

Emulsification

IN 1925, Seifriz¹ made a number of interesting observations on the emulsification of hydrocarbon oils with water, using casein as emulsifier. He showed, for example, that oils ranging in density from 0.664 to 0.820 gave stable emulsions of the oil-in-water type; those of density 0.857 to 0.895 gave stable emulsions of the water-in-oil type; while oils intermediate in density gave emulsions which separated immediately. So far as we are aware, no adequate explanation of these results has been offered, but a simple explanation is possible on the basis of recent developments in the study of the liquid state.² The hypothesis to be advanced has important consequences for the theory of emulsification and detergent action.

Liquids are no longer to be regarded as structureless, and in the case of aliphatic compounds, the tendency to incipient crystallisation increases with the length of the carbon chain. The resistance to dispersion of liquids composed of long-chain molecules must therefore increase with the chain length, that is, in the case of the paraffins, with the density of the oil. Hence the inversion of emulsion type observed by Seifriz is due simply to the increased resistance to dispersion of paraffins of high molecular weight, caused by incipient crystallisation.

When oils and related compounds are spread as a thin film on a solid surface, the tendency to incipient crystallisation manifests itself in the form of adhesion to the surface. In this case, removal of oil by means of soap solution is conditioned by the magnitude of adhesion and interfacial tension, as shown by the following experiments.

A mineral oil was subjected to repeated fractional distillation to obtain nine fractions of increasing boiling point. Each fraction was then used to oil a wool fabric, which was afterwards scoured with soap and soda solution, using a standard mechanical technique. The amount of oil remaining in the fabric was found

Percentage by weight of Oleyl Alcohol in mixture.	Oil-water Interfacial Tension (dynes/cm.)	Residual Oil (per cent on weight of wool)
0.0	47.9	2.50
2.5	20.9	1.81
5.0	19.1	0.61
6.0	18.9	0.58
10.0	20.2	0.57
15.0	19.6	0.83
20.0	19.1	1.14
40.0	..	2.20
55.0	16.1	2.88
70.0	15.5	3.25
85.0	14.7	3.36
100.0	14.4	2.66

to increase with the boiling point of the fraction, according to a law which indicates that the difficulty of removing oil increases in proportion to the length of the molecule.

Although the preceding results serve to indicate the importance of the adhesion factor, the difficulty of removing mineral oil from a solid surface such as wool is due mainly to high interfacial tension. Oleyl alcohol on the other hand, possesses a low interfacial tension, but is even more difficult to remove than mineral oil. This result must be referred to adhesion of a very high order, due to the polar character of the molecule and its high molecular weight.³ Mixtures of mineral oil and oleyl alcohol are as a rule more easily removed than either oil alone. This important result serves to discriminate between the two factors of adhesion and interfacial tension, and is illustrated

by the data of the accompanying table, obtained by oiling a wool fabric with 5 per cent by weight of each mixture, the fabric being then scoured as before, and the residual oil estimated by ether extraction.

As might be expected from the preceding results, both mineral oil and oleyl alcohol were found to be difficult to emulsify with soap solution, but the mixture of mineral oil and 6 per cent oleyl alcohol, for example, gave an extremely stable emulsion under similar conditions.

In conclusion, it is evident that the formation of emulsions, especially in the case of oils and related compounds of high molecular weight, is not determined simply by the magnitude of the interfacial tension and the formation of a stable adsorbed film at the interface. The cybotactic condition of the liquid to be dispersed is of equal importance in ordinary emulsification; while, in scouring processes, related adhesion phenomena acquire exceptional significance.

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¹ Seifriz, *J. Phys. Chem.*, **29**, 587; 1925.

² Stewart, *Reviews of Modern Physics*, **2**, 116; 1930.

³ Hardy, *Phil. Trans.*, A, **230**, 1; 1931.

Inhibition of Enzymes by Carcinogenic Compounds

EXPERIMENTS carried out in this laboratory¹ have shown that 1:2:5:6-dibenzanthracene and 5:6-cyclo-penteno-1:2-benzanthracene are the most carcinogenic of pure compounds yet described. The action of these compounds and of certain non-carcinogenic hydrocarbons on the oxidising enzymes of yeast and muscle has been studied. The carcinogenic and other hydrocarbons dissolved in benzene or toluene were shaken up with enzyme preparations; and the effect on the activity of the enzyme measured. In no case was indophenol oxidase of yeast or muscle affected by any such treatment.

The oxidation of lactate by lactic dehydrogenase of yeast or muscle was, however, inhibited by a dilute solution of the hydrocarbon in benzene or toluene which had been exposed to air and light. Exposure to air in the dark, or to light out of contact with air, was ineffective. Solutions activated by exposure to ultra-violet light became coloured yellow or brown and non-fluorescent. The amount of inhibition produced in this way on a yeast lactic dehydrogenase by several hydrocarbons treated in a comparable manner was as follows:

	Percentage Inhibition of Enzyme.	
Toluene control	0	
(1) Anthracene	30	Non-carcinogenic.
(2) 1:2-Benzanthracene	28	"
(3) Chrysene	26	"
(4) 5:6-cyclo-Penteno-1:2-benzanthracene	55	Carcinogenic.
(5) 1:2:5:6-Dibenzanthracene	62	"
(6) Polycyclic hydrocarbon from coal tar	74	More carcinogenic than (4) and (5).

In each case, 0.005 mgm. of the hydrocarbon was added to 1 c.c. of enzyme solution, which reduced 1 c.c. of 1/5000 methylene blue in the presence of lactate in 10 minutes at 40°. The maximum concentration of hydrocarbon is thus 1 part in 400,000.

The inhibitory action is greatest in the case of the carcinogenic compounds. The inhibition in the case of anthracene is not due to the presence of dianthracene, as this compound is quite inactive. 1:2:5:6-Dibenzanthracene was recovered unchanged after treatment which converts anthracene into dianthracene.