

CHROM. 3361

## Chromatography on ion exchange papers

## XXIII. Further results on ion exchange with organic solvents\*

Our previous work with ion exchange papers and mixtures of aqueous acids and organic solvents<sup>1</sup> has been extended to cover a wider range of solvents. Previously only alcohols and acetone had been studied, and we wanted to investigate more polar solvents (acetic acid and ethyl acetate), a very non-polar solvent (benzene) and phenol (an aromatic polar solvent).

The ion exchangers examined were a cationic sulphonic resin (Amberlite SA-2 paper), an anionic quaternary ammonium resin (Amberlite SB-2 paper), and a cellulose anion exchanger (Macherey, Nagel quaternary ammonium cellulose paper); control chromatograms were also run on ordinary (Whatman No. 1) filter paper. The techniques employed were those described previously<sup>1</sup>.

TABLE I

$R_F$  VALUES OF INORGANIC IONS IN MIXTURES OF AQUEOUS HCl AND ACETIC ACID (FROM 0% TO 80%) (HCl = 2.4 N THROUGHOUT)

Papers: SA-2 = Amberlite SA-2 paper (sulphonic resin paper)

SB-2 = Amberlite SB-2 paper (strongly basic quaternary ammonium resin paper)

MN = Macherey Nagel strongly basic ion exchange cellulose paper with quaternary ammonium groups

W 1 = Whatman No. 1 pure cellulose paper

Metal ion	Paper	% HAc			
		0	30	50	80
Fe(III)	SA-2	0.57	0.51	0.36	0.10-0.53
	SB-2	0.57	0.04	0.05	0
	MN (basic)	0.87	0.72	0.55	0.75
	W 1	1	0.82	0.68	0.73
Co(II)	SA-2	0.46	0.39	0.33	0.04-0.55
	SB-2	1	1	0.15; 0.84	0
	MN	0.92	0.88	0.69	0.42
	W 1	1	0.85	0.72	0.46
Ni(II)	SA-2	0.46	0.39	0.33	0.32
	SB-2	1	1	0.78	0.41
	MN	0.92	0.88	0.74	0.33
	W 1	1	0.85	0.72	0.30
Cu(II)	SA-2	0.59	0.61	0.59	0.49
	SB-2	0.75	0.20	0.06	0
	MN	0.89	0.80	0.62	0.42
	W 1	1	0.84	0.72	0.43
Ba(II)	SA-2	0.04	0.06	0.05	0.04
	SB-2	1	0.92	0.88	0.81
	MN	1	0.81	0.89	0.68
	W 1	0.89	0.71	0.64	0.67

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\* Parts XX, XXI and XXII of this series are notes in *J. Chromatog.*, 21 (1966) 499; 22 (1966) 200; and 29 (1967) 306.

TABLE I (continued)

Metal ion	Paper	% HAc			
		0	30	50	80
Zn(II)	SA-2	0.04-0.47	0.04-0.51	0.04-0.44	0-0.31
	SB-2	0	0	0	0
	MN	0.55	0.42	0.43	0.42
	W 1	1	1	1	0.51
Sr(II)	SA-2	0.26	0.16	0.09	0.06
	SB-2	1	1	1	0.62
	MN	0.88	0.85	0.77	0.60
	W 1	0.90	0.82	0.69	0.57
Ce(III)	SA-2	0.10	0.03	0.01	0.01
	SB-2	1	1	1	0.70
	MN	1	1	0.84	0.49
	W 1	1	0.90	0.69	0.62
La(III)	SA-2	0.13	0.06	0	0.02
	SB-2	1	1	1	0.76
	MN	1	1	0.84	0.52
	W 1	1	0.86	0.76	0.60
Sm(III)	SA-2	0.12	0.06	0.01	0.02
	SB-2	1	1	1	0.70
	MN	1	1	0.82	0.45
	W 1	1	0.90	0.69	0.59
ReO <sub>4</sub> <sup>-</sup>	SA-2	0.50	0.64	0.66	0.56
	SB-2	0.03	0.08	0.12	0.17
	MN	0.57	0.61	0.65	0.72
	W 1	0.70	0.73	0.72	0.59
TcO <sub>4</sub> <sup>-</sup>	SA-2	0.19	0.39	0.45	0.17-0.50
	SB-2	0	0.01	0.03	0.03
	MN	0.60	0.60	0.60	0.64
	W 1	0.65	0.69	0.73	0.58
AuCl <sub>4</sub> <sup>-</sup>	SA-2	0.03	0.10	0.10	0.21
	SB-2	0	0	0	0.01
	MN	0.28	0.44	0.48	0.67
	W 1	0.47	0.64	0.67	0.58

Benzene holds so little HCl that the paper strips were moistened with aqueous HCl so as to obtain conditions similar to those in equilibrium experiments.

The results obtained are given in Tables I-IV. Acetic acid has the same effect as a polar alcohol, *i.e.* it fixes hydrated ions more strongly, increases the complexation of reversible chloro complexes, and desorbs anions soluble in organic solvents (*e.g.* ReO<sub>4</sub><sup>-</sup>). Benzene does not extract any of the ions tested to any great extent. We were surprised that even ReO<sub>4</sub><sup>-</sup> and AuCl<sub>4</sub><sup>-</sup> are preferentially held on the resin.

Phenol does not extract any of the ions examined, with the exception of Rb, Cs, ReO<sub>4</sub><sup>-</sup> and TcO<sub>4</sub><sup>-</sup>. Ethyl acetate also generally gave low *R<sub>F</sub>* values even with ions otherwise readily extractable such as AuCl<sub>4</sub><sup>-</sup>.

TABLE II

$R_F$  VALUES OF SOME INORGANIC IONS ON A STRONG ANIONIC RESIN (SB-2) PAPER MOISTENED WITH 2.4 N HCl AND DEVELOPED WITH BENZENE

Metal ion	$R_F$
AuCl <sub>4</sub> <sup>-</sup>	0
ReO <sub>4</sub> <sup>-</sup>	0
Co	0.01
Cu	0.02
Ni	0.05
Sr	0.04
La	0.04
Fe	0
Ce	0.03

TABLE III

$R_F$  VALUES OF SOME INORGANIC IONS WITH MIXTURES OF PHENOL AND AQUEOUS HCl OF VARIOUS CONCENTRATIONS (1:1)

Papers: SA-2 = Amberlite SA-2 paper (sulphonic resin paper)

SB-2 = Amberlite SB-2 paper (strongly basic quarternary ammonium resin paper)

MN = Macherey Nagel strongly basic ion exchange cellulose paper with quarternary ammonium groups

W 1 = Whatman No. 1 pure cellulose paper

Ion	Paper	2N HCl	3N HCl	4N HCl
Fe	SA-2	0	0	0
	SB-2	0.02T*	0.01	0
	MN	0T	0.02	0.01
	W 1	0.02	0.02	0.01
Co	SA-2	0	0	0.01
	SB-2	0.05T	0.02	0.03
	MN	0.03T	0.03	0.03
	W 1	0.02T	0.02	0.02
Ni	SA-2	0	0	0
	SB-2	0.04T	0.02	0.03
	MN	0.02T	0.03	0.01
	W 1	0.02	0.02	0.01
Cu	SA-2	0	0	0.01
	SB-2	0.04T	0.02	0
	MN	0.03T	0.02	0.01
	W 1	0.03	0.02	0.02
Sm	SA-2	0	0	0
	SB-2	0.05T	0	0.04
	MN	0.05T	0	0.01
	W 1	0.01	0	0.01
La	SA-2	0	0	0
	SB-2	0.05T	0	0.04
	MN	0.03T	0	0.01
	W 1	0.02	0	0

\* T = Tail or elongated spot.

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TABLE III (continued)

Ion	Paper	2N HCl	3N HCl	4N HCl
Ce	SA-2	0	0	0
	SB-2	0.05T	0	0.02
	MN	0.04T	0	0.02
	W 1	0.02	0	0-0.14
Sr	SA-2	0	0	0
	SB-2	0	0	0.04
	MN	0.03T	0	0.01
	W 1	0.01	0	0
Ba	SA-2	0	0	0
	SB-2	0	0	0.02
	MN	0	0	0
	W 1	0.03	0	0
Zn	SA-2	0	0.03	0
	SB-2	0	0.02	0
	MN	0	0.03	0
	W 1	0	0	0
K	SA-2	—	—	—
	SB-2	0.15	0.15	0.16
	MN	0.10	0.16	0.09
	W 1	0.08	0.10	0.06
Rb	SA-2	—	—	—
	SB-2	0.33	0.42	0.41
	MN	0.34	0.41	0.33
	W 1	0.23	0.24	0.22
Cs	SA-2	—	—	—
	SB-2	0.72	0.77	0.73
	MN	0.71	0.64	0.70
	W 1	0.44	0.48	0.33
ReO <sub>4</sub> <sup>-</sup>	SA-2	0.23	0.23	0.23T
	SB-2	0	0.01	0
	MN	0.26	0.28	0.24
	W 1	0.27	0.29	0.22
TcO <sub>4</sub> <sup>-</sup>	SA-2	0.07	0.07	0.06
	SB-2	0	0	0
	MN	0.26	0.20	0.19
	W 1	0.27	0.20	0.19
AuCl <sub>4</sub> <sup>-</sup>	SA-2	0-0.10	0-0.14	0-0.10
	SB-2	0	0	0
	MN	0.17	0.26	0.13
	W 1	0.30	0.30	0.23

TABLE IV

 $R_F$  VALUES OF SOME INORGANIC IONS WITH MIXTURES OF ETHYL ACETATE AND AQUEOUS HCl (1:1)

Papers: SA-2 = Amberlite SA-2 paper (sulphonic resin paper)

SB-2 = Amberlite SB-2 paper (strongly basic quarternary ammonium resin paper)

MN = Macherey Nagel strongly basic ion exchange cellulose paper with quarternary ammonium groups

W 1 = Whatman No. 1 cellulose paper

<i>Ion</i> *	<i>Paper</i>	<i>2N HCl</i>	<i>3N HCl</i>
Fe	SA-2	0.05-0.32	0-0.30
	SB-2	0-0.11	0-0.06
	MN	0.07-0.35	0-0.22
	W 1	0.09-0.29	0-0.18
Cu	SA-2	0.02	0
	SB-2	0	0
	MN	0.01	0
	W 1	0.01	0
AuCl <sub>4</sub> <sup>-</sup>	SA-2	0.06T	0.07-0.23
	SB-2	0.02	0.03
	MN	0.03-0.15	0.06-0.25
	W 1	0.26-0.51	0.23-0.61
Zn	SA-2	0.05	0.10T
	SB-2	0	0
	MN	0.03	0.04
	W 1	0.06	0.11
TcO <sub>4</sub> <sup>-</sup>	SA-2	0.04	0.05
	SB-2	0.01	0
	MN	0.04	0.05
	W 1	0.06	0.06
ReO <sub>4</sub> <sup>-</sup>	SA-2	0.05	0.09
	SB-2	0.01	0
	MN	0.04	0.07
	W 1	0.06	0.08

\* K, Rb, Cs, Co, Ni, Sm, Sr, La, Ce, Ba all have  $R_F = 0$  on all papers and in all solvents.

The results presented here do not seem to have any analytical applications. However previously published data did find use in explaining the mechanisms involved in ion exchange with organic solvents<sup>2</sup> and the present results might also find use in this direction.

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