

most instances, the glass formed on replacement is not stable. In some cases, the glass is completely disintegrated and in others the glass cracks on cooling. Sodium may be replaced by silver to a depth of approximately 0.1 mm. without cracking.

2. On replacing sodium by silver under the action of a potential, a sharp boundary is formed between the sodium and the silver ions. From the rate of motion of the boundary, the speed of the ions under a unit potential gradient has been determined. The speed of the ions increases greatly with increasing temperature, corresponding to the increased conductance of the glass with increasing temperature.

3. The fraction of the total sodium present in the glass, which takes part in the conduction process, has been determined from the depth of penetration of the boundary and from the amount of electricity passing, as well as from the change in the weight of the tube. It has been found that from 74% to 82% of the total sodium present in an ordinary soda-lime glass takes part in the conduction process. The remainder of the sodium is either not in a charged state or otherwise the ions are held in fixed position. The fraction ionized, as defined in this way, increases slightly with the temperature between 278° and 343°.

4. The results obtained are discussed and some inferences are drawn relative to the nature of rigid substances of the electrolytic type.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY, No. 152]

## THE INTERFACIAL TENSION BETWEEN GELATIN SOLUTIONS AND TOLUENE<sup>1</sup>

BY S. E. SHEPPARD AND S. S. SWEET

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In a technical paper<sup>2</sup> on "Colloidal Fuels" one of the authors made a suggestion as to the emulsoid colloid state, which was developed more fully in a letter to *Nature*.<sup>3</sup> The essential feature of the hypothesis put forward was that the micelles, or multimolecular units of such colloid systems, are formed, and their growth and aggregation determined by "the orientation of definite atom groups, entirely in the sense of the theory of molecular orientation due to structure proposed for surface and interfacial tension phenomena by W. B. Hardy,<sup>4</sup> W. D. Harkins<sup>5</sup> and I. Langmuir."<sup>6</sup>

<sup>1</sup> Paper read at the Birmingham meeting of the American Chemical Society, April, 1922.

<sup>2</sup> Sheppard, *J. Ind. Eng. Chem.*, **13**, 37 (1921).

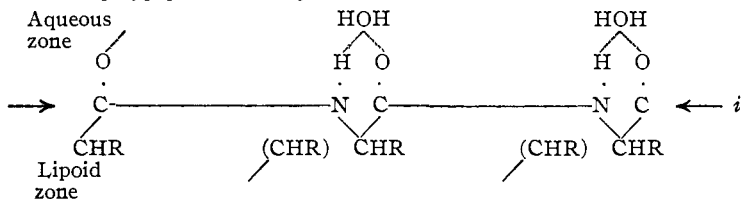
<sup>3</sup> Sheppard, *Nature*, March 17, 1921, p. 73.

<sup>4</sup> Hardy, *Proc. Roy. Soc.*, **81A**, 610 (1912).

<sup>5</sup> Harkins, Davies and Clark, *This Journal*, **39**, (a) 354, (b) 541 (1917).

<sup>6</sup> Langmuir, *ibid.*, **39**, 1848 (1917).

"The genesis of a micelle, as multimolecular unit of a colloid system, may be regarded as a consequence of equilibrium, usually incomplete, between homochemical solution forces and heterochemical forces, the former tending to dissociate and decompose the chemical molecule, the latter resisting decomposition. In the case of proteins the most probable general type of linkage, according to H. A. Plimmer<sup>7</sup> is of the form,  $\text{NH}_2\text{CHR}\cdot\text{CO}\cdot(\text{NH}\cdot\text{CHR}\cdot\text{CO})_n\cdot\text{NH}\cdot\text{C}(\text{COOH})\text{HR}$ , when  $n$  refers to the degree of polypeptide condensation and R is an alkyl or other substituent group. On the hypothesis suggested here we may, imperfectly, represent the redistribution of this in the presence of water for the polypeptide chain by



In this the arrows indicate the direction of an imagined plane or infra-molecular interface  $i$  separating the hydrophilic groups  $\begin{matrix} \text{C}-\text{N} \\ \cdot \cdot \\ \text{O} \text{ H} \end{matrix}$  which are consolute with water (in virtue of residual affinities tending to complete the amino and carboxyl groups), from the hydrophobe or hydrocarbon groups,  $-\text{CHR}$ . Not only in a single protein molecule, but also to a variable extent between molecules, we may admit that this primary orientation leads to mutual attraction between water-soluble and water-insoluble groups, respectively. Without any actual cleavage of the molecule, we have orientation and a straticchemical field of force which is of a similar character, in essence, to crystallization, but results in incomplete instead of complete equilibrium. The hydrocarbon or lipid atom groups will approach the fluid or the solid state according to molecular weights and constitution; hence, the system may be likened, in one aspect, to a sub-molecular emulsion, the lipid groups tending to form interconnected sheets of atom groups necessarily permeable to water and water solutes, although mechanically developing a stress resisting rupture in virtue of the fields of attraction and repulsion induced. The micelles are the smallest multimolecular units thus built up."

The following brief survey indicates the present status of the question. A somewhat destructive criticism of the foregoing hypothesis by Dr. J. W. McBain<sup>8</sup> was shortly followed, in the same journal<sup>9</sup> by N. K. Adam's observations on monomolecular films of palmitic acid on water and aqueous alkali solutions. They confirmed the theory of the orientation of soap molecules in surfaces and micelles, suggested by Harkins, Davies and Clark.<sup>5</sup> Further, the structure of the soap micelle proposed by Adam was quite in accord with Sheppard's suggestion that orientation determined the growth of the micelle. More recently, J. Loeb<sup>10</sup> has explained the stability of protein solutions and the difference between gel formation and precipitation by reference to an orientation hypothesis of the protein molecule. Loeb's "watery" groups and "oily" groups correspond, respectively, to the "hydrophilic" and "hydrophobe" or "hydrocarbon" groups of Sheppard's note. Finally, it may be noted that E. J. Witzemann,<sup>11</sup> in an interesting paper considers

<sup>7</sup> Plimmer, "Chemical Constitution of the Proteins," Longmans, Green and Co., 1912, vol. II, p. 2.

<sup>8</sup> Ref. 3, p. 74.

<sup>9</sup> Adam, *Nature*, 107, 286 (Apr. 28) (1921).

<sup>10</sup> Loeb, "Proteins and the Theory of Colloidal Behavior," 1922, p. 283.

<sup>11</sup> Witzemann, *J. Phys. Chem.*, 26, 201 (1922).

that orientation at surfaces, as shown by soaps, is of less importance for proteins and polysaccharides. Generally, however, his argument supports a chemical view of the biocolloids.

Whatever the increased consideration gained for the hypothesis by these contributions, it remains actually a working hypothesis, to be tested by definite consequences capable of experimental verification. These consequences reach in two directions—on the one hand, the behavior of emulsoid colloids toward their thermodynamic environment;<sup>12</sup> on the other, fundamental chemical changes (oxidation-reduction, substitution, etc.). On the first count, the surface and interfacial tensions of emulsoid colloids are of particular interest. It is known that when weak solutions of gelatin are shaken with immiscible solvents such as benzene, gasoline, toluene, etc., gelatin, still considerably hydrated, tends to be precipitated and aggregated as an interfacial layer.<sup>13</sup>

It appeared desirable to investigate this more fully, in particular as a function of hydrogen-ion concentration. The properties of gelatin as an emulsifying agent for kerosene have been studied by H. N. Holmes and W. C. Child<sup>14</sup> in relation to (a) the surface tension of the gel-oil interface, (b) determination of whether or not gelatin is absorbed to form a concentration layer around the oil droplets, and (c) viscosity of the solution. The present investigation, while not at variance with their results, shows that in such studies the hydrogen-ion concentration may be a determining factor. This is to be expected, but the relation of the property to hydrogen-ion concentration in the present case is somewhat different from those instanced by Loeb and others. It will be remembered that in the cell protoplasm we have a complex lipid-protein interface, so that the property in question is physiologically important, as also industrially, in relation to certain processes for preparing glue and gelatin.

## Experimental

### Shaking Out: Foam and Emulsion Stabilities

The gelatin used for these experiments was an ash-free iso-electric gelatin, relatively free from hydrolysates; it was prepared by a method described in a paper "The Elasticity of Purified Gelatin Jellies as a Function of Hydrogen-ion Concentration."<sup>15</sup>

The adjustment of the hydrogen-ion concentration, when changed from the iso-electric value, was effected with hydrochloric acid on the acid side and sodium hydroxide on the alkaline side. The shaking experiments were made in a water thermostat controlled to 0.1°, the bottles

<sup>12</sup> On the orientation theory, their electromagnetic environment.

<sup>13</sup> Winkelblech, *Z. angew. Chem.*, **18**, 1953 (1906). See also W. Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 260.

<sup>14</sup> Holmes and Child, *THIS JOURNAL*, **42**, 2049 (1920).

<sup>15</sup> Sheppard, Sweet and Benedict, *THIS JOURNAL*, **44**, 1857 (1922).

being rotated at 120 r.p.m. and containing a weighed amount of glass beads. Preliminary experiments at 30° with 1.0, 0.1 and 0.01% concentration of gelatin, in which 50 cc. was shaken with an equal volume of benzene (redistilled, b. p. 80.3°), showed that a foam or cream of hydrous gelatin separated in the benzene layer just above the gelatin solution, but that the formation of this seemed to depend considerably upon the presence of air. The relative volumes of the phases are given in the following table.

TABLE I

Temp.	SHAKING EXPERIMENTS								
	30° gelatin			40° gelatin			50° gelatin		
	%	%	%	%	%	%	%	%	%
	1.0	0.10	0.01	1.0	0.10	0.01	1.0	0.10	0.01
Aqueous layer....	40	45	50	30	45	50	40	40	45
Benzene.....	0	5	40	10	30	40	0	40	45
Cream.....	60	50	10	60	25	10	60	20	10

The "cream" or interfacial layer consists of benzene dispersed in (and protected by) hydrous and aerated gelatin, and is partly a stabilized foam.

TABLE II

## STABILITY OF GELATIN FOAMS

Temp. $P_H$	30°		40°	
	Foam Cc.	Half period Sec.	Foam Cc.	Half period Sec.
1.29	40	45	25	30
3.80	40	50	25	45
4.34	40	75	30	90
4.58	40	150	30	120
4.78	40	180	35	150
4.82	60	180	40	180
4.87	70	300	35	180
5.00	70	300	40	180
5.10	70	300	40	150
5.20	50	300	35	90
5.39	40	240	30	60
7.60	40	150	25	60
10.30	35	90	30	45
12.20	40	60	30	30

On taking precautions to keep out air (using toluene in place of benzene), boiling out the solutions and the toluene prior to sealing,<sup>16</sup> it was found possible to shake the liquid without much separation of the gelatin in the toluene, although considerable toluene was emulsified in the gelatin solution.

<sup>16</sup> Narrow-mouthed glass-stoppered bottles were used; they were sealed first with gelatin and over this with sealing wax. Glass tubes nearly always cracked.

An investigation was then made of the stability of a gelatin-air foam as a function of hydrogen-ion concentration. Using 1.0% solutions of the ash-free gelatin, measurements of the hydrogen-ion concentration were made electrometrically, at 30° and 40° after the gelatin solutions had been heated for 30 minutes at 70°. Fifty cc. of each solution was shaken for 2 minutes in a stoppered graduated cylinder, then the volume of foam was read immediately and the time taken for this to fall to one-half. The results are given in Table II and Fig. 1.

It is evident from this that the foam is most stable in the region of the iso-electric point; that is, at this point the reduction of the surface tension of water-air by gelatin is greatest.

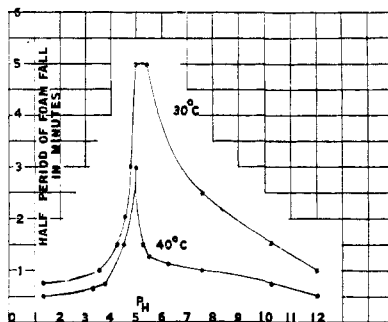


Fig. 1.

### Drop-number Experiments with Toluene

The interfacial tension between gelatin solutions, of varying hydrogen-ion concentration and toluene was determined by measuring the drop number of the gelatin solution falling through the toluene from a Traube stalagmometer. Harkins, formula<sup>17</sup> and tables were used to compute the

interfacial tension  $T$  in dynes. According to this,  $T = \frac{(M-m)g}{2\pi r \psi \left(\frac{r}{\sqrt{1/3}}\right)}$

where  $r$  is the radius of orifice,  $g$  the gravity,  $M$  the mass of drop,  $m$  the mass displaced by drop,  $\psi$  = function tabulated by Harkins. The accuracy obtained in this way was not high, the probable error on the value of  $T$  being from 1 to 2%. But, even using the specially purified gelatin described, the reproducibility of this material is at present of lower order than this. Hence, there would be no point in striving for the precision possible by the drop-weight method with pure chemical substances.<sup>5b</sup> The tables of data are omitted and the results given in the form of curves. In Figs. 2 to 5 are shown the values of the drop numbers in toluene, of water and 1.0% gelatin solution, respectively, as a function of hydrogen-ion concentration (Sørensen values).

The measurements were made at temperatures of 30°, 35°, 40° and 50°; after the solutions had been kept at these temperatures for the times indicated in the figures. The whole stalagmometer was jacketed, and the temperature maintained constant by circulating water from the thermostat.

<sup>17</sup> Harkins and Brown, THIS JOURNAL, 41, 518 (1919).

It will be seen that all the curves for gelatin lie above the water curve for the same temperature but have a somewhat similar outline; thus, the strongly acid and strongly alkaline solutions  $2 < P_H > 10$  show rapid increase in the drop number (or rapid decrease of the interfacial tension),

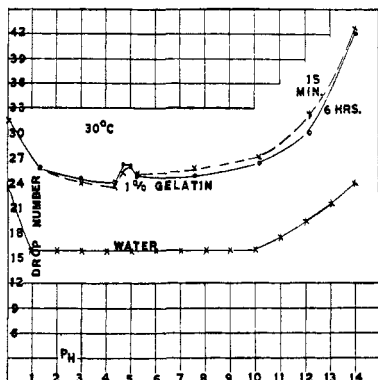


Fig. 2.

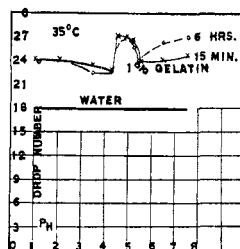


Fig. 3.

while between these limits the value varies not at all with water, with gelatin in a manner to be discussed.

As regards the marked change outside  $2 < P_H > 10$ , it must be remembered that these solutions are becoming, respectively, conc. solutions of hydro-

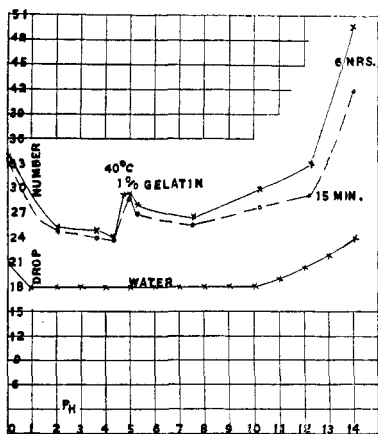


Fig. 4.

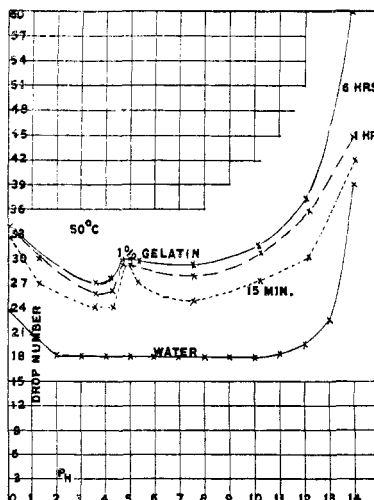


Fig. 5.

chloric acid, and sodium hydroxide. How far the phenomena with water alone at these limits are affected by traces of impurities was not ascer-

tained in these experiments, but the reproducibility was sufficient to exclude the possibility of casual contamination.<sup>18</sup>

All the gelatin-containing solutions show a characteristic "kink" or break in the region of the iso-electric point, the maximum reduction of interfacial tension (see Fig. 6) being at  $P_H$  4.8. Further, also differing from the plain water systems, there is a change with time, and this time process alters progressively with temperature. At 30°, while there was found but little change between 15 minutes and 6 hours on the acid side, on the alkaline side there was a slight increase of interfacial tension. At 35° this change was in the opposite direction, while at 40° and 50°, although there was little change noted at the iso-electric point, on both the acid and alkaline sides there was a noticeable decrease of interfacial tension with time, becoming greater with rising temperature.

It is possible that the slight regression at 30° is of the same character as the viscosity increase with time at such temperatures, noted by Davis and Oakes<sup>19</sup> and considered by them to be evidence of a transition point between sol and gel forms. A more complete study of the time factor is required before its bearing upon this question can be stated. The progressive changes at 40° and 50° are most probably evidence of hydrolysis of the gelatin. As such they do not appear to be in good agreement with the results of J. H. Northrop<sup>20</sup> who found the velocity of hydrolysis of gelatin between  $P_H$  2 and  $P_H$  10 to be approximately constant. Northrop, however, followed the complete hydrolysis chemically, as increase of uncombined amino or carboxyl groups, by formol titration. It is possible that the change of physical properties does not run entirely parallel with

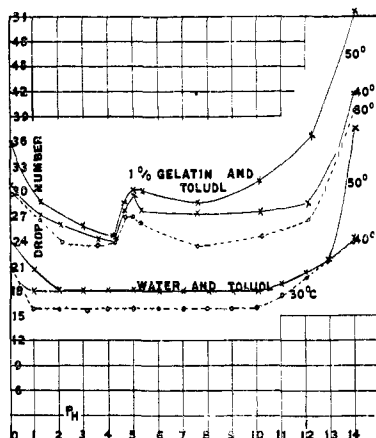


Fig. 6.

<sup>18</sup> Harkins and Humphrey [THIS JOURNAL, 38, 242 (1916)], studying the effect of acids, bases and salts on the interfacial tension of aqueous solution-benzene, found for HCl and H<sub>2</sub>SO<sub>4</sub> values increasing very slightly with concentration up to 1 equivalent per liter. Reducing their concentrations, from ionization data, to  $P_H$  values, we find  $T=34.18$  for  $P_H=7$  to  $T=34.23$  for  $P_H=1.0$ , for HCl:H<sub>2</sub>O. With regard to NaOH and KOH, they state: "These bases lower the surface tension slightly, and the results obtained at any one time, when the same solution of the base is used, agree well, but when different solutions of the base are used, or when the solution has been allowed to stand for some time the results vary."

<sup>19</sup> Davis and Oakes, THIS JOURNAL, 44, 464 (1922).

<sup>20</sup> Northrop, J. Gen. Physiol., 3, 715 (1921).

this.<sup>21</sup> Also, in the experiments referred to, Northrop maintained the hydrogen-ion coefficient sensibly constant throughout the hydrolysis.<sup>22</sup> The outstanding decrease of interfacial tension to toluene at the isoelectric point is in agreement with the hypothesis discussed in the earlier

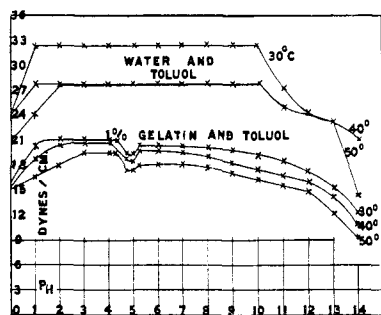


Fig. 7.—Interfacial tension.

part of the paper, since the polar groups of the gelatin molecule would be least active at this point, and the presentation of these in the surface reduced.

There remain two results not obviously in agreement with orientation theories. First, there is the rapid decrease of the interfacial tension of the gelatin solutions for  $1 < P_H > 10$ . But, this effect was also shown by the straight aqueous solutions, as already noted, and requires further investigation on its own account.<sup>23</sup> Second, there is the

decrease of  $T$  with time, supposedly due to hydrolysis. Since the hydrolysis tends to increase the number of free polar groups, it would seem that it should increase the interfacial tension to toluene. But at the same time, as shown by viscosity data, the breakdown of the molecule goes with a reduction of aggregation. Just as the interphase film of palmitic acid on alkaline solutions<sup>9</sup> breaks down into aggregates probably having hydrocarbon chains in the center and carboxyl groups on the surface, so we may suppose that with gelatin solutions on hydrolysis either with acid or alkali, the dispersity is increased, in the sense that the intramolecular networks or films<sup>24</sup> formed by coalescing lipid atom groups would be broken down, and aggregates formed having these groups in the center

<sup>21</sup> An investigation on viscosity, to be published, shows a similar result.

<sup>22</sup> Direct measurements by the electrometric method, gave the following results, for the change of Sørensen values of 1% ash-free gelatin under the conditions of our experiments.

Original $P_H$	After 6 hours at 40°	After 6 hours at 50°
2.00	2.02	2.04
4.91	4.98	...
4.87	...	4.90
11.02	11.09	...
11.40	...	11.40

These solutions were *not* buffered, and the results show that variation of hydrogen-ion concentration was insignificant over the time considered and at the temperatures in question.

<sup>23</sup> See Ref. 5. Strictly, therefore, its bearing on the orientation theory awaits complete explanation of the cause of this effect.

<sup>24</sup> Extended in 3 dimensions, instead of 2 only.



and polar groups ( $-\text{NH}_3^+ \dots$  or  $-\text{COO}^- \dots$ ) on the surface; but the more this progressed, that is, the smaller these aggregates, the greater becomes the ratio of surface to volume, so that the attraction of the toluol for the lipid atom groups could come increasingly into play, resulting in the decrease of  $T$  observed.

The great sensitivity of interfacial tension of gelatin in the immediate neighborhood of the iso-electric point appears of some importance in regard to the physical chemistry of muscular motion. Harkins, Davies and Clark<sup>5</sup> considered from their experiments on the benzene-water interface that change of hydrogen-ion concentration would be insufficient to produce changes of interfacial tension accounting for muscular movement;<sup>25</sup> but the depression of interfacial tension at the iso-electric point of gelatin and hence, presumably, of other proteins, affords the type of change required.

#### Summary<sup>26</sup>

1. The relation of the orientation of specific atom groups in the molecule to the emulsoid colloid state is discussed.
2. The separation of gelatin at a benzene-water interface was investigated, and found to be affected by presence of air.
3. The stability of gelatin-air foam was found to be greatest at the iso-electric point.
4. The interfacial tension between aqueous gelatin solutions of various hydrogen-ion concentrations and toluene was measured. The lowering of the tension by gelatin increases rapidly at the iso-electric point. Secondary phenomena due to hydrolysis were observed.

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<sup>25</sup> In a later paper, Harkins and Ewing [THIS JOURNAL, **41**, 1977 (1919)] noted that there is a rapid change of surface tension near the neutral point when certain polar groups are present. This was found with dichloro-ethyl sulfide (mustard gas) and chloroform.

<sup>26</sup> *Addendum*.—After this paper had been prepared for publication we received *Proc. Roy. Soc.*, **101A**, July 1, 1922, containing a paper by H. Hartridge and R. A. Peters on "Interfacial Tension and Hydrogen Ion Concentration," p. 348. This investigation did not cover gelatin but, in agreement with our results on toluene, they found the interfacial tension between water and benzene to be unaffected by hydrogen-ion concentrations between  $P_{\text{H}}$  5.6 and 7.4. Their general conclusions are in harmony with those of our paper. Our attention has also been called, by Dr. Arthur B. Lamb, to papers by V. Bermann, and W. Windisch and V. Bermann, in *Wochschr. Brauerei*, **36**, 319 (1919) and **37**, 109, 153 (1920) on "Conditions requisite for head-formation by beerwort," to which, however, we have not yet had access.