

Loci of Emulsion Polymerization: The Diffusion of Organic Molecules from Emulsion Droplets through an Aqueous Phase into Soap Micelles

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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

Loci of Emulsion Polymerization: The Diffusion of Organic Molecules from Emulsion Droplets through an Aqueous Phase into Soap Micelles

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February 4, 1946

AN important problem of emulsion polymerization in soap solutions is to determine the rate of diffusion of molecules from the surface of oil emulsion droplets through the aqueous phase into the position in which they are caught, i.e., in a soap micelle. The method used to determine the rate of diffusion is extremely simple and was outlined in an unpublished paper by Vinograd, Fong, and Sawyer.¹ They measured by the use of a microscope the diameters of small drops of oil "submerged in soap solutions" and found that their diameters "decline linearly with time until 99 percent of the drop passes into the aqueous phase."

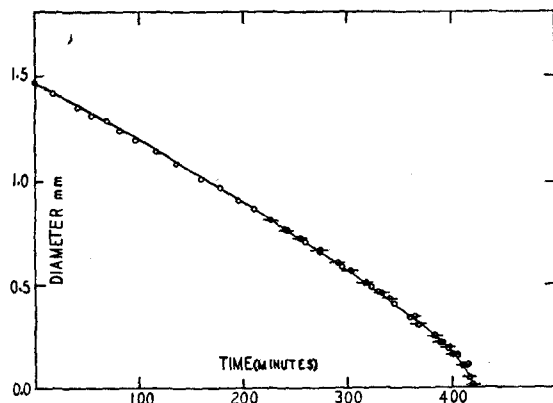


FIG. 1. Diffusion of ethyl benzene into 12.2 percent potassium laurate at 40°C. A second curve starting with a smaller initial drop diameter has been superimposed on the curve for the drop with a larger drop diameter by adding 226 minutes to the time axis.

Our work indicates a different relation: the rate of decrease of the diameter of the oil drop *increases with time* (Figs. 1 and 2), i.e., as the drop grows smaller. The rate of decrease of diameter for a drop of ethyl benzene in 12.2 percent potassium laurate solution at 40°C was increased from -0.00260 mm to -0.00430 mm per minute by a decrease in the diameter from 1.4 mm to 0.25 mm. The rate of diffusion is about twice as high at 40° as at 25°C.

In private communications to the writers Professor P. Debye has developed a theory for the diffusion of molecules from an oil drop into a soap solution. From the picture proposed by him the more rapid decrease of diameter for small than for large drops is what would be expected. His theory introduces a quantity defined by the relation:

$$\Delta^2 = D/\alpha,$$

in which D is the diffusion constant for the oil; in the special case cited, ethyl benzene, and α is a constant such that αdt is the number of molecules of the oil which are caught per cc during the time dt by the soap at a place where the concentration of the oil is n . The quantity Δ is then representative for the characteristic thickness of the diffusion layer.

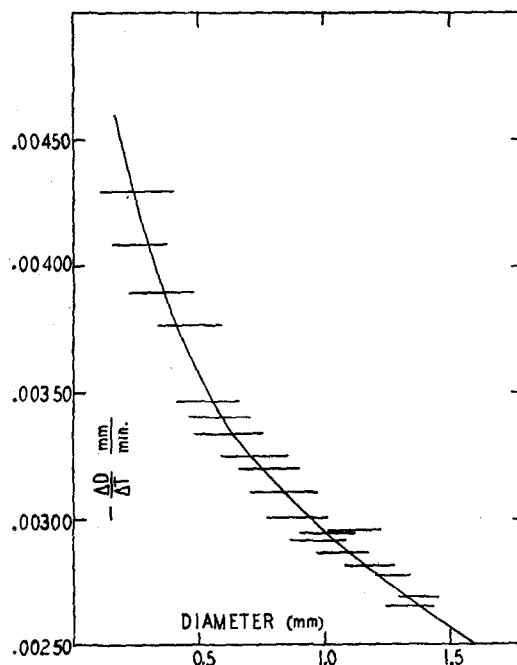


FIG. 2. Chord plot of data of Fig. 1, showing increase in the rate of diffusion with decrease in the size of the drop.

It is of interest that the calculated value of Δ found by the use of the linear variation of the diameter d of the drop of ethyl benzene is of the order of 50A, while from a representative curve, similar to that of Fig. 1 except that the concentration of the potassium laurate was 10.6 per-

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

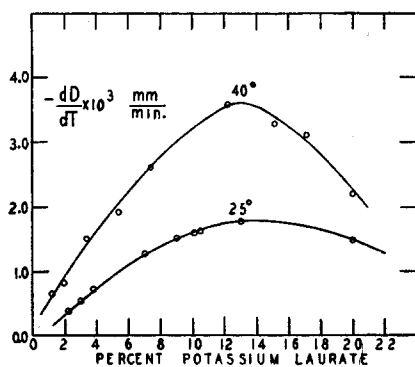


FIG. 3. Diffusion of ethyl benzene into potassium laurate as a function of soap concentration at a constant drop diameter of 0.5 mm.

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.