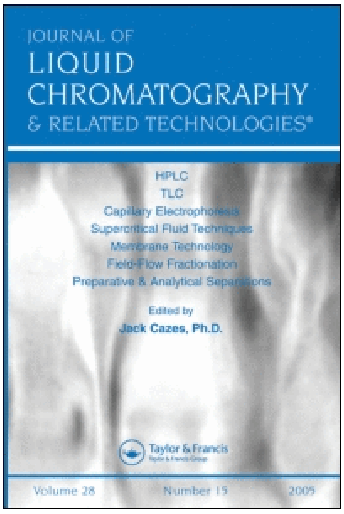

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Chromatographic Separation of Anions on Papers Impregnated with Hydrous Titanium Oxide

K. V. Surendra Nath[a]; S. N. Tandon[a]
[a] Chemistry Department, University of Roorkee, Roorkee, India

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CHROMATOGRAPHIC SEPARATION OF ANIONS ON PAPERS IMPREGNATED WITH HYDROUS TITANIUM OXIDE

K. V. Surendra Nath and S. N. Tandon*
Chemistry Department
University of Roorkee
Roorkee-247 667, India

ABSTRACT

Chromatographic behaviour of different anions on hydrous titanium oxide papers has been investigated in a variety of aqueous and non-aqueous solvent systems. Some anions like F^-, PO_4^{3-}, SO_4^{2-}, VO_4^{3-}, MnO_4^-, AsO_4^{3-} and WO_4^{2-} are strongly retained on these papers. Based on the R_f values data it was possible to attain some difficult separations.

INTRODUCTION

Alberti (1) and Qureshi (2) in their review articles have highlighted the advantages of papers impregnated with inorganic ion exchangers. Hydrous oxides of polyvalent metal ions are capable of behaving both as cation and anion exchangers but the papers impregnated with these materials have been mostly used for the separation of cations. Relatively less information exists on their use for the separation of anions. Sakodinsky and Lederer (3) reported a comparative study of the chromatographic behaviour of a few anions on hydrated iron (III), titanium (IV) and zirconium (IV) oxide papers. Singh and Tandon (4) studied the behaviour of various anions on hydrated zirconium oxide (HZO) papers in aqueous solvent systems and achieved some separations. Ghatuary and Sen (5) employed hydrated tin oxide (HSnO) paper for the separation of some polyvalent anions. Papers impregnated with hydrated titanium oxide (3,6) have been used for the removal of uranium from sea water and for the separation of some cations including uranium and cationic complexes. In the absence of any detailed study on the use of hydrated titanium oxide papers for the separation of anions the authors took up a systematic investigation of the behaviour of a number of anions both in aqueous and mixed solvent systems. The results were interesting and it was possible to achieve several topical separations on these papers.

EXPERIMENTAL

Preparation of Hydrous Titanium Oxide Papers:

Whatmann No.1 chromatographic paper strips (28 cm x 2 cm) were dipped in 0.10M solution of $TiCl_4$ (E.Merck) in 4NHCl for 30 sec. These were blotted with filter paper to remove excess of liquid and air dried. The papers were then dipped into 10% ammonia for 45 sec, agitating carefully to avoid any uneven precipitation. The dried papers were then washed several times with distilled water and air dried overnight. The uniformity of impregnation of hydrous titanium oxide in the paper was checked by determining titanium (IV) in one sq.cm. pieces of the strips of the same paper and of different lots. Titanium impregnation ~~was found~~ to be fairly uniform 1.7 ± 0.1 mg/sq.cm. and the papers give reproducible R_f values.

Solvent System/Composition:

(1) 0.10M $NaNO_3$
(2) 0.10M NaCl
(3) 0.10M NaAc
(4) 0.10M Na_2SO_4
(5) 1.0M Na_2SO_4
(6) 0.10M Na_2CO_3
(7) 1.0M Na_2CO_3
(8) 0.10M $NaHCO_3$
(9) Acetone-3M NH_4OH (1:1) V/V
(10) Acetone-3M NH_4OH (7:3) V/V
(11) Acetone-n-butanol - 3M NH_4OH (4:3:3) V/V/V
(12) Acetone-methanol-3M HCl (4:3:3) V/V/V
(13) Acetone-n-butanol- 3M HCl (4:3:3) V/V/V
(14) Acetone-ethyleneglycol-3M HCl (4:3:3) V/V/V
(15) Acetone-ethanol-20% acetic acid (4:3:3) V/V/V
(16) Acetone-n-butanol-20% acetic acid (4:3:3) V/V/V

Corresponding serial numbers for solvent systems are used in the Tables -1 and 2.

Procedure:

The development of anions was carried out in glass jars by the method of ascending chromatography keeping the diameter of the spots within 5 mm. The anions were identified by spraying appropriate reagents (7).

RESULTS AND DISCUSSION

The hR_f values of the anions in different aqueous and mixed solvent systems are given in Table - 1. The various separations achieved are listed in Table - 2. In the case of chloride it was checked that the associated cation does not have any significant effect on the R_f value.

TABLE 1. hR_f Values of Different Anions in Various Aqueous and Mixed Solvent Systems

Anions	Solvent Systems															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Fluoride	(-)	(-)	(-)	49t	45t	60t	(-)	(-)	49	43	45	45t	43t	71t	7	3
Chloride	100	(-)	100	100	85	100	100	100	81	63	67	(-)	(-)	(-)	57	47
Bromide	100	(-)	100	100	79	100	100	100	85	74	71	(-)	(-)	(-)	65	55
Iodide	93	95	92	85	74	90	93	98	92	87	82	90	73	92	78	66
Thiocyanate	86	91	85	78	69	81	82	83	96	96	85	92	80	94	83	78
Chlorate	100	100	100	100	88	100	100	100	100	89	82	92	74	98	83	69
Bromate	100	100	100	100	83	100	100	100	91	75	58	(-)	(-)	(-)	59	43
Iodate	52	64	60	66	45	73	89	71	57	35	26	0	0	0	0	0
Phosphate	0	0	0	0	0	0	76t	0	0	0	0	0	0	0	0	0
Vanadate	5	58t	0	0	0	12t	0	12t	71t	0	22t	37t	22t	0	0	41t
Chromate	19	15	60	25	13	85	96	85	55	15	24	79	71	87	20	22
Permanganate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Arsenate	0	12t	0	0	10t	0	0	0	5t	5t	0	3t	0	0	0	0
Molybdate	28	55t	45	21t	13t	85	96	85	71	23	25	21t	0	55t	0	0
Tungstate	3	12t	0	0	0	11t	0	12t	21t	20t	5t	0	0	0	0	0
Sulphate	100	(-)	100	(-)	(-)	100	(-)	(-)	61	0	12	41t	38	(-)	0	0
Thiosulphate	100	(-)	100	(-)	(-)	100	(-)	(-)	71	35	33	82	69	(-)	33	21
Persulphate	100	(-)	100	(-)	(-)	100	(-)	(-)	93	95	71	98	92	(-)	80	53
Ferrocyanide	75	73	82	88	95t	90	90	87	90t	8	18	49t	7	21t	0	0
Ferricyanide	100	100	100	100	100	100	100	100	100	75	54	75	51	57	65t	31

t = tailing ; (-) = could not be identified

TABLE 2. Various Separations on Hydrous Titanium Oxide Paper

Anions Separated	Solvent System Used
CrO_4^{2-} - PO_4^{3-}	6,8,9,12,13
CrO_4^{2-} - VO_4^{3-}	6,8,9,12,13
CrO_4^{2-} - WO_4^{2-}	6,8,9,12,13
CrO_4^{2-} - AsO_4^{3-}	6,8,9,12,13
CrO_4^{2-} - MoO_4^{2-}	12,13
MoO_4^{2-} - PO_4^{3-}	6,8,9
MoO_4^{2-} - VO_4^{3-}	6,8
MoO_4^{2-} - WO_4^{2-}	6,8,9
MoO_4^{2-} - AsO_4^{2-}	6,8,9
I^- - IO_3^-	1-16
ClO_3^- - IO_3^-	3,4,6
BrO_3^- - IO_3^-	3,4,6
ClO_3^- - BrO_3^- - IO_3^-	5,10,11,15
SO_4^{2-} - $S_2O_3^{2-}$ - $S_2O_8^{2-}$	9-16
$Fe(CN)_6^{4-}$ - $Fe(CN)_6^{3-}$	1-4,6-8,10-16
CrO_4^{2-} - VO_4^{3-} - PO_4^{3-}	12
CrO_4^{2-} - MoO_4^{2-} - WO_4^{2-}	9
CrO_4^{2-} - MoO_4^{2-} - VO_4^{3-}	14
CrO_4^{2-} - MoO_4^{2-} - PO_4^{3-}	12,13,14
VO_4^{3-} - WO_4^{2-} - PO_4^{3-}	9
F^- - Cl^- - Br^- - I^- - CNS^-	10,11,15,16
CrO_4^{2-} from a mixture of AsO_4^{3-}, WO_4^{2-}, PO_4^{3-}, MnO_4^- and VO_4^{3-}	6,8,9,12,13
MoO_4^{2-} from a mixture of AsO_4^{3-}, WO_4^{2-}, PO_4^{2-}, MnO_4^- and VO_4^{3-}	6,8,9,12

Amongst the halides F^- is strongly retained on these papers both in aqueous and mixed solvents. This may be attributed to the strong complexation of F^- with titanium (IV). In aqueous solvents there is no definite trend in the R_f values of halides, however, in the mixed solvents it follows the order $F^- < Cl^- < Br^- < I^- < SCN^-$. Good resolutions of halides were achieved with solvent systems 5, 10, 11, 15, 16. Irrespective of the nature of the solvent system the R_f values of the oxyhalide ions follow the order $IO_3^- < BrO_3^- < ClO_3^-$. The separation of ClO_3^-, BrO_3^- and IO_3^- was achieved effectively with mixed solvent systems 9, 10, 11 and 15 and that of IO_3^- from ClO_3^- or BrO_3^- even with the different aqueous salt solutions. Since IO_3^- is retained strongly it can be separated from I^- also.

Generally the oxyanions like PO_4^{3-}, VO_4^{3-}, CrO_4^{2-}, MnO_4^-, AsO_4^{3-}, MoO_4^{2-} and WO_4^{2-} do not move much from the point of application on HTiO papers. This is in conformation to the observation of Kraus (8) who has remarked that these oxyanions are strongly adsorbed by various hydrous oxide exchangers. Singh and Tandon (4) and Ghatuary and Sen (5) observed similar behaviour of some of these anions on HZO and HSnO papers. However, it is interesting to note that CrO_4^{2-} and MoO_4^{2-} show a significant movement in aqueous solutions of carbonate, bicarbonate or chloride and in mixed solvents having either ammonia or HCl as one of its component. Thus some interesting separations involving CrO_4^{2-} and MoO_4^{2-} anions can be achieved with the solvent systems 6, 7, 8, 9, 12, 13 and 14. The R_f values of different anions of sulphur eg. SO_4^{2-}, $S_2O_3^{2-}$ and $S_2O_8^{2-}$ in mixed solvent systems show the trend $SO_4^{2-} < S_2O_3^{2-} < S_2O_8^{2-}$, but in aqueous media all these anions move to the solvent front.

Amongst $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ the latter attains a brown colour on HTiO papers and is preferentially retained. The development of brown colour is attributed to surface precipitation (3).

These two anions can be conveniently separated in various aqueous and mixed solvents.

Strong retention of F^-, PO_4^{3-}, SO_4^{2-}, VO_4^{3-}, MnO_4^-, AsO_4^{3-} and WO_4^{2-} could be either due to adsorption, complexation or precipitation. It has been observed that the R_f values of different anions invariably increase with increase in concentration of Na_2CO_3 solution and this may be due to apparent loss of anion exchange capacity. For separations which can be achieved both in aqueous and mixed solvents the former should be preferred because it takes much shorter time (15-20 min.) to accomplish them.

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