

phenolphthalein as indicator. Samples of higher content of acetic acid were analyzed for vinyl acetate by adding a measured excess of bromine water followed by potassium iodide, and titrating the liberated iodine with standard thiosulfate solution.

From the known composition of the initial mixture, the composition of the aqueous layer as determined by analysis, and the curve showing the solubility relationships, the composition of the vinyl acetate layer is found. The straight line between the initial gross composition and the composition of the aqueous layer is extrapolated to the solubility curve; the intersection is the composition of the vinyl acetate layer.

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EMULSION TYPE

JOEL H. HILDEBRAND

Department of Chemistry, University of California, Berkeley, California

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Although the factors influencing emulsion type have long been the subjects of discussion, it can hardly be said even now that the apparent conflicts have been settled. The situation indicates, I believe, that no single theory of emulsion type will suffice, in view of the various factors operating and the wide differences in the emulsifying agents used. Three of these theories assume that the type is determined by a natural direction of curvature of the interfacial film of emulsifying. One, the "oriented-wedge theory" (1, 3, 4), applies to monomolecular films, another applies to solid skins, and a third to solid particles (5). In each of these cases there is reason to believe that curvature in one direction yields a lower energy than curvature in the other; hence this direction is undoubtedly one factor in determining which liquid shall be the enclosed phase.

There are two reasons, however, for seeking additional factors. One is that the force tending to produce curvature is extremely small in view of the thinness of the film. A second and far stronger objection is that there is no mechanism whereby droplets of oils as insoluble in water as those ordinarily used can assume the theoretical equilibrium size. A droplet that is too big cannot spontaneously shrink; it can only become bigger by coalescence, an irreversible process. I wish to suggest, therefore, that attention be focused on the processes of emulsification and coalescence, rather than upon equilibrium considerations involved in curvature of minimum energy. The more or less violent agitation used to form an emulsion must give at the outset globules of both kinds, so that between them we have both kinds of film, some of water, some of oil.

Let us consider, first, films stabilized by monomolecular layers of soap such as we have in emulsions of oil in water. The soap is highly adsorbed at the interfaces, greatly lowering the interfacial tension. Suppose, now, that the film is suddenly stretched and threatens to break at some point. The fresh solution thereby exposed, or at least the region of less oriented soap molecules, has a higher interfacial tension; hence the film automatically strengthens itself wherever a break is threatened. The oriented soap layer is then replenished by further adsorption from the solution. Thus far there is nothing new about the explanation. A further question naturally arises, however. Why does the film resist rupture better when the soap in the interfaces comes from the film solution, here the water, than when it comes from the larger reserve in the droplet? The answer I suggest is that the resistance to sudden rupture is much stronger if the emulsifying agent is present in the film liquid, which is the external phase, than if it is in the larger mass of emulsified drop, the internal phase. The reason for this is that there is very little soap available in a thin film to migrate to the new surface and weaken it, while there is an ample supply if it is soluble in the liquid outside of the film. This can be verified by a simple calculation based on the figures of Griffin (2). A permanent emulsion of oil in water can be prepared with 0.0125 molal sodium oleate. Such a solution would contain 7.5×10^{18} molecules per cubic centimeter. The area occupied by a molecule in the interface was found to fall between 20 and 40 \AA^2 . Let us select the mean, 30 \AA^2 . Two faces of such a soap film, each of 1 cm^2 , would then contain 7×10^{14} molecules. The ratio of this number to the number per cubic centimeter is approximately 10^{-4} , that is, to fill with soap 1 cm^2 of new double film surface would exhaust all the dissolved soap in a layer 10^{-4} cm . thick. We may infer from the thickness of soap films in air that films as thin as this may easily occur between the oil drops of a concentrated emulsion. In order for two drops to coalesce, the separating film of the outer phase would have to become even thinner at the point of threatened coalescence, and this would be resisted more strongly when the emulsifier is dissolved in the film than when it is dissolved in the droplets.

We are thus led to an explanation for a rule that has long been held on a purely empirical basis, so far as I am aware, i.e., that an emulsifying agent tends to render the phase in which it is soluble the outside phase. This is not inconsistent with the oriented-wedge theory, since the larger end of the molecular wedge tends to determine the solubility. Indeed, the rule can be stretched to cover the behavior of solid powder emulsifiers, since the solid is in a sense more soluble in the better wetting liquid. A thin layer of the outer liquid is much better protected against rupture if the solid particles project chiefly into the interior of the film, i.e., if the particles are mainly on the outside of the emulsified droplets. Colloidal emulsifiers

may be regarded as intermediate between dissolved but superficially adsorbed emulsifiers on the one hand and solid powder emulsifiers on the other.

We may fairly conclude that the different theories are not essentially antagonistic but rather are different factors in a rather complex mechanism. This analysis is intended not as a denial of any of these factors but to emphasize and account for the survival of films of one liquid over films of the other during the process of emulsification, and to point out that this survival may be a principal factor in determining which liquid shall become the outer phase.

SUMMARY

The various factors which contribute to the stability of one type of emulsion rather than the inverse type are supplemental rather than rival. The direction of film curvature for minimum energy has probably been over-emphasized at the expense of the more mechanical forces operating during the emulsification process. The rupture of a film separating two droplets can be resisted by a larger rise in interfacial tension at the threatened point if the reserve emulsifying agent is dissolved in the liquid forming the film, i.e., the external phase, owing to the lower rate of adsorption in that case.

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CALCULATION OF ACTIVITIES OF RADIOACTIVE SUBSTANCES IN SERIES DISINTEGRATIONS

D. E. HULL

*School of Chemistry, Institute of Technology, University of Minnesota,
Minneapolis, Minnesota*

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It is the object of this paper to present a set of formulas which enable one to calculate quickly the activity of any member of the three naturally occurring radioactive series at any time after any arbitrary initial conditions. The method of calculation has proved to be of convenience to the author, and the required formulas are given for the benefit of others who may find them of use.