[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

A Study of the Reaction between Dodecyl Bromide and Thiosulfate Ion Solutions of Dodecylammonium Bromide[1]

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In the reaction between dodecyl bromide and thiosulfate ion in solutions of dodecylammonium bromide it has been found that rate constants calculated on the basis of concentrations expressed as mole reactant per mole micelle are more consistent than when the concentrations are expressed as moles per liter of solution. The rate constant calculated on the micellar basis was found to vary with the concentrations of reactants and dodecylammonium bromide as follows: (1) The rate constant is independent of the thiosulfate concentration up to a value of 0.041 mole thiosulfate per mole of micelle, but increases at higher thiosulfate concentrations. (2) The rate constant increases with increasing concentration of dodecylammonium bromide. (3) The rate constant decreases with increasing dodecyl bromide concentration. (4) The rate constant increases when decyl alcohol is solubilized in the micelle in addition to the other reactants. The first variation is tentatively explained on the basis of a distribution of thiosulfate ion between those fixed rigidly on the micelle and those present in the double layer.

In reactions taking place in solutions of colloidal electrolytes the reactants may be in the water, absorbed on the micelle, or solubilized in the micelle depending on the nature of the reactant. If the reactant is a small ion, such as sodium ion or bromide ion possessing the same sign of charge as the colloidal ions forming the micelle, it will be located in the water. An ion of charge opposite to that possessed by the aggregating ion will be adsorbed as a counter-ion on the micelle. The completeness of this adsorption depends on the concentration of this ion, the concentrations and nature of other ions which may serve as counter-ions on the micelle, the water solubility of the compounds formed by the counter ions, the temperature, and the critical concentration of the colloidal electrolyte.

Reactants which are neutral molecules may exist in the water or be solubilized in the micelle depending on the nature of these molecules. Molecules which are solubilized are characterized by low water solubility, but relatively great hydrocarbon solubility. It has been suggested by Harkins and co-workers[2a,b,3] that solubilization occurs in two ways in the micelle, the molecules may align themselves in the palisades of the micelle or may be held in the sandwich layer in the middle of the micelle. Molecules which are solubilized in the palisades have a polar group such as the hydroxyl group attached, *e.g.*, to a hydrocarbon group, like dodecyl alcohol. Non-polar molecules such as benzene are solubilized in the sandwich layer.

The study reported here was made to determine the kinetics of a reaction between a solubilized neutral molecule and an ion existing essentially only as a counter-ion on the micelle.

It is desirable for this type of study to avoid the use of a reaction involving transfer of electrons (*i.e.*, oxidation–reduction) because of the possibility of complications from radical formation. The substitution reactions undergone by the normal alkyl halides appeared to be the best suited to our purpose. These reactions have been studied by a number of investigators[4] and been found to follow second order kinetics and to be bimolecular reactions.

The substitution of the thiosulfate ion for the bromide atom on *n*-dodecyl bromide was selected for this study. Dodecyl bromide was selected because it has the same chain length as the colloidal electrolyte that was used, namely, dodecylammonium bromide. Thiosulfate ion was chosen since it forms an insoluble salt with dodecylammonium ion. The substitution reaction may be written

$$RBr + S_2O_3^{=} \rightarrow RS_2O_3^{-} + Br^{-}$$

in which R denotes dodecyl. The products are the ion of a Bunte salt, $RS_2O_3^-$, and the bromide ion. Dodecylammonium bromide was chosen as the colloidal electrolyte to provide a minimum change in the composition of the ion atmosphere surrounding the micelle. The dodecylammonium bromide was always present in large excess with respect to the reactants so that no great change in the counter-ion concentration occurred during the reaction. The ion of the Bunte salt which is formed is similar in nature to the aggregating ion of the typical colloidal electrolyte and, therefore, may be expected to remain in the micelle after being formed, especially since its charge is opposite to the charge of the aggregating ions in the micelle. At the beginning of the reaction the micelle will consist of dodecylammonium ions oriented with their axes parallel to each other with dodecyl bromide molecules dispersed among them. The thiosulfate ions will be located almost entirely on the surface of the micelle, the bromide ions constituting a diffuse layer around the micelle. At the end of the reaction the micelle will consist of dodecylammonium ions oriented with axes parallel with ions of the Bunte salt dispersed among them probably as an insoluble salt composed of the $C_{12}H_{25}S_2O_3^-$ and dodecylammonium ions. Since no turbidity appeared in the reaction mixtures during the reactions, it is probable that the reaction products are retained in the micelle by solubilization. The only counter-ions present will be the bromide ions.

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(1) This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Synthetic Rubber Program of the United States Government.

(2) (a) R. W. Mattoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys.*, **15**, 209 (1947); (b) W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Colloid Sci.*, **1**, 105 (1946).

(3) W. D. Harkins, R. W. Mattoon and R. Mittleman, *J. Chem. Phys.*, **15**, 762 (1947).

(4) (a) E. A. Moelwyn-Hughes, *Chem. Revs.*, **10**, 241 (1932); (b) P. J. Hardwick, *J. Chem. Soc.*, 141 (1935); (c) H. A. C. McKay, THIS JOURNAL, **65**, 702 (1943); (d) H. Seelig and D. E. Hull, *ibid.*, **64**, 940 (1942); (e) J. L. LeRoux, C. S. Lu, S. Sugden and R. H. K. Thompson, *J. Chem. Soc.*, 536 (1945); (f) E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, **37**, 279 (1941); (g) E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1576 (1933); (h) I. Dostrovsky and E. D. Hughes, *ibid.*, 164 (1946).

The reactions were run at 50° to provide adequate solubility of dodecylammonium bromide and of dodecylammonium thiosulfate in the micelle.

It has been shown[5] that in substitution reactions in homogeneous solution involving the normal alkyl halides, the energy of activation is independent of the chain length and that the second-order rate constant does not vary greatly with chain length from propyl to cetyl halides. Thus for the purposes of this discussion we may obtain a sufficiently accurate value of the rate constant for the reaction between thiosulfate and dodecyl bromide in homogeneous solution by extrapolating the data of Crowell and Hammett[6] for the reaction between thiosulfate ion and *n*-propyl bromide in 44% ethanol from 37.5 to 50°, the temperature used in our experiments, by means of the activation energy which they obtained. This gives a value of the rate constant at 50° of 0.29 liter mole^{-1} min.$^{-1}$ for 44% ethanol solutions initially containing 0.100 *M* sodium thiosulfate and 0.036 and 0.059 *M* *n*-propyl bromide. The value of the second-order rate constant, k_2, was found to decrease 1 to 2% when the initial concentration of alkyl bromide was increased from 0.045 to 0.055 *M*. This same effect was observed by Haywood[7] in the reactions between alkyl iodides and benzyl oxide ion and by McKay[4c] in the exchange of radioactive iodide with the iodine molecule on alkyl iodides. The latter found that on increasing the initial concentration of alkyl iodide from 0.91 to 4.01 the rate constant decreased by 27% when the initial concentration of sodium iodide was 0.60 *M*. This decrease in rate constant with increasing concentration of alkyl halides has not yet been explained in a satisfactory manner.

The rate constant given above for the reaction between *n*-propyl bromide and thiosulfate is somewhat higher than the rate constant for the reaction between *n*-dodecyl bromide and thiosulfate ion but is probably only about 15% higher if this reaction follows the same behavior found for a number of other substitution reactions of alkyl halides.[5]

Interpolation for the dielectric constant of a 44 weight per cent. ethanol–water solution from the data given by Harned and Owen[8] gives a dielectric constant for this medium of 45.8. Taking with Debye[9] the dielectric constant at the surface of the micelle to be the average of the dielectric constants of water and the hydrocarbon gives a value of 40. Thus, as nearly as can be estimated, our investigation of the substitution reaction between thiosulfate ion and dodecyl bromide has been made in a medium of the same dielectric constant as that of the medium used by Crowell and Hammett[6] in their study of the reaction between thiosulfate ion and propyl bromide. No correction is necessary then for the effect of dielectric constant on the rate constant when we compare our results with theirs.

Experimental

The dodecylammonium bromide was prepared by passing 99.2% pure tank hydrogen bromide into an alcoholic solution of dodecylamine. The dodecylamine used was a sample obtained from Armour and Co. and was fractionally distilled under reduced pressure through a column twenty inches long. The dodecylammonium bromide was recrystallized twice from absolute ethanol and dried in a vacuum desiccator over anhydrous magnesium perchlorate.

The dodecyl bromide was obtained from Halogen Chemicals Co. and was fractionated under reduced pressure through a thirty-inches long column. The fraction collected boiled over a 0.4° range.

A stock 0.1000 *M* thiosulfate solution was prepared from Mallinkrodt A.R. sodium thiosulfate. This solution was standardized against pure potassium iodate. A stock solution of iodine which was 0.09938 *N* was standardized against the stock 0.1000 *M* sodium thiosulfate. Dilute iodine solutions for titrating the samples taken from the reaction mixtures were prepared daily by diluting the stock iodine solution.

The reaction mixtures were prepared, except for slight variations to be noted later, as follows: A solution of the desired concentration of dodecylammonium bromide was prepared by weighing out the dry solid and dissolving it in hot conductivity water. This solution was transferred to a volumetric flask and the solution made up to volume at 50.0°. The dodecyl bromide was delivered from a weight pipet made from a ten-ml. Pyrex hypodermic syringe by sealing a Corning micro stopcock with a capillary tip onto the tip of the syringe. The syringe containing dodecyl bromide was weighed, the dodecyl bromide delivered into a Pyrex glass bottle of approximately 125 ml. capacity and the syringe reweighed, the amount of dodecyl bromide being determined by difference. One-hundred milliliters of dodecylammonium bromide solution was pipetted into the bottle containing the dodecyl bromide, the stopper set firmly in place, and the neck of the bottle and stopper tightly wrapped with rubber electrician's tape to hold the stopper firmly in place. The bottle was then placed in a 50.0 ± 0.05° thermostat and rotated end-over-end for a period of at least one hour to solubilize the dodecyl bromide in the dodecylammonium bromide solution. Experiments reported later showed that one hour agitation provided solubilization equilibrium. After solubilization of the dodecyl bromide the bottle was removed and as rapidly as possible the tape was cut off, the stopper removed, an appropriate volume of 0.1000 *M* sodium thiosulfate solution pipetted into the bottle, the stopper replaced, the bottle shaken vigorously, the neck and stopper retaped and the bottle replaced in the thermostat providing end-over-end agitation. These latter operations required approximately two minutes to perform. The bottle containing the reaction solution was left rotating in the thermostat until just prior to the time the first sample was taken for analysis when the bottle was removed from the thermostat, the tape cut off, and the bottle placed in another thermostat at 50.0 ± 0.05° where it was not agitated.

Ten-ml. samples were removed for analysis by pipet. The samples were added to 30 ml. of absolute alcohol and titrated amperometrically with 0.001988 *M* iodine solution, except where noted later, the end-point being determined by means of a rotating platinum micro-electrode maintained at +0.1 v. with respect to the saturated calomel reference half cell.

The point of zero time was taken as the time at which the sodium thiosulfate solution was added to the dodecyl bromide solution. As will be seen later, this did not correspond to the actual zero time, apparently because of the cooling of the solution at the time the thiosulfate solution was added and the time for the thiosulfate to attain adsorption equilibrium with the micelles. The initial concentrations of reactants and the concentration of dodecylammonium bromide were calculated by assuming the volumes of the dodecylammonium bromide solution, containing solubilized dodecyl bromide, and the sodium thiosulfate solution were additive. The variations in rate constants in this system are great enough that any error introduced by this assumption cannot influence to any appreciable extent the validity of the conclusions drawn from the data.

Results

The first variable investigated was the dodecylammonium bromide concentration. For this set

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(5) (a) J. B. Conant and R. E. Hussey, THIS JOURNAL, **47**, 476 (1925); (b) J. A. Mitchell, *J. Chem. Soc.*, 1792 (1937).

(6) T. I. Crowell and L. P. Hammett, THIS JOURNAL, **70**, 3444 (1948).

(7) P. C. Haywood, *J. Chem. Soc.*, **121**, 1904 (1922).

(8) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N.Y., 1943, p. 118.

(9) P. Debye and R. M. Hagen, Report to Office of Rubber Reserve, April, 1949.

of experiments the dodecyl bromide concentration was kept equal to the thiosulfate concentration and the ratio of thiosulfate concentration to dodecylammonium bromide concentration was kept constant. The reaction solutions were prepared in the following manner. Two hundred ml of a 0.500 *M* dodecylammonium bromide solution was prepared and sufficient dodecyl bromide weighed in to make the solution 0.01133 *M* in dodecyl bromide. This solution was placed in a bottle which was rotated in the thermostat for two hours to solubilize the dodecyl bromide. Portions of this solution were pipetted into 100-ml. volumetric flasks and diluted to volume at 50° to give solutions which were 0.375, 0.250, 0.125, 0.075 and 0.050 *M* in dodecylammonium bromide and containing proportionate concentrations of dodecyl bromide. These solutions were transferred to reaction bottles and placed in the 50° thermostat providing agitation and left for one hour to allow the solution to equilibrate. The bottles were then removed from the thermostat and an amount of 0.1000 *M* sodium thiosulfate solution added so that the concentration of thiosulfate was equal to the dodecyl bromide concentration. The bottles were restoppered and returned to the thermostat and rotated until just before the first sample was removed for analysis. The remainder of the procedure was the same as described previously.

The rate constants for these runs evaluated graphically are given in Table I.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION BETWEEN THIOSULFATE AND DODECYL BROMIDE IN SOLUTIONS OF DODECYLAMMONIUM BROMIDE AT 50.0 ± 0.05°

Initial concn. $S_2O_3^=$ = initial concn. dodecyl bromide = constant × concn. dodecylammonium bromide

Concn. dodecylammonium bromide (mole/liter)	Second-order rate constant $K, \frac{\text{liter}}{\text{mole-min.}}$	"Micellar" rate constant, K'
0.346	0.817	0.288
.237	1.058	.244
.122	1.833	.200
.0737	3.15	.189
.0494	4.73	.169

To investigate possible reasons for the increase in the second-order rate constant with decreasing dodecylammonium bromide concentration shown in Table I, reactions were run in which the concentrations of dodecylammonium bromide and thiosulfate were held constant and the concentration of dodecyl bromide was varied. Two sets of runs were made, the first set at a dodecylammonium bromide concentration of 0.238 *M* and a second set at a dodecylammonium bromide concentration of 0.119 *M*. In both sets of runs the thiosulfate concentration was 0.00476 *M*. The method of preparation of the solutions was that given earlier.

Second-order rate constants for these runs are given in Table II.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION BETWEEN THIOSULFATE AND DODECYL BROMIDE IN 0.238 AND 0.119 *M* DODECYLAMMONIUM BROMIDE SOLUTIONS AT 50° FOR VARIOUS INITIAL CONCENTRATIONS OF DODECYL BROMIDE

Initial concn. $S_2O_3^=$ = 0.00476 *M*; 0.238 *M* dodecylammonium bromide

Initial concn. dodecyl bromide (mole/liter)	Second-order rate constant, K	Micellar rate constant, K'
0.00174	1.202	0.272
.00252	1.046	.239
.00337	1.141	.260
.00551	1.157	.267
.00554	1.120	.259
.00724	1.036	.240
.00732	1.011	.234
.01068	0.712	.168
.01082	.856	.202
.01082	.855	.202
.01457	.682	.164
.01460	.701	.168
.01488	.684	.164
.01492	.692	.166
.01520	.666	.160
.01719	.597	.144
.02355	.525	.130
.02888	.492	.125
.03290	.463	.119
0.119 *M* Dodecylammonium bromide		
0.00182	1.818	0.196
.00336	1.962	.214
.00486	1.747	.194
.00648	1.540	.173
.00806	1.410	.161
.00982	1.220	.142
.01132	1.179	.138
.01297	1.088	.130
.01538	0.968	.119
.02019	.907	.114

The data for the five runs listed in Table II at approximately 0.015 *M* dodecyl bromide concentration and 0.238 *M* dodecylammonium bromide concentration were obtained not only to test the variation of rate constant with initial concentration of dodecyl bromide but also to find the effect of various periods of agitation of the dodecylammonium bromide solution with the dodecyl bromide prior to the addition of the thiosulfate. The time of shaking prior to adding the thiosulfate was varied from 1 to 27 hours. The rate constants for these runs are presented in Table III.

TABLE III

THE EFFECT OF TIME OF SHAKING PRIOR TO ADDITION OF THIOSULFATE ON SECOND-ORDER RATE CONSTANT FOR THE REACTION BETWEEN DODECYL BROMIDE AND THIOSULFATE AT 50°

Time of shaking in hours	Initial concn. of dodecyl bromide (b)	Second-order rate constant	Difference from K = $1.350 - 44.7b$, %
1.0	0.01488	0.684	−0.1
2.0	.01460	.701	+1.3
3.0	.01520	.666	−0.7
7.8	.01492	.692	+1.3
27.0	.01457	.682	−2.4

The last column in Table III shows the per cent. difference between the experimentally determined rate constant and the rate constant given by the empirical relation, $K = 1.350 - 44.7b$, where b is the initial concentration of dodecyl bromide. This equation represents the relationship between the second-order rate constant and the initial concentration range 0.006 to 0.018 M dodecyl bromide. It can be seen from the data in Table III that shaking for one hour is sufficient to establish solubilization equilibrium. The experiments also show that the dodecyl bromide undergoes no appreciable side reactions with the water or dodecylammonium bromide.

The final variation investigated was the variation in rate constant obtained when the thiosulfate concentration was varied, the concentration of dodecyl bromide and dodecylammonium bromide remaining constant. Two sets of runs were made to study this effect. For the first set a 0.250 M dodecylammonium bromide solution was prepared at 50° and 200 ml. of this solution pipetted into a bottle containing 1.3106 g. of dodecyl bromide. This bottle was placed in the 50° thermostat and agitated for 13 hours. Fifty-ml. portions of this solution were then pipetted into each of five bottles and various amounts of water at 50° added by pipet, the volume of water being such that, when the thiosulfate solution had been added, the total volume in each case would be 105 ml. These bottles were then put into the 50° thermostat and agitated for about one hour before the thiosulfate solution was added. After addition of thiosulfate the bottles were again agitated until immediately before taking the first sample as in all other runs.

For the second set of experiments the make up of the reaction solutions was essentially the same as described above with the exception that both the dodecyl bromide and thiosulfate were made up in dodecylammonium bromide before mixing.

The second-order rate constants for the runs are given in Table IV.

TABLE IV

SECOND-ORDER RATE CONSTANTS FOR THE REACTION BETWEEN THIOSULFATE AND DODECYL BROMIDE IN SOLUTIONS OF 0.119 M DODECYLAMMONIUM BROMIDE AT 50° FOR VARIOUS INITIAL CONCENTRATIONS OF THIOSULFATE

Initial concentration dodecyl bromide = 0.00963 M

Initial concn., $S_2O_3^=$	Second-order constant, K	Micellar rate constant, K'
0.002057	1.313	0.151
.00476	1.284	.148
.00762	1.625	.194
.00952	1.957	.225
.01429	2.327	.291
Initial concentration dodecyl bromide = 0.00458 M		
0.00244	1.628	0.187
.00365	1.634	.188
.00610	1.927	.222
.00731	2.063	.237
.00853	2.385	.274

It is of interest to note that in all cases the reactions follow second-order kinetics even though in the run with 0.0143 M thiosulfate the solution was slightly turbid during the entire run.

Discussion

The reaction between dodecyl bromide and thiosulfate in a solution of dodecylammonium bromide is of interest for in this aqueous medium we presumably know the location of the reactants. Though no figure can be given for the water solubility of dodecyl bromide in water, an estimate can be made as to its order of magnitude. Since the mercaptide group is more hydrophilic than bromide, the water solubility of dodecyl bromide would be expected to be somewhat less than the solubility of dodecyl mercaptan, which is soluble in water to the extent of approximately 10^{-6} M at 50°.

The lowest concentration of dodecyl bromide in the present work was 0.00174 mole per liter. Under the experimental conditions used in the rate of reaction experiments, solutions which were 0.238 M in dodecylammonium bromide and approximately 0.03 M with respect to dodecyl bromide appeared completely clear to the unaided eye. Thus, when the concentration of dodecyl bromide is 0.00174 M, the micelle must be only about one-fifteenth saturated to the bromide while the concentration in water must be negligibly small.

Dodecylammonium thiosulfate is soluble in water to the extent of about 10^{-3} mole per liter at 50°.[10] This solubility is reduced to about 10^{-5} molar in the neighborhood of the critical concentration of dodecylammonium bromide by the common ion effect. As the concentration of dodecylammonium bromide is increased, the solubility of dodecylammonium thiosulfate increases. This increase in solubility is attributed to solubilization of dodecylammonium thiosulfate by replacing bromide ions with thiosulfate ions in the dodecylammonium bromide micelle. The solubility of dodecylammonium thiosulfate in the true aqueous phase, however, must remain constant at a concentration of approximately 10^{-5} molar above the critical concentration. The lowest concentration of thiosulfate used was approximately 2.3×10^{-3} M; thus, at this concentration, the upper limit to the percentage of thiosulfate in the water is four-tenths.

For our purposes we may consider that all the dodecyl bromide is in the micelles and all the thiosulfate ions are present as counter ions of the micelles.

It has been pointed out that the second-order rate law is adhered to by the reaction systems reported in this paper. The second-order rate constant, however, decreases steadily with increasing dodecyl bromide concentration, the initial concentration of all other components remaining constant. The magnitude of the decrease of the rate constant suggested that it might be associated with the manner in which the dodecyl bromide is solubilized in the micelle.

It has been shown[2b,3,11] that long chain alcohols are solubilized by aligning the hydrocarbon chain in the palisades of the micelle with the hydrophilic end of the molecule oriented toward the water, *i.e.*, the alcohol molecules are oriented in the same manner as the long chain ions making up the micelle. Other molecules which do not possess polar character are solubilized in the sandwich

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[10] I. M. Kolthoff and W. F. Johnson, THIS JOURNAL, **74**, 22 (1952).

[11] R. W. Mattoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys.*, **16**, 644 (1948).

layer of the micelle. Thus it seems likely that in the case of dodecyl bromide solubilized in dodecylammonium bromide micelles the dodecyl bromide is preferentially solubilized in the palisades. The hydrophilic character of the bromide group not being so great as the hydrophilic character of the hydroxyl group, there is a possibility that part of the dodecyl bromide is solubilized in the sandwich layer, or that after saturation of the palisades layer solubilization in the sandwich layer starts.

On the basis of the above considerations a number of kinetic expressions were derived and tested involving solubilization of the dodecyl bromide either in the palisades or the sandwich layer. None of these schemes explained the observed variation in rate constant with dodecyl bromide concentration.

It was pointed out previously that the dodecyl bromide and the thiosulfate must be almost entirely in or on the micelle. The most likely locus of reaction is, therefore, the micelle. If the reaction does take place entirely in the micelle, the concentration of the reactants should have been expressed in terms of the concentration in the micelle in the expression for the rate constant.

We can take $(C - C_0 + b)$ to be the total moles of micellar material per liter of solution, where C is the dodecylammonium bromide concentration, C_0 the critical concentration of the dodecylammonium bromide, and b the initial concentration of the dodecyl bromide. The reaction product remains in the micelle so that the moles of micellar material remain constant during the reaction. The relation between the second-order rate constant and the micellar rate constant can easily be shown to be

$$K' = (C - C_0 + b)K$$

where K' = rate constant calculated on the basis of moles reactants per mole of micelle, and K = rate constant calculated on the basis of moles reactants per liter of solution.

In deriving the above expression the assumption has been made that the concentration of micellized dodecylammonium bromide is given by the total concentration minus the critical concentration. This assumption is consistent with the e.m.f. data of the silver, silver laurate half cell[12] and has been used by Debye and Hagen[9] and Anacker[13] for the interpretation of light scattering by solutions of detergents.

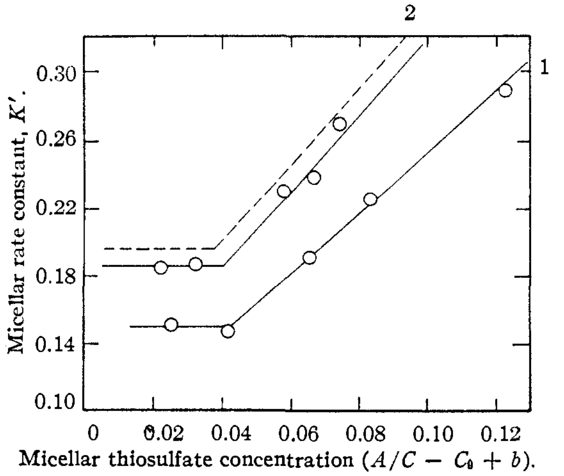

Fig. 1.—Micellar rate constant *vs.* micellar thiosulfate concentration at 50.00 ± 0.05°: (1) initial dodecyl bromide concentration = 0.0830 mole/mole micelle; (2) initial dodecyl bromide concentration = 0.0412 mole/mole micelle.

Micellar rate constants calculated from the above expression have been given for the various runs in Tables I, II and IV.

Micellar rate constants are plotted as a function of the micellar concentration of thiosulfate in Fig. 1 for the experiments in 0.119 M dodecylammonium bromide in which the dodecyl bromide concentration was kept constant. It is seen that the two curves have the same general shape. Correcting the lower curve for the difference in rate constant caused by the difference due to difference in dodecyl bromide concentration, the dotted lines shown in Fig. 1 are obtained. This dotted curve essentially coincides with the upper curve, showing the two sets of runs to be mutually consistent.

The micellar rate constant as a function of dodecylammonium bromide concentration is shown in Fig. 2. In the range of concentrations investigated the micellar rate constant increases linearly with dodecylammonium bromide concentration, a 7.5-fold increase in dodecylammonium bromide concentration producing a 1.7-fold increase in the rate constant.

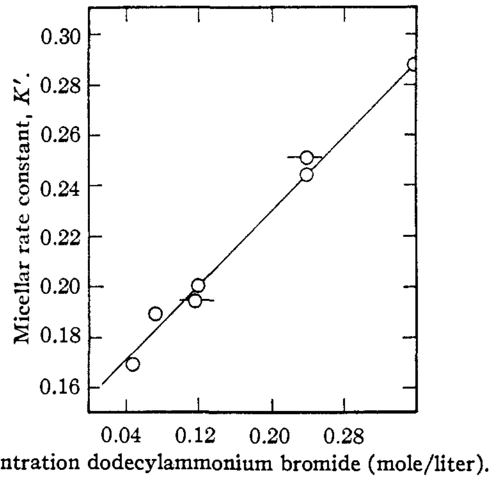

Fig. 2.—Micellar rate constant *vs.* dodecylammonium bromide concentration: -○-, interpolated from Fig. 3.

In substitution reactions of this type it has been found that the rate constant for the ion is greater than the rate constant for the undissociated molecule.[14] Second-order rate constants calculated on the basis of the total concentration of the substituting component for reactions in homogeneous solution increase with dilution.

Assuming that part of the thiosulfate ions in the ion atmosphere around the micelle is associated very closely with the dodecylammonium ions, whereas the remainder is located at somewhat

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[12] I. M. Kolthoff and W. F. Johnson, *J. Phys. Colloid Chem.*, **52**, 22 (1948).

[13] E. W. Anacker, Report to Office of Rubber Reserve, 1948.

[14] A. E. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Press, 1948, p. 12.

greater distance from the surface of the micelle, a distribution between these two locations exists If the thiosulfate "ions" which are close to the surface of the micelle are bound tightly enough that they exist not as ions but as neutral dodecylammonium thiosulfate molecules, they may be expected to give a lower rate constant than those thiosulfate ions existing further away from the surface of the micelle. The rate constant will remain constant as long as a constant "distribution coefficient" is maintained. Any change in this distribution coefficient would then produce a change in the rate constant calculated on the basis of a constant distribution of the thiosulfate ion.

The concentration at which the rate constant begins to increase (0.041 mole thiosulfate per mole micelle) would correspond to that at which the distribution coefficient for the thiosulfate ion is no longer constant. At this concentration relatively more thiosulfate ions are found in the diffuse part of the double layer. As the concentration of dodecylammonium bromide is increased the micellar rate constant also increases indicating that the distribution of the thiosulfate ions becomes increasingly more favorable toward the double layer.

Micellar rate constants are plotted as a function of micellar concentration of dodecyl bromide in Fig. 3. There is a slight difference in the rate constants for reactions run in 0.119 and in 0.238 *M* dodecylammonium bromide solutions. The difference between the two sets, however, is not great. Since the micellar concentration of thiosulfate was not the same, this difference is perhaps to be expected. The agreement is close enough to indicate that the rate constant for reactions in which the reactants are solubilized in solutions of colloidal electrolytes must be calculated on the basis of micellar concentration rather than on the basis of concentrations expressed in terms of moles per liter of solution.

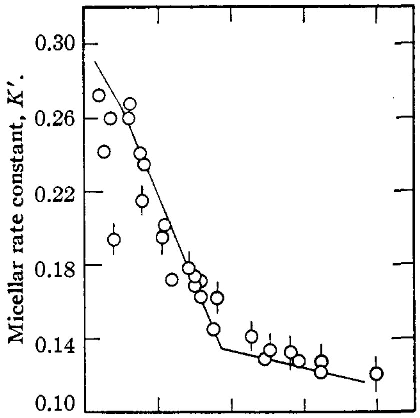

Fig. 3.—Micellar rate constant *vs.* initial micellar concentration of dodecyl bromide at 50.00 ± 0.05°: ○, 0.238 *M* dodecylammonium bromide; ϕ, 0.119 *M* dodecylammonium bromide.

TABLE V

RATE CONSTANTS FOR THE REACTION BETWEEN THIOSULFATE ION AND DODECYL BROMIDE FOR VARIOUS CONCENTRATIONS OF ADDED *n*-DECYL ALCOHOL AT 50°

Initial concn. $S_2O_3^{=}$ = 0.00476 *M*, concn. dodecylammonium bromide = 0.238 *M*

Concn. decyl alcohol (mole/liter)	Initial concn. dodecyl bromide (mole/liter)	*K'*
0.000	0.01068	0.168
.00827	.01050	.191
.01599	.01113	.199
.02376	.01047	.233
.04043	.01058	.291

One series of experiments was run in which the concentration of dodecylammonium bromide, sodium thiosulfate and dodecyl bromide were kept constant and decyl alcohol added to the solution in various amounts. The data for these runs are given in Table V and are plotted in Fig. 4.

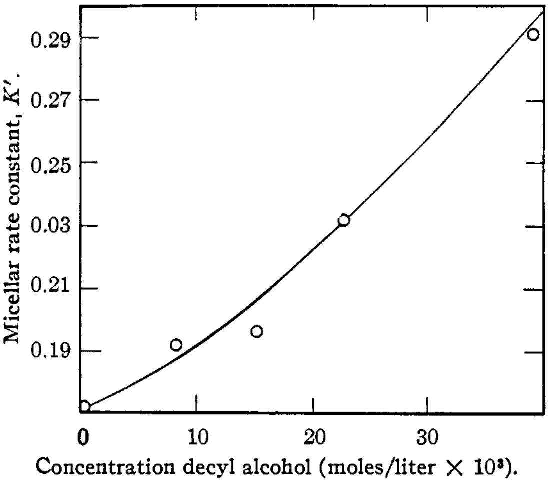

Fig. 4.—Micellar rate constants *vs.* decyl alcohol concentration for the reaction between dodecyl bromide and thiosulfate ion at 50.00 ± 0.05°: initial concentration thiosulfate ion = 0.00476 *M;* initial concentration dodecyl bromide = (1,067 ± 19) $\times 10^{-5}$ *M;* concentration dodecylammonium bromide = 0.238 *M.*

It is seen from these data that the rate constant increases with increasing decyl alcohol concentration. It has been thought that part of the decrease in rate constant with increasing dodecyl bromide concentration might be due to a reduced rate of diffusion of the dodecyl bromide molecules in the micelle as the micelle became more nearly saturated with the solubilized material. The decyl alcohol was added with the intent that it would produce essentially the same physical effect and at the same time not enter into the reaction.

The variations in the rate constant with concentration of dodecyl bromide and decyl alcohol cannot be explained at present. In homogeneous solution the rate constant for substitution reactions involving the *n*-alkyl halides decreases as the concentration of alkyl halide increases, though the decrease is not so great as in the reaction run under our conditions.

Though we are unable to interpret fully the observed variations in rate constant, it is of some interest to compare the rate constant obtained in solutions of dodecylammonium bromide with the rate constant for the reaction in homogeneous solution. Assuming the density of the micelle to be 0.9, an approximate value of the rate constant in terms of moles reactants per liter of micelle can be calculated. Making this calculation it is found that the rate constants lie between 0.068 and 0.033 liter micelle mole^{-1} min.$^{1-}$. These values are approximately one-fourth to one-tenth the value of 0.29 liter mole^{-1} min.$^{-1}$ to be expected on the basis of the work of Crowell and Hammett.[6]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Effect of Inert Gases on the Quenching of Fluorescence in the Gaseous State[1a,b]

BY H. G. CURME[2] AND G. K. ROLLEFSON

The quenching of the fluorescence of β-naphthylamine by carbon tetrachloride in the gas phase has been studied with respect to its dependence on the wave length of the exciting light and on the concentration of gases which are not in themselves quenchers. It has been found that the quenching constant is about one-fourth as large when $\lambda = 2537-2650$ Å. is used for excitation than when $\lambda = 3130$ is used. This fact is in accord with Neporent's observations on the lifetimes with these modes of excitation. The addition of ethane or cyclohexane causes the apparent quenching constant to increase and it appears to approach a limiting value. This limit is independent of the nature of the added gas and of the light used for excitation. Such behavior is explained by assuming that the effect of the added gas is to deactivate the photoexcited molecule to the lowest vibrational state of the first excited level. These facts are represented by a set of processes for which rate constants are deduced. The dependence of the apparent quenching constant on the concentration of the added inert gas has been expressed in terms of these constants and it is shown that the theoretical curve is in good agreement with the experimental observations.

Introduction

It is a well known fact that the fluorescence of a substance dissolved in a non-polar solvent is usually independent of the frequency of the exciting light. This observation is explained by saying that the vibrational energy of the photoexcited molecule is removed by contact with the solvent molecules so rapidly that all transitions which lead to the emission of light occur from the lowest vibrational level of the excited state. On the other hand the fluorescence of substances in the gaseous state often shows a marked dependence on the frequency of the exciting radiation. This dependence may take the form of a variation in the quantum yield of fluorescence, a variation of the quenching constant or changes in the energy distribution in the fluorescence spectrum. If the explanation for the lack of such effects in the liquid state is correct it should be possible to eliminate them in the gaseous state by adding inert gases which will not quench the fluorescence but will remove vibrational energy from the excited state. In this paper we wish to present the results of some studies of the fluorescence of β-naphthylamine in which this goal has been achieved.

Experimental

A conventional d.c. resistance bridge circuit was used to measure fluorescent intensities relative to the intensity of a monitoring beam received by a 935 phototube; this arrangement eliminated errors which might be introduced by fluctuations of the light source. Light from the source was collimated by a lens and the beam split by a quartz plate. A portion of the beam passed through the filters, F_2, to the 935 phototube. The remainder passed through the filters F_1, described below, to the fluorescence cell and fluorescent light passed through the filters F_3, also described below, to a 931A photocell.

A 45-volt B.battery was used to power the 935 phototube while the 600–1000 volt stabilizing power supply described by Zimm[3] was used as a power source for the 931A tube. 50,000 ohm resistors were used between the dynodes of the 931A. The resistance legs of the bridge were set at 10,000 ohms and the bridge was balanced with a Rubicon portable galvanometer with a resistance of 1500 ohms and a sensitivity of 6×10^{-10} amp./mm. A bucking electromotive force across the resistance arm of the bridge in series with the 931A tube was adjusted until the galvanometer showed no deflection while the entire apparatus was dark. When both photocells were illuminated the balance reading of the bridge was then proportional to the photocurrent from the tube 931A. Tests with screens and filters showed that the response of both tubes and of the bridge was quite linear. In typical operating conditions the current through the 935 tube was about one microampere and that through the 931A tube ranged from one tenth to one microampere. The bridge could easily be balanced to half a per cent. of its total reading. Some variations in sensitivity of the tube with time were noted but these introduced no errors since unquenched and quenched readings were made within minutes of one another. Both phototubes were cooled with jets of compressed air.

The fluorescence cell was immersed in a heating-bath of Dow-Corning silicone oil "DC 200," 100 centistokes viscosity grade. This bath was found to transmit ultraviolet as far as the 2537 A. mercury line at elevated temperatures over a long period of time. The oil was contained by a rectangular 2.5-liter copper vessel with Corning 7910 windows. Temperature was controlled to within about one degree by varying the input to a 250-watt cartridge type heater immersed in the rapidly stirred bath. Temperatures were read on a 100–150 degree thermometer immersed in the oil. The oil bath was surrounded by two inches of glass wool insulation except at the windows where a dead space of two inches was maintained.

β-Naphthylamine.—Eastman Kodak Co. β-naphthylamine (m.p. 109.9°) was purified by sublimation at 180° in a stream of nitrogen. The purified material melted at 110.3°.

Carbon tetrachloride was purified three times by the method of Fieser.[4] The purified material distilled at a constant temperature of 76.6°.

Isoöctane was graciously provided by the Shell Development Co. After one pass through a silica gel column and distillation the liquid was found to be transparent at wave lengths longer than 2250 Å.

Commercial cyclohexane was passed through a silica gel

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(1) (a) From the Ph.D. thesis of H. G. Curme. (b) For material supplementary to this article order Document 3337 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) Eastman Kodak Co. Fellow 1949–1950. Present address: Research Laboratory, Eastman Kodak Co., Rochester, N. Y.

(3) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

(4) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 365.