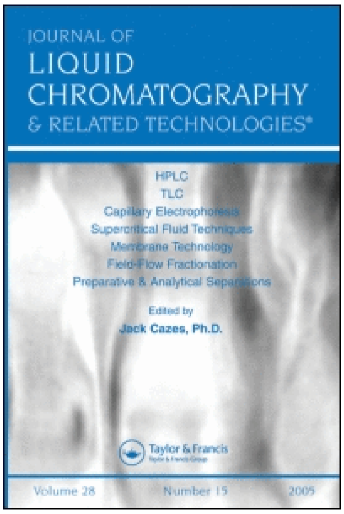

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PLAIN THIN-LAYER CHROMATOGRAPHY OF SOME HERBICIDES AND RELATED COMPOUNDS ON ADMIXTURE OF BARIUM SULFATE AND CALCIUM SULPHATE IN MIXED SOLVENTS

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ABSTRACT

Some carboxylic herbicides and plant growth regulators such as benzoic acid, 4-chlorophenoxyacetic acid, cinnamic acid, 2,4-D, indole-3-acetic acid, indolepropionic acid, α-naphthaleneacetic acid, β-naphthaleneacetic acid, β-naphthoxyacetic acid, phenoxyacetic acid, TCA and 2,4,5-T have been separated on $BaSO_4$-$CaSO_4$ (1:1) coatings in mixed solvent systems. Quantitative separations of indole-3-acetic acid (100 µg) from 50-100 µg of benzoic acid, α-naphthaleneacetic acid and 2,4,5-T have been carried out successfully.

INTRODUCTION

Calcium sulphate was used for the separation of carboxylic herbicides by plain (P-TLC)[1], ion-pair reverse-phase (IP-RP TLC)[2], sequential (S-TLC)[3] and two-dimensional (2D-TLC)[4] thin-layer chromatographies. P-TLC on admixture of $CaSO_4$ and

$BaSO_4$ [5] was used for the separation of a number of carboxylic acids such as cinnamic, citric, indole-3-acetic, maleic, malic, malonic, β-naphthaleneacetic, β-naphthoxyacetic, oxalic, phenoxyacetic, salicylic and tartaric in single solvent systems. It was reported in our previous paper[6] that the separation potential of $BaSO_4$-$CaSO_4$ coatings can be enhanced by impregnating the coating with coconut oil.

Literature shows that a number of papers were devoted to separate carboxylic herbicides by TLC on silufol[7,8] or a 2:3 mixture of silica gel and Kieselguhr[7], and preadsorbent silica gel layers[9] impregnated with $AgNO_3$ in mixed solvent systems. However separation potential of $BaSO_4$-$CaSO_4$ coatings in mixed solvent systems has not been tested so far.

Therefore, in continuation to our previous work, now such an attempt has been made. The results obtained are discussed in this paper.

EXPERIMENTAL

Apparatus

Stahl apparatus with a universal applicator, glass plates (20 x 3 cm), glass jars (25 x 5 cm), Bausch and Lomb spectronic-20 spectrophotometer, centrifugal machine (Baird & Tatlock Ltd.,England), magnetic stirrer (Sunvic,U.K.), glass coated magnetic bars (approx.length 0.8 cm), temperature controlled electric oven (Tempo,India), lambda pipette, conical flask 10 ml etc. were used.

Chemicals

Ferric chloride anhydrous (Rambaxy, India); methanol (Glaxo, India); perchloric acid (Merck, India) and bromophenol blue, herbicides and plant growth regulators were from Sigma, U.S.A. All other reagents used were of analytical grade.

Preparation of Plates

A slurry containing $BaSO_4$ (50 g), $CaSO_4$ (50 g) and distilled water (130 ml) was applied to the glass plates with the applicator to give a film thickness of 0.50 mm. The plates were first allowed to dry at room temperature and then in an oven at 110°C for one hour.

Preparation of Reagent for indole-3-acetic acid (IAA) Determination

The reagent is prepared by mixing 1 ml of 0.5M ferric chloride solution in 50 ml of 35% (v/v) perchloric acid.

Spotting of Test Solutions and R_f Values

Test solutions (1% ethanolic) were spotted onto the plates with a fine capillary. For determination purpose 100 µg of IAA (10 µl of 1% methanolic solution) and varying amounts of benzoic acid, α-naphthaleneacetic acid and 2,4,5-T such as 50 µg to 100 µg (5 µl-10 µl of 1% methanolic solutions) were applied. The spots were dried with the help of a hot air blower and then the plates were developed.

For tailing, the front limit (RI) and the rear limit (RT) were measured while for compact spots R_f values were calculated in the usual way[3].

Identification Method

The herbicides and growth regulators on plates were visualized by spraying ethanolic alkaline solution of bromophenol blue (0.1%).

Quantitative Separation of IAA

Known volumes of standard solution of IAA were applied on TLC plates. The plates were developed in carbon tetrachloride-propanol (100:0.5) solvent system. Previously indicated portions of the coating were scratched with a spatula and collected in a conical flask (10 ml capacity), 2.5 ml of methanol were added into it, the mixture was stirred for 5 min, and then transferred in the centrifuge tube. The conical flask was washed with 0.5 ml of methanol and the washings were transferred into the same centrifuge tube. The solid portion was removed by centrifugation and IAA was determined in clear solution by the following method[10]. The freshly prepared reagent (2 ml) was added into the centrifugate dropwise but rapidly with continuous agitation and the system was placed in dark for one hour for colour development. Finally the absorbance was measured at 510 nm against a blank containing methanol (3 ml) and reagent (2 ml).

RESULTS

The separations achieved on $BaSO_4$-$CaSO_4$ coatings using mixed solvent systems are recorded in Table 1. Results of quantitative separations of IAA from benzoic acid, α-naphthaleneacetic acid and 2,4,5-T are given in Table 2.

Table 1 - Separations achieved on $BaSO_4$-$CaSO_4$ (1:1) coatings in different solvent systems.

Compound separated	From compounds	Solvent system
BOA(0.6)	β-NTAA(0.25), PAA(0-4.5)	Benzene-Dioxan(50:1)
IAA(0.35)	BOA(0.75), NXAA(0.75)	Benzene-Dioxan(20:1)
IPA(3-5.5)	BOA(0.75), NXAA(0.75)	Benzene-Dioxan(20:1)
IAA(0.6)	BOA(0.8), NXAA(0.85)	Benzene-Dioxan(20:2)
IPA(0.6)	BOA(0.8), NXAA(0.85)	-do-
BOA(0.7)	IAA(0.25)	Benzene-Ethylacetate(20:1)
IPA(1-5)	α-NTAA(0.75)	Benzene-Ethylacetate(20:2)
IAA(2.5-6)	BOA(0.92), NXAA(0.85)	Benzene-Propanol(50:1)
IPA(0.58)	BOA(0.92), α-NTAA(0.83), TCA(0.9)	-do-
β-NTAA(0.6)	BOA(0.92), NXAA(0.85)	-do-
BOA(0.75)	CPAA(0.5), PAA(1-5)	Carbon tetrachloride-Dioxan(20:1)
IAA(0-2)	BOA(0.75), α-NTAA(0.7)	-do-
IPA(0-4)	BOA(0.75), α-NTAA(0.7), NXAA(0.65)	-do-
β-NTAA(0.4)	BOA(0.75), α-NTAA(0.7)	-do-
BOA(0.9)	CPAA(0.65), PAA(0.65)	Carbon tetrachloride-Dioxan(20:2)

(continued)

(Table 1 continued)

Compound separated	From compounds	Solvent system
IAA(0-3.5)	BOA(1), CPAA(0.9), CIA(0.85), 2,4-D(1), α-NTAA(0.85), β-NTAA(0.75), NXAA(0.85), PAA(0.85), TCA(1), 2,4,5-T(0.9)	Carbon tetrachloride-Propanol(50:1)
IPA(0.5)	BOA(1), CIA(0.85), α-NTAA(0.85), NXAA(0.85)	-do-
IAA(0.7)	BOA(1), CPAA(1), CIA(1), 2,4-D(1), α-NTAA(1), β-NTAA(1), NXAA(1), PAA(1), TCA(1), 2,4,5-T(1)	Carbon tetrachloride-Propanol(20:1)
IPA(0.85)	BOA(1), CIA(1), α-NTAA(1), β-NTAA(1), NXAA(1)	-do-
BOA(0.8)	IAA(0.3), IPA(1-4)	Chloroform-Dioxan(50:1)
TCA(0.85)	PAA(3-6)	-do-
IAA(1-5)	BOA(0.7), NXAA(0.8)	Chloroform-Dioxan(20:1)
IPA(1-4.5)	BOA(0.6), CIA(0.55), α-NTAA(0.55), NXAA(0.6)	Chloroform-Ethyl acetate(20:1)
α-NTAA(0.8)	IAA(0.5), IPA(0.6)	Chloroform-Ethyl acetate(80:20)
NXAA(0.85)	IAA(0.5), IPA(0.6)	-do-
IAA(0.74)	BOA(1), CIA(0.93), α-NTAA(1), NXAA(0.95)	Chloroform-Propanol(100:1)
IPA(0.75)	α-NTAA(1), NXAA(0.95)	-do-

Abbreviations used are BOA = benzoic acid, CPAA = 4-chlorophenoxyacetic acid, CIA = cinnamic acid, 2,4-D = 2,4-dichlorophenoxyacetic acid, IAA = indole-3-acetic acid, IPA = indole propionic acid, α-NTAA = α-naphthaleneacetic acid, β-NTAA = β-naphthaleneacetic acid, NXAA =βnaphthoxyacetic acid, PAA = phenoxyacetic acid, TCA = trichloroacetic acid and 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid. R_f values are given in parantheses.

IAA(1.5-5)	BOA(0.9), CIA(0.85), α-NTAA(0.85), NXAA(0.85)	Carbon tetrachloride-Dioxan(20:2)
IPA(0-6.5)	BOA(0.9), CIA(0.85), α-NTAA(0.85), NXAA(0.85)	-do-
β-NTAA(0.55)	BOA(0.9), α-NTAA(0.85), NXAA(0.85)	-do-
IAA(0.65)	BOA(0.9), CIA(0.85), 2,4-D(0.8), NXAA(0.9), 2,4,5-T(0.85)	Carbon tetrachloride-Dioxan(80:20)
BOA(0.7)	IAA(0-1), IPA(0-2), β-NTAA(0.15), PAA(0-4)	Carbon tetrachloride-Ethyl acetate(20:1)
BOA(0.8)	CPAA(0.5), IAA(0.25), IPA(0.5), β-NTAA(0.3), PAA(3-6)	Carbon tetrachloride-Ethyl acetate(20:2)
CIA(0.65)	IAA(0.25)	-do-
BOA(0.85)	CPAA(0.55), IAA(0.3), IPA(1-5), PAA(3-6)	Carbon tetrachloride-Ethyl acetate(80:20)
IPA(1-5)	CIA(0.75), α-NTAA(0.75), NXAA(0.75)	-do-
IAA(0)	BOA(0.6), CIA(0.45), α-NTAA(0.45), 2,4,5-T(0.3)	Carbon tetrachloride-Propanol(100:0.5)
IPA(0-2)	BOA(0.6), CIA(0.45), α-NTAA(0.45), NXAA(0.4)	-do-
IAA(0-2)	BOA(0.82), CPAA(0.5), CIA(0.78), α-NTAA(0.74), PAA(0.54)	Carbon tetrachloride-Propanol(100:1)

Table 2 - Quantitative chromatographic separation of indole-3-acetic acid from other acids using carbon tetrachloride-propanol (100:0.5) as solvent system.

Amount of acids (µg) separated on TLC		Absorbance at 510 nm				Average value	Standard deviation	Coefficient of variation
IAA	Other acids	x_1	x_2	x_3	x_4	(µ)	(σ)	(C.V.)
100	-	0.44	0.48	0.46	0.48	0.4650	0.0191	4.117
	BOA							
100	50	0.44	0.42	0.48	0.52	0.4650	0.0443	9.536
100	75	0.40	0.45	0.50	0.46	0.4525	0.0411	9.089
100	100	0.46	0.43	0.48	0.50	0.4675	0.0298	6.387
	α-NTAA							
100	50	0.48	0.50	0.50	0.46	0.4850	0.0191	3.947
100	75	0.46	0.50	0.48	0.46	0.4750	0.0191	4.030
100	100	0.50	0.45	0.49	0.46	0.4750	0.0238	5.011
	2,4,5-T							
100	50	0.44	0.47	0.48	0.48	0.4675	0.0189	4.048
100	75	0.48	0.50	0.50	0.48	0.4900	0.0115	2.356
100	100	0.45	0.44	0.46	0.48	0.4575	0.0170	3.732

Abbreviations are defined in table 1.

To calculate analytical parameters the following relations were used

$$\sigma = \sqrt{\frac{(x_1-\mu)^2 + (x_2-\mu)^2 + \ldots}{n - 1}}$$

$$C.V. = \frac{\sigma \times 100}{\mu}$$

where σ = standard deviation; $x_1, x_2, \ldots$ = measured values, μ = average value, n = number of sets and C.V. = coefficient of variation.

DISCUSSION

Previous publications[1-5] from this laboratory show that calcium sulphate and barium sulphate are good TLC materials. Thin layers of barium sulphate are not as good as that of calcium sulphate alone. Admixtures of barium sulphate and calcium sulphate give uniform, smooth and stable layers and have very good separation potential for carboxylic acids.

The time of development[5] of TLC plate increases with the increasing percentage of barium sulphate in the admixtures and the admixture containing barium sulphate-calcium sulphate (1:1,w/w) is most suitable for thin-layer chromatographic studies. The above admixture can be used for separating carboxylic herbicides in single solvent systems. The separation potential is limited due to tailing nature of the herbicides in some of the solvents such as benzene, carbon tetrachloride and chloroform. However, compact spots with R_f value 1 were obtained in dioxan, ethyl acetate and propanol and some binary separations were obtained in distilled water.

A number of tertiary and quaternary separations were achieved on $BaSO_4$-$CaSO_4$ (1:1) coatings impregnated with coconut oil[6] in water while organic solvents were found to be ineffective. The separation potential increases with increasing percentage of coconut oil used for impregnation. Unfortunately the time of development also increases with increasing percentage of coconut oil.

Table 1 shows $BaSO_4$-$CaSO_4$ can be used for several binary separations of carboxylic herbicides and related compounds using mixed solvent systems. The following separations, which are not possible on $BaSO_4$-$CaSO_4$ as well as on $BaSO_4$-$CaSO_4$ impregnated with coconut oil in single solvent systems, can be achieved in mixed solvent systems: BOA from CPAA; IAA from BOA, CIA, CPAA, 2,4-D, α-NTAA, β-NTAA, NXAA and 2,4,5-T; β-NTAA from α-NTAA and NXAA; IPA from BOA, CIA and NXAA (table 1).

Data recorded in Table 2 show that IAA can be separated quantitatively from BOA, α-NTAA and 2,4,5-T in carbon tetrachloride-propanol (100:0.5).

CONCLUSION

Admixture of $BaSO_4$-$CaSO_4$ (1:1) is a good thin-layer chromatographic material. It can be used for some binary separations of carboxylic herbicides and related compounds in water as developer. The above admixture impregnated with coconut oil can be used for ternary and quaternary separations using water as developer. Many binary separations which are not possible in single solvent systems as well as on impregnated coatings, can be achieved on the same admixture by mixed solvent systems.

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