In Table Ia are given the c values for heptane on various non-porous solids and also the pressure ranges over which the HJ plots were found to be applicable. These c values range from 19 to 174. Although, as pointed out by Emmett, the lower relative pressure limit at which the HJ plot is linear lies above $p/p_0 = 0.35$ when c is about 25 or less, nevertheless a straight line HJ plot is obtained over a considerable range at higher pressures (Fe_3O_4, Ag (untreated), Ag (reduced), Cr (untreated) and Sn (untreated) are examples). The range of linearity is in general considerably larger for the HJ than for the BET method. Furthermore, the slopes of these HJ plots yield area values which are in moderately good agreement with those obtained by the standardized BET method. Emmett[8] states, "good agreement between BET (using 16.2 sq. Å. as the cross-sectional area of the nitrogen molecule) and the Harkins–Jura plots will be obtained *only* for c values between 100 and 150." The experimental data for n-heptane on the 21 non-porous solids included in this paper appear to indicate that this is not the exact criterion for the c values when n-heptane is used.

During the course of this work with n-heptane a number of area determinations have been made on samples whose total areas were only 1 sq. meter. It appears probable that a moderately accurate area measurement could be obtained on a sample whose total area is about 0.25 sq. meter.

IV. Summary

1. The values for the areas of 21 non-porous solids calculated from n-heptane adsorption isotherms at 25° by the Harkins–Jura (HJ) relative method and by the Brunauer, Emmett and Teller (BET) method (standardized by use of a solid of known area as determined by the HJ absolute method) are in satisfactory agreement, although the BET values of c vary from 19 to 174. The value of k, the constant used in the HJ relative method, is 16.9 (or 18.2 more rarely) for n-heptane at 25°. The effective cross-sectional area (σ_m) of n-heptane at 25° used in the calculation of areas by the BET method is, as determined by us, 64 sq. Å.
2. Similar agreement for a smaller number of solids is obtained using the isotherms of n-hexane at 0°. The value of k for n-hexane at 0°, 14.3, and of σ_m, 58.9 sq. Å., are probably less accurate than those for n-heptane.
3. The values for the areas of several non-porous solids calculated from the adsorption isotherms of n-heptane or n-hexane are in satisfactory agreement with those calculated from the adsorption isotherms of nitrogen and with those obtained by the HJ absolute method.
4. The method is described for the calculation of the effective molecular cross-sectional area of an adsorbate (σ_m).
5. With higher values of the BET constant c the condensed phase of the HJ method forms at relatively low values of p/p_0 for n-heptane, and at low values of c at higher values of p/p_0.

CHICAGO, ILL. RECEIVED DECEMBER 15, 1949

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

The Locus of the Initiation in an Emulsion Polymerization Recipe Containing Ferrous Iron and Benzoyl Peroxide*

BY I. M. KOLTHOFF AND MADOLYN YOUSE

In recent years several papers[1] have been published on the emulsion polymerization of butadiene (75) and styrene (25) using an organic peroxide which is soluble in monomers and some reducing system in the aqueous layer. In these systems the free radicals which initiate polymerization are produced by the reaction of ferrous iron with the organic peroxide. In some recipes ferrous iron is the only reducing substance present while in other recipes a reducing organic substance such as a reducing sugar is present. The main function of sugars such as glucose or fructose is to reduce continuously the ferric iron formed; on the other hand, it has been shown in this Laboratory that with more active sugars, such as dihydroxyacetone or scylloinosose, the direct reaction between the sugar and the peroxide may be of major importance in initiating polymerization. The peroxides which have been used most successfully are cumene hydroperoxide (denoted below as CHP) and benzoyl peroxide (BP). One of the notable differences in these two peroxides is that cumene hydroperoxide is soluble in water to the extent of 13.9 grams per liter (0.0914 molar), while benzoyl peroxide is practically insoluble in aqueous solutions. From work carried out in this Laboratory[2] it is evident that with CHP, the locus of formation of free radicals is the aqueous layer. It has been proposed by Wall and Swoboda[3] that with BP the locus of the reaction is the organic layer, the

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* 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.

(1) W. Kern, *Die Makromoleculare Chem.*, **1**, 199 (1948); E. J. Vandenberg and G. E. Hulse, *Ind. Eng. Chem.*, **40**, 932 (1948).

(2) I. M. Kolthoff and A. I. Medalia, *J. Polymer Sci.*, in press.

(3) F. T. Wall and T. J. Swoboda, THIS JOURNAL, **71**, 919 (1949).

reaction being that of BP with an oil soluble ferrous soap. Quite generally, the term organic layer is used loosely in the literature on emulsion polymerization. According to the theory proposed by Harkins[4] the micelles of the emulsifier in the aqueous layer solubilize monomers and are the locus of the polymerization reaction during the early stages of conversion of monomer to polymer. When dealing with recipes containing activators like organic peroxides or hydroperoxides which are oil-soluble but slightly soluble in water, solubilization of these activators with the monomers occurs. Thus, monomers and activators are present as a separate layer, but also in the water layer in the micelles. If the concept of "monomer layer" employed by Wall and Swoboda is replaced by the "oil core in the micelle," there would not be any conflict with regard to the locus of the initial polymerization reaction.

In order to interpret the mechanism of the type of recipes under consideration, it is highly desirable to know more precisely the exact locus of the initiation reaction.

It does not seem plausible that in an emulsion polymerization free radicals would be formed in the organic layer while the polymerization proper occurs in the aqueous layer. In polymerizations of this type all the polymer formed is present in the latex which is a suspension of the polymer particles in the aqueous layer. In order to avoid confusion in terminology we use the term layer instead of phase.

In the present paper it is shown that in an emulsion polymerization with a redox recipe with BP as the oxidizing agent, the locus of the reaction is the aqueous layer and not the organic layer.

Considerable work had been carried out in this laboratory with the following benzoyl peroxide-ferrous iron redox type of recipe which is based on that of Marvel and co-workers.[5]

General recipe:

Ingredients	Amounts in grams
Butadiene	75
Styrene	25
Water	180
Detergent	5
BP	Variable
Ferrous sulfate heptahydrate	Variable
Pyrophosphate	Variable
Sulfole mercaptan	0.30

The results of polymerizations carried out with the above recipe, with variations in the concentrations of ingredients and with variations in the type of detergent used, will be reported elsewhere. Only a few results are discussed in the present paper in substantiation of the proposed locus of the initiation reaction.

In the section on solubility of ferrous salts of detergents in organic solvents evidence is given that the initiation reaction in the polymerization occurs in the aqueous layer. In the section dealing with the reaction between benzoyl peroxide added as a solid or as a benzene solution and ferrous iron in a detergent solution it is shown that both in the presence and absence of pyrophosphate solubilized benzoyl peroxide reacts rapidly with ferrous iron. In detergent solutions below the critical concentration a slower reaction takes place in the aqueous layer between ferrous iron and benzoyl peroxide suspended as a solid or as an emulsion by shaking with a benzene solution. The mechanism of this reaction is of importance in a quantitative interpretation of the efficiency of the free radicals in the emulsion polymerization reaction.

Materials and Analytical Procedures Used

The benzoyl peroxide used (Eastman Kodak Company) had a purity of 98.0% as determined by the method of Nozaki.[6] Potassium myristate and potassium caprate were prepared by neutralization of the Eastman white label fatty acids with potassium hydroxide in hot alcohol, followed by recrystallization from alcohol and vacuum drying to constant weight. Sodium oleate was prepared by neutralization of oleic acid obtained from Dr. W. C. Ault of the Eastern Regional Laboratories. The SF flakes (mixture of the sodium soaps of oleic, palmitic and stearic acids) were obtained from Procter and Gamble and the sodium dodecane sulfate from Dr. Richardson of the Research Laboratory of Procter and Gamble.

The method of preparation of the suspensions of the ferrous soaps in inert solvents consisted of mixing, in an air-free atmosphere, hot aqueous solutions of ferrous sulfate added to the fatty acid soap solutions followed by the addition of the organic solvent. The precipitation reactions were carried out in 4 oz. bottles which were sealed with screw caps containing a Buna N gasket covered with aluminum foil. When butadiene was used as the organic liquid, the aqueous suspension of ferrous soap was cooled before the addition of the butadiene. Samples of solutions of ferrous soaps in benzene and chloroform were removed for analysis in a nitrogen atmosphere with nitrogen-filled pipets. An aqueous solution of 5 M trichloroacetic acid was used for the extraction of the ferrous iron from the organic liquid. With butadiene solutions, a right angle tube fitted with a needle on one end and a stopcock and needle on the other was used for the extraction of the sample. The bottle containing the butadiene solution was clamped in position and one of the needles was inserted through the cap into the liquid while the second needle was inserted into an air-free capped bottle containing 5 ml. of nitrogen-bubbled 5 M trichloroacetic acid solution in water which was cooled in *Dry Ice*-alcohol. On turning the stopcock a sample was drawn into the cooled bottle. The aqueous extracts obtained from ferrous oleate and the ferrous salt of SF flakes solutions in organic solvents were titrated with ceric sulfate by a standard procedure. Aqueous extracts from ferrous myristate solutions had such a low iron content that the latter was determined colorimetrically with *o*-phenanthroline.

In part of the work the ferrous iron was determined in the monomer layer after a charge had been polymerized to low conversions. In order to assure complete absence of peroxide, these charges had to be prepared with traces of CHP instead of BP. The recipe used was similar to that given with 5.0 parts of potassium myristate, 1.0 part of potassium pyrophosphate, 0.008 part of CHP in place of BP, varying amounts of iron, and with the addition of

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[4] W. D. Harkins, *J. Chem. Phys.*, **13**, 381 (1945); **14**, 47 (1946); THIS JOURNAL, **69**, 1428 (1947).

[5] C. S. Marvel, R. Deanin, C. G. Overberger and B. M. Kuhn, *J. Polymer Sci.*, **3**, 128 (1948).

[6] K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

0.07 part of dihydroxyacetone. Analysis of the monomer layer of polymerization charges of low conversion was carried out in a manner similar to that described above for the determination of ferrous iron in butadiene. In all such experiments the charges used showed a sharp separation of monomer and aqueous layers. The charges were centrifuged before sampling to remove any suspended matter.

Experiments were carried out in which the reaction of benzoyl peroxide and ferrous iron was studied in detergent solutions in the absence of an organic layer. The solutions were prepared in a nitrogen atmosphere by dissolving such amounts of solid soap, with or without solid pyrophosphate, as to give the desired concentrations on addition of a given volume of air-free conductivity water and solid BP. After specified times an air-free solution of ferrous sulfate was added to the detergent mixture. The mixtures were rotated end over end at 35 r. p. m. in a 30° thermostat. At the end of the reaction period 10 ml. of an air-free solution of 4 *N* sulfuric acid was added to precipitate the fatty acid soap, then 50 ml. of benzene was added to dissolve the fatty acid and BP. Analysis of the ferrous iron remaining in the aqueous layer was carried out according to standard procedures using potassium dichromate or ceric sulfate. Analysis of the BP extracted in the benzene solution was carried out according to the method of Nozaki.[6]

In the two-phase system the reaction mixtures were prepared by delivering known volumes of air-free solutions of BP in benzene and air-free aqueous solutions with the aid of nitrogen-filled pipets into the oxygen-free reaction vessel. The mixtures were rotated at 35 r. p. m. on a 30° thermostat for the specified reaction time. At the end of the reaction period sufficient air-free 4 *N* sulfuric acid was added to precipitate the fatty acid soap and acidify the mixtures. Analyses of the aqueous solution for ferrous iron and the benzene solution for BP were carried out as described above. In such systems in which sodium dodecane sulfate was used as detergent, only the ferrous iron was determined since this detergent is not precipitated by the addition of acid. The entire emulsion mixture was used for the determination of the iron. The best method of analysis for these mixtures was found to be titration with ceric sulfate using barium diphenylamine sulfonate as indicator.

Solubility of Ferrous Salts of Fatty Acids and Dodecane Sulfate in Organic Solvents.—In a discussion of metallic soap–solvent systems, S. B. Elliot[7] mentions that it is highly doubtful whether any true solutions are ever obtained of metallic soaps in organic solvents though various degrees of dispersion are exhibited.

It has been reported by Wall and Swoboda[3] that apparent solutions of the ferrous soap of SF flakes in benzene and chloroform have been prepared with ferrous iron concentrations of the order of 0.05 molar. Following the directions of Wall and Swoboda for the preparation of the ferrous soaps of SF flakes and of oleate and working in the absence of oxygen, we obtained dark green gels with either benzene or chloroform as solvents. Centrifuging did not affect the gels and heating to 50° increased the gel viscosity. After standing for several days at room temperature, the gel obtained with SF flakes separated and the ferrous iron concentration of the pale green solution (benzene) was determined and found to be of the order of 0.001 molar. With the ferrous soap of sodium oleate, standing at room temperature had no effect on the gel while standing at 0° reduced the viscosity and brought about the precipitation of some of the ferrous soap. Analysis of the supernatant liquid showed the ferrous iron content of this apparent solution (benzene) to be of the order of 0.02 molar. When butadiene was used as a solvent for ferrous oleate, a dark green suspension was obtained. Neither standing, cooling, or centrifuging yielded a clear solution so no determination of ferrous iron was made.

Similar experiments were carried out with ferrous myristate. There was no apparent gel formation with this soap. Pale green suspensions of ferrous myristate were obtained in a number of organic liquids (benzene, chloroform, butadiene, styrene, and isoprene); these suspensions settled out on centrifuging and analysis of the colorless organic liquid showed, in all experiments, a ferrous iron concentration of the order of 3×10^{-5} molar. With a dried precipitate of ferrous myristate (absence of air) similar values were obtained.

Polymerization Experiments

In all BP–ferrous iron recipes which are of practical value, excess pyrophosphate is used so that the ferrous iron in the charge is present as the soluble pyrophosphate complex which does not precipitate the fatty acid soap. Considering that the solubility of solid ferrous myristate in the monomer is of the order of 10^{-5} molar it would seem that in the presence of excess pyrophosphate the ferrous iron extracted from the aqueous to the monomer layer must be negligibly small. Actual determinations of ferrous iron in the monomer layer of charges showing a distinct phase separation at low conversions were made. In charges containing 0.004 molar (0.1 part per 100 parts of monomers) ferrous iron and 0.017–0.051 molar (1–3 parts per 100 parts of monomers) pyrophosphate, no ferrous iron could be detected in the monomer layer.

Further evidence that the reaction of benzoyl peroxide and ferrous iron in recipes of the kind described does not take place in the monomer layer is obtained from comparison of the conversion-time curves *1* and *4* of Fig. 1, which were obtained when potassium myristate and sodium oleate were used for polymerizations with otherwise identical recipes. While ferrous oleate has a solubility approximately 300 times greater than that of ferrous myristate, the conversion–time curve obtained for the charge containing this soap does not show a higher initial rate of conversion as would be expected if the reaction between ferrous iron and BP takes place in the monomer layer.

Sodium dodecane sulfate, a detergent, the ferrous salt of which is freely soluble in water, has been used in polymerization charges. No ferrous iron was detectable in the monomer layer of a charge of low conversion prepared with this detergent and with a ferrous iron concentration of 0.15 molar in the aqueous phase. Nevertheless, good rates of conversion are obtained with this detergent in charges containing sodium pyrophosphate (curve 3, Fig. 1).

The most conclusive evidence that the reaction of ferrous iron and BP takes place in the aqueous layer is obtained from polymerizations carried out with cetyldimethylbenzylammonium chloride (CBAC), a cationic detergent. Good initial rates of conversion were obtained when this detergent was used in a recipe similar to that described with sodium hydroxide in the place of pyrophosphate (Curve 6, Fig. 1). Slightly lower rates were obtained with this detergent in the absence of sodium hydroxide. Pyrophosphate could not be used as it precipitates with the cationic detergent.

Reaction between BP and Ferrous Iron: (a) Absence of an Organic Solvent.—Benzoyl peroxide is, practically speaking, insoluble in water at room temperature, the saturation value being considerably less than 10^{-4} molar. The following experiments show that BP is solubilized by myristate solutions and that the solubilized BP reacts very rapidly with ferrous myristate. Two grams of solid BP was shaken for one hour with 50 ml. of a 0.10 molar solution of potassium myristate. At this time the detergent solution was filtered, acidified and extracted with benzene. The concentration of the BP in the myristate solution was 0.0012 molar. The equilibrium value of solubilization could not be determined since turbid solutions were obtained after long periods of rotation which did not give clear filtrates. When ferrous iron was added to the clear soap solution containing solubilized BP, a rapid reaction between the white precipitate of ferrous myristate and BP could be seen to take place by the immediate appearance of the orange-red color of ferric myristate.

Experiments were then carried out with systems con-

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[7] S. B. Elliot, "The Alkaline Earth and Heavy Metal Soaps," Reinhold Publ. Corp., New York, N. Y., 1946.

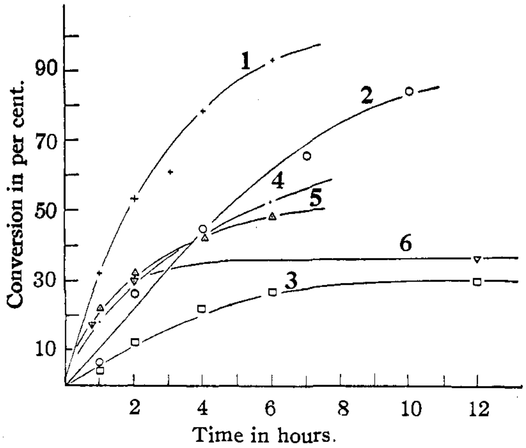

Fig. 1.—Conversion time curves obtained with a benzoyl peroxide–ferrous iron redox recipe with 0.063 part of BP, 0.10 part of $FeSO_4 \cdot 7H_2O$, and 5 parts of various detergents: 1, ×, 5 parts K myristate + 3 parts $K_4P_2O_1$; 2, ⊙, 5 parts SF flakes + 3 parts $Na_4P_2O_7 \cdot 10H_2O$; 3, □, 5 parts NaC_{12} sulfate + 3 parts $Na_4P_2O_7 \cdot 10H_2O$; 4, ●, 5 parts Na oleate + 3 parts $K_4P_2O_7$; 5, ◬, 5 parts Na oleate + 3 parts $Na_4P_2O_7 \cdot 10H_2O$; 6, ⩢, 5 parts CBAC + 0.02 parts NaOH + 0.3 parts BP + 0.2 parts $FeSO_4 \cdot 7H_2O$.

taining various detergents, ferrous iron and solid benzoyl peroxide. At various times after the addition of ferrous iron to these systems, the amounts of ferrous iron and BP reacted were determined. The results of these experiments are summarized in Table I. All experiments were carried out in the absence of air.

TABLE I

REACTION OF FERROUS IRON AND BP IN 50 ML. OF DETERGENT SOLUTION IN THE ABSENCE OF ORGANIC LIQUIDS

Mixtures were rotated at 30° for specified times. Column A under "Time of Rotation" (A) gives the number of hours of shaking of solid BP with detergent solution before addition of iron; column (B) gives the time after addition of iron

Detergent	*M*	$K_4P_2O_7$, *M*	Time of rotation A	Time of rotation B	Amounts taken in millimoles Fe^{+2}	Amounts taken in millimoles BP	Amounts found after reaction, millimoles Fe^{+2}	Amounts found after reaction, millimoles BP
None (blank)		...	..	24	0.940	2.06	0.945	1.99
None (blank)		0.20	..	24	0.975	2.06	.970	2.00
K Myristate	0.10	...	..	24	1.12	..	.96	..
K Myristate	.10	...	24	1	0.940	2.06	.270	1.53
K Myristate	.10	...	24	24	.940	2.06	.117	1.41
K Myristate	.15	...	24	1/4	.975	1.24	.259	0.64
K Myristate	.15	...	24	24	.975	1.24	.045	0.49
K Myristate	.10	0.20	24	1/4	.975	2.06	.565	1.50
K Myristate	.10	0.20	24	24	.975	2.06	.289	1.13
K Myristate	.15	...	0	1/4	.880	2.06	.572	1.72
K Myristate	.15	...	0	1	.880	2.06	.390	1.60
K Caprate	.08	...	50	1	.531	1.03	.305	0.91
NaC_{12} sulfate	.10	0.10[a]	0	24	.642	1.24	.059	..
CBAc[b]	.10	...	24	27	1.090	1.24	.480	..

[a] $Na_4P_2O_7 \cdot 10H_2O$. [b] CBAC = cetyldimethylbenzyl ammonium chloride (Winthrop Chemical Company).

It is seen that with and without pre-shaking of the BP a rapid reaction occurs between ferrous myristate and BP. The reaction is also rapid when ferrous iron is present in the form of a soluble complex with pyrophosphate.

One experiment is reported with potassium caprate just below the critical concentration. From this experiment it may be concluded that BP, when present in fine suspension in a detergent solution, reacts with a measurable rate with ferrous iron. This reaction, however, is markedly slower than that between solubilized BP and ferrous iron.

Sodium dodecane sulfate forms a water soluble ferrous salt. When a solution of this detergent containing ferrous iron is shaken with BP, a slow reaction takes place with the BP and ferrous iron and the mixture becomes violet in color. Apparently by free radical oxidation a substance of phenolic character is formed which yields a violet complex with the ferric iron. In Table I the result of one experiment is reported in which the reaction was allowed to occur in the presence of pyrophosphate. The reaction rate in the presence of pyrophosphate is so great that there seems to be little doubt but that the reaction takes place between ferrous iron and solubilized BP.

An experiment is given in which the cationic detergent CBAC was used. A measurable rate was found between BP and ferrous iron in this detergent solution. Insufficient experiments have been run with this detergent to allow a conclusion as to whether the reaction is entirely between suspended BP and ferrous iron or whether solubilized BP also participates. In any case the reaction takes place in the aqueous layer.

(b) **Presence of an Organic Solvent.**—Another set of experiments was carried out with systems containing a detergent, ferrous iron, and a benzene solution of benzoyl peroxide. Such systems are comparable to those used in actual polymerizations with the exception of the fact that the monomer is replaced by an inert organic solvent. The reaction of ferrous iron and BP in systems containing a fatty acid soap are summarized in Table II.

In the experiments with fatty acid soaps, pyrophosphate had to be added to prevent the reaction between ferrous myristate and BP from taking place in the benzene layer. Although the ferrous myristate is practically insoluble in benzene, it seems to be wetted better by benzene than by water. Upon shaking an aqueous suspension of ferrous myristate with benzene the precipitate becomes suspended in the benzene. When the benzene contains BP, the suspended precipitate reacts with a fairly large rate and an orange-red solution of ferric myristate in benzene is obtained.

In all experiments reported in Table II enough pyrophosphate was added to the soap containing systems to keep all the iron in the aqueous layer in the form of a complex. Evidence has already been given that in the presence of pyrophosphate the reaction occurs in the aqueous and not in the organic layer. In striking confirmation of this conclusion are results of experiments with sodium dodecane sulfate, the results of which are given in Figure 2. It is seen that pyrophosphate (curve 3) greatly accelerates the rate of reaction of ferrous iron. If ferrous dodecane sulfate were shaken out in the benzene and reacted there with the BP, the presence of pyrophosphate would greatly decrease the reaction rate whereas it has just the opposite effect.

TABLE II

REACTION OF FERROUS IRON IN AQUEOUS DETERGENT SOLUTION WITH BENZOYL PEROXIDE IN BENZENE

Reaction mixtures composed of 10 ml. of aqueous solution and 10 ml. of 0.2 *M* BP solution in benzene. All reaction mixtures were shaken for one and one-half hours at 30° before analyzing

Soap	*M*	$K_4P_2O_7$, *M*	Molarity of $FeSO_4 \cdot 7H_2O$ Initial	Molarity of $FeSO_4 \cdot 7H_2O$ Final
K Myristate	0.005	0.05	0.0109	0.0056
K Myristate	.005	.10	.0104	.0048
K Myristate	.10	.05	.0109	.00014
K Myristate	.10	.10	.0104	.0023
K Myristate	.10	.15	.0104	.00060
K Caprate	.05	.05	.0104	.0039
Na oleate	.005	.05	.0107	.0022
Blank	...	.10	.0142	.0133

From the experiments carried out in the absence of an organic solvent it follows conclusively that suspended BP reacts with ferrous iron in the detergent solutions. Other conditions being the same the rate of reaction increases with increasing detergent concentrations and also with the solubilizing power of the detergents. However, a definite reaction also is found below the critical concentration where the detergent acts only as an emulsifier and not as a solubilizer. This result is not surprising since the rate of reaction would be expected to increase with an increase in the surface exposed by the BP. In agreement with this conclusion are the results of experiments carried out in the presence of benzene. Potassium myristate in 0.005 molar solution and potassium caprate in 0.05 molar solution are below the respective critical concentrations, but act as good emulsifiers at those concentrations. A measurable rate of reaction of ferrous iron and BP which is considerably greater than the blank is found at these concentrations. It is seen that the rate of reaction in 0.10 molar myristate is greater than in 0.005 molar myristate. This is attributed to the solubilized BP. When the pyrophosphate concentration in a 0.10 molar myristate solution is increased from 0.05 to 0.15 molar, the rate of reaction decreases somewhat. This effect of pyrophosphate deserves further systematic study.

The rate of reaction found in 0.005 molar oleate is somewhat greater than in 0.005 molar myristate. This is not surprising since the critical concentration of sodium oleate is of the order of and less than 0.001M. If the reaction between ferrous iron and BP would take place in the benzene layer, a considerably greater rate of reaction would have been expected with oleate since ferrous oleate is of the order of 300 times more soluble in benzene than is ferrous myristate. Thus, these results substantiate again the conclusion that the reaction takes place in the aqueous layer in the presence of pyrophosphate.

Acknowledgment.—The authors are indebted to Dr. A. I. Medalia for his interest and constructive discussions and to Mrs. Alma Blazic for carrying out polymerization experiments.

Summary

It has been shown that the reaction between ferrous iron dissolved in aqueous pyrophosphate solution and BP dissolved in organic solvents occurs in the aqueous layer. Evidence has been given that both solubilized and emulsified BP reacts with ferrous iron.

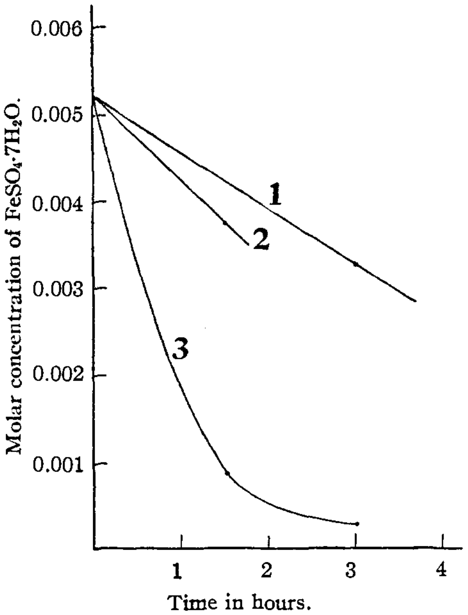

Fig. 2.—Reaction between ferrous iron in 0.10 M aqueous solution of sodium dodecane sulfate and BP in benzene solution. Mixtures composed of 30 ml. of aqueous solution 0.0051 M in $FeSO_4 \cdot 7H_2O$ and 25 ml. of benzene solution 0.05 M in BP. Reaction studied at 30° in the absence of air: 1, mixture contained 0.05 M acetic acid in aqueous layer; 2, mixture as described; 3, mixture contained 0.036 M $Na_4P_2O_7 \cdot 10H_2O$ in aqueous layer.

The most conclusive evidence that the aqueous layer is the locus of the reaction of BP and ferrous iron in an emulsion polymerization recipe is derived from experiments with the cationic detergent, CBAC. With this detergent no organic soluble iron can be formed but the polymerization reaction occurs with a reasonable rate.

MINNEAPOLIS, MINNESOTA RECEIVED DECEMBER 9, 1949

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

The Quenching of Fluorescence. Deviations from the Stern–Volmer Law

BY HAROLD BOAZ AND G. K. ROLLEFSON

The fluorescence of a gas or solution is said to be quenched if the intensity of that fluorescence is diminished by the addition of another substance which does not undergo any net reaction with the fluorescent substance. It is of course possible that the quenching process may involve some reaction between the photoactivated molecule and the quencher but both molecules must ultimately return to their original states. Some possible mechanisms for the quenching process have been discussed in a previous paper.[1] In this paper we wish to present data dealing with systems which deviate from the law derived by Stern and Volmer in 1920 and to show how these deviations can be accounted for in a simple manner.

Stern and Volmer considered the quenching process to be a bimolecular reaction which competes with the radiative process and all other molecular processes. On this basis they derived an equation which can be put in the form

$$I_0/I = 1 + k_q(Q) \qquad (1)$$

in which I_0 is the intensity of fluoresence in the

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[1] G K. Rollefson and H. Boaz, *J. Phys. Colloid Chem.*, **52**, 518 (1948).