

Distribution of Cr(VI) Particles in Acid Solutions

By R. Šarmaitis, V. Dikinis, V. Rezaite and V. Stasiukaitis

The experimental dependence of the apparent constant of formation of polychromium particles (K_{3p}) on pH was determined by the static ion chromatography method. The equilibrium forms of Cr(VI) particles were estimated in solutions of acids. The effect of the presence of substituted chromates on distribution of equilibrium forms of chromic acid was evaluated. The change of acidic properties of Cr(VI) solutions was calculated with introduction of anions of various acids into their composition.

A model of CrO_3 solution has been proposed by the authors.¹ It takes account of the law of conservation of neutrality, equilibrium in the presence of polychromates, material balances of Cr(VI), and both total and free acidity, as well as the acidity formed (or bonded) at stages of CrO_3 solution titration by alkali.

Solution of a set of equations according to the model proposed made it possible to estimate the formation constants of $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ particles, using numerical methods. The division of polychromic acids into $\text{H}_2\text{Cr}_3\text{O}_{10}$ and $\text{H}_2\text{Cr}_4\text{O}_{13}$ is conventional.² Accordingly, it is expedient to determine every apparent constant of formation of polychromic particles (K_{3p}) on the basis of experimental data and to express their total concentration in terms of $\text{Cr}_3\text{O}_{10}^{2-}$ particle concentration.

Pure CrO_3 solutions are very seldom used in practice. Electrolyte compositions used and meant for depositing chromate coatings, chromium plating and etching, contain anions of other organic and inorganic acids in addition to chromic acid (*i.e.*, in essence, they are mixtures of solutions of acids).

It is suggested that in the case of concentrated CrO_3 solutions, the equilibria occurring in them, in the presence of other acids, are modified, because substituted chromates, such as CrO_3Cl^- , CrSO_7^{2-} , HCrPO_7^{2-} and $\text{H}_2\text{CrPO}_7^-$ are developed.³ The chromium plating theory of J.P. Hoare^{4,5} is widely used. According to this theory, Cr(VI) is reduced to metallic Cr at the cathode by the products of interaction between the ions of trichromic acid, $\text{HCr}_3\text{O}_{10}^-$, and those of HSO_4^- . There is good reason to calculate the equilibrium in solutions of chromic acid, in the presence of anions of other acids, to predict their acidic properties and availability of substituted chromates.

Experimental Procedure

To determine experimentally the apparent constant of formation of polychromic particles, the chromic acid solution model was used, plus the static variant of the ion exchange chromatography described in detail and discussed in our previous paper.¹ The anionite AB-17 (manufactured in Russia) was used in the form of the chloride salt (the fraction > 0.3 mm). From 0.7 to 10 g/L of the anionite was added to acidified ($C_{\text{H}^+} = 0.01$ to 0.4 mol/dm³) solutions of chromic acid ($C_{\text{Cr(VI)}} = 0.05$ to 0.2 mol/dm³) and agitated by a magnetic stirrer for 5 to 30 min. The quantity of the anionite added was the amount necessary to absorb Cr(VI) completely, with an excess of 15 percent. After separating the anionite in the

filtrates, the Cr(VI) content was determined by the classical method of iodometric titration by sodium thiosulfate. The Cl^- evolved was determined mercurimetrically, using sodium nitroferrocyanide as an indicator. The total acidity (C_{H^+}) was determined by alkaline potentiometric titration.

The concentration of Cr(VI) [$\Delta C_{\text{Cr(VI)}} \equiv C_{\text{Cr(VI)}}$] and that of bound acidity ($C_{\text{H}^+} - C_{[\text{H}^+]}$) were calculated from the difference between the initial concentration and the concentration determined after anion exchange experiments. The quantities of chromic acid particles absorbed by the anionite ($\Delta C_{\text{Cr(VI)}}$) and the Cl^- evolved were recalculated for the stock solution. It should be noted that the concentration of Cl^- evolved in CrO_3 solutions free from other acids corresponds to the concentration of free acid $C_{[\text{H}^+]}$ (*i.e.*, $\Delta C_{\text{Cl}^-} \equiv C_{[\text{H}^+]}$). It should also be noted that the pH of the chromic acid solution does not change in the experiments on anion exchange. In this connection, the equilibria between the particles of chromic acid do not change markedly in the course of the experiments (5-30 min).

The experimental data on determination of $C_{\text{Cr(VI)}}$, C_{H^+} , $C_{[\text{H}^+]}$ and $C_{\text{H}^+} - C_{[\text{H}^+]}$ were substituted into the corresponding equations of material balances of the authors' model of chromic acid solution.¹ When solving these equations together with equations of electrical neutrality, the data on the presence of condensed chromic acid particles greater than 2 in the solution were obtained. The apparent constant of formation of polychromic particles, $\text{Cr}_n\text{O}_{3n+1}^{2-}$ ($n > 2$), was calculated as $\text{Cr}_3\text{O}_{10}^{2-}$ and its dependence on pH was also determined.

All concentrations are given in moles ($M = \text{mol/dm}^3$). With either increase or decrease in pH of CrO_3 solutions, to calculate their composition, it was assumed that the electrical neutrality of the solutions is retained on introduction of either univalent Na^+ (NaOH) or Cl^- (HCl) ions, respectively.

Results and Discussion

The table lists a part of the experimental data obtained by investigating the polyforms of chromic acid and shows the values of K_{3p} by solving the set of

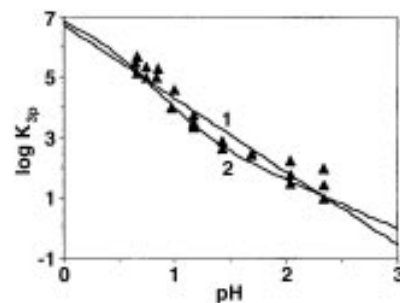


Fig. 1—Dependence of the apparent constant of formation of polychromic particles (K_{3p}) on pH (calculated as $\text{Cr}_3\text{O}_{10}^{2-}$). Curve 1 calculated by Eq. (1); curve 2 by Eq. (2).

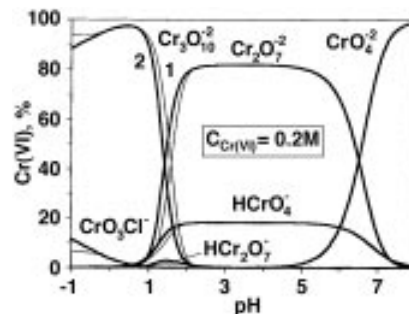


Fig. 2—Percentage distribution of Cr(VI) in equilibrium forms of chromic acid as a function of pH, taking into account K_{3p} by Eq. (1) for curve 1 and Eq. (2) for curve 2.

equations describing the model of chromic acid solution by the authors.¹ It should be noted that, when solving these equations, the influence of the contribution made by polychromic acids on the distribution of Cr(VI) in the solution is reflected through the particles of $\text{Cr}_3\text{O}_{10}^{2-}$, according to the equation

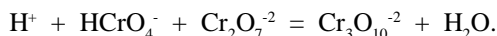


Figure 1 shows the dependence of K_{3p} on the pH of the Cr(VI) solution. A simplified approximation for the straight-line dependence calculated by the method of least squares (curve 1) is expressed by the equation

$$\log K_{3p} = 6.736 - 2.416 \cdot \text{pH} \quad (1)$$

A more exact analytical description of the experimental data of curve 2 is written as

$$\log K_{3p} = 4 - \text{pH} - \frac{8}{\pi} \cdot \arctan uv \quad (2)$$

where $u = 1.4 \text{ pH} - 2.2$ and $v = 0.6 - 0.4 \text{th}(u + 1)$.

Figure 2 shows calculations of Cr(VI) particle distribution in 0.2 M solution, depending on its pH by the model¹ and taking into account K_{3p} by Eq. (1) and (2). Extrapolation of the approximating curves shown in Fig. 1 is usually correct within no more than a tenth of the range under investigation. As it follows from the data of Fig. 2, however, there are actually no polychromic particles when the pH of a Cr(VI) solution exceeds 2. The difference in Cr(VI) distribution in

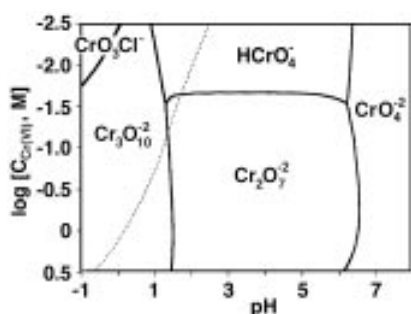


Fig. 3—The region of relative predominance of the equilibrium form of chromic acid, depending on Cr(VI) concentration and pH. The dashed line represents dependence of solution pH on CrO_3 concentration.

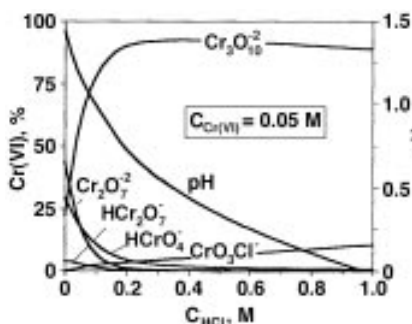


Fig. 4—Percentage distribution of Cr(VI) in equilibrium forms of chromic acid and change of solution pH as a function of HCl concentration.

the particles of either $\text{Cr}_2\text{O}_7^{2-}$ or $\text{Cr}_3\text{O}_{10}^{2-}$, depending on the application while calculating equations (1) or (2), is particularly significant when changing the pH of a Cr(VI) solution from 1 to 2.

It should be noted that under alkaline titration of Cr(VI) solutions (when calculating the total acidity), one mole of $\text{Cr}_2\text{O}_7^{2-}$ generates 2H^+ moles, and one mole of $\text{Cr}_3\text{O}_{10}^{2-}$ generates 4H^+ moles.¹ This circumstance should be taken into account when calculating (e.g., the gradient of total acidity concentrations in the diffusion layer during corrosion of zinc in chromating solutions with initial pH ranging from

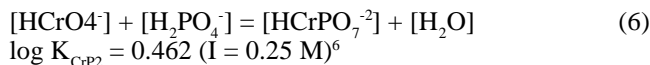
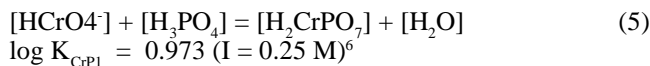
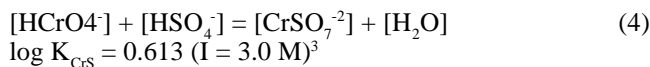
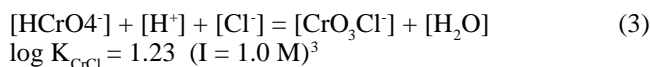
Values of the Apparent Constant
Of Polychromic Acids Formation (K_{3p})
Calculated as the Constant of $\text{Cr}_3\text{O}_{10}^{2-}$ Formation
Temp 25 °C, Anionite AB-17, Conc. in mol/dm³

		Experiment		Calc. Values	
$C_{\text{Cr(VI)}}$	$C_{[\text{H}^+]}$	$C_{\text{H}^+} - C_{[\text{H}^+]}$	C_{HCl}	C_{H^+}	K_{3p}
0.0051	0.0050	0.0050	-	0.0102	1.440
0.0100	0.0100	0.1000	-	0.0200	1.800
0.0249	0.0240	0.2580	-	0.0498	2.500
0.0521	0.0444	0.0571	-	0.1042	2.670
0.0518	0.0389	0.0633	0.05	0.1536	3.447
0.0514	0.0341	0.0657	0.10	0.2028	4.000
0.0502	0.0293	0.0663	0.15	0.2504	5.317
0.0491	0.0244	0.0647	0.20	0.2982	5.000

1 to 2). The employment of equation (2) in calculations helps avoid significant errors in such cases.

Figure 3 shows distribution of dominating particles in a Cr(VI) solution, depending on $C_{\text{Cr(VI)}}$ and pH. The dependence of the solution pH on the chromic acid (CrO_3) concentration is shown as a dashed line. It should be noted that with increase in acidity ($\text{pH} < 1$) of the solution within a wide range of Cr(VI) concentration (0.003 to 3.0 M) the polychromate of $\text{Cr}_3\text{O}_{3n+1}$ (with $n > 2$) is the dominating particle of Cr(VI).

Estimation of the apparent constant of formation of polychromic acid particles is based on the solution model described earlier¹ and on a generally accepted concept of the effect of the solution ionic strength on that model. To estimate equilibria in solutions of chromic acid in the presence of substituted chromates, the following equilibria were taken into account, in addition to those previously described:¹



As can be seen from the calculated data, the equilibrium concentrations of substituted chromates CrO_3Cl^- and CrSO_7^{2-} make up a negligible part of equilibrium concentrations of chromic acid particles within a wide range of concentrations of HCl (Fig. 4) and H_2SO_4 (Fig. 5) in 0.05 M solution of CrO_3 . Quite a different picture is observed when phosphoric acid is introduced into the solution of CrO_3 (Fig. 6). The equilibrium concentration of the substituted chromate $\text{H}_2\text{CrPO}_7^{2-}$ constitutes about 60 percent of equilibrium concentrations of Cr(VI) particles in the presence of 0.05 M CrO_3 in 1 M H_3PO_4 . This circumstance should be taken into account when analyzing the influence of Cr(VI) solution composition on electrochemical processes proceeding during corrosion of metals in Cr(VI)-containing media, as well as in the course of chromating and chromium plating of metals.

To estimate the conditions of substituted chromate formation, calculations were carried out for solutions of Cr(VI)

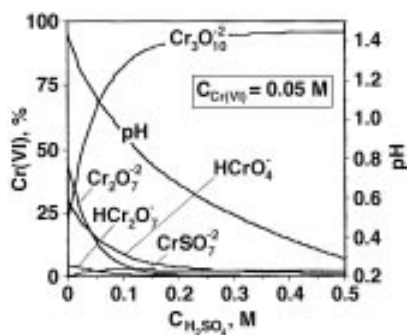


Fig. 5—Percentage distribution of Cr(VI) in equilibrium forms of chromic acid and change of solution pH as a function of H_2SO_4 concentration.

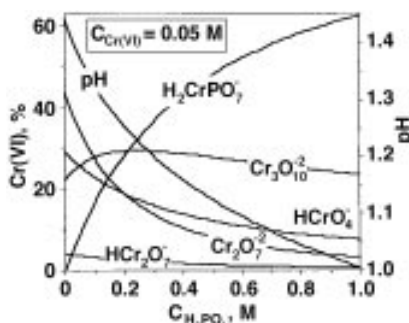


Fig. 6—Percentage distribution of Cr(VI) in equilibrium forms of chromic acid and change of solution pH as a function of H_3PO_4 concentration.

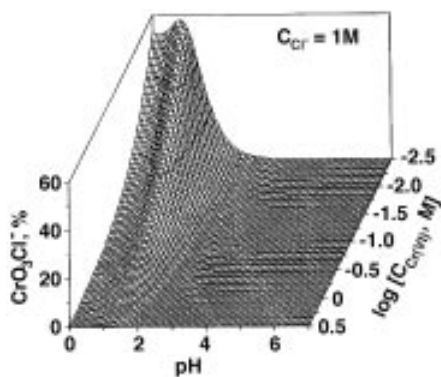


Fig. 7—Percentage distribution of CrO_3Cl^- in solution of 1 M Cl^- as a function of pH and concentration of Cr(VI).

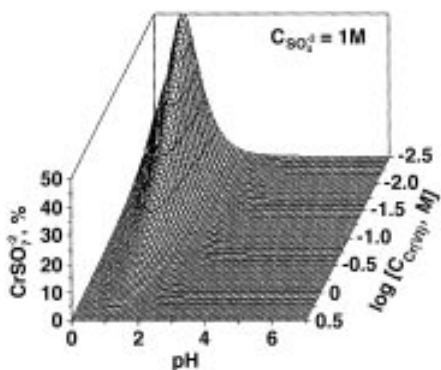


Fig. 8—Percentage distribution of $CrSO_7^{2-}$ in solution of 1 M SO_4^{2-} as a function of pH and concentration of Cr(VI).

within wide ranges of CrO_3 concentrations and acidities. Figures 7-10 show the data obtained when calculating the equilibrium concentrations of substituted chromates, depending on concentrations of the free acid (pH) and Cr(VI) in 1 M solution of hydrochloric, sulfuric and phosphoric acids. It follows from the calculation data that it is possible to predict the presence of an appreciable amount of substituted chromates of CrO_3Cl^- kind (Fig. 7) and of $CrSO_7^{2-}$ (Fig. 8) one only in strongly acid solutions and in very dilute [with respect to Cr(VI)] solutions. When the solution pH exceeds 2, both chloride- and sulfate-substituted chromates are actually absent over the whole range of Cr(VI) concentrations (0.003 to 0.3 M).

$H_2CrPO_7^-$ (Fig. 9) is the dominating equilibrium particle of Cr(VI) within the pH range from 1 to 2 in solutions of CrO_3 containing phosphoric acid, and the particle $HCrPO_7^{2-}$ (Fig. 10) predominates in the range of 2.5 to 5.5. This is true for solutions containing less than 0.1 M Cr(VI). According to Haigh *et al.*, no substituted chromates are formed in solutions of chromic acid containing HNO_3 , $HClO_4$ and CH_3COOH .

There are no data in the literature on equilibrium constants of formation of substituted chromates in solutions of chromic acid involving H_3BO_3 , NH_2CH_2COOH , $HCOOH$ and NH_4SO_3H . Their presence in solutions of Cr(VI), however, significantly alters the acidic properties of the solution. As an example, Fig. 11 shows the calculated data of the influence of acids of different nature on the change in the total acidity of Cr(VI) solution, depending on its initial pH. Considering that many electroplating processes that use solutions of Cr(VI) for treating metal surfaces consume a considerable amount of H^+ ions, the data analogous to those shown in Fig. 11 should help to choose the optimum solution composition in accordance with its acidic properties.

The calculations carried out for this study show that because of alkalization of the near-surface layer during corrosion of metals in acid solutions of Cr(VI), both composition and equilibrium concentrations of various ionic forms of chromic acid will differ significantly from the bulk solution composition. The mechanisms involving numerous possible ways of the course of homogeneous and heterogeneous reactions of oxidation by Cr(VI) are often conditioned by the diversity of Cr(VI) particles.⁷ Therefore, the data obtained should be considered in analytical determinations, investigations of corrosion of metals, electrodeposition of chromium and metal polishing.

Summary

The experimental dependence of the apparent constant formation of polychromium particles (K_{sp}), calculated as $Cr_3O_{10}^{2-}$, on pH was determined by the static ion chromatography method. The equilibrium forms of Cr(VI) particles were estimated in solutions of acids. The effect of the presence of substituted chromates on distribution of equilibrium forms of chromic acid was evaluated.

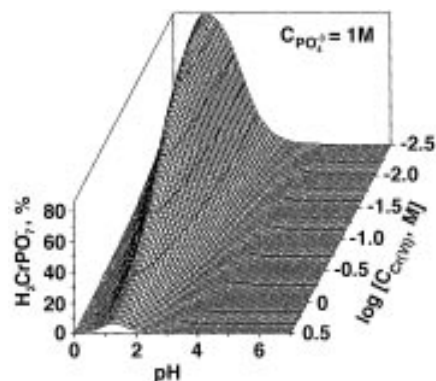


Fig. 9—Percentage distribution of $H_2CrPO_7^-$ in solution of 1 M PO_4^{3-} as a function of pH and concentration of Cr(VI).

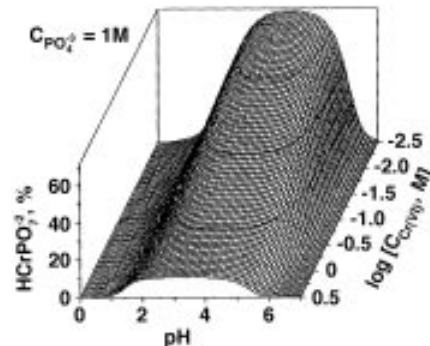


Fig. 10—Percentage distribution of $HCrPO_7^{2-}$ in solution of 1 M PO_4^{3-} as a function of pH and concentration of Cr(VI).

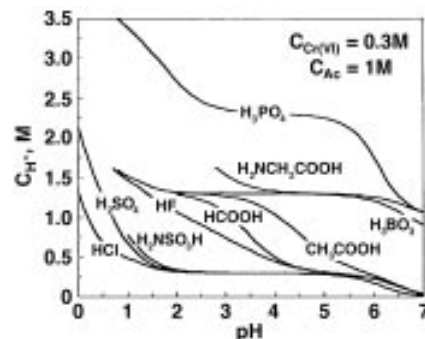


Fig. 11—Dependence of the total acidity CH_+ of 0.3 M Cr(VI) solution on its pH and the presence of anions of acids (Ac).

The change of acidic properties of Cr(VI) solutions was calculated with introduction of anions of various acids into their composition.

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