Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Haworth, D. T. and Liu, Tai-Ching(1976) 'Thin-Layer Chromatography of Some Ferrocene Derivatives and Other Cyclopentadienyl Organometallics', Separation Science and Technology, 11: 4, 329 — 334
To link to this Article: DOI: 10.1080/01496397608085325
URL: http://dx.doi.org/10.1080/01496397608085325

SEPARATION SCIENCE, 11(4), pp. 329–334, 1976

Thin-Layer Chromatography of Some Ferrocene Derivatives and Other Cyclopentadienyl Organometallics

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Abstract

Microcrystalline cellulose as an absorbent in inorganic thin-layer chromatography has been successfully applied to the separation of various ferrocene derivatives and organometallics containing cyclopentadiene. The effect of gross dielectric constant versus the R_F value is also discussed as well as the analogy between silica-gel chromatographic separations.

Work in our laboratory has shown that microcrystalline cellulose can be successfully used as an absorbent in inorganic thin-layer chromatography (*1*, *2*). Its application to the separation of organometallic compounds containing cyclopentadienyl is reported here. A TLC one-dimensional separation technique on microcrystalline cellulose was developed which allows the separation of 10 ferrocene-type compounds and 10 cyclopentadienyl organometallic compounds.

Schlögl and co-workers have used silica gel in the separation of ferrocene derivatives (*3*). Their investigations also include oxidation and isomer separation (*4*, *5*). Several mono- and disubstituted ferrocenes were also separated on silica gel by Tanikawa and Arakawa. They concluded that cellulose could not be used for an absorbent (*6*). A comparison of R_F values of some ferrocene compounds and their benzenoid analogs separated on silica indicated that the ferrocene analog had a lower R_F value than the corresponding phenyl compound (*7*). TLC on alumina for some ferrocene derivatives has also been reported (*8*). Unlike the silica gel and alumina layers, the microcrystalline cellulose plates used in this study do not have to be heated to activate them.

EXPERIMENTAL

Plate Preparation

The microcrystalline cellulose slurry was prepared and spread on 20 × 5 cm plates at a thickness of 0.75 mm as previously reported (*9*, *10*).

Solution Preparation and Application

Benzene or chloroform solutions [0.5 to 1.0 (w/v) %] of the various ferrocenes and benzene or water solutions of the various cyclopentadienyl organometallics were applied to the microcrystalline-coated glass plates by capillary syringes. They were allowed to dry before insertion into the chromatographic tank (Desaga type). Except for the ferrocene carboxylic acid which is light sensitive, the ferrocene solutions were stable; however, most of the organometallic solutions decomposed within a few hours.

Solvent Systems and Detection

The solvent systems were prepared from redistilled or reagent grade chemicals listed in Table 1. Since the ferrocenes are colored, special visualizing procedures are not necessary; ferrocene is yellow, monoacylferrocenes are orange, diacyl and monobenzoyl derivatives are red. Less

TABLE 1

Solvent Systems Used In TLC Separations

No.	Solvent system	No.	Solvent system
1	Pentane	7	Methanol: water (10:80)
2	Acetone	8	Methanol: water (10:40)
3	Methanol	9	Methanol: water (10:1)
4	Water	10	Methanol: water (10:2)
5	Toluene	11	Methanol: water (10:2.5)
6	Ether: methanol (30:1)	12	Methanol: water (10:3)

TABLE 2

R_F Values of Ferrocene Derivatives Separated by TLC Using Microcrystalline Cellulose

Solvent system	Fc[a] (yellow)	Fc(COCH$_3$) (orange)	Fc(COCH$_3$)$_2$ (red)	Fc(COC$_6$H$_5$) (red)	Fc(COC$_6$H$_5$)$_2$ (dark red)	Fc(COOH) (pale brown)	Fc(COOH)$_2$ (pale (orange)	Fc(CHO) (orange)	Fc(HgCl) (pale yellow)	Fc(HgCl)$_2$ (light brown)
1	1.00	1.00	0.66	1.00	0.64	0.00	0.00	—	0.55	0.00
3	—	—	—	—	—	—	—	—	0.95	0.00
4	—	0.80	0.79	0.00	0.00	0.92	0.42	0.80	—	0.00
5	1.00	—	—	—	—	0.74	0.00	—	—	—
6	1.00	0.88	0.33	1.00	0.84	—	—	—	—	—
7	—	0.87	—	0.00	—	—	—	—	—	—
11	1.00	—	—	—	—	—	—	—	0.29	0.00

[a] Fc = Fe(C$_5$H$_5$)$_2$.

TABLE 3

R_F Values of Cyclopentadienyl Organometallic Compounds Separated by TLC Using Microcrystalline Cellulose

Solvent system	Fe(cp)$_2$ (yellow)	Ni(cp)$_2$ (pale brown)	Ti(cp)Cl$_3$ (green-yellow)	Tl(cp) (pale brown)	cpCo(CO)$_2$ (brown)	Zr(cp)$_2$Cl$_2$ (colorless)	Fe(Pϕ_2)$_2$ (orange)	cpFe(CO)$_2$I (dark green)	Hg[cpCr(CO)$_3$]$_2$ (green)	[cpFe(CO)$_2$]$_2$ (dark red)
1	1.00	1.00	—	0.00	—	—	—	—	—	—
2	1.00	—	—	—	—	0.11	1.00	—	1.00	—
3	—	0.86	—	0.00	—	—	—	—	—	—
8	—	—	—	—	—	—	0.00	0.60	—	0.00
9	0.94	0.71	0.00	—	—	—	—	—	—	—
10	—	—	—	0.00	0.81	—	—	—	—	—
12	1.00	—	—	—	0.50	—	—	—	—	—

intensively colored ferrocene derivatives were detected in an iodine chamber yielding brown spots on a white background. The cyclopentadienyl organometallics were also detected by their color or by insertion into the iodine chamber. The R_F values (Tables 2 and 3) are averages of five runs. The color in parenthesis in Tables 2 and 3 is the color of the detected spot.

Dielectric Constant Studies

The dielectric constant measurements were obtained on a Sargent Model V ocsillator. A standarization curve (instrument reading vs dielectric constant) was prepared using reagent-grade chemicals.

RESULTS AND DISCUSSION

R_F Value and Functionality

From the data given in Tables 2 and 3 it appears that the polarity of the solvent as well as the polarity of various solutes is the major factor governing solubility and adsorption. Thus most of the separations by TLC can be explained in terms of increased polarity with an increase in the number of functional groups. For example; in the less polar ether: methanol (30:1) solvent system (No. 6), the nonpolar ferrocenes move to the top of the plate whereas the more polar monoacetyl and diacetyl ferrocenes had R_F values of 0.88 and 0.33, respectively. This trend is also shown by comparison of the separation of mono- and disubstituted ferrocenes containing acetyl, benzoyl, carboxylic acid, or chloromercuri groups in nonpolar solvent systems. This trend is also verified in separation of the more symmetrical benzoylferrocene vs acetylferrocene.The former does not move in a polar solvent system of methanol: water (No. 7) whereas the latter gave an R_F value of 0.87. Further evidence for this trend is in the TLC separation of the less polar ferrocene compounds with their benzenoid derivatives (7); for example, C_6H_5CHO moved farther (0.75 R_F) than FcCHO (0.30 R_F) in benzene–acetone (30:1). Similar conclusions are also obtained on comparison of ferrocenes with different functional groups separated in the same solvent system. In pentane (No. 1) movement of the diacetyl- and dibenzoylferrocene is obtained when chromatogramed with the dicarboxylic acid derivative. A reversal of this movement is obtained by using water (No. 4) as the solvent system.

This trend is also shown for the cyclopentadienyl organometallics.

TABLE 4

A Comparison of Dielectric Constants to R_F Values for Acetylferrocene and Benzoylferrocene

Solvent system[a] H_2O:methanol	ε	R_F	
		$Fc(COCH_3)$	$Fc(COC_6H_5)$
1:0	80.4	0.00	0.85
1:9	74.5	0.00	0.87
1:8	74.5	0.00	0.87
1:7	73.5	0.00	0.93
1:6	72.0	0.27	0.83
1:5	72.5	0.36	0.85
1:2	67.0	0.86	0.96
1:1	60.0	0.95	0.96
2:1	51.5	1.00	1.00
4:1	46.5	1.00	1.00
0:1	33.6	1.00	1.00

[a] Solvent ratio by volume.

TABLE 5

Dielectric Constant Studies vs R_F Value for 1,1′-DiacetylFc and 1,1′-Fcdicarboxylic acid

Solvent system[a] acetone:methanol	ε	R_F	
		$Fc(COCH_3)_2$	$Fc(COOH)_2$
1:0	19.5	1.00	0.00
10:1	20.5	1.00	0.00
10:2	21.3	1.00	0.00
10:3	21.8	1.00	0.00
10:4	22.5	1.00	0.00
1:1	25.2	0.97	0.00
1:2	27.7	0.96	0.35
1:3	28.5	0.95	0.45
1:6	30.7	0.82	0.66
1:8	31.0	0.77	0.70
1:20	31.2	0.75	0.71
0:1	32.5	0.75	0.74

[a] Solvent ratio by volume.

$Fe(Cp)_2$ and $Ni(Cp)_2$ move in pentane; however, the more polar Tl(cp) does not move. The ionic character of $(cpFe(CO_2)^+(I)^-$ accounts for its migration in water vs the dimer of $cpFe(CO)_2$. The one case where polarity is not as important as solubility in the solvent and adsorption on the microcrystalline cellulose is the TLC separation of $Fe(cp)_2$ and $Ni(cp)_2$.

Dielectric Constant Studies

Tables 4 and 5 show typical data taken on comparison of TLC separation with the gross dielectron constant of the solvent. While our previous data has shown that acetylferrocene and benzoylferrocene can be separated in water but not in methanol, the movement of the acetyl derivative with decreased dielectric constant (increased methanol) is shown in Table 4. This same effect is shown in Table 5 for the separation of 1, 1′-diacetylferrocene and 1, 1′-ferrocene dicarboxylic acid in various acetone–water solvent systems. One concludes that there exists a certain range in which the dielectric constant falls in order to obtain a satisfactory separation for any given set of compounds in solvent systems which consist of the same components but different compositions.

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Received by editor November 10, 1975