EMULSIONS. PART II. PARTIAL COAGULATION OF A STANDARD EMULSION IN SODIUM OLEATE SOLUTION BY SALTS OF SOME BI- AND HIGHERVALENT METALS.

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Hatschek * noticed that $ZnSO_4$ was less efficient as a coagulating agent for emulsions in solutions of sodium oleate than $CaCl_2$ or $BaCl_2$ when the quantity of electrolyte added was insufficient to react with all the soap present. However, we know of no systematic study of the partial coagulation of emulsions by electrolytes. The coagulation of the standard emulsion in $N/30$ sodium oleate studied in Part I [1] by varying quantities of salts of bi- and highervalent metals is described in this paper.

Determination of the Volume of Oil Thrown Out.

100 to 150 c.c. of standard emulsion was prepared and left for 10 minutes to allow foam to collapse. Then 7·5 c.c was run into graduated centrifuge tubes (Fig. 1). Between 0·2 and 1·0 c.c. of $N/10$ coagulating solution (1 c.c. was equivalent to the sodium oleate in 7·5 c.c. of emulsion) was added to the tubes. Immediately after the addition, each tube was stoppered and turned upside down five times to complete mixing. After half an hour, and again after 48 hours, the tubes were centrifuged for 5 minutes at 2000 r.p.m., and the volumes of oil separated read on their graduated necks. Since the volume of oil thrown out varied from fractions of 1 to 4·5 c.c., centrifuge tubes with different diameters of neck were used. Duplicate determinations were usually made. The presence of jelly at the interface between emulsion and separated oil was sometimes troublesome, particularly when HCl or luteocobaltic chloride were the coagulating agents. Since jellies usually contain only a small proportion of solid, they were included in the volume of oil separated. Such jellies affected the measurements most when a large proportion of the emulsion was broken. Reshaking the tubes after 24 hours did not alter the volume of oil separated when 0·6 c.c. or less of electrolyte had been added, but when 0·8 or 1 c.c. had been added it was usually increased.

FIG. 1.

The decinormal solutions of the various electrolytes used as coagulating agents were prepared, when possible, from " Analar " materials. The Al in the $Al_2(SO_4)_3$ and the Th in the $Th(NO_3)_4$ solution were determined
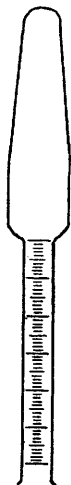
* Private communication.
[1] A. R. Martin and R. N. Hermann. This vol., p. 25.

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gravimetrically. The Cu contents of the solutions of copper salts were checked electrolytically. The solutions of $MgCl_2$ and $Mg(NO_3)_2$ were prepared by decomposition of the MgO (analar) with acid, and those of $CaCl_2$, and on one occasion of $BaCl_2$ by similar decomposition of the pure carbonate. Hexol salt (hexol-hexaethylenediamine tetracobaltic nitrate, which yields a hexavalent kation) was prepared from cobalt nitrate and ethylenediamine according to the directions of Werner.[2]

TABLE I.

C.c. 0·1 N Electrolyte Added.		Volume of Oil Separated from Standard Xylene Emulsion. (Total Volume of Oil Present, 4·5 c.c.)							
		HCl.	ZnSO₄.	MgSO₄.	MgCl₂.	Mg(NO₃)₂.	CaCl₂.	SrCl₂.	BaCl₂.
a.	1·0	—	2·91	2·17	3·54	3·87	2·84	2·90	3·48
b.	1·0	4·32	4·42	2·97	4·20	4·19	3·39	3·85	4·35
a.	0·8	—	1·49	1·50	2·25	2·19	1·38	1·84	1·97
b.	0·8	2·91	1·69	1·96	2·77	2·66	1·66	2·03	2·28
a.	0·6	—	0·38	1·01	1·50	1·50	1·01	1·28	1·38
b.	0·6	2·14	0·72	1·20	1·75	1·75	1·22	1·47	1·56
a.	0·4	—	0·24	0·70	0·98	1·05	0·70	0·80	0·83
b.	0·4	1·27	0·37	0·78	1·10	1·15	0·88	0·94	0·98
a.	0·2	—	0·16	0·36	0·53	0·55	0·35	0·43	0·43
b.	0·2	0·66	0·23	0·39	0·54	0·55	0·46	0·49	0·54

		CuSO₄.	CuCl₂.	CoCl₂.	Al₂(SO₄)₃.	Th(NO₃)₄.	"Luteo."	"Hexol."	
a.	1·0	4·00	4·23	2·91	2·63	4·43	4·45	4·17	
b.	1·0	4·30	4·38	4·30	3·47	4·43	4·45	4·32	
a.	0·8	2·05	2·63	0·99	2·13	3·24	4·45	2·19	
b.	0·8	2·20	3·24	1·55	2·27	3·24	4·45	2·91	
a.	0·6	1·40	1·68	0·77	1·61	1·49	1·94	1·69	
b.	0·6	1·40	1·74	0·97	1·80	1·70	2·41	2·16	
a.	0·4	0·94	1·02	0·49	0·89	0·80	1·38	0·91	
b.	0·4	0·94	1·13	0·69	1·09	0·97	1·41	1·25	
a.	0·2	0·47	0·56	0·27	0·30	0·44	0·58	0·43	
b.	0·2	0·47	0·57	0·35	0·43	0·55	0·71	0·59	

a = c.c. of oil coagulated after 30 to 60 minutes.
b = c.c. of oil coagulated after 2 to 3 days.

In Table I are recorded experiments with a standard xylene emulsion (xylene is preferable to benzene for such work because it is less volatile). The xylene was " sulphur free ". In Table II are recorded similar experiments carried out at Utrecht, which differed only in that at one time and with the same preparation of emulsion the coagulating powers of the same quantity of different electrolytes were determined instead of those of different quantities of the same electrolyte. In Utrecht more powerful centrifuging was employed (10 mins. at 3000 r.p.m.). Some characteristic results are shown graphically in Fig. 2.

[2] A. Werner, *Ber.*, 1907, **40**, 2113.

TABLE II.

C.c. 0.1 N Electrolyte Added.		Volume of Oil Separated from Standard Xylene Emulsion. (Total Volume of Oil Present, 4.5 c.c.)						
		$ZnSO_4$.	$MgCl_2$.	$CaCl_2$.	$SrCl_2$.	$BaCl_2$.	$Al_2(SO_4)_3$.	$Th(NO_3)_4$.
a.	1.0	2.97	3.23	3.19	3.32	3.59	3.91	3.49
b.	1.0	3.20	4.05	3.63	3.58	3.63	4.35	3.99
c.	1.0	4.50					4.35	4.45
a.	0.8	1.09	2.24	2.07	2.34	2.72	3.12	2.99
b.	0.8	1.70	2.81	2.21	2.41	3.13	3.20	3.09
c.	0.8	2.45					4.43	3.67
a.	0.6	0.70	1.55	1.30	1.48	1.51	2.09	1.80
b.	0.6	0.79	1.58	1.33	1.52	1.58	2.17	1.80
c.	0.6	1.06					2.20	2.07
a.	0.4	0.35	1.02	0.83	0.86	1.07	1.48	1.09
b.	0.4	0.50	1.02	0.83	0.89	1.07	1.48	1.09
c.	0.4	0.50					1.52	1.09
a.	0.2	0.19	0.53	0.46	0.40	0.49	0.51	0.49
b.	0.2	0.29	0.53	0.46	0.43	0.49	0.53	0.49
c.	0.2	0.29					0.53	0.49

a = c.c. of oil coagulated after about 3 hours.
b = c.c. of oil coagulated after 24 hours, without reshaking.
c = c.c. of oil coagulated after 48 hours, tubes reshaken before centrifuging.

1 . $CuCl_2$
2 . $MgCl_2$
3 . $BaCl_2$
4 . $CuSO_4$
5 . $ZnSO_4$
6 . $CaCl_2$

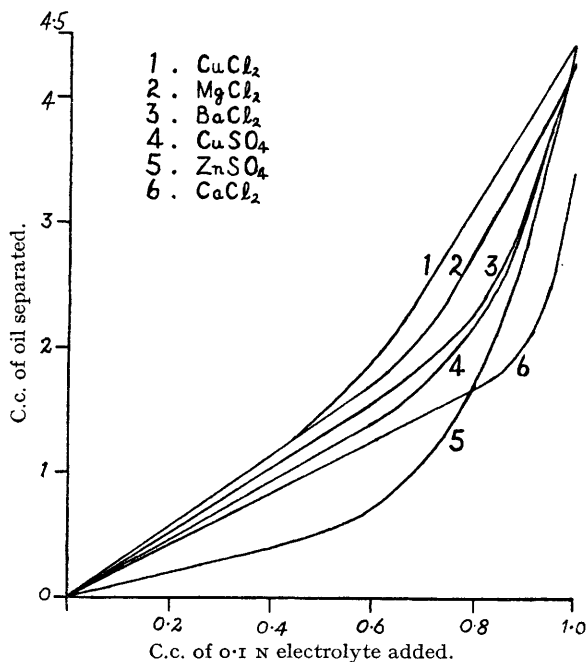C.c. of oil separated.

C.c. of 0.1 N electrolyte added.

FIG. 2.

Discussion.

If the sodium oleate adsorbed is insufficient for a satisfactory interfacial film, it may be expected that the interfacial area will be diminished by oil separation until such a film can be maintained at the reduced interface (the nature of the interfacial film in standard benzene emulsions has been described in Part I[1]; in xylene emulsions it is probably very similar—droplet sizes are the same). Owing to the shape of an adsorption isotherm, the proportion of the adsorbed film destroyed is, at first, less

than the proportion of all the sodium oleate destroyed by the coagulating salt. But when all the sodium oleate has been destroyed, there cannot be any film left. Consequently, the curve relating volume of oil separated to amount of coagulating salt added is convex to the axis representing the latter quantity—as was always found.

However, this simple theory cannot account for the different coagulating powers of equivalent quantities of various salts observed when these are insufficient completely to break the emulsion. There are few obvious regularities in these specific effects, beyond the order $Ca^{++} < Sr^{++} < Ba^{++}$ for the coagulating powers of the chlorides of the alkaline earths, which is the reverse of the lyotropic series. The effect of valency is slight, and sometimes it is overruled completely, as in hydrochloric acid, which is one of the most powerful coagulants, although both its ions are univalent.

Water-in-oil emulsions formed by soaps of bi- and highervalent metals are too unstable to have influenced the results appreciably, except possibly in the case of magnesium, and, furthermore, the mixture must be shaken after addition of coagulating (inverting) salt to produce them. For instance, when W/O emulsions were prepared by adding to portions of a standard benzene emulsion coagulating salts equivalent to the sodium oleate present, shaking and homogenising, only with magnesium soap was a relatively stable and rather viscous W/O emulsion formed—the bulk of the others broke after a few minutes. Moreover, when mixed soaps obtained by adding quantities of a number of salts equivalent to 50, 60 and 80 % of the sodium oleate in solution were used to emulsify xylene by the standard procedure, magnesium soaps were again exceptional. In the absence of magnesium stable O/W emulsions were formed in the first two cases, and only when 80 % of the sodium oleate had been decomposed was a W/O emulsion obtained —and this broke almost immediately. In each experiment involving magnesium a W/O emulsion was formed, which began to break down after about half an hour. If the tendency of metal soaps to form W/O emulsions had determined the specific effects previously referred to, all salts except those of magnesium would have behaved in much the same way, which was not the fact. One is consequently driven to the idea that the extent to which the interfacial film is destroyed in partial coagulation varies with the nature of the added salt. The reaction between salts of bi- and highervalent metals and sodium oleate was therefore studied.

The Reaction between Salts of Bi- and Highervalent Metals and Sodium Oleate in Emulsions.

(i) Copper.—The oil separated by copper salts was a clear blue, independent of its nature. But interaction of equivalent quantities of sodium oleate and copper salts in aqueous solution followed by extraction by an oil gave not a trace of colour to the organic liquid ; only after prolonged standing did the copper soap become to some extent oil-soluble. However, addition of oleic acid or sodium oleate, which would give some oleic acid by hydrolysis, made the copper oleate dissolve immediately in the oil. The colour is destroyed by mineral acids, and somewhat less readily by alkali. Although the reaction between sodium oleate and copper salts in aqueous solution gave practically a normal oleate of copper, all the soaps derived from emulsions contained a considerable excess of oleic acid.

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A slight excess of $N/10$ $CuSO_4$ was added to a large quantity of standard benzene emulsion. The vessel was immediately turned upside down five times and left for an hour. The separation of the benzene was then completed by centrifuging. On evaporation of the benzene a dark green oil was obtained, which solidified to a soft wax of the same colour. This was dissolved in ether and decomposed by shaking with dilute H_2SO_4. The oleic acid in the ethereal layer was finally titrated with $N/10$ alkali (for details see Part I, p. 27) and the Cu in the aqueous layer and washings determined electrolytically.

On mixing equivalent quantities of sodium oleate and $CuSO_4$ in aqueous solution, a greenish precipitate was formed, which had to be left for 24 hours before it could be filtered. The light blue-green soap thus obtained was, after pressing, dry to the touch and soluble in benzene. When placed in an oven at 105°, however, large quantities of liquid water separated and left a dark green waxy solid like that obtained on evaporating the benzene separated from an emulsion. This was also analysed.

The results of these analyses are given in Table III (oleate expressed as oleic acid), together with that of the residue from the benzene separated when copper salt equivalent to 80 % of the sodium oleate had been added to the emulsion (thus breaking about one half of it). The first two specimens contained traces of sodium.

TABLE III.

Specimen.	Ratio of Molecules of Oleic Acid to Atoms of Copper.
1. From fully broken emulsion	2·67
2. From fully broken emulsion	2·73
3. From partly broken emulsion	2·43
4. From reaction in aqueous soln.	1·99

If there is oleic acid in the copper soap, there must be the equivalent of metallic hydroxide in the aqueous phase. Therefore, in the second experiment, the solid left in the water and at the interface was analysed. It contained one atom of copper to 0·39 molecules of oleic acid. This basic copper oleate may produce a little unstable W/O emulsion. The separated water was neutral.

The coloured solutions of copper soaps in organic liquids appear to be sols of copper oleate peptised by oleic acid. Soyenkoff [3] has studied similar sols of iron and nickel soaps, and Lawrence [4] has reported complexse of sodium and calcium stearates and fatty acids in " Nujol ". The more concentrated solutions obtained by dissolving the waxy copper soaps in an organic liquid were a clear deep emerald instead of blue like the dilute solutions separated from emulsions. The emerald solutions given by the copper soap from an emulsion and by the material prepared in aqueous solution before and after drying in the oven were identical in appearance. Drying over calcium chloride did not change their colour. So although some water may be present it does not play an essential role. Under the microscope (dark field, × 700) only a few small particles in Brownian movement were visible. The reason why the soap prepared in aqueous solution became oil-soluble on keeping is not clear. It may have been partial loss of water (cf. Pink's work on magnesium oleate [5]) or liberation of oleic acid. The corresponding sols of copper stearate were very much less stable.

The reactions when a copper salt is added to our emulsion may therefore be pictured as follows. In the water a basic copper oleate is precipitated by reaction with the alkaline sodium oleate (in Part I it

[3] B. Soyenkoff, *J. Physical Chem.*, 1930, **34,** 2518.
[4] A. S. C. Lawrence, *Trans. Faraday Soc.*, 1939, **35,** 702.

has been shown that about 12 per cent. of all the sodium oleate is hydrolysed). Copper oleate is formed at the interface by reaction with the sodium oleate there, and this copper oleate, together with some from the aqueous phase, goes into colloidal solution in the oil, peptised by the oleic acid which was present at the interface. Some basic copper oleate remains in the water.

(ii) **Aluminium.**—On completely breaking a standard benzene emulsion with aluminium sulphate, a colourless solution of aluminium soap in benzene was obtained, which on evaporation yielded a yellowish, transparent, rubber-like substance, which contained 1 atom of aluminium to 4·94 molecules of oleic acid (aluminium weighed as oxide). The separated water was neutral and free from aluminium. The solid suspended in the water and the jelly at the interface together contained 1 atom of aluminium to 0·88 molecules of oleic acid.

(iii) **Zinc.**—The main product was in solution in the separated oil, from which it was recovered as a yellowish-white powdery solid, which contained 1 atom of zinc to 2·05 molecules of oleic acid (zinc weighed as pyrophosphate). The separated water was milky, not alkaline, and contained no zinc in solution. It was centrifuged for an hour—the small amount of solid obtained contained zinc and oleic acid. There was no jelly.

(iv) **Magnesium.**—After an emulsion had been broken by magnesium sulphate, the separated water held an opaque white suspension much thicker than in the case of zinc. This suspension was alkaline, and formed the greater part of the reaction-product. Under the microscope it appeared very heterodisperse with particles up to 2 μ across. After it had been poured several times through the same filter, a clear filtrate was obtained, which was no longer alkaline. The suspended material was probably magnesium oleate stabilised by magnesium hydroxide. It is this suspension which stabilises the W/O emulsions so readily formed in the presence of " magnesium soap " (p. 33). Pink[5] has shown that whilst anhydrous magnesium oleate is soluble in benzene, it is precipitated as an hydrated soap on addition of water. Evaporation of the separated benzene gave a yellowish acidic oil consisting of magnesium oleate and oleic acid.

We shall now consider the effect of the reactions described above on the coagulating powers of metallic ions. If a copper salt is added to our emulsion, the interfacial film of acid-soap is destroyed not only by conversion of sodium oleate to copper oleate, but also by removal of oleic acid to peptise the copper oleate in the oil. Consequently, more of the interfacial film is destroyed than if normal copper oleate had been precipitated, and copper salts are powerful coagulants. The fact that when the copper salt added is less than the equivalent of the sodium oleate the excess of oleic acid in the separated oil is smaller (specimen 3, Table III) may be interpreted as due to a competition between the undestroyed sodium oleate and the copper oleate for the oleic acid in the film of acid-soap. The large coagulating power of aluminium sulphate can similarly be traced to the high ratio of oleic acid to aluminium in the oil thrown out. On the other hand, zinc oleate does not remove any oleic acid from the interfacial film. So less of the film is destroyed and zinc sulphate is a poor coagulant. When the coagulating electrolyte is equivalent to all the sodium oleate present, such effects should not alter the volume of oil thrown out, for in all cases there should be no sodium

[5] R. C. Pink, *J. Chem. Soc.*, 1938, 1252 ; 1939, 619.

oleate left. The fact that magnesium salts are more powerful coagulants than calcium salts may be due to the formation of some unstable W/O emulsion, which later breaks.

Influence of Dilution of the Emulsion.

The volumes of oil thrown out from a standard emulsion and from two emulsions diluted in different ways, which nevertheless contained the same amount of sodium oleate, were compared. The diluted emulsions were (A) a standard xylene emulsion diluted with an equal volume of water immediately before addition of the coagulating solution (50 c.c. standard emulsion + 50 c.c. water = 100 c.c. emulsion A) ; and (B) an emulsion prepared in the standard way but with a diluted sodium oleate solution (20 c.c. $N/30$ sodium oleate + 50 c.c. water + 30 c.c. xylene = 100 c.c. emulsion B). In Table IV are recorded the volumes of oil thrown out from these emulsions by a number of salts, together with the volumes thrown out at the same time from a standard emulsion (column C).

TABLE IV.

C.c. 0·1 N Electrolyte Added.	Volume of Xylene (c.c.) from/after				
	A.		B.		C.
	3 hours.	24 hours.	3 hours.	24 hours.	24 hours.
$CuSO_4$.					
1·0	4·42	4·42	4·36	4·45	4·43
0·8	1·68	2·12	1·68	1·90	2·45
0·6	1·00	1·06	1·00	1·06	1·75
0·4	0·64	0·64	0·68	0·76	1·17
0·2	0·30	0·34	0·34	0·34	0·57
$ZnSO_4$.					
1·0	—	4·32	—	4·37	4·30
0·8	—	2·05	—	3·74	2·94
0·6	—	0·25	—	0·34	0·76
0·4	—	0·13	—	0·07	0·41
0·2	—	0·09	—	0·05	0·20
$CaCl_2$.		17 hours.		17 hours.	17 hours.
1·0	—	2·79	—	3·36	2·87
0·8	—	1·10	—	1·77	1·88
0·6	—	0·63	—	0·68	1·44
0·4	—	0·40	—	0·48	0·96
0·2	—	0·20	—	0·17	0·43
$Al_2(SO_4)_3$.					
1·0	—	4·34	—	4·28	4·35
0·8	—	3·10	—	3·68	3·12
0·6	—	1·62	—	1·84	2·28
0·4	—	0·98	—	1·08	1·48
0·2	—	0·40	—	0·34	0·63

When the quantity of coagulating salt was small, the volume of oil separated was much reduced by dilution. This means that less of the interfacial film had been destroyed, probably because a larger proportion of the reaction had occurred in the bulk of the aqueous phase with precipitation of normal copper oleate. When the coagulating salt was equivalent to the sodium oleate, all the interfacial film was destroyed and the emulsion was

completely broken, whether it was diluted or not. The slight difference between the behaviours of the diluted emulsions A and B may be due to jelly, for there was no such difference when coagulating with copper sulphate, which forms no jelly. Bhatnagar [6] noticed that more salt was required to cause inversion when an emulsion was diluted without altering the quantity of sodium oleate present.

Influence of the Nature of the Anion.

The differences in coagulating power between salts with the same kation but different anions, such as $MgSO_4$, $MgCl_2$, $Mg(NO_3)_2$, $CuSO_4$, and $CuCl_2$ (Table I) was confirmed by experiments on the same xylene emulsion with $CuSO_4$, $CuCl_2$, $Cu(NO_3)_2$. The coagulating power of a sulphate is less than that of the corresponding chloride and nitrate, which are equal. This fact can be correlated with the degree of dissociation of these salts. The sulphates of bivalent metals such as Cu and Mg are far from being completely dissociated at the concentrations used, whilst the dissociation of the chlorides and nitrates is practically complete.[7] A given concentration of the sulphate therefore produces a smaller concentration of bivalent kations than does an equivalent concentration of the chloride or nitrate. It may be supposed that this leads to a larger proportion of the reaction occurring in the aqueous phase in the case of a sulphate and so, as suggested in the previous section, to the coagulation of less oil. For the larger the concentration of an ion the greater will be the extent to which it penetrates the atmosphere of sodium ions around a droplet and reacts at the interface, and this, owing to the removal of oleic acid into the oil by the metal oleate formed, results in the destruction of more of the interfacial film of acid-soap than reaction in the aqueous phase.

Influence of the Nature of the Oil.

Since the character of the interfacial film depends to some extent on the nature of the oil (Part I), addition of the same quantity of coagulating salt to standard emulsions made with different oils may cause the separation of different volumes of oil. For instance, on adding 0·5 c.c. of N/10 copper sulphate to 7·5 c.c. portions of standard emulsions of heptane and decyl alcohol the volume of oil separated in the former case was 1·31 c.c., and in the latter 2·32 c.c. Although the heptane emulsion was much the coarser, it was less sensitive to addition of coagulating salt than the finely divided emulsion of decyl alcohol. However, it has been shown in Part I that in standard emulsions of the higher aliphatic alcohols almost all the soap is at the interface. Such emulsions must be extraordinarily sensitive to coagulating salts, for there is little reserve of soap in solution to maintain the interfacial film.

Summary.

Experiments on the partial coagulation of a standard emulsion of xylene and other oils in sodium oleate solution by salts of bi- and higher-valent metals are reported. The extent to which the interfacial film of

[6] S. S. Bhatnagar, *J. Chem. Soc.*, 1921, **119**, 61.
[7] C. W. Davies, *The Conductivity of Solutions*, 2nd ed., London, 1933, pp. 110, 138.

acid-soap is destroyed by the formation of sols of metal-soap in the organic liquid peptised by oleic acid is shown to be an important factor in determining the volume of oil thrown out when the quantity of coagulating salt is less than equivalent to the sodium oleate.

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