

Loci of Emulsion Polymerization: Diffusion of Organic Molecules from Emulsion Droplets through an Aqueous Phase into Polymer Latex Particles

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cent, Debye calculated that Δ is about .06 mm or 6×10^6 Å. What is now needed is to make certain that all of the conditions in our experiments are in accord with what is demanded by Debye's theory, which is developed on the basis of a spherical drop suspended in the soap solution.

On account of the difference between the density at 25°C of ethyl benzene (0.862) and of the soap solution (1.0082 for 12.2 percent potassium laurate) there is a slight departure of the drops from the spherical form. However, the drop becomes more spherical as it becomes smaller, and, coincidentally, the curvature in the diffusion curve of Fig. 1 increases. Also, while photographs of the profile of the drop have been taken, there has been as yet no accurate determination of the area of contact between the top of the drop and the glass plate against which it rests.

A drop of ethyl benzene suspended in an aqueous 10.6 percent solution of soap is covered with a tightly packed monolayer of molecules of soap with the $C_{12}H_{25}$ -chain oriented toward the oil and the $-COO^-K^+$ toward the aqueous phase. The monolayer of soap is about 16 Å thick (neglecting the relatively few K^+ ions which form the outer part of the diffuse ionic layer). Such a very thin diffusion layer ($\Delta \sim 50$ Å) would allow capture of ethyl benzene molecules by only the edges of those soap micelles which are in contact with the surface of the oil drop. In a 10.6 percent solution of potassium laurate about 15 percent of the volume is filled with solubilizing micelles (provided almost all of the soap is present as solubilizing micelles, which is not certain).*

The variation of the rate of diffusion of ethyl benzene is shown in Fig. 3 as a function of soap concentration at a

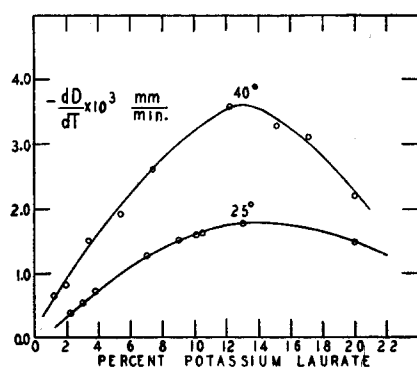


FIG. 3. Diffusion of ethyl benzene into potassium laurate as a function of soap concentration at a constant drop diameter of 0.5 mm.

constant drop diameter of 0.5 mm and at 25°C and 40°C. Both curves exhibit a maximum at a soap concentration of about 15 percent. The rate of diffusion of an oil into a soap solution is increased greatly by the presence of small amounts of salts such as potassium chloride.

¹ September 11–15, 1944, Meeting of the American Chemical Society.
* Note: Vinograd has communicated to us a mathematical analysis by Dr. J. N. Wilson, based on Fick's equation for diffusion. According to Wilson, a constant rate of change of the diameter of the drop, such as that obtained by Vinograd, represents a value of Δ such that $\Delta/d < 1$, i.e., a thin diffusion layer.

Loci of Emulsion Polymerization: Diffusion of Organic Molecules from Emulsion Droplets through an Aqueous Phase into Polymer Latex Particles

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February 4, 1946

IN recent communications Harkins¹ has developed a general theory of the loci of reaction in emulsion polymerization. According to this theory, when micellar soap is present, most of the polymer particle *nuclei* are initiated by polymerization of monomer layers of the general order of 10 Å thick, solubilized in soap micelles. The polymer molecules thus formed are sufficiently large to be ejected from the micelles into the aqueous phase outside, where they form extremely small (size *unknown*, possibly of the order of 25 Å diameter) polymer particle nuclei, which dissolve monomer. Such polymer-monomer particles become the locus in which, under ordinary conditions, almost all of the polymer is synthesized.

That the particles thus formed are extremely small was shown by an experiment in which 0.75 g of styrene was completely dissolved in 100 g of a 6 percent solution of potassium laurate. All of the styrene, except the small amount dissolved in the aqueous phase, was present in the micellar oil layers. After complete polymerization, the polymer appeared outside the micelles, but the solution, due to the small size of the polymer-latex particles, was almost as clear as the initial soap solution. The particles were so small that no method yet used has given their size.

However, when the same amount of styrene was polymerized in either (1) water alone or (2) a solution of the soap at 0.2 percent concentration (below the critical concentration for micelles), the solution became extremely opaque and very white, indicative of very large polymer particles. The extremely thin micellar oil layers in the presence of a higher concentration of soap—6 percent or more in this case—allow only very small polymer particles to form. However, if more and more styrene is emulsified in the 6 percent soap solution, and polymerization caused to proceed by the use of a catalyst, etc., the solution becomes more and more opaque as the polymer particles become larger. They may, for example, attain diameters of 1000 Å or even more. Data obtained by use of the electron microscope, from light scattering and by surface tension methods, which show the rate of growth of the polymer particles with the yield of polymer have been obtained and will be presented in later papers.

It is obvious that such small polymer particles cannot change into large particles with a constantly increasing total mass of polymer, unless monomer is constantly added to the polymer particles, while the monomer thus added undergoes polymerization. If all of the above is true, there must be a constant diffusion of monomer molecules from the emulsion oil droplets into the polymer particles after their ejection from the soap micelles. If polymer particles free from monomer become saturated with an oil such as ethyl benzene, which does not polymerize, the diffusion occurs in both directions and the monomer droplets no longer decrease in size.

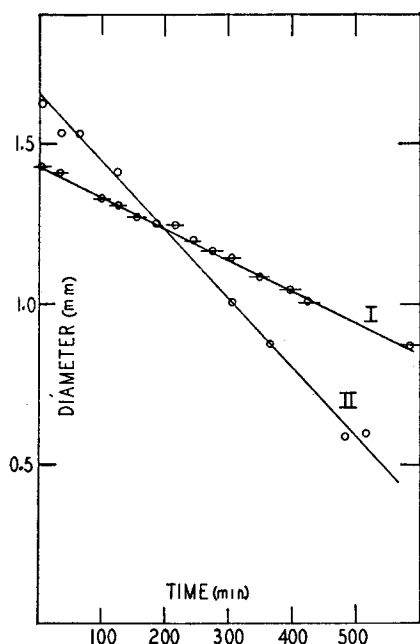


FIG. 1. Diffusion of ethyl benzene into latex solutions at 25°C. Curve I: 98 percent conversion. Curve II: 67 percent conversion.

Experiments were carried out in which polymer particles were substituted for the soap micelles used in the earlier work. The polymer particles were formed from a mixture of 75 percent isoprene and 25 percent styrene in a soap solution with an initial soap concentration of 3 percent and 100 parts monomer to 180 parts water. Samples of latex were used at 67 and 98 percent conversion to polymer. The former already contained 33 percent and the latter only 2 percent of monomer.

The rate of diffusion at 25°C from a drop of ethyl benzene with an initial diameter of 1.5 mm but calculated as the slope of the best straight line was found to be 2×10^{-3} mm decrease of diameter per minute in the polymer solution of 67 percent conversion and 1.0×10^{-3} mm in that of 98 percent conversion. These diffusion rates are not very accurate on account of the difficulty encountered in the observation of the boundary of the drop due to the opacity of the solution. Within the limits of Fig. 1 the rate of decrease of diameter of the drop is linear, but it seems probable that the rate will be found to increase as the drop decreases still further in diameter.

In these polymer solutions no micellar soap and very little dissolved soap is present. On account of the extremely great area of the latex particles almost the whole of the soap is adsorbed at the interface between the latex particles and the aqueous phase.

The relations presented in this and in the preceding letter are often neglected in the development of the kinetics of emulsion polymerization. When 3 percent soap with 100 g of monomer and 180 g of water is used, all free monomer commonly disappears by solution in the polymer particles by the time the yield of polymer reaches about 60 percent.

¹ W. D. Harkins, *J. Chem. Phys.* 13, 381 (1945); 14, 47 (1946).

The Critical Concentration for the Formation of Micelles as Indicated by the Absorption Spectrum of a Cyanine Dye *

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February 7, 1946

RECENTLY Sheppard and Geddes¹ reported that the absorption spectrum of aqueous pinacyanol chloride is shifted from that exhibited in aqueous solution to that characteristic of its solutions in non-polar solvents by the addition of cetyl pyridinium chloride. They consider that the "addition of a micelle-forming hydrophile colloid effects conversion of the dye from an aggregated—probably dimeric—to a monomeric state." We have determined the absorption spectra of the same cyanine dye in aqueous solutions of potassium laurate and potassium myristate of varying soap concentration at a dye concentration of 1×10^{-4} molar and a temperature of 25.6°. The extremely rapid change in the spectrum in each of these soap solutions is found to occur at the critical concentration for the formation of micelles, and this appears to give the simplest method for the determination of the critical concentration.

With increasing soap concentration, the observed spectra show a very pronounced shift over a short range of concentration to the form typical of the dye solutions in a non-polar medium. With potassium laurate the spectrum is markedly different from that of the dye in water at a soap concentration of 1×10^{-3} molar. In more concentrated solutions a band appears at 4800Å; this band disappears

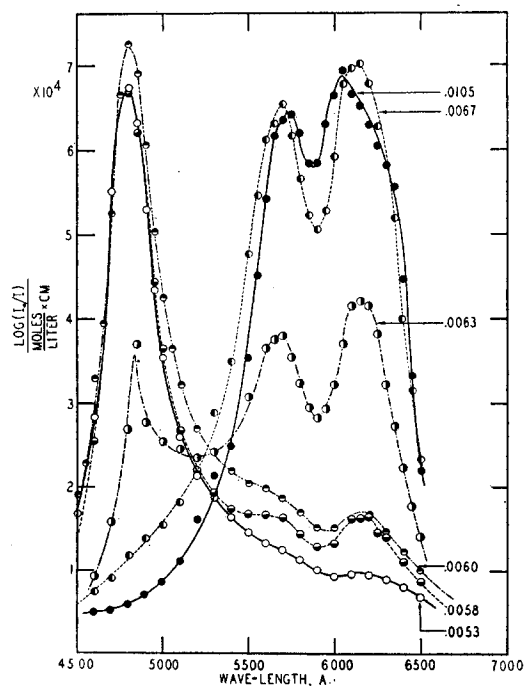


FIG. 1. Absorption spectra of 1×10^{-4} pinacyanol chloride in aqueous potassium myristate solutions.