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Short Communication

Salting-out thin-layer chromatography of transition metal complexes

I. Investigation of the behaviour of mixed aminocarboxylato cobalt(III) complexes on silica gel

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ABSTRACT

Twenty-four mixed aminocarboxylato cobalt(III) complexes of anionic and neutral types, containing nitro ligands with or without ammonia ligands and belonging to six homologous series, were investigated by salting-out thin-layer chromatography on silica gel, using seven ammonium sulphate solutions in water. In most cases it was established that a decrease in the R_F values of the complexes accompanied increasing salt concentration of the solvent systems used. A positive linear dependence between the R_M [log $(1/R_F - 1)$] values of the complexes and the mol percent (mol fraction × 100) of ammonium sulphate in the solvent systems used was found. Finally, a positive linear dependence between the R_M values of the complexes of a homologous series and the number of carbon atoms in the hydrophobic part of a complex was also established. To explain these results, a mechanism based on hydrophobic interaction between the sorbate and the sorbent is proposed.

INTRODUCTION

In several recently published papers by Lederer and co-workers [1–4] the effect of the salt concentration in the water developer on the R_F values of many classes of organic compounds obtained by paper chromatography and thin-layer chromatography (TLC) on cellulose was investigated. It was found that increasing the salt concentration decreased the R_F values of the studied compounds (salting-out TLC). The same effect has been also investigated on some transition metal complexes using paper chromatography [5–6] and TLC on silica gel [7], but in these cases a similar trend was not observed. For this reason we wanted to determine if a salting-out effect can also occur in the case of transition metal complexes. To this end we chromatographed on silica gel some of complexes containing hydrophobic hydrocarbon moieties with ammonium sulphate solutions in water in a wide range of concentrations. Silica gel was chosen because, as established in an earlier paper [8], this sorbent is capable of non-specific hydrophobic interac-

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tions with some metal acetyl-acetonato complexes from water–organic solvents [8].

EXPERIMENTAL

The syntheses of the complexes were performed according to procedures given in the literature (Table I), and the chromatographic procedure is described in an earlier paper [9]. The solutions of different concentrations of ammonium sulphate (Merck, Darmstadt, Germany) in water were used for chromatographic development. The chromatography was carried out at 20 ± 2°C.

RESULTS AND DISCUSSION

The results obtained are given in Table I. They show that the investigation was carried out with eleven neutral and thirteen anionic mixed cobalt (III) complexes, belonging to six homologous se-

TABLE I

R_F × 100 VALUES OF THE INVESTIGATED COMPLEXES

No.	Complex[a]	Optical activity[b]	Ref. for synth.	Ammonium sulphate content in solvent system used						
				1.1	2.2	3.3	4.4	5.5	6.6	7.7 mol%
				0.63	1.14	1.69	2.20	2.66	3.10	3.48 mol/dm^3
cis-(NO_2), *trans* (N)-[Co $L_2(NO_2)_2$]$^-$										
1	L = gly		10	99	99	99	97	98	95	97
2	L = S-ala	+	10	96	94	89	87	82	78	73
3	L = S-abu	+	11	88	82	76	70	62	51	45
4	L = S-nva	+	11	73	66	58	44	31	22	21
5	L = S-nle	+	11	52	46	32	17	12	9	6
cis (NO_2), *trans* (N)-[Co $L_2(NO_2)_2$]$^-$										
6	L = iabu		11	89	84	79	70	60	49	44
7	L = S-val	+	11	78	73	63	53	40	29	25
8	L = S-leu	+	11	60	53	44	29	19	12	11
9	L = S-ile	+	11	68	51	47	32	22	15	12
cis (O), *trans* (NH_2)-[Co $L_2(NO_2)NH_3$]										
10	L = gly		12	98	99	99	97	98	97	99
11	L = S-ala	+	12	92	92	89	85	84	83	79
12	L = S-abu	+	13	79	80	69	63	62	61	46
13	L = S-nva	+	13	55	52	46	31	21	18	11
14	L = S-val	+	13	61	59	56	44	36	31	24
mer-[Co $L(NO_2)_3NH_3$]$^-$										
15	L = gly		14	98	98	97	97	97	97	97
16	L = S-ala	–	14	97	96	95	93	93	93	89
17	L = S-abu	–	14	95	93	91	85	82	79	70
18	L = S-nva	–	14	92	87	82	74	65	60	52
cis $(NO)_2$, *trans* (NH_2, NH_3)-[Co $L(NO_2)_2$ $(NH_3)_2$]										
19	L = gly		12	98	96	97	97	97	97	98
20	L = S-ala	+	12	97	92	95	94	93	93	87
21	L = S-abu	+	12	94	88	90	85	83	76	75
trans (NO_2), *cis* (NH_3)-[Co $L(NO_2)_2$ $(NH_3)_2$]										
22	L = gly		12	99	95	97	97	97	96	97
23	L = S-ala	+	12	98	94	94	93	93	91	91
24	L = S-abu	+	12	93	89	89	83	82	77	76

[a] gly = glycine; S-ala = (*s*)-alanine; S-abu = (*s*)-aminobutyric acid; S-nva = (*s*)-norvaline; S-nle = (*s*)-norleucine; iabu = isoaminobutyric acid; S-val = (*s*)-valine; S-leu = (*s*)-leucine; S-ile = (*s*)-isoleucine.

[b] Sign of optical rotation at 589 nm.

ries, using seven solvent systems comprising ammonium sulphate solutions of various concentrations in water. From Table I it is seen that, under the experimental conditions applied, in 80% of the cases increasing of the salt concentration in the solvent system resulted in a decrease in the R_F values of the complexes. This decrease is in accordance with the results obtained by salting-out TLC of numerous organic compounds on cellulose [1–4]. Considering the composition of the complexes that do not exhibit the aforementioned effect, it may be noted that they contain the glycinato anion as an aminocarboxylato ligand. On this basis it could be assumed that the absence of the aforementioned effect is due to a small hydrophobic part of such complexes, which results in insufficient non-specific hydrophobic interaction between such sorbates and the siloxane groups of the sorbent, which are hydrophobic, unlike to silanol groups [15]. This assumption is in accordance with the fact that this effect increases with the degree of chain branching in aminocarboxylato ligands in a homologous series of the investigated complexes [16].

In addition, we established in most cases a linear dependence of the R_M [log (1/R_F − 1)] values of the complexes on the mol percent (mol%) of ammonium sulphate in the solvent system used for cases for which $R_M > -1.00$ (see Fig. 1). This allows the

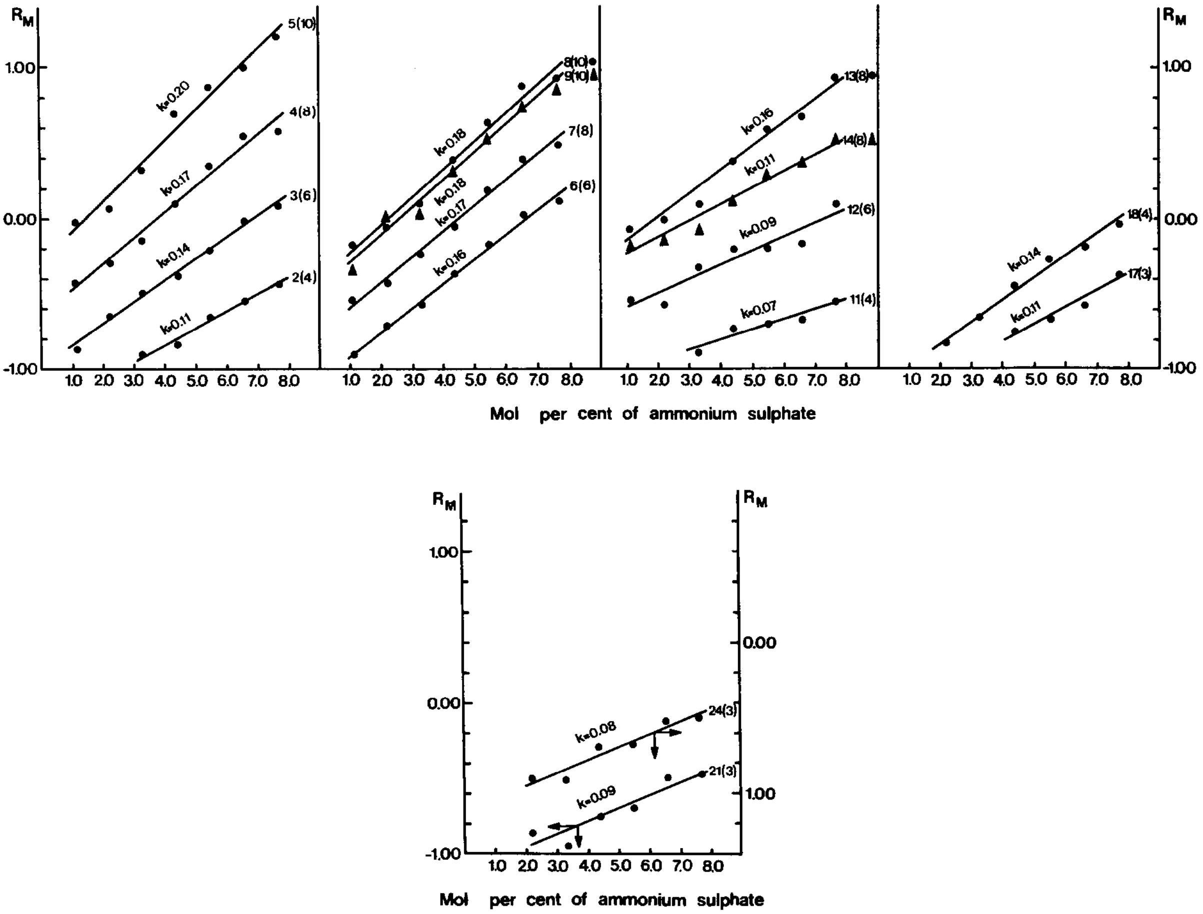

Fig. 1. Dependence of the R_M values of the complexes on ammonium sulphate mol%. Numbers beside the lines represent the complexes used from Table I and the number of the corresponding carbon atoms in the hydrophobic part of a complex (given in brackets); k refers to the corresponding slopes.

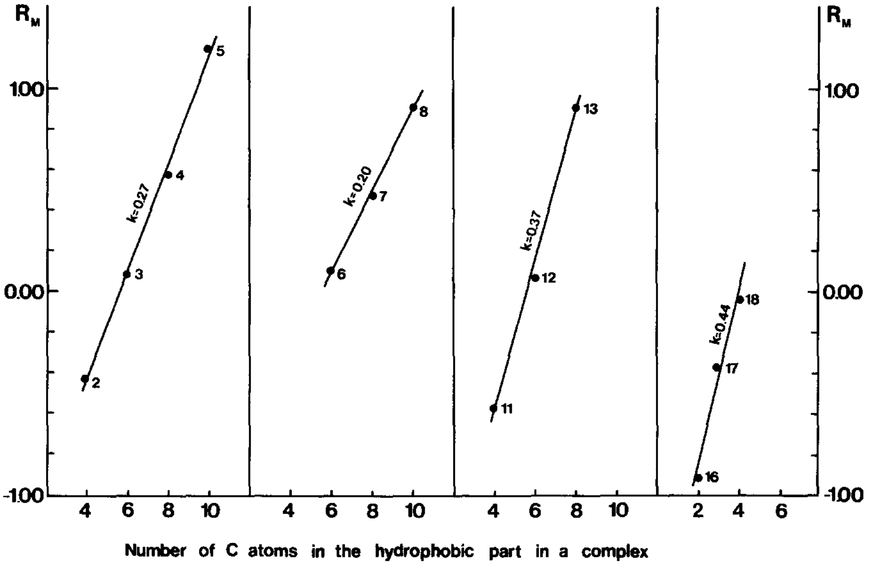

Fig. 2. Dependence of the R_M values of the complexes on the number of carbon atoms in the hydrophobic part in a complex obtained with 7.7 mol% ammonium sulphate solution. Numbers on the lines represent the complexes used from Table I. k as in Fig. 1.

possibility of using the slopes of the resultant straight lines as a determinant of salting-out efficiency. From Fig. 1 it is seen that the slopes of the straight lines increase within a homologous series, which is in accordance with the increase in the hydrophobic part of the molecules in the series.

A linear dependence of the R_M values on the number of carbon atoms in the hydrophobic part of the complexes of the same homologous series, shown in Fig. 2, was also found. From Fig. 2 it is seen that the slopes of the individual straight lines are different. This means that a change of one carbon atom results in a different change in the R_M value in different homologous series of the complexes depending on the other constituents of the complex and their distribution.The aforementioned correlations represented in Figs. 1 and 2 are similar to those previously obtained by column liquid chromatography [17–20], in which linear plots of log k' capacity factor *versus* the number of repeated units in a sorbate or the modifier or additive concentration in the mobile phase have beeen reported.

Finally, we compared the selectivities obtained using the most diluted and the most concentrated solutions of ammonium sulphate (1.1 and 7.7 mol%, respectively). For this reason, in Fig. 3 we have shown the mutual dependence of the R_M values obtained with these two solutions for three series of complexes for which suitable values for such a presentation were obtained. The linear correlation shown on the figure is a consequence of the previously described linear correlation between log k' (R_M) and the number of the sorbate repeated units [17–20]. Since the slopes of all three straight lines are greater than 1, this means that the log of the separation factor [8] for two adjacent members in

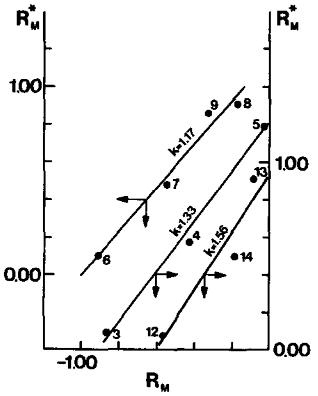

Fig. 3. Dependence of the R_M values of the investigated complexes obtained with 1.1 (R_M) and 7.7 mol% (R_M*) ammonium sulphate solution. Numbers on the lines represent the complexes from Table I. k as in Fig. 1.

all three series of complexes is greater for more concentrated ammonium sulphate solutions.

On the basis of all the above it may be concluded that silica gel can be also applied for salting-out TLC, in spite of considerable differences between the properties of this sorbent and those of earlier applied cellulose. In addition, it may be concluded that salting-out TLC on silica gel can also be applied for the separation of transition metal complexes.

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