

285. *Ionic Interchange in Stearic Acid Sols and the Mechanism of Coagulation.*

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ACHAR and USHER (J., 1927, 1875) have shown that, when a colloidal suspension of stearic acid is treated with a neutral salt, acid appears in the intermicellar liquid. Their observations indicate that the effect is due to the displacement, by the salt kations, of hydrogen ions produced by the ionisation of the surface molecules of the stearic acid particles. In the present investigation the influence of the nature of the salt kation, and of other factors, upon the degree of this ionic interchange has been studied, in particular with reference to the influence of electrolytes upon the stability of the sol. The coagulating power of a salt is found to be closely correlated with the tendency of the kation to displace hydrogen ion, and the results support the view that the interchange is of primary importance for a general theory of coagulation (cf. Verwey, *Chem. Reviews*, 1935, **16**, 363).

EXPERIMENTAL.

Colloidal Stearic Acid.—The sols were prepared by Mukherjee's method (*J. Mysore University*, 1935, 4984). Stearic acid (m. p. 69.4°) was obtained by double recrystallisation of "specially pure" material (B.D.H.) from methyl alcohol, the product being dried over phosphoric oxide. Methyl alcohol was treated with magnesium turnings and fractionated, the product being neutral to litmus. 2.4 G. of stearic acid in 200 c.c. of alcohol were added to

700 c.c. of boiling conductivity water. The resulting sol was freed from alcohol by further heating, and filtered to remove coarse particles. The concentrations of the sols, found by drying to constant weight, were :

Sol.....	A	B	C	D	E
G. per litre	1.36	2.25	2.07	2.41	2.26

When the sol was boiled, the stearic acid gradually coarsened, and collected at the surface of the liquid. This accounts for the low concentration of sol A, which was boiled for 1.5 hours, as compared with 0.3 hour in the case of C, D, and E. The sols were perfectly stable at room temperature. On agitation, they gave a pronounced streaky appearance.

Coagulation Values.—Equal volumes (4.0 c.c.) of sol and salt solution were simultaneously pipetted into a small test-tube in such a manner that the streams of liquid intermingled. The tube was closed with a glass stopper, the contents shaken vigorously for 5 minutes, and then kept at room temperature for 18 hours. This procedure gave very uniform results.

At sufficiently high concentrations of the coagulant, the whole of the stearic acid flocculated and rapidly collected at the surface, so that the underlying liquid (U.L.) became quite clear in a few minutes. Over a range of lower concentrations, the U.L. was definitely turbid even after 18 hours, but on filtering through a Jena fritted glass filter of porosity 3 (pore diameter 20–30 μ), a perfectly clear liquid was obtained. In these cases the sol was completely coagulated in the sense that isolated colloidal particles were no longer present. Such particles would have appeared in the filtrate, since in the absence of coagulant the sol passed through this filter unchanged. Apparently the process of aggregation had either ceased or become exceedingly slow at the stage when the aggregates were still small enough to form a stable coarse suspension. At still lower concentrations coagulation occurred, as shown by the accumulation of stearic acid at the surface of the liquid, but was incomplete, since the U.L. (or filtrate) showed streaks when shaken. The proportion of coagulated acid decreased with decrease in the concentration of coagulant, but for a given concentration appeared to be practically the same after 18 hours as shortly after the introduction of the coagulant. In one or two instances a partially coagulated sol was left undisturbed for several days without undergoing any perceptible change. It is evident that the stearic acid sols show the phenomenon of "fractional coagulation."

TABLE I.

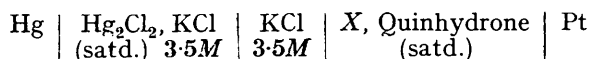
Determination of Coagulation Values.

Sol.	Electro-lyte.	Concn. $\times 10^3$.	Nephelometer reading.*	Coag. value.	Sol.	Electro-lyte.	Concn. $\times 10^3$.	Nephelometer reading.*	Coag. value	
C	K ₂ SO ₄	44	35–32		E	K ₂ SO ₄	50	32–31		
		50	21–19				55	21–22		
		56	8–7.5				58	10–13		
		62	7–8	0.053			62	6–7	0.060	
	Na ₂ SO ₄	56	28–26			MgSO ₄	10	>100		
		62	18–16				20	25–21		
		72	7–8.5	0.067			22	7.5–9		
	Li ₂ SO ₄	62	32–31			D	H ₂ SO ₄	25	6–8	
			71	18–19					31	8–9
		83	9–8					0.179	>100	
100		10		0.358	85–81					
125		7.5	0.077	0.537	23–21					
				0.627	16–17					
				0.716	11–10.5	>7.16 $\times 10^{-4}$				

* Reading for water = 6–8.

The "coagulation value" of an electrolyte was taken as the minimum concentration necessary to produce complete coagulation (*i.e.*, to give a perfectly clear filtrate with a filter of porosity 3) in 18 hours. A Zeiss nephelometer, in conjunction with a Pulfrich photometer, was used to detect the point at which the filtrate became quite free from colloid. The determinations (in duplicate) are recorded in Table I. As elsewhere in this paper, salt and acid concentrations are expressed as g.-equiv. per litre of the mixture of sol and electrolyte.

Ionic Interchange.—Equal volumes of sol and salt solution were thoroughly mixed in a glass-stoppered tube or bottle, the mixture kept for 18 hours, the stearic acid removed, and the concentration of the sulphuric acid in the remaining liquid determined electrometrically by means of the cell



where *X* is the experimental solution. The e.m.f. values given by salt solutions containing known quantities of sulphuric acid were measured (Table II), and curves drawn from which the actual quantity of hydrogen ion liberated from the suspension could be read off.

The stearic acid was removed, to minimise contamination of the electrode, and also because the sol was partially coagulated by the quinhydrone, with liberation of hydrogen ion. Unless the U.L. was quite clear (in which case a sample was simply withdrawn by pipette) the stearic acid was removed by filtration through a Jena fritted-glass filter of porosity 4 (pore diameter 5–10 μ). This filter was found to hold back the colloidal acid itself, except for a small amount of extremely fine particles. Control experiments showed that the glass filter adsorbed hydrogen ion to a small extent, and error from this source was avoided by rejecting the first 20 c.c. of filtrate.

The e.m.f. values were measured by means of a Tinsley potentiometer reading to 0.1 mv., used in conjunction with an Onwood galvanometer, and a Tinsley standard cell (N.P.L. certificate). The apparatus was set up in a constant-temperature room maintained at $14^\circ \pm 0.15^\circ$. Readings were commenced 20 mins. after the assembly of the cell, and found to be very steady. In some preliminary experiments, air, freed from carbon dioxide by passage through several soda-lime towers, and containing water vapour at the correct pressure, was bubbled for several hours through the experimental solution. As this procedure did not change the e.m.f. value, no precautions were taken to exclude carbon dioxide in the subsequent work. Each e.m.f. value given (in mv.) in the tables is the mean of at least two determinations. With few exceptions duplicates agreed to within 1.0 mv.

For the accurate measurement of the low concentrations of acid involved, certain special precautions were necessary. Jena- or Pyrex-glass apparatus was employed throughout the investigation. The sols and solutions were prepared from conductivity water of $\kappa > 1.2 \times 10^{-6}$ mho. The acid found to be present in the commercial salts (A.R. except in the case of lithium sulphate) was reduced by recrystallisation or neutralisation.

TABLE II.
E.M.F. values (millivolts) for salt-sulphuric acid mixtures.

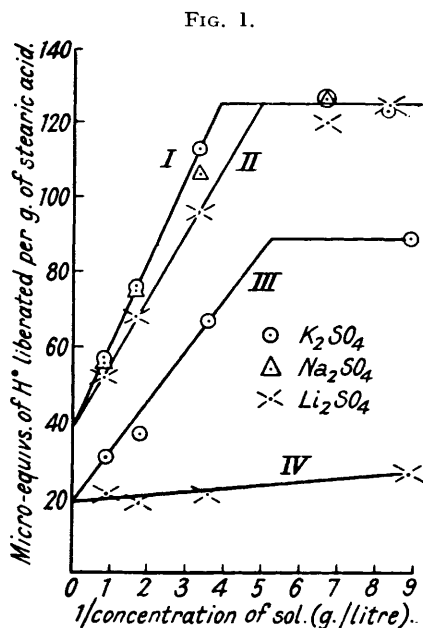
		Concn. of salt = 0.5.									
<i>a</i> *	0.0	8.95	17.9	35.8	59.6	89.5	119.3	179	358	716	
<i>b</i> *	102.6	110.3	120.3	129.9	150.7	170.6	—	197.0	216.2	234.8	
<i>c</i> *	101.6	107.1	116.0	128.0	149.7	170.8	—	—	—	—	
<i>d</i> *	103.2	113.2	120.9	136.0	156.8	—	—	201.4	221.0	240.7	
<i>e</i> *	74.6	82.0	85.0	96.9	—	117.7	133.6	181.3	219.2	243.4	
		Concn. of salt = 0.25.					Concn. of salt = 0.05.				
<i>a</i>	0.0	8.95	17.9	35.8	44.7	0.0	6.7	8.95	17.9	35.8	
<i>b</i>	115.6	125.5	135.8	152.4	164.2	147.4	153.2	—	168.8	181.0	
<i>c</i>	113.9	122.6	134.7	154.0	165.3	145.6	153.7	—	167.5	180.0	
<i>d</i>	120.7	129.5	137.6	156.4	—	147.6	154.5	—	168.0	179.8	
<i>e</i>	—	—	—	—	—	132.9	144.3	—	161.3	179.3	
		Concn. of salt = 0.10.					Concn. of salt = 0.01.				
<i>b</i>	126.1	144.4	154.0	168.2	—	152.9	—	168.3	178.5	—	
<i>c</i>	123.8	140.2	151.2	170.6	—	150.7	—	164.5	175.6	—	
<i>d</i>	127.9	140.4	151.4	172.2	—	152.0	—	165.1	177.9	—	
<i>e</i>	121.6	—	140.4	162.4	—	148.1	—	—	179.8	—	

* *a* = concn. of $H_2SO_4 \times 10^6$; *b*, *c*, *d*, *e* = e.m.f. values for K_2SO_4 , Na_2SO_4 , Li_2SO_4 , and $MgSO_4$ respectively.

Influence of Sol Concentration.—Table III contains data showing the variation in the degree of interchange as the sol (D) was diluted, the salt concentration being kept constant (0.5 g.-equiv./l.). Col. 1 gives the number of g. of stearic acid in 1 l. of sol + salt solution. For each salt, 2l. of stock solution (containing 1 g.-equiv./l.) were prepared from the recrystallised material, and sufficient of the residual acid neutralised (by the addition of a negligibly small volume of a solution of the corresponding hydroxide) to reduce the e.m.f. given by a 0.5N-solution of the salt to about 100 mv. In Fig. 1, the amount of hydrogen ion liberated from 1 g. of stearic acid is plotted against the reciprocal of the concentration of the sol (Curves I and II). The e.m.f. given by a mixture of equal volumes of a saturated solution of purified stearic acid and of 0.1 or 0.5N-potassium sulphate (introduced to increase the conductivity for the purpose of

measurement) was found to be practically identical with that given by the salt alone. Hence only a negligible quantity of hydrogen ion was present in the intermicellar liquid of the pure sol.

The curves are of exactly the same type as that obtained by Achar and Usher (*loc. cit.*), who, however, give a much higher value—340, as against 125—for the maximum amount of



Sol D, I and II. Sol B, III and IV. Concentration of salt = 0.5N.

that under these conditions 0.5N-potassium sulphate contained 38, and 0.5N-lithium sulphate 46, micro-equivs. per litre more acid than after neutralisation. Measurements were also made

TABLE III.

Variation of interchange with sol concentration.

Concn. of sol.	E.m.f.			Concn. of liberated H ⁺ , × 10 ⁶ .			Micro-equivs. of H ⁺ liberated from 1 g. of stearic acid.		
	K.	Na.	Li.	K.	Na.	Li.	K.	Na.	Li.
1.205	155.6	154.8	157.3	69	67	63	57	56	52
0.603	140.6	137.9	141.7	46	45	41	76	75	68
0.301	131.4	127.0	130.9	34	32	29	113	106	96
0.151	118.7	116.0	120.4	19	19	18	126	126	120
0.121	115.8	111.6	118.8	15	14	15	123	(116)	125

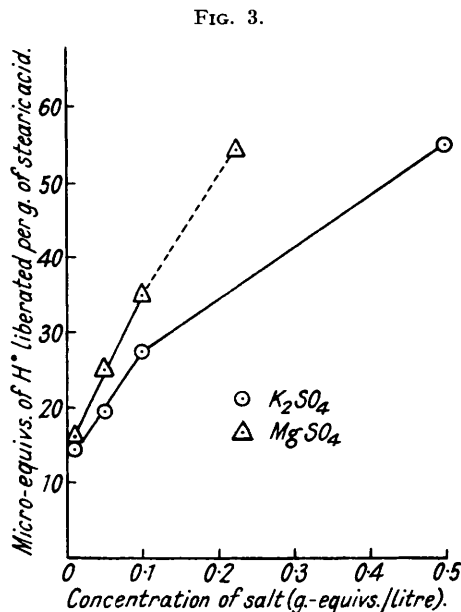
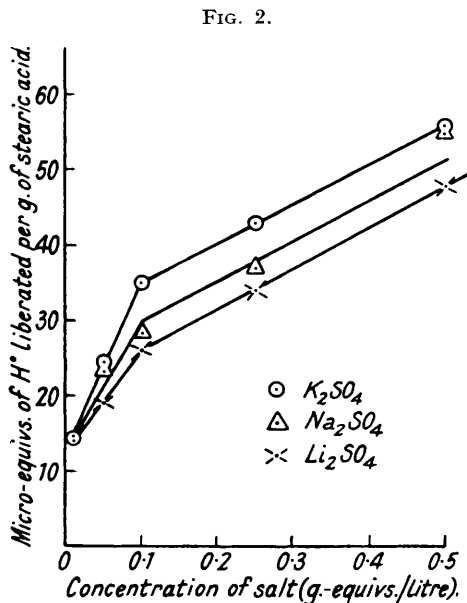
with potassium sulphate solutions to which sulphuric acid had been added. Equal volumes of sol B and 1.0N-salt were mixed, and the concentration of liberated acid in the mixture found to be 23×10^{-6} N when 58×10^{-6} N-acid, and nil when 134×10^{-6} N-acid, was present.

TABLE IV.

Influence of acidity on interchange.

Concn. of sol.	E.m.f.		Concn. of liberated H ⁺ , × 10 ⁶ .		Micro-equivs. of H ⁺ liberated from 1 g. of stearic acid.	
	K.	Li.	K.	Li.	K.	Li.
1.125	159.0	162.7	35	24	31	21
0.563	149.7	153.3	21	11	37	19
0.281	148.3	150.2	19	6	67	21
0.112	142.3	148.2	10	3	89	27

Influence of Nature and Concentration of Salt.—Table V shows the amounts of hydrogen ion liberated at various concentrations of the sulphates of potassium, sodium, lithium, and magnesium, the concentration of the sol being constant. The corresponding curves are given in Figs. 2 and 3.



Sol E. The point for 0.5N-MgSO₄ is plotted with the scale reduced to half; the slope of the broken line is therefore less than the true slope.

TABLE V.
Influence of nature and concentration of salt.

Concn. of salt.	E.m.f.					Micro-equivs. of H ⁺ liberated from 1 g. of stearic acid.				
	Sol. C.			Sol E.		Sol C.			Sol E.	
	K.	Na.	Li.	K.	Mg.	K.	Na.	Li.	K.	Mg.
0.50	148.7	147.3	148.7	152.0	136.4	56	55	48	55	109
0.25	161.0	157.6	155.7	—	—	43	37	34	—	—
0.10	168.0	164.3	163.0	165.1	164.7	35	28.5	26	27.5	35
0.05	174.6	172.1	168.6	171.0	172.0	24.5	23	19	19.5	25
0.01	174.9	172.2	173.5	175.0	178.8	14.5	14.5	14	14	16

State of Dispersion.—The amount of hydrogen ion liberated per g. of stearic acid under comparable conditions was found to vary only slightly from sol to sol; e.g., the values obtained for the action of 0.5N-potassium sulphate on undiluted sol were 56, 57, and 55 micro-equivs. for sols C, D, and E respectively (Tables III and V). It would therefore appear that the sols were very reproducible in respect of average particle size. The following observations, however, showed that they were polydisperse. A quantity of sol C was passed through a fritted-glass filter of porosity 4, 25 c.c. of the clear filtrate were mixed with 25 c.c. of salt solution, and the acidity determined. The following results were obtained :

Salt.	Concn.	E.m.f.	Concn. of liberated H ⁺ , × 10 ⁶ .	Salt.	Concn.	E.m.f.	Concn. of liberated H ⁺ , × 10 ⁶ .
K ₂ SO ₄	0.25	130.2	13.5	Na ₂ SO ₄	0.05	152.0	5.0
	0.50	112.0	11.0		0.10	140.4	9.0
Li ₂ SO ₄	0.05	152.1	4.5		0.25	129.4	14.0
	0.25	133.8	13.5				

They show that ionic interchange was occurring with colloid which had not been retained by the filter. It was further ascertained that after 160-fold dilution of sol C, the liquid was still

definitely opalescent. Hence if the sol was monodisperse, the maximum concentration of hydrogen liberated in the filtrate would be less than $125 \times 2.07/160 =$ approx. 2 micro-equivs. per litre. Since the actual figure was above 13.5, it must be concluded that the sol was polydisperse, the finest particles being small enough to pass the filter.

DISCUSSION.

Achar and Usher (*loc. cit.*) explain the variation in the amount of hydrogen ion liberated from 1 g. of stearic acid on diluting the sol (Table III) as due to the progressive dissociation of the surface molecules of the colloidal particles. The influence of added sulphuric acid (Table IV) is consistent with this view, since if the surface dissociation is that characteristic of a weak acid, it will be substantially decreased by small amounts of a strong acid, and the ionic interchange accordingly diminished at all concentrations of the sol. It will be seen that up to the point of maximum liberation of hydrogen ion, the graphs in Fig. 1 conform to the equation $y = ax + b$. Apparently the limit b , to which the liberated hydrogen tends as the sol becomes more concentrated, is the fraction of hydrogen ion which would be split off the surface if the potassium sulphate were present within the double layer alone. Thus, in the case represented by Curve I (Fig. 1), where $b = 38$ and the maximum interchange is 125, about two-thirds, $(125-38)/125$, of the available molecules of stearic acid would be undissociated under these conditions. It follows that the degree of surface dissociation in the pure sol must be much less than 33%, since in the presence of 0.5*N*-sulphate the dissociation is markedly enhanced by the formation of bisulphate ion. Data are lacking for the evaluation of b in the case of 0.01*N*-potassium sulphate, where the formation of bisulphate ion is relatively small, but the value will be less than 14.5 (Table V). Hence, in the pure sol less than 1 in $125/14.5$, or 1 in 9, of the ionisable surface molecules is actually dissociated. According to the present method of deduction, however, the data indicate that this is the order of magnitude of the dissociation. McBain and Peaker (*Proc. Roy. Soc.*, 1929, *A*, **125**, 394; McBain and Dubois, *Z. Elektrochem.*, 1931, **37**, 651; Dubois and Roberts, *J. Physical Chem.*, 1931, **35**, 3070) have deduced the same order of magnitude from their measurements of the conductivity of a mono-layer of stearic acid on water. It should be pointed out that the observed maximum liberation of 125 micro-equivs. of hydrogen ion per g. of stearic acid may be lower than the true value for perfectly neutral salt, owing to incomplete neutralisation of the acid in the salts actually employed. This factor may possibly account for the difference between the above value and that reported by Achar and Usher.

In order completely to coagulate the sol by means of sulphuric acid, a concentration of about $720 \times 10^{-6}N$ was required (Table I), but aggregation of some of the particles occurred even at $36 \times 10^{-6}N$. It is probable that the fractional coagulation is due to the polydisperse nature of the sol, a higher concentration of coagulant being necessary in the case of the smaller particles than in that of the larger (cf. Odén, *Nova Acta Upsala*, 1913, *iv*, **3**, 55; Müller, *Koll.-Chem. Beih.*, 1928, **26**, 306; Thiessen, Thater, and Kandelaky, *Z. anorg. Chem.*, 1929, **180**, 11). The simplest interpretation of the effect is that the number of stearic acid molecules per unit area of surface which are oriented with the carboxyl group in contact with the water, and hence able to dissociate, increases with decrease in particle size. If for a given concentration of sulphuric acid, the proportion of such molecules actually dissociated is independent of particle size, it follows that the smaller the particle, the higher will be the concentration of acid necessary to reduce the surface density of charge to the minimum value required for coagulation. The observation that in the presence of $134 \times 10^{-6}N$ -sulphuric acid no measureable amount of hydrogen ion was displaced by 0.5*N*-potassium sulphate might be thought to invalidate the assumption that the coagulation of the sol by acid is the result of decrease in the surface dissociation. However, the experimental error in the determination of the liberated hydrogen ion under the above conditions is large enough to conceal what may well be a significant degree of ionic interchange. Hence, it may be assumed that the dissociation is not completely suppressed by $134 \times 10^{-6}N$ -sulphuric acid. That the requisite concentration is probably much higher than this is indicated by the experiments of Langmuir and Schaeffer (*J. Amer. Chem. Soc.*, 1936, **58**, 284), who determined the composition of

films of stearic acid spread on buffered solutions containing barium ion. It was found that at p_H values not greater than 3 (approx.) the mono-layer consisted entirely of fatty acid, whereas when the p_H was increased beyond 3, conversion into barium stearate occurred, becoming complete at about p_H 11. Moreover, Schulman and Hughes (*Proc. Roy. Soc.*, 1932, A, 138, 430) have shown that the "surface potential" of a mono-layer of myristic acid varies with the p_H of the substrate in a manner consistent with the view that ionisation of the film sets in when the p_H is increased beyond some value between 3 and 4. The minimum concentration of acid producing complete coagulation corresponds to a p_H lying within these limits, and hence it is reasonable to suppose that, in the case of the smallest particles, a large proportion of the surface molecules is favourably oriented for ionisation, so that the character of the surface approximates to that of a mono-layer.

The graphs in Figs. 2 and 3 show at once that when the salt kations are arranged according to either coagulating power (Table I) or tendency to displace hydrogen ion, the sequence is the same, *viz.*, $Mg > K > Na > Li$. That the two effects are closely related is definitely shown by comparison of the amounts of hydrogen ion liberated at the respective coagulation concentrations, as obtained by interpolation. It will be seen from Table VI

TABLE VI.

Sol.	Salt.	Coagulation value.	Micro-equivs. of H' per g. of stearic acid, liberated at coagulation point.	$\frac{1}{\sqrt{\mu}}$. *	Relative thickness of double layer.
C	Li ₂ SO ₄	0.077	23.0	2.94	1.00
	Na ₂ SO ₄	0.067	24.0	3.15	1.07
	K ₂ SO ₄	0.053	24.5	3.55	1.20
E	K ₂ SO ₄	0.060	21.5	3.33	1.13
	MgSO ₄	0.021	18.5	4.88	1.66

* See below.

that the liberation of hydrogen ion by the alkali-metal salts (sol C) varies by not more than 4% from the mean value (23.8), although the coagulation values for the sodium and lithium salts are respectively 26 and 45% greater than that for potassium sulphate. Thus, within the experimental error, the degree of ionic interchange at the coagulation point is the same for all three kations. The difference in the amounts of hydrogen liberated by potassium and magnesium (sol E) probably exceeds the apparent variation due to experimental error. However, the most important point is that, although the coagulation value for potassium is three times that for magnesium, the liberated hydrogen in the case of both kations lies within 8% of the mean value (20).

It is commonly supposed that the stability of a lyophobic sol depends upon the thickness of the ionic atmosphere surrounding the individual particle. When the atmospheres of two particles interpenetrate, a repulsive force arises from the resistance offered by the atmospheres to distortion, so that the particles do not approach closely enough for the forces of attraction to predominate. Thus an electrolyte coagulates the sol by reducing the thickness of the atmosphere to some critical value. On the assumption that $1/\kappa$ (the value of the equivalent radius of the ionic atmosphere in the theory of Debye and Hückel) may be regarded as a measure of the thickness of the ionic atmosphere about a colloidal particle (cf. Müller, *Koll.-Beih.*, 1928, 26, 285; Henry, *Proc. Roy. Soc.*, 1931, A, 133, 106), it follows that $1/\sqrt{\mu}$ (where μ is the ionic strength of the electrolyte present) should have the same value for all electrolytes at their respective coagulation values. That this does not hold in the present instance will be seen from the data in Table VI. Moreover, since the degree to which hydrogen ion is liberated varies with the nature of the replacing ion, it is evident that specific attractive forces exist between this ion and the surface of the particle.

Since equivalence in ionic interchange at the coagulation point has been observed in the case of both sulphur (Bolam and Muir, J., 1934, 754) and stearic acid sols, it would appear that the phenomenon is of primary importance for a general theory of coagulation. The simplest interpretation of the results is that coagulation occurs only when some definite fraction of the stabilising ions forms either undissociated molecules or associated

ion-pairs (McBain and Peaker, *loc. cit.*; Hartley, *Trans. Faraday Soc.*, 1935, **31**, 164) with the kations of the coagulant. It seems difficult to account for the equivalent interchange on the assumption that coagulation may result from simple contraction of the ionic atmosphere, as postulated by Müller (*loc. cit.*), Verwey (*loc. cit.*), and Weiser (*J. Physical Chem.*, 1935, **39**, 1163).

As the concentration of salt is increased beyond the coagulation value, the amount of hydrogen ion liberated also increases, probably because the surface acid is further dissociated owing to the formation of bisulphate ions. It seems feasible to account for part, at least, of the observed difference in interchange at the coagulation point in the case of potassium and magnesium (Table VI) on the same grounds. Coagulation by potassium occurs when the concentration of sulphate ion is higher than in the case of magnesium, and the surface dissociation is correspondingly greater. Complete replacement at the coagulation point is observed with dialysed sulphur sols (Bolam and Muir, *loc. cit.*), which are also stable in the presence of high concentrations of mineral acid. This contrast with the behaviour of stearic acid sols suggests that the stabilising polythionic acid is highly dissociated.

SUMMARY.

(1) The influence of the following factors upon the liberation of hydrogen ions from the surface of colloidal particles of stearic acid has been investigated: (i) concentration of sol, (ii) acidity, (iii) concentration, and (iv) nature of salt. The coagulative action of acids and salts has also been examined.

(2) In general, the results support Achar and Usher's view that the surface molecules of the particles dissociate in the manner of a weak acid, and that the hydrogen ions so produced undergo interchange with the salt kations.

(3) It is shown that the coagulating power of a salt is closely correlated with the tendency of the kation to displace hydrogen ion from the surface of the particles. The bearing of the results upon the theory of coagulation is discussed.

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