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ION-EXCHANGE PAPER CHROMATOGRAPHY OF INORGANIC IONS

PART XXVIII. SOME INVESTIGATIONS OF THE "PERCHLORATE EFFECT"

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SUMMARY

The "perchlorate effect" has been examined for several chromatographic systems. There is considerable desorption due to the presence of perchlorate in adsorption and ion-exchange systems. The "perchlorate effect" is not limited to perchlorate; it is exhibited to a lesser extent by nitrate but not by sulphate. No effect due to perchlorate was observed in partition systems (*n*-butanol–acid–water solvents) and in paper electrophoresis (aqueous mineral acid as electrolyte).

INTRODUCTION

In several recent publications from this laboratory¹⁻³, we have shown that the electrophoretic and ion-exchange behaviour of inorganic ions is influenced by the presence of oppositely charged ions even if no complex formation takes place. Most of the effects are known under the name of ion-pair formation or outer-sphere complexing, but the actual magnitude of the effects had not been appreciated sufficiently.

This work led us to examine the influence that the presence of one anion could have on the behaviour of another anion, *i.e.*, the interaction of the same kind of charge.

There is frequent mention in the literature that in anion exchange some very strongly held anions, *e.g.*, PtCl_6^{2-} , which cannot be eluted with HCl from a column (usually of Dowex 1), are eluted readily with HClO_4 . This effect also has consequences in equilibrium studies where lower constants are obtained when perchlorate is used as an inert medium. A good summary of the literature can be found in the book by MARCUS AND KERTES⁴ under the heading "The perchlorate effect". It seems that most workers consider the effect to be due to the strong affinity of perchlorate for anion exchangers, but the chapter by MARCUS AND KERTES concludes that "a complete quantitative explanation of the perchlorate effect is still lacking...".

There are isolated observations (for example⁵ for HTcO_4 and HReO_4) that the perchlorate effect is not limited to anion exchangers.

We therefore felt that a more extensive study of the effect of perchlorate in various separation systems would be interesting, and report our results here.

EFFECTS PRODUCED BY CONTINUOUS VARIATION OF THE CHLORIDE:PERCHLORATE RATIO AT LOW IONIC STRENGTH

In equilibrium studies, mixtures of, for example, chloride and perchlorate are often used in order to study the effect of the chloride ion at constant ionic strength. We therefore chromatographed compounds containing what we thought to be two representative anions, namely HAuCl_4 and H_2PdCl_4 , in such mixtures at total concentrations of 1 *N*, 2 *N* and 3 *N* on various papers. The results with mixtures of HCl-HClO_4 are shown in Table I and those with mixtures of LiCl-LiClO_4 in Table II. The latter mixtures were kept at pH 1 so as to avoid hydrolysis of the metal chloride complexes studied.

These results are best discussed with graphical representations of R_F value versus concentration of ClO_4^- . Fig. 1 shows clearly that there is a "perchlorate effect" for HAuCl_4 on simple cellulose filter-paper with an increase in the R_F value from

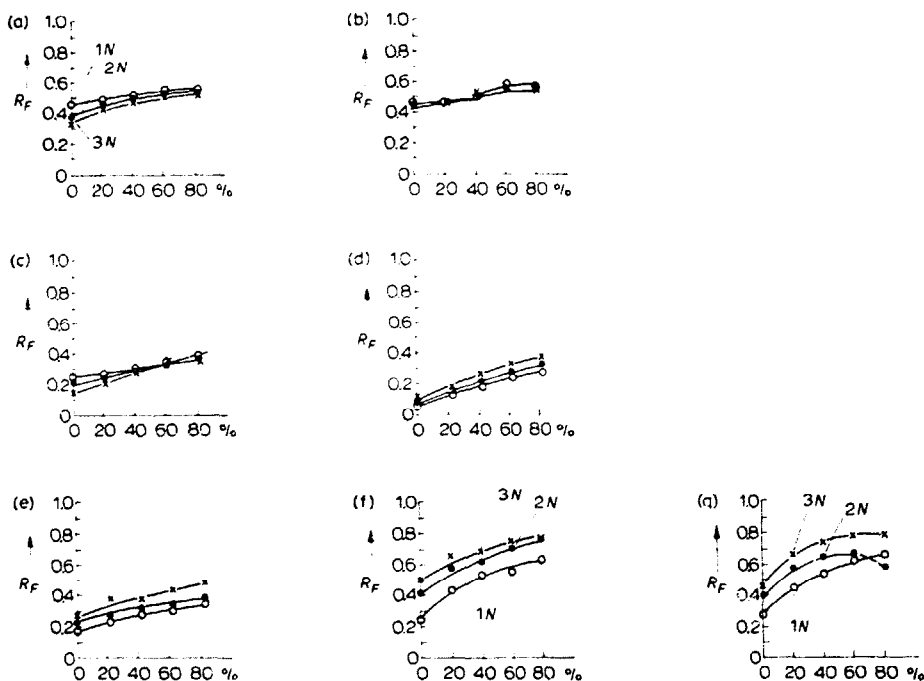


Fig. 1. R_F values of chlorauric acid and chloropalladous acid plotted against the perchlorate concentration in HCl-HClO_4 mixtures and in LiCl-LiClO_4 mixtures on several cellulose papers. (a) Chlorauric acid on Whatman No. 1 paper with 1 *N*, 2 *N* and 3 *N* HCl-HClO_4 mixtures. The lines almost coincide. (b) Chlorauric acid on Whatman No. 1 paper with 1 *N*, 2 *N* and 3 *N* LiCl-LiClO_4 mixtures. The R_F values in the 3 *N* mixture are slightly lower. (c) Chlorauric acid on carboxymethylcellulose paper with 1 *N*, 2 *N* and 3 *N* LiCl-LiClO_4 mixtures. There are small differences but only at low perchlorate concentrations. (d) Chlorauric acid on Whatman DE-20 paper with 1 *N*, 2 *N* and 3 *N* HCl-HClO_4 mixtures. (e) Chlorauric acid on Whatman DE-20 paper with 1 *N*, 2 *N* and 3 *N* LiCl-LiClO_4 mixtures. In (d) and (e) there are slightly higher R_F values at higher concentrations of electrolyte. (f) Chloropalladous acid on Whatman DE-20 paper with 1 *N*, 2 *N* and 3 *N* HCl-HClO_4 mixtures. Note the considerable differences between the three curves which are not found with chlorauric acid. (g) Chloropalladous acid on Whatman DE-20 paper with 1 *N*, 2 *N* and 3 *N* LiCl-LiClO_4 mixtures.

TABLE I

R_F VALUES OF CHLORAUIC ACID AND CHLOROPALLADOUS ACID ON VARIOUS PAPERS IN HCl-HClO₄ MIXTURES

Acid	Paper ^a	Total constant concentration in mixture (N)	HCl:HClO ₄ in mixture (%)				
			100:0	80:20	60:40	40:60	20:80
Chlorauric	Whatman No. 1	1	0.48	0.48	0.52	0.59	0.56
	Whatman No. 3MM		0.49	0.47	0.52	0.54	0.53
	Whatman CM 50		0.27	0.29	0.33	0.38	0.35
	Whatman DE-20		0.18	0.25	0.27	0.30	0.35
	Amberlite SB-2		0	0	0	0	0
	Amberlite SA-2		0.02	0.07	0.10	0.11	0.14
	Amberlite WB-2		0	0.02	0.03	0.04	0.05
	Amberlite WA-2	0.22	0.28	0.32	0.36	0.38	
Chloro-palladous	Whatman No. 1	1	0.82	0.88	0.79	0.85	0.86
	Whatman No. 3MM		0.88	0.80	0.90	0.87	0.83
	Whatman CM 50		0.77	0.82	0.86	0.81	0.87
	Whatman DE-20		0.27	0.44	0.53	0.56	0.63
	Amberlite SB-2		0	0.11	0.24	0.35	0.37
	Amberlite SA-2		0.04	0.29	0.28-0.57	0.24-0.54	0.20-0.50
	Amberlite WB-2		0	0	0	0	0
	Amberlite WA-2	0-0.28	0-0.39	0-0.38	0-0.51	0-0.46	
Chlorauric	Whatman No. 1	2	0.45	0.48	0.52	0.53	0.51
	Whatman No. 3MM		0.44	0.48	0.51	0.50	0.54
	Whatman CM 50		0.24	0.22	0.28	0.30	0.40
	Whatman DE-20		0.22	0.27	0.33	0.35	0.38
	Amberlite SB-2		0	0	0	0	0
	Amberlite SA-2		0.02	0.07	0.12	0.17	0.15
	Amberlite WB-2		0	0.03	0.05	0.07	0.08
	Amberlite WA-2	0.21	0.23	0.28	0.32	0.34	
Chloro-palladous	Whatman No. 1	2	0.79	0.83	0.81	0.81	0.82
	Whatman No. 3MM		0.80	0.87	0.88	0.80	0.84
	Whatman CM 50		0.71	0.74	0.75	0.79	0.82
	Whatman DE-20		0.42	0.59	0.62	0.71	0.78
	Amberlite SB-2		0	0.24	0.46	0.55	0.58
	Amberlite SA-2		0.11	0.54	0.69	0.68	0.68
	Amberlite WB-2		0	0.01	0.01	0.01	0.01
	Amberlite WA-2	0.42	0.62	0.68	0.67	0.69	
Chlorauric	Whatman No. 1	3	0.46	0.49	0.56	0.57	0.56
	Whatman No. 3MM		0.43	0.49	0.55	0.56	0.53
	Whatman CM 50		0.24	0.29	0.29	0.32	0.35
	Whatman DE-20		0.26	0.38	0.37	0.43	0.47
	Amberlite SB-2		0	0	0.01	0.01	0.01
	Amberlite SA-2		0.03	0.13	0.15	0.16	0.24
	Amberlite WB-2		0.01	0.03	0.05	0.09	0.10
	Amberlite WA-2	0.16	0.22	0.23	0.32	0.33	
Chloro-palladous	Whatman No. 1	3	0.82	0.84	0.81	0.86	0.84
	Whatman No. 3MM		0.76	0.85	0.79	0.82	0.83
	Whatman CM 50		0.67	0.70	0.78	0.75	0.82
	Whatman DE-20		0.50	0.67	0.68	0.74	0.77
	Amberlite SB-2		0.01	0.35	0.55	0.66	0.69
	Amberlite SA-2		0.19	0.74	0.78	0.80	0.75
	Amberlite WB-2		0.02	0.02	0.04	0.04	0.03
	Amberlite WA-2	0.47	0.62	0.58	0.73	0.80	

^a Whatman No. 1 and 3MM are pure cellulose papers, Whatman CM 50 is a carboxymethyl-cellulose paper, Whatman DE-20 is a diethylaminoethylcellulose paper, Amberlite papers contain ca. 50% of a resin, SB-2 is a strong anion exchanger, SA-2 is a sulphonic cation exchanger, WB-2 is a weak anion exchanger and WA-2 is a carboxylic resin.

TABLE II

R_F VALUES OF CHLORAUIC ACID AND CHLOROPALLADOUS ACID ON VARIOUS PAPERS IN LiCl-LiClO₄ MIXTURES AT pH 1

Acid	Paper	Total constant concentration in mixture (N)	LiCl:LiClO ₄ in mixture (%)				
			100:0	80:20	60:40	40:60	20:80
Chlorauric	Whatman No. 1	1	0.49	0.49	0.52	0.54	0.54
	Whatman No. 3MM		0.45	0.45	0.51	0.49	0.50
	Whatman CM 50		0.20	0.27	0.30	0.34	0.39
	Whatman DE-20		0.08	0.14	0.19	0.25	0.29
	Amberlite SB-2		0	0	0	0	0
	Amberlite SA-2		0.01	0.06	0.11	0.11	0.12
	Amberlite WB-2		0	0.02	0.03	0.03	0.03
	Amberlite WA-2		0.10	0.11	0.11	0.15	0.16
Chloro-palladous	Whatman No. 1	1	0.84	0.86	0.84	0.80	0.88
	Whatman No. 3MM		0.85	0.88	0.89	0.90	0.92
	Whatman CM 50		0.77	0.79	0.85	0.83	0.87
	Whatman DE-20		0.45	0.44	0.53	0.61	0.65
	Amberlite SB-2		0	0.05	0.10	0.12	0.10
	Amberlite SA-2		0.02	0-0.29	0-0.45	0-0.45	0-0.34
	Amberlite WB-2		0	0	0	0	0
	Amberlite WA-2		0.07	0.08	0.11	0.11	0.11
Chlorauric	Whatman No. 1	2	0.39	0.45	0.50	0.52	0.58
	Whatman No. 3MM		0.39	0.43	0.41	0.43	0.51
	Whatman CM 50		0.20	0.27	0.31	0.30	0.36
	Whatman DE-20		0.68	0.14	0.24	0.29	0.34
	Amberlite SB-2		0	0	0	0	0
	Amberlite SA-2		0.02	0.09	0.09	0.10	0.13
	Amberlite WB-2		0	0.02	0.05	0.09	0.07
	Amberlite WA-2		0.09	0.10	0.20	0.25	0.25
Chloro-palladous	Whatman No. 1	2	0.83	0.83	0.80	0.83	0.90
	Whatman No. 3MM		0.84	0.82	0.84	0.85	0.89
	Whatman CM 50		0.73	0.76	0.84	0.86	0.88
	Whatman DE-20		0.40	0.58	0.64	0.66	0.57
	Amberlite SB-2		0	0-0.30	0-0.44	0-0.56	0-0.59
	Amberlite SA-2		0.06	0.57	0.63	0.63	0.63
	Amberlite WB-2		0	0	0	0	0
	Amberlite WA-2		0-0.25	0-0.36	0-0.43	0-0.50	0-0.57
Chlorauric	Whatman No. 1	3	0.33	0.43	0.48	0.52	0.54
	Whatman No. 3MM		0.32	0.42	0.47	0.48	0.57
	Whatman CM 50		0.15	0.21	0.30	0.33	0.33
	Whatman DE-20		0.11	0.19	0.28	0.34	0.37
	Amberlite SB-2		0	0	0	0	0
	Amberlite SA-2		0.03	0.05	0.07	0.12	0.14
	Amberlite WB-2		0	0.02	0.06	0.09	0.10
	Amberlite WA-2		0.08	0.13	0.17	0.21	0.22
Chloro-palladous	Whatman No. 1	3	0.82	0.82	0.87	0.87	0.87
	Whatman No. 3MM		0.79	0.84	0.80	0.89	0.83
	Whatman CM 50		0.72	0.79	0.83	0.83	0.90
	Whatman DE-20		0.47	0.66	0.73	0.78	0.79
	Amberlite SB-2		0	0-0.50	0-0.77	0-0.78	0-0.80
	Amberlite SA-2		0.12	0.70	0.75	0.80	0.77
	Amberlite WB-2		0	0	0	0	0
	Amberlite WA-2		0-0.23	0-0.61	0-0.61	0-0.83	0-0.83

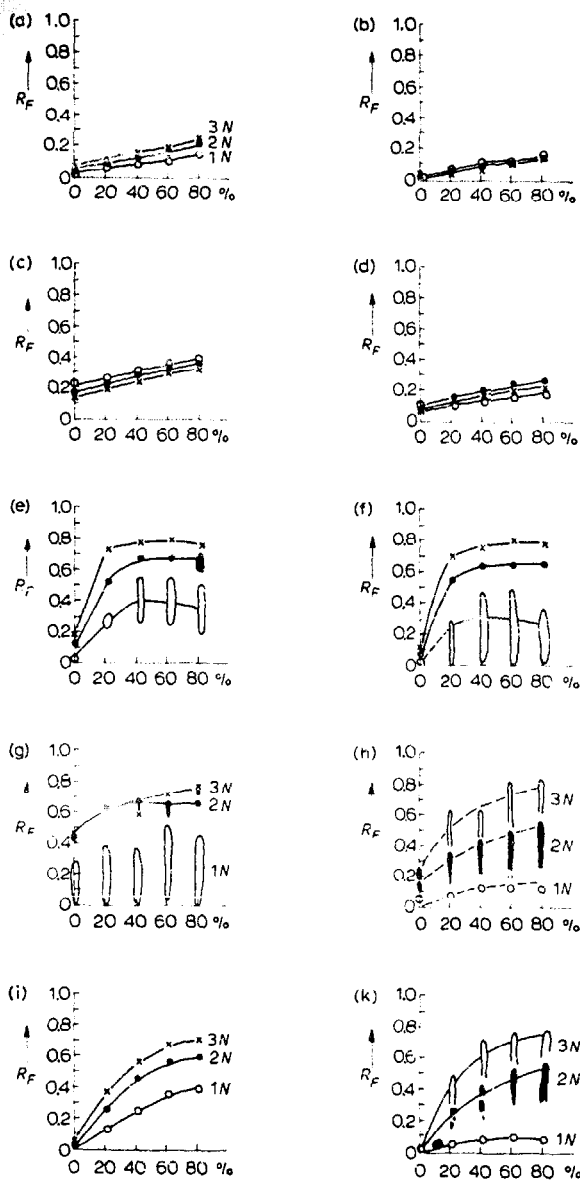


Fig. 2. R_F values of chlorauric acid and chloropalladous acid plotted against perchlorate concentration in HCl-HClO₄ mixtures and LiCl-LiClO₄ mixtures at pH 1 on several resin papers. (a) Chlorauric acid on Amberlite SA-2 paper with HCl-HClO₄ mixtures. (b) Chlorauric acid on Amberlite SA-2 paper with LiCl-LiClO₄ mixtures. (c) Chlorauric acid on Amberlite WA-2 paper with HCl-HClO₄ mixtures. (d) Chlorauric acid on Amberlite WA-2 paper with LiCl-LiClO₄ mixtures. (e) Chloropalladous acid on Amberlite SA-2 paper with HCl-HClO₄ mixtures. (f) Chloropalladous acid on Amberlite SA-2 paper with LiCl-LiClO₄ mixtures. (g) Chloropalladous acid on Amberlite WA-2 paper with HCl-HClO₄ mixtures. (h) Chloropalladous acid on Amberlite WA-2 paper with LiCl-LiClO₄ mixtures. (i) Chloropalladous acid on Amberlite WA-2 paper with HCl-HClO₄ mixtures. (k) Chloropalladous acid on Amberlite SB-2 paper with LiCl-LiClO₄ mixtures.

TABLE III

R_F VALUES OF INORGANIC IONS ON VARIOUS PAPERS COMPARING 4 N HCl, 3 N HCl + 1 N HClO₄, 3 N HCl + 1 N HNO₃ AND 3 N HCl + 1 N H₂SO₄ AS ELUENTS

Paper	Ion	4 N HCl	3 N HCl + 1 N HClO ₄	3 N HCl + 1 N HNO ₃	3 N HCl + 1 N H ₂ SO ₄
Whatman No 3MM	Au(III)	0.46	0.52	0.51	0.46
	Pd(II)	0.80	0.84	0.80	0.77
	Hg(II)	0.83	0.88	0.86	0.79
	Bi(III)	1.00	1.00	1.00	0.92
	Cd(II)	0.92	0.93	0.94	0.92
	Sb(III)	0.91	0.87	0.86	0.84
	Fe(III)	0.88	0.89	0.89	0.90
	UO ₂ ²⁺	0.83	0.82	0.83	0.86
	Zn(II)	0.85	0.90	0.92	0.88
	Ga(III)	0.88	1.00	1.00	0.92
	Tl(III)	0.81	0.82	0.80	0.78
	Pt(IV)	0.86	0.85	0.85	0.81
	CrO ₄ ²⁻	0.61	0.68	0.65	0.60
	ReO ₄ ⁻	0.73	0.84	0.82	0.68
	SB-2 resin	Au(III)	0.00	0.00	0.00
Pd(II)		0.07	0.48	0.09	0.25
Hg(II)		0.00	0.20	0.00	0.00
Bi(III)		0.04	comet	0.03	0.03
Cd(II)		0.05	0.43	0.07	0.04
Sb(III)		0.05	0.19	0.03	0.04
Fe(III)		trails	trails	trails	trails
UO ₂ ²⁺		0.25	0.70	0.16	0.53
Zn(II)		0.03	0.39	0.07	0.05
Ga(III)		0.03	0.32	0.20, trail	0.09
Tl(III)		0.00	0.02	0.00	0.00
Pt(IV)		0.00	0.06	0.09	0.00
CrO ₄ ²⁻		0.00	0.00	0.00	0.00
ReO ₄ ⁻		0.15	0.46	0.24	0.14
SA-2 resin		Au(III)	0.04	0.11	0.05
	Pd(II)	0.30	0.82	0.50	0.32
	Hg(II)	0.18	0.80	0.30	0.13
	Bi(III)	trails	0.85, comet	trails	trails
	Cd(II)	0.90	0.90	trails	trails
	Sb(III)	0.42, comet	0.81	0.46, comet	0.40, comet
	Fe(III)	0.74	0.78	0.77	0.79
	UO ₂ ²⁺	0.57	0.57	0.54	0.63
	Zn(II)	0.48	0.87	0.71	0.61
	Ga(III)	0.47	0.56	0.62	0.57
	Tl(III)	0.17	0.43	0.13	0.08
	Pt(IV)	0.19	0.77	0.26	0.21
	CrO ₄ ²⁻	0.17, comet	0.42, comet	0.23, slight comet	0.18, comet
	ReO ₄ ⁻	0.57, slight comet	0.78	0.67	0.55, comet

TABLE IV

R_F VALUES OF INORGANIC IONS ON VARIOUS PAPERS COMPARING 6 N HCl, 5 N HCl + 1 N HClO₄, 5 N HCl + 1 N HNO₃ AND 5 N HCl + 1 N H₂SO₄ AS ELUENTS

Paper	Ion	6 N HCl	5 N HCl + 1 N HClO ₄	5 N HCl + 1 N HNO ₃	5 N HCl + 1 N H ₂ SO ₄
Whatman No. 3MM	Au(III)	0.48	0.53	0.52	0.43
	Pd(II)	0.72	0.77	0.74	0.72
	Hg(II)	0.78	0.82	0.80	0.72
	Bi(III)	0.90	0.95	0.93	0.92
	Cd(II)	0.92	0.85	0.92	0.90
	Sb(III)	0.87	0.80	comet	0.84
	Fe(III)	0.85	0.80	0.81	0.74
	UO ₂ ²⁺	0.78	0.78	0.75	0.72
	Zn(II)	0.93	0.94	0.92	0.95
	Ga(III)	1.00	1.00	1.00	1.00
	Tl(III)	0.83	0.84	0.82	0.78
	Pt(IV)	0.74	0.80	0.75	0.75
	CrO ₄ ²⁻	0.05	0.70	0.65	0.57
	ReO ₄ ⁻	0.77	0.79	0.78	0.74
	SB-2 resin	Au(III)	0.00	0.00	0.00
Pd(II)		0.05	0.42	0.11	0.06
Hg(II)		0.02	0.18	0.03	0.01
Bi(III)		0.03	comet	0.06	0.02
Cd(II)		0.04	comet	0.06	0.03
Sb(III)		0.04	comet	0.00	0.03
Fe(III)		0.00	0.05	0.00	0.00
UO ₂ ²⁺		0.02	comet	0.03	0.04
Zn(II)		0.05	comet	0.07	0.03
Ga(III)		0.00	0.00	0.00	0.00
Tl(III)		0.03	0.02	0.00	0.00
Pt(IV)		0.00	0.03	0.00	0.00
ReO ₄ ⁻		0.23	0.59	0.29	0.22
SA-2 resin	Au(III)	0.04	0.12	0.05	0.04
	Pd(II)	0.44	0.76	0.50	0.38
	Hg(II)	0.30	0.81	0.38	0.28, slight comet
	Bi(III)	comet	0.94, slight comet	comet	comet
	Cd(II)	0.90, comet	0.96	comet	0.90
	Sb(III)	comet	0.86, slight comet	comet	comet
	Fe(III)	comet	comet	comet	comet
	UO ₂ ²⁺	0.39	0.64, slight comet	0.35	0.52
	Zn(II)	0.74	0.90	0.73	0.60
	Ga(III)	0.97	0.18	0.12	0.13
	Tl(III)	0.17	0.44	0.19	0.15
	Pt(IV)	0.18	0.81	0.22	0.19
	ReO ₄ ⁻	0.65	0.80	0.70	0.62

It is therefore evident that much more data are needed in order to be able to explain the effect of perchlorate, but we can already conclude:

(1) the "perchlorate effect" is not limited to anion exchangers but can also occur on neutral (cellulose) supports, sulphonic and carboxylic resins;

(2) the desorbing effect of perchlorate may even be higher in systems that do not involve anion exchangers;

(3) one of the consequences of the perchlorate effect may be comet formation and this may vary from substance to substance and also with the concentration of the eluent used.

PAPER ELECTROPHORETIC EXPERIMENTS

Fig. 3 shows electropherograms of a mixture of Ni^{2+} , HAuCl_4 and H_2PdCl_4 in various mixtures of HCl-HClO_4 of total concentration $1 M$ in a Camag high-voltage apparatus operated at $300 V$ for $2 h$ at 3° on Whatman No. 1 filter-paper.

TABLE V

THE EFFECT OF LARGE HClO_4 CONCENTRATIONS ON THE ADSORPTION OF INORGANIC IONS ON RESIN PAPERS FROM MIXTURES OF $1 N \text{HCl} +$ VARIOUS CONCENTRATIONS OF HClO_4

Paper	Ion	$1 N \text{HCl}$	$1 N \text{HCl} +$ $3 N \text{HClO}_4$	$1 N \text{HCl} +$ $4 N \text{HClO}_4$	$1 N \text{HCl} +$ $5 N \text{HClO}_4$	$1 N \text{HCl} +$ $6 N \text{HClO}_4$
SA-2 resin	Au(III)	0.03	0.22	0.22	0.22	0.22
	Pd(II)	0.04	0.81	0.81	0.78	0.74
	Hg(II)	0.08	0.90	0.87	0.87	0.84
	Bi(III)	0.19, slight comet	0.93	0.95	0.95	0.93
	Cd(II)	0.60	0.90	0.98	0.98	0.91
	Sb(III)	0.31	0.74	0.73	0.71	0.64
	Fe(III)	0.11	0.03	0.00	0.61	0.30
	UO_2^{2+}	0.19	0.30	0.23	0.18	0.13
	Zn(II)	0.19, elon- gated spot	0.83	0.91	0.91	0.91
	Ga(III)	0.05	0.41	0.44	0.33	0.18
	Tl(III)	0.09	0.39	0.37	0.34	0.27
	Pt(IV)	0.10	0.88	0.83	0.80	0.81
	ReO_4^-	0.38	0.80	0.80	0.85	0.78
SB-2 resin	Au(III)	0.00	0.01	0.02	0.02	0.03
	Pd(II)	0.01	0.74	0.71	0.72	0.68
	Hg(II)	0.00	0.52	0.59	0.62	0.61
	Bi(III)	0.00	0.73, elon- gated	0.80, elon- gated	0.82	0.78, elon- gated
	Cd(II)	0.08	0.80	0.83	0.83	0.78
	Sb(III)	0.03	0.29	0.32	0.32	0.30
	Fe(III)	0.00	0.03	0.94, elon- gated	0.94, elon- gated	0.10, elon- gated
	UO_2^{2+}	0.65	0.70	0.60	0.71	0.68
	Zn(II)	0.08	0.67	0.75	0.75	0.75
	Ga(III)	0.06	0.06	0.96	0.97-0.87, two spots	0.05
	Tl(III)	0.00	0.02	0.03	0.03	0.03
	Pt(IV)	0.00	0.26	0.31, elon- gated	0.33, elon- gated	0.33, elon- gated
	ReO_4^-	0.06	0.64	0.70	0.75	0.74

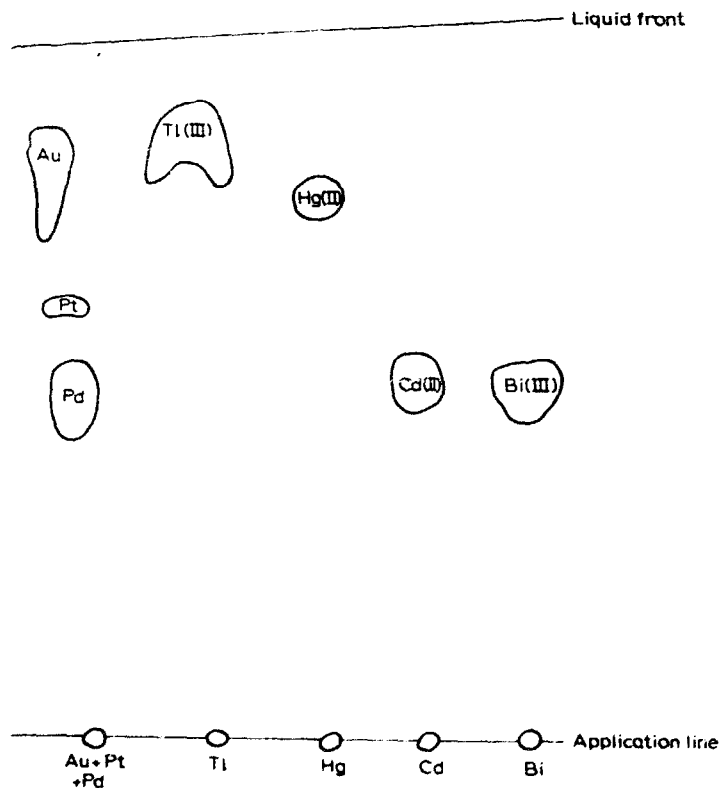
TABLE VI

R_F VALUES OF INORGANIC IONS IN *n*-BUTANOL-HCl-HClO₄-WATER (100:10:10:80) ON WHATMAN No. 1 PAPER

Development for 23 cm.

Ion	R_F value	Ion	R_F value
Pb(II)	0.13	Au(III)	1.0
Cu(II)	0.12	Tl(III)	1.0
Cd(II)	0.56	UO ₂ (II)	0.20
Bi(III)	0.41	Th(IV)	0.04
Hg(II)	0.91	Ti(IV)	0.18
As(III)	0.54	Zr(IV)	0.0
Sb(III)	0.62	Ga(III)	0.21
Sn(IV)	0.72	In(III)	0.25
Al(III)	0.07	Be(II)	0.33
Fe(III)	0.17	V(V)	0.24
Zn(II)	0.59	Mo(VI)	0.40
Mn(II)	0.10	ReO ₄ ⁻	1.0
Co(II)	0.10	SeO ₃ ²⁻	0.64
Ni(II)	0.09	SeO ₄ ²⁻	0.51
Pt(IV)	0.64	TeO ₃ ²⁻	0.22
Pd(II)	0.48	TeO ₄ ²⁻	0.00

(a)



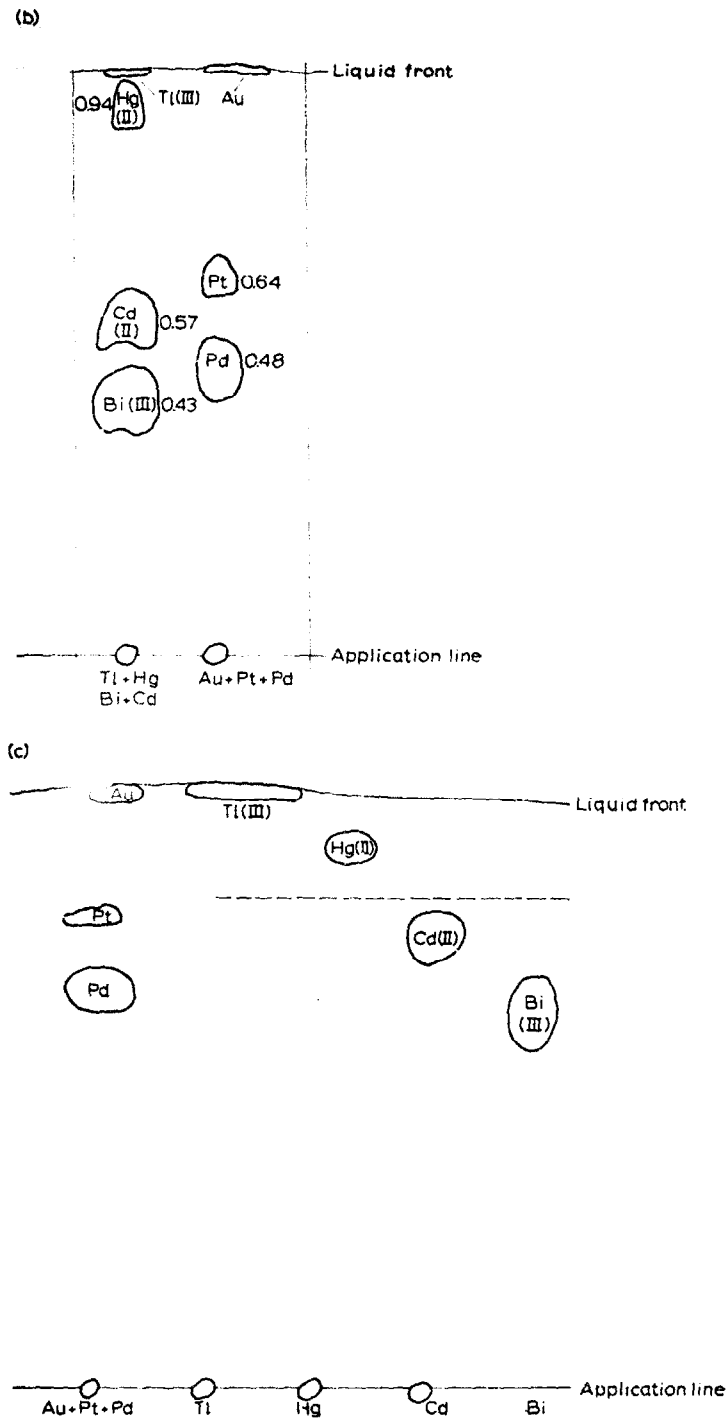


Fig. 4. Chromatograms of some inorganic ions on Whatman No. 1 paper: (a) with *n*-butanol-HCl-water (100:10:90); (b) with *n*-butanol-HCl-HClO₄-water (100:20:10:80); (c) with *n*-butanol-HCl-water (100:20:80).

Evidently, whatever differences there may be, they are below the order of accuracy of the electrophoretic runs. The small differences due to the lowered adsorption of HAuCl_4 on to cellulose paper seems to be annulled by other effects. Electrophoresis with electrolyte of concentration more than 1 *N* gives rather high currents in the Camag apparatus and not very satisfactory electropherograms.

COMPARISON OF PERCHLORATE WITH OTHER IONS

We were also interested to establish whether the "perchlorate effect" is really unique for perchlorate or whether other anions might have the same effect. In order to be able to survey a range of anionic chloro-complexes, we carried out two series of experiments, one with a total acidity of 4 *N* and the other of 6 *N*, as shown in Tables III and IV. We compared here the R_F values in 4 *N* HCl with mixtures that were 3 *N* in HCl and 1 *N* in another acid, and 5 *N* in HCl and 1 *N* in another acid.

Comet formation was quite extensive in some instances in this work also.

The carboxylic resin paper WA-2 was examined, but we do not report any results here as we believe that this resin was decomposed during chromatography with HCl- HNO_3 mixtures.

The general conclusions from these results are as follows.

Not only perchlorate but also nitrate can produce a "perchlorate effect". The "nitrate effect" is always much smaller than the "perchlorate effect", varying from 10% to 50% of the perchlorate effect. Sulphate, when replacing part of the HCl, has no noticeable effect on the R_F values.

The uranyl ion presents an exception in all systems because of the tendency of perchlorate, nitrate and sulphate to form complexes that are more stable than the chloro-complexes. This property could be useful in the separation of UO_2^{2+} from other ions.

THE EFFECT OF HIGH CONCENTRATIONS OF PERCHLORATE

So far we have only investigated the perchlorate effect with relatively low concentrations. The results given in Table V give an idea of the result when various amounts of HClO_4 up to 6 *N* are added to 1 *N* HCl.

Generally, a maximum is reached at relatively low perchlorate concentrations and the effect is then either constant or even decreases at higher perchlorate concentrations. Some comment has to be made on the behaviour of Ga(III) and Fe(III) shown in this table as these ions are essentially cationic in 1 *N* HCl. On the sulphonic resin paper, they are desorbed by HClO_4 and the R_F values decrease from 3 *N* to 6 *N* HClO_4 , which is a similar effect to that observed with cations in aqueous solutions of HClO_4 only⁶.

On the anion-exchange resin they remain on the liquid front until rather high HClO_4 concentrations and are adsorbed strongly from 1 *N* HCl to 6 *N* HClO_4 . This adsorption at high HClO_4 concentrations is unexpected and needs further investigation.

The "perchlorate effect" therefore reaches its maximum in most instances at relatively low perchloric acid concentrations, and at higher concentrations it remains constant or may even diminish.

PARTITION CHROMATOGRAPHY

Mixtures of *n*-butanol-HCl-water and *n*-butanol-HClO₄-water have been studied extensively as solvents in partition paper chromatography. Very few results with mixed acids in *n*-butanol-acid-water systems are given in the literature⁷.

We have tried here to compare *n*-butanol-1 *N* HCl and *n*-butanol-2 *N* HCl with *n*-butanol equilibrated with an aqueous solution 1 *N* with respect to HCl and 1 *N* with respect to HClO₄. There are no considerable differences between the mixed HCl-HClO₄ solvent and one prepared with 2 *N* HCl, but there are small changes in *R_F* values due to slightly different complexing of some metals that might make this solvent analytically attractive. The *R_F* values obtained are shown in Table VI and separations of some typical mixtures are shown in Fig. 4.

Hence no evidence of a "perchlorate effect" could be observed in a partition system consisting of *n*-butanol saturated with aqueous acid.

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