(6.7%, calculated as an equimolar mixture of *n*-hexane and hexene-1) and 15.3 g. (82.9%) of *n*-dodecane, b. p. 213–216°, n^{25}_{D} 1.4214. Egloff gives for *n*-dodecane, b. p. (760 mm.) 216.2 and n^{20}_{D} 1.42182.[3]

Identification of the Fraction of b. p. 60–70°.—All of the material of b. p. 60–70° collected in the series of runs was combined and cooled to −5° in a mixture of ice and salt. Bromine in carbon tetrachloride was added in drops until a faint bromine color persisted for a few minutes. The carbon tetrachloride was distilled off and the residue distilled under reduced pressure; yield, 4.8 g. of 1,2-dibromohexane, b. p. (38 mm.) 103–106°, $n^{18.2}_{\mathrm{D}}$ 1.5006, $d^{22.5}_{22}$ 1.5498. Dykstra, Lewis and Boord give for 1,2-dibromohexane, b. p. (36 mm.) 103–105°, $n^{13.5}_{\mathrm{D}}$ 1.50601, d^{20}_{20} 1.56322.[4]

After redistilling the lower boiling material through a 75-cm. Vigreux column three times, there was obtained a small fraction, b. p. 66–68°, n^{25}_{D} 1.4072. A Beilstein test showed the presence of halogen. The properties indicate that this material was *n*-hexane contaminated with a little carbon tetrachloride. Egloff gives for *n*-hexane, b. p. (760 mm.) 68.8°, n^{20}_{D} 1.37506.[5] The amount of material was too small to permit further purification.

Reaction after Elimination of the By-products in the Formation of the Grignard Reagent.—*n*-Hexylmagnesium bromide was prepared in the usual manner. The ether and all volatile products were removed by distillation and then 4 g. of *n*-dodecane was added and the distillation continued until no more liquid came over. The residue was taken up in 200 cc. of dry ether and caused to react with silver bromide as described above. There were obtained in this way 1.9 g. of the fraction b. p. 60–70° and 4.7 g. of *n*-dodecane, b. p. 213–216°.

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(3) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Company, New York, N. Y., 1939, p. 80.

(4) H. B. Dykstra, J. F. Lewis and C. E. Boord, This Journal, **52**, 3401 (1930).

(5) G. Egloff, ref. 3, p. 36.

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Solubilizing and Detergent Action in Non-Ionizing Solvents

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Now that it has been established that insoluble materials may dissolve in dilute aqueous solutions of solubilizers or detergents, to form stable colloidal solutions as distinguished from mere suspensions or emulsions, it becomes evident that this must be a general possibility for all solvents. Many indications of this are to be found in technical literature[1] and Freundlich[2] adduces a number of probable examples. Strict proof that such solubilization is possible would be of great scientific as well as technical significance. It would then remain to find appropriate solubilizers for taking up and reorganizing given materials in various media.

It is a cognate but different phenomenon that, as McBain and Woo[3] showed, spontaneous emulsification may occur, either of oil into water or of water into oil, without mechanical effort. Solubilizers, however, produce true reversible equilibria in contrast to temporary emulsions or mere protected particles.

The present note adduces a series of upwards of two hundred qualitative observations which serve the purpose of demonstrating that solubilizing does occur in non-aqueous solvents. Many solubilizers or detergents that operate in water are likewise effective in other solvents, provided that they are themselves soluble therein. Many are not soluble and a very few, even if soluble, do not exhibit solubilizing action in certain non-aqueous solvents. Solubilizers include substances that are not aqueous detergents such as rubber in benzene.

The experimental procedure has been to take approximately 1% solutions of pure or commercial detergents as supplied by the makers and add solid dye. Solubilization is indicated by the almost immediate coloration of the liquid. It is well known that admixture with a second solvent of 1% only slightly affects the solvent power of an ordinary solvent,[3a] whereas here it is affected by orders of magnitude. Likewise a solid dye cannot as such yield emulsions. The use of crystalline dye avoids mere suspension of colloidal particles of dye. The subject of solubilization is best discussed in connection with aqueous systems with regard to which there is now a good deal of information and in which we have conducted some critical experiments, whereas this note refers to most of what is available with regard to non-aqueous systems. It is sufficient here to point out that the dye is not dissolved as single molecules of dye, but that the colloidal particles must be organized from both dye and detergent. Direct X-ray evidence for this has been presented for benzene in the lamellar micelles of ordinary aqueous soap solutions.[4]

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(1) For example, U. S. Patents 2,097,773 and 2,147,713 for imparting fluorescence to petroleum products; possibly also the anti-bloom agents mentioned by Clayton, Black, Johnson and Morse, *Nature*, **138**, 801 (1936); and soaps used in dry cleaning.

(2) H. Freundlich, "Kapillarchem.," Akad. Verlagsges., Leipzig, 1932, 4th edition, Vol. II, p. 532.

(3) J. W. McBain and T.-M. Woo, *Proc. Roy. Soc.* (London), **A163**, 182 (1937).

(3a) For example, in the present case, alcohol is not appreciably effective until 15–20% is added to toluene, or glacial acetic acid 4–8%; whereas lauryl sulfonic acid is highly effective with only 0.2% used.

(4) H. Kiessig and W. Philippoff, *Naturwiss.* **27**, 593 (1939).

Most of our tests have been carried out with *n*-heptane, and with benzene or toluene. As materials to be solubilized therein we have used eosin, fluorescein, crystal violet, Calcomine Orange 2R (sodium *p*-sulfo-*o*-toluene-azo-β-naphthol), all of which are quite insoluble in heptane, and also chlorophyll which is soluble only in traces.

These are solubilized in *n*-heptane by a series of condensation products of diethanolamine and fatty acids, the higher fatty acid condensates being especially effective; by an oil soluble polyether alcohol; by diglycol laurate and stearate, the latter more so on warming (in all cases tested for the effect of heat, both in aqueous and non-aqueous systems, solubilizing was much greater at higher temperatures); sulfonated petroleum soaps, except for crystal violet in one particular soap. A naphthenate solubilized eosin, but fluorescein only on warming and not crystal violet. Sodium resinate, a polyglycerol ester, and a polyethylene glycol were only slightly effective even on warming, due to insolubility. Laurylpyridinium iodide had no effect on eosin or crystal violet, and very little on fluorescein when warmed. The well-known aqueous solubilizer, the sodium sulfonate of dioctylsuccinic ester, is remarkable in that it is highly soluble in heptane, but has practically no effect on eosin or fluorescein. However, it does solubilize crystal violet.

Although thymotic acid, oleic acid, acetic acid, chloroform, carbon tetrachloride and petroleum ether are readily soluble in *n*-heptane, their dilute solutions did not solubilize. The following are themselves insufficiently soluble: sulfonated castor oils, laurylpyridinium iodide, cetyltrimethylammonium bromide, ammonium linoleate, sodium deoxycholate, deoxycholic acid, potassium lauryl sulfoacetate, a sodium alkyl naphthalene sulfonate and a mixture of alkyl sodium sulfates.

The calcium and zinc salts of diisopropylsalicylic acid readily dissolve methylene blue in toluene. However, in cold *n*-heptane the action is less and requires many hours whereas it is instantaneously effective on warming.

Eosin, methylene blue and crystal violet were used with benzene and toluene. Here the dioctyl sulfosuccinate solubilized crystal violet and methylene blue, but scarcely affected eosin. A sodium alkyl naphthalene sulfonate, diglycol stearate and laurate in particular, the naphthenate, the polyglycerol ester, a number of diethanolamine fatty acid condensates, the petroleum sulfonates, zinc and calcium stearate all solubilize. Laurylpyridinium iodide and a mixture of sodium alkyl sulfates were less effective, least with methylene blue hydrochloride. Cetyltrimethylammonium bromide was effective in cold toluene with methylene blue, but required warming for the others. Sodium resinate solubilized except for methylene blue in benzene, where it also required warming for eosin. Potassium lauryl sulfoacetate, dehydrocholic acid and deoxycholic acid in benzene had a slight effect on warming, except for eosin, the methylene blue being strongest in the dehydrocholic acid. Oleic acid, although itself soluble, dissolved no dye. Sodium lignin sulfonate, sodium laurate, sodium oleate and sodium deoxycholate are themselves insoluble. On warming, methylene blue dissolves in toluene solution of sodium oleate with a red color. Upon cooling this becomes a blue jelly and if placed in contact with water gives a striking display of spontaneous emulsification.[3]

In mineral oil (Squibb) methylene blue and crystal violet are solubilized by 0.2% lauryl sulfonic acid at 80°, but not at room temperature; compare the Type III surface tension curve found by M. E. Laing McBain and Perry.[5] Upon warming, sodium oleate and sodium deoxycholate become sufficiently soluble to do likewise. In toluene and chloroform 0.2% laurylsulfonic acid solubilizes methylene blue.

We may venture the conclusion that it is possible to solubilize almost any material in almost any solvent, as desired. A good solubilizer should be effective in concentrations of 1% or less.

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(5) M. E. Laing McBain and L. H. Perry, THIS JOURNAL, **62**, 989 (1940).

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The Synthesis of a New Dimethyl-β-methylglucoside

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It has recently become desirable to synthesize a crystalline derivative of 2,4-dimethylglucose for comparison with some of the hydrolytic products obtained from a methylated type III pneumococcus polysaccharide.[1] Starting with the known 3-tosyl-2,4,6-triacetyl β-methylgluco-

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[1] The results of these experimental investigations will be described in a separate publication.