

# THE EFFECT OF GLYCERINE ON THE EQUILIBRIA OF HYDRATED SOAP SYSTEMS

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SOAP, as we understand the term today, presents so many singular aspects of complexity that it becomes possible, and in fact necessary, to study it from varying points of approach. One of the most fruitful techniques has grown out of the phase viewpoint which considers soaps, commercial or otherwise, as definite systems of matter in which definite soap phases distribute themselves in equilibrium with one another.

During the boiling of soap, the system in the kettle is usually regarded as one of three components, soap, water and electrolyte. Actually, of course, there are other components present, and there is one which has always been of considerable importance in the process because it is itself a by-product of that process. This component is glycerine. It forms during the "killing" or saponification and is present in varying amounts during each of the washes, strong change, graining changes, and pitches.

It has been customary since the days of Merklen to say that glycerine does not exert any very profound influence on the equilibria of the soap kettle, and in fact it is seldom present in amounts of more than about 5 per cent to 8 per cent of the total kettle system.

The influence of glycerine on the fields of stability of soap phases such as neat soap, middle soap and nigre is however still a matter of conjecture, although the soft potash soap and liquid soap processes often point to effects far more important than those encountered in the routine boiling of soda soaps. In neither the potash nor the soda soaps, however, has the influence of glycerine been adequately studied.

The present paper is concerned with glycerine and its effect on hydrated sodium tallow soap, both in the presence of and the absence of electrolyte.

## Experimental Method and Materials

The experimental method is essentially that described by Ferguson and Richardson.

All systems were prepared in

Ind. Eng. Chem. 24, 1329-36 (1932).

sealed pyrex tubes which could be held at constant temperature until equilibrium was attained. Thus in studying the system Tallow soap—H<sub>2</sub>O—glycerine weighed quantities of the three components were added to the tube, which, after sealing, was immersed in a thermostat at 90° C. When equilibrium resulted the phases present were noted and removed for analysis. From such results, Table I and the phases dia-

bichromate method.

*The System Tallow Soap—H<sub>2</sub>O—Glycerine—90° C*

In the first place the simplest system to be considered is made up of tallow soap—water and glycerine, at one temperature, 90° C. It would, of course, be possible to have a simpler system, namely soap and glycerine; but even though this system could be studied and graphically represented over a range of

TABLE I.  
The System: Tallow Soap-Glycerine-H<sub>2</sub>O; 90° C.

Total System	Top Layer			Bottom Layer		
	R.S.	Glyc.	H <sub>2</sub> O	R.S.	Glyc.	H <sub>2</sub> O
1 G.	10.0	90.0	0.0	Phases at Equil. 90° C.		
2 G.	20.0	80.0	0.0	Clear fluid nigre (30° firm transp. gel)		
3 G.	30.0	70.0	0.0	Clear fluid nigre (30° firm transp. gel)		
4 G.	40.0	60.0	0.0	38.3	61.7	0.0
5 G.	50.0	50.0	0.0	39.8	60.2	0.0
6 G.	60.0	40.0	0.0	Gummy middle soap		
7 G.	70.0	30.0	0.0	Neat-middle (stiff)		
8 G.	80.0	20.0	0.0	Solid and some neat (Powder), solid		
9 G.	90.0	10.0	0.0	(Powder), solid		
10 G.	68.0	4.4	27.6	Clear fluid neat (30° C. opaque solid)		
14 G.	68.0	7.6	24.4	Clear fluid neat, more vis. than 10 G. and 15 G.		
15 G.	68.0	10.0	22.0	Clear fluid neat less vis. than 14 G.		
17 G.	68.0	15.0	17.0	Clear fluid neat		
18 G.	68.0	20.0	12.0	Clear fluid neat		
19 G.	68.0	25.0	7.0	No separation of glycerine but mass is granular		
20 G.	20.0	20.0	60.0	Clear fluid nigre		
21 G.	25.0	20.0	55.0	Clear fluid nigre		
22 G.	30.0	20.0	50.0	39.6	18.8	28.7
23 G.	35.0	20.0	45.0	Middle-nigre		
24 G.	40.0	20.0	40.0	Middle-little nigre		
25 G.	45.0	20.0	35.0	Middle		
26 G.	50.0	20.0	30.0	Middle		
27 G.	55.0	20.0	25.0	Middle		
28 G.	60.0	20.0	20.0	Neat-middle		
29 G.	65.0	20.0	15.0	Neat-middle		
30 G.	28.3	71.7	00.0	Edge of Middle-Nigre Boundary		

gram No. 1 were constructed. Similar procedure was followed in the more complex system Tallow Soap—H<sub>2</sub>O—Glycerine—NaCl; 90°.

The method of preparation of the soap has been given in the earlier paper. The soap was made directly from tallow fatty acids of the following characteristics:

42.4 titre  
213 sap. value  
50.0 I. V.

The glycerine was double distilled anhydrous glycerine of 1.2600 gravity 25°. It was neutral to phenolphthalein in alcoholic solution.

Analytical soap methods were those previously described. Glycerine was determined by the

temperature it would be of limited practical interest because either the soap or the glycerine or both are invariably associated with water.

The diagram which follows (Figure I) represents all mixtures of tallow soap—glycerine and water at 90° C., and shows the phases which

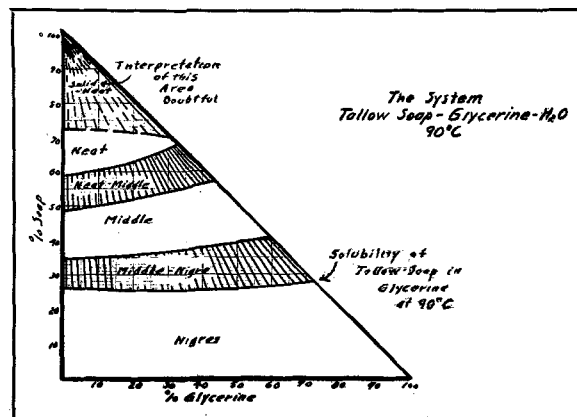


FIGURE 1

are present, and with what they are in equilibrium.

The diagram indicates clearly that no new phases are produced by glycerine. On the contrary it shows a remarkable similarity in the effect of glycerine on soap as compared to the effect of water on soap. At 90° if dry tallow soap is added to water a saturated solution or nigre is formed at a concentration of about 26 per cent soap, and the saturation phase is middle (or gum) soap. If dry tallow soap is added to glycerine the solution becomes saturated at 28 per cent soap and again the saturation phase is middle soap.

The solutions or nigrés which form all over the nigre area are homogeneous soap solutions, in water along the left boundary, in glycerine along the right boundary, and in glycerine-water mixtures elsewhere. Their properties differ in dependence on the composition. As an example, the nigrés along or near the right boundary (*i. e.*, low in water) are able to form transparent, rather rigid gels when cooled to room temperature while, nigrés along the left boundary (high in water, low in glycerine) when treated likewise form opaque masses. The influence of glycerine on soap equilibrium at lower temperatures is thus very marked, and the influence on transparency and gel rigidity is pronounced even in sodium soap systems.

The area of middle soap is somewhat more extended as the glycerine content increases, but neat soap is barely able to form at 90° when no water is present.

The upper portion of the diagram, labelled solid—neat, representing very concentrated systems with respect to soap, is drawn in dotted lines. The interpretation of this area is extremely difficult and

problematical. The extent of hydration of the solid form of soap, considered by McBain to be such

J. Chem. Soc. 119, 1374-83 (1921), as to yield definite hydrates, is in our opinion far from conclusively proven, and until further investigation either confirms or disproves this conception we prefer to indicate the upper area as doubtful.

Contrary to implications of earlier literature the diagram shows that

Handbuch Oel-Fette, Ubbelohde III, 2, p. 182, 186.

glycerine cannot salt out tallow soap into the usual soap equilibria, neat-nigre or neat-lye. In fact neat soap cannot exist in equilibrium with nigre or lye under any conditions in the present system containing glycerine, water and soap free from electrolyte. Glycerine behaves to

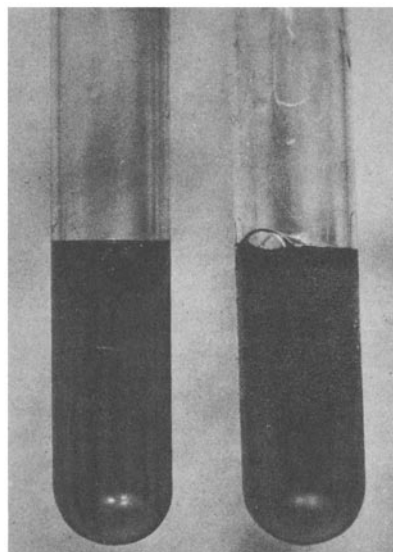


FIGURE 2

ward soap exactly as does water. Addition of either water or glycerine to neat soap produces first middle (or gum) soap, and finally nigre

or soap solution. The photograph, figure 2, represents separations of middle soap over nigre in the middle-nigre area along the right boundary. No water is present and the separations refer to nigrés made up of tallow soap dissolved in glycerine, in equilibrium with middle soap containing tallow soap and glycerine.

### The Effect of Glycerine on the Electrolyte Required to Salt Out Soap

The presence of glycerine in a soap system makes it more difficult to salt out the soap. Many years ago in kettle experiments Merklen showed that the limiting lye in-

Die Kernseifen, Ger. Trans. by Goldschmidt. Halle (1907).

creases in NaCl concentration when glycerine is present in the kettle.

In recent years Kawakami has confirmed Merklen's conclusions.

J. Soc. Chem. Ind. Japan. Oct., 1931, p. 398, series B.

As a result of his experiments Kawakami concludes that upon raising the glycerine content of a soap system from 0 to 5 per cent, the NaCl content of the limiting lye will increase from 2.5 per cent to 2.8 per cent.

In the work of Merklen and Kawakami the results were referred to changes in the concentration of the limiting lye. The present work has to do with the effect of glycerine on the neat-nigre boundary, that is to say, the effect of glycerine on the electrolyte required to salt out into neat soap over nigre.

In Table II and Figure 3 are shown the percentages of NaCl required to produce a separation of neat-nigre in a 25 per cent tallow soap-water solution at various tem-

TABLE III  
The System: Tallow Soap—Glyc.—NaCl—H<sub>2</sub>O; 90° C.  
Ratio  $\frac{\text{Glyc.}}{\text{Soap}} = .10$

No.	R. S.	Total System			Phases 90° C.	R. S.	Top Layer			
		Glyc.	NaCl	H <sub>2</sub> O			Glyc.	NaCl	H <sub>2</sub> O	% solution
30G	20.0	2.0	4.0	74.0	neat-nigre	63.4	...	1.36	...	...
31G	20.0	2.0	4.5	73.5	neat-nigre	61.2	.99	1.45	36.4	2.7
32G	20.0	2.0	5.0	73.0	neat-nigre-lye	63.9	.90	1.07	34.1	2.5
33G	20.0	2.0	6.0	72.0	neat-lye	65.2	.85	1.3	32.7	2.6
34G	20.0	2.0	7.0	71.0	neat-lye	64.3	.90	1.7	35.1	2.7
40G	20.0	2.0	9.0	69.0	neat-lye	62.8	.91	2.96	35.3	2.7
41G	20.0	2.0	12.0	66.0	neat-lye (curdy)	67.7	.80	3.36	28.6	2.8
42G	20.0	2.0	16.0	62.0	neat-lye (curdy)	67.6	.92	5.05	26.3	3.5
35G	50.0	5.0	1.5	43.5	neat-nigre	66.9	2.84	.20	30.1	..
36G	50.0	5.0	2.0	43.0	neat-nigre-lye	67.6	3.1	.98	28.3	11.0
37G	50.0	5.0	2.5	42.5	neat-lye	69.5	2.9	1.06	26.5	11.3
38G	50.0	5.0	3.0	42.0	neat-lye	70.7	2.4	1.2	25.7	9.4
39G	50.0	5.0	3.5	41.5	neat-lye	66.5	3.0	1.9	28.6	10.5
43G	50.0	5.0	4.5	40.5	neat-lye	67.6	3.0	1.95	27.5	10.9
44G	50.0	5.0	6.5	38.5	neat-lye	67.1	3.35	3.3	27.2	12.6
45G	50.0	5.0	10.0	35.0	neat-lye (curdy)	69.0	3.3	5.13	22.6	14.6

TABLE II

Tube	% Soap	% NaCl	% H <sub>2</sub> O	% Glyc.	Temp. at which neat-nigre forms. °C.
1...	25.0	2.5	72.5	0.0	81.0
2...	25.0	3.0	72.0	0.0	100.0
3...	25.0	3.5	71.5	0.0	129.0
4...	25.0	2.5	69.5	3.0	71.7
5...	25.0	3.0	69.0	3.0	92.8
6...	25.0	3.5	68.5	3.0	118.0
7...	25.0	2.5	66.5	6.0	62.0
8...	25.0	3.0	66.0	6.0	84.5
9...	25.0	3.0	65.5	3.5	109.5
10...	25.0	2.5	63.5	9.0	53.5
11...	25.0	3.0	63.0	9.0	71.0
12...	25.0	3.5	62.5	9.0	98.5

peratures in the presence of varying quantities of glycerine.

It is evident that the influence of glycerine, in quantities up to 9 per cent, is not very great although the NaCl concentration necessary to produce heterogeneity is definitely raised for each increase in glycerine content. At 100° C. the effect is such that an increase in glycerine content of 3 per cent raises the electrolyte needed for salting out by about .3 to .4 per cent.

It should be observed that the curves in Fig 3 denote also the temperatures at which, on cooling, a homogeneous nigre will be converted into a heterogeneous system of neat-nigre.

**The Distribution Ratio of Glycerine**

*The System, Tallow Soap—H<sub>2</sub>O—Glycerine—Na Cl; 90°C.*

When tallow is completely saponified with NaOH solution, a system is formed that contains soap, water, electrolyte and glycerine. The glycerine content of the system is related to the soap content approximately as 1:10.

Note: The ratio of glycerine to soap is constant in the total system no matter what the water content of the lye used for saponification or what the final dilution of the system at the end of saponification. Thus:

$$\frac{860 \text{ g. tallow} + 120 \text{ g. NaOH} \rightarrow 898 \text{ g. soap} + 92 \text{ g. glycerine}}{\text{glycerine}} = .103$$

This constant ratio makes it possible to

study a system of great practical interest which contains four components, but in which two of the components are held in unchanging proportion relative to one another. If no fractionation occurred, the system could be considered in its essential aspects as one of three components. Actually some fractionation of glycerine between the soap and the lye is known to take place, but it will be found that if the system is plotted in terms of soap, NaCl and water, that the compositions of the separated phases in general fall on a straight line through the total system.

Now if to various tallow soap—water solutions (containing 10 per cent glycerine relative to soap) increasing quantities of NaCl are added, it is possible to produce all of the equilibria involved in the soap boiling process. Accordingly, after phase segregations have occurred, the glycerine content of the phases can be determined and the distribution ratio calculated. The distribution ratio of glycerine between curded soap and lye has been determined by Kawakami.

J. Soc. Chem. Ind. Japan 34, 186-8 (1931).

His results apply to a limited range of salt concentrations and do not involve separations of nigre.

Bergell makes the statement that the proportion of glycerine in the water of the lye layer relative to the glycerine in the water of the soap layer is independent of the quantity of glycerine in the vessel, and in general is equal to 1.1.

Seif. Ztg. 61, 814-5 (1934).

In the present work tallow soap solutions containing 10 per cent

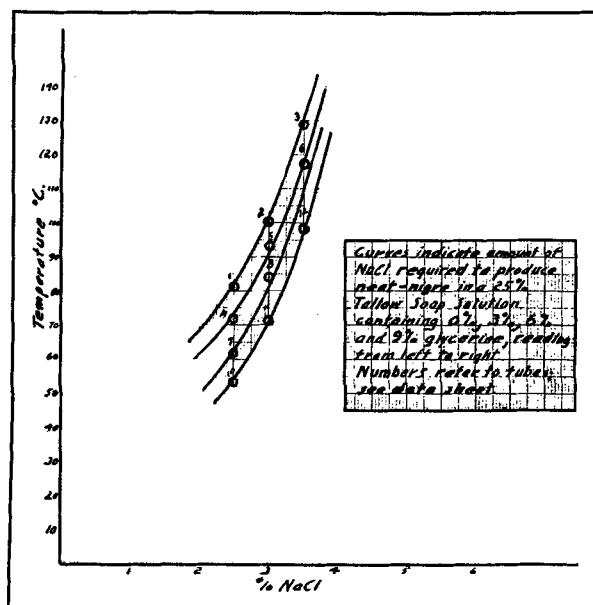


FIGURE 3

glycerine have been salted out with proper NaCl concentrations to produce not only the usual curdy soap over lye of the salt washes but the other equilibria of the kettle, namely, neat-nigre, neat-nigre-lye and neat-lye. Thus we have separations which enable a distribution ratio to be calculated over a wide range of salt concentrations. (Varying strengths of grain.)

Table III brings together the results.

The figures in columns 1 to 4 indicate the concentration required to salt out 50 per cent or 20 per cent tallow soap solutions into various phases. The glycerine, soap, salt and water contents of the phases are given in appropriate columns.

Two separate ratios have been calculated as follows:

$$a = \frac{\% \text{ glycerine in the soap rich layer}}{\% \text{ glycerine in the water rich layer}}$$

TABLE III—Continued  
The System: Tallow Soap—Glyc.—NaCl—H<sub>2</sub>O; 90° C.

Nigre Layer				Lye Layer				Ratio		Distribution Ratio, Glyc. in Soap / Glyc. in Lye
R. S.	Glyc.	NaCl	H <sub>2</sub> O	R. S.	Glyc.	NaCl	H <sub>2</sub> O	Glyc. in H <sub>2</sub> O of Lye	Glyc. in H <sub>2</sub> O of Soap	
11.4	1.95	4.7	81.9	...	...	..	...	...	...	..
8.7	2.67	5.4	83.2	...	...	..	...	1.18	1.27	.37
7.5	2.07	6.5	83.1	.09	2.9	6.7	91.3	1.27	3.3	.29
...	...	..	..	.10	2.95	7.9	90.0	1.22	3.3	.31
...	...	..	..	.09	2.9	7.15	87.9	1.11	3.0	.36
...	...	..	..	.13	2.54	12.1	85.2	1.11	3.1	.32
...	...	..	..	.11	2.5	15.5	81.9	.95	3.3	.35
...	...	..	..	.10	2.56	20.6	76.7	Ave. 1.15	...	.33
27.1	7.92	3.3	71.7	...	...	..	...	...	...	.36
...	...	..	..	.8	10.1	6.95	82.2	1.11	12.2	.31
...	...	..	..	.48	9.8	8.25	81.5	1.07	12.0	.30
...	...	..	..	.46	9.0	9.5	81.0	1.17	11.1	.27
...	...	..	..	.45	9.6	10.7	79.2	1.14	12.1	.31
...	...	..	..	.37	10.3	12.5	76.8	1.21	13.3	.29
...	...	..	..	.28	10.1	16.9	72.7	1.10	13.9	.33
...	...	..	..	.23	9.9	23.2	66.6	1.01	14.8	.33
...	...	..	..	...	...	..	...	Ave. 1.12	...	.31

$$b = \frac{\% \text{ glycerine in the water of the lye}}{\% \text{ glycerine in the water of the soap}}$$

Ratio—*a*—represents the true distribution ratio of the glycerine between the phases. In certain tubes the phases present are neat soap and nigre. The distribution ratio between these two phases is .36. When neat-nigre-lye is present, the distribution ratio between the neat and lye is .31 and this ratio holds for all strengths of electrolyte in the

layer. Thus no matter how "soft" the grain or how "hard" the grain the ratio remains fairly constant. It is likewise independent of the absolute amount of glycerine in the system, within the limits of the experiment, for an average ratio of .33 is found for the tubes contain 2 per cent glycerine at the start, and an average ratio of .31 for tubes initially containing 5 per cent glycerine.

The ratio—*b*—which refers to the glycerine in the water of the layers averages approximately 1.13. It varies somewhat from tube to which may be due to the fact that water was determined by difference and combined errors may center here. However, the results seem to show an approach to a ratio of about 1.0 as the electrolyte strength increases or as the soap becomes more grainy.

## THE CHARACTERISTICS OF KAPOK OIL

From the Laboratories of  
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By VIRGIL C. MEHLENBACHER

WITHIN the last half decade kapok oil has assumed such a position in the vegetable oil industry as to make further knowledge of its composition and characteristics most desirable. Information relating to the source of kapok oil is readily available in the literature, so that no further mention will be made of this. (1) Jamieson and McKinney recently reported an analysis of kapok oil, but in view of the fact that the total available information regarding the constants and characteristics of this oil is comparatively meager, it was thought best to proceed with a report of this investigation, which had already been begun. (2)

The sample of oil which was used for the analysis, in this case, represented a shipment into this country of several hundred tons from Japan. It was of normal character, comparing favorably in quality and similar in action and characteristics to several previous shipments which had been received. This lot of oil was classed as semi-refined as received, but was re-refined and filtered before analysis to insure the use of a purely refined product for the development of the analytical and physical data.

The chemical characteristics and physical constants of the glycerides are given in Tables I and II.

TABLE I

Free Fat Acids as Oleic (F.A.C.)	0.06%
Color Reading (F.A.C.—Lovibond)	
35 yellow	4.4 red
Color Reading (after F.A.C.)	
bleach) 20 yellow	1.5 red
Halphen Test (F.A.C.)	Positive
Besson Test (3)	Positive

Saponification Number (F.A.C.)	191.2
Iodine Number (Wijs—F.A.C.)	100.5
Thiocyanogen Number (F.A.C.)	70.95
Acetyl Value (F.A.C.)	26.8
Unsaponifiable Matter (F.A.C.)	0.53
Iodine Number of Unsaponifiable Matter (Wijs—F.A.C.)	42.8
Specific Gravity at 15° C. (Westphal)	0.920
Refractive Index (Zeiss Butyro @ 40° C.)	57.60

No crystals were obtained with acetic anhydride when using the AOAC alcohol extraction method for phytosterol.

The oil exhibited the normal degree of fluorescence which is almost characteristic for the so-called oriental oils.

From the iodine number and thiocyanogen value of the oil, the olein and linolein content was calculated, assuming, of course, the complete absence of other unsaturants.

The solid fatty acids were separated by the lead salt ether method (Twitchell Modified—F.A.C.) and calculated to the glycerides, using as the equivalent factor the value 95.5. The composition of the oil as indicated by these analyses is given in Table III.

TABLE III

	Per cent
Olein glyceride (calculated)	48.2
Linolein glyceride (calculated)	34.1
Solid glycerides (corrected)	
(Twitchell Modified—F.A.C.)	16.3
Unsaponifiable Matter (F.A.C.)	0.53

If the saturated glycerides are calculated from the values given above for unsaponifiable matter, olein, and linolein, a figure varying from the solid glycerides, as obtained by actual analysis, by 0.87

per cent, results. This is probably within the limits of the accuracy of the methods used. No attempt was made to isolate individual solid acids.

The fat acids were separated from the oil and the physical constants also determined on these. The data follow in Table IV.

TABLE IV

Titer (F.A.C.)	30.4
Refractive Index (Zeiss Butyro @ 40° C.)	45.40
Iodine Number (Wijs—F.A.C.)	102.2
Saponification Number (F.A.C.)	199.5
Melting Point (F.A.C.)	35.4° C.
Soluble acids as Butyric (A.O.A.C.)	0.7%
Insoluble acids (Hehner—A.O.A.C.)	94.3%

So far as we know, no one has made any report on attempts to refine kapok oil. Jamieson and McKinney have suggested that due to the smaller amount of non-oil constituents present in kapok oil than in cottonseed oil, correspondingly lower losses should result. (4) Our experience in the laboratory refining of many samples representing several hundred thousand pounds of kapok oil has indicated that equivalent results are easily obtainable, but we have not been able to prove any great superiority in this respect.

After considerable experimentation with the reactions of kapok oil in various methods of refining, two factors of importance were developed. An agitation period of greater duration than that required by regular hot pressed cottonseed oil was vitally necessary for a good "break" or separation of the saponified material, and extended high temperature agitation was most essen-