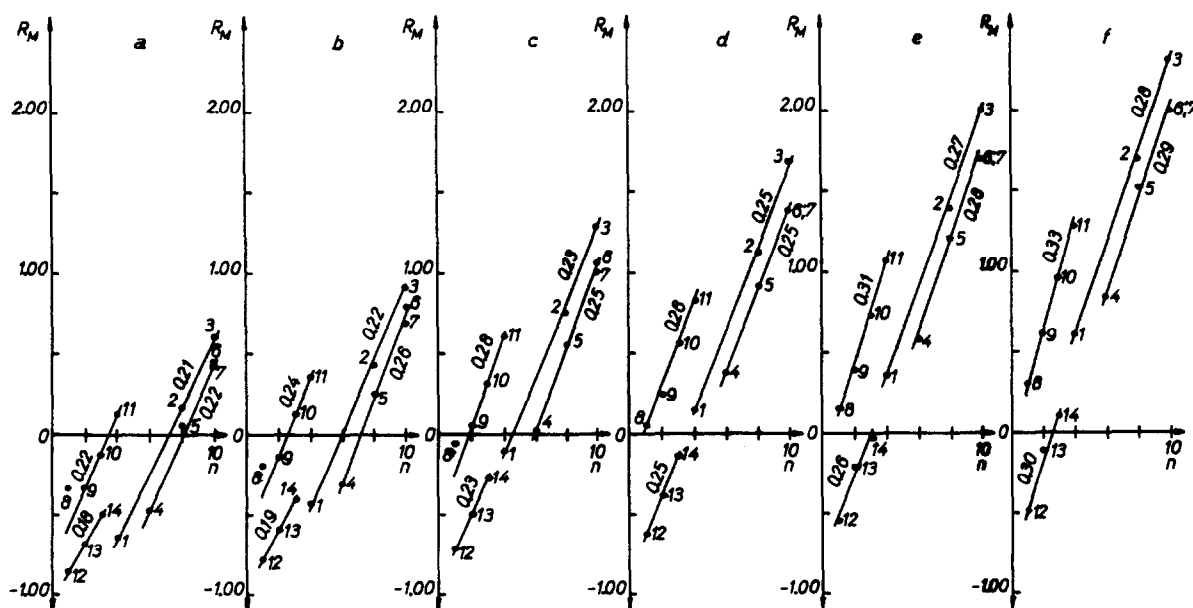

Fig. 2. Dependence of the R_M values of the investigated complexes on the number of carbon atoms in the hydrocarbon part of the complex (n) in chromatographic separations with ammonium sulphate solutions containing (a) 0.92, (b) 1.88, (c) 2.89, (d) 3.97, (e) 5.12 and (f) 6.36 mol% of the salt. Numbers adjacent to the points denote the numbers of the complexes in Table I; the numbers above or below the straight lines denote their slopes.

Finally, in order to present quantitatively the difference in the selectivity of the solvents used for various groups of complexes, the dependence of the logarithm of the separation factors (α) on the concentration (mol%) of ammonium sulphate in the solvent is shown in Fig. 3. Log α, which is numerically equal to the difference in the R_M values between two adjacent members of a homologous series [20], was calculated from the corresponding regression straight lines shown in Fig. 2. Fig. 3 shows that the separation factor on PANS for all four groups of complexes investigated increases with increasing mole per cent of ammonium sulphate in the solvent system, and that there is a linear dependence between its logarithm and the mol% of the salt. It is noticeable that for each investigated salt concentration the logarithms of the separation factors of individual groups of complexes containing two aminocarboxylato ligands (complexes 1–3 and
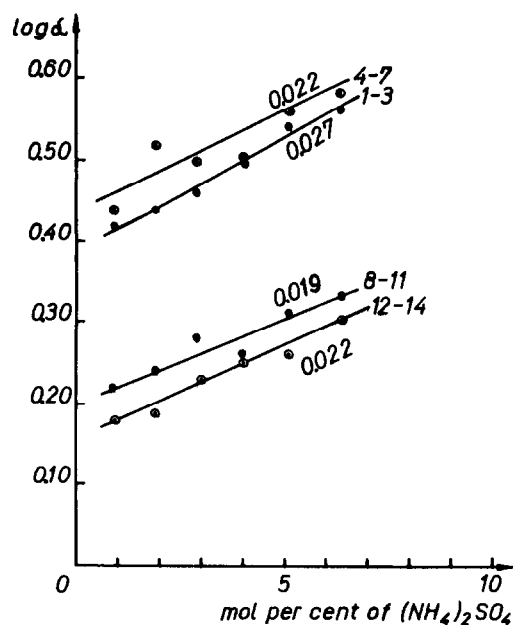
4–7) are about double the values obtained for other homologous series of complexes containing only one aminocarboxylato ligand. This can be explained by the fact that in the former instance two adjacent members of the series differ by two but in the latter instance by only one CH_2 group.

It may be concluded that the separation of the investigated complexes by SOTLC on PANS is based on non-specific hydrophobic interactions, which is in accord with the results obtained by Lederer and co-workers [1–5] on cellulose and also with those obtained in our previous study on silica gel [6].

Fig. 3. Dependence of the logarithms of the separation factors (α) of the investigated groups of complexes on mol% of ammonium sulphate in the solvent system used. The numbers on the right of the lines denote the numbers of the complexes in Table I; the numbers above or below the lines denote the slopes of the straight lines.

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