(formation of a C–C bond in the cyclopentenyl radical of ~81 kcal. and loss of a double bond of ~57 kcal., taking into account 7 kcal. in strain energy in the ring and a loss of 15.4 − 12.6 = 2.8 kcal. in stabilization energy in going to the cyclic product). The entropy difference between the two radical intermediates is not expected to exceed 5 to 7 e.u. The A factor for ring opening (A_d) can be estimated to 10^{13} in accordance with most other reactions involving unimolecular bond breaking. The A factor for ring closure (A_c) is therefore about $\sim 10^{12}$. The equilibrium between the linear and cyclic radicals is way over on the side of the cyclopentenyl radical. The fact that only small amounts of cyclic products are formed must mean that the cyclization reaction requires a high activation energy. The magnitude of this activation energy E_c can be estimated from the relative rates of ring closure *vs.* HI attack on the pentadienyl radical. The product analysis shows that not more than ~1% of the total reaction products were found to be cyclopentene. This means that the rate of HI attack on the pentadienyl radical (k_b) is about 100 times faster than the rate of ring closure (k_c) to form the isomeric cyclopentenyl radical.

$$\frac{k_b'(\mathrm{HI})}{k_c} \approx 100 \approx \frac{(10^{8\pm1})(10^{-1.5\,\pm\,0.5/\theta})(10^{-5})}{10^{12}10^{-E_c/\theta}}$$

Previous experiences with HI attack on radicals[12a-d] yield the above value of k_b' (units of l. mole^{-1} sec.$^{-1}$).

From the fact that we lose practically no iodine during the course of the reaction and from the sensitivity of the iodine measurements, one may assume that (HI) $\lesssim$ 0.5 torr. For A_c we use the value of 10^{12} mentioned earlier. For a mean temperature of 450°K. this yields 24 kcal. for E_c', the activation energy for ring closure. This value seems to be reasonable. Together with the estimated exothermicity of 14 kcal., it leads to a value of about 38 kcal. for the activation energy of the reverse reaction, ring opening of cyclopentenyl to form the pentadienyl radical. This can be compared with the recently reported values of 37 kcal. for the similar ring opening of cyclopentyl radical to form 1-penten-5-yl radical.[21] This latter reaction is endothermic by about 17 kcal.

(d) Rotation in the Pentadienyl Radical. Conformational changes in the radical intermediate are expected to be reasonably fast. The barrier to rotation can be estimated to be not more than 6–7 kcal. Only about 3 kcal. of stabilization energy are given up in forming the pentenyl radical, which should have a barrier to rotation of about 3 kcal. (judging from similar molecules).[22] This then means that the 1,3-pentadiene formed should be in equilibrium with respect to the geometrical isomers. In addition we know from earlier measurements of the kinetics[5a] and the equilibrium[11] between *cis* and *trans* $PD_{1,3}$ that the iodine catalyzed geometrical isomerization of 1,3-pentadiene is very fast at the temperatures and iodine concentrations used in this work. Yet we do not find the geometrical isomers of $PD_{1,3}$ in equilibrium concentrations. We believe that this arises from small stereospecific losses while quenching and collecting the sample. This conclusion is supported by the reported material defects.

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(22) H. G. Silver and T. L. Wood, *Trans. Faraday Soc.*, **59**, 588 (1963).

Determination of the Dissociation Rate of Dodecylpyridinium Iodide Micelles by a Temperature-Jump Technique[1a,b]

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Abstract: The rate of dissociation of the dodecylpyridinium iodide micelle in aqueous solution was studied by a temperature-jump technique in order to investigate the kinetic aspects of micellization. A relaxation process with a concentration-dependent half-life was observed above the critical micelle concentration. The temperature dependence of the rate constant k, which corresponds to dissociation of the first monomer from the micelle, can be described by the equation $\ln k = -1750/RT + 6.91$ over the range 8–22°. A mechanism has been proposed which is consistent with the characteristics of micellization, and possibly involving an activation process in which water is ordered around a monomer as it leaves the micelle. The techniques applied in this investigation should be applicable in general for studies of the association of macromolecules.

Although numerous studies have been made to elucidate the equilibrium aspects of micellization, the kinetics of micellization have been neglected. This is probably due to the fact that the rate of micellization is so fast that it cannot be followed by conventional techniques.[3-5]

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(2) (a) National Institutes of Health Postdoctoral Fellow of the National Cancer Institute, 1963-1965; (b) National Institutes of Health Postdoctoral Fellow of the National Institute of General Medical Sciences, 1964-1966.

(3) G. S. Hartley, *Trans. Faraday Soc.*, **31**, 199 (1935).
(4) G. A. Phillips and A. S. Porter, *Vortraege Originalfassung Intern. Kongr. Grenzflaechenaktive Stoffe, 3, Cologne, Germany*, 1, 239 (1960) (published 1961); *Chem. Abstr.*, **57**, 6049*f* (1962).
(5) P. Mukerjee and K. J. Mysels, *J. Am. Chem. Soc.*, 77, 2937 (1955).

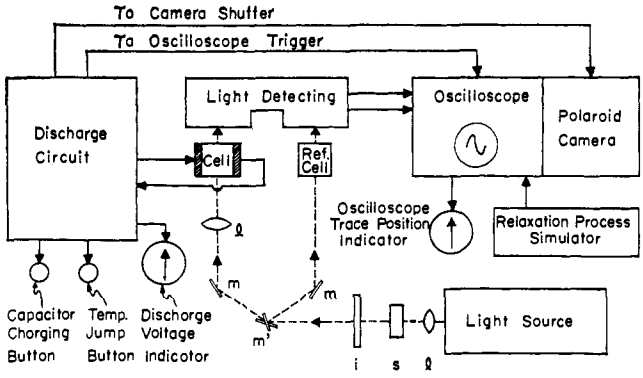

Figure 1. Schematic diagram of the temperature-jump apparatus: m = mirror, m′ = double mirror, l = lens, i = interference filter, s = shutter. For simplicity the temperature control units and the power supplies are not represented.

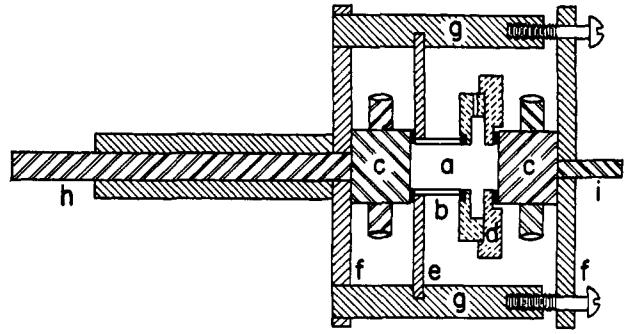

Figure 2. Diagram of the cell assembly: a = solution space, b = rectangular quartz cell with open ends, c = hollow brass electrodes (platinum-coated at the solution sides) with outlets for circulating coolant liquid, d = circular filling chamber with outlet for syringe needle (made from two plexiglass spacers, cemented together), e = high-voltage insulator plate to prevent arcing between electrodes, f and g = insulating plates and clamps, h = high-voltage plug with insulator shaft, i = ground lead. The black filled-in areas indicate rubber washers. The direction of the observation light beam is perpendicular to the plane of the diagram.

The purpose of this paper is to demonstrate that the temperature-jump technique is well suited for making the required kinetic measurements to study the rate of dissociation of the micelle formed from dodecylpyridinium iodide (DPI), and to interpret the observed relaxation times in terms of a suitable mechanism. DPI was chosen because a large spectral change accompanies its micellization[6,7] and thus provides a self-indicator of the micellization process. Alternatively, a more general method of using a dye as an indicator was found to yield equivalent results. It is considered that these findings demonstrate the feasibility of conducting kinetic experiments to study the association of macromolecules by making use of presently available "fast reaction" techniques.

Experimental Section

Materials. Dodecylpyridinium bromide (DPB) was obtained from K & K Laboratories, Inc., and DPI was prepared from DPB by crystallization twice from saturated KI solutions and twice from water. The product was dried and stored over $CaCl_2$ in a dark bottle in an evacuated chamber. A light yellow color, which appeared upon storage of dry DPI (apparently due to traces of iodine or triiodide[8]), could be removed from the aqueous solutions by adding sodium thiosulfate at a concentration of 1×10^{-4} *M* to the solvent without appreciably changing the critical micelle concentration (c.m.c.),[7] or perceptibly affecting the relaxation times. Therefore, the sodium thiosulfate was omitted in most of our kinetic studies.

1-Methylpyridinium iodide (MPI) was prepared from methyl iodide (Columbia Organic Chemicals, Co.) and reagent grade pyridine according to Kosower.[8]

Brom phenol blue (BPB) was purchased from National Aniline Division of Allied Chemical Corp.

Laboratory deionized distilled water and reagent grade salts were used. Solutions were prepared by dissolving a weighed amount of material in a volumetric flask and diluting to volume. Correction was not made for moisture content of the samples since they were stored over $CaCl_2$.

Equilibrium Measurements. Spectral studies were performed with a Cary Model 14 recording spectrophotometer, which was equipped with two Haake circulating pumps so that the temperature of each compartment could be controlled independently. The c.m.c. of DPI was determined by noting the optical density change which accompanies micellization at 287 mμ[6,7] in a thermostated Beckman Model DU spectrophotometer with 2-mm. and 1-cm. quartz cells, depending on the range of concentrations.

Temperature-Jump Measurements. In the temperature-jump technique, the temperature is changed very rapidly by means of electric heating. This produces a displacement of the equilibrium with an attendant rapid reattainment of equilibrium at the higher temperature. The kinetics of this process are followed by spectrophotometric observation of the changes in concentration of one of the species taking part in the equilibrium. The modified temperature-jump apparatus used was developed from the basic designs of Czerlinski, Eigen, and de Maeyer.[9,10] The major components of the instrument are represented in Figure 1. This drawing also indicates some of the major principles involved in its operation.

A critical part of the temperature-jump instrument is the cell. The main functions of this component are to hold the solution to be analyzed in the path of the observation beam and to provide electrodes for conducting the heating current. With considerable care to minimize undesirable effects (nonuniform heating, shock waves, etc.), a cell accommodating only 2 ml. of solution was constructed. Inside this cell the distance is 1.57 cm. between the electrodes and their surface area exposed to the solution is 0.9 cm.[2] For cleaning purposes, the cell can be taken apart and reassembled with rapidity and ease. The temperature of the test solution is controlled within $\pm 0.1°$ by circulating ethanol from a Haake thermostat through the hollow electrodes. During a series of temperature-jump experiments, only about 6 min. is necessary to change the solution, equilibrate at the desired temperature, and prepare the cell for the next temperature jump. The details of the cell construction can be seen from Figure 2.

In the discharge circuit a 0.1-μf. capacitor bank, charged to 25 kv., is discharged through the cell by means of a thyratron tube (for details see Appendix). The customary calculation,[10] using these capacitance and voltage values with the dimensions of the cell discussed above, yields for the theoretical maximum temperature rise, induced by the electric current in the solution, 5.4°, Considering the assumptions involved in this calculation, it is estimated that the actual temperature rise is $5.2 \pm 0.2°$.

In this instrument the rapidity of the heating process can be characterized by a relaxation time τ_H, which can be estimated from the simple relationship[10] $\tau_H = {}^1/_2RC$, where R and C are the resistance and capacitance of the discharge circuit, respectively. By making the assumptions that resistances, other than those of the cell and of the 10-ohm resistor used in the circuit, and capacitances, other than that of the capacitor bank, are negligible, relaxation times of 17×10^{-6} and 3×10^{-6} sec. were calculated for 328- and 48-ohm cell resistances, respectively. Actual measurements, using very rapidly equilibrating systems as indicators and solutions with the same cell resistances as above, showed relaxation times of 20×10^{-6} and 4×10^{-6} sec., respectively.

For the experiments discussed in this work a 250-w. xenon–mercury arc light source (Hanovia D-510B-1) was used. The

(6) W. D. Harkins, H. Krizek, and M. L. Corrin, *J. Colloid Sci.*, **6**, 576 (1951).
(7) P. Mukerjee and A. Ray, *J. Phys. Chem.*, **67**, 190 (1963).
(8) E. M. Kosower, *J. Am. Chem. Soc.*, 77, 3883 (1955).
(9) G. Czerlinski and M. Eigen, *Z. Elektrochem.*, **63**, 652 (1959).
(10) M. Eigen and L. de Maeyer, "Technique of Organic Chemistry," Vol. 8, Part II, Interscience Publishers, Inc., New York, N. Y., 1963, p. 895.

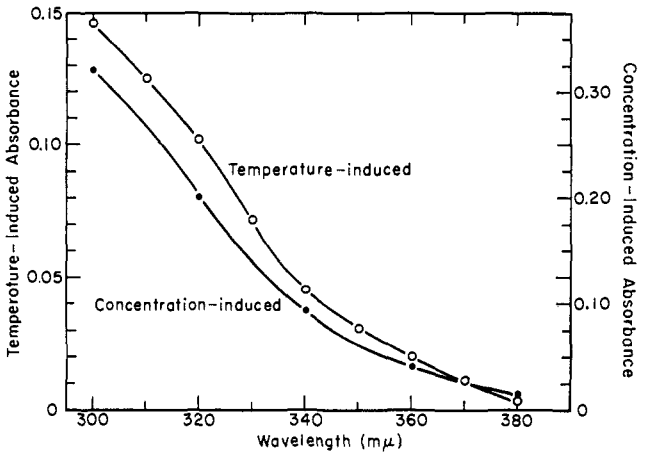

Figure 3. Difference spectra of the dodecylpyridinium iodide micelle: open circles represent results obtained with an 8.4 × 10^{-3} *M* solution in 0.1 *M* KCl + 0.0001 *M* sodium thiosulfate at 10°, measured against the same solution at 14°; the filled circles represent the spectrum obtained by Mukerjee and Ray[7] in 0.0001 *M* sodium thiosulfate using a solution *slightly* above the c.m.c. in the reference compartment and a solution *significantly* above the c.m.c. in the test compartment.

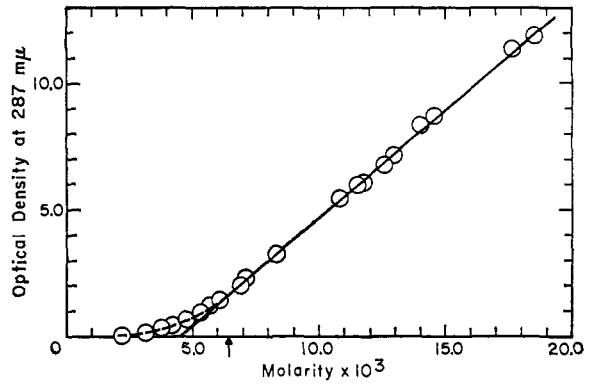

Figure 4. Optical density at 287 mμ for 1-cm. path length as a function of DPI molarity in 0.1 *M* KCl at 22°. The arrow on the abscissa indicates the c.m.c. which was calculated from the kinetic results. The straight line was computed from the data for which the concentration was above 7.0 × 10^{-3} *M*.

lamp was operated on d.c. using specially built, stabilized power supplies. The paths of the light beams from the source to the photomultipliers are indicated in Figure 1. The electrically operated shutter is used to minimize the exposure of the sample to the intense light source. The lenses in the light path are made of crystalline quartz and the mirrors have aluminized surfaces. The separation of the desired monochromatic light from the essentially white light of the lamp is achieved by interference filters (also shown in Figure 1) purchased from Bausch and Lomb, Inc. and from Baird-Atomic, Inc. Their transmission at peak wave length varies from 10 to 35%, and the half-width of their transmitted band varies from 25 to 17 mμ depending on whether they are first- or second-order types. The role of the reference cell placed in the path of the reference beam is to facilitate the balancing of the two light beams. During the experiments, the sample and reference cells were filled with the same solution.

Light-intensity changes are converted to voltage variations by the detecting circuit which utilizes two photomultipliers (RCA 1 P28) in a self-balancing arrangement (for details see Appendix). To avoid saturation, only six of the possible nine dynode stages are used. The photomultipliers are shielded from the electromagnetic wave generated by the sudden high-voltage current to such extent that the observed longest signal "blackout" following the discharge is only about 2 × 10^{-6} sec. The output signals of the detecting circuits are fed to the oscilloscope (Analab No. 1100 with Type 200 plug-in) and can be displayed on the screen at various sweep rates. The automatically operated Polaroid camera is coupled to the oscilloscope by a periscope attachment. The peak-to-peak noise level observed at the 366-mμ wave length is about 10^{-3} optical density unit. The relaxation process simulator represented in Figure 1 is used mostly in the analysis of reactions faster than those encountered in the present study. The operation and use of this unit will be discussed in detail in a forthcoming publication.

Results

Equilibrium Measurements. Mukerjee and Ray[7] have reported an ultraviolet difference spectrum which they considered to be characteristic of the DPI micelle. This spectrum was obtained by comparing two DPI solutions; one solution *slightly* above the c.m.c. (and therefore consisting primarily of monomer) was used as the reference to compare with another solution *appreciably* above the c.m.c., the latter containing the same concentration of monomer as the reference solution. The spectrum is presented in Figure 3 (filled circles). Data below 300 mμ are not presented, but they are available in the paper of Mukerjee and Ray.[7] Using these data, one selects a single wave length (*e.g.*, 287 mμ) at which there is appreciable difference in absorption between monomer and micelle, and thus can determine the c.m.c. The c.m.c. of DPI in salt-free water was found to be 5.40 × 10^{-3} *M* at 25°, in agreement with the value[7] of 5.26 × 10^{-3} *M* recently reported. This value for the c.m.c. was obtained as the point of intersection of the extrapolation of the two lines which represent the optical density of the monomer (below the c.m.c.) and of the micelle (above the c.m.c.). It will be shown in the Discussion that this is not the best way to obtain the c.m.c. of DPI from absorbancy data, but we wish to demonstrate at this point that our material is similar to that used by other workers.

Since 0.1 *M* KCl was used for most of the temperature-jump experiments, the c.m.c. of DPI was also determined in 0.1 *M* KCl from the concentration dependence of the optical density at 287 mμ at 22°. The results are presented in Figure 4. It may be seen that considerable curvature exists below 6.5 × 10^{-3} *M*, and a linear relationship between optical density and molarity results above this concentration. The straight line drawn in Figure 4 was computed by the method of least squares from the absorption data for solutions more concentrated than 7.0 × 10^{-3} *M*. The slope of this line, which is less in 0.1 *M* KCl than in water, is considered to represent the absorption coefficient of the micelle. It is also believed that the onset of linearity at about 6.5 × 10^{-3} *M* is the proper point to designate as the c.m.c. of DPI. This value for the c.m.c. is in good agreement with the one indicated in Figure 4 by the arrow, which was obtained from the analysis presented in the Discussion of the kinetic results. The c.m.c. determined by the onset of linearity is obviously larger than that obtained by the extrapolation method previously discussed. The curvature below the c.m.c. must be related to charge-transfer effects studied by Kosower and co-workers.[11]

It must be pointed out here that, owing to the presence of KCl in the solution, some fraction of the iodide counterions of the micelles is expected to be replaced by chloride ions.[12] The data displayed in Figure 4 can be

(11) E. M. Kosower, "The Enzymes," Vol. 3, Part B, Academic Press Inc., New York, N. Y., 1960, pp. 171-194.

conveniently used to ascertain the importance of this effect. Along the abscissa the ratio of the concentration of iodide ions to that of chloride ions is changing rapidly. Therefore, the fact that the curve is linear above the c.m.c. must be interpreted to mean that the changing iodide–chloride concentration ratio does not affect the absorption spectrum of the micelles; since the initial curvature seen in Figure 4 is also present in chloride ion free DPI and MPI systems (data not shown here), it cannot be a manifestation of the chloride–iodide exchange effect. In further discussions it will be assumed that this replacement by chloride ion is present but is relatively unimportant for the pertinent phenomena; hence, the aggregates will be referred to simply as DPI and not as DPI (Cl) micelles.

The temperature dependence of the c.m.c. of aqueous DPI was determined at 5, 25, 33, and 38°. The c.m.c. increased and the absorbancy of the micelle decreased with increasing temperature over this temperature range. Changing the temperature produces the spectral change shown in Figure 3 (open circles). This spectrum may also be considered to be typical of the micelle. It was obtained by placing an 8.4×10^{-3} *M* DPI solution in 0.1 *M* KCl + 1×10^{-4} *M* sodium thiosulfate in each compartment of the Cary spectrophotometer, and adjusting the reference cell to 14° and the sample cell to 10°. The two spectra shown in Figure 3 are superimposable within experimental error, showing that the spectrum induced by a concentration difference is the same as that produced by a temperature difference. In a related experiment, the reversibility of the absorbance change of a solution of DPI in 0.1 *M* KCl, which was above the c.m.c., was demonstrated by raising the temperature from 5 to 35° and cooling back to 5° again.

Kinetic Studies. Conditions were arranged in the temperature-jump apparatus to produce a rapid rise in temperature of 5.2 ± 0.2°. This led to a change in optical density which corresponded to about 90% of that observed in equilibrium studies over the same temperature interval. (The failure to observe 100% of the optical density change is attributed to stray light in the temperature-jump apparatus.) Such experiments were carried out over a range of concentrations of DPI to determine the relaxation time as a function of concentration. Most measurements were made at 366 mμ, since the optical density at 287 mμ was too high for observations with concentrated DPI solutions; however, at low concentrations, the measurements were made at both 366 and 287 mμ.

The ionic strength of the solutions was controlled with KCl. In most of our studies 0.1 *M* KCl was used. However, higher salt concentrations were employed in some experiments in order to reduce the heating rate, and to determine the ionic strength dependence of the observed relaxation times.

Typical oscilloscope traces, which were obtained below the c.m.c., slightly above the c.m.c., and with a nearly saturated solution are presented in Figures 5a, b, and c, respectively. It may be seen from Figure 5a[13]

(12) J. M. Corkill and J. F. Goodman, *Trans. Faraday Soc.*, **58**, 206 (1962).

(13) A wave length of 287 mμ was used in this case in order to obtain a greater total optical density change with such a dilute solution. The fast step can also be seen at 366 mμ, but the total optical density change is smaller than at 287 mμ.

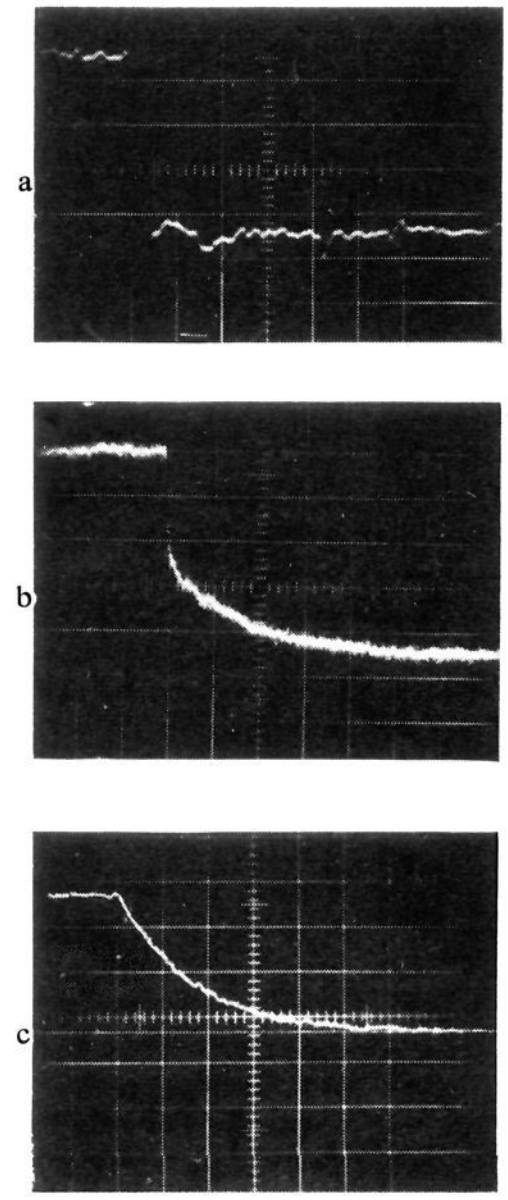

Figure 5. Typical relaxation effects of dodecylpyridinium iodide solutions initially at 10°. The abscissa represents the time scale, and the ordinate is in arbitrary units proportional to absorbancy for small optical density changes. The observed relaxation effect corresponds to a decrease in absorbance with time: (a) 2.5×10^{-3} *M* in 0.5 *M* KCl, λ = 287 mμ, sweep rate = 10 μsec./division; (b) 7.5×10^{-3} *M* in 0.5 *M* KCl, λ = 366 mμ, sweep rate = 500 μsec./division; and (c) 22.0×10^{-3} *M* in 0.1 *M* KCl, λ = 366 mμ, sweep rate = 100 μsec./division.

that a rapid change in optical density occurs below the c.m.c. with a relaxation time less than 1×10^{-5} sec.$^{-1}$. This fast step is still seen with solutions slightly above the c.m.c. (Figure 5b), but is now followed by a slow relaxation process which appears to be associated with changes in the monomer–micelle equilibrium. It may be noted that the slow step is not observed below the c.m.c. Figure 5c indicates that, far above the c.m.c., only the slow step is observed. The proportion of the total optical density change observed during a temperature jump, which corresponded to the fast step, decreased with increasing concentration above the c.m.c. up to about 15×10^{-3} *M* DPI, where it essentially disappeared.

The curves of Figures 5b and c may be used to compute a relaxation time. For this purpose, a horizontal line in Figure 5c was drawn through the tail end of the relaxation curve to represent the equilibrium optical density of the solution following the temperature jump, OD_f. The optical density of the relaxing solution after *t* μsec. may be represented by OD_t. Since the plots of $\ln (OD - OD_f)$ *vs.* *t* were linear, the relaxation process can be characterized by a *single* relaxation time τ, which is equal to the negative reciprocal of the slope. Typical plots are given in Figure 6 for a solution which

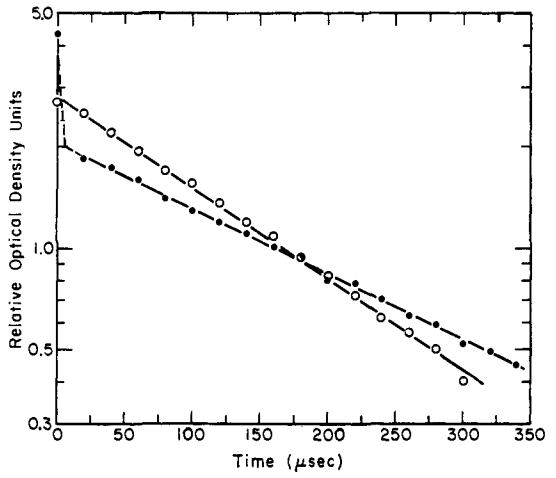

Figure 6. Plot of log ($OD_t - OD_f$) *vs.* t for dodecylpyridinium iodide solutions in 0.1 M KCl with an initial temperature equal to 10° and wave length of 366 mμ. Concentration for open circles = 22.0×10^{-3} M, and for filled circles = 9.08×10^{-3} M. Units of time which are plotted for the 9.08×10^{-3} M experiment are one-half the observed values in order to represent the data on a single abscissa. The dashed line arises from the fast process.

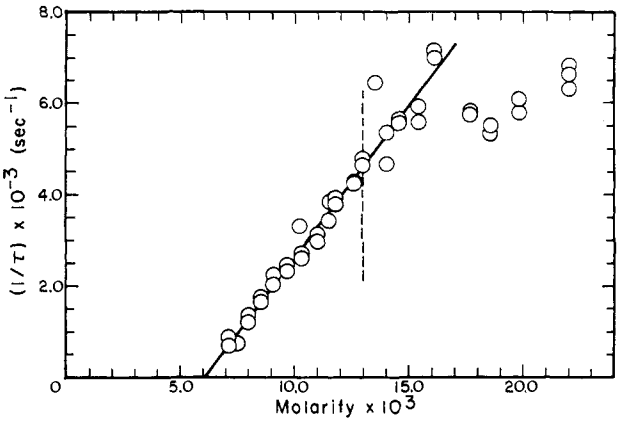

Figure 7. Plot of $1/\tau$ *vs.* molarity for dodecylpyridinium iodide in 0.1 M KCl with initial and final temperatures of 10° and 15.2°, respectively, and a wave length of 366 mμ. The line drawn represents the one of best fit including the data up to the point of the broken vertical line.

exhibits only the slow reaction (open circles) and for a solution which shows both the fast and the slow reaction (filled circles). The relaxation curve for the slow step is clearly first order for at least 85% of the total absorbancy change. Multiple regression analysis with all the data for the slow step yielded a multiple correlation coefficient[14] of 0.997 ± 0.002, indicating that the observed linearity is highly significant.

The results obtained for the concentration dependence of the reciprocal of the relaxation time are given in Figure 7. The radii of the points represent the standard deviation of the calculated line drawn through the data below 13×10^{-3} M.

The computed relaxation times were independent of the wave length used to obtain them. However, the per cent of the total optical density change (which corresponded to the fast step for solutions above the c.m.c.) was greater at 287 mμ than at 366 mμ.

A few temperature-jump experiments were carried out with the DPI–BPB system. In order to minimize the possible effect of the dye on the micellization equilibrium of DPI, only trace amounts (10^{-5}–10^{-4} M) of BPB were used. The relaxation process was followed at a wave length of 578 mμ. In these experiments none of the oscillograms obtained showed the fast step, but the slow step was present in every case. The relaxation times for the slow step were identical with those which were obtained on the pure DPI system using light of wave lengths 287 and 366 mμ for observation.

Although temperature jumps were made with fresh solutions for obtaining all of the results which are given in Figure 7, it was found that the same relaxation spectra were observed on successive jumps with the same solutions. However, this was true only for the more concentrated solutions, since evidence of photoaging was noted upon repeated jumps with solutions of concentrations about equal to and less concentrated than the c.m.c. This result led us to expose the sample to the light source the minimum amount of time when conducting a temperature-jump experiment, even with the more concentrated solutions.

Experiments were also performed in order to determine the temperature dependence of the relaxation time. Four sets of solutions ranging from 7.1 to 9.6 $\times 10^{-2}$ M were adjusted to 3°, and four sets of solutions ranging from 8.1 to 11.0 $\times 10^{-3}$ M were adjusted to 17° prior to heating. The variation of $1/\tau$ with molarity could again be described by a straight line with slope and intercept equal to 6.27×10^5 (μsec. M)$^{-1}$ and -3680 μsec.$^{-1}$, respectively, for the 3° runs, and 6.65×10^5 (μsec. M)$^{-1}$ and -4270 μsec.$^{-1}$, respectively, for the 17° runs.

In order to determine the effect of ionic strength on the relaxation time of the slow step, solutions of DPI (ranging in concentration from 7.1 to 12.5 $\times 10^{-3}$ M) were prepared at KCl concentrations of 0.1, 0.3, and 0.5 M. No effect of ionic strength on τ was observed.

Temperature jumps were also made with DPB at 287 mμ. This wave length was used because the optical density of aqueous DPB solutions increases sharply with increasing concentration at the reported c.m.c.[15] when absorbancy is measured at 287 mμ. Both the rapid and the slow reaction were observed with 1.9×10^{-2} M DPB solutions in 0.5 M KCl. A solution of DPB as concentrated as 3.4×10^{-2} M in 0.1 M KCl was examined, and the relaxation time of the slow step was of the order of 2 msec.

The results of temperature-jump experiments with methylpyridinium iodide solutions showed only the fast reaction when solutions ranging in concentration from 3.0 to 4.5 $\times 10^{-2}$ M were used. The change in optical density was in a direction similar to the changes noted with DPI, in agreement with spectrophotometric observations. When a concentrated solution of 9.1 $\times 10^{-2}$ M was examined, no relaxation process was found.

Discussion

The formation of micelles from DPI monomers has been demonstrated by various methods.[6,7,16,17] The

(14) G. W. Snedecor, "Statistical Methods," 4th Ed., The Iowa State College Press, Ames, Iowa, 1946, p. 347.

(15) J. E. Adderson and H. Taylor, *J. Colloid Sci.*, **19**, 495 (1964).
(16) H. C. Parreira, *Anais Acad. Brasil. Cienc.*, **32**, 207 (1960).
(17) G. C. Kresheck, H. Schneider, and H. A. Scheraga, *J. Phys. Chem.*, **69**, 3132 (1965).

c.m.c. determined by light scattering[16] is 5.6×10^{-3} M in water; the micelle appears spherical[16] and has a molecular weight[16] of 32,700 at the c.m.c. Application of various spectrophotometric methods[6,7] yielded a c.m.c. in water of $5.0–5.6 \times 10^{-3}$ M; a c.m.c. of 5.9×10^{-3} M was observed by a conductivity method.[17]

The temperature dependence of the c.m.c. of DPI reported in this study receives support from the observation of Mukerjee and Ray[7] that the c.m.c. of DPI is higher at 45° than at 25°. Adderson and Taylor[15] reported that the c.m.c. of DPB also increases with increasing temperature above 15°.

It appears that the fast optical density changes observed on the temperature-jump oscillograms with DPI, MPI, and DPB solutions (but not with the DPI–BPB system) are due to the direct perturbation of the ion pair and charge-transfer equilibria[11,18] by the temperature jump. Since the relative intensity of the absorption change arising from this step gradually decreases as the monomer–micelle concentration ratio decreases, it is possible that the dissociation of the ion pairs of the nonassociated monomers represents a major factor in this observed fast optical density change. It is also conceivable that dimerization equilibria[19] could contribute to this absorption change; this latter effect, however, may be expected to make only a small contribution to the absorbency change, because large perturbances of the absorption spectra are unlikely in a tail-to-tail type dimerization.

We interpret the slow steps seen on the temperature-jump oscillograms as relaxation processes due to the perturbation of the monomer–micelle equilibrium by the temperature change. In other words, we believe that the gradual decrease of the optical density simply indicates a decrease in the micelle concentration. The experimentally observed increase in the c.m.c. with increasing temperature would require that the micelle concentration decrease during the temperature jump. Figure 3 corroborates this view, by indicating that the temperature difference spectrum of the system is the same as the spectrum of the micelles. The disappearance of the slow step below the c.m.c. for DPI and DPB solutions, and its complete absence in the case of nonmicelle-forming MPI solutions, are further proofs that the slow process is connected with micellization. The most convincing evidence, however, comes from the BPB experiments. Owing to the solubilization of the dye–detergent salt inside the micelles,[5] the extinction coefficient of brom phenol blue at 578 mμ changes with the concentration of the micelles present. The temperature-jump experiments on the DPI–BPB system showed exactly the same relaxation at 578 mμ as the slow step with DPI alone at 287 mμ. Thus, since the absorption changes of two entirely different chromophoric groups gave the same relaxation times, it must be concluded that the slow reaction is due to the changes in micelle concentration and not to some other reactions involving the charge-transfer complex chromophore.

In water, the observed c.m.c. of DPI[6,7] is smaller than that of DPB[15] by a factor of about two. The observed relaxation times also vary by about the same order of magnitude. Finally, the minimum in the temperature dependence of the c.m.c. is also different for these two compounds. It is considered that the observed differences in the behavior of these two surfactants are related to the facility with which iodide is desolvated (relative to bromide) prior to becoming associated with the charged micelle surface. This view seems to be in agreement with the recent proposals of Mysels and Princen[20] and Schick.[21]

Mechanism. In order to express the relaxation time (or times) of a slightly perturbed chemical equilibrium in terms of reactant concentrations and rate constants, the mechanism of the individual reactions taking part in the equilibrium must be known. In favorable cases, when the mechanisms are not very complex, explicit expressions can be derived in order to determine the rate constants of the individual reactions from the experimental data.[10] Since the details of the reactions involved in the monomer–micelle equilibria of the DPI system are not known, a mechanism had to be assumed to interpret the observed relaxation times. In seeking this mechanism only those reaction schemes were considered which were in full agreement not only with the kinetic data but also with the general characteristics of micelle equilibria, *e.g.*, the phenomenon of critical micelle concentration, preponderance of monomers and micelles over the other possible intermediate species, etc. There have been several theories published in the literature about the formation of micelles.[22–28] Since most mechanisms derived directly from these treatments would yield very complex rate expressions which could not be checked by experimental data, a simple mechanism was chosen which is essentially based on the mass-action concept of stepwise aggregation. The details of the assumed mechanism are as follows.

The aggregation of monomers leading to the formation of micelles (n-mers) is the net result of $n - 1$ reversible bimolecular steps.

$$\left.\begin{array}{l} A + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 \\ A_2 + A \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} A_3 \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ A_i + A \underset{k_{i+1,i}}{\overset{k_{i,i+1}}{\rightleftharpoons}} A_{i+1} \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ A_{n-2} + A \underset{k_{n-1,n-2}}{\overset{k_{n-2,n-1}}{\rightleftharpoons}} A_{n-1} \\ A_{n-1} + A \underset{k_{n,n-1}}{\overset{k_{n-1,n}}{\rightleftharpoons}} A_n \end{array}\right\} \quad (1)$$

The role of equilibria involving the reactions of intermediate species such that

$$A_j + A_k \rightleftharpoons A_{j+k} \quad (2)$$

is assumed to be negligible

It is a good approximation to assume that, in a typical monomer–micelle equilibrium above the c.m.c.,

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(24) M. J. Vold, *J. Colloid Sci.*, **5**, 506 (1950).
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(28) D. C. Poland and H. A. Scheraga, *ibid.*, **69**, 2431 (1965).

the following is true

$$[A] \gg [A_2] \gg [A_3] \gg \ldots \gg [A_{n-2}] \gg [A_{n-1}] \quad (3)$$

and

$$[A_n] \gg [A_2] \quad (4)$$

where the brackets represent concentrations. In order for the mechanism represented by eq. 1 to satisfy eq. 3 and 4, certain conditions concerning the rate constants and monomer concentration must be met. Equation 3 is fulfilled by the proposed mechanism if eq. 5 holds.

$$\frac{k_{i,\,i+1}}{k_{i+1,i}}[A] \ll 1 \quad \text{for } 1 \leqq i \leqq n-2 \quad (5)$$

In order to demonstrate the inequality of (4), we express the concentration of micelles in terms of the monomer concentration with the aid of the set of equilibria represented by eq. 1 as

$$[A_n] = \frac{k_{12}k_{23}\ldots k_{i,i+1}\ldots k_{n-2,n-1}k_{n-1,n}}{k_{21}k_{32}\ldots k_{i+1,i}\ldots k_{n-1,n-2}k_{n,n-1}}[A]^n \quad (6)$$

Substituting into eq. 4 the quantities $(k_{12}/k_{21})[A]^2$ for $[A_2]$ and eq. 6 for $[A_n]$ we obtain

$$k_{n,n-1} \ll k_{n-1,n}\prod_{i=2}^{n-2}\frac{k_{i,i+1}}{k_{i+1,i}}[A]^{n-2} \quad (7)$$

as the condition under which eq. 4 will hold.

Since the aggregation number reported for several micelle equilibria is relatively large[29-31] (about 80 for the DPI system[16]), eq. 6 predicts a very rapid increase in $[A_n]$ with increasing [A] (*e.g.*, for $n = 80$, a 1% increase in monomer concentration more than doubles the micelle concentration). If, in addition, eq. 5 and 7 also hold true, then this mechanism would account for the existence of a c.m.c., *i.e.*, the sudden appearance of micelles at a critical concentration. We can also show that a rapid increase in $[A_n]$, from zero to a very large value, with increasing [A] implies that the monomer concentration is essentially independent of the total concentration, and equal to the c.m.c., at and above the c.m.c. This may be demonstrated by recognizing that any incremental amount of monomer added to the system will appear as an extremely small increase in [A] and a relatively large increase in $[A_n]$ in order to satisfy the requirement that $[A_n]$ increase very rapidly with [A]. Thus, the added amounts of monomer will leave the equilibrium monomer concentration changed only very little, and $[A_n]$ will increase *linearly* with the total detergent concentration. If eq. 5, 6, and 7 hold, then the c.m.c. should be chosen as the point of onset of linearity in a plot of optical density *vs.* total concentration; this was the basis for the determination of the c.m.c. from the data in Figure 4.

It has been shown recently by n.m.r. studies[32] that the hydrocarbon chains inside the micelle are under much higher pressure than in the solution. Under these conditions the removal of the first detergent molecule from the intact micelle could be much slower than that of the subsequent ones from a broken-up micelle. Assuming that the bimolecular collisions involved in the stepwise buildup of the micelles are fast, diffusion-controlled reactions, the relatively slow dissociation of the first monomer from the micelle would imply that the last step in eq. 1 equilibrates much more slowly than do the other steps; in essence, the decomposition of the micelle is the rate-limiting step for the relaxation process. By making this assumption, eq. 1 can be written as

$$\left.\begin{aligned}(n-1)A &\underset{l}{\overset{l'}{\rightleftharpoons}} A_{n-1} \quad \text{fast}\\ A_{n-1} + A &\underset{k_{n,n-1}}{\overset{k_{n-1,n}}{\rightleftharpoons}} A_n \quad \text{slow}\end{aligned}\right\} \quad (8)$$

where l' and l are related to the rate constants of the first $n-2$ steps; the ratio l'/l may be called L. For the slow last step

$$\frac{d[A_n]}{dt} = k_{n-1,n}[A_{n-1}][A] - k_{n,n-1}[A_n] \quad (9)$$

It can be seen from eq. 8 that, from the point of view of the slow last step

$$[A_{n-1}] = L[A]^{n-1} \quad (10)$$

By defining

$$z = [A] - [A]_e \text{ and } x = [A_n] - [A_n]_e \quad (11)$$

where the subscript e designates equilibrium concentrations and the other values are instantaneous concentrations during the perturbation of the equilibrium, the substitution from eq. 10 and 11 into eq. 9 yields

$$\frac{d[A_n]}{dt} = \frac{dx}{dt} = k_{n-1,n}L\{[A]_e + z\}^n - k_{n,n-1}\{[A_n]_e + x\} \quad (12)$$

Expanding in a power series, we obtain

$$\frac{dx}{dt} = k_{n-1,n}L[A]_e^n + k_{n-1,n}Ln[A]_e^{n-1}z + \ldots - k_{n,n-1}[A_n]_e - k_{n,n-1}x \quad (13)$$

By the definition of equilibrium, the first and penultimate terms cancel. It follows from eq. 3 and 4 and from the stoichiometry of eq. 1 that $z = -nx$. Substituting these relations in eq. 13, we obtain

$$\frac{dx}{dt} = -k_{n-1,n}Ln^2[A]_e^n\left[\frac{x}{[A]_e} + \ldots\right] - k_{n,n-1}x \quad (14)$$

Since $x/[A]_e$ is small, eq. 14 reduces to

$$\frac{dx}{dt} = -(k_{n-1,n}\,Ln^2[A]_e^{n-1} + k_{n,n-1})x \quad (15)$$

Treating eq. 15 as a first-order differential equation, with appropriate boundary conditions, we obtain the relaxation time τ.

$$\frac{1}{\tau} = k_{n,n-1} + k_{n-1,n}\,Ln^2[A]_e^{n-1} \quad (16)$$

Since

$$[A_n]_e = L\frac{k_{n-1,n}}{k_{n,n-1}}[A]_e^n \quad (17)$$

(29) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press Inc., New York, N. Y., 1963.
(30) J. M. Corkill and K. W. Herrmann, *J. Phys. Chem.*, **67**, 934 (1963).
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(32) J. Clifford and B. A. Pethica, in R. H. Ottewill and G. D. Parfitt, *Nature*, **196**, 940 (1962).

eq. 16 reduces to

$$\frac{1}{\tau} = k_{n,n-1} + k_{n,n-1}n^2\frac{[A_n]_e}{[A]_e} \quad (18)$$

By neglecting the concentration of intermediate species (eq. 3), the total concentration of the surfactant can be expressed as $a = [A]_e + n[A_n]_e$. Substitution into eq. 18 yields

$$\frac{1}{\tau} = k_{n,n-1} + k_{n,n-1}n\left(\frac{a}{[A]_e} - 1\right) = -k_{n,n-1}(n-1) + \frac{nk_{n,n-1}}{[A]_e}a \quad (19)$$

This mechanism is equivalent to the steady-state assumption with regard to the intermediate species.

It must be noted that the same expression for $1/\tau$ can also be derived from the following mechanism based on a one-step n-molecular aggregation

$$nA \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A_n \quad (20)$$

An n-molecular reaction (eq. 20) is highly improbable compared to a series of bimolecular reactions (eq. 1). Therefore, we may dismiss the mechanism of eq. 20 from further consideration. On the other hand, it is conceivable that other mechanisms, besides those of eq. 1 and 20, could lead to the expression in eq. 19.

In order to apply eq. 19 to the interpretation of the experimental data, an additional assumption must be made, *viz.*, that n does not change significantly over the temperature range used in the temperature-jump experiment, and that the micelles are monodisperse. While the distribution of n values and their temperature dependence could be taken into account, the mathematics would become too complicated to handle in a simple manner. On the other hand, the kinetic data are consistent with a unique and constant value of n since the plot of ln $(OD_t - OD_f)$ *vs.* t would depart significantly from the observed linearity if n varied.

Since, for all practical purposes, $[A]_e$ is constant above the c.m.c.,[28-31] eq. 19 predicts a linear relationship between the reciprocal of the relaxation times and the total surfactant concentration. Figure 7 demonstrates that the kinetic measurements on the DPI system at 15.2° are in agreement with this prediction. The data obtained at 8.2 and 22.2° indicated a similar linear behavior. The deviations above 13×10^{-3} M may be due to interactions between micelles, which are reported to change the micelle shape,[30] aggregation number,[28] etc. These effects were not taken into account in the mechanism discussed here. It is also noteworthy that the high-concentration points of Figure 7 are not much below the solubility limit of DPI.

It can be seen from eq. 19 that, if n is known, $k_{n,n-1}$ can be calculated from the intercept of the $1/\tau$ *vs.* a plot. It was reported by Parreira[16] that the aggregation number of DPI micelles in aqueous solution at 25° is 87. Using this value and the intercept data, these rate constants can be obtained. The results of these calculations are given in the second row of Table I. The accuracy of these numbers depends on the errors of the determination of n (not available in the published paper) and, of course, on the validity of eq. 19.

Table I. Rate Constants and C.m.c. Values Calculated from Kinetic Data

Temp., °C.	8.2	15.2	22.2
$k_{n,n-1}$, sec.$^{-1}$	43	47	50
C.m.c., M (*i.e.*, $[A]_e$)	5.9×10^{-3}	6.1×10^{-3}	6.5×10^{-3}

The temperature dependence of the first-order rate constant is represented by eq. 21.

$$k_{n,n-1} = 9.96 \times 10^2 \exp\left(\frac{-1750 \text{ cal./mole}}{RT}\right) \quad (21)$$

The activation energy and the pre-exponential factor were derived from the usual Arrhenius plot.

Equation 21 indicates that both the frequency factor and the activation energy are unusually low compared to other first-order reactions (*e.g.*, $A \sim 10^{13}$ sec.$^{-1}$ and $E_a \sim 30$ kcal./mole). These low values may arise if the activation process, in which the monomer leaves the micelle, involves the formation of ordered water around the monomer; *i.e.*, there would be negative contributions to the entropy and enthalpy of activation. In addition, if the process is diffusion controlled, this would also lead to a low activation energy.[33]

Equation 19 also indicates that the c.m.c., equal to $[A]_e$, can be determined from the ratio of the intercept to the slope of the $1/\tau$ *vs.* a plot. The results of these calculations are given in the third row of Table I. The value of the c.m.c. at 22.2° is the same as the one obtained by the spectroscopic method (6.5×10^{-3} M) under the same conditions. The failure to observe the slow relaxation step at 6.4×10^{-3} M is also consistent with the conclusion that the c.m.c. is above 6.4×10^{-3} M. The increase of the c.m.c. with increasing temperature is also in agreement with the conclusions of the equilibrium studies discussed in a previous paragraph.

Acknowledgments. It is a pleasure to acknowledge helpful discussions with Dr. W. P. Bryan during the construction of the temperature-jump apparatus, and to thank Mrs. E. Stimson for calculating the relaxation times from the temperature-jump photographs.

Appendix

Detailed drawings of some electronic parts of the temperature-jump apparatus have been deposited with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C., where they may be obtained by ordering Document 8584 and remitting $1.25 for microfilms or $1.25 for photoprints. Make checks payable to: Chief, Photoduplication Service, Library of Congress.

The drawings contain: (Appendix A) Figure 8, diagram of the discharge circuit; (Appendix B) Figure 9, diagram of the detecting circuit.[34]

(33) Reference 10, p. 1033.

(34) NOTE ADDED IN PROOF. Dr. R. H. Ottewill has called our attention to a paper entitled Studies on the Rate of Micelle Breakdown in Solution, by M. J. Jaycock and R. H. Ottewill, presented at the International Congess of Surface Activity, Sept. 1964. Using a stopped-flow conductance apparatus, they found that the rate of breakdown was "very fast with a half-life of the order of, or less than, 10 milliseconds."