ADSORPTION OF GELATIN BY PRECIPITATED HYDROXIDES.

By J. G. Kane.

INTRODUCTION.

It is well known that substances like gelatin, gum arabic and dextrin will prevent the precipitation of very fine particles. This stabilizing action has been attributed by Bechhold, Zsigmondy, Loeb and others, to the protective action of gelatin and similar substances which are adsorbed by the fine particles on their surfaces. Thus, each particle is surrounded by the stabilizer and a stable unit is formed owing to the forces of adsorption. This force will exist in both the cases when either gelatin in solution is brought in contact with the fine precipitate after complete precipitation, or when the precipitate is allowed to form in the presence of gelatin. In the former case adsorption takes place and in the latter peptisation takes place, the difference being only in the effective total surface formed. The forces by which they are caused are of the same nature. The object of the present investigation was to study fairly accurately the amounts of gelatin adsorbed by activated charcoal, silica gel, and hydroxides of iron, aluminium and nickel. For this purpose a rapid and accurate method for determining the quantity of gelatin in solution was developed (*cf.* Kane and Watson, *Jour. Soc. Chem. Ind.*, 1929, **48**, 335T), the results of which are reproduced for ready reference.

TABLE I (*Series I*).

Refractive Index of Gelatin Solutions at 21° C.

Gm. gelatin per 100 gm water	Gm. gelatin per 100 c.c. of solution	Difference in micrometer readings	$\delta n_D \times 10^5$	$\delta n_D \times 10^5$/gm. weight	$\delta n_D \times 10^5$/gm. volume
0·122	0·122	2·80	22	180	180
0·202	0·201	4·65	37	183	184
0·320	0·318	7·30	58	181	182
0·526	0·524	12·15	96	182	183
0·710	0·705	16·25	130	183	184
0·879	0·872	19·95	159	181	182
1·330	1·316	30·10	240	180	182
1·784	1·754	40·40	323	181	184

TABLE I (*Series II*).

Refractive Index of Gelatin Solutions at 29° C.

Gm. gelatin per 100 gm. water	Gm. gelatin per 100 c.c. of solution	Difference in micrometer readings	$\delta n_D \times 10^5$	$\delta n_D \times 10^5$/gm. weight	$\delta n_D \times 10^5$/gm. volume
0·780	0·772	18·15	143	183	185
1·130	1·116	26·10	207	183	185·5
1·592	1·566	36·60	291	183	186
2·406	2·356	54·95	439	182·5	186·3
3·215	3·137	72·85	584	181·7	186·2

In Table II given below, the refractometric methods of estimating gelatin as used by other workers have been compared with respect to their practical application.

TABLE II.

Worker	Instrument used	Agreement of the values in terms of R.I. × 10^5	Practical limit of accuracy %	Temp. control	δn_D/gm. × 10^5
Frei ..	P.R. with single cell	± 10	± 0·2	required	177
Walpole ..	Z I.R.	± 2	..	,,	182·4 (17·5° C.)
Hart .	,,	± 8	± 0·1	,,	183 (20° C.)
Authors ..	P.R. with double cell	± 1	± 0·01	not required	182·5 (21° C.)

P.R. = Pulfrich Refractometer. Z.I.R. = Zeiss Immersion Refractometer.

EXPERIMENTAL.

Kahlbaum's 'Gold Label' gelatin (1.8% ash) was used. Solutions were made by first soaking the gelatin in water and then heating to 60° C. on a water-bath and filtered, and the strengths of the filtrates determined by the method described previously. Dilute solutions were prepared from these by the addition of requisite quantity of water. Norite charcoal used was a commercial sample. Silica was prepared by hydrolysing methyl silicate, heating the whole mass to 100° C. so as to remove the methyl alcohol. A sample of silica gel was also prepared by the usual double decomposition of sodium silicate with acid. Aluminium hydroxide was precipitated from a solution of potassium alum by ammonia. Ferric hydroxide was precipitated from a solution of ferrous ammonium sulphate by ammonia. Nickel hydroxide was precipitated from nickel sulphate solution by caustic soda. All the precipitates were washed well with water. A part from each was preserved moist and the rest dried. The dried hydroxides and the dry adsorbents, *viz.*, Norite charcoal and silica, were powdered, sieved through 100-mesh to remove coarse particles and were heated at 100° C. to constant weight.

The adsorbent was weighed out into bottles and equal volumes of the gelatin solutions added to each. The bottles were shaken for half an hour (which was enough for obtaining equilibrium) at the room temperature and centrifuged. The concentration changes in the gelatin solutions were determined by the differential method described previously.

(1) *Adsorption by Norite Charcoal.*—Table III shows the results obtained when 1 gm. of charcoal was treated with 10 c.c. of gelatin solution. i shows the difference in micrometer readings in minutes, for water and the initial gelatin solution. This gives the values of C_0 the initial concentration. i' shows the difference in micrometer readings in minutes, for the initial and final (C) gelatin solutions $(C_0 - C)$.

TABLE III.

(C_0)		$(C_0 - C)$		(C) Final strength % in water
i	Strength %	i'	Strength % in charcoal	
(1) 3·00	0·130	2·35	0·102	0·028
(2) 4·00	0·174	3·05	0·133	0·041
(3) 5·00	0·217	3·75	0·163	0·054
(4) 6·00	0·261	4·55	0·198	0·063
(5) 8·00	0·348	5·80	0·252	0·096
(6) 10·00	0·435	7·15	0·311	0·124

(2) *Adsorption by Silica* (prepared from methyl silicate) is shown in Table IV. 0.2 gm. silica was treated with 10 c.c. of gelatin solution.

TABLE IV.

(C_0)		(C_0 – C)		(C) in water strength %
i	Strength %	*i'*	Strength % in silica	
(1) 1·00	0·048	0·85	0·037	0·011
(2) 1·50	0·065	1·00	0·043	0·022
(3) 2·00	0·087	1·20	0·052	0·035
(4) 2·95	0·128	1·40	0·061	0·067
(5) 4·05	0·176	1·45	0·063	0·113
(6) 5·00	0·217	1·55	0·067	0·150
(7) 5·90	0·257	1·70	0·074	0·183
(8) 7·80	0·339	1·90	0·083	0·256
(9) 9·90	0·430	2·10	0·091	0·339

(3) The adsorption by the hydroxides of aluminium, iron and nickel in moist as well as dry conditions was next investigated.

(*a*) *Moist Adsorbents.*

Aluminium Hydroxide.—A weighed quantity of aluminium hydroxide was shaken with 10 c.c. gelatin solution of approximately 0.4% strength. After shaking, the whole mixture was found to have changed into a sol, from which only a part of the hydroxide settled after centrifuging. Even by taking more dilute solutions of gelatin, the formation of sol could not be prevented. Hence, no adsorption measurements were possible in this case.

Ferric Hydroxide.—Table V gives the adsorption results obtained with different weights of two samples of ferric hydroxide containing

TABLE V.

	Weight of moist $Fe(OH)_3$ gm.	Dry $Fe(OH)_3$ gm.	Water accompanying the moist hydroxide gm.	Altered strength %	Gelatin adsorbed gm.
No. I	1·412	0·407	1·005	0·380	0·0378
	2·468	0·712	1·756	0·360	0·0335
No. II	5·530	1·230	4·300	0·300	0·0265
	7·310	1·620	5·690	0·270	0·0259

28.9 and 22.2% of $Fe(OH)_3$. In each case 10 c.c. of gelatin solution of 0.426% strength were added.

Nickel hydroxide containing 22.32% $Ni(OH)_2$ was shaken with 10 c.c. of 0.426% gelatin solution. The results are as follows:

Wt. of moist $Ni(OH)_2$ gm.	Dry $Ni(OH)_2$ gm.	Water accompanying the hydroxide gm.	Altered strength %	Gelatin adsorbed gm.
3·170	0·710	2·460	0·340	0·0296

Due to the water accompanying the moist hydroxide, the initial strength of the gelatin solution was altered; a correction is made for this and the true strength as obtained is given under the column 'altered strength'. The values given under 'gelatin adsorbed' have been calculated from the changes in strength observed refractometrically.

(*b*) *Dry adsorbents* were shaken with 10 c.c. of 0.426% gelatin solution. The following results were obtained:

TABLE VI.

Substance	Weight gm.	Initial quantity of gelatin gm.	Amount of gelatin adsorbed gm.
$Al(OH)_3$	1	0·0426	Changes into a sol
Al_2O_3	1	,,	0·0190
$Fe(OH)_3$	1	,,	0·0130
Fe_2O_3	1	,,	very little
$Ni(OH)_2$	1	,,	very little
NiO	1	,,	nil
SiO_2 (from methyl silicate)	0·2	,,	0·009
SiO_2 (from sodium silicate)	1	,,	0·016
Charcoal	1	,,	0·031

DISCUSSION.

The equilibrium curves for charcoal and silica have been plotted from the values given in Tables I and II. Since very dilute solutions of gelatin have been used, the Freundlich equation $x/m = KC^{1/n}$ ought to be applicable in the two cases. On plotting log x/m against log C, straight lines are obtained. For charcoal, values of K and $1/n$ in the equation $\log x/m = \log K + 1/n \log C$, are K, 0 15, $1/n$, 0.75.

In the case of silica, however, the results are not very concordant.

Coming to a consideration of the results obtained with moist $Fe(OH)_3$, given in the table, it seems strange that the adsorption of gelatin is the more, the smaller the weight of $Fe(OH)_3$ taken.

TABLE VII.

Wt. of dry $Fe(OH)_3$ gm. (*a*)	Concn. of gelatin % (*b*)	Gelatin adsorbed gm.	I *a*/*b*	II *a*/*b*/1·07	III (W)
(1) 1·620	0·270	0·0259	6·00	5·61	1·620/·407 = 4
(2) 1·230	0·300	0·0265	4·10	3·93	1·230/·407 = 3
(3) 0·712	0·360	0·0335	1·98	1·85	0·712/·407 = 1·75
(4) 0·407	0·383	0·0378	1·07	1	0·407/·407 = 1

Column I in Table VII gives the ratio *a*/*b* while column II gives the same ratio recalculated on taking the last value of *a*/*b* as unity. Column III shows the proportionate increase in the weight of the hydroxide. The calculations given show the interrelationship of the various factors involved.

When the gelatin solution is added to the precipitated hydroxide, the latter are deflocculated due to the peptising influence of gelatin, of gelatin, thus affording a greater space for the adsorption of gelatin. The dispersion will be greater, greater the gelatin concentration, and smaller, larger the weight of the hydroxide. The dispersion varies inversely as the value of *a*/*b*. The adsorption of gelatin, therefore, will be proportional to $\frac{W}{a/b}$.

It must, however, be remembered that the above expression is only an approximation of the true state. The gelatin disperses a part of the hydroxide whereby the surface is increased. With a continual dispersion and consequent increase of the surface, more and more of gelatin is adsorbed until finally the strength of the remaining gelatin solution is not sufficient to exert any dispersive influence on the remaining hydroxide; thus (*a*) and (*b*) do not remain constant. Therefore, the factor *a*/*b* continually changes its value in the whole process. Table VIII shows the calculated and observed values of adsorption, which are found to be of the same order. The values have been calculated starting with the experimental value of 0.0378 gm. obtained for the adsorbed quantity of gelatin in the 4th case of Table VII, the values of *a*/*b* and W having been taken as unity.

TABLE VIII.

Calculated value of the adsorbed quantity of gelatin gm.	Experimental value gm.
(1) $\frac{0\cdot0378 \times 4}{5\cdot61} = 0\cdot0269$	*0·0259*
(2) $\frac{0\cdot0378 \times 3}{3\cdot93} = 0\cdot0288$	*0·0265*
(3) $\frac{0\cdot0378 \times 1\cdot75}{1\cdot85} = 0\cdot0357$	*0·0335*

TABLE IX.

	gm. of gelatin adsorbed by (from 0·0426 gm. of gelatin)		
	Al	Fe	Ni
Moist hydroxide .	changed into a sol	0·0335	0·0296
Dry hydroxide ..	partly changed into a sol	0·0130	very little
Dry oxide ..	0·0190	very little	nil

It will be seen from Table IX that the adsorption capacities of hydroxides and oxides are in the order Al > Fe > Ni. The moist hydroxide adsorbs more than the dry one, which again is stronger than the oxide in adsorption power.

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SUMMARY.

1. The amounts of gelatin adsorbed from dilute solutions by charcoal, silica and hydroxides of aluminium, iron and nickel have been measured refractometrically.
2. The Freundlich equation has been applied to the adsorption by charcoal and silica. While the adsorption isotherm for charcoal agrees with the equation, a distinct break is observed in the case of silica. This may be due to a change of the degree of association in the two phases (the adsorbent and the solvent).

3. The hydroxides of aluminium, iron and nickel which are easily peptised have been found to adsorb appreciable quantities of gelatin. The surface forces causing adsorption and peptisation are identical and there is a close relation between adsorption and peptisation.

4. Ferric hydroxide shows an increase in the amount adsorbed with decreasing weight. This is explained on the basis of dispersion of the hydroxide by the gelatin solution and verified by a simple formula.

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