Salicylate and 5-Sulfosalicylate Complexes of Chromium(II)[1a]

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The chromous complexes with salicyclic and 5-sulfosalicylic acids represent two of the most powerful reducing agents stable in aqueous solution. pH titrations indicate two salicylate ions per chromium in the complex, with $pk_1 = 8.41$ and $pk_2 = 6.95$ in 3 F sodium perchlorate. The corresponding constants of the closely related 5-sulfosalicylate complexes are $pk_1 = 7.14$ and $pk_2 = 5.74$. The salicylate complex gives an anodic polarographic wave with a half-wave potential of -1.33 v. vs. s.c.e. at pH 12. The chromous EDTA complex, with an anodic half-wave potential of -1.48 v. at pH 12, is a more powerful reducing agent than any yet observed.

In a polarographic study of complexes of chromous ion with various ligands,[2] we have noted the existence of a salicylate complex with an anodic half-wave potential of -1.23 v. vs. s.c.e. On the basis of the half-wave potential, this complex was considered to be one of the most powerful reductants known in aqueous solution. This paper describes a more thorough investigation of the nature of this complex. By means of potentiometric studies we have arrived at the formula and the stepwise formation constants of this system of complexes as well as for the closely related 5-sulfosalicylate system.

Experimental

Reagents.—Chromous perchlorate solutions were prepared from potassium dichromate, Primary Standard grade. The latter was dissolved in perchloric acid and reduced to chromic perchlorate with hydrogen peroxide. The resulting solution contained 0.1 F chromium(III) and 0.25 F perchloric acid and was introduced into a three compartment electrolysis cell. The mercury cathode and external platinum foil anode were separated by coarse sintered glass disks from the center salt bridge. A small flow of air-free 3 F perchloric acid was maintained through the bridge to reduce cross contamination. All operations from this point were performed under a slight positive pressure of purified nitrogen. An electrolysis current of 0.5–0.7 amp. was maintained by manual regulation of the applied voltage (20–30 v.). This gave a current density of 0.03 amp./cm.². The electrolysis was continued for 30 minutes after it appeared that the chromic ion had been entirely reduced. The electrolysis vessel was connected directly to the Stone-type storage buret[3] with all glass fittings. Throughout the electrolysis a current of nitrogen flushed the entire apparatus. The chromous content of the solution was determined by titration with potassium iodate[3] or by reduction of ferric ion and subsequent titration of the ferrous ion produced with standard dichromate solution. The chromic content was determined spectrophotometrically or by difference between the chromous content and total chromium. The molar absorbancy of chromium(III) in these solutions is 15 at the 415 mμ peak. Chromium(II) is essentially transparent in this region with an absorbancy of less than 0.2. The chromic content was never more than 1% of the total and was ignored. Hydrogen ion was determined by potentiometric titration with ethylenediamine.

Chromous solutions prepared in the above manner showed no increase in chromic ion for periods up to two months.[4] The solution of chromous chloride used for the earlier work[2] was restandardized after being undisturbed for ten years. The titer, which had decreased by 1.0% in the first six months, decreased by only 0.2% in the following ten years, showing that carefully prepared chromous solutions are far more stable than commonly believed.

Sodium perchlorate, Reagent grade, was used without further purification for the polarographic supporting electrolyte. A small contamination of acid was removed by four-fold recrystallization for the pH titrations.

Salicylic acid was purified by sublimation. The 5-sulfosalicylic acid (Eastman White Label) was found to be 99.4% pure by acid assay and was used without further purification. All other chemicals were reagent grade.

pH **Measurements.**—We define pH as the negative logarithm of the hydrogen ion *concentration*. In all of this work unless otherwise noted, there was a large excess of inert salt present so that the ionic strength did not vary appreciably. A calibration curve was determined relating the millivolt response of a glass–calomel electrode pair to known hydrogen ion concentrations. The linear response was verified and the electrodes were recalibrated daily.

In the polarographic work, a Beckman Model G pH meter was used operating on the millivolt range. The glass electrode was an experimental type with very small sodium ion correction, kindly furnished by Beckman Instruments, Inc. The calomel electrode was saturated with sodium chloride and was pressurized with a reservoir of sodium chloride solution connected to the side arm of the electrode and placed 50 cm. above. The small flow of solution (100 ml./month) aided in rapidly establishing a reproducible junction potential.

For the pH titrations, a Radiometer Model PHM4b pH meter (Radiometer, Copenhagen) was used. With this instrument and the electrodes described above, we obtained a precision of a few tenths of a millivolt.

Polarography.—Polarograms were automatically recorded on a calibrated Sargent Model XXI Polarograph, without damping. The cell was a modified three-compartment H-cell[5] thermostatted at 25.0 ± 0.1°. The calomel electrode was saturated with sodium chloride and the center compartment was filled with 6 F sodium perchlorate. The potential between the calomel electrode of the polarographic cell and a Beckman fiber-type, potassium chloride calomel electrode immersed in 1 F sodium chloride in the test solution compartment of the cell was 2 ± 1 mv., the Beckman electrode being positive. A correction for this difference has not been made in the data reported here. The capillary had a flow rate of 1.957 mg./sec.; drop time varied from 4 to 5.5 seconds depending on potential and was measured accurately at the proper potential in the determination of the diffusion current constant. Solutions were deaerated by bubbling with nitrogen which had passed through a chromous sulfate scrubbing tower, a tube filled with hot copper turnings and a distilled water scrubber. Potentials were measured vs. the saturated sodium chloride calomel electrode with a Gray Instrument Company potentiometer, Model E-3062H, and are considered accurate to ± 3 mv.

Discussion

pH **Titrations of the Chromous Salicylate System.**—As Bjerrum has shown,[6] measurements of the pH of solutions of metal ions and complexing agents which are bases can be interpreted to give information about the formulas and stability constants of the complexes formed in the system.

We assume complexation reactions in this system to be

(1) (a) Portions of this work were supported by the National Science Foundation. (b) du Pont Teaching Fellow, 1958–1959. Abstracted from the dissertation submitted by William P. Schaefer to the Graduate Division, University of California, Los Angeles, in partial fulfillment of the requirements for the degree Doctor of Philosophy.

(2) R. L. Pecsok and J. J. Lingane, THIS JOURNAL, **72**, 189 (1950).

(3) H. W. Stone, *Anal. Chem.*, **20**, 747 (1948).

(4) K. Schug and E. L. King, THIS JOURNAL, **80**, 1090 (1958).

(5) R. L. Pecsok and R. S. Juvet, Jr., *Anal. Chem.*, **27**, 165 (1955).

(6) J. Bjerrum, ''Metal Ammine Formation in Aqueous Solution,'' P. Haase and Sons, Copenhagen, 1941.

$$Cr^{++} + HSal^- = CrSal + H^+ \qquad (1)$$

$$CrSal + HSal^- = CrSal_2^- + H^+ \qquad (2)$$
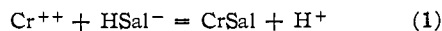
and we can write

$$k_1 = \frac{(Cr^{++})(Sal^-)}{(CrSal)} \quad (3) \qquad k_2 = \frac{(CrSal)(Sal^-)}{(CrSal_2^-)} \quad (4)$$

In order to obtain $\bar{n}$, the average number of ligands bound per metal ion, we start with the complexation reaction (equations 1 and 2) and assume that each ligand which combines must release one hydrogen ion and that there are no bi-nuclear species formed. The equations given below are written for a maximum value of $\bar{n}$ (N) of 2, but the final result is independent of the value of N chosen for the derivation. We have for charge balance in the system

$$2(Cr^{++}) + (Na^+) + (H^+) = (HSal^-) + 2(Sal^-) +$$
$$2(CrSal_2^-) + (ClO_4^-) + (OH^-) \quad (5)$$

and for the material balances

$$\Sigma_{Cr} = (Cr^{++}) + (CrSal) + (CrSal_2^-) \qquad (6)$$

$$\Sigma_{Sal} = (H_2Sal) + (HSal^-) + (Sal^-) + (CrSal) +$$
$$2(CrSal_2^-) \quad (7)$$

The two ionization equilibria for salicylic acid are

$$K_1 = \frac{(H^+)(HSal^-)}{(H_2Sal)} \quad (8) \qquad K_2 = \frac{(H^+)(Sal^-)}{(HSal^-)} \quad (9)$$

We must now solve these equations for total bound ligand concentration (which is equal to (CrSal) plus 2(CrSal$_2^-$)). The total bound ligand concentration obtained in this way is divided by the total chromous ion present, giving

$$\bar{n} = \frac{(H^+)^2 + K_1(H^+) + K_1K_2}{\Sigma_{Cr}[2(H^+)^2 + K_1(H^+)]} \left[2\Sigma_{Cr} + (Na^+) + (H^+) - \frac{K_w}{(H^+)} - (ClO_4^-) - \Sigma_{Sal} \left(\frac{K_1(H^+) + 2K_1K_2}{(H^+)^2 + K_1(H^+) + K_1K_2} \right) \right]$$
$$(10)$$

This equation, which is similar to the equations developed by Martell and Calvin,[7] has on the right hand side only known or easily calculated quantities and hydrogen ion concentration. The latter is measured, $\bar{n}$ calculated, and the results plotted vs. pSal.

The solution of the equation given above for $\bar{n}$ is exceedingly tedious when many experimental data are available. For this reason, use was made of the FORTRAN automatic coding system and the IBM 709 computing system located at the Western Data Processing Center (Graduate School of Business Administration, University of California, Los Angeles). All data were calculated with the aid of this machine.[8]

Preliminary experiments were made in media of low, uncontrolled ionic strength and $\bar{n}$ determined by a graphical method.[7] This was plotted against a pSal which is very approximate. The results of two of these experiments are reproduced as Fig. 1b in order to show the long flat portion of the curve at $\bar{n} = 2.0$. No data are given below $\bar{n} = 0.5$, because at this point the pH is such that the bisalicylate–salicylic acid buffer is becoming operative and the measurements made on graphs become very

(7) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Englewood Cliffs, New Jersey, 1952.

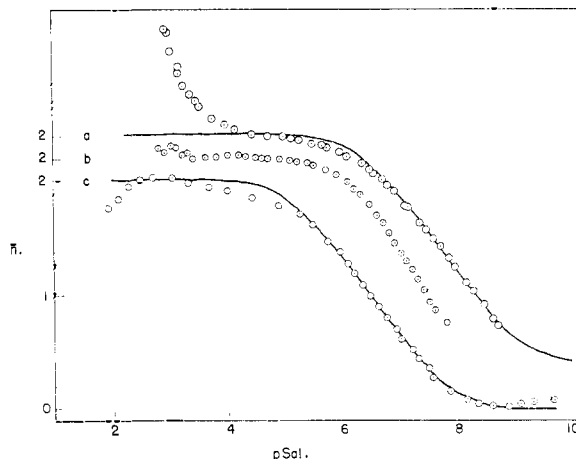(8) The writers are grateful to Mr. Lowell Wood of U.C.L.A. for preparing the program for these calculations.

Fig. 1.—Formation curves of the chromous salicylate and 5-sulfosalicylate complexes: a, for salicylic acid in 3 F sodium perchlorate; b, for salicylic acid at uncontrolled ionic strength; c, for 5-sulfosalicylic acid in 1 F sodium perchlorate. (Curves b and a are displaced by 0.2 and 0.4 $\bar{n}$ units, respectively; solid lines represent the theoretical curves for formation constants selected.)

unreliable. It was for this reason that an algebraic means of determining $\bar{n}$ was sought in the hope that, with accurate pH measurements, the curve could be extended through 0.5 in order to obtain there a value of k_1 for the complex. This requires, of course, a precise knowledge of the dissociation constants (particularly the first) of salicylic acid. pK_1 is given in the compilation of Bjerrum, Schwarzenbach and Sillen[9] as 3.86; the original work of Ågren gave this same number as determined by titration with a properly calibrated glass electrode in 3 F sodium perchlorate solution.[10] However, the present writers' calculation of pK_1 from the value of K_1 given by Ågren, viz., (0.718 ± 0.005) × 10^{-3}, gives a value of pK_1 of 3.144 ± 0.003. The figure obtained in this work from a similar series of titrations was 3.183 ± 0.014; this latter figure was used in all calculations. All values quoted and all titrations performed herein refer to 3 F sodium perchlorate.

pK_2 of salicylic acid was given in the same work[10] as 13.12 ± 0.05, calculated from spectrophotometric data. The spectra of these species were examined in this study and it seemed that a great deal of effort would be required for us to improve upon the accuracy of Ågren's value; it was therefore taken as given. Ågren also determined the ion product of water in 3 F sodium perchlorate and pK_w was taken as listed,[10] 14.15 ± 0.01.

With the necessary data at hand, several titrations were made and the results plotted. The best of these plots are reproduced as Fig. 1a; the increase above $\bar{n} = 2$ continues to at least $\bar{n} = 8$. From these data the stability constants of the complexes were calculated. As the curves obtained by the algebraic solution of the equation for $\bar{n}$ do not level off at 2.0 as predicted, it was assumed that something used in the computation was at fault.

(9) J. Bjerrum, G. Schwarzenbach and L. Sillen, "Stability Constants, Part I, Organic Ligands," The Chemical Society, London, 1957.

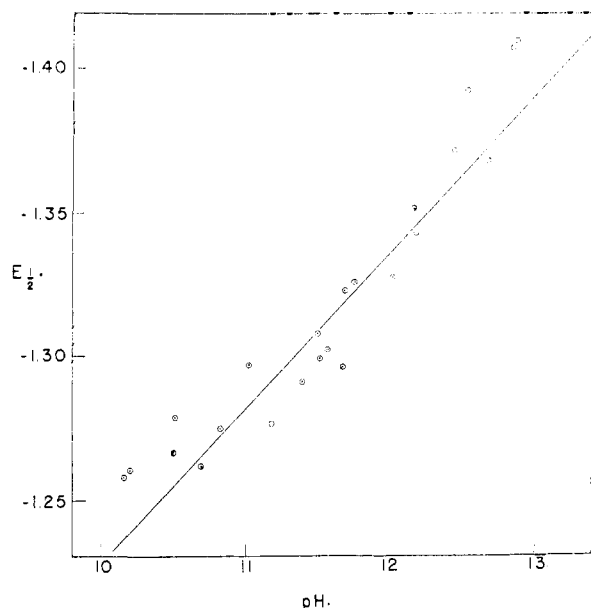(10) A. Ågren, Acta Chem. Scand., 8, 1059 (1954); 9, 49 (1955).

Fig. 2.—Half-wave potential of the chromous salicylate complex as a function of pH. (The line is drawn with the theoretical slope, 59 mv./pH unit.)

This could be either the measurement of pH in basic regions, giving erroneous values for hydrogen ion concentration, or an incorrect value of pK_2 of salicylic acid. Small changes in either of these (say, $\pm$ 0.03 log unit) can alter the entire shape of the $\bar{n}$ curve in this basic region. The maximum value of $\bar{n}$ was taken as 2.0 from the data of Fig. 1b, and only the descending portion of the curve below $\bar{n} = 2$ in Fig. 1a was used for the stability constant computations.

Irving and Rossotti[11] have devised a method of calculation which makes use of more of the experimental data than Bjerrum's method of successive approximations. Using their table of correction factors, the successive dissociation constants of the complex were calculated. The resulting values of pk_1 and pk_2 are posted in Table I.

TABLE I

DISSOCIATION CONSTANTS OF THE CHROMOUS SALICYLATE COMPLEXES CALCULATED FROM VARIOUS POINTS ON THE FORMATION CURVE

$\bar{n}$	pk_1	$\bar{n}$	pk_2
0.9	8.41	1.1	6.98
.8	8.41	1.2	6.96
.7	8.41	1.3	6.96
.6	8.41	1.4	6.92
.5	8.40	1.5	6.91
Value taken	8.41		6.95

pH Titrations of the Chromous Sulfosalicylate System.—By means of similar experiments and computations, the formation curve of the chromous 5-sulfosalicylate complexes was determined (Fig. 1c). The necessary titrations were made in 1 F sodium perchlorate solution with a recalibrated glass electrode. pK_w was taken as 13.76 by calculation from the data of Harned and Owen[12] for 0.974

(11) H. Irving and H. S. Rossotti, J. Chem. Soc., 3397 (1953).

(12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 2nd Ed., Reinhold Publishing Co., New York, N. Y., 1950, p. 578.

M sodium bromide, the solution which most closely resembled our solution. pK_2 and pK_3 of the acid were determined from titrations as 2.329 $\pm$ 0.004 and 11.389 $\pm$ 0.012, respectively. Using again the correction tables of Irving and Rossotti,[11] pk_1 and pk_2 of the sulfosalicylate complexes were determined and are posted in Table II. The peculiar hump in the plot of $\bar{n}$ vs. $pSal$ at $pSal = 5$ is real, and the shape of the curve is not affected by varying the values of K_2 and K_3 of the sulfosalicylic acid or K_w. Presumably some mixed hydroxy complex is being formed in this region, causing the curve to depart from the theoretical. Mixed complexes (as well as binuclear ones) cannot be treated by Bjerrum's methods.

TABLE II

DISSOCIATION CONSTANTS OF THE CHROMOUS 5-SULFOSALICYLATE COMPLEXES CALCULATED FROM VARIOUS POINTS ON THE FORMATION CURVE

$\bar{n}$	pk_1	$\bar{n}$	pk_2
0.9	7.11	1.1	5.78
.8	7.13	1.2	5.77
.7	7.10	1.3	5.80
.6	7.17	1.4	5.72
.5	7.22	1.5	5.62
Value taken	7.14		5.74

Polarography of the Chromous–Salicylate System.—A series of polarograms was taken at a constant pH of 12.5 and with a total salicylate concentration varying from 0.01 to 1.0 F. The half-wave potential varied by no more than ±0.01 v. As Fig. 2 shows, the half-wave potential does, however, vary with pH and becomes more negative by about 60 mv. as the pH increases by one unit. The slight discrepancy of 100 mv. between the half-wave potential reported here and that reported in the earlier study[2] is caused by the use of a greater concentration of gelatin in the previous work.

All polarograms plotted in Fig. 2 were checked for reversibility by plotting log $[i - (i_d)_a]/[(i_d)_c - i]$ vs. E_{de}. The slope varied from 53 to 65 mv. per log cycle and was close to the theoretical value of 59 mv. except in the presence of maximum suppressor. Although from the above observations the anodic wave appears to be reversible, all attempts to obtain a cathodic wave for the reverse process failed. The chromic–salicylate complex produced by controlled potential oxidation of the chromous complex at a large mercury anode was not polarographically reducible. Preparations from chromic ion, salicylate and sodium hydroxide also gave a non-reducible complex regardless of the order of mixing. We conclude that the chromic salicylate complex produced by oxidation at the d.m.e. is stable for periods of the order of the drop time but reaches equilibrium slowly with respect to another species. The latter species is very likely a form of hydrous chromic hydroxide, although a precipitate was not observed and chromic hydroxide can be peptized in the presence of basic salicylate to yield an apparently soluble species.

Because of the slow attainment of an equilibrium state of the chromic complex, it is not possible to use the polarographic data to calculate stability constants. However the data can be interpreted

in a qualitative sense. The independence of half-wave potential on salicylate concentration and the dependence on pH show that the number of salicylate ions is the same in both the chromous and chromic complexes and that one hydrogen ion is released (or one hydroxide consumed) in the oxidation. It is reasonable to think that, if a water molecule were coördinated to the chromous ion, when this ion is oxidized the increased central positive charge would promote the ionization of one of the water protons. Such a reaction is proposed to account for the observed behavior. Chromous ion is characteristically four-coördinate but like cupric ion can accept another ligand.[13] It is thought that two salicylate ions occupy four of the coördination positions in a square-planar arrangement and the fifth position above the plane holds a water molecule bound more loosely. Then, at the d.m.e., the reaction proposed is

$$CrSal_2H_2O^- = CrSal_2OH^- + H^+ + e^- \quad (11)$$
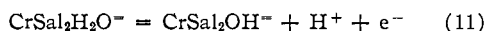
The anodic limiting current was shown to be diffusion controlled and was found to be precisely linear with concentration in the range from 0.04

(13) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

to 0.28 mF chromium(II). The diffusion current constant, I, of the complex in 3 F sodium perchlorate at pH 12 is -1.05.

It was mentioned earlier that the very negative anodic half-wave potential of the chromous salicylate complex showed it to be one of the most powerful reductants known in aqueous solution. It was thought that this property could lead to certain practical applications and for that reason the present study was initiated. In the course of this investigation, a very brief study of the ethylenediaminetetraacetate complex of chromous ion was made, and it was found that above pH 12, this complex has an anodic half-wave potential of -1.48 v. $vs.$ s.c.e. The wave was apparently reversible and the half-wave potential was not a function of pH or of EDTA concentration in this region. Between pH 12 and 8, the half-wave potential decreased to -1.24 v., indicating that one hydrogen ion per electron is involved in the oxidation in this region. Below pH 8 no studies were made; the solutions turn purple and begin evolving hydrogen gas when they are made too acid. However, it seems clear that the chromous EDTA complex in basic media is an even more powerful reducing agent than the salicylate complex.

Mononuclear and Polynuclear Complex Formation by Manganese(II) and Zinc(II) Ions with 2,3-Dimercapto-1-propanol: The Behavior of the E$_r$ Function with Mercaptide[1a]

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Manganese(II) and zinc(II) ions react with 2,3-dimercapto-1-propanol to form complexes of the type MDMP and MDMP$_2^-$. The formation constants of these species are $1.7 \times 10^{+5}$ and $2.7 \times 10^{+10}$, respectively with manganese(II) and are $3 \times 10^{+13}$ and $2 \times 10^{+23}$ with zinc(II) at 30° and at an ionic strength of 0.10 M. For the bis DMP complexes the difference in the free energies of complex formation corrected for the hydration energies of the aqua ions, the George E_r function, has the largest value of any that can be calculated from data found in literature. This seems to be the result of a larger increase in the strength of σ bonds in the series Mn(II) through Zn(II) with mercaptide than with the more common ligands having oxygen or nitrogen donor groups. The value of E_r is roughly proportional to the number of mercaptide groups coördinated to the metal ions. Polynuclear complexes are also formed by zinc(II) and DMP. The data indicate that a "core plus links" series, $(ZnDMP_2)\cdot(ZnDMP)_n^-$, is formed. The stability of the dimer (the first member of this series) is less than that for the corresponding dimeric nickel(II) DMP complex. This appears to be due to the greater importance of π bonding in the nickel(II)-polynuclear complexes.

The ligand field stabilization energies for a number of complexes of the divalent metal ions of the first transition series have been shown[2-4] to be related to the difference in the free energies of formation of the corresponding Mn(II) and Zn(II) complexes. This difference after correction for the hydration energies of the aqua metal ions is designated E_r.[5] Its value gives direct evidence of the course of the almost linear[4] monotonic function in the series Mn(II)–Zn(II) that would describe the stabilities

(2) P. George, *Rec. trav. chim.*, **75**, 671 (1956)

(3) D. L. Leussing, THIS JOURNAL, **80**, 4180 (1958).

(4) P. George and D. S. McClure, Progress in Inorganic Chemistry, Vol. I, F. A. Cotton, ed., Interscience Publishing Co., New York, N. Y., 1959.

(5) This has been designated as Δ in ref. 3.

of the intervening ions in the absence of ligand field stabilization. A comprehensive examination of the stabilities of a large number of complexes with different ligands reveals that E_r increases with the coordination O<N<S and its use, together with ligand field stabilization energies, as a tool diagnostic of the number and kind of coordinated groups has been demonstrated.[4]

The value of E_r represents essentially the free energy for the reaction $Zn_g^{++} + MnL_{naq.} \rightarrow ZnL_{naq.} + Mn^{++}$ and is almost entirely determined by the difference in the heats of formation of the solvated complexes. Because the effect of the ligand activity is absent, or at least minimized, and the activities of the metal ions are the same, changes in E_r with different ligands are more significant of changes in the metal ion-donor atom bond strengths than are changes in just the formation constants, the reason being that changes