CHROM. 5825

The paper electrophoretic study of ion-pair formation. VIII
The behaviour of Co(III) complexes in solutions of chromate and dichromate

The formation of outer-sphere complexes between a wide range of anions and a series of Co(III) of varying size of ligands (*viz.* $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(dipyridyl)_3^{3+}$ and $Co(o\text{-phenanthroline})_3^{3+}$) has been studied in this laboratory[1,2] by means of high voltage paper electrophoresis, and generally monovalent anions form stronger outer-sphere complexes with increase of ionic size (both for the Co(III) complex and the anion) while divalent anions notably sulphate and thiosulphate reverse the order to $Co(en)_3^{3+} < Co(NH_3)_6^{3+} < Co(o\text{-phen})_3^{3+} < Co(dipyridyl)_3^{3+}$. This reversal is most probably due to hydrogen bond formation of amino groups of the ligand with the anion.

So far no data on the behaviour of chromate have been obtained and we felt that these would be interesting in order to complete the picture.

Experimental and results

High voltage paper electrophoresis employing a Camag apparatus was used as described in previous papers[1,2]. The cobalt complexes could be detected with ammonium sulphide. The electrophoretic movement in various concentrations of chromate and at various pH values is shown in Fig. 1. There is a remarkable difference between acid solutions and neutral and alkaline solutions. In the first the order of electrophoretic movement is that normally encountered with monovalent acids such as perchloric acid while in neutral and alkaline solutions the sequence is that found with sulphate or thiosulphate.

We were thus interested whether the difference is inherent in an equilibrium of the type

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^-$$

or whether it was due to the polymerization of chromate to di- and possibly trichromate.

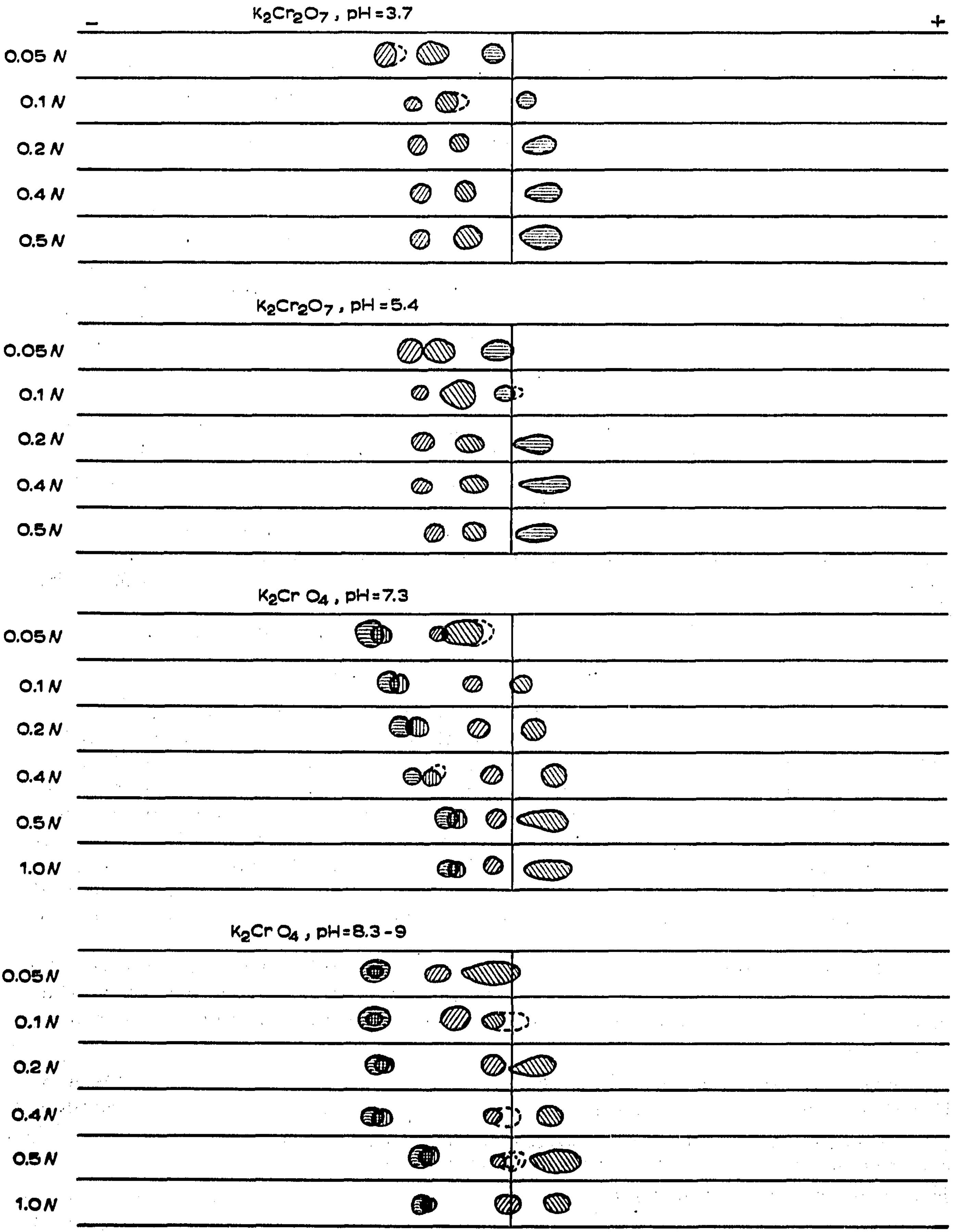
If it were due to the $HCrO_4^-$ a similar effect should occur with sulphate at low pH values where HSO_4^- is present. However, as shown in Fig. 2 acid sulphate behaves essentially identically to neutral sulphate (whereas chromate at pH 5.4 does not). Another possible effect was suggested: OH^- could effectively compete in ion-pair formation in the solutions above pH 7. That this is not likely is shown in Fig. 3 where the movement of cobalt complexes in trichloroacetate at three different pH values shows no great change. It thus appears that the formation of ion pairs between the dichromate ion and cobalt complexes is radically different from that between chromate and cobalt complexes.

There is a number of plausible explanations for this difference, however the scope of this note is merely to report on the phenomenon observed. We believe that interesting results should also be obtained with other polyanions and intend to work in this direction.

Laboratorio di Cromatografia del C.N.R., L. OSSICINI
Via Romagnosi 18 A, Rome (Italy) S. BICHI

1 M. MAZZEI AND M. LEDERER, *J. Chromatogr.*, 31 (1967) 196.
2 M. LEDERER AND M. MAZZEI, *J. Chromatogr.*, 35 (1968) 201.

Received November 18th, 1971



−
+
$K_2Cr_2O_7$, pH = 3.7
0.05 N
0.1 N
0.2 N
0.4 N
0.5 N
$K_2Cr_2O_7$, pH = 5.4
0.05 N
0.1 N
0.2 N
0.4 N
0.5 N
K_2CrO_4, pH = 7.3
0.05 N
0.1 N
0.2 N
0.4 N
0.5 N
1.0 N
K_2CrO_4, pH = 8.3-9
0.05 N
0.1 N
0.2 N
0.4 N
0.5 N
1.0 N

Fig. 1

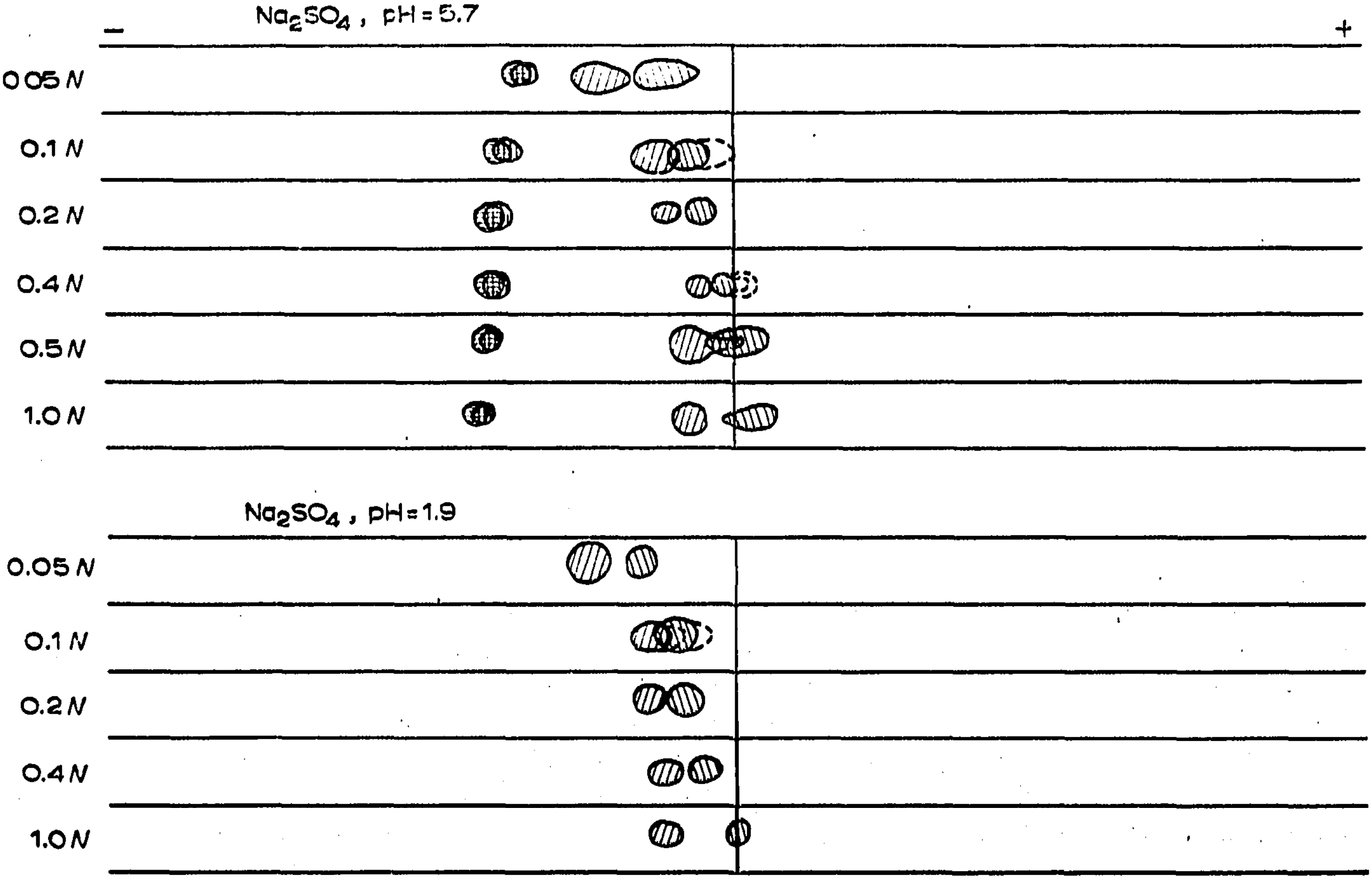


Fig. 2. High voltage electrophoresis of some cobalt complexes in solutions of sulphate at two pH values. At pH 1.9 the complexes with dipyridyl and *o*-phenanthroline decomposed and are not shown. Voltage, 1500 V; temperature, 6°; time, 30 min; on Whatman No. 1 paper. The symbols are the same as in Fig. 1.

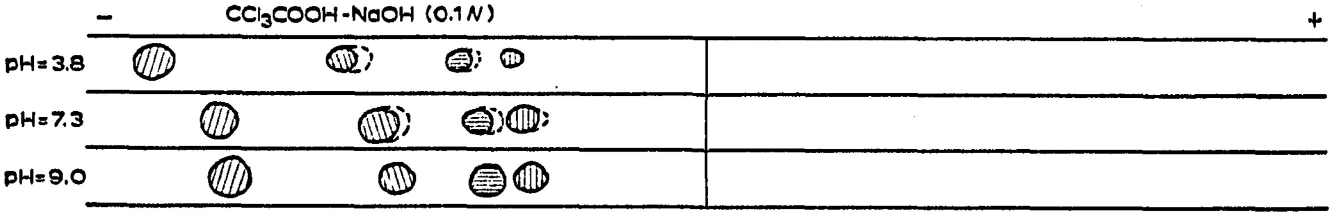


Fig. 3. High voltage electrophoresis of some cobalt complexes in trichloroacetate at various pH values. Voltage, 1500 V; temperature, 6°; time, 30 min; on Whatman No. 1 paper. The electrolytes were trichloroacetic acid–sodium hydroxide mixtures 0.1 *N* suitably adjusted to various pH values. The symbols are the same as in Fig. 1.

Fig. 1. High voltage electrophoresis of some Co(III) complexes in solutions of chromate and dichromate at various pH values. Apparatus, Camag; voltage, 1500 V; temperature, 8°; time, 30 min; on Whatman No. 1 paper. 0.5 *N* and 1 *N* solutions were run with 1000 V only. In the case of 0.5 *N* dichromate the temperature had to be raised to 16° to avoid crystallization during electrophoresis. Diagonal lines (top right to bottom left), $Co(NH_3)_6^{3+}$; diagonal lines (top left to bottom right), $Co(en)_3^{3+}$; horizontal lines, Co $(o\text{-phen})_3^{3+}$ and vertical lines, Co $(dip)_3^{3+}$.