This is to certify that Mr ADAM I. S. DUNCAN, a candidate for the degree of Ph.D., successfully sustained an oral examination by a Committee of the Department on the subject of his thesis on 20 April, 1936.

                              Chairman of Committee.

11 May, 1936.
_____

IONIC INTERCHANGE IN STEARIC ACID SOLS

AND THE MECHANISM OF COAGULATION.

by

ADAM INNES SMITH DUNCAN, B.Sc.

Thesis presented for the

degree of

Ph.D.

May, 1936.

C O N T E N T S.

INTRODUCTION.

In many instances the electrical charge on the particles in lyophobic sols may be attributed to the fixation of ions at the surface of the particles. It is evident that these ions must hold, by electrostatic attraction, an equivalent amount of ions of opposite charge ("contra-ions" or "Gegenionen") in the neighbourhood of the surface, so that an "ionic double layer" is formed.
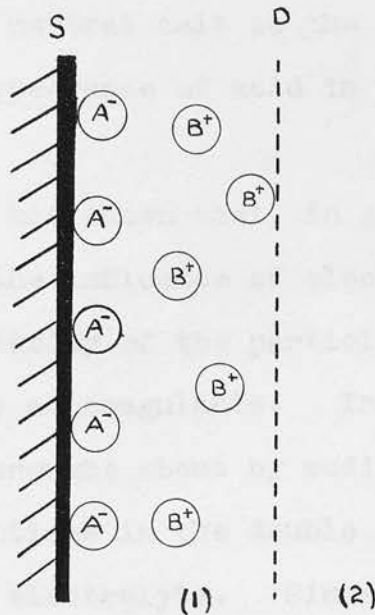
Thus, if the surface (S) is negatively charged by the attachment of anions A^-, the outer layer will consist of kations B^+, which are free to move in the adjacent liquid to a distance (SD) from the surface determined by the attraction of the fixed ions. The concentration/

concentration of the kations will therefore be greater in the double layer (1) than in the intermicellar, or external, liquid (2). In general, conditions can be secured which result in the difference being very marked. Now, it is evident that when an electrolyte with kation (C^+) other than B^+, is introduced into the aqueous phase, some of B^+ will be replaced by C^+, and become free to diffuse into the external liquid. This is the process termed "ionic interchange", "base exchange", or "exchange adsorption" ("Austausch-adsorption"). If the kations B^+ are hydrogen ions, the addition of neutral salt to the sol will thus result in the appearance of acid in the intermicellar liquid.

Experience has shown that, in general, parallelism exists between the influence of electrolytes upon the cataphoretic velocity of the particles of a sol, and their efficiency as coagulants. This indicates that coagulation is brought about by modification of the electrical conditions in the double layer, by the presence of the electrolyte. Since these conditions must depend upon the nature and concentrations of the ions within the region of the double layer, it is reasonable to suppose that the study of ionic inter-change may materially assist in elucidating the mechanism of coagulation. Despite considerable investigation, however, there is a wide divergence of opinion/

opinion with regard to the importance of ionic inter-
change in the coagulation process.[1,2] No doubt this is
due, in part at least, to the relative complexity of
the systems investigated, which include arsenious
sulphide sol[3], platinum sol[4], silver iodide sol[1], and
sulphur sol[2]. It therefore appeared desirable to
study the phenomenon in the case of a more simple
system.

Colloidal stearic acid was selected as appro-
priate for the purpose. Very stable sols may be
prepared by mixing a methyl alcohol solution of the
acid with water at a suitable temperature. On
elimination of the alcohol, by heating, the sol con-
sists simply of solid particles of stearic acid
dispersed in an exceedingly dilute, though saturated,
aqueous solution of stearic acid. Achar and Usher[5]
have shown that when neutral salt is added to the
sol, acid appears in the intermicellar liquid. This
is comprehensible, since at least part of the particle
surface must be composed of molecules of stearic acid
orientated/

1. Verwey and Kruyt, Z. physikal Chem., 167 A (1933)
   312. Verwey, Chem. Reviews, 16 (1935) 363.

2. Weiser and Gray, J. Phys. Chem., 39 (1935) 1163.
   Bolam and co-workers, J.C.S. (1932), 2684; (1933),
   1022; (1934), 754.

3. Freundlich, Joachinsohn, and Ettisch, Z. physical
   Chem., 141A, (1929), 249.
   Rabinovitch and Kargin, Trans. Faraday Soc., (1935)
   31, 50. Weiser and Gray, J.Phys. Chem., 36, 1932,2796.

4. Pennycuik, J.C.S., 1929, 618: Kolloid-Zeitsch, 54,
   (1931) 21.

5. Achar and Usher, J.C.S., 1927, 1875.

orientated with their carboxyl groups in contact with
the liquid. By the ionisation of these molecules a
double layer is formed, the inner part consisting of
stearate anions embedded in the particle surface, and
the outer, of mobile hydrogen ions. Hence when a
neutral salt is introduced, interchange will occur
between the salt kations and the hydrogen ions. Achar
and Usher studied the influence of (1) concentration
of sol and (2) concentration of salt upon the degree
of interchange. From their data they conclude that
the "surface ionisation" of the particles resembles
that of a weak acid; that is to say only a small
fraction of the ionisable surface molecules are
actually ionised.

The present work deals with (1) the dependence of
the degree of interchange upon (a) concentration of
sol, (b) concentration of salt, (c) nature of salt, and
(d) acidity of system and (2), the degree of interchange
at the coagulation point of the sol. In the following
an account is given of the experimental work, and the
bearing of the results upon current views with regard
to the mechanism of coagulation is discussed.

EXPERIMENTAL.

MATERIALS AND APPARATUS.

Preparation of Stearic Acid Sols.

Several sols were prepared during the course of this investigation, and the method adopted by Mukherjee[1] was used. Stearic acid of "specially pure" quality as supplied by B.D.H. Ltd. was recrystallised twice from neutral methyl alcohol, and dried in a vacuum dessic- ator. The melting point of this acid was 69.4°C.[2] Methyl alcohol was first treated with magnesium turnings to remove water, then distilled, the middle fraction taken and redistilled. The middle fraction of the re- distillate was neutral to litmus,and was used for the purification of the stearic acid and the preparation of the sols.

2.4 grams of stearic acid were dissolved in 200 mls. of neutral methyl alcohol by heating to boiling point on a water bath, the solution being added to 700 mls. of boiling conductivity water contained in a large Jena beaker, and a milk-like suspension was obtained. Boiling was continued to evaporate the methyl alcohol, and the total volume of liquid kept constant/

1. Half-yearly. Journal of the Mysore University, - 1935, - P. 4984
2. M.P. = 69.2°C. Proc. R. Soc. 125, (1929) P. 394.

constant by the addition of boiling conductivity water.
According to Mukherjee (loc. cit.), departure from the
above or a lowering of the solution temperature reduces
the sol concentration, while at temperatures below
$69^{\circ}C$, no sol is formed.

In the present work it was found that prolonged
boiling, after the addition of the methyl alcohol
stearic acid solution, decreased the concentration of
stable sol, e.g. the concentration of sol B is much
less than the other sols; - (see page 7). Boiling
for a quarter of an hour after the addition of the
stearic acid solution gave a sol whose concentration
was similar to that obtained by Achar and Usher. (loc.
cit.). The sols prepared in this way were allowed to
stand for three days, and any coarse particles not in
colloidal suspension, quickly came to the surface of
the liquid, and the sol was removed from the coarse
particles by means of a siphon. Sols were stored
in Jena glass bottles and protected from the light;
they were very stable, and their degree of coarsening
over a period of six months was extremely small.

Estimation/

Table 1.

Composition of Sols.

Sol.	Wt. of stearic acid, in grams, after 1st Heating.	2nd Heating.	3rd Heating.	Grams of Stearic acid / litre.	Mean.
B.	0.0340	-	-	1.36	1.36
C.	0.0563	0.0561	0.0561	2.24	2.25
"	0.0569	0.0564	0.0565	2.26	
D.	0.0524	0.0521	0.0521	2.08	2.07
"	0.0519	0.0513	0.0515	2.06	
E.	0.0611	0.0601	0.0603	2.41	2.41
F.	0.0569	0.0568	0.0568	2.27	2.26
"	0.0564	0.0565	0.0563	2.25	

Estimation of the Stearic acid content of the Sols.

The method of drying to constant weight was employed. This gave accurately reproducible values.

25 mls. of the sol were pipetted into a weighed Pyrex evaporating basin, and the water removed by evaporation on the steam bath. It was observed that the stearic acid was almost completely coagulated when the volume of the liquid was reduced to approximately a quarter. After heating to apparent dryness, the basin was cooled in a dessicator and the stearic acid weighed. This procedure was repeated until constant weight was obtained. The data is given in Table I.

9.

Chemical Reagents.

With the exceptions of lithium sulphate and lithium hydroxide, the salts, acids, and alkalies, employed throughout the research were of A.R. quality.

The mercury for the calomel electrode was twice washed in nitric acid, dried and distilled in vacuo. Calomel was prepared electrolytically[1] from this mercury and A.R. hydrochloric acid, and when formed by this process was heavily laden with finely divided mercury. This was shaken with repeated changes of a 3.5 N KCl solution before being placed in the calomel half-cell. Potassium chloride was recrystallised twice and dried in an air-oven at $120^{\circ}C$ for several hours.

The quinhydrone, prepared by the method of Biilman and Lund[2], was repeatedly washed with ice-cold water until free from acid, dried over calcium chloride in a vacuum dessicator, and kept in a well stoppered bottle.

Pure conductivity water was made in the following way. Distilled water containing potassium permanganate and barium hydroxide was redistilled in an all Pyrex glass apparatus, the first 500 mls of the distillate being rejected, and the middle fraction, - approximately 1000 mls - collected. Water thus produced was of a specific conductivity not greater than 1.20×10^{-6} mho.

1 Clark:- Determination of Hydrogen Ions.
2 Biilman and Lund:- Annales de Chemie. 15, 128, 1928.

Glass-Ware.

Since the amount of hydrogen ion to be measured
was very small, it was imperative that the liquids
under investigation should not be brought in contact
with any acidic or basic surface. Hence only Pyrex
or Jena glass ware was used in this investigation.
Ordinary soda-glass was found to be quite unsatisfac-
tory. Before use, all glass ware was cleaned with
chromic acid, thoroughly washed with distilled water,
steamed-out for several hours, and finally dried in a
steam oven.

Volume Measurements.

Six Pyrex pipettes were used, each one being kept
for a particular operation. They were cleaned in the
above manner, and the following calibration data show
the reproducibility of the volume measurements.

2 ml. Pipettes.

Used for Salt Solutions.		Used for Sols.	
Wt. of water delivered. (grams)	Divergence from mean. (grams)	Wt. of water delivered. (grams)	Divergence from mean. (grams)
1.9826	+ 0.0027	1.9778	+ 0.0006
1.9781	- 0.0018	1.9770	- 0.0002
1.9812	+ 0.0013	1.9758	- 0.0014
1.9789	- 0.0010	1.9783	+ 0.0011
1.9786	- 0.0013		
Mean:- 1.9799		Mean:- 1.9772	
Temp. 17°C.		Temp. 18°C.	

10 ml. Pipettes.

Used for Salt Solutions.		Used for Acid Solutions.	
Wt. of Water delivered. (grams)	Divergence from mean. (grams)	Wt. of Water delivered. (grams)	Divergence from mean. (grams)
9.984	+ 0.008	9.961	- 0.006
9.982	+ 0.006	9.958	- 0.009
9.962	- 0.014	9.972	+ 0.005
9.978	+ 0.002	9.976	+ 0.009
Mean :- 9.976	Temp. 16°C.	Mean:- 9.967	Temp. 16°C.

13.

25 ml. Pipettes.

Used for Salt Solutions.		Used for Sol.	
Wt. of Water delivered. (grams)	Divergence from mean. (grams)	Wt. of Water delivered. (grams)	Divergence from mean. (grams)
24.986	+ 0.003	24.988	+ 0.009
24.990	+ 0.007	24.989	+ 0.010
24.993	+ 0.010	24.972	- 0.007
24.965	- 0.022	24.967	- 0.012
24.982	- 0.001		
Mean:- 24.983 Temp. 17°C.		Mean:- 24.979. Temp. 14°C.	

Three Pyrex graduated flasks were employed, the volumes of which did not differ from 100 mls.,
250 mls., and 1000 mls., respectively by more than 0.05 per cent.

E.M.F. Determinations.

The concentration of acid in the solutions under examination was determined by means of the quinhydrone electrode[1] in conjunction with a 3.5 N calomel electrode, connection being made by means of a 3.5 N KCl bridge, thus:-

$$\text{Hg} \left| \begin{array}{cc} \text{Hg}_2\text{Cl}_2, & \text{KCl} \\ \text{(solid)} & \text{3.5 N} \end{array} \right| \begin{array}{c} \text{KCl} \\ \text{3.5 N} \end{array} \left| \begin{array}{c} \text{X,} \end{array} \right. \begin{array}{c} \text{Quinhydrone} \\ \text{(solid)} \end{array} \left| \text{Pt. foil.} \right.$$

Where X = solution of unknown acidity. The circuit employed was of the ordinary Poggendorff type, the principal components being a high sensitivity moving coil galvanometer (Gambrell), a Tinsley "Ionisation" potentiometer reading to 0.10 millivolts, and a Tinsley standard Weston cell (N.P.L. calibration).

A specially designed quinhydrone cell of about 7 mls. capacity was constructed from a pyrex ground glass joint A, as shown in Fig. 1. The siphon tap B was thoroughly ground in with a silica paste to give a perfect fit, so that the use of vaseline or other lubricant was avoided. Cleaning and drying with alcohol and ether was found to give erratic readings, due/

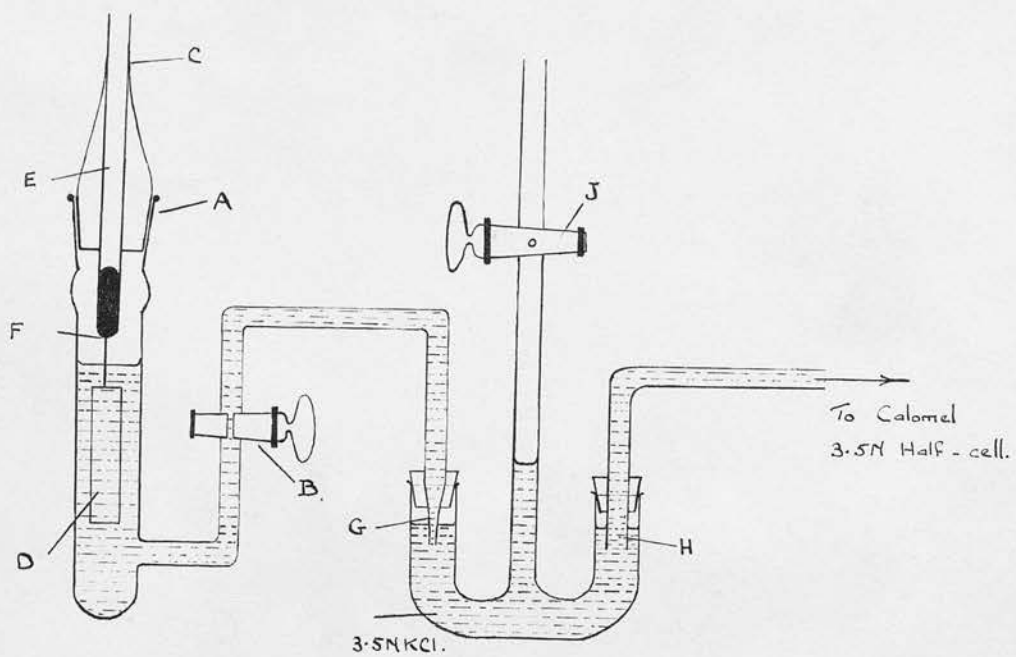1. Biilman. Annales de Chemie 15, (1921) p.128.

Fig. 1.

due probably to impurities in these liquids. The
platinum electrode was a narrow strip of polished
platinum D , welded to a short length of platinum wire
F , which was fused into a piece of Pyrex glass tubing
E , (0.5 cm. diam.) An internal seal was made with
the ground glass joint at C. The platinum-glass
junction was thoroughly tested[1] for any leakage or
crack and found to be perfect. When not in use, the
platinum electrode was kept in conductivity water.
Before each determination the platinum electrode was
washed and heated in an alcohol flame.

This electrode vessel had the following advantages:-
(1) It consisted entirely of Pyrex glass.
(2) It was simple in design and therefore easily
cleaned and dried.
(3) The electrode could be cleaned by heating in an
alcohol flame[2] without risk of fracture.

The electrode vessel dipped into the bridge at
G , containing 3.5 N KCl, while contact was made with
the calomel cell at H. The combination was mounted on
an earthed metal sheet, in a constant temperature room,
the temperature being regulated to $14^{\circ}C$ ($\pm 0.15^{\circ}$). The
composition/

1 Morgan, Lambert, and Campbell. J.A.C.S. I. 1931,p.453.

2 Havorka and Dearing. J.A.C.S. 56, p.243 1934.

composition of the atmosphere in this room was more or less constant. There were no fumes of any description and the only burner used was the alcohol flame for heating the platinum electrode.

The liquid under investigation was saturated with quinhydrone by shaking for five minutes with excess of the solid in a Jena glass stoppered bottle. All voltages were read twenty minutes after assembly of the cell. In any given case the e.m.f. was quite constant, and the data in the following pages show that the degree of reproducibility was satisfactory. To ascertain whether the presence of carbon dioxide had any influence upon the results, several experiments were carried out in the following manner. Air, freed from carbon dioxide by passage through several soda-lime towers, and at the same vapour pressure as that of the experimental solution, was bubbled through the latter for several hours. It was found that this treatment in no way affected the values of the e.m.f.

In order to test the calomel cell, and the quin-
hydrone, a solution of known P_H was taken and the
values determined at different periods during the
research.   The solution was an $\frac{M}{10}$ aqueous solution
of secondary sodium citrate (B.D.H.)   Two solutions
from different bottles were used.

No. of Experiment.	E.M.F. (Volt)	Mean.	Biilman's Value.
1	0.1674		
2	0.1672	0.1673	
3	0.1673		
4	0.1683		0.1678
5	0.1680		
6	0.1683	0.1682	
7	0.1681		
8	0.1682		

Experiments 1, 2 and 3 were carried out with
solution A, while the remainder were obtained with
the other sample B.

Preparation of Salt Solutions.

Solutions of potassium, sodium, and lithium sulp-
hates prepared directly from the commercial salts were
found to be distinctly acid, for the e.m.f. value
obtained with the salt solution itself decreased on
recrystallisation of the salt, as will be seen from
Table 2.   Preliminary work showed that it was neces-
sary to reduce the acidity of the salt solutions very
considerably, and since elimination of the acid by
recrystallisation of the salt was a lengthy process,
the stock solutions of potassium, sodium, and lithium
sulphates used for most of the work were prepared in
the following manner. To two litres of a solution,
containing one gram equivalent of recrystallised salt
per litre, a small volume of carbonate - free solution
of the corresponding hydroxide was added, so that the
residual acid was neutralised to an extent which re-
duced the e.m.f. to about 0.1000 volt in a solution
0.5 N with respect to salt. (Salts X_3, Y_3, and Z_3,
Tables 3, 5, 6).

The magnesium sulphate was found to be much less
acid than the alkali metal sulphates, and a single
recrystallisation sufficed for the preparation of a
satisfactory solution without the addition of alkali.

Table 2.

Influence of recrystallisation on acidity of

salt solutions.

Salt.	Number of recrystal- lisations.	Conc. of solution.	E.M.F. (volt.)	Mean.
K_2SO_4 (X.)	0	0.25	0.1505	
			0.1510	
			0.1508	
			0.1489	0.1503
" (X₁)	3	0.25	0.1341	
			0.1348	
			0.1349	
			0.1328	
			0.1331	
			0.1344	0.1340
" (X₂)	4	0.25	0.1377	
			0.1377	
			0.1351	
			0.1356	0.1365
	4	0.50	0.1339	
			0.1342	
			0.1350	
			0.1345	0.1344
Na_2SO_4 (Y.)	0	0.25	0.1615	
			0.1622	
			0.1628	
			0.1611	0.1619

Table 2 (contd.)

Salt.	Number of recrystal-lisations.	Conc. of solution.	E.M.F. (volt.)	Mean.
Li_2SO_4 (Z.)	0	0.25	0.1899	
			0.1906	
			0.1906	
			0.1904	
			0.1908	0.1905
" (Z1)	3	0.25	0.1743	
			0.1746	
			0.1745	0.1745
" (Z2)	5	0.25	0.1455	
			0.1458	0.1457
	5	0.50	0.1475	
			0.1451	
			0.1465	
			0.1467	0.1464

IONIC INTERCHANGE.

Determination of Liberated Acid.

Equal volumes of sol and salt solution were mixed
and shaken in a glass-stoppered bottle or tube, the
mixture allowed to stand for 18 hours, the stearic acid
separated off (see below) and the e.m.f. given by the
residual liquid measured.

In order to deduce the actual concentration of
liberated acid from the e.m.f., it was necessary to
know the relation between these quantities at the par-
ticular concentration of salt in question. This re-
lation was obtained by measuring the e.m.f.'s for a
series of salt solutions to which known amounts of
sulphuric acid had been added. For this purpose a
stock solution of sulphuric acid was prepared from A.R.
acid and carefully standardised with carbonate-free
Sodium hydroxide. By dilution of this acid solution
(0.3581 N),solutions of suitable concentrations were
obtained. Finally, mixtures made from equal volumes
of acid and salt solutions were used for the actual
measurements. The data are reproduced in Tables 3 - 8,
and Figs. 2 - 5. It will be seen that smooth graphs
were obtained, from which the concentration of acid
corresponding to a given value of the e.m.f. could be
read off with the requisite degree of accuracy.

In all tables the concentrations of salts and acid
are expressed in terms of gram equivalents per litre.

Table 3.

Potassium Sulphate. (X₃).

Conc. of Salt.	Conc. of acid X 10^6.	E.M.F. (Volt)	Mean.
0.5	–	0.1026	
	–	0.1012	
	–	0.1038	
	–	0.1024	
	–	0.1025	
	–	0.1029	0.1026
	8.95	0.1108	
	"	0.1097	0.1103
	17.90	0.1210	
	"	0.1195	0.1203
	35.80	0.1301	
	"	0.1289	
	"	0.1285	
	"	0.1310	
	"	0.1292	
	"	0.1320	0.1299
	59.60	0.1511	
	"	0.1502	0.1507
	89.50	0.1710	
	"	0.1703	0.1706
	179.00	0.1968	
	"	0.1971	0.1970
0.25	–	0.1159	
	–	0.1153	0.1156
	8.95	0.1261	

Potassium Sulphate (X3) cont.

Conc. of Salt.	Conc. of acid X 10⁶	E.M.F. (Volt)	Mean.
0.25	8.95	0.1261	
	"	0.1250	0.1255
	17.90	0.1365	
	"	0.1351	0.1358
	35.80	0.1526	
	"	0.1522	0.1524
	44.70	0.1645	
	"	0.1639	0.1642
0.10	-	0.1260	
	-	0.1262	
	-	0.1262	0.1261
	8.95	0.1446	
	"	0.1442	0.1444
	17.90	0.1542	
	"	0.1537	0.1540
	35.80	0.1685	
	"	0.1679	0.1682
0.05	-	0.1477	
	-	0.1471	0.1474
	6.70	0.1535	
	"	0.1530	0.1532
	17.90	0.1692	
	"	0.1684	0.1688
	35.80	0.1807	
	"	0.1807	
	"	0.1815	
	"	0.1812	0.1810

Potassium Sulphate (X_3) Contd.

Conc. of Salt.	Conc. of acid X 10^6	E.M.F. (Volt)	Mean.
0.01	-	0.1531	
	-	0.1522	
	-	0.1538	
	-	0.1526	0.1529
	8.95	0.1685	
	"	0.1682	
	"	0.1682	0.1683
	17.90	0.1776	
	"	0.1795	
	"	0.1785	0.1785

Table 4.

Potassium Sulphate (X_2).

Conc. of Salt.	Conc. of acid X 10^6.	E.M.F. (Volt)	Mean.
0.5	4.50	0.1382	
	"	0.1378	0.1380
	8.95	0.1403	
	"	0.1415	0.1409
	11.92	0.1456	
	"	0.1448	0.1452
	17.90	0.1497	
	"	0.1489	0.1493
	35.80	0.1593	
	"	0.1595	0.1594

Table 5.

Sodium Sulphate (Y3).

Conc. of Salt.	Conc. of acid X 10^6	E.M.F. (Volt.)	Mean.
0.5	–	0.1011	
	–	0.1005	
	–	0.1019	
	–	0.1015	
	–	0.1028	
	–	0.1017	0.1016
	8.95	0.1075	
	"	0.1067	0.1071
	17.90	0.1165	
	"	0.1155	0.1160
	35.80	0.1278	
	"	0.1267	
	"	0.1268	
	"	0.1310	
	"	0.1292	
	"	0.1275	
	"	0.1271	0.1280
	59.60	0.1501	
	"	0.1493	0.1497
	89.50	0.1708	
		0.1709	0.1708
0.25	–	0.1141	
	–	0.1137	0.1139
	8.95	0.1230	
	"	0.1222	0.1226
	17.90	0.1341	
	"	0.1354	0.1347

Sodium Sulphate (Y₃)   Contd.

Conc. of Salt.	Conc. of acid X 10⁶	E.M.F. (Volt.)	Mean.
0.25	35.80	0.1545	
	"	0.1536	0.1540
	44.70	0.1657	
	"	0.1650	0.1653
0.10	–	0.1242	
	–	0.1234	0.1238
	8.95	0.1409	
	"	0.1395	0.1402
	17.90	0.1516	
	"	0.1508	0.1512
	35.80	0.1708	
	"	0.1705	
	"	0.1704	0.1706
0.05	–	0.1459	
	–	0.1453	0.1456
	6.70	0.1541	
	"	0.1534	0.1537
	17.90	0.1675	
	"	0.1676	0.1675
	35.80	0.1801	
	"	0.1798	0.1800
0.01	–	0.1510	
	–	0.1505	0.1507
	8.95	0.1648	
	"	0.1643	0.1645
	17.90	0.1753	
	"	0.1760	0.1756

Table 6.

Lithium Sulphate (Z3).

Conc. of Salt.	Conc. of acid X 10^6	E.M.F. (Volt)	Mean
0.5	-	0.1028	
	-	0.1019	
	-	0.1038	
	-	0.1042	0.1032
	8.95	0.1126	
	"	0.1138	0.1132
	17.90	0.1210	
	"	0.1208	0.1209
	35.80	0.1365	
	"	0.1356	0.1360
	59.60	0.1568	
	"	0.1568	0.1568
	179.0	0.2013	
	"	0.2015	0.2014
	358.0	0.2209	
	"	0.2211	0.2210
	716.0	0.2405	
	"	0.2408	0.2407
0.25	-	0.1212	
	-	0.1203	0.1207
	8.95	0.1288	
	"	0.1301	0.1295
	17.90	0.1381	
	"	0.1372	0.1376
	35.80	0.1567	
	"	0.1561	0.1564

Lithium Sulphate (Z3) cont.

Conc. of Salt.	Conc. of acid. X 10^6.	E.M.F. (Volt)	Mean.
0.10	–	0.1285	
	–	0.1273	0.1279
	8.95	0.1408	
	''	0.1401	0.1404
	17.90	0.1513	
	''	0.1515	0.1514
	35.80	0.1725	
	''	0.1719	0.1722
0.05	–	0.1478	
	–	0.1475	0.1476
	6.70	0.1548	
	''	0.1542	0.1545
	17.90	0.1685	
	''	0.1676	0.1680
	35.80	0.1802	
	''	0.1798	
	''	0.1792	0.1798
0.01	–	0.1521	
	–	0.1518	0.1520
	8.95	0.1647	
	''	0.1655	0.1651
	17.90	0.1780	
	''	0.1778	0.1779

Table 7.

Lithium Sulphate (Z$_2$)

Conc. of Salt.	Conc. of acid. X 10^6	E.M.F. (Volt).	Mean
0.5	6.70	0.1490	
	"	0.1489	0.1490
	8.95	0.1515	
	"	0.1510	0.1513
	17.90	0.1555	
	"	0.1574	0.1565
	35.80	0.1674	
	"	0.1662	
	"	0.1684	0.1674

Table 8.

Magnesium Sulphate.

Conc. of Salt.	Conc. of acid X 10^6	E.M.F. (Volt)	Mean.
0.5	–	0.0771	
	–	0.0775	
	–	0.0771	
	–	0.0710	
	–	0.0701	0.0746
	8.95	0.0824	
	"	0.0816	0.0820
	17.90	0.0850	
	"	0.0850	0.0850
	35.80	0.0948	
	"	0.0995	
	"	0.0990	
	"	0.0942	0.0969
	89.5	0.1179	
	"	0.1174	0.1177
	119.3	0.1337	
	"	0.1335	0.1336
	179.0	0.1817	
	"	0.1820	
	"	0.1809	
	"	0.1807	0.1813
	358.0	0.2189	
	"	0.2194	0.2192
	716.0	0.2435	
	"	0.2433	0.2434
	1260.0	0.2582	
	"	0.2585	0.2584

Magnesium Sulphate. (contd.)

Conc. of Salt.	Conc. of acid X 10^6.	E.M.F. (Volt)	Mean
0.10	–	0.1210	
	–	0.1221	0.1216
	17.90	0.1406	
	"	0.1402	0.1404
	35.80	0.1626	
	"	0.1621	0.1624
0.05	–	0.1331	
	–	0.1326	0.1329
	6.70	0.1445	
	"	0.1441	0.1443
	17.90	0.1612	
	"	0.1614	0.1613
	35.80	0.1792	
	"	0.1793	0.1793
0.01	–	0.1481	
	–	0.1481	0.1481
	17.90	0.1796	
	"	0.1802	
	"	0.1798	0.1798
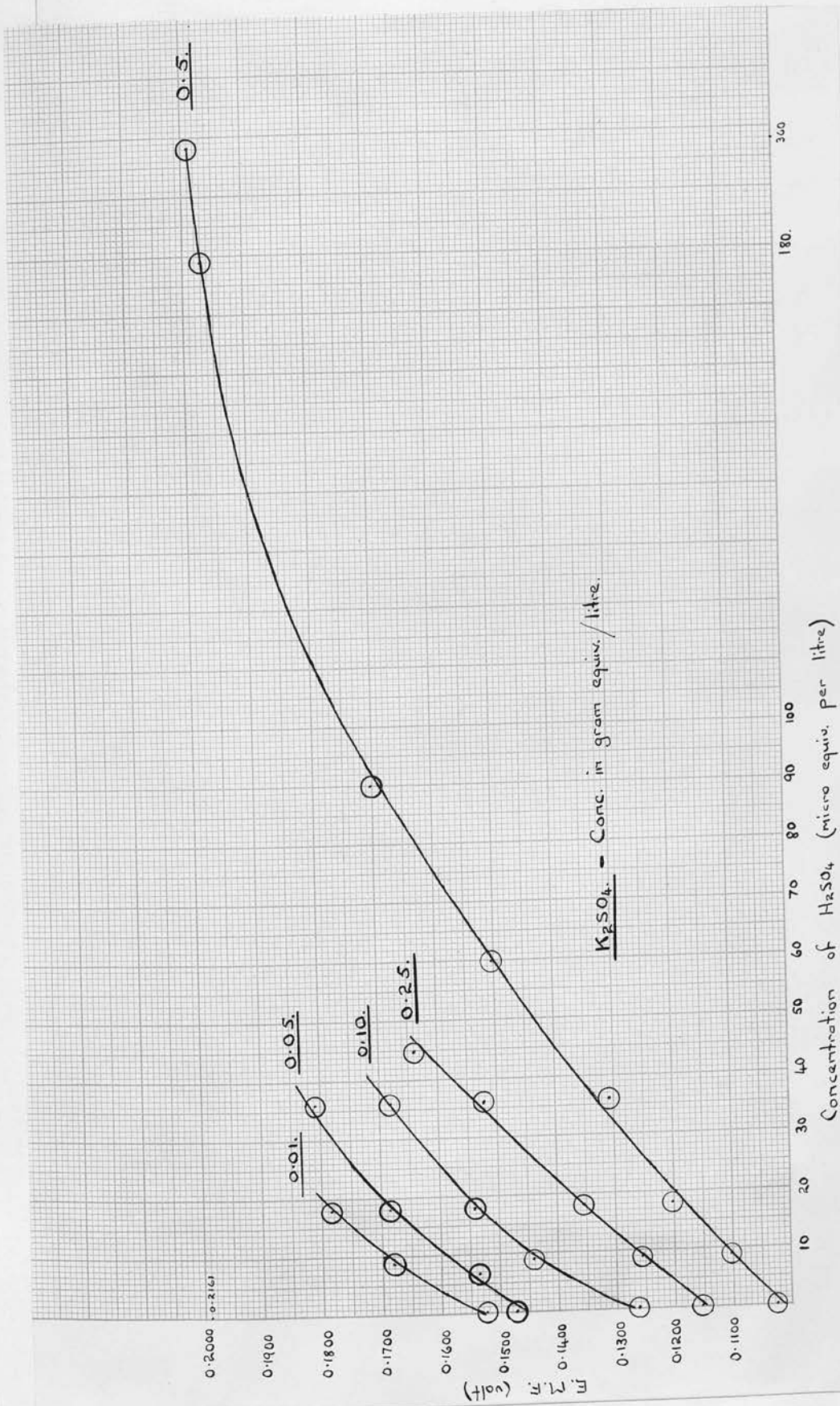
Fig. 2.
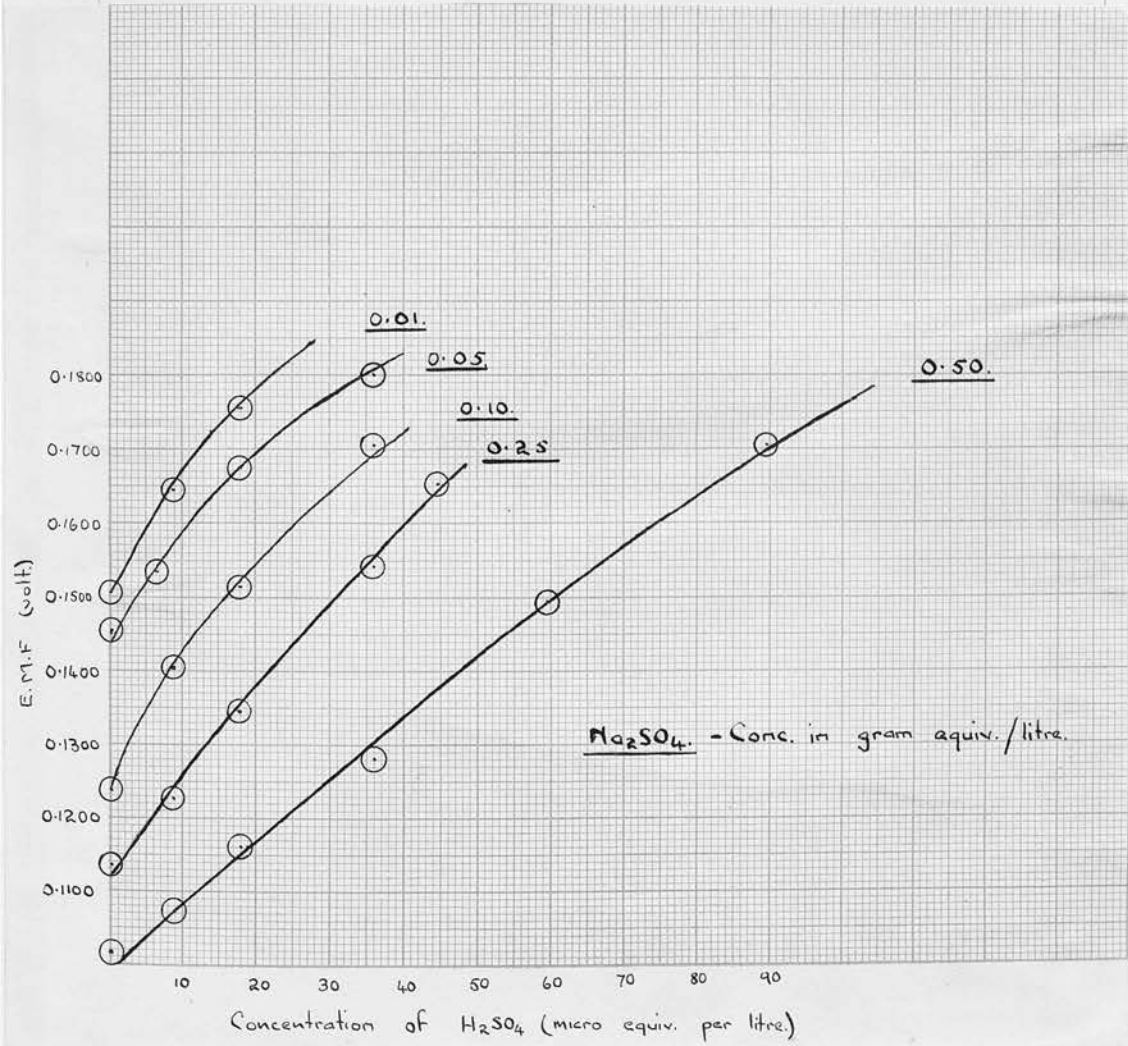
Fig. 3.
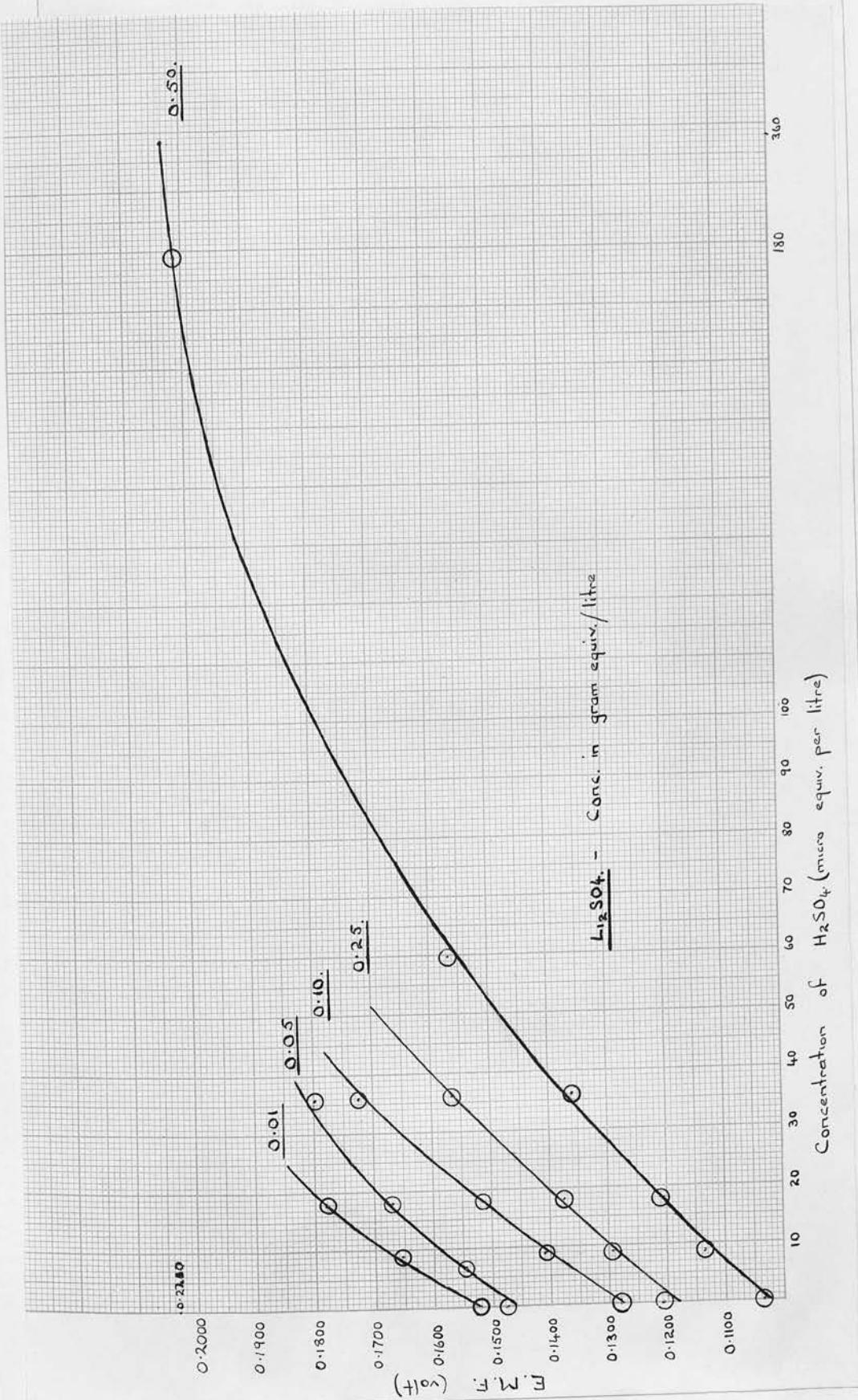
Fig. 4.
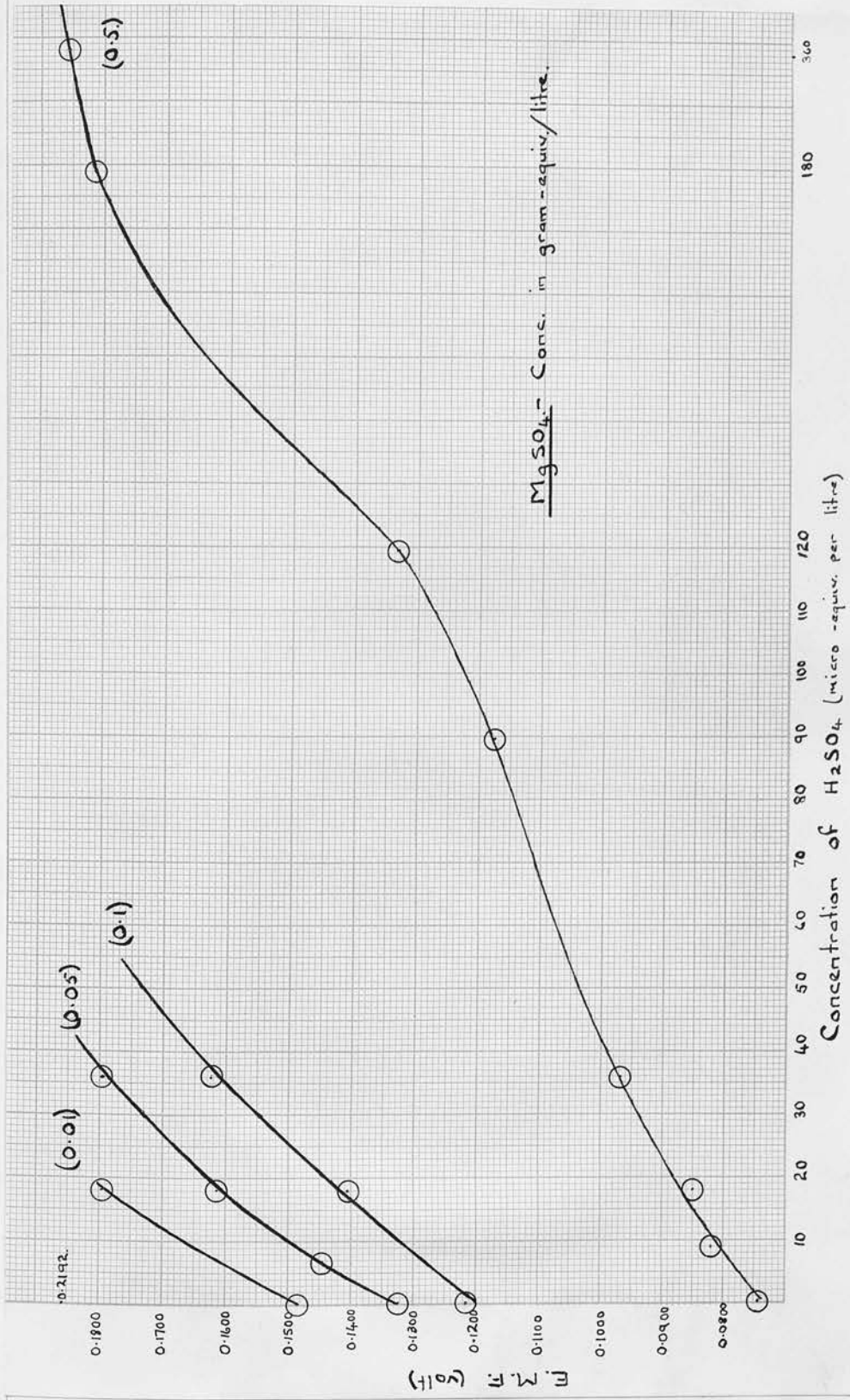
Fig. 5.

Method of Separation.

It was thought desirable to separate the stearic
acid from the aqueous phase for two reasons. In the
first place Achar and Usher (loc. cit.) have pointed
out that coagulated acid tends to adhere to the plat-
inum electrode, thereby vitiating the potential deter-
mination. In the second place it was observed by the
author that the quinhydrone had a definite coagulating
action on any colloidal acid present, which (see later)
would probably be accompanied by an increase in the
acidity of the aqueous phase beyond that produced by
the added salt.

The method of separation was varied according to
the concentration of salt employed. At sufficiently
high concentrations the whole of the stearic acid rose
to the surface of the solution, leaving a perfectly
clear underlying liquid, samples of which could be
easily removed by means of a pipette. At lower con-
centrations of salt, however, the underlying liquid was
turbid, due to the presence of either uncoagulated col-
loid, or coagulum in the form of a coarse suspension
(see later).

Achar and Usher (loc. cit.) in similar experiments
on stearic acid sols used "ashless" filter papers as a
means of separating the stearic acid coagulum from the
intermicellar liquid. Since "ashless" filter papers
result from treatment with acid, there appeared to be
a risk of hydrogen ion being displaced from such paper.
The/

The following experiments were therefore performed.

(1)   25 mls of K_2SO_4 (X_2) solution were added to 25 mls Sol B, the mixture shaken for 5 minutes and allowed to stand for 18 hrs. Coagulation was complete, the underlying liquid being quite clear. The liquid was filtered through a 9 cm. "ashless" filter paper, (Schleicher and Schüll Blue band.) the first 10 mls. of filtrate being rejected, and the remainder collected. An experiment was also carried out similar to the above but in this case the clear underlying liquid was removed by means of a pipette. The following figures were obtained.

Liquid.	Conc. of Salt.	E.M.F. (volt).	Mean.
Filtered	0.50	0.1697	
	"	0.1692	0.1695
Unfiltered	0.50	0.1531	
	"	0.1538	0.1535

It will be observed that the filtered liquid was actually more acid than the unfiltered; the difference in acidity being 26 micro equi./l. (see fig. 2.)

(2)   Experiment (1) was repeated, the first 25 mls collected and the e.m.f. determined. The final 25 mls. was also collected and its e.m.f. determined.

Liquid	Conc. of Salt.	E.M.F. (volt)	Mean.
1st 25 mls. Filtrate.	0.50	0.1783	
"	"	0.1786	0.1785
2nd 25 mls. Filtrate.	0.50	0.1559	
"	"	0.1556	0.1557

The difference in conc. of acid is 49 micro-equi./l.(fig2) and it will be observed that the e.m.f. of the un-filtered liquid in expt. (1) corresponds with that of the 2nd 25 mls. filtrate in (2). It would appear there-fore that the presence of salt increases the conc. of acid on filtering through an "ashless" filter paper.

(3)   25 mls. of the salt solutions, K_2SO_4 (X) and Li_2SO_4 (Z) were filtered through two separate filter papers, (5 cm. diam) which had been previously washed with conduct-ivity water and dried. The first few mls. were re-jected in each case, and the e.m.f. of the subsequent filtrates determined.

Salt	Conc. of Salt.	E.M.F. volt.		Mean.
		Before filt-:ration.	After filt-:ration.	
$K_2 SO_4$ X.	0.25	0.1503	0.1611	
"	"	From Table.2.	0.1615	0.1613
Li_2SO_4 Z.	0.25	0.1905	0.1932	
"	"		0.1936	0.1934

For K_2SO_4 (X) the increase in conc. of acid on filtra-tion is 12 micro equi./l. (See fig. 2).

Obviously/

Obviously, salt displaces hydrogen ion from the filter paper, and the following experiment confirms this.

(4)   100 mls. of K_2SO_4 (X_2) solution were filtered through an "ashless" filter paper of 5 cm. diameter. The first 25 mls. were collected and its e.m.f. determined. Succeeding 25 mls. fractions were also collected, with the exception of the final 24 mls, which were unfiltered, and the following results obtained.

Conc. of Salt.	E.M.F.		No. of Fraction (25 mls.)
	Before filtr-:ation.	After filtra-:tion.	
0.25	0.1365	0.1638	1
"	From table. 2.	0.1384	2
"		0.1377	3
"		0.1377	Unfiltered.

The increase in the conc. of acid is 26m.eq./l for the first fraction, while succeeding fractions show an e.m.f. which is similar to the figure obtained for salt which was unfiltered.

(5)   Sol B was filtered through an "ashless" filter paper, 25 mls. of filtered sol were shaken with 25 mls. K_2SO_4 X_2, and the clear intermicellar liquid was removed by means of a pipette.

Conc. of Salt.	E.M.F. volt.	Mean.
0.50	0.1535	
"	0.1527	0.1531

The above results prove conclusively that salt dis-
placed hydrogen ion from the filter paper, and that for
salt solutions containing 0.5 gm. equi./l. it was nec-
essary to reject at least the first 25 mls. of filtrate.
It is also to be observed that filtration of the sol
through "ashless" filter paper before salt is added in
no way affects the results, showing that the stearic
acid did not displace hydrogen ion from the filter paper.
Since washing the filter paper with conductivity water
did not remove the acid, the production of acid can
only be due to ionic interchange between the hydrogen
ion in the filter paper, and the cation of the added
salt.

Ultimately filtration by means of Jena fritted
glass filters was tried and proved to be an excellent
means of separation. Rather surprisingly, it was found
that filters of porosity 4, held back not only stearic
acid in coarse suspension, but also the great bulk of
the colloidal material (i.e. all except the very finest
particles). This was a great convenience since the
disadvantages of ultrafiltration could be avoided.
Actually a filter of the Buchner type was used, the
liquid/

liquid being drawn through by slight suction at the
rate of about 1 drop per 5 seconds, and collected in a
Jena filter-flask. The first drop or two of filtrate
was always colloidal enough to be distinctly turbid,
but thereafter the filtrate was quite clear. Since the
average diameter of the filter pores is given by the
makers as 5 - 10 microns, it would appear that the
action of the filter was probably due to adsorption of
the stearic acid on the glass, so that the effective
size of the pores was considerably decreased. Undoubt-
edly the stearic acid gradually blocked the pores, since
after about 25 mls. of liquid had been filtered, the
rate of filtration became perceptibly slower, and by
the time 50 mls. were collected, filtration became
extremely slow, even under very strong suction.

Before use, the filters were rinsed thoroughly with
hot hydrochloric acid, and then with water to remove
loose particles and accumulated dust. Washing with
distilled water was continued for several hours. The
filters and receivers were steamed out in the usual
manner. Stearic acid was removed from the fritted
glass by treatment with boiling absolute alcohol fol-
lowed by washing with conductivity water. Boiling
absolute alcohol was used as a solvent for all glass
ware contaminated with stearic acid.

Influence of Concentration of Sol.

Sol C was used to investigate the effect on the ionic interchange, of diluting the sol. The salt solutions were prepared from K_2SO_4 (X_2) and Li_2SO_4 (Z_2). Equal volumes of salt solution and diluted sol were mixed in every case, the concentration of the salt in the mixtures being uniformly 0.5 gm. equi./l. At all the dilutions considered, coagulation was complete with this concentration of salt. Hence the system was allowed to stand for 18 hrs., and the underlying liquid then removed by means of a pipette. In the following tables, the figure given under "Dilution" is the value of the ratio:

Concentration of original undiluted sol.

Final concentration of sol in mixture.
Thus when the sol is undiluted, the dilution is 1 ; when equal volumes of salt solution and original sol are added to each other, the dilution is 2 and so on.

44

Table 9 .

Effect of Dilution of Sol   (Sol C.).

Potassium Sulphate   (X$_2$) (See Fig 2&4)

Conc. of Salt.	Dilution of Sol.	E.M.F. (volt.)	Mean.	Conc. of liberated H$^+$ ion X 10^6.
0.5	2	0.1590		
"	"	0.1590	0.1590	35
"	4	0.1498		
"	"	0.1495	0.1497	21
"	8	0.1485		
"	"	0.1480	0.1483	19
"	20	0.1426		
"	"	0.1420	0.1423	10
Lithium Sulphate (Z$_2$).				
0.5	2	0.1627		
"	"	0.1628	0.1627	24
"	4	0.1530		
"	"	0.1535	0.1533	11
"	8	0.1502		
"	"	0.1501	0.1502	6
"	20	0.1484		
"	"	0.1479	0.1482	3

Exactly similar experiments were carried out with Sol
E. Solutions K_2SO_4 (X_3), Na_2SO_4 (Y_3) and Li_2SO_4 (Z_3)
were employed.

Table 10 .

Effect of Dilution of Sol. (Sol E.)
Potassium Sulphate (X_3). (Fig. 2)

Conc. of Salt.	Dilution of Sol.	E.M.F. (volt)	Mean.	Conc. of liberated H^+ ion X 10^6.
0.5	2	0.1558		
"	"	0.1553	0.1556	69
"	4	0.1403		
"	"	0.1408	0.1406	46
"	8	0.1316		
"	"	0.1309	0.1314	34
"	16	0.1193		
"	"	0.1180	0.1187	19
"	20	0.1154		
"	"	0.1162	0.1158	15

Table 11.

Sodium Sulphate (Y₃). (Fig. 3)

Conc. of Salt.	Dilution of Sol.	E.M.F. (volt)	Mean	Conc. of liberated H^+ ion $\times 10^6$.
0.5	2	0.1550		
"	"	0.1546	0.1548	67
"	4	0.1391		
"	"	0.1368	0.1379	45
"	8	0.1272		
"	"	0.1268	0.1270	32
"	16	0.1168		
"	"	0.1152	0.1160	19
"	20	0.1115		
"	"	0.1117	0.1116	14

Table 12.

Lithium Sulphate. (Z₃) (Fig. 4)

Conc. of Salt.	Dilution of Sol.	E.M.F. (volt)	Mean.	Conc. of liberated H^+ ion $\times 10^6$.
0.5	2	0.1578		
"	"	0.1568	0.1573	63
"	4	0.1416		
"	"	0.1417	0.1417	41
"	8	0.1300		
"	"	0.1317	0.1309	29
"	16	0.1205		
"	"	0.1202	0.1204	18
"	20	0.1180		
"	"	0.1195	0.1188	15

Influence of Nature and Concentration of Salt.

In every case 25 mls. of sol were shaken for five minutes with 25 mls. of salt solution, the mixture allowed to stand for 18 hours, the stearic acid separated off, and the e.m.f. for the clear liquid determined.

Table 13.

Determinations with Sol D.

Potassium Sulphate. (X_3) (Fig. 2)

Conc. of Salt.	E.M.F. (volt.)	Mean.	Conc. of liberated H^+ ion X 10^6.
0.50	0.1492		
"	0.1481	0.1487	58.0
0.25	0.1611		
"	0.1608	0.1610	44.0
0.10	0.1685		
"	0.1676	0.1680	36.0
0.05	0.1751		
"	0.1742	0.1746	25.0
0.01	0.1735		
"	0.1737		
"	0.1742		
"	0.1765		
"	0.1763		
"	0.1750	0.1749	15.0

Table 14.
Sodium Sulphate. (Y_3) (Fig 3)

Conc. of Salt.	E.M.F. (volt)	Mean.	Conc. of liberated H^+ ion $\times 10^6$.
0.50	0.1472		
"	0.1474	0.1473	57
0.25	0.1581		
"	0.1571	0.1576	38
0.10	0.1646		
"	0.1640	0.1643	30
0.05	0.1720		
"	0.1722	0.1721	23
0.01	0.1730		
"	0.1715		
"	0.1721	0.1722	14

Table 15.
Lithium Sulphate. (Z_3) (Fig. 4)

Conc. of Salt.	E.M.F. (volt)	Mean.	Conc. of liberated H^+ ion $\times 10^6$.
0.50	0.1492		
"	0.1481	0.1487	51
0.25	0.1560		
"	0.1555	0.1557	35
0.10	0.1634		
"	0.1626	0.1630	28
0.05	0.1689		
"	0.1682	0.1686	19
0.01	0.1730		
"	0.1740	0.1735	14

Table 16.

Determinations with Sol F.

Potassium Sulphate. (X3) Fig 2.

Conc. of Salt.	E.M.F. (volt)	Mean.	Conc. of liberated H^+ ion $\times 10^6$.
0.50	0.1524		
"	0.1516	0.1520	63
0.10	0.1647		
:	0.1654	0.1651	32
0.05	0.1710		
"	0.1709	0.1710	22
0.01	0.1748		
"	0.1752	0.1750	15

Table 17.

Magnesium Sulphate. (Fig 5).

Conc. of Salt.	E.M.F. (volt)	Mean.	Conc. of liberated H^+ ion $\times 10^6$.
0.50	0.1363		
"	0.1365	0.1364	123
0.10	0.1652		
"	0.1643	0.1647	40
0.05	0.1716		
"	0.1725	0.1720	29
0.01	0.1790		
"	0.1785	0.1788	18

COAGULATION VALUES.

Procedure.

The procedure adopted for the purpose of
observing the influence of the various electrolytes
upon the stearic acid sols was as follows: Equal
volumes (4 mls.) of sol and salt solution were mixed
in a small test-tube (pyrex). In order to minimise
local variations in concentration, the liquids were
discharged simultaneously at approximately the same
rate from small pipettes (2 mls: pyrex) in such a
manner that the streams of liquid intermingled. The
tube was closed with a glass stopper, the mixture
shaken vigorously for 5 minutes and then allowed to
stand at room temperature for 18 hours. This procedure
gave very consistent results.

As already indicated, above a certain relatively
high concentration of 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 certain range of
concentration somewhat below this the U.L. was still
definitely turbid, even after 18 hours, but on filter-
ing through a Jena fritted glass filter of porosity 3,
pore diameter = 20 to 30 microns, a perfectly clear
filtrate was obtained. In these cases the colloid was
to be regarded as completely coagulated in the sense
that none of the primary colloidal particles were
present/

present as separate individuals. Such particles
would have appeared in the filtrate since the stearic acid
sols themselves 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 coarse
suspension.

At still lower concentrations coagulation occur-
red, as evidenced by the accumulation of stearic acid
at the surface of the liquid, but was incomplete, since
the filtrate obtained with a 3 porosity filter gave
the "Schlieren" effect on agitation, which denoted the
presence of colloidal stearic acid. The proportion of
coagulated to uncoagulated acid decreased with decrease
in the concentration of coagulant, and for a given
concentration of coagulant appeared to be practically
the same after 18 hours as shortly after the intro-
duction of the coagulant. In one or two instances
a partially coagulated sample of sol was left undis-
turbed for several days without further change occurring.
Thus stearic acid sols show the phenomenon of "fract-
ional coagulation".

The "coagulation value" of an electrolyte was
taken as the minimum concentration necessary to pro-
duce complete coagulation, as described above, in 18
hours, i.e., which gave a perfectly clear filtrate with
a 3 porosity filter. Since at concentrations of
coagulant slightly below the coagulation value very
small/

PLAN of NEPHELOMETER.

Capacity of cell, approx. 1 ml
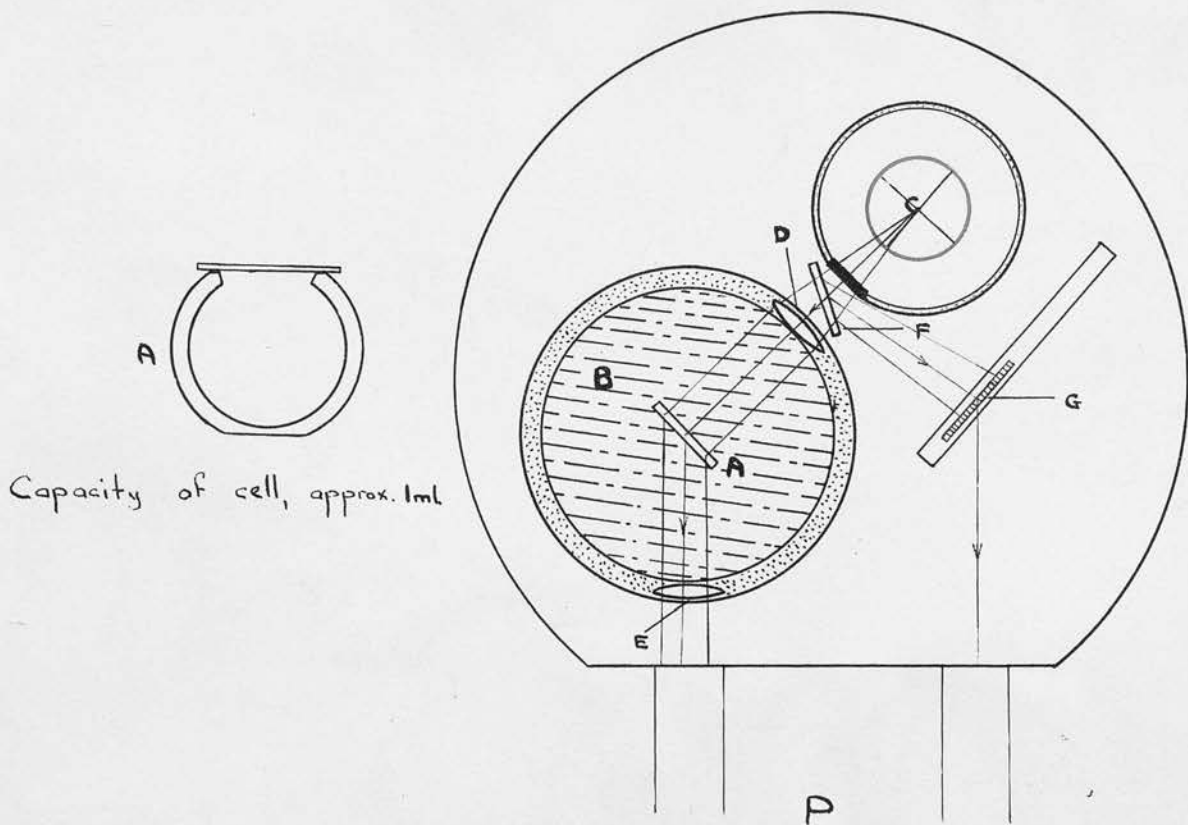
Fig. 6.

small quantities of colloid appeared in the filtrate, a Zeiss nephelometer, in conjunction with a Pulfrich photometer, was employed to detect the point at which the liquid became quite free from colloid. By this means it was found possible to determine the coagulation values to within a few per cent.   The tables (19 - 21), show that it was possible to detect very small concentrations of sol, by merely holding the tube containing the liquid against a suitable background e.g. a sol diluted 200 times was still colloidal in appearance. Near the coagulation value it was sometimes difficult to tell whether or not the liquid was opal - escent, and in this respect the nephelometer was useful.

Nephelometric Determinations.

The liquid to be examined was contained in the plane sided glass cell A. (Fig 6.), which was placed in the water chamber B. Light from the filament lamp C entered B through one lens D in the form of a pencil of uniform square cross-section.   The light scattered by colloidal particles in the cell left the water chamber through the other lens E. Part of the light from the lamp was reflected before entering the water chamber, at a glass plate F, and passed through the opal glass disc G. The intensities of the two beams, the one of light scattered by the particles of the colloidal solution, the other that transmitted by the opaque glass were compared by means of a Pulfrich photometer/

photometer P. Since the coagulation value was taken
as the minimum concentration of coagulant necessary
to give a water-clear liquid, the readings were com-
pared with that for water (= 6 to 8.). Before each
experiment, the glass cell was thoroughly cleaned with
a piece of muslin soaked in absolute alcohol, and dried.

Coagulation of Sol D. - Preliminary Observations.

Table 18.

Salt	Conc. of Salt.	Appearance of U.L.	
		After 60 mins.	After 18 hrs.
$K_2SO_4(X_3)$	0.50	Clear.	Clear
	0.25	"	"
	0.125	"	"
	0.083	V. Slight turbidity	"
	0.072	Slight turbidity	Slight turbidity
	0.050	Turbid.	Turbid.
$Na_2SO_4(Y_3)$	0.25	Clear	Clear
	0.125	"	"
	0.100	Slight turbidity	Slight turbidity
	0.072	" "	" "
	0.062	Turbid	Turbid.
	0.050	"	"
$Li_2SO_4(Z_3)$	0.50	Clear	Clear
	0.25	"	"
	0.166	"	"
	0.125	Slight turbidity	V. Slight turbidity.
	0.083	Turbid	Turbid
	0.050	"	"

Table 19.

Sol D. - Coagulation Values for $K_2SO_4 \cdot (X_3)$, $Na_2SO_4 \cdot (Y_3)$, and $Li_2SO_4 (Z_3)$.

Salt	Conc. of Salt.	Appearance of U.L. before filtration.	Appearance of U.L. after filtration.	Nephelometer reading.	Coag. Value.
K_2SO_4.	0.062	Slightly turbid	Perfectly clear	7. 8.	
	0.056	"	"	8. 7.5	
	0.050	Increased turbidity	Slightly colloidal; "schlieren" effect evident	21. 19.	0.053
	0.044	"	Slightly colloidal "schlieren" effect evident	35. 32.	
Na_2SO_4	0.072	Slightly turbid	Perfectly clear	7. 8.5	
	0.062	Turbid.	Slightly colloidal, - "schlieren" effect evident.	18. 16.	0.067
	0.056	Increased turbidity	Slightly colloidal "schlieren" effect evident	28. 26	
Li_2SO_4	0.125	Very slight turbidity	Perfectly clear	7.5	
	0.100	Slightly turbid	Perfectly clear.	10	
	0.083	"	"	9 8	0.077
	0.071	Increased turbidity	Slightly colloidal "schlieren" effect evident	18. 19	
	0.062	"	Colloidal and "schlieren" effect evident	31. 32.	

Table 20.

Sol F. - Coagulation Values for $K_2SO_4.(X_3)$ and Mg SO_4

Salt	Conc. of Salt	Appearance of U.L. before filtration.	Appearance of U.L. after filtration	Nephelometer reading.	Coag. Value.
MgSO4	0.031	Practically clear. A few coag. particles still in suspension.	Perfectly clear.	8. 9.	
	0.025	Slightly turbid	"	6. 8.	
	0.022	"	"	7.5 9.	0.021
	0.020	Increased turbidity	Slightly colloidal: - "schlieren" effect evident.	25. 21.	
	0.010	Colloidal.	Colloidal with distinct "schlieren" effect.	Over 100.	
K2SO4	0.062	Slightly turbid	Perfectly clear.	6. 7.	
	0.058	"	Slight opalescence, but no "schlieren" effect.	10. 13.	
	0.055	Increased turbidity	Slightly colloidal. "schlieren" effect evident.	21. 22.	0.060
	0.050	"	Slightly colloidal.	32. 31.	

Table 21.

Sol E. - Coagulation Value of H_2SO_4.

Conc. of H_2SO_4 X 10^4	Appearance of U.L. before filtration.	Appearance of U.L. after filtration	Nephelometer Reading.
17.90	Coagulation took place immed. sol + cold were shaken. U.L. perfectly clear after 10 minutes	Filtration unnecessary. Coagulation complete.	-- --
7.16	Slightly turbid.	Filtrate appeared clear, - when held against a dark surface, there was just the suspicion of a slight opalescence. No "schlieren" effect.	11.0. 10.5.
6.27	Slightly colloidal.	Only very slightly colloidal.	16 17
5.37	Colloidal.	Slight opalescence, "schlieren" effect observed.	23 21
3.58	Colloidal.	Filtrate definitely colloidal.	85 81
1.79	Brisk shaking was necessary to bring about coagulation. Turbid.	Colloidal.	Over 100.

Coagulation Value for H_2SO_4 may be taken as slightly above 7.16×10^4 gm. equiv/l.

. . . .

DISCUSSION.

Reproducibility of Sols.

It would appear that the method employed in the preparation of sols was satisfactory from the point of view of reproducibility.   As will be seen from Table I (p.7), the concentration of the sol did not vary greatly from preparation to preparation, with the exception of sol B, which was boiled to an excessive extent (see p.6).   Moreover the liberation of hydrogen ion by K_2SO_4 (X_3) solutions was practically the same for sols D and F at all concentrations of the salt (see later).   Again, the amount of hydrogen ion liberated per _gram_ of stearic acid by 0.5N K_2SO_4 (X_3) was found to differ only very slightly for sols D, E, and F, the values being 56, 57, 56 micro-equiv. per litre, res- pectively.   Finally it may be mentioned that the coagulation value for K_2SO_4 (X_3) in the case of sol D was much the same as the value obtained in the case of sol F.

The intermicellar liquid in all cases was simply a saturated solution of stearic acid.   A quantity of coarse purified stearic acid was treated with conduct- ivity water and the acidity of the extract determined. Actually equal volumes of extract and K_2SO_4 (X_3) solutions were mixed, and an e.m.f. determination carried/
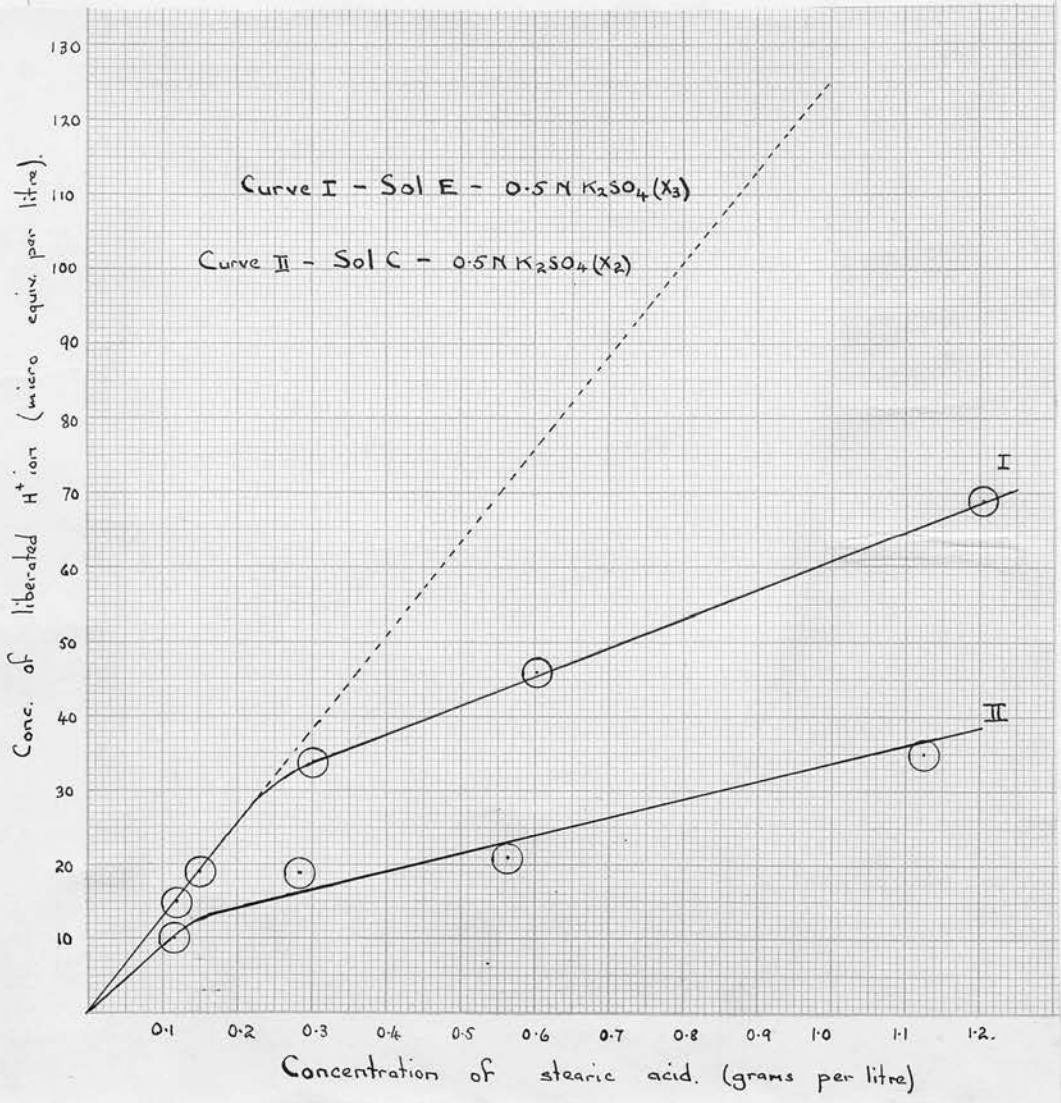
Fig. 7.

carried out in the usual way.   The e.m.f. values
obtained show that the hydrogen ion concentration of
the extract was negligible.

Conc. of salt	E. M. F. (Volt)	
	Extract + K_2SO_4	K_2SO_4 (alone)
0.05	0.1485	0.1474
	0.1480	
0.25	0.1168	0.1156
	0.1156	

Hence the e.m.f. values given by mixtures of <u>sol</u> and
salt solution directly represent the amount of liber-
ated acid.

In the following discussion, the sols are considered
as being strictly comparable except where otherwise
stated.

Influence of Concentration of Sol on Degree of
Ionic Interchange.

It will be convenient in the first place to
consider the curve I in Fig.7 (see Table 10, p.45),
which shows the variation in concentration of acid
liberated/

liberated by 0.5N K_2SO_4, with change in the sol concentration. The curve consists of two straight-line portions, with an inflection at a sol concentration of about 0.25 gms. per litre. It appears feasible to account for the change in direction of the curve in the following manner.

When ionic interchange occurs, the concentration of hydrogen ion near the surface is lowered so that further ionisation of the surface stearic acid will occur. Such ionisation will continue to an extent depending upon the ratio between the volumes of the surface layer and of the external liquid. The actual distribution of hydrogen ion will be that characteristic of a Donnan equilibrium, since the stearate ions are equivalent to non-diffusible ions separated from the external liquid by a hypothetical membrane situated at the boundary of the double layer. According to the Donnan principle, when the concentration of salt is sufficiently high the concentration of hydrogen ion will be the same at the surface as in the intermicellar liquid. Hence, it is reasonable to suppose that with 0.5N salt, the whole of the hydrogen ion will be replaced at high dilutions of the sol, since the concentration of free hydrogen ion is not great enough to form any unionised surface stearic acid. For the range of sol concentration where these conditions apply, the concentration of liberated acid abviously should be proportional/

Curve I – Sol E – $0.5 N K_2 SO_4 (X_3)$

Curve II – Sol C – $0.5 N K_2 SO_4 (X_2)$
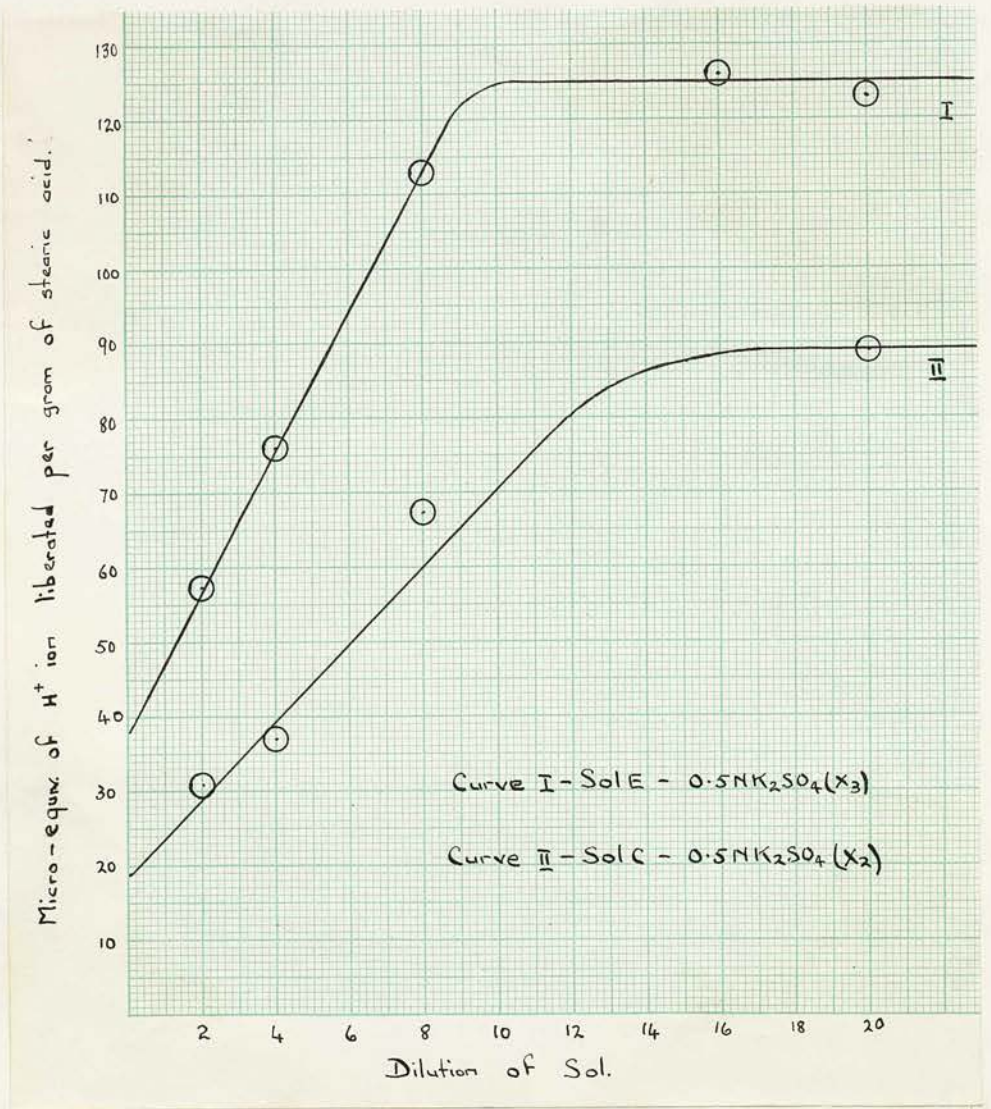
Fig. 8.

Conc. of Sol.		Dilution	Micro-equiv. H^+ ion liberated / gm. stearic acid.	
E.	C.		By K_2SO_4 (X_3)	By K_2SO_4 (X_2)
1.205	1.125	2	57	31
0.602	0.563	4	76	37
0.301	0.281	8	113	67
0.151	–	16	126	–
0.120	0.112	20	123	89

proportional to the concentration of the sol, as actually is the case. It is also evident that the amount of acid liberated per gram of stearic acid will be constant in this case. This is clearly shown by the curve I in Fig.8.

When the sol concentration exceeds approximately 0.25 gms. per litre (Dilution = 10), the equilibrium concentration of acid is such that a proportion of the surface remains unionised, so that the ionic inter-change is incomplete and becomes progressively smaller as the concentration of the sol is increased. Hence the experimental curve for the concentration of liberated acid falls below the curve representing com-plete replacement, indicated by the dotted line in Fig.7. Moreover as can be seen from the figure, the hydrogen ion liberated per gram of stearic acid decreases quite regularly as the sol increases in concentration.

Influence of Acidity.

The curve II shown in Fig.7 was obtained with 0.5N K_2SO_4, prepared from salt (X_2), (see Table 9, p.44). It will be seen that the curve is of the same type as the curve I, but the slopes of the two portions are distinctly less and the point of inflection occurs at a lower value of sol concentration, about 0.15 gms. per litre.

As/

As already indicated (p.44) the salt solution
used in this case was definitely more acid than that
used for curve I, the difference in acidity being 38
micro equi./l.[*] in a 0.5N K_2SO_4 solution.   In con-
formity with the considerations put forward in the
preceeding section, it is reasonable to ascribe the
decrease in liberated acid to suppression of the
surface ionisation by the small amount of acid present
in the salt solution.   From the curve II in Fig.8 it
appears that the hydrogen ion liberated per gram
becomes constant at a value well below that in the case
of curve I.   It is difficult to account for this on
any other assumption than that the higher acidity of
the salt solution prevents complete ionisation of the
surface stearic acid.

[*]
The value of the e.m.f. for 0.5N K_2SO_4 (X_2) is given
in table 2, and according to Fig.2, corresponds to
the above acidity.   It is also to be observed that
the acid-salt values given in Table 4 for 0.5N K_2SO_4 (X_2)
fall on the curve for 0.5N K_2SO_4 (X_3) in Fig.2.
Hence the hydrogen ion liberated in K_2SO_4 (X_2)- sol
solutions may be obtained from Fig.2.
Similar considerations apply to Lithium Sulphate (Z_2)
Table 7; Fig.4).

The curves in Fig.9 for similar experiments with
Lithium Sulphate support the above conclusions.
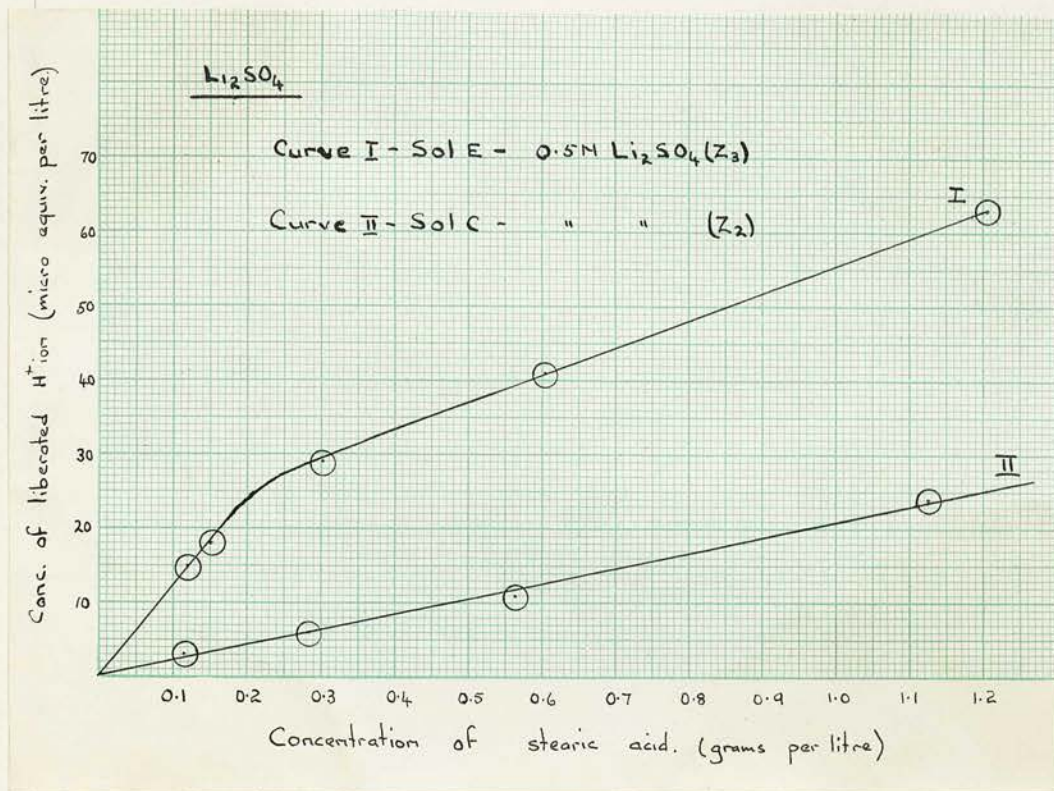
Fig.9

Curve I represents the data obtained with the salt
solution (Z_3) i.e. comparable with K_2SO_4 (X_3) and it
will be seen that the curve is much the same as curve
I in Fig.8.   Curve II in Fig.9 was obtained with
Li_2SO_4 (Z_2) which contained 46 micro equiv. of acid/l
in a 0.5N solution, and it will be observed that the
concentration of liberated acid falls below that shown
in Fig.8, curve II.   The effect of the acid in the
case of Li_2SO_4 is so great that even at the highest
dilution/
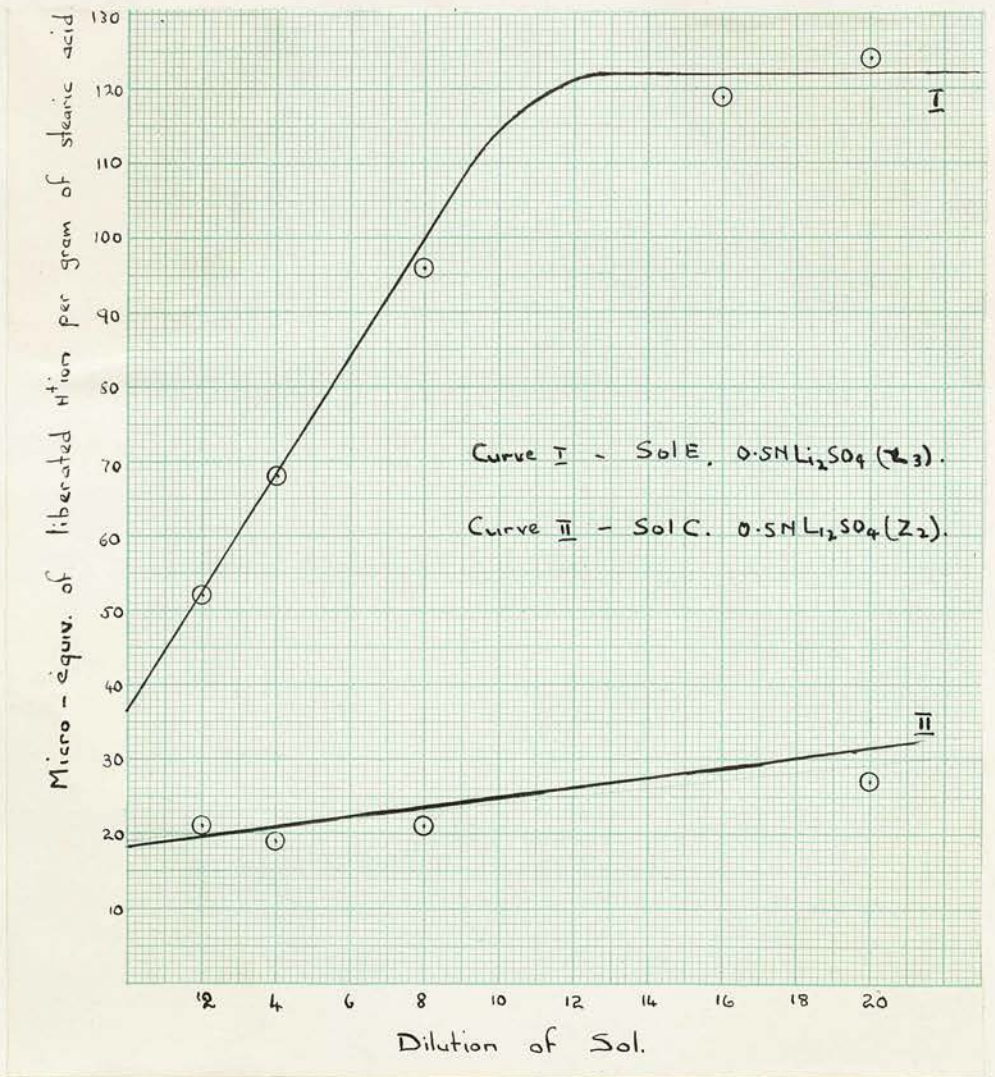
Fig. 10.

Conc. of Sol.		Dilution	Micro-equiv. H^+ ion liberated / gm. of stearic acid.	
E.	C.		By Li_2SO_4 (Z_3)	By $Li_2 SO4$ (Z_2)
1.205	1.125	2	52	21
0.602	0.563	4	68	19
0.301	0.281	8	96	21
0.151	—	16	119	—
0.120	0.112	20	124	27

dilution of sol (Fig.10), the ionic interchange per gram
of stearic acid does not much exceed that for the
undiluted sol.

Mention may be made here of some experiments in
which sulphuric acid solution was added to the salt
solution, along with K_2SO_4 to keep the solution at the
required concentration. Equal volumes of these
solutions were added to equal volumes of Sol C and the
coagulum separated. The results were as shown below.
It will be seen that when the concentration of sul-
phuric acid is 140 micro-equiv./l., no liberation of
hydrogen ion can be detected. Presumably under these
conditions the surface ionisation is very small.

Conc. of Salt	Conc. of H_2SO_4 $X10^6$	E.M.F. (volt)	Conc. of liberated H^+ - ion $X10^6$
0.5	58	0.1649	
"	"	0.1642	24
"	140	0.1887	
"	"	0.1886	-

A 0.5N K_2SO_4 (X_3) solution gave a displacement of
hydrogen ion of 57 micro-equiv. per gram of stearic
acid, the value being approximately the same for three
different sols. It is to be observed that the corres-
ponding value obtained by Achar and Usher (loc. cit.)
was/
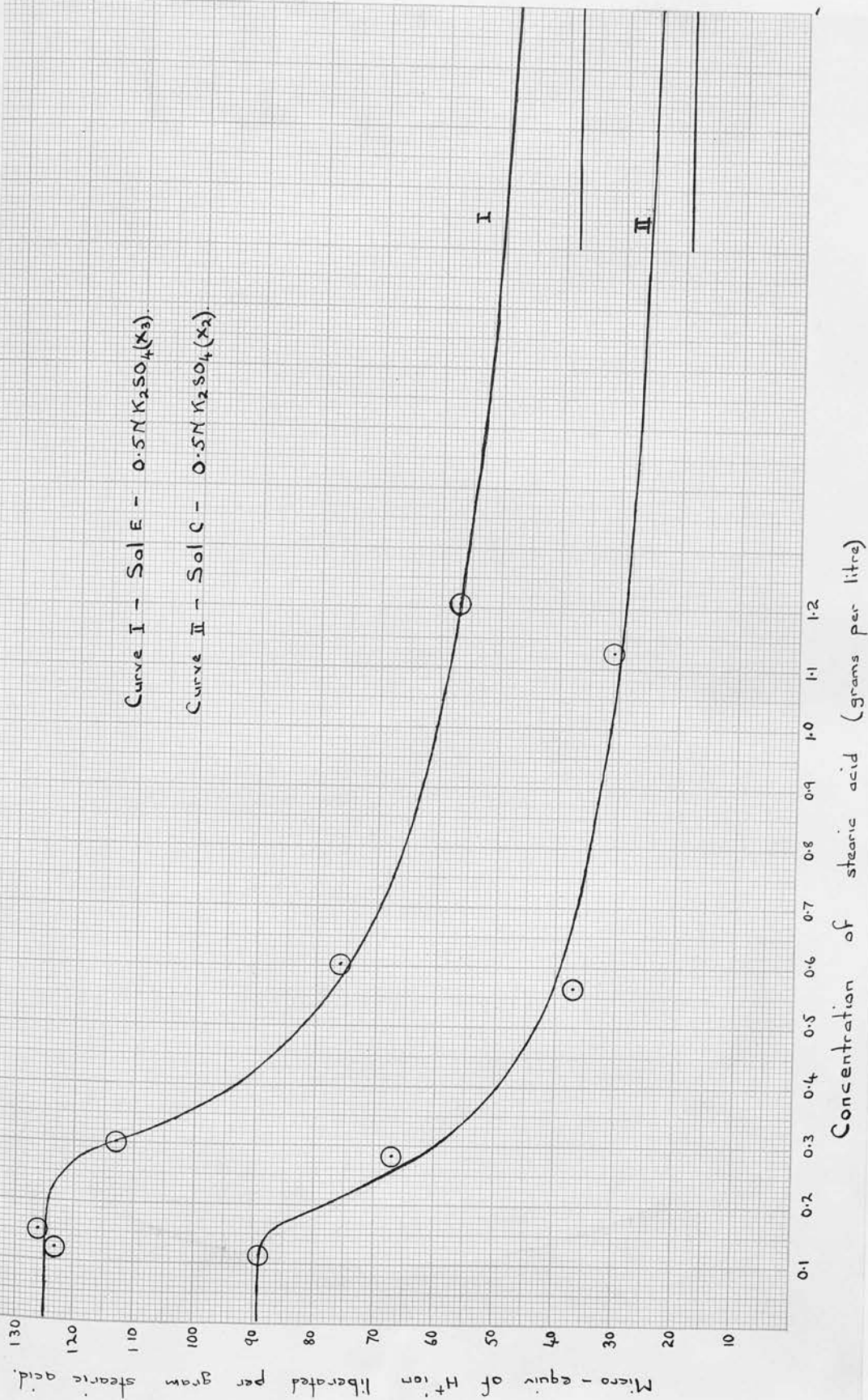
Fig. 11.

was 90.6, that is to say widely different from the
above.   There is a possibility that the difference
is due, at least in part, to the use by Achar and
Usher of "ashless" filter paper in the separation of
the coagulated stearic acid.   As has been shown
(page 38 etc.) a considerable amount of acid is dis-
placed from such filter paper by 0.5N salt.   An
alternative explanation is that the salt used by the
above experimenters contained less acid than $K_2SO_4(X_3)$,
since as has been shown in the preceeding pages,
increase in the acidity of the salt suppresses the
displacement of hydrogen ion from the stearic acid
particles.   It should be added that the curves
obtained by Achar and Usher were of the same type as
those obtained in the present instance.

Formulation of Interchange.

In Fig.11 the liberation of hydrogen ion per
gram of stearic acid is plotted against concentration
of sol.   At first horizontal, the curves become
hyperbolic being then represented by the general
equation,

$$y = \frac{a}{x} - b,$$

where y = hydrogen ion liberated from one gram of
stearic acid and x = concentration of sol.   The
values/

values of the constants a and b are given below. It
appears that the limiting value b to which the amount
of liberated hydrogen ion tends as the sol becomes
more concentrated decreases with increase in the
acidity.

TABLE.

Curve	a	b	Salt
I	22.7	38	$0.5N\ K_2SO_4\ (X_3)$
II	12.2	19	$0.5N\ K_2SO_4\ (X_2)$

At the present stage of the research it was
hardly feasible to explain the true significance of
the constants in the above equation.   It may be
suggested that b represents the proportion of union-
ised potassium stearate at the surface of the
particles. $\frac{a}{x}$ would then represent the fraction of
interchange which gives rise to ionised potassium
stearate.   This fraction would decrease with increase
in sol concentration, owing to the progressive
formation of unionised stearic acid.

State of Dispersion of Stearic Acid in Sols.

That the sols were polydisperse was shown in the
following/

following manner.   Pure sol was filtered through a
Jena fritted glass filter porosity 4, a portion of the
clear filtrate mixed with an equal volume of salt
solution and the acidity determined in the usual way.
From the data given in the accompanying Table (curve
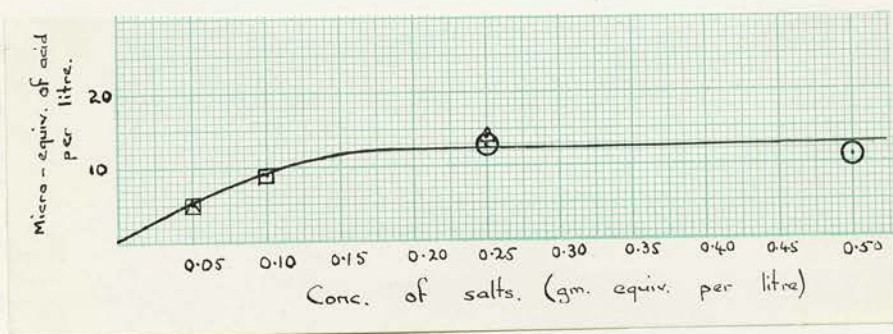in Fig 12), it will be seen that the acidity of the

F$_{IG}$. 12.

mixture increased with increase in salt concentration
to a maximum value of about 13 micro-equiv. per litre
for all three salts.

Salt.	Conc. of Salt.	E.M.F. (volt)	Micro-equiv. of acid / litre
Li$_2$SO$_4$	0.05	0.1522 0.1522	5
△	0.25	0.1346 0.1330	14
Na$_2$SO$_4$	0.05	0.1522 0.1518	5
	0.10	0.1404 0.1404	9
□	0.25	0.1287 0.1300	13
K$_2$SO$_4$	0.25	0.1301 0.1304	13
○	0.50	0.1116 0.1125	11

The explanation of this effect must be that
some of the stearic acid particles passed through the
filter so that ionic interchange occurred on the
addition of salt.   It appears however that these
particles were extremely fine,   When the sol was
diluted 160 fold, the liquid was still definitely
colloidal in appearance.   Hence if the particles were
uniform in size, the amount of colloid which had
passed through the filter would have to be less than
$\frac{1}{160}$th part of the total, since the filtrate was quite
clear.   That is to say, the maximum acidity observed
could not exceed $\frac{125 \times 2.4}{160}$ = approx. 2 micro equiv.
per litre, whereas the actual concentration of liber-
ated acid was approx. 13 micro-equiv./l.   It must be
concluded that the filtrate contained particles with
a capacity for interchange which was greatly above
the average of 125 micro equiv./gm. of stearic acid.
In other words, the size of these particles was
either much less than the average particle size, or
the number of ionisable molecules per unit area of
their surface was above the average.   It seems
likely that both factors are involved since it may be
expected that once the nucleus of the particle is
formed, its tendency to grow will depend upon the
degree of orientation of the molecules at its surface.
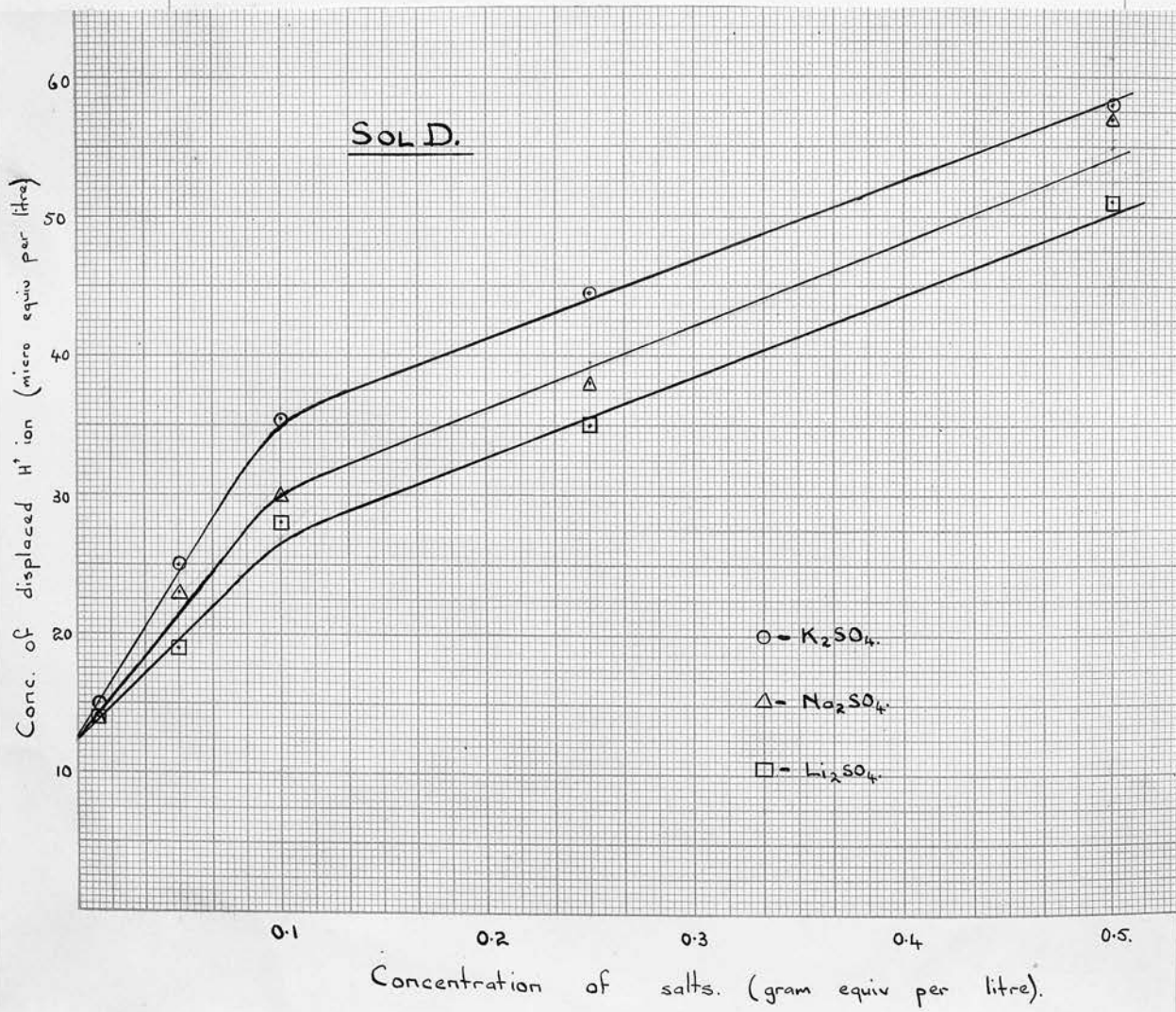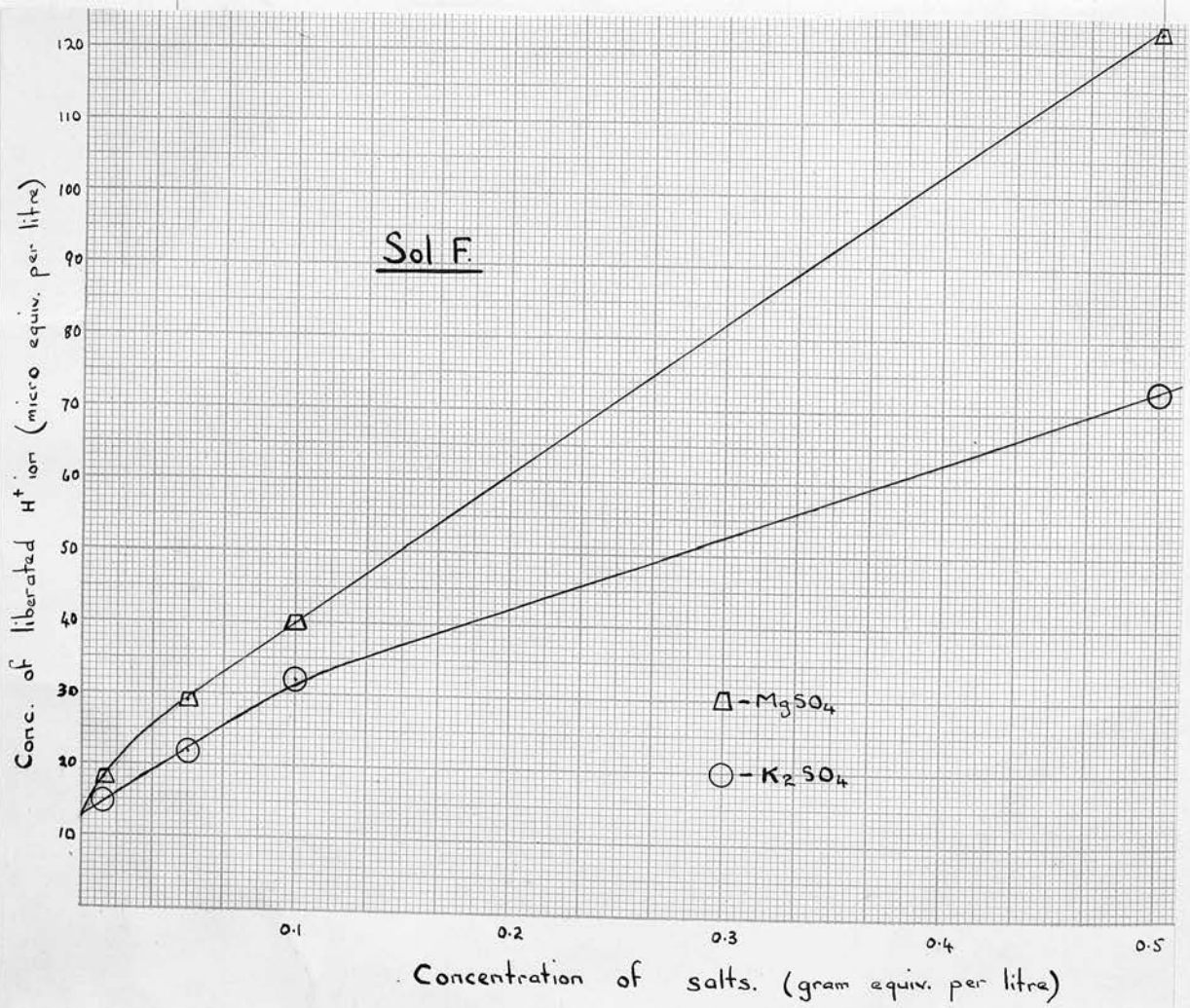The properties of films and crystals of stearic
acid/

Fig. 13.

Fig. 14.

acid suggest that molecules of the acid are less likely
to become attached to a surface consisting of carboxyl
groups than to one of paraffin chains.

Influence of Concentration of Salt on Degree
of Interchange.

The curves in Figs. 13 and 14 show the variation
in the concentration of liberated hydrogen ion with
change in the salt concentration for the sulphates of
lithium, sodium, potassium and magnesium (see Tables
13 to 17).   We may consider the curve for K_2SO_4 in
Fig.12 as representative, since all the curves are of
the same general form.   The hydrogen ion concen-
tration rises to a value of approx. 12.5 m.eq./l at
some extremely small concentration of the salt,
comparable with that of the liberated acid.   This is
understandable since the hydrogen ion concentration
in the intermicellar liquid (I.L.) tends to equal that
of the potassium ion if the interchange is of the
simple nature referred to in the introduction.   Hence
at very small salt concentrations the concentration
of liberated acid will be approximately that of the
potassium ion remaining in the I.L..   The ionic
interchange over this range of salt concentration will
be accompanied by increased ionisation of the surface
stearic/

stearic acid.   Apparently however, when the concen-
tration of liberated acid reaches 12.5, further ioni-
sation becomes increasingly difficult, but the actual
course of events involves several factors.   In the
first place, the increasing concentration of sulphate
ion promotes interchange since an increasing propor-
tion of hydrogen ion will be removed from the sphere
of action by the formation of HSO_4^- ion.   In the
second place, it is probable that unionised potassium
stearate is being formed at the surface of the
particles. (see later).

Coagulation by Salts.

The essential features of the well-known theory
of coagulation proposed by Freundlich[1]   some years
ago may be formulated as follows: (1) in order to
coagulate a sol the charge on the particles must be
reduced to a definite value, (2) the neutralisation
of the charge is brought about by the "adsorption" of
the oppositely charged ions of the coagulant.
According to this theory, therefore, in the case of
negatively charged particles, the same amount (in
equivalents) of salt kation should be taken up by the
particles at the coagulation point, irrespective of
the nature of the salt.   In 1929 Freundlich, Joachim-
sohn and Ettisch[2] found, however, that the amount
of kation adsorbed by colloidal arsenious sulphide at
the/

the coagulation point varied very considerably from
salt to salt, a result which was confirmed by Weiser [3]
in a series of careful investigations.

In view of these results the tendency has been to
regard Freundlich's theory as fundamentally unsound.
It appears, premature, however, to reject the theory
solely on the basis of inequality in kationic adsorption
at the coagulation point, since the taking up of the
salt kation may be the result of more than one process.
We must in fact distinguish between ionic interchange
on the one hand and certain other processes which can
occur along with it.   For instance molecules of the
foreign electrolyte may become attached to those parts
of the particle surface unoccupied by the stabilising
ions.   The total amount of kation taken up by the
particle will exceed that involved in the interchange,
and hence will exceed the amount of original kation
liberated from the surface.   As Rabinovitch and Kargin [4]
have pointed out, lack of equivalence between the
amount of kation taken up by the particles and the
amount/

1. Freundlich and Gann, Kolloid chem. Beih. 8 (1916) 127.

2. Freundlich, Joachimsohn and Ettisch, Z. physikal
   Chem., 141A, (1929) 249.

3. Weiser, Contribution to Alexander's "Colloid Chemistry
   Vol.1 (1926), 600.

4. Rabinovitch and Kargin, Trans. Faraday Soc., 31,
   (1935), 50.

amount of hydrogen ion liberated has been frequently
encountered.   It therefore seems reasonable to regard
constancy in the amount of hydrogen ion liberated by
different salts at their respective coagulation
values as the criterion of Freundlich's theory, rather
than constancy in the amount of salt kation which is
held by the micelles.

A number of investigations have been carried out
with the object of deciding whether ionic interchange
and coagulating action are in any way related.   In
general it has been found that the coagulation powers
of kations show the same sequence as their tendencies
to interchange, but the data as a whole do not indicate
that the degree of interchange at the coagulation
points follows any simple rule.

The figures obtained in the present investigation
are given below. (See also Tables 19 to 21 and Figs.
13 and 14).

Sol.	Salt.	Coagulation value.	Conc. of liberated H^+ - ion (micro equiv. per litre)
D	Li_2SO4	0.077	23.5
	Na_2SO_4	0.067	25.0
	K_2SO_4	0.053	25.0
F	K_2SO_4	0.060	24.0
	M_gSO_4	0.021	22.0

In/

In the case of sol D, the concentration of liberated hydrogen ion varies by not more than 5 per cent from a mean value of 24.5, although the coagulation value for sodium sulphate is 26 per cent, and that for lithium sulphate 45 per cent greater than the coagulation value for potassium sulphate. In the case of sol F, the hydrogen ion concentration lies within 5 per cent of a mean value of 23, while the coagulation value of potassium sulphate is three times that of magnesium sulphate.

Since the apparent variations in ionic interchange are of the same order as the experimental error, it may be said that in the case of a given stearic acid sol, the degree of interchange at the coagulation point is the same for the sulphates of lithium, sodium, potassium and magnesium.

According to Freundlich's theory, the necessary condition for coagulation is that the charge on the particles be reduced by the coagulant. An alternative theory, advocated by Verwey [1] and others, assumed that coagulation is the consequence of a decrease in the "thickness" of the double layer, the actual surface density of the charge being unaffected by the presence of the electrolyte. On this view, presumably the particles in a stable sol do not aggregate/

1. Verwey, Chem. Reviews, 16 (1935) 363.

aggregate because their ionic atmospheres offer
resistance to deformation and prevent the particles
from approaching closely enough for their attractive
forces to become operative. Decrease in the average
thickness of the ionic atmosphere permits of closer
approach, and if below a certain value, of actual
adhesion. Now the quantity $1/\kappa$, 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 double layer[1].
This will therefore be proportional to $\frac{1}{\sqrt{\mu}}$
where μ is the ionic strength of the electrolyte
present in the sol.

On the basis of the foregoing the value of $\frac{1}{\sqrt{\mu}}$
should be the same for all electrolytes at their
coagulation values. That this was not the case in
the present instance will be seen from the following
figures.

Sol.	Salt	$\frac{1}{\sqrt{\mu}}$	Relative thickness of double layer
D	Li_2SO_4	2.94	1.00
	Na_2SO_4	3.15	1.07
	K_2SO_4	3.53	1.20
F	K_2SO_4	3.33	1.13
	M_gSO_4	4.88	1.66

It/

1. Henry, Proc. Royal Soc. A, 133, (1931) 106.

It is evident that there exists some specific action of the salt kation, which may be very marked. Moreover it is reasonable to suppose that this factor is also responsible for the differences shown by the salts in the capacity for liberating hydrogen ion from the micelles; particularly as the ionic interchange at the coagulation point is the same for all four salts, under comparable conditions.

This raises the question of the mechanism of the interchange. It cannot consist merely in the replacement of a portion of the mobile hydrogen ions of the double layer by mobile salt kations. If this were the case, the exchange at any given salt concentration should be the same for all salts, at least at high concentrations when differences in the distribution of ions of different valency, due to the Donnan effect, will be negligible. To explain the dependence of the degree of interchange upon the nature of the replacing ion, it is frequently suggested that the ions in the diffuse layer differ in respect to their average distance from the surface. This is really equivalent to postulating a specific ionic interaction. For example Jenny[1] assumes that each mobile ion of the double layer oscillates within a given space ("oscillation cell"), the average volume of which is characteristic of the valency and nature of/

1. Jenny, J. Phys. Chem., 40 (1936) 501.

of the ion.   Exchange is considered to occur only
when an ion of another species slips between the
surface and the original ion.   In effect one species
of ion "occupies" a proportion of the surface to the
exclusion of the other ion, since although not
actually fixed upon the surface it approaches the
same more closely on the average.   According to this
the equality in the amounts of hydrogen ion liber-
ated by different salts at their coagulation values
implies that the average distance of approach to the
surface, or the "oscillation volume" of the replacing
ions is the same at the coagulation point;   i.e. the
coagulation is due to compression of the double
layer.   The alternative is, of course, that the
replacing ions occupies a proportion of the surface
by forming either undissociated molecules (or else
ion - pairs) with the stabilising ions.[1]   According
to this the equality in the amounts of hydrogen ion
liberated by different salts at their coagulation
values implies that at the coagulation point, the
charge on the particles has been reduced to the same
extent in all cases;   i.e. Freundlich's theory is in
principle, valid.   Further investigation is required
to decide between these alternatives, but it is clear
that/

1. McBain and Peaker, Proc. Royal Soc., A 125,
    (1929) 394.

that, on either view, the interchange is of primary
importance in the coagulation process, and not merely
incidental to it, as maintained by Verwey (loc. cit.)

Coagulation by Acids.

As will be seen from Table 21, the sols were very
sensitive to hydrogen ions.   Sulphuric acid produced
partial coagulation even at a concentration of
179×10^{-6} N*, while the coagulation value was complete
at about 716×10^{-6}N.   The obvious explanation is
that the added acid suppresses the dissociation of the
surface stearic acid molecules and so "discharges"
the particles to the required extent.

That the degree of dissociation in the pure sol
has a low value is suggested by the manner in which
the ionic interchange varies with change on the con-
centration of sol or salt.   Moreover the measurements
by McBain and Peaker (loc. cit.) of the conductivity
of a monomolecular film of stearic acid on water,
indicate that approximately only one in every nine of
the molecules is dissociated.   Also Schulman and
Hughes[1]/

* A trace of coagulation was observable even at
  72×10^{-6}N acid.

1. Schulman and Hughes, Proc. Royal Soc. A <u>138,</u>
   (1932) 430.

have shown that the "surface potential" of a mono-
layer of myristic acid commences to fall off at a P_H
value of the substrate between 2 and 4, whereas the
potential for a film of ethyl myristate remains
unchanged even at high values of the P_H.   Evidently
the molecules of the acid film dissociate, the degree
of dissociation becoming appreciable within the above
range of P_H, which includes the value (about 3) at
which sulphuric acid brings about complete coagulation
of the sol.   It is of interest to note that Langmuir
and Schaeffer[1] found that no formation of barium
stearate occurred in a film of stearic acid spread on
a solution of barium salt when the P_H lay between 2
and 4.   As the P_H was increased beyond 4, the barium
content of the film increased, complete conversion
into barium stearate occuring at $P_H = $ " .

The wide range of concentration over which coag-
ulation by sulphuric acid takes place is probably due
to the polydispersity of the sols.   Assuming (1)
that the number of ionisable molecules per unit area
of surface increases with decrease in particle size,
and (2) that the proportion actually ionised is the
same for any one concentration of sulphuric acid, it
follows that the surface density of the charge will
be/

1.   Langmuir and Schaeffer, J.A.C.S., _58_, (1936) 284.

be reduced to the extent necessary for coagulation by a lower concentration of acid in the case of large particles than in the case of small.

The interchange effected by 0.5N potassium sulphate (X_3) appears to be negligible when the concentration of sulphuric acid present is 140×10^{-6}N (see p. 68), i.e. at a value well below the coagulation value of the acid. It might therefore appear that the action of the acid involves more than the suppression of the surface dissociation. However it should be pointed out that with 140×10^{-6}N acid present, the experimental error is sufficient to obscure a liberation of hydrogen ion amounting to about 8×10^{-6}N, which is a third that produced by the salts at their coagulation values.

SUMMARY.

(1) The production of acidity in stearic acid sols by neutral salts has been investigated by means of the quinhydrone electrode.

(2) The variation in the degree of ionic interchange with variation in (1) concentration of sol, (2) concentration of salt, (3) acidity, and (4) nature of salt has been studied.

(3) The influence of electrolytes upon the stability of the sol has been examined, and the conclusion reached that there is a close connection between the coagulative ability of a salt and the tendency for it to liberate hydrogen ions.

(4) The results have been discussed with reference to the general theory of coagulation.