

## Short Communications

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### Chromatography on ion-exchange papers

#### XI. The salting-out effect in the adsorption of inorganic anions

The adsorption of anions (such as  $\text{AuCl}_4^-$ ) on ion exchangers usually increases with the concentration of LiCl or other chlorides but decreases with the concentration of HCl.

This increased adsorption with LiCl was observed on both anion exchange resins<sup>1</sup> and cation exchange resins<sup>2,3</sup> and seems contrary to what would be expected in ion exchange equilibria which are supposed to obey the law of mass action.

By comparing the adsorption of numerous metal ions on various anion exchangers (resins and cellulose exchangers) we concluded<sup>4</sup> that at least two mechanisms are involved, namely electrostatic attraction (or ion exchange) and a "physical" adsorption akin to extraction with liquid solvents.

As no data were available for the effect of salts such as LiCl on cellulose exchangers we have now carried out a preliminary investigation taking perrhenate and chloroaurate as typical anions and observing the change of adsorption with the change in the LiCl concentration on a range of neutral, cationic and anionic supports. From the results given below it appears that the salting-out effect is quite independent of possible electrostatic attraction and occurs on all supports. Indeed it seems that anion exchange and salting-out are competitive on anion exchangers.

#### *Experimental*

The various papers given in Table I were developed by the ascending technique with solutions being 1, 2, 4 and 8 *N* with respect to LiCl and 0.1 *N* to HCl (the latter to prevent hydrolysis of  $\text{AuCl}_4^-$ ). Ion exchange papers were all washed twice with 2 *N* HCl and water, and air dried.

Perrhenate was detected by spraying with a solution of  $\text{SnCl}_2$  and KCNS in 5 *N* HCl and the gold by spraying with a solution of  $\text{SnCl}_2$  in HCl.

The papers in Table I are in the order of decreasing  $R_F$  values and this order is approximately the same for both ions.

Perrhenate does not change its  $R_F$  values appreciably on neutral or acid supports with an increase in the LiCl concentration and decreases them on anion exchangers as would be expected from an adsorption obeying the law of mass action.

Chloroaurate decreases its  $R_F$  values on all supports with increasing LiCl concentration, the least decrease occurring with aminoethylcellulose which also in our studies with HCl<sup>4</sup> proved to combine the least adsorption affinity with anion exchange properties. DEAE cellulose already shows a stronger salting-out effect presumably due to the presence of the non-polar ethyl groups on the nitrogen atoms.

The sequence of adsorption differs for the two ions only for the two cellulose anion exchangers. The aminoethylcellulose has a higher exchange capacity (and

TABLE I

 $R_F$  VALUES OF  $\text{ReO}_4^-$  AND  $\text{AuCl}_4^-$  ON VARIOUS PAPERS DEVELOPED WITH SOLUTIONS OF LiCl

Paper	Perrhenate				Chloroaurate			
	1N LiCl	2N LiCl	4N LiCl	8N LiCl	1N LiCl	2N LiCl	4N LiCl	8N LiCl
Whatman paper P20 (cellulose phosphate)	diffuse zone at liquid front				0.61	0.50	0.48	0.32
Whatman No. 1 paper (pure cellulose)	0.67	0.66	0.64	0.67	0.43	0.36	0.30	0.23
Amberlite WA-2 paper (containing 45% of Amberlite IRC-50, an acrylic resin with COOH groups)	0.59	0.55	0.50	0.56	0.16	0.15	0.11	0.08
Whatman paper DE 20 (diethylaminoethylcellulose)	0.40	0.47	0.50	0.60	0.13	0.12	0.11	0.06
Whatman paper AE 30 (aminoethylcellulose)	0.40	0.43	0.46	0.55	0.15	0.15	0.13	0.12
Amberlite SA-2 paper (containing 45% of Amberlite IR-120, a nuclear sulphonic resin on styrene base)	0.32	0.36	0.36	0.32	0	0	0	0
Amberlite WB-2 paper (containing 45% of Amberlite IR 4B, a phenolic weak base resin)	0.04	0.06	0.07	0.07	0	0	0	0
Amberlite SB-2 paper (containing 45% of Amberlite IRA-400, a strong base styrene resin)	0	0	0	0.02	0	0	0	0

hence adsorbs  $\text{ReO}_4^-$  stronger) and the additional ethyl groups increase the adsorption of  $\text{AuCl}_4^-$  on DEAE-cellulose even at lower LiCl concentrations.

Cellulose phosphate adsorbs anions less than cellulose which could be expected since highly polar groups are present in the first. The acrylic (carboxylic) resin Amberlite WA-2 adsorbs less strongly than cellulose anion exchangers and even less than a nuclear sulphonic resin. Evidently the network plays a considerable role in the adsorption on these resins.

The low  $R_F$  values of  $\text{AuCl}_4^-$  on anion exchange and sulphonic resins does not permit any conclusions, however, for these resins equilibrium studies have already been recorded<sup>1-3</sup> and confirm the general picture here presented.

Work on a large number of metal ions with various exchangers and LiCl as solvent is in progress and will be described later.

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