Journal of Chromatography, 111 (1975) 452–455
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CHROM. 8372

Note

A comparison of several silica gel pre-coated thin layers for the separation of some cobalt(III) complexes

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(Received April 21st, 1975)

There have been several reports[1–4] on the wide differences in behaviour encountered when using pre-coated silica gel thin layers obtained from various sources; these dealt with several classes of organic compounds and with such solvent systems as benzene–ethanol–acetone–acetic acid[2] and benzene–diethyl ether[3]. It has also been pointed out that as many as 100 different types of silica gel are at present available[5], and this poses a problem when attempts are made to devise new separations or to repeat published work. The most important question is, when a separation is unsuccessful on a given pre-coated silica gel thin layer, should another type of support be used or should other types of silica gel plates be tested?

To illustrate this problem in another field, we report here work on the separation of Co(III) complexes carried out in conjunction with studies of thermal reactions in the solid state. We wanted to separate four complexes*, *viz.*, the *cis*- and *trans*-forms of $Co(en)_2Cl_2^+$ and those of $Co(en)_2(OCOC_6H_5)_2^+$. Although there are separations in the literature[6,7] for the *cis*- and *trans*-forms of $Co(en)_2Cl_2^+$, to our knowledge, no separations involving the *cis*- and *trans*-forms of $Co(en)_2(OCOC_6H_5)_2^+$ have been reported. In order to obtain further results on the behaviour of the various pre-coated thin layers, we also chromatographed the following complexes: *cis*- and *trans*-$Co(en)_2(OCOCH_3)_2^+$, $Co(en)_3^{3+}$ and $Co(o\text{-phen})_3^{3+}$.

EXPERIMENTAL

The complexes were prepared as described in the literature, the *trans*- and *cis*-forms of $Co(en)_2Cl_2^+$, as perchlorate, according to Bailar[8]; the two forms of $Co(en)_2(OCOC_6H_5)_2^+$, as nitrate, according to Aprile *et al.*[9]; those of $Co(en)_2(OCOCH_3)_2^+$, as perchlorate, by the method of Linhard and Stirn[10]; $Co(en)_3^{3+}$, as chloride, and $Co(o\text{-phen})_3^{3+}$, as perchlorate, as described by Work[11] and by Prosperi *et al.*[12], respectively.

The following ten types of pre-coated silica gel plates were used: (1) Camag (Muttenz, Switzerland) No. 30079; (2) Merck (Darmstadt, G.F.R.) 60; (3) Schleicher & Schüll (Dassel, G.F.R.) G 1500; (4) Woelm (Eschwege, G.F.R.) SiO_2;

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* The following abbreviations are used: en = ethylenediamine; *o*-phen = ortho-phenanthroline; $OCOC_6H_5$ = benzoato; $OCOCH_3$ = acetato.

(5) Baker (Phillipsburg, N.J., U.S.A.) IB-2; (6) Eastman-Kodak (Rochester, N.Y., U.S.A.) No. 13179; (7) Macherey, Nagel & Co. (Düren, G.F.R.) MN- Polygram SIL-G; (8) MN-Polygram SIL-N-HR; (9) Carlo Erba (Milan, Italy) Stratocrom SIF-RS; and (10) Serva (Heidelberg, G.F.R.) Silufol UV 254.

The mobile phases used (M_1, M_2 and M_3) were, respectively, 96% ethanol–methanol–25% aqueous ammonium acetate–1 *N* acetic acid in methanol (30:70:5: 0.3)[13], formamide–methanol–70% perchloric acid (40:60:0.1)[14], and dimethyl sulphoxide–methanol–70% perchloric acid (40:60:0.5)[15].

Conditions

Portions (1–3 μl) of 0.5–1 % solutions of the complexes in the mobile phase were applied to the plates, and development was carried out in Desaga chambers, the mobile phases being placed in the chambers 18 h before development. Ascending development was carried out at 20–22° for 10 cm, and the spots were detected by spraying with ammonium polysulphide solution.

RESULTS AND DISCUSSION

Preliminary work on the mixture to be separated was carried out with columns of ion-exchange resins and carboxymethylcellulose, but no satisfactory results were obtained. We therefore decided to try the solvents used by Seiler *et al.*[13] and by Druding and Hagel[14,15], with silica gel thin layers.

The results are shown in Fig. 1, which shows the R_F values of the various complexes, except for $Co(en)_3^{3+}$ and $Co(o\text{-phen})_3^{3+}$, the time of development (for 10 cm) and the height of the "acid front" when this was present; this "front" was detected by the line of eluted impurities and by spraying with universal indicator. The reproducibility of R_F values was reasonably good, being ±0.02 to 0.04 on all the layers.

In spite of considerable variation in R_F with solvent M_1, good separations could be attained on all layers both for the dichloro and the dibenzoato complexes, but there was no separation of the diacetato complexes. Both $Co(en)_3^{3+}$ and $Co(o\text{-phen})_3^{3+}$ remained in the region of $R_F \simeq 0$. In this solvent, the dichloro complexes yielded more than one spot, presumably because of substitution reactions, so that M_1 was unsuitable for our purpose.

In solvent M_2, separations of the *cis–trans* pairs depended largely on the layer used, some giving separations and others not. Excellent separations were obtained with the Merck layer, and the Camag and Erba layers also gave separations, but with considerable streaking. In this solvent (M_2), even on the Merck layer, the mixture of the two dichloro and the two dibenzoato complexes gave only three spots, as the *trans*-dichloro and the *cis*-dibenzoato complexes overlapped. The two diacetato complexes were not separated, and the R_F value for $Co(en)_3^{3+}$ varied considerably from layer to layer being 0 on the Camag, Merck, Erba and Serva layers and 0.33 on the MN layer (on the other layers, this complex gave streaks). The $Co(o\text{-phen})_3^{3+}$ always remained near or at the point of application.

In solvent M_3 there was an "acid front" (as already noted by Druding and Hagel[14]), which varied considerably with the type of layer, as did the R_F values of the complexes. On the Merck and Camag layers, there were excellent separations of the dichloro complexes (this agrees with the results obtained by Druding and Hagel[14]),

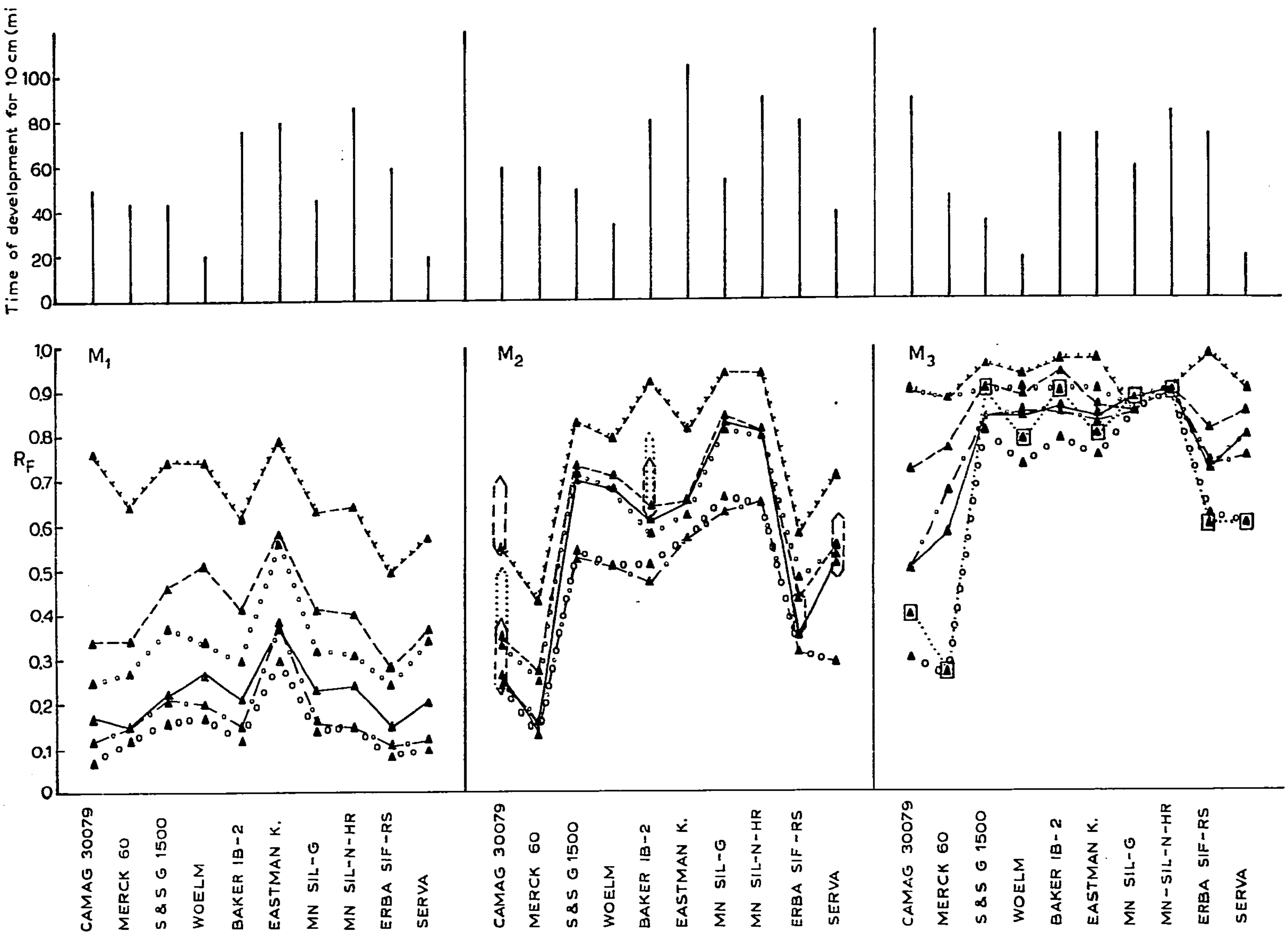

Fig. 1. R_F values (▲) for Co(III) complexes and times of development for 10 cm on silica gel pre-coated plates from various manufacturers. ———, *cis*-$Co(en)_2Cl_2^+$; – – –, *trans*-$Co(en)_2Cl_2^+$; ⊥⊥⊥, *trans*-$Co(en)_2(OCOC_6H_5)_2^+$; ○○○, *cis*-$Co(en)_2(OCOCH_3)_2^+$; o-o-o, *trans*-$Co(en)_2(OCOCH_3)_2^+$; □·····, secondary "acid front". For compositions of solvents M_1, M_2 and M_3, see text.

but on the MN layers, all the complexes except Co(*o*-phen)$_3^{3+}$ moved near the acid front. On some layers, solvent M_3 gave good separations of the *cis*- and *trans*-diacetato complexes. The species Co(en)$_3^{3+}$ and Co(*o*-phen)$_3^{3+}$ remained near $R_F = 0$ on the Camag layer; on the Merck layers they were both at $R_F = 0.15$, on the Eastman-Kodak layer at $R_F = 0.75$ and on all the other layers they were separated, the Co(en)$_3^{3+}$ always moving faster.

Experiments with other solvent mixtures, such as acetone-water-70% perchloric acid (80:20:1) or (80:20:0.1), methanol-ethanol-water-70% perchloric acid (70:30:5:0.3), all yielded a second "front", which varied considerably from one layer to another (and, of course, with the acid concentration); however, no useful separations of the four complexes could be obtained.

We had hoped to establish some correlation between the physical properties of the pre-coated thin layers (*e.g.*, grain size, binder, activity of the layers) and their chromatographic properties. However, we could not obtain sufficient information from the manufacturers for this purpose. The binder apparently exerts no great effect, as similar results were obtained on MN SIL-G and MN SIL-N-HR with two different polymer binders. The Serva layer seems to be less suitable for use with the types of solvent employed by us.

To conclude, in the separation of Co(III) complexes, the type of silica gel thin layer used has enormous influence on the separation achieved, R_F values varying as much as from 0 to 0.9. Thus, when attempting new separations, one should not limit the experiments to only one type of layer.

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