

TABLE III

VALUES OF SOME THERMODYNAMIC PROPERTIES OF THE ESTER-WATER INTERFACES

Temp., °C.	Methyl chloroacetate			Ethyl chloroacetate			n-Propyl chloroacetate			n-Butyl chloroacetate		
	$d\gamma_i/dt$	L	E	$d\gamma_i/dt$	L	E	$d\gamma_i/dt$	L	E	$d\gamma_i/dt$	L	E
26.8	-0.0552	16.61	28.51	-0.0341	10.26	26.16	-0.0344	10.35	30.15	-0.0362	10.89	33.29
42.6	-.0614	19.38	29.38	-.0421	13.29	28.69	-.0470	14.84	34.04	-.0397	12.53	34.33
55.2	-.0663	21.77	31.97	-.0484	15.89	30.69	-.0572	18.78	37.38	-.0424	13.92	35.12
70.4	-.0722	24.80	33.70	-.0562	19.30	33.20	-.0693	23.80	41.50	-.0458	15.73	36.43

facial tensions decrease with increasing temperature, but not linearly. Since the interfacial tension is influenced by mutual solubility of the liquid compounds, and the solubility is in turn dependent on the temperature, it is to be expected that departure from strict linearity is due, at least partially, to the solubility factor. With the aid of the empirical equations, it was possible to calculate the entropy ($d\gamma_i/dt$), latent heat (L), and total energy (E) attending the formation of 1 sq. cm. of the interfacial surfaces over the temperature range given. These are shown in Table III, with all energy values expressed in ergs.

Since for saturated surfaces, the latent heat L is related to the temperature coefficients by the equation $L = -T(d\gamma_i/dt)$, the latent heat may be positive or negative—positive when the interfacial tension decreases with the temperature and negative when it increases. The esters of this series have positive values of L , and it is evident, therefore, that energy is utilized when the interface is extended. The effect of increasing the length of the ester chain on the solubility of the

compound is clearly reflected in the increasing values of the interfacial tension in passing from the methyl to the butyl ester at any given temperature. It might be expected, therefore, that the methyl ester of the fluorine substituted acetic acid would be completely soluble in water. This was found to be the case.

Summary

The interfacial tensions of the methyl, ethyl, *n*-propyl and *n*-butyl esters of monochloroacetic acid were measured against water at the temperatures 26.8, 42.6, 55.2 and 70.4°, and the procedure briefly described. Density and interfacial tension data for these temperatures are tabulated in respective tables. An empirical equation relating the interfacial tension and temperature was formulated for each of the esters. The equations were applied in the calculation of the entropy, latent heat, and total energy of formation per sq. cm. of the interface, and these values were presented in a table.

DETROIT, MICHIGAN

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Copolymerization in Emulsion¹

BY F. T. WALL, R. E. FLORIN AND C. J. DELBECQ

A great many copolymerization systems have been investigated up to the present time, and it appears that in most instances the compositional relationships involved are adequately described by a copolymerization equation^{2,3,4} which in differential form is

$$\frac{dM_1}{dM_2} = \frac{M_1(r_1M_1 + M_2)}{M_2(M_1 + r_2M_2)} \quad (1)$$

In the above equation M_1 and M_2 represent the unreacted amounts of the two monomers and r_1 and r_2 are ratios⁵ of certain specific reaction rate constants characteristic of the particular system. From its derivation it might be expected that equation (1) would hold only for single phase polymerizations; it is observed empirically, however, that it also describes emulsion

copolymerizations providing r_1 and r_2 are given proper values which are generally different from those observed for single phase reactions. It is a matter of some interest, therefore, to ascertain the reasons for the success of equation (1) in emulsion systems assuming that it has more than empirical validity. Theoretically equation (1) should hold in the immediate environment of the reaction providing M_1 and M_2 are taken as concentrations in that neighborhood. This suggests that an explanation of why the equation works for the over-all system might be obtained by examining such factors as monomer solubilities in those regions of an emulsion which might conceivably serve as reaction loci.

As a result of some earlier work by Wall and co-workers⁶ on the emulsion polymerization of rubber-like copolymers, it was suggested that the polymerization reaction might occur in the aqueous phase. Under those circumstances,

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

(2) Mayo and Lewis, *THIS JOURNAL*, **66**, 1594 (1944).

(3) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

(4) Wall, *THIS JOURNAL*, **66**, 2050 (1944).

(5) Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).

(6) Wall, Powers, Sands and Stent, *THIS JOURNAL*, **70**, 1031 (1948).

equation (1) would hold providing r_1 and r_2 are replaced by r_1' and r_2' where $r_1' = r_1k$ and $r_2' = r_2/k$ and k is the distribution coefficient of the monomers between the oil and aqueous phases. Although this was a possible explanation in some instances, the evidence was not sufficient to prove or disprove the hypothesis. Fordyce and co-workers^{7,8} favored an oil phase mechanism for several emulsion copolymerizations because of the close agreement between the reactivity ratios for emulsion and bulk systems. Harkins,⁹ on the other hand, without recourse to copolymer composition studies suggested the soap micelles and polymer-monomer particles as seats of reaction. The present work was undertaken in an effort to get more information about the reaction locus through copolymer composition measurements. An analogous type of study with emphasis on modifier activity and its dependence on phase relationships has been carried out by Smith.¹⁰

The monomer system chosen for this investigation was styrene and methyl methacrylate which was investigated by Mayo and Lewis² in bulk polymerizations. Our composition studies were carried out for polymerizations in benzene solution and in emulsion at 35°. In addition we examined the distribution of the two monomers between the various regions in the emulsion system: namely, oil droplets, water solution, and soap micelles. In the discussion which follows, r_1 and r_2 will refer to the monomer reactivity ratios observed for benzene solution polymerizations and r_1' and r_2' will be the apparent values for emulsion reactions. In every instance styrene will be considered monomer 1 and methyl methacrylate monomer 2.

Experimental

1. Materials Used. Styrene.—The Dow Chemical Company product was purified by the procedure of Price and Adams¹¹ and was stored at -15 to 0° for periods up to ten days.

Methyl Methacrylate.—The Rohm and Haas product was shaken with portions of 5% sodium hydroxide until no further color developed, then washed with water, dried overnight with anhydrous magnesium sulfate, and distilled under 100 mm. pressure with nitrogen ebullition. The pure material was stored at -15 to 0° for periods up to ten days.

Benzene.—Reagent grade A. C. S. thiophene-free benzene was used without further treatment.

Benzoyl Peroxide.—Obtained from Eastman Kodak Company and recrystallized from chloroform.

***n*-Dodecyl Mercaptan.**—This material was supplied by the Organic Chemistry Division of the University of Illinois.

Potassium Persulfate.—Baker and Adamson, reagent grade.

Emulsifier.—Procter and Gamble, SF Flakes.

(7) Fordyce, *THIS JOURNAL*, **69**, 1903 (1947); Fordyce and Chapin, *ibid.*, **69**, 581 (1947).

(8) Fordyce and Ham, *ibid.*, **69**, 695 (1947); and *J. Polymer Sci.*, **3**, 891 (1948).

(9) Harkins, *THIS JOURNAL*, **69**, 1428 (1947).

(10) Smith, *ibid.*, **68**, 2059, 2064 and 2069 (1946).

(11) Price and Adams, *ibid.*, **67**, 1674 (1945).

Nitrogen.—Tank nitrogen was purified in a column of hot finely divided copper by the procedure of Meyer and Ronge.¹²

2. Polymerizations.—Styrene and methyl methacrylate were copolymerized in benzene solution and in emulsion at 35°, using monomer ratios of 3.847, 1.000 and 0.2402. The emulsion polymerization technique was similar to that of Wall and co-workers,⁸ using crown cap bottles fitted with self-sealing gaskets. The solution reactors were 250-ml. all-glass vessels bearing two stopcocks lubricated with Nonaq, protected externally with common stopcock grease, and held in place with rubber bands. The emulsion recipe consisted of 60 g. of monomers, 105 g. of 3% soap solution, 10 ml. of 3% potassium persulfate solution, and 0.21 g. of dodecyl mercaptan; for solution polymerizations, the recipe was 60 g. of monomers, 50 g. of benzene, and 1.000 g. of benzoyl peroxide. In the charging operation, care was taken to remove oxygen by cooling the reactor in ice-salt mixture and subjecting it to repeated evacuation followed by introduction of nitrogen. For the emulsion mixtures the evacuation and nitrogen treatment were also applied to warm solutions of soap and persulfate which were then frozen before adding the other ingredients.

The emulsion reactors were directly sampled by a syringe; the solution reactors were allowed to discharge into a vial, from which the products were drawn at once into a syringe. The polymers were isolated by precipitation in methanol containing about 0.1 g. of potassium iodide and 0.5 g. of hydroquinone per liter. The samples were subsequently purified by three successive precipitations by methanol from benzene solutions followed by evaporation of a frozen benzene solution according to the method of Mayo and Lewis.¹³ The dry copolymer was weighed to measure conversion and its composition determined by combustion analysis. The treatment of the data was essentially that of Wall, Powers, Sands and Stent,⁶ but all compositions were finally converted from a weight to a mole basis. The copolymer compositions were calculated using experimental, rather than theoretical, carbon analyses for pure polystyrene and pure polymethyl methacrylate, each of which were prepared by the same techniques that were employed for copolymerizations.

Measurement of Monomer Distribution in Water.—About 30 g. of monomer mixture was equilibrated with 50 g. of distilled water in a 35° thermostat over a period of five hours interrupted by frequent shaking. The mixture was transferred to a separatory funnel, kept in an oven at 35 ± 2° for thirty minutes, and cautiously separated. The water layers in equilibrium with mixtures rich in styrene were slightly turbid and accordingly were centrifuged for ten minutes. Samples of the water layer were pipetted off and a 10-ml. portion was used for an interferometric determination of methyl methacrylate. Because of the low solubility of styrene in water, no correction was made for its presence in this interferometric measurement. Another sample was diluted with an equal volume of 95% ethanol for a spectrophotometric determination of styrene. The styrene determination was performed with a Beckmann ultraviolet spectrophotometer at 2840 Å. Standards were prepared from a stock solution containing styrene, ethanol, and water. The spectra of styrene and methyl methacrylate (the latter was not found in a search of the literature) are shown in Fig. 1.

From the results of the above-described measurements, monomer distribution coefficients were calculated according to the formula

$$K_w = (M_1/M_2)_{\text{water}} / (M_1/M_2)_{\text{oil}} \quad (2)$$

4. Measurement of Monomer Distribution in Soap Micelles.—Weighed amounts (0.10 to 5.00 g.) of styrene and methyl methacrylate were added to a measured volume of a 3% soap solution in a Babcock milk tube fitted with a sealed closure. After equilibration by one hour of rotation at 29 r. p. m. in a 35° thermostat, the tubes were

(12) Meyer and Ronge, *Z. angew. Chem.*, **52**, 637 (1939).

(13) Mayo and Lewis, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

centrifuged thirty minutes at 1200 r. p. m. (equivalent to 400 g) with interruptions at ten-minute intervals for re-heating. (Equilibration for times up to four hours and centrifuging as long as two hours did not alter the results.) The volume of the oil phase recovered by centrifugation was measured from the graduations on the tube, and its composition was determined by a refractive index measurement. From these data the weight of each monomer recovered could be calculated. The recovered amounts equal monomer present in the oil phase, and the differences between the initial and recovered amounts represent the equilibrium amount of monomer present in soap solution. The amount of each monomer in the micelles of the solution is calculated by subtracting, from the total dissolved, the amount which would be dissolved in a water phase in equilibrium with the final oil phase. (For this purpose it was necessary to know the distribution in pure water.)

Distribution coefficients for monomers in soap micelles were then calculated according to the equation

$$K_m = (M_1/M_2)_{\text{micelle}} / (M_1/M_2)_{\text{oil}} \quad (3)$$

Results and Discussion

The data for the solution polymerization of styrene and methyl methacrylate are summarized in Table I. From these data, using methods

TABLE I

SOLUTION POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE

Re-actant mole ratio M_{10}/M_{20}	Time, hours	Conversion, %	Polymer % carbon	Polymer mole ratio M_1/M_2	Moles styrene remaining M_{1r}	Moles methacrylate remaining M_{2r}	
3.847	0	0			0.4609	0.1189	
	23.5	4.54	83.56	2.650	.4417	.1126	
	23.5	4.57	83.74	2.727	.4416	.1124	
	46.3	8.67	83.53	2.638	.4243	.1059	
	46.5	8.69	83.80	2.753	.4264	.1073	
	71.0	12.81	83.33	2.557	.4073	.0988	
	71.0	12.79	83.76	2.735	.4094	.1010	
	95.5	16.50	83.83	2.766	.3904	.0943	
	95.5	16.85	83.76	2.762	.3891	.0935	
	1.000	0	0			.2938	.2937
23.25		5.02	76.60	1.044	.2788	.2793	
23.25		5.19	76.40	1.019	.2785	.2787	
47.0		9.81	77.12	1.113	.2635	.2664	
47.0		9.95	76.76	1.065	.2637	.2655	
71.75		14.69	76.40	1.019	.2503	.2511	
71.75		14.71	76.48	1.029	.2500	.2511	
94.25		18.89	76.67	1.053	.2268	.2302	
94.25		18.30	76.37	1.015	.2396	.2404	
0.2402		0	0			.1152	.4795
		23.25	7.41	69.25	0.403	1.026	.4482
		23.25	7.45	68.90	.383	1.030	.4475
		23.25	7.45	69.65	.428	1.020	.4486
		46.75	14.52	68.80	.377	.0916	.4170
	46.75	14.58	69.50	.418	.0898	.4186	
	46.75	14.58	69.30	.406	.0902	.4181	
	71.25	21.55	69.43	.414	.0778	.3892	
	71.25	21.71	69.41	.413	.0776	.3884	
	71.25	21.71	68.92	.384	.0795	.3865	
	94.5	28.42	68.87	.381	.0687	.3575	
	94.5	28.65	69.30	.406	.0662	.3588	
	94.5	28.65	69.52	.420	.0650	.3599	
	∞	95.5	18.39	92.25	∞ (polystyrene)		
0	19.25	20.25	59.60	0 (polymethyl methacrylate)			

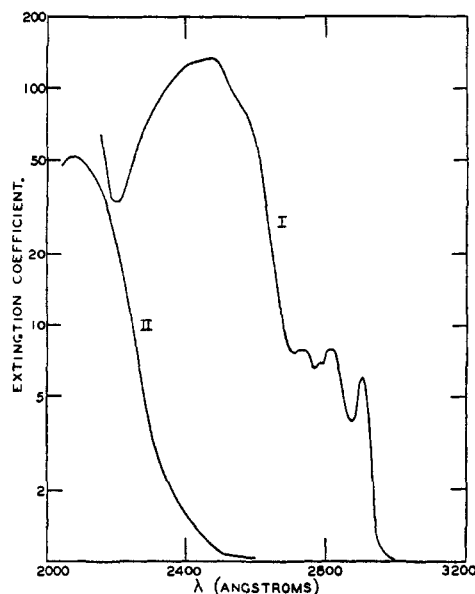


Fig. 1.—Ultraviolet absorption spectra of styrene (I) and methyl methacrylate (II) dissolved in 95% ethanol.

described earlier, we have calculated the reactivity ratios to be $r_1 = 0.50 \pm 0.02$ and $r_2 = 0.44 \pm 0.02$. Table II lists the data for emulsion polymerizations of the same monomers, from

TABLE II

EMULSION POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE

Re-actant mole ratio M_{10}/M_{20}	Time, hours	Conversion, %	Polymer % carbon	Polymer mole ratio M_1/M_2	Moles styrene remaining M_{1r}	Moles methacrylate remaining M_{2r}	
3.847	0	0			0.4609	0.1198	
	0.75	8.33	83.90	2.810	.4252	.1070	
	1.25	17.44	83.92	2.819	.3861	.0931	
	1.33	9.98	83.91	2.814	.4181	.1045	
	1.83	19.38	84.15	2.927	.3769	.0910	
	1.83	28.4	84.01	2.860	.3388	.0770	
	2.25	35.4	84.08	2.893	.3081	.0669	
	2.42	28.5	84.35	3.026	.3362	.0785	
	2.83	36.8	84.28	2.991	.3003	.0660	
	1.000	0	0			.2938	.2938
1.08		5.95	76.41	1.019	.2761	.2765	
1.25		13.95	76.64	1.048	.2519	.2537	
1.58		19.94	76.56	1.038	.2343	.2363	
1.58		13.37	76.64	1.048	.2537	.2554	
2.00		25.3	76.71	1.057	.2175	.2216	
2.08		20.60	76.27	1.001	.2347	.2334	
0.2402		0	0			.1152	.4795
		2.16	17.4	68.15	0.3380	.0892	.4024
		2.42	12.60	69.16	.3950	.0941	.4259
	2.92	32.4	68.64	.3650	.0638	.3387	
	3.17	28.8	68.47	.3556	.0705	.3534	
	3.50	43.6	68.30	.3462	.0487	.2874	
	3.67	37.7	67.98	.3289	.0598	.3112	
	∞	2.00	40.9	92.18	∞ (polystyrene)		
0		4.75	3.49	59.70	0 (polymethyl methacrylate)		

which we calculate $r_1' = 0.56 \pm 0.02$ and $r_2' = 0.50 \pm 0.02$. The parameters for solution polymerization should be substantially equal to those observed in bulk and can be compared with values obtained by Lewis and co-workers¹⁴ (extrapolated to 35°), namely, $r_1 = 0.485$ and $r_2 = 0.43$.

Table III and Figs. 2 and 3 give the equilibrium solubilities of styrene and methyl methacrylate in water as functions of the oil phase composition. From these data we find that K_w is of the order

TABLE III

DISTRIBUTION OF STYRENE AND METHYL METHACRYLATE BETWEEN OIL PHASE AND WATER AT 35°

Oil phase, weight % styrene	Water phase, weight % styrene	Water phase, weight % methyl methacrylate	K_w
0	0	1.48	
20.0	.006	1.040	0.208
33.3	.009	0.866	.021
50.9	.013	.655	.019
66.6	.020	.447	.022
80.0275	
100.0	.026	0	

of 0.02. Thus if the water phase were the principal locus of reaction in an emulsion polymerization, we should obtain

$$r_1' = r_1 K_w = 0.50 \times 0.02 = 0.010$$

$$r_2' = r_2 / K_w = 0.44 / 0.02 = 22.0$$

Since the values differ quite markedly from our experimental values, it would appear that the water phase cannot be an important reaction site.

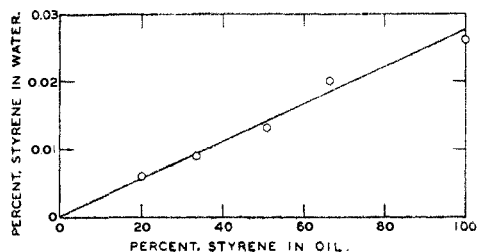


Fig. 2.—Solubility of styrene in water.

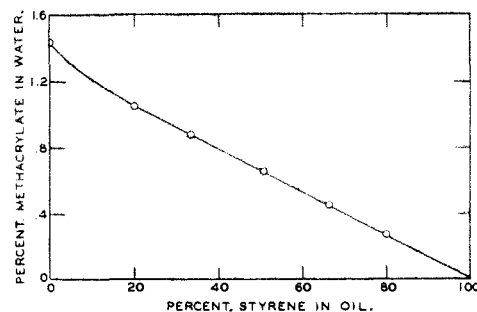


Fig. 3.—Solubility of methyl methacrylate in water.

Table IV and Fig. 4 give the equilibrium distributions of styrene and methyl methacrylate

(14) Lewis, Walling, Cummings, Briggs and Mayo, *THIS JOURNAL*, **70**, 1519 (1948).

TABLE IV
DISTRIBUTION OF STYRENE AND METHYL METHACRYLATE BETWEEN OIL PHASE AND MICELLES OF 3% SF FLAKES SOAP AT 35°

Oil wt. %	Total grams dissolved in 100 cc. soap solution		Grams dissolved in micelles of 100 cc. soap solution		Weight ratio M_1/M_2		K_w
	M_1	M_2	M_1	M_2	In oil	In micelle	
0	3.67	0	2.25	0
0	3.62	0	2.20	0
14.5	3.10	.226	2.00	0.170	0.170	0.113	0.665
20.2	3.01	.346	1.99	.253	.253	.174	.688
22.0	2.93	.367	1.94	.282	.282	.189	.671
36.5	2.47	.661	1.66	.575	.575	.399	.694
36.5	2.44	.675	1.63	.575	.575	.414	.720
40.0	2.31	.675	1.54	.667	.667	.437	.655
61.0	1.472	.963	0.963	1.56	1.56	1.00	.641
72.2	1.018	1.09	.652	2.60	2.60	1.67	.642
79.0	0.865	1.16	.590	3.76	3.76	1.97	.524
86.2	0.597	1.15	.415	6.25	6.25	2.76	.442
88.2	0.513	1.22	.358	7.47	7.47	3.42	.458
100	...	1.40	0
100	...	1.40	0
100	...	1.38	0

between the oil phase and the micelles of a 3% soap solution. Since the styrene in the water

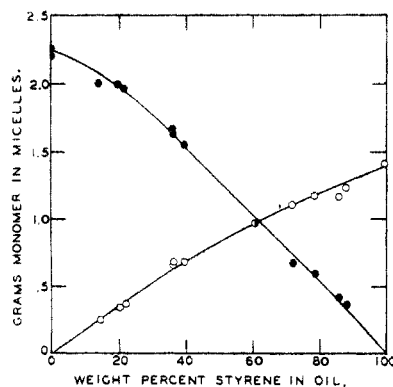


Fig. 4.—Solubility of styrene (open circles) and methyl methacrylate (solid circles) in soap micelles.

layer is almost entirely in the micelles, no correction for its solubility in soap-free water is necessary. Figure 5 shows a plot of K_m , the distribu-

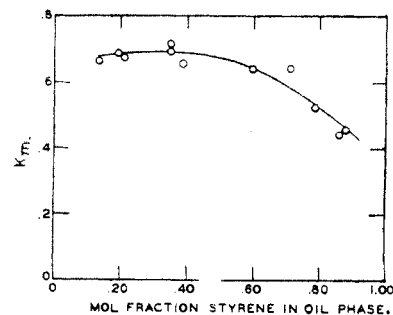


Fig. 5.—Solubility distribution coefficient of styrene and methyl methacrylate in soap micelles.

tion coefficient between oil phase and micelles, as a function of oil phase composition. It is found that K_m is not constant, but taking an average value (for the monomer ratios used) as 0.7, and considering these "equilibrium" micelles as the locus of reaction, we should find

$$r_1' = r_1 K_m = 0.50 \times 0.07 = 0.35$$

$$r_2' = r_2 / K_m = 0.44 / 0.7 = 0.63$$

Since these values are likewise significantly different from the experimental values, it would appear that the equilibrium micelles are not important reaction loci.

From the point of view of monomer reactivity ratios, it would appear from the above results that the oil phase would be the principal reaction locus for the system studied. According to Harkins,⁹ however, the reaction starts in the soap micelles, but as soon as some polymer forms, monomer will dissolve in the polymer, and the reaction will continue in the resulting monomer polymer particles. Since the composition of the monomer dissolved in the monomer-polymer particles can reasonably be expected to be nearly the same as that of the oil phase, it is easily seen why the polymerization would appear to take place in the "oil phase" as far as monomer reactivity ratios are concerned.

At extremely low conversions, however, the copolymer composition should approach that predicted from micelle compositions. To test this idea, we carried out six additional experiments with conversions ranging from 0.24 to 9.0%. In performing these experiments, especially those for the lowest conversions, extreme

precautions had to be taken to remove oxygen from the system. This was necessary since the initial polymer formed would otherwise have been contaminated with oxygen, for it is used up in the induction period as if it were a comonomer.

These experiments, which will not be described in detail, did show composition shifts in the direction predicted by assuming the micelles to be the reaction locus. However, the copolymer compositions never reached the theoretical limit expected for micellar reactions, and were always closer to the oil phase values. Nevertheless, considering the experimental difficulties encountered, there seems to be general compatibility with Harkins' views⁹ with respect to the changing nature of the reaction locus.

Summary

Copolymerization and solubility studies have been carried out on styrene and methyl methacrylate for the purpose of learning more about the mechanism of emulsion polymerization. The copolymerizations were carried out both in solution and in emulsion for three different monomer ratios and the compositions of the resulting copolymers determined. In addition the solubility distribution coefficients for the monomers between oil, water, and soap micelles were measured. These results have been correlated and are in substantial agreement with Harkins' theory of the locus of an emulsion polymerization, namely, that most of the polymerization occurs in the swollen polymer-monomer particles after the initial reaction in the micelles.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY]¹

The Heterogeneous Methanolysis of Native and Mercerized Cotton Cellulose²

BY RICHARD E. REEVES, LAURENCE W. MAZZENO, JR., AND CARROLL L. HOFFPAUR

In continuing studies on the acid-catalyzed heterogeneous-methanolysis of cotton cellulose^{3,4} two effects have been observed which are capable of quantitative evaluation; first, the introduction of acid-labile methoxyl groups into the insoluble cellulose, and second, the dissolution of a portion of the cellulose into the methanolysis reagent. Methanolysis is here regarded as the sum of these two effects.

In the present investigation purified native cotton cellulose and mercerized cotton cellulose

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Some of the data in this manuscript were presented before the Cellulose Division at the 114th meeting of the American Chemical Society, Portland, Oregon, September 1948, in a paper entitled "The Methanolysis of Cotton Cellulose."

(3) Hoffpaur and Reeves, *Anal. Chem.*, **21**, 815 (1949).

(4) Reeves, Schwartz and Giddens, *THIS JOURNAL*, **68**, 1383 (1946).

have been subjected to methanolyses at different temperatures and the reactions have been followed in the region when 0.1 to 5% of the total glucose units have become involved in reaction. Throughout this region a constant temperature coefficient was found for the rate of methanolysis of native fiber; for mercerized fiber the temperature coefficient was essentially constant, but clearly smaller than that observed for the former substrate. This difference between native and mercerized celluloses extends from the earliest observations to the last.

At equal extents of reaction differences in rate with temperature constitute the temperature coefficient and through this are related to the apparent energy of activation of the rate controlling step of the reaction. For the methanolysis of native cotton cellulose the apparent energy of activation is 24 kilocalories per mole;