

IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

Part III. Colloidal Prussian Blue.

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Received November 23, 1935.

IN papers published by Desai and collaborators¹ it has been shown that changes which are produced in the charge on colloidal particles during dialysis are not so simple as is usually supposed and that the results of viscosity and stability cannot always be utilised for getting an idea about the charge on colloid particles. The results of simultaneous measurements of cataphoretic speed, stability and viscosity of colloidal solutions of ferric and thorium hydroxide have been given in Parts I (Desai and Borkar¹) and II (B. N. Desai and A. K. Desai¹) respectively. It will be seen from the results that the behaviour of both the sols as regards dialysis, dilution and critical potential is similar; the viscosity changes on dialysis and in presence of electrolytes have, however, been found to be different. In the present paper similar simultaneous measurements taken with colloidal prussian blue are presented.

Experimental.

Prussian blue was precipitated by adding slowly and without stirring a 2% solution of potassium ferrocyanide to a 2% solution of ferric chloride.² The precipitate was allowed to stand for about 15 minutes, filtered and peptised by shaking vigorously with a 2% oxalic acid solution in one case and a 5% oxalic acid solution in the other. The sol so obtained was filtered four times through a double-fold of filter in order to attain as far as possible uniformity of particle size and better constancy of conductivity.³

The sol was dialysed in parchment paper bags which were previously kept soaked in distilled water for 3 to 4 days. The outer water was changed once a day. No prussian blue passed out during dialysis; oxalic acid and traces of ferric chloride were however detected in the dialysate. Dialysis was carried out in dark room in order to avoid effect of light on the sol. The amount of prussian blue in the sol did not change to any appreciable extent during dialysis.

The cataphoretic speed was measured by Mukherjee's improved U-tube method. The dialysate made equi-conducting by addition of potassium chloride in the initial stages of dialysis and by addition of oxalic acid in the later stages was found to be quite satisfactory as an upper liquid. The difference between the direct and reverse movements of the boundary was never more than 3 to 4%. In all the tables of results, the cataphoretic speed (mean of direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre $\times 10^5$. The concentration of the electrolytes is expressed in millimoles per litre.

Viscosity was measured by using an Ostwald viscometer. The results of viscosity have been expressed in terms of the viscosity of distilled water at the temperature of the experiment as unity.

The stability was determined by finding out the amount of the electrolyte necessary to give instantaneous coagulation. The flocculation values are expressed in millimoles of the electrolyte in total volume, *i.e.*, 30 c.c.'s in this case.

All the measurements of cataphoretic speed and viscosity were made at a temperature of 30° C.

Results and Discussion.

A. Effect of ageing.—Sols dialysed for 6 and 25 days were removed and stocked in resistance glass flasks covered with black paper and the cataphoretic speed (cat. speed) was determined at different periods. The results are given in the following table:—

TABLE I.

Sol dialysed for 6 days		Sol dialysed for 25 days	
Age in days	Cat. speed	Age in days	Cat. speed
0	39.20	0	38.60
30	37.00	20	38.30
40	36.90	38	31.55
143	36.90	104	27.90
216	36.60	173	27.40
262	36.00	218	27.20

It will appear that in the case of the sol dialysed for 6 days, the cat. speed first decreases and then remains constant for a certain period after

which it again decreases, while for the sol dialysed for 25 days, the cat. speed first decreases very slowly, then rapidly and afterwards again slowly when kept for longer periods. The decrease in the cat. speed on ageing might possibly be due to preferential adsorption of the coagulating ions.

In order to minimise the effect of ageing, all the experiments were carried out in as short a time as possible.

B. Changes in cataphoretic speed, stability and viscosity with the progress of dialysis.—The results of these experiments are given in Tables II and III.

TABLE II.
Sol peptised with 5% oxalic acid solution.

Period of dialysis in days	Cat. speed	Relative viscosity	Flocculation values with KCl
3	38.10	1.027	7.06
6	41.60	1.000	5.80
10	42.05	0.996	4.20
12	42.90	1.005	2.74
15	50.30	1.008	1.20
19	21.50	1.009	0.50
23	13.10	1.014	0.10

TABLE III.
Sol peptised with 2% oxalic acid solution.

Period of dialysis in days	Cat. speed	Relative viscosity	Flocculation values with KCl
4	39.00	1.014	4.84
9	41.10	1.009	4.20
14	44.10	1.004	2.64
18	43.60	1.005	1.28
27	38.00	1.012	..
30	27.00	1.014	..
34	19.50

It will appear from Tables II and III that with the progress of dialysis the cat. speed first increases and reaches a maximum after which it gradually decreases, while the relative viscosity first decreases and reaches a minimum after which it gradually increases. The stability as determined by flocculation values with KCl continuously decreases with the progress of dialysis.

Desai and co-workers¹ have explained a first increase and then a decrease in the cat. speed with dialysis by assuming that the process of dialysis (during which the amount of peptising agent in the sol continuously decreases) can be considered roughly as a reverse of the process of adding small increasing amounts of the peptising agent to the colloid so far as the influence of the electrolyte on the cat. speed is concerned. If this analogy is correct one would expect that on adding small increasing amounts of oxalic acid, which is the peptising agent in the present case, to the prussian blue sol, the cat. speed should first increase and then decrease. That this is actually the case will be clearly seen from the results given in Table IV.

TABLE IV.

Cat. speed of colloidal prussian blue (peptised with 2% oxalic acid solution and dialysed for 25 days) in the presence of varying amounts of oxalic acid.

Amount of oxalic acid	Cat. speed
0.000	26.95
0.013	35.00
0.037	37.50
0.125	39.40
0.250	40.80
1.250	35.70
3.750	31.90
12.500	30.70

It will also appear that the cat. speed and the stability do not apparently go hand in hand till the maximum value of charge is reached during dialysis as in the case of ferric and thorium hydroxide sols investigated by Desai and co-workers.¹ In the present case, the decrease in the flocculation values with the progress of dialysis in spite of an increase in charge might be due to an increase in the preferential adsorption of the stabilising (oxalate) ions in the presence of KCl (electrolyte added for flocculation value determinations) as well as a change in the size of the colloid particles during dialysis.

According to v. Smoluchowski,⁴ the greater the electric charge on the colloidal particles the greater will be the viscosity of the sol, while according to Dhar and co-workers,⁵ other things being identical, a decrease in electric charge on colloid particles causes an increase in hydration and necessarily in the viscosity of the sol. From the results given in Table III it will appear that the viscosity and cat. speed changes with the progress of dialysis completely support Dhar's view, but in the case of the sol peptised with 5% oxalic acid the maximum in the cat. speed and minimum in viscosity have not occurred at the same stage of dialysis—a fact against Dhar's view. The results do not support v. Smoluchowski's view.

On comparing the results given in Tables II and III it will appear that a higher value of cat. speed is obtained for the sol peptised with 5% oxalic acid solution than for the one peptised with 2% oxalic acid solution. There is an advantage in peptising prussian blue with concentrated solution of oxalic acid in that sols so obtained have finer particles and are more stable than those obtained by using dilute solutions of oxalic acid. The sols peptised with concentrated solutions of oxalic acid are, however, not suitable for charge measurements as the boundary becomes diffused due to the disturbances caused by vigorous electrolysis once the current is passed through the sol. In the experiments to be described further only prussian blue sols prepared by using 2% oxalic acid solution have therefore been used.

C. Changes in the cataphoretic speed and stability of colloidal prussian blue dialysed and diluted to different extents.—Sols of different concentrations were prepared by adding requisite amounts of conductivity water to the original dialysed sol. The original sol has dilution 1; dilutions of other sols have been obtained from the value of the ratio $\frac{\text{total volume of the diluted sol}}{\text{actual volume of the original sol}}$. The results of these experiments are given in the following table.

TABLE V.

Figures in columns 'a' and 'b' give values of cat. speed and flocculation (with KCl) respectively.

Period of dialysis in days	Dilution										
	1		1.33		2		4		5.33	8	
	a	b	a	b	a	b	a	b	a	a	b
3	38.70	5.20	40.30	4.70	42.50	4.16	39.00	3.36	35.75	30.10	3.16
8	40.60	4.32	41.10	4.04	41.10	3.50	37.70	2.58	35.00	30.10	2.20
13	43.20	3.24	42.20	2.84	40.50	2.20	36.10	1.12	33.80	28.60	0.36
17	42.50	1.70	40.90	1.28	38.70	0.66	35.00	0.14	32.50	27.00	..
21	41.05	..	40.00	..	37.60	..	33.60	..	31.30	25.90	..
26	37.10	..	35.40	..	32.30	..	24.20	..	22.30	21.50	..
30	27.50	..	25.80	..	23.05	..	21.00	..	20.60

The following conclusions can be drawn from the results given in the table :—

- (1) With the progress of dialysis the cat. speed (vertical columns 'a') first increases and then decreases for sols having dilutions 1 and 1.33, while it continuously decreases for sols having dilutions 2, 4, 5.33 and 8.
- (2) On diluting the sol, the cat. speed (values given in columns 'a'—horizontal rows) first increases and then decreases for sols dialysed for 3 and 8 days, while it continuously decreases for sols dialysed for 13, 17, 21, 26 and 30 days.
- (3) The stability of the sol as determined by flocculation values (given in columns 'b') continuously decreases with the progress of dialysis (vertical columns) and dilution (horizontal rows).

These results are thus exactly similar to those obtained with colloidal ferric and thorium hydroxide.¹ The changes in cat. speed on dilution have been explained by Desai and co-workers¹ by assuming similarity between processes of dilution and dialysis so far as the changes in the amount of the peptising electrolyte are concerned (the amount of the electrolyte in the sol decreases both during dialysis and dilution). According to this view samples of the sol which contain initially an amount of the peptising electrolyte more than that corresponding to the maximum in the cat. speed—concentration curve with that particular electrolyte (in this case the curve

obtained by plotting results given in Table IV) will show first an increase and then a decrease in cat. speed on further dialysing or diluting the sol; samples of sol which contain initially an amount of the peptising electrolyte equal to or less than that corresponding to the maximum in the cat. speed concentration curve of the colloid with that particular electrolyte will show a continuous decrease in cat. speed on further dialysing or diluting the sol. Further according to their view the maximum value of the cat. speed should occur at smaller and smaller dilution with the progress of dialysis and that the maximum value of cat. speed on dialysis should not differ appreciably from the maximum value of cat. speed on dilution. The present results completely support their view-point because (i) the maximum value of cat. speed on dialysis having occurred either on the 13th day or between the 8th and 13th day, the cat. speed on dilution has first increased and then decreased in the case of sols dialysed for 3 and 8 days and continuously decreased for sols dialysed for 13 days or longer, (ii) there is no appreciable difference between the maximum value on dialysis, *i.e.*, 43.20 and dilution, *i.e.*, 42.50, and (iii) the maximum value of the cat. speed has occurred at dilution 2 for sol dialysed for 2 days, and between 1.33 and 2 for that dialysed for 8 days.

It is also clear from the results that changes in stability on dilution and dialysis do not always give an idea about changes in cat. speed of the colloidal particles.

It may be mentioned here that for prussian blue dialysed for 3, 8 and 13 days, on diluting the sol the viscosity is found to decrease first rapidly and then slowly and afterwards shows a tendency to become constant. In the case of sols dialysed for periods longer than 13 days, on diluting the sol the viscosity first decreases and then increases. From changes in the cat. speed on dilution of sols dialysed to different extents (Table V) it will be clear that neither the view of Dhar⁵ nor of v. Smoluchowski,⁴ can individually explain the changes in cat. speed and viscosity observed in these experiments. As stated by Desai and co-workers,¹ one should also consider changes in hydration, the amount of electrolyte and the shape and size of particles to explain these results.

D. Measurements of cataphoretic speed from the point of view of critical potential.—A summary of results obtained in these experiments is given in Table VI.

TABLE VI.

Electrolyte	Initial cat. speed	Initial increase of cat. speed	Cat. speed at which coagulation begins	Concentration of electrolyte at which coagulation begins
HCl	38.70	3.60	27.50	0.125
KCl	37.30	7.30	26.20	2.500
MgCl ₂ *	37.05	nil	27.85	0.075
	36.35	nil	26.75	0.750
MgSO ₄ *	27.90	nil	22.20	0.125
	36.90	nil	24.50	1.250

* Results taken with two different samples of sol.

It will appear from the results that in the case of the electrolytes with univalent coagulating ions the cataphoretic speed first increases and then decreases when small increasing amounts of electrolyte are added to the sol, while with electrolytes with bivalent coagulating ions, the initial increase is not noticed at all. The initial increase in cat. speed is due to preferential adsorption of the similarly charged ions as stated before. The preferential adsorption of the similarly charged ions is not observed with MgCl₂ and MgSO₄ because of the bivalency of the coagulating ions.¹ Further as H-ions act as better coagulating agent than K-ions the initial increase in the cat. speed is smaller in the former case than in the latter.

The value of the cat. speed at which coagulation begins in different cases lies between 22.20 and 27.85, the maximum difference in the initial cat. speed being 10.80. According to Powis⁶ coagulation begins only when the electrokinetic potential or the electric charge is lowered to a certain absolute value characteristic of each colloid. Mukherjee and co-workers⁷ have, however, concluded that there is no critical potential characteristic of coagulation of a colloid by an electrolyte as suggested by Powis. Desai and co-workers¹ have observed that in the case of the colloidal ferric and thorium hydroxide coagulation begins at about the same value of the cat. speed for different electrolytes although the concentration of the electrolyte corresponding to that cat. speed is quite different in different cases. The present results also support the idea of critical potential at least for the electrolytes tried in this investigation because coagulation has begun at about the same value of cat. speed in different cases; slight variations in the critical values might be

due to the differences in the nature of the stabilising ions as suggested by Desai and co-workers.¹

E. Influence of sunlight on cataphoretic speed of colloidal prussian blue dialysed to different extents.—For these experiments equal volumes of sol were removed in resistance glass beakers (of same capacity) which were kept covered with glass plates and exposed to sunlight for different periods. Any loss due to evaporation was made good by addition of conductivity water. The results of these experiments are given in Table VII.

TABLE VII.

Sol dialysed for 10 days		Sol dialysed for 21 days	
Exposure in hours	Cat. speed	Exposure in hours	Cat. speed
0	44.30	0	42.70
1	43.90	1	37.80
3	37.90	2	36.20
		5	34.10
		10	33.60
		29	27.60

It will appear from the results that the cat. speed decreases on exposure to sunlight. According to Miss S. Roy and Dhar⁸ the prussian blue sol becomes more stable (stability as determined by flocculation values) on exposure to light. They have further stated that the greater stability is due to agglomeration as inferred from the absorption-spectra of sol exposed to sunlight. It is not clear how stability can increase as a result of agglomeration because ordinarily one would expect that the greater the size of particles the smaller the stability of the sol as a smaller amount of electrolyte would be required to reach a given degree of turbidity when the particles are big than when they are relatively small. The fact that agglomeration takes place on exposure will also be supported by the following observations.

TABLE VIII.

Period of dialysis in days	Time after which sol coagulates on exposure
0	1 to 1.5 mins.
1	2.5 to 3 „
7	17 „
10	3 to 4 hours
21	> 29 „

It will appear that in the first four cases exposure has given rise to agglomeration, *i.e.*, coagulation. Agglomeration has however resulted in a decrease of stability—a fact not agreeing with observations of Miss S. Roy and Dhar.⁸ In the case of the sol dialysed for 21 days no sign of coagulation appears even on exposing it for 29 hours.

According to Laderer and Hartleb,⁹ Berlin blue hydrosols are decolourised when exposed to visible light. It may be stated that in our case no decolourisation of the sol was noticed upto an exposure of 29 hours to sunlight, in the case of sol dialysed for 21 days. They have, however, stated that electrolytes decrease the time of flocculation by irradiation. This observation is supported by the results given in Table VIII because the sol dialysed for 21 days and containing very little of oxalic acid does not coagulate even on exposure of 29 hours, while sols dialysed for shorter periods and containing relatively large amounts of oxalic acid coagulate on exposure to sunlight even for very short periods.

The changes in cat. speed on exposure are probably due to action of sunlight on oxalic acid which gives rise to a change in the nature of the intermicellary liquid.

It may be mentioned that viscosity of the sol is found to decrease on exposure to sunlight—a fact which would seem to support v. Smoluchowski's view.

Summary.

The cat. speed of colloidal prussian blue (prepared by peptisation with oxalic acid) with the progress of dialysis first increases and then decreases, while the stability as determined by flocculation values with KCl

continuously decreases. The cat. speed on dilution first increases and then decreases in some cases while it continuously decreases in others; the stability on dilution is found to decrease continuously in all the cases. These results of dialysis and dilution are exactly similar to those obtained with colloidal ferric and thorium hydroxide investigated by Desai and co-workers.

The changes in the cat. speed and viscosity under different conditions show that neither the view of Dhar nor of v. Smoluchowski can individually explain the results.

The idea of critical potential is supported.

The cat. speed of the sol decreases on ageing and exposure to sunlight, sols dialysed for short periods even coagulating when exposed to sunlight for a couple of minutes.

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