

composition on the curd phase boundary. If curd phase consisted of one or more definite hydrates these tie-lines would have had to converge to the points representing the compositions of the hydrates. In this connection it might also be mentioned that in an earlier paper McBain⁵ himself has commented on the fact that the water content of soap curd appears to vary continuously with the concentration of the electrolyte used to salt it out.

Summary

An isopiestic vapor pressure method has been developed which is suitable for studying soap systems at high temperatures and high soap concentrations where the usual methods based on ob-

servations of phase changes or analysis of phases are inapplicable due to non-separation of phases. By means of vapor pressure measurements in a pure single soap system at 90°, it has been demonstrated (a) that curd phase can exist in true reversible equilibrium with neat soap, and that the two are separate phases; (b) that no stoichiometric hydrates occur in the system at 90°, the curd phase varying continuously in water content.

The complete equilibrium diagram has been drawn for the system sodium palmitate-sodium chloride-water at 90°.

The formation and appearance of curd fibers have been described.

IVORYDALE, OHIO

RECEIVED JUNE 3, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Preparation of Some Higher Alkylglucosides

BY C. R. NOLLER AND W. C. ROCKWELL

The following records the preparation and some properties of *n*-hexyl-, *n*-octyl-, *n*-nonyl-, *n*-decyl- and *n*-dodecylglucoside. These compounds were synthesized in order to make available for physical-chemical investigations pure surface-active compounds of known constitution that have suitable solubility characteristics and do not ionize in aqueous solutions.

The method of synthesis was essentially that of Fischer and his co-workers,¹ namely, the condensation of acetobromoglucose with the appropriate alcohol and hydrolysis of the tetraacetyl derivative to the alkyl glucoside. One important change was made in the method of deacetylating the tetraacetates, namely, the replacement of hydrolysis using barium hydroxide or ammonium hydroxide by catalytic transesterification² with methyl alcohol and sodium methoxide. In this way the time of hydrolysis is greatly reduced and the isolation of the pure glucoside is simplified.

It will be noted from the tables that while the melting points of the tetraacetyl derivatives are fairly sharp, those of the alkyl glucosides especially from octyl up are over a very wide range. This was noted by Fischer and Helferich,¹ who stated

that they were unable to explain the phenomenon. We have noted that during a melting point determination the solid changed to a semi-transparent state at the lower temperature noted. On further raising the temperature little change took place until the higher temperature was reached when sharp melting to a clear liquid occurred. It appears to us that the lower temperature marks the transition from the solid to the liquid-crystal state and the higher temperature the transition from the liquid-crystal to the liquid state.

n-Hexylglucoside is very soluble in water and its aqueous solutions show little tendency to foam on shaking. As the length of the alkyl group increases the foam-producing ability is greatly increased, the nonyl-, decyl- and dodecylglucosides giving very stable foams. The solubility in water decreases, the dodecylglucoside being only sparingly soluble in cold water but readily in hot water. Cetylglucoside was reported by Fischer and Helferich¹ as being insoluble in water.

It was not determined whether these glucosides are hydrolyzed by emulsion but the work of Fischer and Helferich and the observed negative rotations would indicate that they are β -glucosides.

Experimental

Pentaacetylglucose and Acetobromoglucose.—When pentaacetylglucose was prepared according to the proced-

(1) Fischer and Raske, *Ber.*, **42**, 1465 (1909); Fischer and Helferich, *Ann.*, **383**, 68 (1911).

(2) Fischer and Bergmann, *Ber.*, **52**, 852 (1919); Zemlín and Paesli, *ibid.*, **62**, 1613 (1929).

ure of Fischer,³ using 100-g. quantities of glucose, charring took place due to the heat of the reaction. This was obviated by adding the glucose in portions of about 10 g. at such a rate that the temperature did not rise above 110°. Glucose hydrate may be used instead of the anhydrous glucose recommended by Fischer without changing the yield or quality of the product.

Considerable trouble was encountered in the preparation and storage of acetobromoglucose. Of the various procedures reported in the literature and modifications which were tried, the method of Freudenberg, Noe and Knopf⁴ gave the best results.

Tetraacetylalkylglucosides.—A mixture of 0.15 mole of the pure alcohol, 0.02 mole of acetobromoglucose, 200 cc. of absolute ether and 0.025 mole of freshly prepared, dry silver oxide⁵ in a tightly stoppered flask was shaken mechanically for two hours. At the end of this time a small sample gave no precipitate when tested with silver nitrate solution. The ether solution was filtered through a thin layer of diatomaceous earth on a Büchner funnel, the ether evaporated and the excess alcohol removed by steam distillation. Upon cooling the residue in the flask, the crude tetraacetylglucoside congealed and was filtered and crystallized from dilute aqueous methyl alcohol. The products frequently came down as a milky emulsion which crystallized on cooling in an ice-bath. The yields varied from 40 to 60% of the calculated amount. The properties and analyses of the individual compounds are given in Table I. The specific rotations were determined in methyl alcohol solution.

TABLE I
TETRAACETYLALKYLGLUCOSIDES

Alkyl radical	M. p., °C.	[α] ²⁰ _D	Saponification equivalent	
			Calcd.	Found
<i>n</i> -Hexyl	51–52.5	–22.4	108.1	106.7
<i>n</i> -Octyl	53–54	–21.7	115.1	116.5
<i>n</i> -Nonyl	39.5–40.5	–20.9	118.6	118.4
<i>n</i> -Decyl	47.5–48.5	–21.5	122.1	123.0
<i>n</i> -Dodecyl	58.5–59.5	–18.8	129.1	131.0

(3) Fischer, *Ber.*, **49**, 584 (1916).

(4) Freudenberg, Noe and Knopf, *ibid.*, **60**, 241 (1927).

(5) Helferich and Klein, *Ann.*, **460**, 225 (1926).

Alkylglucosides.—To a solution of 0.01 mole of tetraacetylalkylglucoside in 100 cc. of absolute methyl alcohol was added 2 cc. of a 0.1 *N* solution of sodium methylate in methyl alcohol. The solution was boiled for one-half hour under a reflux condenser protected by a calcium chloride tube and the methyl alcohol then removed under reduced pressure. The sirupy residue was taken up in hot ethyl acetate and on cooling in a freezing mixture the glucoside crystallized and was filtered and washed with petroleum ether. Considerable difficulty was encountered in crystallizing the crude glucosides since there was a tendency to separate as a gel. The dodecylglucoside crystallized best from water. The properties and analyses of the glucosides are given in Table II, the rotations being determined in methyl alcohol solution. The analyses for glucose were made by hydrolyzing the sample with dilute sulfuric acid and determining iodimetrically the amount of glucose formed. We are indebted to Mr. S. Kinsman for the rotations and analyses of the alkylglucosides.

TABLE II
ALKYLGLUCOSIDES

Alkyl radical	M. p., °C.	[α] ²⁰ _D	% glucose after hydrolysis	
			Calcd.	Found
<i>n</i> -Hexyl	88–91	–33.7	68.1	68.9
<i>n</i> -Octyl	65–99	–30.3	61.6	62.2
<i>n</i> -Nonyl	65–118	–28.8	58.8	58.3
<i>n</i> -Decyl	75–130	–27.8	56.2	56.3
<i>n</i> -Dodecyl	77–137	–24.7	51.7	51.2

Summary

n-Hexyl-, *n*-octyl-, *n*-nonyl-, *n*-decyl- and *n*-dodecylglucosides and their tetraacetates have been prepared in a pure state. Aqueous solutions of the glucosides from octyl through dodecyl foam on shaking but dodecylglucoside is only slightly soluble in cold water. These glucosides should be of value in physical-chemical investigations where a non-ionizing surface-active substance is desired.

STANFORD UNIVERSITY, CALIF. RECEIVED MAY 25, 1938