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THIN-LAYER CHROMATOGRAPHY OF β-DIKETONES AND THEIR METAL CHELATES

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SUMMARY

The thin-layer chromatographic behaviour of β-diketones and their metal chelates on silica gel HR in different single solvents were studied. Ten β-diketones and twelve metal chelates, *viz.*, iron(III), cobalt(III) and chromium(III) derivatives of acetylacetone, benzoylacetone, thenoyltrifluoroacetone and benzoyltrifluoroacetone, were investigated, using five developing solvents, *viz.*, carbon tetrachloride, toluene, benzene, dichloromethane and diethyl ether.

It was found that the chromatographic behaviour of compounds containing a $-CF_3$ functional group was different from those that did not, and that there was a correlation between the behaviour of metal chelates and the ligand.

In addition, the effects of the solvents used as the developer were compared in terms of solubility parameters.

INTRODUCTION

Thin-layer chromatography (TLC) has the advantages of simplicity, rapidity and high sensitivity, but relatively little has been published on its application to organometallic compounds. Several studies on the TLC of metal chelates have been published, *e.g.*, on ferrocene derivatives[1,2], metal–EDTA complexes[3] and metal dithizonates[4–6], diethyldithiocarbamates[7–10] and α-nitroso-β-naphtholates[11].

Metal chelates are very useful in the determination and separation of some metal ions by colorimetry, titration, solvent extraction, etc., and the combination of the advantages of TLC with the use of metal chelates should extend the analytical utility of these compounds further. In order to develop such a combination satisfactorily, systematic studies on the chemical and physical properties of metals, ligands and solvents used as the developer or eluent, and other chromatographic conditions, are necessary, as have been carried out previously for solvent extraction techniques.

We have carried out systematic studies on the TLC of β-diketones, which represent one of the most frequently used types of chelating agents in analytical chemistry, and their metal chelates. As is well known, β-diketones have two tautomers in keto and enol forms, as shown in Fig. 1, and the latter forms some metal derivatives. Applications of some β-diketones on silica gel layers have been

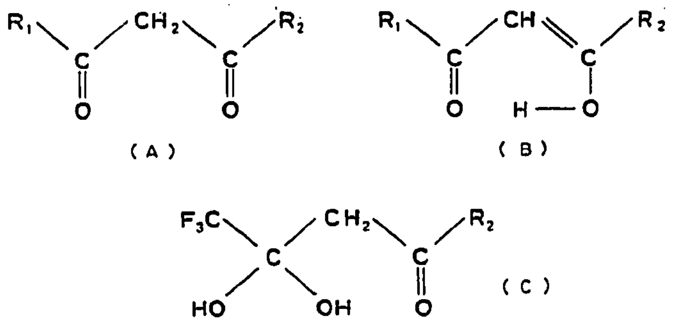

Fig. 1. Different forms of β-diketones. (A) keto form; (B) enol form; (C) hydrated form of a β-diketone containing a CF_3 substituent.

reported[12], and the behaviour of β-diketone–metal chelates have been investigated, *e.g.*, acetylacetone[3], and trifluoroacetylacetone chelates[13]. However, these studies seem to be incomplete, and more systematic studies are required.

In the present work, the TLC behaviour of ten β-diketones and twelve metal chelates on silica gel HR using various developing solvents were investigated in order to establish the correlation between the behaviour of a chelating agent and its metal chelates. β-Diketones applied are grouped into three classes according to the substituent functional groups present, indicated as R_1 and R_2 in Fig. 1, as follows:

Class I: R_1 and R_2 are alkyl or aryl; *e.g.*, acetylacetone (AA), benzoylacetone (BA) and dipivaloylmethane (DPM);

Class II: either R_1 or R_2 is –O-alkyl or –N-aryl; *e.g.*, ethyl malonate (EM), ethyl acetoacetate (EAA) and acetoacetanilide (AAA);

Class III: one of the groups is trifluoromethyl; *e.g.*, trifluoroacetylacetone (TFA), benzoyltrifluoroacetone (BFA), furoyltrifluoroacetone (FTA) and thenoyltrifluoroacetone (TTA).

The behaviour of the metal chelates of AA, BA, TTA and BFA was also investigated. The former two ligands belong to class I and the latter two to class III. Iron(III), chromium(III) and cobalt(III) were selected as the metals for the formation of chelate compounds with such ligands; they are typical transition metals, and the chelates formed are neutral and readily soluble in many organic solvents.

EXPERIMENTAL

β-Diketones

The β-diketones used are listed in Table I. BA, AAA, EM and EAA were obtained from Wako Pure Chemicals (Osaka, Japan) and the others from Dojindo Co. (Kumamoto, Japan). Most of these commercial materials were purified by either distillation or sublimation, and were dissolved in *n*-hexane, except for the poorly soluble AAA, which was dissolved in benzene.

Metal chelates

$Fe(AA)_3$, $Cr(AA)_3$ and $Co(AA)_3$ were available commercially (Dojindo Co.). $Fe(BA)_3$, $Fe(TTA)_3$ and $Fe(BFA)_3$ were prepared by the reaction of the ligands with

TABLE I

β-DIKETONES USED IN THE PRESENT WORK

β-Diketone	*Abbreviation*	*R_1**	*R_2**	*Purification***	*Sample solution (mg per 5 ml of n-hexane)*
Acetylacetone	AA	CH_3	CH_3	D	22.76
Benzoylacetone	BA	CH_3	C_6H_5	S	28.315
Dipivaloylmethane	DPM	$(CH_3)_3$	$(CH_3)_3$	—	27.60
Acetoacetanilide	AAA	CH_3	$NH \cdot C_6H_5$	—	23.315***
Ethyl malonate	EM	C_2H_5O	OC_2H_5	D	35.20
Ethyl acetoacetate	EAA	CH_3	OC_2H_5	D	20.19
Trifluoroacetylacetone	TFA	CF_3	CH_3	—	24.50
Benzoyltrifluoroacetone	BFA	CF_3	C_6H_5	S	28.435
Furonyltrifluoroacetone	FTA	CF_3	2-Furyl	—	34.0
Thenoyltrifluoroacetone	TTA	CF_3	2-Thiophenyl	S	24.530

* Shown in Fig. 1.

** D = distillation; S = sublimation.

*** Dissolved in benzene.

iron(III) nitrate buffered by sodium acetate[14], and $Cr(BA)_3$, $Cr(TTA)_3$ and $Cr(BFA)_3$ by the reaction of the ligands with chromium nitrate involving the hydrolysis of urea[15]. $Co(BA)_3$, $Co(TTA)_3$ and $Co(BFA)_3$ were obtained by the reaction of the ligands with $Na_3[Co(CO_3)_3] \cdot 3H_2O$ with the addition of dilute nitric acid[16]. Each of the crude reaction products was purified by rapid chromatography on an acid-washed alumina column in order to remove unreacted ligand and unidentified metal complexes, as described by Fay and Piper[17,18]. The materials were characterized by C and H ultimate analysis. Each sample solution contained *ca.* 30 mg of a metal chelate in 1 ml of benzene solution.

Developing solvents

Commercially obtained carbon tetrachloride, toluene, benzene, dichloromethane and diethyl ether were purified by distillation after ordinary chemical treatment.

Preparation of TLC plates

The silica gel used in the present work must be of high purity because of the high reactivity of β-diketones. Silica gel HR (E. Merck, Darmstadt, G.F.R.) was used to prepare the plates without any binder so as to avoid undesirable influence due to the binder. For the coating of five plates, each of dimensions 20 × 20 cm, a homogeneous slurry of 30 g of silica gel HR with 65 ml of redistilled water was employed, using a Stahl-type spreader to adjust the layer thickness to 300 μm. The coated layer was air-dried for 2 h, activated for 1 h at 105° and applied after cooling for 2 h.

The activity of the layer was checked by using standard dyes ("Test Mix", Wako Pure Chemicals). The R_F values determined using benzene as a developer were 0.54, 0.21 and 0.02 for butter yellow, Sudan Red G and indophenol, respectively. The results showed that the activity of the layer corresponds to Brockman II–III.

Procedure

The chromatography was carried out at a temperature of 25 ± 1°. Portions of 1–2 μl of each sample solution were spotted 20 mm from the lower edge of the layer, with 15 mm between neighbouring spots. The development was carried out in a sandwich chamber with an internal width between the plates of 2 mm. Each plate was dipped about 10 mm into the solvent and the length of running from the starting point to solvent front was 120 mm. After development, the chromatographed plate was exposed in air in order to remove the impregnated solvent. The spots of β-diketones were made visible with iodine vapour, while the metal chelates were detected by their characteristic colours. For each system, at least five runs were carried out.

RESULTS AND DISCUSSION

TLC of β-diketones

Chromatograms obtained for β-diketones in various solvents are shown in Fig. 2.

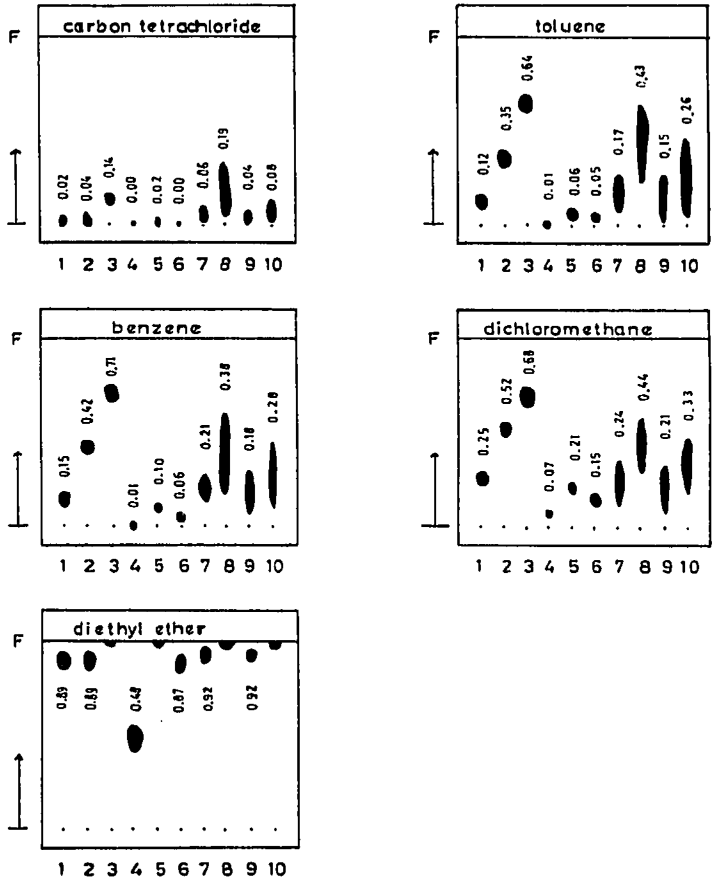

Fig. 2. Thin-layer chromatograms of β-diketones on silica gel HR, carried out in various solvents: 1, AA; 2, BA; 3, DPM; 4, AAA; 5, EM; 6, EAA; 7, TFA; 8, BFA; 9, FTA; 10, TTA. F indicates solvent front. The values adjacent to the spots show the R_F values at the centres (mean of five measurements).

With diethyl ether as the developer, most of the test materials move near to the solvent front, which suggests that this solvent is too strong for use as a developer for these compounds. The chromatographic behaviour can be summarized as follows. The compounds belonging to class I (AA, BA and DPM) give even ellipsoidal spots, and the R_F values increase in the order AA < BA < DPM. They are separated completely from each other using toluene, benzene and dichloromethane. The spots of the class II compounds can be observed distinctly on the chromatographic layer, none of them having a large R_F value in comparison with those of class I compounds in the same solvent. The R_F values of class I and II β-diketones increase in the following order, independent of the solvent: AAA < EAA < EM < AA < BA < DPM.

Compounds of class III give very diffuse spots (tailing), contrary to the situation with other classes. For example, with benzene as developer, the ranges of the R_F values from the front to the rear edges of the spots are 0.28–0.13, 0.60–0.17, 0.28–0.08 and 0.44–0.12 for TFA, BFA, FTA and TTA, respectively. Such diffuse and faint spots result in less accurate determinations of the R_F values and compounds in this class are never separated from each other under these conditions. The reason for the specific behaviour of β-diketones in this class can be explained as follows. These compounds contain trifluoromethyl substituents and it is known that such β-diketones are easily converted into hydrated forms (Fig. 1C) in the presence of water[19]. As silica gel contains a large amount of water (5 and 15% in silica gel corresponding to Brockman activity II and III, respectively[20]), the hydrated β-diketones must predominate on the chromatographic layer. This is consistent with the following experimental results for TTA. (*i*) A cyclohexane solution of TTA gives absorption maxima at 338 nm (shoulder) and 314 nm, but after spotting on the silica gel layer, it gives further maxima at 268 nm and *ca.* 298 nm (shoulder). TTA hydrate* dissolved in wet dioxane gives absorption maxima at *ca.* 264 and 286 nm (Fig. 3). It is known that the enol form of TTA shows absorption maxima at 338 and 314 nm, and the keto hydrated form at 292

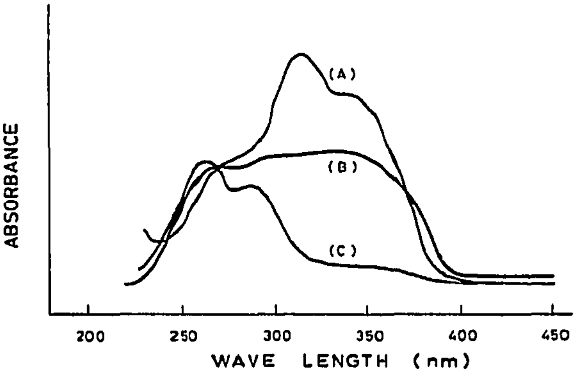

Fig. 3. UV absorption spectra of TTA. (A) cyclohexane solution; (B) TTA spotted on silica gel layer; (C) TTA hydrate dissolved in wet dioxane (TTA concentrations not identical).

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* TTA hydrate was prepared as described by King and Reas[21].

and 266 nm in *n*-hexane[19]. (*ii*) The resultant chromatogram of TTA is the same as that of TTA hydrate in benzene. On the basis of such a spectrophotometric comparison, the chromatographic behaviour of FTA can be explained in a similar manner.

The R_F values of β-diketones belonging to class III increase independent of the solvent in the order FTA < TFA < TTA < BFA.

TLC of metal chelates

Chromatograms and R_F values of metal chelates in various solvents are shown in Fig. 4. Iron chelates migrate with extensive tailing, which makes the determination of accurate R_F values difficult. It is obvious that the mobility of metal chelates of trifluoromethyl-containing β-diketones of class III, *i.e.*, TTA and BFA, is very different from that of the chelates of AA and BA in class I.

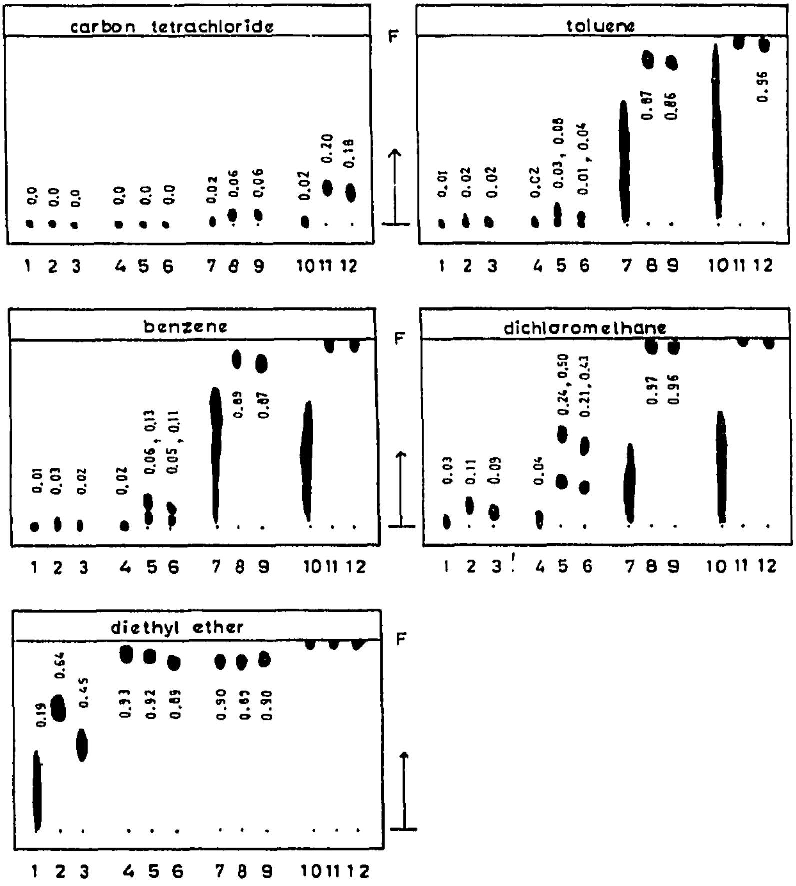

Fig. 4. Thin-layer chromatograms of metal chelates on silica gel HR: 1, $Fe(AA)_3$; 2, $Cr(AA)_3$; 3, $Co(AA)_3$; 4, $Fe(BA)_3$; 5, $Cr(BA)_3$; 6, $Co(BA)_3$; 7, $Fe(TTA)_3$; 8, $Cr(TTA)_3$; 9, $Co(TTA)_3$; 10, $Fe(BFA)_3$; 11, $Cr(BFA)_3$; 12, $Co(BFA)_3$. The values adjacent to the spots show the R_F values at the centres (mean of five measurements).

With toluene or benzene, $M(TTA)_3$ and $M(BFA)_3$, where M represents a metal, move near to the solvent front, while $M(AA)_3$ and $M(BA)_3$ remain near the origin. Especially with chromium and cobalt chelates, the R_F values of $M(TTA)_3$ and $M(BFA)_3$ are higher than those of the corresponding ligands. However, with $M(AA)_3$ and $M(BA)_3$, opposite results are obtained. From the standpoint of the ligands, the difference in the chromatographic behaviour of metal chelates can be summarized as follows. The chelates $M(AA)_3$ are the most difficult to move, and it is necessary to use dichloromethane or diethyl ether in order to obtain reasonable running. The chelates $M(BA)_3$ were more mobile than $M(AA)_3$. Chromium and cobalt chelates are separated into double spots and, according to the solubility data[17], these spots might be assigned to the *cis*- (upper spot) and *trans*- (lower) isomer, respectively. $M(TTA)_3$ and $M(BFA)_3$ are very mobile. Chromium and cobalt chelates move near to the solvent front in all of the solvents except carbon tetrachloride, and the R_F values of $M(BFA)_3$ are higher than those of $M(TTA)_3$. The mobility sequence of metal chelates with different ligands is the same as that of the corresponding free ligands. Of the various metal chelates formed with a particular ligand, the R_F values increase, independent of the solvent, in the order iron < cobalt < chromium.

Effects of the developing solvents

The elution power of the solvent has generally been discussed on the basis of the polarity of the solvent, and the dielectric constant (ε) or dipole moment (μ) is frequently adopted as a criterion. An eluotropic series of the solvents proposed by Trappe[22] or Strain[23] might be useful in the present work. However, we have attempted to discuss the elution power of the solvents from the point of view of dissolving power. One of the properties of a solvent is the solubility parameter, as defined in regular solution theory[24]. Solubility parameters have been applied successfully to studies of solvent extraction[25-27], and a few applications to chromatography have been reported[28,29]. Physical properties, including solubility parameters, of the solvents used are listed in Table II. The relationship between the R_M values of β-diketones and the solubility parameter of the solvents, δ, is shown in Fig. 5, where R_M is defined by

TABLE II

PHYSICAL PROPERTIES OF SOLVENTS

Solvent	*Dielectric constant, ε, at 20° (ref. 30)*	*Dipole moment, μ (Debye units) (ref. 30)*	*Solubility parameter, δ, at 25° (ref. 24)*
Carbon tetrachloride	2.238	0.00	8.6
Toluene	2.379*	0.39	8.9
Benzene	2.284	0.00	9.15
Dichloromethane	9.08	1.55	9.7
Diethyl ether	4.335	1.15	7.4

* At 25°.

$$R_M = \log(1/R_F - 1)$$

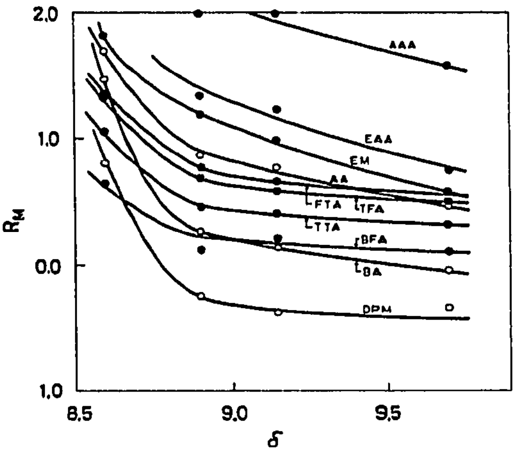

Fig. 5. Dependence of the R_M values of β-diketones on the solubility parameter (δ) of the developing solvent.

It can be seen that the greater the solubility parameter, the smaller is the R_M value (the greater the R_F value), except for diethyl ether. The solubility parameter of diethyl ether is 7.4, which is the smallest of those studied, but the R_F value for this solvent is the highest. In the case of diethyl ether, a different factor must be considered. The effects of the solvents in the TLC of metal chelates are similar to those in the TLC of β-diketones. With the exception of diethyl ether, the increase in the R_F values of β-diketones and metal chelates is parallel to the increase in solubility parameters, and not parallel to the increase in either the dielectric constant (ε) or dipole moment (μ). This suggests that the solubility parameter is a very useful approach in the elucidation of the elution power of solvents in chromatography. The mobility of all sample materials depends on the developing power of solvents, in the order carbon tetrachloride, toluene, benzene, dichloromethane and diethyl ether.

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