

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OREGON]

THE EMULSIFYING PROPERTIES OF GELATIN SYSTEMS

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That gelatin will act as an emulsifying agent is generally known, but extensive investigations of this property of gelatin have been very few. Holmes and Child,¹ in the study of emulsifying properties of gelatin, found that the maximum lowering of surface tension should be secured; that an excess of strong acids, bases or liquefying salt should not be added; and that the viscosity should not be greatly increased above that of water in order to obtain good emulsions. Working with kerosene-water emulsions, they did not find any convincing evidence that gelatin particles were withdrawn from the solutions to form adhesion layers about the oil droplets. Their conclusion was that the leading factor in an oil-water emulsion with the aid of gelatin is viscosity, not maximum, but the most favorable viscosity.

In this investigation it was desired to determine (a) how the emulsifying properties vary with the gelatin content, (b) the effect of P_H on the emulsifying properties of gelatin, and (c) the extent of the adsorption of gelatin in the interface of the emulsion.

Experimental Procedure

The gelatin used (U. S. Gelatin Company) was purified by first soaking in 1/128 molar acetic acid, then in distilled water, and finally electro-dialyzing until a minimum current flowed. The solutions were made more acid or basic as required with hydrochloric acid or sodium hydroxide. The P_H of the resulting solutions was measured electrometrically.

Emulsions were made with 5 cc. of the gelatin solution and 10 cc. of the immiscible liquid in a test-tube. Tubes with a diameter of 2 cm. were used for the study of the influence of P_H , whereas tubes with a diameter of 3.5 cm. were used in the study of the influence of concentration of the gelatin. Because of the influence of the vessel on the emulsion process, this accounts for the fact that values from Table I do not coincide with those given in Table II. The tubes were stoppered and placed in a shaking machine for one hour, at the end of which time they were removed, given 100 shakes by hand, and set aside. Readings were taken from time to time showing the amount of stable emulsion remaining.

Experimental Results

Effect of Concentration of Gelatin.—The concentrations of the gelatin used varied from 0.25 to 1.5%. Experiments were carried out by mixing these gelatin solutions with eight different liquids in the manner described above. These liquids were ethyl acetate, *n*-butyl alcohol, ether, benzene, nitrobenzene, chloroform, carbon tetrachloride and cottonseed oil. The first three did not form emulsions.

Emulsions were also made using gelatin adjusted to P_H 3, and to P_H 6

¹ Holmes and Child, *THIS JOURNAL*, **42**, 1049 (1920).

with the same concentration range of gelatin. The results are given in Table I.

TABLE I
PERCENTAGE STABILITY OF EMULSIONS *vs.* CONCENTRATION OF THE GELATIN

Emulsion	PH of the gelatin	Concentration of gelatin, %					
		0.25	0.5	0.75	1	1.25	1.5
Benzene-water	3.0	20	87	87	100	93	87
	4.7	87	88	87	93	99	95
	6.0	92	94	92	93	97	97
Carbon tetrachloride-water	3.0	0	85	87	90	94	90
	4.7	88	90	93	100	100	100
	6.0	83	83	83	83	87	82
Chloroform-water	3.0	13	73	73	87	90	87
	4.7	87	88	94	97	87	87
	6.0	24	88	88	90	90	87
Nitrobenzene-water	3.0	0	77	26	80	80	53
	4.7	93	94	94	97	97	94
	6.0	77	80	80	87	97	84
Cottonseed oil-water	3.0	80	83	83	67	97	93
	4.7	60	60	60	60	87	60
	6.0	93	93	93	93	93	93

TABLE II
PERCENTAGE STABILITY OF EMULSIONS *vs.* PH OF GELATIN

Emulsion	% Gel.	Time after shaking	PH								
			1.8	2.2	3.1	4.7	5.8	6.4	9.1	10.9	11.2
Chloroform-water	1	1 hour	70	73	67	60	54	57	60	17	3
		3 weeks	20	33	47	53	42	53	63	15	0
Carbon tetrachloride-water	1	1 hour	77	80	27	40	50	60	67	73	14
		3 weeks	33	60	0	26	40	46	53	60	10
Benzene-water	1	1 hour	13	15	17	93	93	43	86	80	74
		3 weeks	3	3	7	80	80	34	74	70	53
Nitrobenzene-water	1	1 hour	0	87	17	24	22	4	20	92	6
		3 weeks	0	80	10	20	18	0	17	87	3
Cottonseed oil-water	1	1 hour	90	93	93	93	93	92	93	93	100
		3 weeks	0	0	0	21	20	24	27	30	100
Chloroform-water	0.5	1 hour	10	30	15	93	87	88	7	87	90
		3 weeks	3	14	5	53	30	50	0	47	60
Carbon tetrachloride-water	0.5	1 hour	3	5	17	100	10	17	13	93	30
		3 weeks	0	0	13	96	2	10	7	80	25
Benzene-water	0.5	1 hour	73	73	44	90	90	23	37	84	93
		3 weeks	33	47	20	87	87	17	33	53	80
Nitrobenzene-water	0.5	1 hour	0	0	8	10	7	10	10	8	7
		3 weeks	0	0	3	3	3	5	5	3	5
Cottonseed oil-water	0.5	1 hour	77	80	94	94	94	94	94	94	97
		3 weeks	0	0	0	7	10	10	14	14	12

Effect of P_H .—The results obtained for the influence of P_H on the emulsifying properties of gelatin are given in Table II. It is to be noted that practically all the experiments show a good stability near the P_H of the dialyzed gelatin, with a minimum and a maximum on each side. Near a P_H of 1 or of 12 there is a second drop in emulsifying properties and beyond this the gelatin loses its emulsifying properties. This effect is not shown in all of the experiments but is shown for at least one concentration of gelatin with each substance.

Cottonseed oil did not give a good emulsion in the 0.5% solutions, even with the most basic solution. In the 1% solution the emulsions were poorest at the most acid and the best at the most basic points.

The Adsorption of Gelatin at the Interface.—In order to determine the extent of adsorption of gelatin at the interface of the emulsions, analyses of the aqueous phase before emulsification were compared with analyses of the first few cc. of aqueous phase that separated from the emulsion as it started to break down. The micro-Kjeldahl method for nitrogen in proteins was used to determine the gelatin content. The results are shown in Table III. It is to be observed that gelatin had been removed from the aqueous phase and concentrated at the interface in the emulsions of carbon tetrachloride, chloroform and benzene with gelatin solutions at P_H 4.72. These emulsions were stable at the end of one hour after shaking. The chloroform emulsion with gelatin solution at P_H 8.13, and the carbon tetrachloride emulsion with gelatin solution at P_H 2.25 were not stable, and Table III shows that there was no adsorption of gelatin at the interface of these emulsions. Apparently gelatin will serve as an emulsifying agent only when conditions are such as favor adsorption at the interface.

TABLE III
REMOVAL OF GELATIN FROM 0.5% SOLUTIONS TO INTERFACE OF EMULSIONS

Solutions analyzed	P_H	% Stability at 1 hour	N in 1 cc. of solution, mg.	Gelatin removed, %
Original	4.72	..	0.8370	..
From carbon tetrachloride	4.72	100	.7786	6.9
From chloroform	4.72	93	.6470	22.6
From benzene	4.72	90	.7299	12.8
Original	8.13	..	.9231	..
From chloroform	8.13	7	.9399	-1.7
Original	2.25	..	.8803	..
From carbon tetrachloride	2.25	0.5	.9058	-2.8

Discussion of Results

In the use of gelatin as an emulsifying agent for oil-water systems, it was found that the concentration of the gelatin between 0.25 and 1.5% at P_H 3, 4.7 and 6 was of little influence on the stability of the emulsion. The outstanding exception to this generalization was found in the case of

0.25% gelatin at P_H 3, where the stability of four of the five emulsions was greatly decreased.

Examination of Table II showing the influence of P_H on emulsifying properties of gelatin solutions shows that if P_H of the gelatin solution is near the isoelectric point stable emulsions are formed. Addition of acid results in less stable emulsions at P_H of about 3, another point of increased stability near 2.5 with a sharp drop when the P_H is further decreased. Addition of alkali results in a sharp decrease in stability near P_H of 6 with a maximum near P_H of 10, and another decrease when P_H rises above 11.

The factors which are generally considered important in the process of emulsification are: (1) mechanical treatment, (2) volume composition, (3) relative densities, (4) character of the walls of the container, (5) viscosity of the components and (6) the interfacial tension. In the experiments carried out the first four of these were kept as constant as possible, so that differences in stability of emulsions formed were probably due to changes in viscosity and interfacial tension. That such is the case can be seen from a comparison of the results obtained with curves showing the relation between viscosity of gelatin solutions and P_H^2 and surface tension *vs.* P_H .³

It is not to be expected that the maximum and minimum stabilities for one combination should exactly coincide with any other, for the nature of the interface is different in each case.

Summary

1. The emulsifying properties of gelatin for oil-water emulsions have been studied with reference to concentration of gelatin, P_H of gelatin solution, and the possible adsorption of gelatin at the interface.

2. It has been found that variation of concentration between 0.25 and 1.5% has little effect at P_H 3, 4.7, 6.

3. Changing the P_H of the gelatin solution affects the emulsifying properties of the gelatin in a manner closely related to the changes of surface tension and viscosity of gelatin solutions with P_H .

4. It has been found that whenever stable emulsions were formed, gelatin was concentrated at the interface.

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² Elmer O. Kraemer, "Colloid Symposium Monograph," 1926, Vol. IV, 102.

³ J. H. St. Johnston and G. T. Peard, *Biochem. J.*, **19**, 281 (1925).