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## Ion-exchange paper chromatography of inorganic ions

### XXVI. The adsorption of $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ on various cation-exchange papers

In two previous papers<sup>1,2</sup> we have shown that complexes of the type  $\text{Co}(\text{NH}_3)_6^{3+}$  are adsorbed by sulphonic resins with an apparent charge of about +5 (if a law of mass action equation is applied) and moreover that on sulphonic cellulose paper they have a charge of only about +2. Both can be explained if one assumes that the sulphonic groups of the resin (acting as if they were present in solution) form outer-sphere complexes with the cobalt complexes, and the degree of complexing varies with the "concentration" of the sulphonic groups.

This note gives additional data on the adsorption of  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Co}(\text{en})_3^{3+}$  on various cation-exchange papers. LiCl was used as eluent in this study, as numerous weak exchangers would not be ionised in HCl solutions. Chromatograms were obtained by ascending development using the  $\text{Li}^+$  form of the various exchange papers in small jars at a temperature of  $20 \pm 1^\circ$  with aqueous solutions of LiCl (A.R.) prepared by suitably diluting a 10 N stock solution. The developed chromatograms were sprayed with ammonium sulphide revealing dark spots for the cobalt complexes.

The "charge" of the complex was obtained graphically by plotting  $R_M$  values against  $\log [\text{LiCl}]$ , and the tangent of the line should then indicate the charge of the metal ion in a law of mass action equation (see ref. 3).

#### Results

On sulphonic resin paper, Amberlite SA-2, the  $R_M$  vs.  $\log [\text{LiCl}]$  plots yield tangents of 3.9 and 3.3 for  $\text{Co}(\text{en})_3^{3+}$  and  $\text{Co}(\text{NH}_3)_6^{3+}$  which are similar to those obtained with HCl on the same paper (namely 4.6 and 4.75, see ref. 1). This is again an example where the charge is above the theoretical value (which should be below 3).

On cellulose phosphate paper (Whatman No. P20) the tangents are 2.1 and 2.2. The usual hydrated trivalent ions such as  $\text{Al}^{3+}$  have such values on the Amberlite

TABLE I

THE CHARGE EXHIBITED BY SOME COBALT COMPLEXES ON CATION-EXCHANGE PAPERS

Cation-exchange paper	Eluent	"Apparent charge" or tangent of the $R_M$ vs. $\log [\text{LiCl}]$ plot for	
		$\text{Co}(\text{NH}_3)_6^{3+}$	$\text{Co}(\text{en})_3^{3+}$
Amberlite SA-2 paper	HCl	4.75	4.6 (from ref. 1)
Amberlite SA-2 paper	LiCl	3.3	3.9
Cellulose phosphate paper Whatman No. P20	LiCl	2.2	2.1
Cellulose citrate paper Whatman No. CT30	LiCl	1.5	1.5
Carboxymethyl cellulose paper Whatman No. CM50	LiCl	1.2	1.2
Zirconium phosphate paper	LiCl		2.4
Sulphonic acid cellulose paper (Macherey, Nagel and Co., Stark Sauer)	HCl	1.6	1.6 (from ref. 2)

sulphonic papers, and these can be considered to be closest to a "normal" behaviour of trivalent cations. Cellulose citrate paper (Whatman No. CT30) and carboxymethyl cellulose paper (Whatman No. CM50) give tangents of 1.5 and 1.2, respectively, and thus approach those obtained on the cellulose sulphonate paper (Macherey, Nagel and Co.; Stark Sauer)<sup>2</sup>.

Zirconium phosphate paper gave rather erratic results perhaps due to a lack of uniformity of the paper employed. The only series of points which can be used to construct a line was obtained with  $\text{Co(en)}_3^{3+}$  on a paper impregnated with 15%  $\text{ZrOCl}_2$  (and precipitated with an excess of phosphoric acid). The tangent is 2.4.

The results are summarised in Table I and show that the "charge" exhibited in the law of mass action equation of the equilibrium of the complexes varies with the exchanger and can have (so far) any value from 5 to 1. If we assume that the adsorption of these complexes is due to outer-sphere complexing, these results appear reasonable as various degrees of outer-sphere complexing with various anions have been noted<sup>4</sup>.

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