Investigation of Thin-Layer Chromatography Properties of Some Transition Metal Complexes Based on Ditiocarbamates

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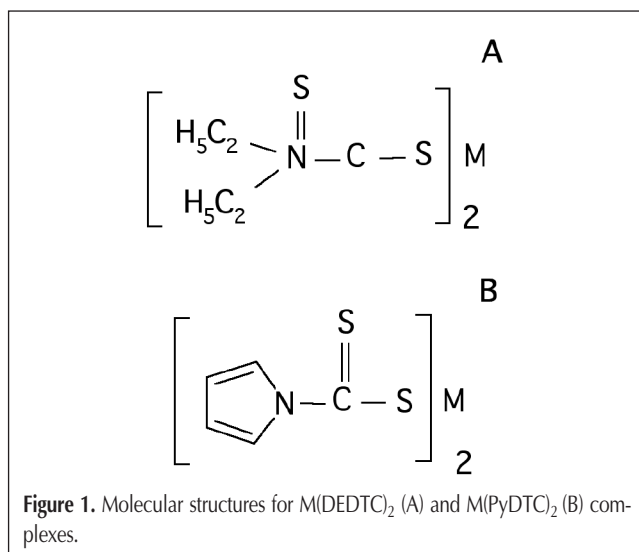
Abstract

Sodium diethyldithiocarbamate (DEDTC) and ammonium pyrolidinedithiocarbamate (PyDTC) are prepared as their Co or Cu (M) complexes [M(DEDTC)$_2$ and M(PyDTC)$_2$, respectively]. The complexes are prepared by reactions of DEDTC and PyDTC with metal (II) nitrates, and they are examined for chromatographic properties using thin-layer chromatography systems. These complexes and their mixtures are spotted on the activated and non-activated 250-μm thick thin layers of commercial silica gel (Si-60GF$_{254}$). Pure toluene and a toluene–cyclohexane mixture (3:1, v/v) are used as mobile phases for running the complexes. These chromatographic systems are successfully used for the qualitative analysis of the corresponding metal cations and the separation of components in both M(DEDTC)$_2$ and M(PyDTC)$_2$ complex mixtures. In addition, non-activated layers are more successful than activated layers. This study may be useful in understanding the effects of stationary and mobile phase properties, retention mechanisms, and the effects of the nature of metal and ligand type on the chromatographic behavior and parameters [e.g., retention factors, theoretical plate numbers, and resolution] of the complexes.

Introduction

The qualitative and quantitative analysis of Cu^{2+} and Co^{2+} cations in environmental media and various samples is challenging for analytical chemists because of the similarities in their properties. Thin-layer chromatography (TLC) is a rapid, easy, and simple separation technique extensively used for organic species but rarely used for inorganic cations. However, TLC has advantages compared with alternative methods. For instance, components of mixture samples can be easily separated without interference. In addition, several samples can be separated simultaneously using TLC, and the positions of spots that appear can be determined with a number of different methods (1–6).

Dithiocarbamate ligands, such as diethyldithiocarbamate (DEDTC) and pyrolidinedithiocarbamate (PyDTC), contain N and S donor atoms, and they form coordinatively saturated complexes with transition metals. The structures of the Cu or Co (M) complexes of DEDTC [M(DEDTC)$_2$] and PyDTC [M(PyDTC)$_2$] are given in Figure 1. These complexes cannot interact chemically with the stationary phase and mobile phase in TLC systems (3–5). Cu (II), Co (II), and other transition metal complexes with dithiocarbamates have been investigated with respect to their structures, reactions, and applications in various fields, including chromatography, by using a variety of analytical techniques (7–13). However, in the literature there are relatively less applications of TLC in the qualitative analysis of metallic cation mixtures (3–5). Additionally, the separability and identification of some metal-DEDTC complexes have also been investigated by sequential TLC–IR systems (14).

In this study, mixtures of M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes were run on activated and non-activated thin layers of silica gel 60GF$_{254}$ (Si-60GF$_{254}$) using two different mobile phases. The retention factors (R_f), theoretical plate numbers (N) and resolution (R) of these complexes were determined and are

Figure 1. Molecular structures for M(DEDTC)$_2$ (A) and M(PyDTC)$_2$ (B) complexes.

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discussed in the context of the variation of stationary phase activation, mobile phase polarity, separation mechanisms, and the nature of the metal, ligand, and complexes.

Experimental

Chemicals, reagents, and materials

Si-60GF$_{254}$, NaDEDTC, NH$_4$PyDTC, Cu(NO$_3$)$_2$, and Co(NO$_3$)$_2$ were purchased from Merck (Darmstadt, Germany). Cu(DEDTC)$_2$, Co(DEDTC)$_2$, Cu(PyDTC)$_2$, and Co(PyDTC)$_2$ complexes were prepared by the reactions of NaDEDTC and NH$_4$PyDTC with Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$. A toluene–cyclohexane mixture (3:1, v/v) and pure toluene were used as the mobile phases. The layers of Si-60GF$_{254}$ were prepared using Loughborough-Griffin & George TLC unikit (Leicestershire, UK). All the chemicals were of analytical grade.

Synthesis of M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes

M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes were prepared by reactions of NaDEDTC and NH$_4$PyDTC with metal (II) nitrates, according to the method described in the literature, and their solutions in chloroform were used as samples for TLC applications (5).

Preparation of thin-layer plates

Slurries of Si-60GF$_{254}$ in water (1:2, w/v) were spread onto clean glass plates (7.5 × 15 cm) with a thickness of 250 μm using a spreader kit. Non-activated plates were obtained by stored them in a closed oven at 25°C for 12 h. After the non-activated plates were taken from the oven, they were immediately used for TLC. Plates were activated by heating them in an oven at 110°C for 2 h.

TLC applications

Two microliter aliquots from each of the complex solutions and their mixtures were spotted with micropipettes on the starting line, which was 2.0 cm from the bottom of the non-acti-vated plates. The original spots on the layers were dried at room temperature for 3 min. A pencil line was marked 5.5 cm above the starting line of each plate. Two developing chambers with 10 × 50 × 20-cm dimensions were used for running. Sixty milliliters of the toluene–cyclohexane mixture (3:1, v/v) was poured into one chamber and 60 mL of pure toluene into the other. The lids of the chambers were closed, and the chambers were allowed to stand for 15 min to ensure that saturation of the air in each chamber with solvent vapor occurred. Then the plates containing the spotted samples were carefully immersed in the developing chambers. When the solvent fronts reached 5.5 cm above the starting line of each plate, the plates were removed and dried. The migration distance of the solvent (Z_f) and of each spot (Z_x), as well as their width (W) were measured. R_f (from $R_f = Z_x/Z_f$), N [from N = 16$(Z_x/W_x)^2$], and R [from R = 2d/(W$_x$ + W$_y$)] were calculated (4,5).

Results and Discussion

In the TLC applications, Z_f and running time were 5.5 cm and 12 min, respectively. The chromatograms of M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes on activated and non-activated Si-60GF$_{254}$ layers are shown in Figures 2 and 3, respectively. As shown in the figures, these complexes are colored and can be easily visualized in the chromatograms. In addition, the spots of the complexes and their mixtures were developed without any tailing or decomposition and were successfully separated into their components.

The effect of stationary phase activation

The separability of mixtures is generally investigated by activated layers in normal-phase TLC applications. Non-activated layers are usually not investigated because of the assumption that the components cannot be successfully separated because of low activity and that they can chemically react with water molecules on the surface of these layers. In this study, the chromatographic behaviors of M(DEDTC)$_2$ and M(PyDTC)$_2$ com-
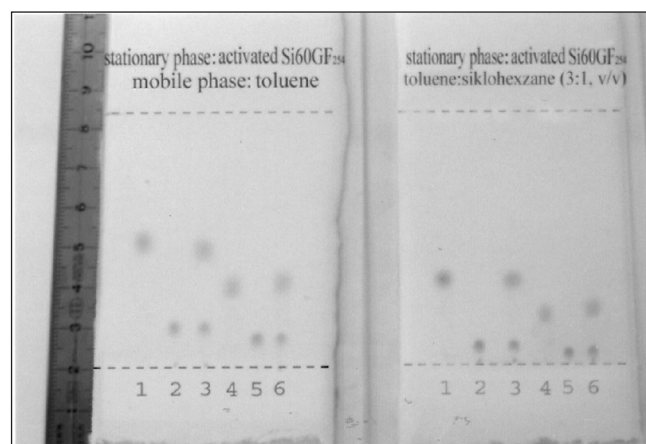

Figure 2. Chromatograms of the complexes and their mixtures on activated Si-60GF$_{254}$ layers. Compound numbers are Cu(DEDTC)$_2$, 1; Co(DEDTC)$_2$, 2; mixture of 1 and 2, 3; Cu(PyDTC)$_2$, 4; Co(PyDTC)$_2$, 5; mixture of 4 and 5, 6.

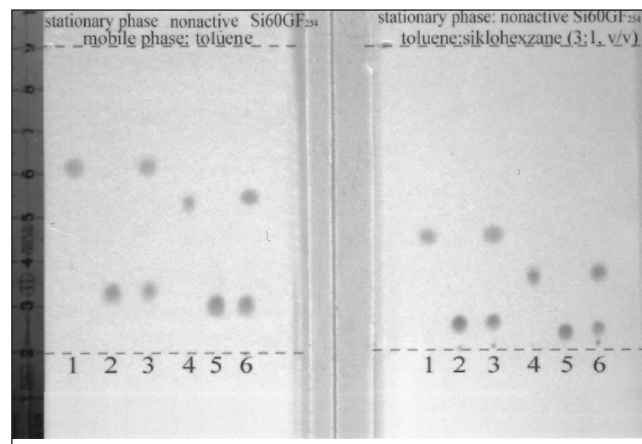**Figure 3.** Chromatograms of the complexes and their mixtures on non-activated Si-60GF$_{254}$ layers. Compound numbers Cu(DEDTC)$_2$, 1; Co(DEDTC)$_2$, 2; mixture of 1 and 2, 3; Cu(PyDTC)$_2$, 4; Co(PyDTC)$_2$, 5; mixture of 4 and 5, 6.

plexes were investigated to give a comprehensive understanding of the effects of activated and non-activated stationary phases. The R_f and N values for these complexes are given in Table I.

As seen from Table I, the R_f and N values of the M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes increase when the activated Si-60GF$_{254}$ layer was replaced by the non-activated Si-60GF$_{254}$ layer, when using the same mobile phase. The surface of the non-activated layer was covered by water molecules. The effectiveness of the Si-OH groups on a non-activated layer was lower than on an activated layer because the Si-OH groups were masked by water molecules. Thus, the activity of a non-activated layer was also lower. In this context, it followed that the increase of the R_f values stemmed from the weakening of the interactions responsible for the retention of complex components because of the decrease in the activity of the layer.

In summary, the chromatographic behavior of the complex components was susceptible to the changing of the activity of the stationary phase. On the other hand, the non-activated layers were more successful than the activated layers because of the higher N values. The original spots of the mixtures on the non-activated layer were more compact than on the activated layers because of the higher water content of the non-activated layers and poor solubility of the complexes in water. Therefore, the spots expand less on the non-activated layers. This means that the overall effects of Eddy diffusion, longitudinal diffusion, and mass transfer were smaller than on the activated layers.

The resolution values of the complexes as a function of stationary phase and mobile phase selection are given in Table II. As seen, the non-activated layers resulted in better resolution than the activated layers when using the same mobile phase. TLC using pure toluene as the mobile phase on the non-activated layer was the most successful of the chromatographic systems because it had the highest resolution value. Thus, the best analytical separation for both M(DEDTC)$_2$ and M(PyDTC)$_2$ was obtained using pure toluene on a non-activated layer.

The effect of mobile phase polarity

As seen in Table I, the R_f and N values of the M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes decreased when pure toluene was replaced by the toluene–cyclohexane mixture (3:1, v/v), when using the same stationary phase. In this context, it follows that the decrease in the R_f values stems from decreasing the mobile phase polarity. This can be explained in the following way: the polarity of toluene is higher than that of cyclohexane because of the π-electron system. Consequently, when the percentage of toluene decreases, the polarity of the solvent system, the interaction of the complex molecules with the mobile phase, and R_f also decrease. On the other hand, pure toluene as the mobile phase was more successful than the toluene–cyclohexane mixture (3:1, v/v) because of the higher N values of the complexes.

As seen in Table II, resolution of Cu(DEDTC)$_2$–Co(DEDTC)$_2$ and Cu(PyDTC)$_2$–Co(PyDTC)$_2$ pairs decreases when pure toluene was replaced by toluene–cyclohexane mixture (3:1, v/v) using the same stationary phase. Based on these results, it follows that the decrease of resolution stems from a decrease of mobile phase polarity. Consequently, pure toluene was more successful as the mobile phase than the toluene–cyclohexane mixture (3:1, v/v).

The effect of retention mechanism

In a chromatographic application, the retention mechanism depends on the liquid preadsorbed on the layer's surface, the nature of the mobile phase, and the properties of the sample components. In this context, the adsorbed water on the surface of non-activated Si-60GF$_{254}$ layers was not miscible with pure toluene or toluene–cyclohexane mixture (3:1 v/v), and the separation of complex molecules was carried out via Nerst distribution equilibriums, as in liquid–liquid chromatography (LLC). In contrast, the surface of the activated Si-60GF$_{254}$ layer was not covered by water, and adsorption equilibriums were established instead of distribution equilibriums between the stationary and mobile phases, as in solid–liquid chromatography (SLC). Therefore, the retention mechanisms of the M(DEDTC)$_2$ and

Table I. R_f and N Data of M(DEDTC)$_2$ and M(PyDTC)$_2$ Complexes

| Complex | Running Time (min) | Activated Layer | | Non-activated Layer | |
		Toluene ($R_f \pm$ SD[†]) (N ± SD)	Toluene–cyclohexane* ($R_f \pm$ SD) (N ± SD)	Toluene ($R_f \pm$ SD) (N ± SD)	Toluene–cyclohexane* ($R_f \pm$ SD) (N ± SD)
Cu(DEDTC)$_2$	12	0.47 ± 0.03 (576 ± 29)	0.31 ± 0.02 (400 ± 20)	0.60 ± 0.03 (1129 ± 57)	0.36 ± 0.01 (625 ± 31)
Co(DEDTC)$_2$	12	0.14 ± 0.01 (324 ± 16)	0.06 ± 0.01 (29 ± 2)	0.27 ± 0.01 (642 ± 32)	0.09 ± 0.01 (64 ± 3)
Cu(PyDTC)$_2$	12	0.31 ± 0.02 (400 ± 20)	0.20 ± 0.01 (169 ± 9)	0.50 ± 0.03 (2178 ± 109)	0.23 ± 0.01 (256 ± 13)
Co(PyDTC)$_2$	12	0.10 ± 0.01 (87 ± 4)	0.05 ± 0.01 (16 ± 1)	0.16 ± 0.01 (121 ± 6)	0.06 ± 0.01 (29 ± 2)

* (3:1, v/v). Number of repeated runs = 3.
[†] SD = standard deviation.

Table II. Resolution Data of Cu(DEDTC)$_2$–Co(DEDTC)$_2$ and Cu(PyDTC)$_2$–Co(PyDTC)$_2$ Complex Couples

| Complex | Activated layer | | Non-activated layer | |
	Toluene R	Toluene–cyclohexane* R	Toluene R	Toluene–cyclohexane* R
Cu(DEDTC)$_2$–Co(DEDTC)$_2$	3.00 ± 0.25	2.30 ± 0.12	3.30 ± 0.17	2.70 ± 0.14
Cu(PyDTC)$_2$–Co(PyDTC)$_2$	1.90 ± 0.10	1.40 ± 0.07	3.40 ± 0.17	1.70 ± 0.09

* (3:1, v/v) mixture. Number of repeated runs = 3.

M(PyDTC)$_2$ complexes are different on activated and non-activated layers.

As shown in Table I, the R_f values of M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes changed when the activated layer was replaced by the non-activated layer and when using pure toluene as the mobile phase. It follows that the change in the R_f values is because of differences in the retention mechanism. This chromatographic behavior pattern is also valid when using the toluene–cyclohexane mixture (3:1 v/v) as the mobile phase.

The effect of the nature of the metal and metal complexes

As seen in Table I, the R_f values of either group complexes show significant difference when the ligands and the mobile and stationary phases are the same. This results from the difference in the electronic structures of the metal atoms. For example, the difference in the R_f values of the Cu(DEDTC)$_2$ and Cu(PyDTC)$_2$ complexes on the non-activated layer using pure toluene was 0.10, whereas it was 0.33 for Cu(DEDTC)$_2$, and Co(DEDTC)$_2$. This showed that the metal in the complex had a greater effect than the ligand on the R_f value. Although the charges, radii, and charge densities of Cu^{2+} and Co^{2+} in aqueous solutions were very similar, their d^7 and d^9 electronic configurations lead to the different physical and chemical properties of the complexes. The wavelength values for maximum reflections of the Cu(DEDTC)$_2$ and Co(DEDTC)$_2$ spots were 273 nm and 325 nm, respectively (3). Thus, it followed that because of these d electron distributions in the metal complexes with the same ligand, the extra stabilization energies decrease from Co^{2+} to Cu^{2+}. Hence, the interactions of the corresponding complexes decrease with the stationary phase, though the interactions with the mobile phase increased in the same order. This relationship was also valid for these metals and their complexes in all the other chromatographic systems.

Conclusion

This study was carried out on mixtures of M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes in order to better understand the effects of stationary phase activation, mobile phase polarity, and retention mechanism, as well as the nature of the metal, ligand, and complexes on the chromatographic parameters (e.g., R_f, N, and R) and to determine the separability of cation mixtures. In light of this study, the following conclusions can be made:

(*i*) M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes do not interact chemically with activated or non-activated Si-60GF$_{254}$ layers and mobile phases in TLC systems. Because the formation rates of the complexes are very high, the applications were carried out in a short time. These complexes are colored and are easily visualized in the chromatograms.

(*ii*) This study shows that it is possible to qualitatively analyze and to satisfactorily separate a mixture Cu^{2+} and Co^{2+} cations using TLC following the complexing of the cations with DEDTC or PyDTC ligands. The best analytical separation for both M(DEDTC)$_2$ and M(PyDTC)$_2$ complexes is obtained when using pure toluene on a non-activated layer.

(*iii*) The R_f, N, and R values of the complexes increase when the activated layer is replaced by the non-activated layer, though the mobile phase is constant. The R_f values increase because the interactions responsible for the retention of the complex molecules weakened because of the decrease in the activity of the layer. The N values increase because of the expansion of the spot on the non-activated layer being less than on the activated layer. This is because of the higher water content of the non-activated layer and lack of solubility of the complexes in water.

(*iv*) The R_f, N, and R values of the complexes decrease when pure toluene is replaced with the toluene–cyclohexane mixture (3:1, v/v) as the mobile phase. It follows that the decrease of the R_f values stems from the decrease of the mobile phase polarity.

(*v*) The separation of M(DEDTC)$_2$ and M(PyDTC)$_2$ molecules on the non-activated layer was carried out via Nerst distribution equilibriums, as in LLC. However, because there is no water covering on the activated layer, adsorption equilibriums are established instead of distribution equilibriums between the stationary and mobile phases, as in SLC.

(*vi*) Although the ligand and mobile and stationary phases were the same, the significant difference in the R_f values of the two group complexes resulted from the difference in the electronic structure of the metal atoms. The metal in the complex has a greater effect on the R_f value than the ligand. Although the charges, radii, and charge densities of Cu^{2+} and Co^{2+} in aqueous solutions are close to each other, their d^9 and d^7 electronic configurations lead to the different physical and chemical properties of the complexes. Thus, when the extra stabilization energies of the metal complexes with the same ligand decrease from Co^{2+} to Cu^{2+}, the interactions of the corresponding complexes with the stationary phase decrease, though the interactions with the mobile phase increase in this order.

Acknowledgments

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