expected to hold for $\gamma_\pm$ of perchloric acid itself, judging from a study of activity coefficients in analogous 1 *M* chloride solutions.[33] Also, the corrections due to ionized phosphoric acid would be less at the higher acidity. Nevertheless an elucidation of the charges on the complex ions would require less accuracy from Baes's values for the formation constants.

The data of Schreyer and Baes on the solubility of uranyl phosphates in phosphoric acid[3,4,34] can be interpreted in terms of a 1:3 uranyl phosphate complex in addition to the lower complexes.[4,6] However, the interpretation of such data is futile whenever charged complexes are concerned unless a constant ionic strength is maintained. An interesting, possibly anomalous, phenomenon is the solubility behavior in phosphoric acid at 6.1 *M* H_3PO_4, the transition point between $UO_2HPO_4\cdot 4H_2O$ and $UO_2(H_2PO_4)_2\cdot 3H_2O$.[3,34] If a neutral 1:3 uranyl phosphate complex were the principal dissolved species at that point, the solubility would be expected to continue to increase there instead of sharply decreasing, as it actually does. The reversed solubility trend might be explained by assuming the average complex to be a polynuclear species, *e.g.*, a 3:5 uranyl phosphate complex. However, evidence confuting the existence of appreciable amounts of such polynuclear complexes at the uranium concentration of the present investigation is supplied by conformance of the uranium solutions to Beer's law at 3.7 *M* H_3PO_4 in the present investigation, the spectrophotometric results of Baes,[6] and the incompatibility of large amounts of polynuclear complexes with the present solvent-extraction data.

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(33) H. S. Harned, THIS JOURNAL, **48**, 326 (1926).

(34) J. M. Schreyer and C. F. Baes, Jr., *ibid.*, **76**, 354 (1954).

[COMMUNICATION NO. 1893 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

The Mechanism of Dye Formation in Color Photography. V. The Effect of a Non-ionic Surfactant on the Ionization of Couplers[1]

BY L. K. J. TONG AND M. CAROLYN GLESMANN

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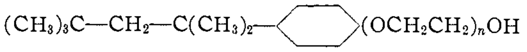
The effect of a non-ionic surfactant on the apparent ionization constant of phenolic and naphtholic hydrogen has been measured by a photometric method. The data have been interpreted by assuming a different solubilization of the acid and salt forms of these compounds. The solubilization constants, defined as distribution coefficients between the micelle and the aqueous phase, were found to be very similar to the corresponding distribution coefficients between *n*-octanol and water. The solubilized salts appear to be completely dissociated.

The dyes in many color photographic systems are products of the oxidative condensation of a developing agent, usually N,N-disubstituted-*p*-phenylenediamines and a coupler, a compound with an active coupling site. In the Kodacolor and Kodak Ektacolor systems, water-insoluble couplers are incorporated in a highly dispersed organic phase, in the aqueous gelatin medium of the photographic emulsion; and the developing agent is supplied to the film from a high-*p*H-bath during processing. The couplers, on contact with the alkaline developer solution, form salts, which presumably are oriented in high concentration at the very large interface. This reaction is probably rapid and reversible; therefore, equilibrium is likely to be established before an appreciable fraction of the coupler reacts with the oxidized developer to form dye.

Dye formation may take place both in the organic phase and at the interface. The relative importance of both sites for color formation depends on many factors, and it was one of our primary objectives in this work to investigate these factors. In this paper and in the next (Part VI) emphasis is placed on the phenomena at the interface. Systems containing micelle-forming colloids are convenient for such studies because of their large surface-to-volume ratio. The colloid used for this investigation was Triton X-100. This material, supplied by Rohm and Haas, is the condensation product of diisobutylphenol and ethylene oxide. From its origin and molecular weight the following formula has been derived



in which *n* has an average of 9.5 units. This surfactant was chosen because its properties as a micelle-forming agent are well known from the investigations of Marsden, Gonick and McBain.[2]

The equilibria of the molecular species involved in dye formation and their distribution are discussed in the present paper, thus laying the foundation for a study of the dye formation in the subsequent communication.

II. Experimental Method and Treatment of Data

The behavior of couplers in the presence of Triton X-100 was studied by means of light absorption and *p*H measurements of coupler solutions containing different concentrations of this colloid. Most of the experiments were carried out with solutions of constant ionic strength (μ = 0.43 to 0.45) and constant potassium ion concentration (0.25 *M*). Therefore, in the following equations, the equilibrium constants are expressed in terms of concentrations, and are equal to the products of the thermodynamic constants and of the activity co-

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(1) For Parts III and IV, see L. K. J. Tong and M. Carolyn Glesmann, THIS JOURNAL, **79**, 583 (1957).

(2) (a) S. S. Marsden and J. W. McBain, *J. Phys. Chem.*, **52**, 110 (1948); (b) E. Gonick and J. W. McBain, THIS JOURNAL, **69**, 334 (1947).

efficients which are assumed to be constant. The concentrations of the substances in the micelles are defined as the amounts of substance solubilized divided by the volume of the micelles. This volume is assumed to be the volume of Triton X-100 added in making up the solution less the volume at the critical micelle concentration (CMC), since this amount of Triton does not contribute to the micelles.

In accordance with Reich's[3] argument, it is further assumed that the volume of the individual micelles is approximately independent of the Triton X-100 concentration; therefore, the total interface is also approximately proportional to the micellar volume, and the following conclusions are equally valid, whether solubilization takes place in the interior of the micelles or at their periphery (adsorption). Let

$(\mathrm{HC})_m$ = concn. of the coupler acid in the micellar region
$(\mathrm{HC})_a$ = concn. of the coupler acid in the aq. region
$(\mathrm{C}^-)_m$ = concn. of the coupler ion in the micellar region
$(\mathrm{C}^-)_a$ = concn. of the coupler ion in the aq. region

The coupler dissociates in the aqueous region, according to eq. 1

$$K_0 = \frac{(\mathrm{C}^-)_a\, 10^{-p\mathrm{H}}}{(\mathrm{HC})_a} \qquad (1)$$

The distribution of substances by solubilization is assumed to be governed by laws analogous to those on which distribution between bulk phases depends. This principle has been discussed by McBain and Hutchinson.[4] We, therefore, set

$$\alpha = \frac{(\mathrm{HC})_m}{(\mathrm{HC})_a} \qquad (2a)$$

and

$$\beta = \frac{(\mathrm{C}^-)_m}{(\mathrm{C}^-)_a} \qquad (2b)$$

For constant (K^+), β should be constant whether the salt is solubilized as (1) dissociated ions with the counterions in the outer layer of the electrical double layer or (2) as ion-pairs in the inner layer. For variable (K^+), however, β should remain constant under situation 1, but should vary in proportion to (K^+) under situation 2. The results in Table V show that β is independent of (K^+), and, therefore, situation 1 is indicated.

Let $(\overline{\mathrm{C}^-})$ and $(\overline{\mathrm{HC}})$ be the over-all concentrations of the salt and acid, defining

$$(\overline{\mathrm{C}^-}) = \frac{v_a(\mathrm{C}^-)_a + v_m(\mathrm{C}^-)_m}{v_a + v_m} \qquad (3)$$

$$(\overline{\mathrm{HC}}) = \frac{v_a(\mathrm{HC})_a + v_m(\mathrm{HC})_m}{v_a + v_m} \qquad (4)$$

where v_a = volume of the aqueous region and v_m = volume of the micellar region. Let

$$V_m = \frac{v_m}{v_m + v_a} \qquad (5)$$

and

$$V_a = \frac{v_a}{v_m + v_a} \cong 1 \text{ since } v_m << v_a \qquad (6)$$

The eq. 2 to 6 lead to

$$(\overline{\mathrm{C}^-}) = (\mathrm{C}^-)_a(1 + \beta V_m) \qquad (7)$$

$$(\overline{\mathrm{HC}}) = (\mathrm{HC})_a(1 + \alpha V_m) \qquad (8)$$

Let us define

$$K = \frac{(\overline{\mathrm{C}^-})\, 10^{-p\mathrm{H}}}{(\overline{\mathrm{HC}})} \qquad (9)$$

Combining eq. 1, 7, 8 and 9, we have

$$\frac{K}{K_0} = \frac{(1 + \beta V_m)}{(1 + \alpha V_m)} \qquad (10)$$

For analytical purposes, eq. 10 can be rearranged into a more useful form

$$\left(1 - \frac{K}{K_0}\right)\frac{1}{V_m} = \alpha\frac{K}{K_0} - \beta \qquad (11)$$

By the use of eq. 11, α and β can be obtained graphically by plotting the left-hand side of the equation *vs.* K/K_0, the two constants α and β are equal to the slope and the negative intercept of the straight line, respectively.

Evaluation of K, as just defined, was made from photometric and *p*H measurements. The molar extinction coefficients for each of the molecular species, C^- or HC, may be different, depending on whether the respective species is present in the aqueous region or in the micellar region. Although changes in *p*H will shift the equilibrium between the molecular species, the distribution coefficient of each of the species between the two regions is assumed not affected. Therefore, as long as V_m is kept constant, it is only necessary to find a wave length where the molar extinction coefficients for the salt and acid forms are sufficiently different in order to measure the ratio $(\overline{\mathrm{C}^-})/(\overline{\mathrm{HC}})$.

To determine K, we set

$$K = \frac{(D - D_a)}{(D_b - D)}\, 10^{-p\mathrm{H}} \qquad (12)$$

where, at a given wave length and with a constant total coupler concentration, D_a is the optical density in an acid solution; D_b is the optical density in a strong basic solution; and D is the optical density in buffers at intermediate and known *p*H values.

III. Results and Discussion

The effect of colloids on dissociation constants of acid indicators has been studied in recent years by Hartley,[5] by Hartley and Roe,[6] by Krishnappa, Doss and Rao,[7] and by Hiskey and Downey.[8] All these investigators, however, used ionic colloids. This introduces complications owing to (1) superimposing the effect of complex formation between the indicator and molecularly dispersed colloids on that of solubilization by the micelles and (2) high zeta-potentials causing a large and uncertain concentration of H^+ near the surface of the micelle.[6] Krishnappa, Doss and Rao interpreted their data entirely on the basis of molecular complexes, confining their results to concentrations below the CMC, but, judging from their data, some of the concentrations reported may have exceeded that limit. In our work, complex formation between colloids and substrates would introduce additional complications in the interpretation of the coupling rate obtained in the presence of the col-

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[3] I. Reich, *J. Phys. Chem.*, **60**, 257 (1956).

[4] M. E. L. McBain and E. Hutchinson, "Solubilization and Related Phenomena," Academic Press, Inc., New York, N. Y., 1955, p. 139.

[5] G. S. Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

[6] G. S. Hartley and J. W. Roe, *ibid.*, **36**, 101 (1940).

[7] T. Krishnappa, K. S. Doss and B. S. Rao, *Proc. Indian Acad. Sci.*, **23**, 47 (1946).

[8] C. F. Hiskey and T. A. Downey, *J. Phys. Chem.*, **58**, 835 (1954).

TABLE I

DEPENDENCE OF DENSITY OF α-NAPHTHOL SOLUTIONS ON pH

A. No Triton X-100 $(\mathrm{K}^+) = 0.25\ M$			B. 0.25% Triton X-100 $(\mathrm{K}^+) = 0.25\ M$			C. 1% Triton X-100 $(\mathrm{K}^+) = 1.00\ M$		
pH	D_{332}	pK	pH	D_{332}	pK	pH	D_{332}	pK
12	1.565		12	1.55		12	1.480	
6	0.028		6	0.093		6.5	0.113	
8.69	.357	9.26	9.51	.491	9.93	9.30	.206	10.44
8.89	.481	9.26	9.72	.661	9.92	9.68	.320	10.43
9.13	.709	9.23	9.90	.822	9.90	10.00	.490	10.42
9.19	.769	9.23	10.11	.995	9.90	10.27	.66	10.45
9.41	.942	9.24	10.29	1.120	9.90	10.61	.95	10.41
9.50	.99	9.28	10.42	1.208	9.94	11.13	1.276	10.36
9.72	1.151	9.29				11.34	1.365	10.30

loids. To minimize these complications, a non-ionic colloid, Triton X-100, was used.

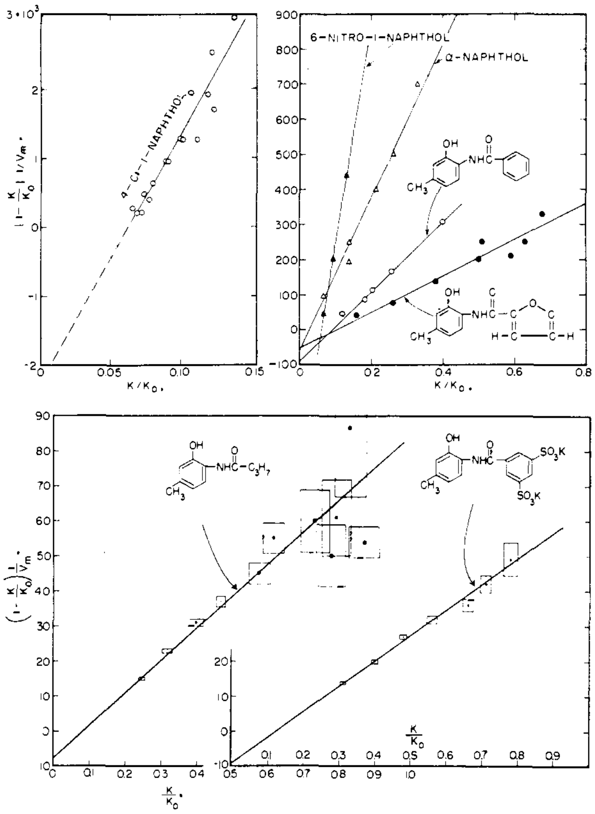
A. Determination of *K*.—Table I shows three examples of α-naphthol measured in solution of different concentration of Triton X-100 as well as at different (K^+) values in order to illustrate the determination of K from photometric and pH measurements. For each set of determinations, the average error of pK calculated by eq. 12 is ± 0.02 unit for measurements within a pH range not greater than 0.5 unit from the average pK. In taking the average, more weight was given to the experiments at a pH very close to the pK of the coupler, because the accuracy of these data is the highest in this region. The average values of pK are listed in Table II. It is evident that K is practically independent of potassium ion concentration and ionic strength within the experimental range indicated.

TABLE II

VARIATION OF pK WITH TRITON X-100 CONCENTRATION

	$(\mathrm{K}^+) = 0.125\ M$ Triton X-100 (vol. %)	pK	$(\mathrm{K}^+) = 0.25\ M$ Triton X-100 (vol. %)	pK	$(\mathrm{K}^+) = 1.00\ M$ Triton X-100 (vol. %)	pK
α-Naphthol	0	9.25	0	9.25	0	9.22
	0.15	9.77	0	9.26	0.20	9.94
	.20	9.88	0.15	9.73	1.0	10.44
	.30	9.98	.20	9.83	2.0	10.61
	.40	10.14	.25	9.93		
	1.00	10.42	.25	9.92		
			.40	10.10		
			.50	10.20		
			.50	10.11		
			1.00	10.42		
4-Cl-1-naphthol	0	8.69	0	8.64	0	8.61
	2.00	10.01	0	8.67	2.00	10.02
			0	8.70		
			0 Av.	8.67		
			0.0825	9.53		
			.0888	9.58		
			.100	9.59		
			.100	9.62		
			.100	9.58		
			.125	9.66		
			.125	9.67		
			.125	9.62		
			.150	9.71		
			.150	9.72		
			.200	9.77		
			.250	9.80		
			.300	9.78		
			.400	9.85		
			.500	9.81		
			.500	9.83		
6-Nitro-1-naphthol	0	8.53	0	8.47	0	8.44
	0.25	9.32	0.25	9.35	0.25	9.33
	.50	9.48	.50	9.49	.25	9.39
	1.00	9.62	2.00	9.63	.50	9.51
	2.00	9.64			1.00	9.59
					2.00	9.64
2,4-Dichloro-1-naphthol	0	7.13	0	7.13	0	6.98
	1.00	8.07	1.0	8.08	1.0	8.00
2-Butyramido-5-methylphenol			0	9.28		
			0.25	9.36		
			.30	9.34		
			.40	9.38		
			.50	9.42		
			.50	9.39		
			.75	9.49		
			1.00	9.52		
			1.50	9.62		
			2.00	9.68		
			3.00	9.77		
			5.00	9.88		
2-Benzamido-5-methylphenol			0.25	9.44		
			.50	9.63		
			.75	9.73		
			1.00	9.78		
			2.00	9.96		
(2-Disulfobenzamido)-5-methylphenol			0	9.23		
			0.50	9.34		
			0.75	9.38		
			1.00	9.41		
			1.50	9.48		
			2.00	9.55		
			3.00	9.63		
			5.00	9.74		
2-(2-Furamido)-5-methylphenol	0	8.97	0	8.94	0	8.92
	0.25	9.21	0.15	9.11	0.25	9.25
	1.00	9.54	.20	9.14	1.00	9.63
	2.00	9.71	.25	9.23	2.00	9.76
			.25	9.17		
			.30	9.24		
			.50	9.36		
			1.00	9.52		
			2.00	9.74		

B. **Determination of the Distribution Constants for Acid, α and Ion β.**—The constants α and β were obtained graphically according to eq. 11. Data for various couplers are plotted in Figs. 1 and 2. Apparently, they are satisfactorily repre-



Figs 1 and 2.—Graphical determination of the distribution constants α and β, according to equation 11.

sented by straight lines as required by the equation. It should be pointed out that accuracy is low at low V_m and/or high K/K_0. At low V_m, the uncertainty is caused mainly by the error inherent in obtaining a small difference from two relatively large quantities, one of them being the CMC of Triton X-100, 0.054 volume %.[9,10]

At high ratios of K/K_0, the factor $(1 - K/K_0)$ becomes uncertain. In Fig. 2, the rectangles represent the magnitude of error caused by ± 0.02 unit in pK (curve on the left) and ±0.01 unit in pK (curve on the right). The lines were drawn within these limits.

C. Distribution of Couplers between *n*-Octanol and Aqueous Buffers.—In this treatment, α and β were postulated as distribution constants of the acid and salt, respectively, between the micellar and the aqueous regions. Comparison of these constants with the distribution constants in organic solvents having properties similar to those of Triton may show the nature of solubilization. The couplers were distributed between the *n*-octanol and aqueous buffers, and the distribution constants, ϕ_{HC}, for the coupler acid are listed in Table III.

Unfortunately, accurate distribution constants of the salts ϕ_{C^-} could not be obtained for most of the couplers for the following reason. In order to determine the distribution constants, the total coupler concentration in each phase is measured and the distribution ratio, R, is expressed as

$$R = \frac{(HC)_S + (C^-)_S}{(HC)_a + (C^-)_a}$$

where the subscripts S and a indicate organic solvent or aqueous phase, respectively. At high pH, $(HC)_a$ can be neglected in comparison with $(C^-)_a$ and the expression becomes

$$R = \frac{(H^+)\phi_{HC}}{K_0} + \phi_{C^-} \qquad (13)$$

Since ϕ_{C^-} is calculated from eq. 13 as a difference between two experimentally determined quantities, its error will be large if its magnitude is relatively small.

Table III

Distribution of Couplers between *n*-Octyl Alcohol and *p*H 6.5 Buffer

Coupler	V_{aq}, cc.	V_{alc}, cc.	(Coupler)aq, $M \times 10^4$	(Coupler)alc, $M \times 10^4$	$\phi_{HC} \times 10^{-3}$
α-Naphthol	250	25	0.556	690	1.24
	250	25	.270	330	1.22
4-Cl-1-naphthol	250	25	.0445	564	12.7
	250	25	.0224	276	12.3
2,4-Dichloro-1-naphthol	500	50	.033	1880	57
6-Nitro-1-naphthol	250	25	.26	845	3.25
	250	25	.139	412	2.97
2-(2-Furamido)-5-methylphenol	500	10	.053	36.9	0.69
2-Butyramido-5-methylphenol	300	10	.112	19.7	.18
2-Benzamido-5-methylphenol	500	10	.254	29.8	1.2
2-(3,5-Disulfobenzamido)-5-methylphenol	25	100	2.0	Est. .04	< .00002

Preliminary experiments indicated that, for most couplers, $R \cong \phi_{HC}(H^+)/K_0$. Table IV shows the distribution of 2,4-dichloro-1-naphthol between *n*-octanol and a strongly alkaline solution. The value of R was found to depend upon the (K^+) and the data can be represented by $R = 0.8 + 25(K^+)_a$. The last term of this expression, ϕ_{C^-}, is proportional to (K^+) because both ions of the salt are extracted together into the bulk organic phase; therefore, $(K^+C^-)_S/(K^+)_a(C^-)_a = 25$. The value 0.8 in the equation agrees with the calculated value of the first term on the right-hand side of eq. 13.

Table IV

Distribution of 2,4-Dichloro-1-naphthol between *n*-Octyl Alcohol and *p*H 12 Buffer, (K^+) Varied

$V_{alc} = 50$ ml., $V_{aq} = 150$ ml.

	Coupler initially in alcohol phase			Coupler initially in aqueous phase		
(K^+), M	(Coupler)aq, $M \times 10^4$	(Coupler)alc, $M \times 10^4$	R	(Coupler)aq, $M \times 10^4$	(Coupler)alc, $M \times 10^4$	R
0.125	2.20	8.4	3.82	1.62	6.36	3.93
.25	1.49	10.5	7.05	1.12	7.86	7.02
.50	0.913	12.3	13.5	0.692	9.15	13.2
1.00	.537	13.4	25.0	.409	9.99	24.4

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(9) S. S. Marsden and J. W. McBain, *J. Phys. Chem.*, **52**, 110 (1948).

(10) E. Gonick and J. W. McBain, This Journal, **69**, 334 (1947).

D. Comparison of the Micellar Distribution Constants α, β and the Bulk Distribution Constants ϕ_{HC}.—The constants α, β and ϕ_{HC} are summarized in Table V. The data show that the constants α and β or the ratio β/α for a given coupler do not vary over an eightfold change of (K^+), but Table IV shows that ϕ_{C^-} is directly proportional to (K^+). This is taken to mean that, in the presence of Triton, the salt is solubilized as dissociated ions (in contrast to ion-pairs) with the counterions in the double layer. The (K^+) in the double layer is proportional to that in the bulk of the aqueous phase, and in solutions of high buffer salt concentration they are nearly equal. Therefore, the effect of (K^+) variation on the activity of the salt in the two regions is also nearly equal. The solubilization of the salts may be regarded as the formation of mixed micelles with the coupler ions hydrated at the surface.

TABLE V

SUMMARY OF CONSTANTS α, β AND ϕ_{HC}

$(K^+) = 0.25$ *M*, $\mu = 0.43$–0.45, unless otherwise noted

Couplers	$\alpha \times 10^{-3}$	$\beta \times 10^{-3}$	$\phi_{HC} \times 10^{-3}$	β/α	$\frac{\phi_{HC}}{\alpha}$
α-Naphthol	2.2 2.4[a] 2.5[b]	0.06 .06[a] .05[b]	1.2	0.027	0.55
4-Cl-1-naphthol	37.0	2.4	12.0	0.065 .048[a] .039[b]	.32
2,4-Dichloro-1-naphthol			57.0	.13 .13[a] .10[b]	..
6-Nitro-1-naphthol	6.2 4.5[a] 6.0[b]	0.38 .30[a] .35[b]	3.0	.061	.48
2-(2-Furamido)-5-methylphenol	0.50 .48[a] .68[b]	.05 .04[a] .05[b]	0.69	.10	1.4
2-Butyramido-5-methylphenol	.095	.008	0.18	.08	1.9
2-Benzamido-5-methylphenol	1.0	.09	1.2	.09	1.2
2-(3,5-Disulfobenzamido)-5-methylphenol	0.070	.009	$<2 \times 10^{-5}$	.13	$<3 \times 10^{-4}$

[a] $(K^+) = 0.125$ *M*. [b] $(K^+) = 1.00$ *M*.

All the couplers, with the exception of 2-(3,5-disulfobenzamido)-5-methylphenol, have values of ϕ_{HC} very nearly equal to their α values, as shown by the α/ϕ_{HC} ratios given in the last column of Table V. The similarity holds over a wide range of values of either term. One may surmise from these data that the solubilized non-ionized acids are located in the interior of the micelles where the environment is similar to the bulk of the octanol. The disulfo compound, however, exhibits a very small ϕ_{HC}/α. This may be explained by a large free energy of hydration of the ionized sulfonate groups, which inhibits extraction into the interior of the alcohol, but does not inhibit solubilization where the hydrated ions may be oriented at the surface of the micelle.

As pointed out by Hiskey and Downey,[8] the shift in the apparent *pK* can be interpreted equally well by either solubilization or complex formation. In the experiments described by Hiskey and Downey, the complex was isolated, and, in the experiments of Krishnappa, Doss and Rao,[7] the surfactant concentrations were low, probably below the CMC. Therefore, the results of both investigations were justifiably interpreted with complex formation. In our case, however, the concept of differential solubilization is preferable because a non-ionic colloid is used at concentrations above the CMC. As further evidence of the similarity of the two interpretations, it is noteworthy that the equation derived by Krishnappa, Doss and Rao expressing the change in *p*H as the same form as eq. 10 expressing the change in *pK*.

IV. Experimental

A. **Ionization.**—Solutions of the couplers in Triton and phosphate buffer ranged in concentration from 10^{-4} to 7.5×10^{-4} *M*. Solutions with a $(K^+) = 0.25$ *M* and lower were prepared by mixing and diluting stock solutions of 0.0833 *M* potassium phosphate (tribasic) containing Triton and 0.25 *M* potassium phosphate (monobasic) containing Triton. Solutions with $(K^+) = 1.0$ *M* were prepared by adding potassium chloride to the same stock solutions.

The densities of the solutions were measured in a Beckman model DU spectrophotometer in the region between 300 and 350 mμ, with the exception of 6-nitro-1-naphthol solutions, which were measured at 520 mμ. The *p*H of the solutions was measured with a Beckman Model G *p*H meter. The solutions were kept in a thermostat at 25° and the absorption cell was surrounded by a jacket through which 25° water was circulated.

B. **Distribution.**—To obtain ϕ_{HC}, the couplers were distributed between *n*-octyl alcohol and *p*H 6.5 phosphate buffer, with (K^+) equal to 0.25 *M* and ionic strength equal to 0.375. With α-naphthol, 4-chloro-1-naphthol and 6-nitro-1-naphthol, weighed amounts of the coupler were dissolved in *n*-octyl alcohol and shaken with the buffer. After clarification by centrifuging, the coupler in the aqueous solution was analyzed by measuring the density of the butyl acetate extract of the dyes formed by coupling with excess 4-amino-2-methyl-N-diethylaniline at *p*H 8. The distributions were measured at two different coupler concentrations.

The phenolic-type couplers were first dissolved in the aqueous *p*H 6.5 buffer and then shaken with the alcohol. The coupler in the aqueous phase was analyzed before and after distribution by the procedure just described.

The 2-(3,5-disulfobenzamido)-5-methylphenol showed an apparent increase in coupler concentration in the aqueous phase after distribution, which was attributed to the extraction of water into the alcohol. A maximum value for the distribution coefficient was estimated after correction for volume change.

Experimental details of the distribution of the acid form of the couplers appear in Table III.

The distribution of 2,4-dichloro-1-naphthol salt (*p*H 12) was found to be dependent on the potassium ion concentration. In this experiment, a weighed amount of the coupler was dissolved in $^1/_{12}$ *M* potassium phosphate (tribasic). After the solution of potassium phosphate (tribasic) was diluted with water or mixed with KCl solution to give the desired (K^+), it was shaken with *n*-octyl alcohol. The coupler in the aqueous phase, after distribution, was analyzed by measuring the optical density of the butyl acetate extract of the dye formed by coupling with excess 4-amino-N-diethylaniline at *p*H 6.5. The distributions at each level of (K^+) were repeated with the coupler initially in the alcohol phase. For details, see Table IV.

C. **Materials.**—Inorganic salts used in preparing the buffers were reagent grade K_3PO_4, KH_2PO_4 and KCl.

The ***n*-octyl alcohol** used in the distribution experiments was Eastman White Label Grade.

The ***n*-butyl acetate** was Eastman Special Grade.

Triton X-100 was purchased from Rohm and Haas Company. The molecular weight and composition of this material have been determined and found to be in reasonable agreement with the information furnished by the manufacturer.

The **α-naphthol** was Eastman White Label Grade, further purified by sublimation, followed by recrystallization from cyclohexane; m.p. 97–99°.

The **2,4-dichloro-1-naphthol** was Eastman White Label Grade, recrystallized from methanol; m.p. 106–107°.

The **6-nitro-1-naphthol**, m.p. 178–180°, was prepared and purified in accordance with the procedure of Hodgson and Turner.[11]

The **4-chloro-1-naphthol**, m.p. 119–120°, was prepared by the method of Kast.[12]

The following compounds were prepared by C. R. Barr, of these Laboratories, using as starting materials commercially available Eastman White Label Grade chemicals. The final products are all crystalline and in acid form except 2-(3,5-disulfobenzamido)-5-methylphenol, which is a dipotassium salt.

2-Benzamido-5-methylphenol.—To a solution of 12.3 g. (0.1 mole) of 2-amino-5-methylphenol[13] and 26 g. (0.2 mole) of quinoline in 150 ml. of dioxane was added, with stirring, at 25°, 15.5 g. (0.1 mole) of benzoyl chloride in 30 ml. of dioxane. The temperature rose rapidly to 40°. The reaction mixture was stirred at room temperature for one hour and then was poured into two liters of 5% hydrochloric acid. The solid product was collected by filtration, dried and recrystallized from ten parts of toluene, giving 15 g. (68%); m.p. 168–169°. *Anal.* Calcd. for $C_{14}H_{13}NO_2$: C, 74.0; H, 5.7; N, 6.2. Found: C, 74.3; H, 5.8; N, 6.4.

2-Butyramido-5-methylphenol.—Prepared as described in the preceding section, this material (10 g., 52%) melted at 114–115° after crystallization from ligroin. *Anal.* Calcd. for $C_{11}H_{15}NO_2$: C, 68.4; H, 7.8; N, 7.3. Found: C, 68.8; H, 7.9; N, 7.4.

2-(2-Furamido)-5-methylphenol.—Prepared similarly to the preceding compound, this material gave a yield of 10 g. (46%); m.p. 167–168°. *Anal.* Calcd. for $C_{12}H_{11}NO_3$: C, 66.4; H, 5.1; N, 6.5. Found: C, 66.8; H, 5.4; N, 6.6.

2-(3,5-Disulfobenzamido)-5-methylphenol Potassium Salt.—To a solution of 18.5 g. (0.15 mole) of 2-amino-5-methylphenol and 15 g. (0.18 mole) of sodium acetate in 300 ml. of 90% acetic acid, 50 g. (0.15 mole) of 3,5-dichlorosulfonylbenzoyl chloride was added, with stirring, at 30°. The temperature rose rapidly to 37°. The reaction mixture was stirred at room temperature for 5 hr. and diluted with 300 ml. of water. The solid was collected, dried and recrystallized from 26 parts of xylene, giving 44 g. (70%) of **2-(3,5-dichlorosulfonylbenzamido)-5-methylphenol**, melting at 173–174°. *Anal.* Calcd. for $C_{14}H_{11}Cl_2NO_6S_2$: N, 3.3. Found: N, 3.2.

To a refluxing solution of 28 g. (0.066 mole) of the dichlorosulfonyl compound in 140 ml. of methyl alcohol, 100 ml. of water was added. The resultant clear solution was heated at reflux for one-half hour and then concentrated to dryness under reduced pressure. The residue was dissolved in 80 ml. of water, and a solution of 13.8 g. (0.066 mole) of barium chloride in 40 ml. of water was added. The mixture was left standing at room temperature overnight, **the barium salt of 2-(3,5-disulfobenzamido)-5-methylphenol** separating in the form of fine, white needles; yield 20 g. (58%). *Anal.* Calcd. for $C_{14}H_{11}NO_8S_2Ba$: C, 32.2; H, 2.1; N, 2.7. Found: C, 32.4; H, 2.5; N, 2.6.

The barium salt (19.9 g., 0.038 mole) was dissolved in 150 ml. of hot water and converted to the potassium salt by the addition of 6.6 g. (0.038 mole) of potassium sulfate in 50 ml. of water. The barium sulfate was collected, and the filtrate was concentrated under reduced pressure. The residue was washed with 50 ml. of methyl alcohol and dried. Crystallization from 30 parts of glacial acetic acid gave 12 g. (68%) of the **dipotassium salt of 2-(3,5-disulfobenzamido)-5-methylphenol**. *Anal.* Calcd. for $C_{14}H_{11}NO_8S_2K_2$: C, 36.3; H, 2.4; N, 3.0. Found: C, 36.1; H, 2.7; N, 2.8.

ROCHESTER, NEW YORK

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The Mechanism of Dye Formation in Color Photography. VI. The Effect of a Non-ionic Surfactant on the Rate of Coupling

BY L. K. J. TONG AND M. CAROLYN GLESMANN

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The kinetics of coupling in the presence of a non-ionic surfactant between phenols (and naphthols) and quinonediimines formed by oxidation of disubstituted-*p*-phenylenediamine have been resolved in terms of simultaneous reactions in the micellar and in the aqueous regions. Both reactions involve the ionized form of the coupler exclusively. A method has been devised for calculating the amount of the reaction in each region.

Introduction

In the preceding paper,[1] the distribution constants α and β were calculated for both the acid and the salt forms of the couplers between aqueous and micellar regions in colloid solutions. The effect of this partition on the rate of coupling with the oxidized developing agent will be discussed in the present paper. The data are interpreted on the assumption that (1) simultaneous and independent reactions occur in the micellar and in the aqueous regions, and (2) the rate in each region is proportional to the product of reactant concentrations determined from the constants α and β.

The symbols have the same meaning as those in Part V of this series.

Since the quinonediimine T^+ is predominantly an hydrophilic cation, it is not solubilized to any great extent in the interior of the micelle; but if the electrical double layer is regarded as part of the micelle, then we can write

$$\gamma = \frac{(T^+)_m}{(T^+)_a} \qquad (1)$$

and

$$(\overline{T^+}) = (1 + \gamma V_m)(T^+)_a \qquad (2)$$

Since the addition of Triton will not, however, remove more than a very small fraction of T^+ from the aqueous region, we can set $(\overline{T^+}) \doteq (T^+)_a$. This assumption is justified by the absence of a measurable influence of Triton X-100 on the rate of deamination of T^+ (see under Results and Discussion).

The coupling rates were measured for the overall solution and the rate constants were therefore calculated in terms of the total concentrations

$$\frac{d(\overline{\text{dye}})}{dt} = k[(\overline{C^-}) + (\overline{HC})](\overline{T^+}) \qquad (3)$$

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[1] For Part V, see L. K. J. Tong and M. Carolyn Glesmann, THIS JOURNAL, **79**, 4305 (1957).