[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Recrystallization of Organic Compounds From Detergent-Water Systems

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Organic compounds with significant water solubilities were purified by a single recrystallization from water containing small amounts of a detergent to yield products of greater purity than derived from a single aqueous recrystallization. This method appears particularly desirable when handling small amounts of material.

In an investigation[2] of an aqueous extract of *Artemisia tridentata* (American sage brush) certain of the naturally-occurring compounds were found to crystallize from the crude extract when a trace amount of a detergent was added, but not in its absence. This observation suggested the possibility of using detergents in facilitating the recrystallization of organic compounds from water.

The recrystallization of organic compounds from water, containing small amounts of detergents, was found to be a useful method of purification, provided that the compounds had a solubility of the order of 0.03 to 2 grams per 100 milliliters of water at room temperatures. Solubility was increased in the detergent-water system to permit recrystallization of substances whose solubilities are of an order of magnitude that aqueous recrystallization would otherwise be impractical. This method is particularly applicable when handling small amounts of materials, since product recovery is unusually high as compared to conventional methods using organic solvents.

This method of recrystallization tended to alter the normal crystal habit of the organic compound. Needles, having high length to width ratios, were frequently formed. This is in agreement with observations of Milone and Cetini,[3] who found that surface-active agents block the growth of crystals in a direction perpendicular to those faces that tend to be of greatest size at the end of crystal growth.

The compounds listed in Table I are representative of those which were recrystallized once from water containing Oronite D-60,[4] an anionic detergent. The stock compounds varied in purity, and those of a higher grade received no enhancement in purification, as indicated by melting points. However, this observation suggested the lack of any appreciable contamination by the detergent. The latter is supported by the suggestion[5] that the maximum adsorption of surface-active agents on solid surfaces is limited and may consist of a monomolecular layer.

The melting point of recrystallized sucrose octaacetate found in this study is considerably higher than those previously reported. Since the compound has been shown[6] to crystallize in two modifications, our compound may be a sample of the higher-melting form. Analysis and optical rotation confirm the chemical identity of the compound.

For comparative purposes, a second anionic detergent, Aerosol OTB,[7] and a nonionic surface-active agent, Triton X-100,[8] were applied. Melting points of once recrystallized products are given in Table II. In general the anionic detergents were equivalent, but nucleation was required to permit crystallization in the presence of Triton X-100, and in three instances crystallization did not occur.

Certain of the compounds applied are frequently recrystallized from water. However, the extent of purification as shown by melting points was found, in general, to be less as shown in Table III. Moreover, the increased solubility in the hot solution using the detergent-water system permitted the recovery of larger amounts of recrystallized materials.

The rate of crystallization of organic compounds with limited water solubility was found to be depressed in the presence of surface-active agents. Davies and Nancollas[9] found that the rate of crystal growth of silver chloride was retarded by sodium dodecylsulfate and cetyltrimethylammonium ion. When crystallizing a highly water-soluble compound, a different effect may be noted. The rate of crystallization of a concentrated solution of sucrose is reported[10] to be unaffected by surface-active agents, but nucleation may be more prolific in their presence. This may explain the statement[11] that an increased crystallization rate is

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[1] Present address, The Texas Co., Beacon, N. Y.

[2] Newman, Ph. D. Dissertation, University of Utah, 1951.

[3] Milone and Cetini, *Gazz. chim. ital.*, **84**, 133 (1954).

[4] A sodium alkylarylsulfonate, Oronite Chemical Co., San Francisco.

[5] Corrin, Lind, Roginsky, and Hawkins, *J. Colloid Sci.*, **4**, 485 (1949); Fava and Eyring, Division of Physical and Inorganic Chemistry, 128th Meeting, ACS, Minneapolis Minn., 1955; Willson, Miller, and Rose, *J. Phys. & Colloid Chem.*, **53**, 357 (1949); and Wolstenholme and Schulman, *Trans. Faraday Soc.*, **46**, 489 (1950).

[6] Duparc and Galopin, *Helv. Chim. Acta*, **13**, 702 (1930); Pictet, *Helv. Chim. Acta*, **13**, 698 (1930).

[7] Sodium dioctylsulfosuccinate, American Cyanamid Co., New York.

[8] An alkyl aryl polyethyleneglycol ether, Rohm and Haas Co., Philadelphia.

[9] Davies and Nancollas, *Trans. Faraday Soc.*, **51**, 823 (1955).

[10] Van Hook and Bruno, *Discussions Faraday Soc.*, **5**, 112 (1949).

[11] King, U. S. Patent 2,591,704, April 8, 1952.

TABLE I

A Single Recrystallization Using Oronite D-60

Compound	Source	Stock	M.p., °C. Observed	Literature[a]
Acetanilide	E[b]-W[c]	114.4–115.1	114.4–114.9	113–114
p-tert-Amylphenol	E-P[d]	91.6–94.0	93.2–94.3	92–93
Anthranilic acid	E-W	144.6–145.6	144.9–145.4	144–146
Benzilic acid	E-W	147.6–149.1	152.8–153.6	150
Benzoin	E-P	125.8–133.0	131.6–132.2	133–134[e]
m-Chloroacetanilide	E-W	76.1–78.0	77.8–78.3	79 (72–73)
trans-Cinnamic acid	E-W	132.5–134.0	132.8–133.0	133
2,4-Dichlorophenoxyacetic acid	M[f]-P	122.4–135.8	142.9–144.9	141 (138)
m-Dinitrobenzene	E-W	90.0–91.0	89.9–90.2	89.6
α-D-Glucose pentaacetate	[g]	95.2–114.5	112.9–113.0	112–113
Hippuric acid	M	184.0–185.0	190.7–191.2	187 (188.5)
D-Mannitol 1,6-dibenzoate	[h]	178.0–179.0	181.5–182.3	182
p-Nitroaniline	E-P	145.5–147.0	146.8–147.5	148
m-Nitrobenzaldehyde	[i]	57.4–58.6	58.0–58.2	58
Phenylacetic acid	E-W	76.8–78.0	77.8–78.2	76–76.5
Sucrose octaacetate	[j]	79.6–84.1	86.3–87.4[k]	70 (75)[l]

[a] Heilbron and Bunbury, *Dictionary of Organic Compounds*, Revised edition, Oxford University Press, New York, 1953. [b] Eastman Organic Chemicals. [c] "White label." [d] Practical grade. [e] Arnold and Fuson, *J. Am. Chem. Soc.*, **58,** 1295 (1936); Benton, Voss, and McCusker, *J. Am. Chem. Soc.*, **67,** 82 (1945); and Buck and Jenkins, *J. Am. Chem. Soc.*, **51,** 2163 (1929). [f] Matheson, Coleman, and Bell. [g] Prepared by undergraduate students by the reaction of glucose and acetic anhydride in the presence of zinc chloride. [h] Prepared by the procedure of Brigl and Grüner, *Ann.*, **495,** 60 (1932). [i] E. Merck, Darmstadt. [j] Prepared from sucrose and acetic anhydride in the presence of pyridine. [k] *Anal.* Calc'd for $C_{28}H_{38}O_9$: C, 49.56; H, 5.64. Found: C, 49.83; H, 5.67. $[\alpha]^{20}_{D}$: reported (Ref. 6), +59.5° (*c*, 2, chloroform); found, +58° (*c*, 2, chloroform). [l] Ref. 6.

TABLE II

Comparison of Detergents

Compound	Stock	M.p., °C. Detergent Aerosol OTB	Oronite D-60	Triton X-100	Literature[a]
Acetanilide	114.4–115.1	116.2–117.0	114.4–115.1	114.6–115.3	113–114
Anthranilic acid	144.6–145.6	144.5–144.8	144.9–145.4	[b]	144–146
Benzoic acid	121.5–123.0	123.0–123.4	121.5–122.0	121.0–122.0	122
Benzoin	125.8–133.0	130.4–131.6	131.6–132.2	131.0–131.8	133–134[c]
m-Chloroacetanilide	76.1–78.0	78.4–78.7	77.8–78.3	[b]	79 (72–73)
trans-Cinnamic acid	132.5–134.0	134.8–135.2	132.8–133.0	134.4–134.8	133
2,4-Dichlorophenoxyacetic acid	122.4–135.8	138.6–139.4	142.9–144.9	[b]	141 (138)
α-D-Glucose pentaacetate	95.2–114.5	112.8–113.1	112.8–113.0	113.4–113.8	112–113

[a] Heilbron and Bunbury, *Dictionary of Organic Compounds*, Revised edition, Oxford University Press, New York, 1953. [b] Crystallization did not occur. [c] Arnold and Fuson, *J. Am. Chem. Soc.*, **58,** 1295 (1936); Benton, Voss, and McCusker, *J. Am. Chem. Soc.*, **67,** 82 (1945); and Buck and Jenkins, *J. Am. Chem. Soc.*, **51,** 2163 (1929).

TABLE III

Comparative Efficiency Using Water and Aqueous Aerosol OTB

Compound	Source	Stock	M.p., °C. Water-OTB	Water	Literature[a]	Amts. recovered from satd. solns. OTB/water
Acetanilide	[b]	113.2–115.2	115.4–116.2	114.2–116.3	113–114	3.1
Benzoic acid	[c]	113.0–120.1	119.8–121.5	118.2–120.1	122	1.5
Benzoin	[d]	125.8–133.0	132.0–133.0	128.4–131.4	133–134	1.7
2,4-Dichlorophenoxyacetic acid	[e]	122.0–136.0	138.2–139.8	136.2–139.0	141 (138)	1.65
β-D-Glucose pentaacetate	[f]	124.0–130.2	131.4–131.8	130.8–131.8	134	1.95
Hippuric acid	[g]	177.2–185.0	189.6–191.0	189.8–191.2	187 (188.5)	2.2
Sucrose octaacetate	[h]	84.6–86.3	86.1–86.4	85.0–86.6	70 (75)[i]	2.25

[a] Heilbron and Bunbury, *Dictionary of Organic Compounds*, Revised edition, Oxford University Press, New York, 1953. [b] Prepared by reaction of aniline and acetic anhydride. [c] Benzoic acid of m.p. 121.5–123.0° contaminated with 5% of *trans*-cinnamic acid. [d] Eastman Organic Chemicals, practical grade. [e] Matheson, Coleman, and Bell, practical grade. [f] Prepared by undergraduate students by reaction of glucose and acetic anhydride in the presence of sodium acetate. [g] Prepared by undergraduate students by benzoylation of glycine. [h] Prepared by reaction of sucrose and acetic anhydride followed by a single recrystallization from ethanol. [i] Ref. 6.

observed when a nonionic, surface-active agent is added to sucrose liquors.

EXPERIMENTAL

General procedure. To crystallize organic compounds by this method, a small amount of detergent was added to distilled water to give approximately a 0.05% solution by weight. (The amount of detergent was not particularly critical and with practice did not require measurement.) The compound to be recrystallized was then added to the solution and the mixture heated. The organic compound slowly went into solution. The amount of solute was adjusted so that at the boiling point the solution was almost saturated. Water or solute, and in some cases more detergent, was added to realize optimum conditions. The solution then was filtered hot. In many cases the compound crystallized immediately upon filtration. In such instances, it was desirable to redissolve the crystals and to permit slower crystal growth for greater purity. The filtrate then was set aside to permit crystallization without stirring or disturbing the solution. Seeding was rarely necessary and in most cases crystallization was complete in about 2 hours. The crystalline material then was filtered through a medium or coarse porosity sintered-glass funnel or a similar filtering device, and washed several times with cold water until the filtrate coming through the funnel did not foam, indicating the removal of the detergent from the crystals.

The stock samples and the recrystallized samples were dried in a vacuum desiccator for approximately one week over anhydrous calcium chloride after which both samples were dried simultaneously in a drying pistol, containing phosphorus pentoxide, by heating with refluxing chloroform (ether for *m*-nitrobenzaldehyde) for 24 hours at 40 mm. pressure. The melting points of both samples then were determined at the same time using an electrically-heated melting point bath, equipped with a total immersion, calibrated Anschutz thermometer.

The comparative recoveries of recrystallized products from water and water-Aerosol OTB were determined by preparing saturated solutions at the boiling point. The solutions were filtered hot, and crystallization was permitted to occur as described in the above. The crystals from the water solution and the detergent solution were collected in tared, sintered-glass crucibles and washed with equal volumes of cold water. The crystals were dried over anhydrous calcium chloride to constant weights in a vacuum desiccator, and the amounts of recovered materials were determined. Small portions were then dried further in a drying pistol and melting points of the stock, of the water-recrystallized, and of the detergent-recrystallized samples were simultaneously determined as described in the above.

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