sometimes accounted for 30-40% of the total number of coulombs passed, and chronopotentiometric end points were poorly defined. The background current may be due to the formation or removal of platinum oxide on the electrode surface. The preconditioning procedure involved carrying out three or four constant current thin-layer electrolyses (at the widest layer thickness to be employed for *n*-value determination) until the transition times became constant. Transition times were then determined at different layer thicknesses for *n*-value determination.

The results of testing the TLE cell with several model compounds in nonaqueous systems are shown in Table I. Sharp chronopotentiometric end points were observed for all systems. *n*-Values listed are average values and were determined within the range of currents indicated. Satisfactory *n*-values were obtained in all systems except at the most positive and negative potentials in DMF and acetonitrile. The high *n*-values observed in these systems were thought to be due to background electrolysis. Such sensitivity to background is expected in TLE in view of the small amount of material (~10⁻⁹ mole) which is electrolyzed within the cell cavity.

The improvement observed when a larger concentration of depolarizer was used further substantiates the suggestion that the high n-values are due to background. Recent work (6,

15, 16) has suggested that for systems in which such background effects may be present, increased accuracy in *n*-value determinations may be obtained by employing a potential step with current integration measuring technique. This approach allows a more accurate measure of the background contribution and of the end point than does chronopotentiometry.

The shifts in $E_{1/2}$ (Table I) suggest that significant current density differences may exist in the TLE cell cavity due to the high resistance of nonaqueous systems. Thus, the effect is smallest in CH₃CN which has a lower resistance than either of the other solvent systems. In no case does the estimation of *n*-values seem to be influenced by *iR* loss. Testing in higher resistance solvents (e.g., glyme) is planned to show whether large current density differences could affect *n*-value determinations. Some indication of the severity of this problem has already been demonstrated (12).

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Aqueous Dissociation Constants of 5-Halo-8-hydroxyquinolines

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8-HYDROXYQUINOLINE and its derivatives are extensively used as reagents in spectrophotometry, fluorometry, solvent extraction, and partition chromatography (I). Although knowledge of the dissociation constants of these compounds is necessary for precise evaluation and application, only limited data of this type are available, especially in aqueous solution. We have, accordingly, studied the 5-halo derivatives to develop the information necessary for further application of these compounds.

Because the 8-hydroxyquinolines are sparingly soluble in water, but have relatively high molar absorptivities, the spectrophotometric technique of Irving *et al.* (2) represents the best method of evaluation.

EXPERIMENTAL

Reagents and Chemicals. 5-Chloro-8-hydroxyquinoline, and 5-iodo-8-hydroxyquinoline were obtained from Aldrich Chemical Co. Melting points were: 5-Cl, 119-120 °C, 5-I, 127-8 °C. Melting points showed no change on vacuum sublimation and recrystallization from 100% ethanol. 5-Bromo-8-hydroxyquinoline was prepared by a direct Skraup synthesis (3), purified by a vacuum sublimation and recrystallized from methanol-water to give a melting point of 125° C (lit $124-125^{\circ}$) (3).

Sodium hydroxide, hydrochloric acid, and sodium chloride stock solutions were prepared using doubly distilled water and reagent grade chemicals. The sodium hydroxide was standardized with potassium acid phthalate; the hydrochloric acid was standardized with sodium hydroxide.

Solutions of 5-halo-8-hydroxyquinolines were prepared by dissolving sufficient solid in 0.499*M* NaOH and diluting to final concentrations of $1 \times 10^{-4}M$ 8-hydroxyquinoline, 0.01*M* NaOH. Stock solutions for analysis were prepared by pipeting 200 ml of stock solution into a 500 ml volumetric flask containing 200 ml of 0.01*M* HCl and sufficient NaCl solution (2.5*M*) to adjust the total ionic strength to the desired value, with a final 8-hydroxyquinoline concentration of $4 \times 10^{-5}M$.

The pH of the solution was adjusted in the following manner: (1) 25 ml samples were withdrawn from the stock solution; (2) one sample was adjusted to pH \sim 2.5 by addition of a drop of concentrated HCl, one sample was adjusted to pH \sim 10 by addition of a drop of 0.499*M* NaOH; (3) by mixing the untreated stock solution with either the acidic or basic solution, pH values in the range of interest were obtained.

Instrumental. pH was measured at 25 °C with a Leeds & Northrup Model 7405 pH meter which had been standardized with 0.0500*M* potassium acid phthalate, and with Beckman pH 7 buffer solution.

Absorbance was measured at 260 m μ with a Beckman Model DB spectrophotometer. This wavelength was selected because it shows the maximum difference in absorbance between the acidic, neutral, and basic species of 8-hydroxyquinolines. Measurements were made in a cell compartment

⁽¹⁾ R. G. W. Hollingshead, "Oxine and Its Derivatives," Vols. I-IV, Butterworths, London, 1954-1956.

⁽²⁾ H. Irving, H. S. Rossotti, and G. Harris, Analyst, 80, 83 (1955).
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Table I. Aqueous Dissociation Constants and Molar Absorptivities of 5-Chloro-8-hydroxyquinoline

Ionic				
strength	0.004	0.050	0.100	0.500
$\epsilon_0 \times 10^{-4}$	1.44	1.45	1.15	1.70
$\epsilon_1 \times 10^{-3}$	5.11	5.19	4.62	5.58
$\epsilon_2 \times 10^{-4}$	1.87	1.74	1.45	2.24
$K_1 \times 10^4$	2.58 ± 0.89	2.32 ± 0.26	2.10 ± 0.80	1.10 ± 0.23
$K_2 \times 10^{10}$	5.31 ± 1.46	8.55 ± 0.07	10.5 ± 3.0	14.7 ± 2.6
\mathbf{pK}_{1}	3.59 ± 0.13	3.63 ± 0.05	3.68 ± 0.14	3.96 ± 0.09
pK_2	9.28 ± 0.10	9.06 ± 0.02	8.98 ± 0.11	8.83 ± 0.08
\pm values represent on	e standard deviation.			

cooled by circulating water to maintain the solution temperature at 25° C. Separate measurements were made to establish conformity to Beer's Law.

Theoretical. The 8-hydroxyquinolines form three species in aqueous solution, denoted by H_2L , HL, and L. Irving *et al.* (2) have shown that, in this case, the absorbance of solutions containing a constant amount of compound is given by:

$$A = bM \frac{\epsilon_0 + \epsilon_1 B_1 \{H\} + \epsilon_2 B_2 \{H\}^2}{1 + B_1 \{H\} + B_2 \{H\}^2}$$
(1)

where {H} is the hydrogen ion activity, as evaluated directly from the pH meter reading (4)—i.e., {H} = $10^{-pH} b$ —is the sample path length, *M* is the stoichiometric concentration, ϵ_0 , ϵ_1 , and ϵ_2 are the molar absorptivities of the species L, HL, and H₂L, respectively, and B_i represents the overall formation constant of the *i*th proton complex—i.e.,

$$B_{1} = \frac{(\text{HL})}{\{\text{H}\}(\text{L})} \quad B_{2} = \frac{(\text{H}_{2}\text{L})}{\{\text{H}\}^{2}(\text{L})}$$
(2)

Values of the five unknowns of Equation 1 can be obtained by solution of five simultaneous equations, but the method is tedious and subject to wide variations due to inherent experimental error. Irving *et al.* (2) have developed a graphical technique for solving Equation 1. We have modified Irving's equations to a form suitable for regression analysis as indicated in the following paragraphs.

From Beer's Law we have $A/b = \epsilon_0 L + \epsilon_1 HL + \epsilon_2 H_2 L(3)$ and from the mass balance relationship

$$M = L + HL + H_2L \tag{4}$$

We assume that (a) below pH 6 the concentration of L is negligible, and (b) above pH 8 the concentration of H_2L is negligible. The following relationships are then obtained directly from Equations 2, 3, and 4:

. .

pH 6 A/bM =

$$\epsilon_1 + \epsilon_2(B_2/B_1)\{H\} - (B_2/B_1)\{H\}(A/bM)$$
 (5)

(4) R. G. Bates, "Determination of pH," pp. 91–92, Wiley, New York, 1964.

Table II. Aqueous Dissociation Constants and Molar Absorptivities of 5-Bromo-8-hydroxyquinoline

Ionic strength	0.004	0.050	0.100
$\epsilon_0 imes 10^{-4}$	1.91	2,00	1.88
$\epsilon_1 \times 10^{-3}$	5.08	3.88	5.66
$\epsilon_2 imes 10^{-4}$	3.04	3.66	3.16
$K_1 \times 10^4$	2.18 ± 0.16	2.37 ± 0.16	2.42 ± 0.18
$K_2 \times 10^9$	1.00 ± 0.04	1.15 ± 0.07	1.30 ± 0.07
pK1	3.66 ± 0.03	3.62 ± 0.04	3.62 ± 0.03
pK_2	9.00 ± 0.03	8.94 ± 0.03	8.89 ± 0.03

 \pm values represent one standard deviation.

$$pH \ 8 \ A/bM = \epsilon_0 + \epsilon_1 B_1 \{H\} - B_1 \{H\} \ (A/bM) \tag{6}$$

which are of the form

$$y = a_1 + a_2 X_1 + a_3 X_1 X_2 \tag{7}$$

The data, in the form of A/bM and $\{H\}$, were processed by an IBM 1620 computer, using IBM program 6.0.003 "SCRAP," to evaluate the coefficients a_1 , a_2 , and a_3 . The dissociation constants were then obtained from the relationship

$$K_2 = 1/B_1$$
 $K_1 = B_1/B_2$ (8)

In order to estimate the thermodynamic dissociation constants, plots were made of pK_1 and $pK_2 vs$. the square root of the ionic strength (5), and extrapolated to zero ionic strength.

RESULTS AND DISCUSSION

Results are shown in Tables I-III, which give molar absorptivities, dissociation constants, and pK values. Table IV lists the thermodynamic pK° values and gives results of other investigations for comparison.

(5) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," p. 32, McGraw-Hill, New York, 1961.

l'able III.	Aqueous Dissociation	Constants and N	Molar Absorptivities	of 5-Iodo-8-h	ydroxyquinoline
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strength	0.004	0.045	0.100	0.450
$\epsilon_0 imes 10^{-4} \ \epsilon_1 imes 10^{-4} \ \epsilon_2 imes 10^{-4} \ K_1 imes 10^{4} \ K_2 imes 10^{9} \ pK_1 \ pK_2$	2.94 1.28 2.73 3.80 ± 1.39 2.59 ± 0.41 3.42 ± 0.20 8.59 ± 0.07	$\begin{array}{c} 1.90\\ 0.80\\ 1.77\\ 1.32 \pm 0.91\\ 1.82 \pm 0.45\\ 2.88 \pm 0.37\\ 8.74 \pm 0.11 \end{array}$	2.75 1.18 2.52 2.47 \pm 0.41 2.61 \pm 0.23 3.61 \pm 0.07 8.58 \pm 0.03	$\begin{array}{c} 2.00\\ 0.95\\ 1.83\\ 1.41\pm 0.23\\ 4.64\pm 1.46\\ 2.85\pm 0.08\\ 8.33\pm 0.14\end{array}$
\pm values represent or	he standard deviation			

Table IV.	Thermodynamic Dissociation Constants of	f
	Substituted 8-Hydroxyquinoline	

		-	
Substituent	pK1°	pK₂°	Ref
None	5.02	9.81	(6)
5-Cl	3.56	9.34	a
5-Br	3.8		(7)
5-Br	3.67	9.02	a
5-I	3.48	8.65	а
5-Sulfonic acid	4.09	8.78	(8)
5-Nitroso	2.36	7.78	(9)
5-Amino	5.9		(7)

Table V. Electron Densities and Pi-Electron Energies

	ϵ_0	€N	E_{π}	$E_{\pi+}$	ΔE_{π}
5-Cl-8-OH	1.910	1.211	19.445	21.639	2.194
5-Br-8-OH	1.909	1.208	18.996	21.190	2.194
5-I-8-OH	1.909	1.208	19.100	21.293	2.193

Table VI. Experimental and Calculated Values of pK1

Substituent	Exptl	Ref	Calcd ^b	Calcd ^c
8-OH	5.05	(7)	4.2	4.5
5-Cl-8-OH	3.52	a	3.0	3.3
5-Br-8-OH	3.68	а	2.9	3.3
5-I-8-OH	3.37	а	3.1	3.4
5-SO3-8-OH	4.05	(7)	3.9	4.3
5-NH2-8-OH	5.67	(7)	5.9	6.3
5-SO3-7-I-8-OH	2.54	(7)	2.8	3.1
5-SO3-7-NO2-8-OH	1.95	(7)	0.7	1.3

^a This work.

^b From Ref. (5).

Calculated with no correction for benzenoid ring.

Table VII. Comparison of —OH Stretching Frequencies with pK Values				
Compound	ν _{OH} (Ref 14)	pK_1	pK2	
8-OH	3416	5.0	10.0 (7)	
5-Cl-8-OH	3414	3.56	9.34 a	
5-Br-8-OH	3415	3.67	9.02 a	
5-I-8-OH	3387	3.48	8,65 a	
5,7-Cl ₂ -8-OH	3396	1.89	(7)	
7-Cl-8-OH	3396	4.0	(7)	
2-Me-8-OH	3408	5.61	10.20 (7)	

The pK₁ values of the 5-halo derivatives show that all three are stronger acids than the parent compound, as expected. The pK₁ values are, however, very nearly identical, showing little difference between the iodo, chloro, and bromo derivatives. pK_2 shows a more definite trend, with acidity increasing in the order Cl < Br < I. Since this is in the direction of decreasing electronegativity of the substituent, we conclude that the π bond forming ability (10) of the halo substituent



Figure 1. π -Electron densities of 5-bromo- and 5-iodo-8-hydroxyquinoline

(resonance effect) is the primary factor in determining acidity when the halogen atom is located on the same ring as the functional group.

For comparison, we have carried out LCAO-MO calculations on the compounds studied. The Hückel approximations (11) were used to simplify the secular determinant, $|\mathbf{H}_{ij} - \mathbf{ES}_{ij}| = 0$, and parameters were selected to correct the carbon sp² AO coulomb and exchange integrals for heteroatoms:

$$H(X_{p_{\pi}}, X_{p_{\pi}}) = H_{cc} + h_x \beta_{cc}$$
$$H(X_{p_{\pi}}, Y_{p_{\pi}}) = k_{xy} \beta_{cc}$$

The exchange terms, k_{zc} , and coulomb parameters, h_z , were those reported by Burton and Davis (12) who have carried out calculations for 8-hydroxyquinoline and certain chloro and bromo derivatives.

The value of k_{xc} was obtained by the method of Burton and Davis. The LCAO energy levels of 5-iodo-8-hydroxyquinoline were calculated as a function of k. The quantity (E – E')/E is then plotted as a function of k_{xc} , where E is the LCAO calculated energy of the first $\pi - \pi^*$ transition for the parent compound and E' is the corresponding energy for the derivative. This is compared with the experimental quantity ($\nu - \nu'$)/ ν , when ν is the spectral frequency at which the first $\pi - \pi^*$ transition of the parent occurs, and ν' is the corresponding frequency for the derivative. The value of k_{xc} is selected for which the two expressions are equal. The value of k_{xc} obtained in this work is 0.75.

Results of these calculations are shown in Figure 1, which shows the electron density for the neutral molecules of 5-Br and 5-I. Values for 5-Cl have been reported by Burton and Davis. Table V summarizes the data for the compounds considered in the present work. There is no significant difference in either the electron density of the nitrogen and oxygen atoms in the different halo compounds, or in the values of $\overline{\Delta E_{\pi}}$ (13), the difference in π electron energy between the protonated (H₂L) and neutral (HL) species. The lack of significant differences is reflected in the closely related pK value of the series.

Perrin (14) has developed an equation for the estimation of

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 ⁽⁹⁾ H. Irving, R. G. W. Hollingshead, and G. Harris, Analyst, 80, 260 (1955).

⁽¹⁰⁾ A. E. Řemick, "Electronic Interpretations of Organic Chemistry," p. 66, Wiley, New York, 1943.

⁽¹¹⁾ A. Streitwieser, "Molecular Orbital Theory," Wiley, New York, 1961.

 pK_1 values of 8-hydroxyquinolines. The pK_1 value is given by

$$pK_1 = 5.25 - 5.90 \Sigma \sigma$$

where $\Sigma \sigma$ represents the summation of σ substituent constants obtained by the method of Dewar and Grisdale (15). For quinoline-type compounds, Perrin has included a σ constant of 0.06 for the benzenoid ring system. We have used this method to estimate pK₁ values of the compounds studied here; results are shown in Table VI. Calculated values are consistently lower than the experimental results. Careful examination of Perrin's own data also shows similar discrepancies for some 8-quinolinols. We, therefore, conclude that the contributions due to the extra ring fused to the pyridine nucleus and to the OH group have been overestimated. The method does, however, predict closely related pK₁'s for the halosubstituted derivatives. Assigning a value of 0.0 for the σ constant of the benzene ring brings the pK₁ values closer to the experimental results (Table VI).

(15) M. J. S. Dewar and P. J. Grisdale, J. Am. Chem. Soc., 84, 3548 (1962).
(16) G. M. Badger and A. G. Moritz, J. Chem. Soc., 1958, 3437.

Badger and Moritz (16) have shown that there is a linear relationship between the —OH stretching frequency of substituted 8-hydroxyquinolines and the Hammett σ constants. Since Perrin's work indicates a linear relationship between σ and pK₁, we would expect that pK₁ should show a linear relationship to ν_{OH} . Such a relationship has been observed (17) for 8-hydroxyquinoline and some of its aza analogs. No correlation is, however, observed for the substituted 8-hydroxyquinolines, as is evident from the data of Table VII.

In summary, thermodynamic pK values have been obtained for 5-bromo-, 5-chloro-, and 5-iodo-8-hydroxyquinoline in aqueous solution at 25° C. Results have been compared with previous work and with suggested methods of estimation of pK values from substituent constants. Molecular orbital calculations have been carried out in order to compare electron distribution and π -electron energy differences with the observed values.

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Spectrophotometric Determination of Silver with Crystal Violet

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THE LITERATURE concerning the use of triphenylmethane dyes has been reported on by Hedrick and Berger (1); these investigators have described conditions for extracting perchlorate, periodate, and alkylbenzenesulfonate. Of the substances investigated they found crystal violet the best reagent and benzene the best solvent for this purpose. Both sulfite and cyanide were found to interfere with the reaction by decolorizing or reacting with the dye.

In spite of the reaction between crystal violet and cyanide it, is possible to make a determination of silver in the concentration range 10^{-6} to $10^{-4}M$ by using crystal violet to extract the silver cyanide complex into benzene provided there is strict attention to procedure.

EXPERIMENTAL

Apparatus. A Unicam SP500 spectrophotometer and either 2.00-cm or 0.50-cm light path cells were used for all absorbance measurements. Borosilicate glass tubes approximately 2.5 mm \times 100 mm with rounded bottoms and glass stoppered tops were used for extraction.

Reagents. Crystal Violet, C.I. 42555, was obtained from British Drug Houses Ltd. All other chemicals were reagent grade.

An approximately $10^{-3}M$ solution of crystal violet was prepared by dissolving 82.2 mg in water and diluting to 200 ml.

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Silver nitrate was stored as a $10^{-3}M$ stock solution. Solutions of $10^{-4}M$ and $10^{-5}M$ were prepared by dilution shortly before use.

Procedure. The solution which is 10^{-6} to $10^{-4}M$ in silver is made $10^{-3}M$ in sodium cyanide and 0.1M in sodium hydroxide. Exactly 10.0 ml of this solution are added to a glass stoppered tube together with 10.0 ml of benzene. Next 1.00 ml of approximately $10^{-3}M$ crystal violet is added. The tube is stoppered immediately and shaken vigorously for exactly 15 seconds. The stopper is removed and the tube centrifuged for 60 seconds. The supernatant benzene layer is removed at once with a pipet and stored in a clean dry glass stoppered vessel. Between 30 and 40 minutes after removing the benzene layer, its absorbance at 600 m μ is measured.

RESULTS AND DISCUSSION

The absorption spectrum of the crystal violet silver cyanide complex shows a maxima at 600 m μ . A calibration curve should be prepared.

A complication is that the reagent is being altered by reacting with the cyanide which is necessary for the formation of the silver cyanide anion. Nevertheless by strict attention to procedure it is possible to get reproducible results.

ANALYSIS FOR BOUND SILVER

Because of the great stability of the hydroxyargentocyanide

$$K_{\rm Hy} = \frac{[\rm Ag^+] [\rm OH^-] [\rm CN^-]}{(\rm OH)^-} = 6 \times 10^{-14}$$

[Ag (CN)]

⁽¹⁾ C. E. Hedrick and B. A. Berger, ANAL. CHEM., 38, 791 (1966).