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The thin-layer and column chromatographic separation of some inorganic anions on microcrystalline cellulose

More than six thousand papers have now been published on the subject of thin-layer chromatography (TLC) in the last eight years[1]. The growth and acceptance of inorganic TLC has been noted by the recent review of LEDERER[2]. Much of the work in inorganic TLC, however, has been done on an absorbent of silica gel or alumina[3]. These separations range from the early simple ion separations of Seiler to the separation of some geometric (cis–trans) isomers of cobalt, platinum and palladium[4].

Work in our laboratory has shown that microcrystalline cellulose (Avicel) can be successfully used as an adsorbent in the separation of common inorganic cations and several geometrical isomers[5,6]. Its application to the synthesis of some substituted β-trichloroborazines has also been noted[7]. The data obtained in these studies indicate that TLC using microcrystalline cellulose is an analog of paper chromatography.

The present work was undertaken to study the chromatographic behavior of 27 inorganic anions using microcrystalline cellulose as the adsorbent. Both thin-layer and column chromatographic separations are reported.

Experimental

Preparation of the plates. The adsorbent was prepared by blending 75 g of microcrystalline cellulose (technical grade, Avicel Sales Division, FMC Corp., Marcus Hook, Pa.) with 227 ml of distilled water in a Waring blender for 15 sec at low speed. The mixture was then pumped on for 2 min by means of a water aspirator and gently shaken to remove the air bubbles. The mixture was spread on 20 × 5 cm glass plates to a thickness of 0.75 mm, allowed to dry overnight and stored in a sodium hydroxide desiccator until ready for use. This mixture prepared 40 plates.

Mixing time and the amount of water used may vary depending on the lot of microcrystalline cellulose. It is our experience that the most uniform plates are best prepared from a rather fluid Avicel slurry. This is a departure from the plate preparation technique originally suggested by WOLFROM et al.[8] and which we reported in our previous paper[5].

Anion preparation and application. The various anions were prepared in 1.0 % (w/v) aqueous solutions from their available sodium or potassium reagent grade salts. All mixtures of the anion solutions were applied to the microcrystalline coated glass by using capillary pipettes and were allowed to dry before insertion into the chromatographic tanks.

Solvent systems. Reagent-grade chemicals were used to make the various solvent systems. These systems were made up to a total volume of 50 or 100 ml. The development time varied from 20 to 70 min.

Detection. Table I summarizes the data of the different detection techniques and reagents used. All of the reagents were applied by a spraying technique. For a multiple detection Table I lists the order of application.

Limits of detection. Ten microliters of successively more dilute solutions of each anion was applied to a TLC plate, developed and detected. In all cases at least 10^{-2} mg of each anion was detectable.

TABLE I

INORGANIC ANION MIXTURES, SOLVENT SYSTEMS, AND R_F VALUES BY THIN-LAYER CHROMATOGRAPHY USING MICROCRYSTALLINE CELLULOSE

No.	Anion mixture	Solvent system (% by volume)	Detection	R_F value
1	BO_3^- F^- Cl^- Br^- I^-	Acetone–ethyl acetate–water (3:1:1)	$AgNO_3$, DCF[a]	0.02 0.11 0.38 0.58 0.93
2	F^- Cl^- Br^- I^-	Acetone–water (4:1)	$AgNO_3$, DCF	0.04 0.15 0.27 0.56
3	$Fe(CN)_6^{4-}$ $Fe(CN)_6^{3-}$ SCN^-	Acetone–ethyl acetate–water (6:1:3)	$FeCl_3$ $FeCl_2$ $FeCl_3$	0.17 0.67 0.97
4	BrO_2^- IO_3^- BrO_3^- ClO_3^-	Ethanol–water–1.5 M NH_3 (6:2:1)	10 % KI in 2 N HCl	0.00 0.36 0.73 0.90
5	PO_4^{3-} $S_2O_3^{2-}$ $Cr_2O_7^{2-}$	Methanol–butanol–water (2:1:1)	$AgNO_3$	0.20 0.36 0.75
6	$HAsO_4^{2-}$ AsO_2^- SO_3^{2-} NO_2^-	Acetone–water–ethyl acetoacetate (6:1:3)	DCF, $AgNO_3$	0.00 0.03 0.05 0.12
7	$C_2O_4^{2-}$ CO_3^{2-}	Methanol–formic acid (100 ml : 10 drops)	DCF, $AgNO_3$, kojic acid, o-coumaric acid	0.00 0.54
8	CO_3^{2-} SO_4^{2-} NO_3^-	2-Butanol–4 N HCl (4:1)	Kojic acid, o-coumaric acid DCF, Laurent's acid, heat DCF, Laurent's acid, heat	0.09 0.59 0.81
9	$S_2O_5^{2-}$ $S_2O_8^{2-}$	Butanol–2-propanol–1.5 M NH_3 (1:2:3)	$AgNO_3$, DCF 10 % KI in 2 N HCl	0.42 0.75
10	CN^- S^{2-}	Methanol–ethylenediamine (100 ml : 10 drops)	DCF, $AgNO_3$	0.15 0.35

[a] Dichlorofluorescein.

Column preparation. Standard burets fitted with a porous glass frit were filled to a length of 10 in. with microcrystalline cellulose. A 0.5 ml sample of a 1.0 % (w/v) solution of the anions was used. A 0.25 in. of sand on top of the column prevented stirring of the adsorbent as the solvent was added. This column gave a flow rate of 12–15 drops per min and was satisfactory for the separation of mixtures 1 and 3 (Table I). Two milliliter fractions from each column were collected, spotted on TLC plates, and analyzed.

Dielectric studies. A Sargent model V oscillometer was used to measure the dielectric constant of various solvent mixtures of acetone, ethyl acetate and water

TABLE II

A COMPARISON OF R_F VALUE, DIELECTRIC CONSTANT, AND DEGREE OF SEPARATION OF $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$ AND SCN^-

Solvent ratio[a]	Degree of separation[b]	ε_i[c]	Average R_F value		
			$Fe(CN)_6^{4-}$	$Fe(CN)_6^{3-}$	SCN^-
50:20:30	excellent	31	0.21	0.60	0.94
50:30:20	good	28	0.03	0.19	0.82
60:10:30	excellent	39	0.17	0.67	0.97
60:20:20	excellent	31	0.02	0.14	0.85
60:30:10	none	21	0.00	0.00	0.55
70:10:20	good	33	0.00	0.13	0.93
70:20:10	fair	24	0.00	0.02	0.70
20:8 :80	none	60	1.00	1.00	1.00
0:80:20	none	13	0.00	0.00	0.00

[a] Mixtures of acetone, ethyl acetate and water.

[b] A predetermined judgment as to the type of separation considering the spreading of the band and differences in R_F values.

[c] At $25.2°$.

used in the separation of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$ and SCN^-. Table II summarizes the data for the correlation between dielectric constant and degree of separation.

Results and discussion

By using the appropriate solvent system, a separation of the anion groups listed in Table I was established. All solvent systems are novel except system No. 2, which has been reported by BARK *et al.*[9] R_F values were taken from an average of at least ten readings.

Plots of R_F value *vs.* percent ethyl acetate for solvent system No. 1, containing 50, 60, 70 and 80 % acetone, indicated that an increase in the percent of ethyl acetate decreases the R_F value of all four anions. Because of the high R_F value of the fluoride ion in system No. 1 as compared to system No. 2, the BO_3^- ion was also included in this separation. The $B_4O_7^{2-}$ ion gave the same R_F value in system No. 1 as the BO_3^- ion.

A large variation in the composition of solvent system No. 3 separated this anion group, however a large amount of spreading occurred. The mixture reported in Table I gave a spread to only 0.04 R_F units per anion.

Of the large number of detecting reagents tried for anion system No. 4 potassium iodide was the most reliable. It gave an instantaneous brown spot for IO_3^-. The bromate ion (BrO_3^-) gave a brown spot about 20 sec later and the ClO_3^- appeared as a light tan color in about 15 min.

No particular difficulties were encountered in separating anion group No. 5.

The use of U.V. light was most helpful in detecting the members of anion group No. 6. Using DCF the spots of $HAsO_4^{2-}$, SO_3^{2-} and NO_2^- were tan, pink and red, respectively and $AgNO_3$ gave a pink color to AsO_2^-. Under U.V. light, the AsO_2^- spot was yellow and the SO_3^{2-} spot became lighter in color.

Attempts to include other anions into system No. 7 resulted in spreading of the $C_2O_4^{2-}$ band. In the absence of these anions the red band of $C_2O_4^{2-}$ gave an R_F value of 0.00 with a small amount of spreading to R_F 0.02.

The detecting reagents of anion system No. 8 proved to be non-reliable in a wide variety of attempted solvent systems. The SO_4^{2-} and NO_3^- anions were best detected by spraying with DCF and Laurent's acid and heating the plates for a few minutes at 110°. A black and light tan band appeared in SO_4^{2-} and NO_3^-, respectively.

In solvent system No. 9 silver nitrate and DCF gave a visible pink to $S_2O_5^{2-}$, which later turned to reddish brown. $S_2O_8^{2-}$ formed a distinct visible brown on a yellow background with potassium iodide.

A visible dark gray and dark brown detected the CN^- and S^{2-} of system No. 10.

Anion mixtures No. 2 and 3 were successfully separated on a chromatographic column. Decreasing the column length from 10 to 6 in. yielded overlapping of I^-, Br^- and Cl^- fractions in the first 2-ml sample.

A comparison of the dielectric constant of solvent system No. 3 before and after a TLC separation of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$ and SCN^- showed no significant change in the gross dielectric constant. It is to be noted from the various mixtures of solvent system No. 3 used that the degree of separation ranged from no separation to excellent. Those mixtures having a dielectric constant in the range of 31–39 units gave the best separation. An increase or decrease in the amount of ethyl acetate or acetone in the mixture caused a considerable change in the dielectric constant and this effect resulted in either no separation or excessive band spreading.

A correlation between dielectric constant and degree of separation of the halide ions, using solvent system No. 1, indicated that excellent separations were obtained with dielectric constants of the solvent mixture in the range of 26–31 and good separation from 28–39.

Conclusions

The data obtained in this study indicate that microcrystalline cellulose can be successfully used to separate a large number of inorganic anions. The method described has been applied to both thin-layer and column chromatography. The TLC plates gave a remarkably hard surface which stands up in a variety of solvents.

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