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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[11] H. Hodgson and H. Turner, *J Chem. Soc.*, 9 (1944).

[12] H. Kast, *Ber.*, **44**, 1337 (1911).

[13] M. C. Sannie and M. H. Lapin, *Bull. soc. chim. France*, 322 (1950).

[COMMUNICATION NO. 1894 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

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

RECEIVED APRIL 2, 1957

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

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

and

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

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

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

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

To resolve the observed rate into its components, we assume

$$(v_{\mathrm{m}} + v_{\mathrm{a}}) \frac{\mathrm{d}(\overline{\mathrm{dye}})}{\mathrm{d}t} = v_{\mathrm{a}}k_{\mathrm{a}}(\mathrm{T}^+)_{\mathrm{a}}(\mathrm{C}^-)_{\mathrm{a}} + v_{\mathrm{m}}k_{1,\mathrm{m}}(\mathrm{T}^+)_{\mathrm{m}}(\mathrm{C}^-)_{\mathrm{m}} + v_{\mathrm{m}}k_{2,\mathrm{m}}(\mathrm{T}^+)_{\mathrm{m}}(\mathrm{HC})_{\mathrm{m}} \quad (4)$$

The terms on the right-hand side of equation 4 express, respectively, the coupling rate of: (1) the coupler ion in the aqueous region, (2) the coupler ion in the micellar region, and (3) the non-ionized coupler acid in the micellar region. The term expressing the coupling rate of the coupler acid in the aqueous phase has been omitted from the equation because from the earlier work[2] it is known to be negligible.

Equation 4 holds equally well whether the reaction takes place in the interior or at the surface of the micelle; for, as long as the size of individual micelles remains constant, the extents of the two regions are proportional to each other. Combining equations 1 to 4 with those in Part V, we have

$$k\,[1 + 10^{(pK - p\mathrm{H})}] = \frac{k_{\mathrm{a}} + k_{1.\mathrm{m}}\,\gamma\beta V_{\mathrm{m}}}{(1 + \beta V_{\mathrm{m}})} + \frac{k_{2.\mathrm{m}}\gamma\alpha V_{\mathrm{m}}(\overline{\mathrm{HC}})}{(1 + \alpha V_{\mathrm{m}})(\overline{\mathrm{C}^-})} \quad (5)$$

If, for a given V_{m}, the second term on the right of equation 5 is zero, the product, $k[1 + 10^{pK - p\mathrm{H}}]$, will be independent of *p*H and will be the specific rate constant based on the total coupler ion concentration. Conversely, if the variation of k with *p*H can be predicted on the basis of $(\overline{\mathrm{C}^-})$ alone, then the second term on the right of equation 5 and also the final term of equation 4 are negligible.

The fractional part of the reaction which takes place in each region can be calculated more conveniently from equation 6, which can be obtained from the earlier equations.

$$k\left[\left(\frac{\alpha(\mathrm{H}^+)}{K_0} + \beta\right)V_{\mathrm{m}}\right] = k_{\mathrm{a}} + \left[k_{1,\mathrm{m}}\beta + k_{2,\mathrm{m}}\frac{\alpha(\mathrm{H}^+)}{K_0}\right]\gamma V_{\mathrm{m}} \quad (6)$$

using $10^{-p\mathrm{H}}$ as (H^+).

Experimental

Coupling rates were determined by steady-state flow methods, either using direct analysis of the end product or comparison with a competing reaction of known kinetics, as described previously.[2] Unless otherwise stated, the method used in the present experiments is the "continuous method," in which the extent of the reaction is measured by the optical density of the dye solution as it passes through the absorption cell at the end of the flow system. All reactions were carried out at 25°.

The solutions were made up as described[2] except that Triton X-100 was added to the alkaline coupler solution. Therefore, the reaction mixtures have, as before, the ionic strength $\mu = 0.375\ M$, and $(\mathrm{K}^+) = 0.19$ to $0.25\ M$.

The molar extinction coefficients of the dyes involving 4-chloro-1-naphthol were obtained from solutions of the purified dyes. In the case of 2-(disulfobenzamido)-5-methylphenol, the molar extinction coefficient of the dye was obtained from the product of the coupling reaction with excess coupler.

All dye solutions containing Triton X-100 were found to obey Beer's law within the dye-concentration range of the experiments. The molar extinction coefficients were independent of the Triton X-100 concentration. The solutions of 2-(disulfobenzamido)-5-methylphenol dye in the absence of Triton X-100 did not obey Beer's law. In this case, the dye concentrations in the reaction mixtures were obtained from empirical calibration curves, using solutions of the same *p*H and ionic strength.

Materials.—The developing agents and couplers used in these experiments were prepared and purified as described in earlier papers of this series. The 4-amino-N,N-diethyl-3-methylaniline hydrochloride[3] is the same sample used in Part III of this series.[2] The 4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline sulfate[4] is the same sample as in Part III of this series. The 4-chloro-1-naphthol is the same sample as in Part V of this series, m.p. 119–120°.[5] The 2-(3,5-disulfobenzamido)-5-methylphenol (dipotassium salt) is the same sample as in Part V of this series.

Results and Discussion

The addition of Triton X-100 does not alter the characteristics of the coupling reactions. Second-order rate plots produced in most cases smooth curves with constant slopes which could be extrapolated through the origin. Second-order rate constants k were calculated according to equation 3, using the total concentrations of the coupler and quinonediimine. Table IA shows that k is

TABLE I

COUPLING RATE BETWEEN 4-CHLORO-1-NAPHTHOL AND 3-METHYL-4-AMINO-N,N-DIETHYLANILINE

A. *p*H 11.03 ± 0.02; initial concn. of reactants varied

0.25% Triton X-100	3-Methyl-4-amino-N,N-diethylaniline $(\mathrm{A})_0 \times 10^4$, *M*	Ferricyanide 2 $(\mathrm{B})_0 \times 10^4$, *M*	4-Chloro-1-naphthol $(\mathrm{C})_0 \times 10^4$, *M*	$k \times 10^{-4}$, *M* l./mole sec.
	2.50	5.00	2.50	9.72
	2.50	2.50	2.50	9.57
	1.25	1.25	2.50	9.22
	5.00	2.50	2.50	9.71
	5.00	5.00	2.50	9.16
	10.00	2.50	2.50	9.50
	2.50	2.50	5.00	9.40
	2.50	2.50	1.25	8.75
			Av.	9.38 ± 0.22
2.0% Triton X-100	2.50	2.50	2.50	5.0
	5.00	5.00	2.50	5.0
	5.00	5.00	5.00	5.1

B. Initial concn. of reactants constant

$(\mathrm{A})_0 = 2.5 \times 10^{-4}\ M$, $(\mathrm{B})_0 = 2.5 \times 10^{-4}\ M$, $(\mathrm{C})_0 = 2.5 \times 10^{-4}\ M$, Triton X-100 varied

Triton X-100 (vol. %)	$k \times 10^{-4}$ (l./mole sec.)	
	*p*H 11.13	*p*H 8.71
0.15	10.4	0.99
.20	9.8	.85
.25	9.4	..
.30	8.6	.68
.40	7.5	.57
.50	7.0	.55
1.00	6.0	.43
1.50	5.4	.40
2.00	5.2	..
2.50	..	.41

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[2] L. K. J. Tong and M. Carolyn Glesmann, (Part III), THIS JOURNAL, **79**, 583 (1957).

[3] (a) J. E. Lu Valle, D. B. Glass and A. Weissberger, *ibid.*, **70**, 2223 (1948); (b) R. L. Bent, J. C. Dessloch, F. C. Duennebier, D. W Fassett, D. B. Glass, T. H. James, D. B. Julian, W. R. Ruby, J. M. Snell, J. H. Sterner, J. R. Thirtle, P. W. Vittum and A. Weissberger, *ibid.*, **73**, 3100 (1951).

[4] A. Weissberger, Eastman Kodak Co., U. S. Patent 2,193,015 (1940).

[5] H. Kast, *Ber.*, **44**, 1337 (1911).

unaffected by variation of the initial concentration of the reactants, by excess ferricyanide, $(B)_0 > (A)_0$, or by excess developing agent, $(A)_0 > (B)_0$. The last two facts have been pointed out in an earlier paper as evidence against mechanisms involving semiquinone in the rate expression. The independence of k on $(C)_0$ indicates that the rate of diffusion of quinonediimine to the micelle is not a controlling factor.

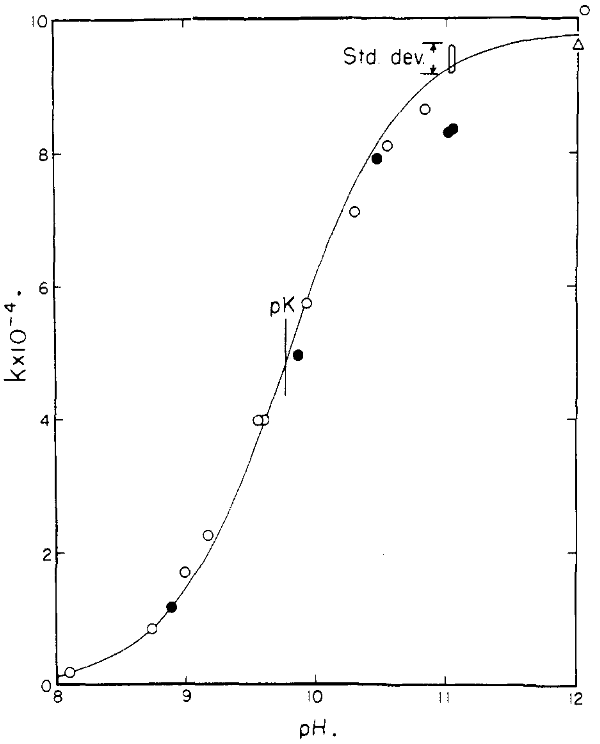
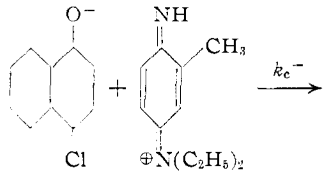


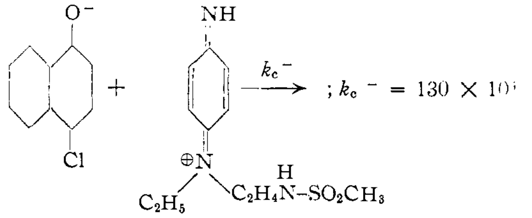
Fig. 1.—Rate of coupling between 4-chloro-1-naphthol and 3-methyl-4-amino-N,N-diethylaniline; Triton X-100 concentration = 0.25 (vol. %); curve calcd; experimental methods: ○, continuous; △, competitive; ●, chemical stop.

At constant Triton X-100 concentration, the rate constants k are proportional to the over-all degree of ionization calculated from K (see Table II, Part V). In Fig. 1, k was calculated as a function of pH for the reaction between 4-chloro-1-naphthol and 3-methyl-4-amino-N,N-diethylaniline, it being assumed that the rate-determining step is



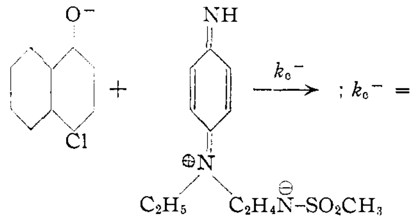
with $pK = 9.78$ for the coupler, and $k_c^- = 9.80 \times 10^4$, the specific rate constant of the ion. In Fig. 2, the rates for the reaction between 4-chloro-1-naphthol and 4-amino-3-methyl-N-ethyl-N-(β-methylsulfoamidoethyl)-aniline have been resolved into the rates of the two reactions: one involving the cation and the other involving the zwitterion of the quinonediimine in the rate-determining step.

Reaction (1)



; $k_c^- = 130 \times 10^4$

Reaction (2)



; $k_c^- = 2.4 \times 10^4$

In the experimental range of pH, reaction 1 is predominant; the sharp peak in Fig. 2 is due to the fact that the pK of the coupler (9.78) is very near the pK of the quinonediimine (9.56).[6]

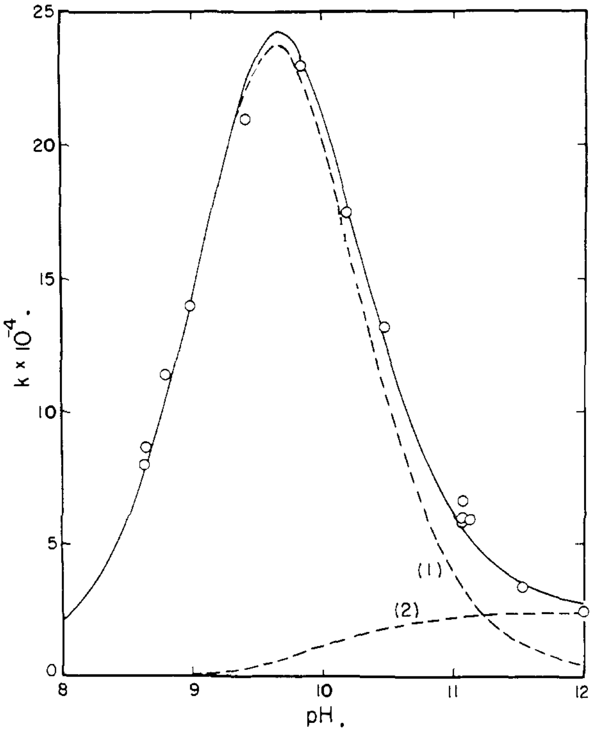
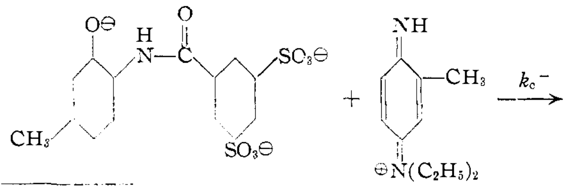


Fig. 2.—Rate of coupling between 4-chloro-1-naphthol and 4-amino-3-methyl-N-ethyl-N-(β-methylsulfoamidoethyl)-aniline. Triton X-100 concentration = 0.25%. Curve 1, coupler ion and the quinonediimine cation; curve 2, coupler ion and the quinonediimine zwitterion; continuous curve, curve 1 + curve 2.

In Fig. 3, log k was plotted *vs.* pH, and the curves were calculated for the reaction having the rate-determining step



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(6) L. K. J. Tong, *J. Phys. Chem.*, **58**, 1090 (1954).

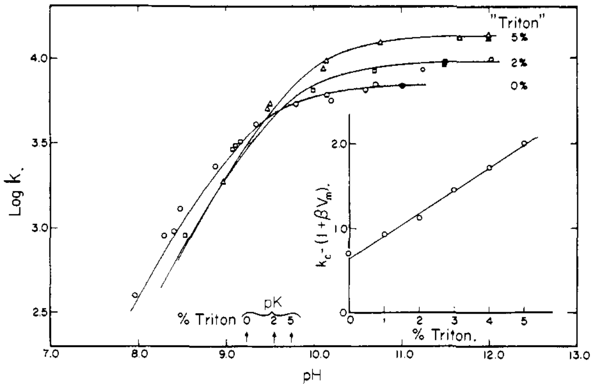

Fig. 3.—Rate of coupling between 5-methyl-2-(3,5-disulfobenzamido)-phenol and 3-methyl-4-amino-N,N-diethylaniline. Triton X-100 concentrations are indicated.

The values of log k_c^- (horizontal asymptotes) increase with Triton concentration, as shown.

The experimental points in Figs. 1 and 2 are in agreement with the calculated lines, within the accuracy of the *p*H measurements. In Fig. 3, the errors are slightly higher than can be expected from the error in *p*H. In the low *p*H region, however, the curves seem to deviate by a constant value in the log *k* scale. They show no tendency to approach a constant value of *k*, which would be expected if any of the rate terms containing (HC) were significant.

At constant *p*H, the rate constants vary with the Triton X-100 concentration, as shown by Table IB. These results were used to calculate the values of the left-hand side of equation 6. In Fig. 4, these data are plotted *vs.* V_m. Although the coupler is ionized only slightly at the lower *p*H values, and almost completely at the high *p*H values, the two sets of data, when plotted, lie practically on the same line. This again shows the insignificance of any term involving the un-ionized coupler in the rate expression. The extrapolated value at $V_m = 0$ is k_a, the rate constant in the aqueous region in equilibrium with the micelles. At any other value of V_m, the ratio $(\mu - k_a)/k_a$ represents the ratio of the reaction rate in the micelle to that in the aqueous region. From Fig. 4 it can be estimated that, in the presence of 2% Triton X-100, 90% of the coupling reaction takes place in the micelles. The effect of the molecularly dispersed Triton X-100 on the coupling rate could be observed by comparing k_a obtained by extrapolation with *k* measured directly in the absence of Triton; unfortunately, the latter cannot be obtained for the reaction shown in Fig. 4, owing to the precipitation of the dye. The reaction shown in Fig. 3, however, has been followed without Triton X-100. The insert in Fig. 3 shows a plot of equation 6, with k_c^- obtained at high *p*H. The point at zero Triton concentration obtained directly agrees well with k_a obtained by extrapolation; this shows that there is no measurable effect of the molecularly dispersed Triton X-100 on the coupling rate. The points at high *p*H in Fig. 3 were either obtained by the "continuous method," corrected for deamination in the calculation, or by the method of competing reactions described earlier, the rate of deamination being used as a standard. The rate of deamination has been found independently to be unaffected by Triton X-100, up to a concentration of 5%. The independence of deamination rate on Triton X-100 concentration indicates that very little quinonediimine has been removed from the aqueous phase by solubilization. This argument is valid except for the improbable situation where the deamination of the solubilized and the unsolubilized quinonediimine would have the same rate. This situation seems improbable, especially since we have found that the presence of an anionic surfactant, *e.g.*, (Duponol) where solubilization is likely to be high, lowers the deamination rate very markedly. The ratios $\gamma k_m/k_a$ for the reactions of 3-methyl-4-amino-N,N-diethylaniline with 4-chloro-1-naphthol, and with 2-(disulfobenzamido)-5-methylphenol are 0.30 and 4.1, respectively. The ratio probably depends on the orientation of the coupler ion in the micelle, which influences the availability of the reactive site of the solubilized coupler. Systematic studies with this point in mind may prove instructive both with respect to problems of solubilization and of reaction kinetics.

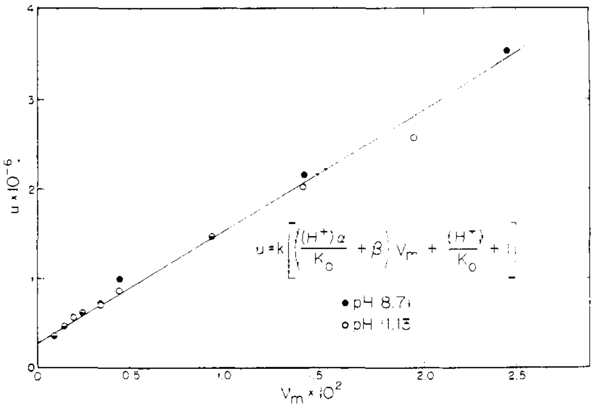

Fig. 4.—Effect of Triton X-100 on coupling rate between 4-chloro-1-naphthol and 3-methyl-4-amino-N,N-diethylaniline *u* (defined in figure) *vs.* V_m.

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