IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS

Part VII. Colloidal Zinc ferrocyanide

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THE last paper[1] of this series contained measurements in the presence and absence of electrolytes of cataphoretic speed, stability and conductivity of colloidal solution of vanadium pentoxide which was dialysed, diluted, allowed to age, and exposed to sunlight to different extents. In the present paper similar results obtained with colloidal solution of zinc ferrocyanide are presented.

Experimental

Zinc ferrocyanide was precipitated by adding a solution of potassium ferrocyanide to a solution of zinc sulphate. The precipitate was filtered and washed with distilled water till free from soluble impurities. It was then suspended in distilled water in a flask, 0·1% solution of potassium ferrocyanide was added to it in small amounts and the mixture shaken vigorously till a clear colloidal solution was obtained. The colloidal solution was filtered through a double fold of filter papers in order to obtain particles of uniform size as far as possible. This sol was then dialysed in parchment paper bags in the usual manner and samples were removed for experiments after different periods of dialysis. Dilaysis was carried out in a dark room to avoid effect of light on the sol. During dialysis potassium and ferrocyanide ions were detected in the dialysate. The concentration of colloidal zinc ferrocyanide was determined from time to time and was found to remain constant during dialysis. In order to minimise the effect of ageing, all the experiments with the same sample of the sol were carried out in as short a time as possible.

The cataphoretic speed and conductivity were determined as before. Dialysate made equiconducting with the sol by the addition of potassium ferrocyanide was used as an upper liquid in cataphoretic speed experiments. In studying the effects of electrolytes on the colloid, the electrolytes were also added to the upper liquid so as to get the same ionic environment. The difference between the direct and reverse movements of the boundary was always within 4 per cent.

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The stability of the sol was determined by finding out the amount of KCl necessary to give instantaneous coagulation as judged by the naked eye when the tube was held against a transluscent background illuminated by an electric lamp.

Experiments on ageing and exposure to sunlight were carried out as in previous work.

All the experiments were carried out at a temperature of 30° C.

Results and Discussion

In all the tables the cataphoretic speed (cat. speed) (mean of direct and reverse movements) is corrected for viscosity and expressed in centimetres per second per volt per centimetre $\times 10^5$. In the experiments on the effect of electrolytes on the colloid, the concentration of the electrolyte is expressed in millimoles per litre of the mixture colloid + electrolyte + water. Dilution is expressed in terms of the ratio

$$\frac{\text{Volume of the diluted sol}}{\text{Volume of the original sol}};$$

the original sol has thus dilution 1. Flocculation values (F.V.) are expressed in millimoles of the electrolyte per litre of the mixture.

Section A: Changes during dialysis.—The results of these experiments are given in Table I.

TABLE I

Days of dialysis	Cat. speed $\times 10^5$	F.V. with KCl	Sp. conductivity $\times 10^6$
3	17·12	0·60	1439·0
8	23·56	0·44	440·2
10	30·72	0·41	..
13	34·08	0·40	212·4
18	37·00	0·39	168·3
21	39·43	0·35	..
25	24·67	0·26	60·9
28	20·58	0·20	50·9

It will be seen from the results that with the progress of dialysis the cat. speed first increases, reaches a maximum, and then decreases as in the case of $Fe(OH)_3$,[2] $Th(OH)_4$,[3] prussian blue,[4] gold[5] and V_2O_5[5] sols investigated

by Desai and co-workers. The colloidal particles of zinc ferrocyanide are —vely charged due to preferentially or primarily adsorbed $Fe(CN)_6''''$ ions, the peptising electrolyte being $K_4Fe(CN)_6$. It will appear from a summary of the results given in Table III in section C that the cat. speed also first increases and then decreases on adding small increasing amounts of $K_4Fe(CN)_6$ to the sol. The changes in cat. speed during dialysis can therefore be explained in the same manner as in the case of the colloidal solutions mentioned above.[1, 5, 6]

The stability as determined by F.V. with KCl continuously decreases with the progress of dialysis although the charge has first increased and then decreased. These results are similar to those obtained with $Fe(OH)_3$[2], $Th(OH)_4$[3], prussian blue[4] and V_2O_5[5] sols and the absence of parallelism between charge and stability in the early stages of dialysis is due to the same considerations as advanced in the previous papers.[1, 2, 3, 4, 6]

With the progress of dialysis the conductivity has continuously decreased. This is mainly due to the decrease in the amount of $K_4Fe(CN)_6$ in the sol during dialysis. The colloidal particles do not seem to contribute to conductivity to any appreciable extent as the conductivity has decreased in the early stages of dialysis when the charge has increased.

Section B: Changes during dilution of sols dialysed for different periods.— In Table II are given the results of these experiments.

It will appear from the results that for all the samples dialysed for a period less than 22 days, the cat. speed on dilution of the sol has first increased, reached a maximum and then decreased. For samples dialysed for 22 days or more, the cat. speed has continuously decreased on dilution of the sol. These results are similar to those obtained with $Fe(OH)_3$[2], $Th(OH)_4$[3] and prussian blue[4] sols where it was observed that for sols dialysed for periods shorter than that corresponding to the maximum in the cat. speed—dialysis curve of the colloid, the cat. speed first increases, reaches a maximum and then decreases on dilution of the sol and continuously decreases for samples of the sol dialysed for larger periods, and can be explained in the same manner.[6]

The conductivity invariably decreases on dilution of the sol and this decrease is mainly due to the decrease in the amount of the electrolyte in the intermicellary liquid.

The stability continuously decreases on dilution of the sol and it is noticed that as in the case of the sols mentioned above, one does not always find charge and stability varying in the same manner.

TABLE II

Days of dialysis	Dilution 1.00			Dilution 1.25		Dilution 1.50		Dilution 2.00			Dilution 3.00			Dilution 5.00		
	Cat. speed × 10⁵	Sp. conductivity × 10⁶	F.V. with KCl	Cat. speed × 10⁵	Sp. conductivity × 10⁶	Cat. speed × 10⁵	Sp. conductivity × 10⁶	Cat. speed × 10⁵	Sp. conductivity × 10⁶	F.V. with KCl	Cat. speed × 10⁵	Sp. conductivity × 10⁶	F.V. with KCl	Cat. speed × 10⁵	Sp. conductivity × 10⁶	F.V. with KCl
3	..	1439·0	0·60	..	1228·0	..	1048·0	..	815·3	0·55	..	503·6	0·50	..	332·2	0·43
6	21·43	..	..	23·20	..	26·56	..	28·80	..	..	24·37	..	..	20·87	..	..
8	23·56	440·2	0·44	28·59	365·4	29·87	307·1	31·79	234·3	0·40	23·54	159·6	0·36	20·94	98·8	0·29
13	34·00	212·4	0·40	34·70	173·5	35·00	142·9	36·10	121·8	0·35	34·80	103·4	0·31	34·10	83·1	0·27
18	37·00	168·3	0·37	37·40	137·4	38·30	119·9	37·90	106·3	0·31	35·80	92·2	0·29	34·90	78·5	0·24
22	28·10	152·3	0·30	26·40	123·9	25·90	117·0	23·00	85·0	0·28	19·80	63·5	0·25	17·60	43·0	0·20
25	24·67	60·9	0·26	23·70	53·6	23·10	48·3	21·90	39·0	0·23	18·50	30·6	0·19	14·30	16·8	0·15

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Section C: Changes in cat. speed of sols (dialysed for different periods) in the presence of electrolytes.—A summary of these results is given in Table III.

TABLE III

Electrolyte	Initial cat. speed	Initial increase of cat. speed	Cat. speed at which coagulation begins	Concentration of electrolyte at which coagulation begins
KCl	23·56* 28·12*	3·88 Nil	10·98 14·25	0·100 0·050
K$_2$SO$_4$	23·56 28·12	4·53 Nil	12·80 15·59	0·075 0·050
MgCl$_2$.	23·56 28·12	6·18 Nil	12·28 19·63	0·050 0·025
MgSO$_4$.	23·56 28·12	6·32 Nil	11·04 15·29	0·050 0·025
K$_4$Fe (CN)$_6$	23·56 28·12	14·04 1·46	No coagulation could be observed.	

* The initial cat. speeds are different because samples of sol dialysed for 8 and 22 days (cat. speed 23·56 × 10^5 and 28·12 × 10^5 respectively) have been used.

It will appear from the results that for the short period dialysed sol the cat. speed first increases and then decreases on adding small increasing amounts of electrolytes whether they contain univalent or bivalent coagulating ions. The initial increase in the cat. speed is due to preferential adsorption of the similarly charged ions as mentioned before. With the sols investigated before in our laboratory, the initial increase in the cat. speed was not noticed with the electrolytes having bivalent coagulating ions. Chaudhury[7] obtained an initial increase in the cat. speed of copper ferrocyanide sol (whose particles are —vely charged) when small increasing amounts of BaCl$_2$ were added to the sol. The causes of this peculiar behaviour of the zinc ferrocyanide sol are not very clear. It may be that the surface of the particles with reference to the similarly charged ions is not so much saturated that some more similarly charged ions are adsorbed due to chemical affinity inspite of the presence of the bivalent coagulating ions.

For the long-period-dialysed sol the initial increase in the cat. speed is noticed only with K$_4$Fe (CN)$_6$ which has a strongly adsorbable ferrocyanide ion. The absence of the initial increase in the cat. speed with other electrolytes having univalent coagulating ions is probably due to the fact that during dialysis the aggregation of the praticles has so changed the

distribution of the ions on the surface of the praticles that the adsorption of the similarly charged ions is not possible except when that ion is strongly adsorbable. It is, however, not understood why zinc ferrocyanide sol should behave in this peculiar manner when the other sols do not show a similar behaviour.

It is also seen from Table III that keeping the coagulating ion the same, the greater the valency of the similarly charged ion, the greater is its preferential adsorption and consequently the larger the initial increase in the cat. speed. As observed with other sols a smaller equivalent amount of electrolyte is necessary for coagulation when the coagulating ions are bivalent than when they are univalent due to greater adsorbability of the former than the latter ions.

It is clear from the results that the range of the cat. speed within which coagulation begins with the various electrolytes varies from 10·98 with KCl to 19·63 with $MgCl_2$. The conception of a critical potential put forward by Powis[8] is thus not supported by the present results (*cf.* Desai and Barve[6]).

Section D: Changes on ageing of sols dialysed for different periods.—The results of these experiments are given in Table IV.

TABLE IV

Age in days	Sol dialysed for 8 days			Sol dialysed for 22 days		
	Cat. speed × 10⁵	Sp. conductivity × 10⁶	F.V. with KCl	Cat. speed × 10⁵	Sp. conductivity × 10⁶	F.V. with KCl
0	23·56	440·2	0·44	28·12	152·3	0·30
30	22·90	401·7	0·36	27·76	147·4	0·27
52	..	..	..	27·05	132·0	0·22
66	21·70	341·5	0·34	..	..	..
68	..	..	..	26·30	127·5	0·19
78	20·80	308·6	0·29	..	..	..
80	..	..	..	25·68	122·8	0·14
90	20·30	299·6	0·27	..	..	..

From the results given in the above Table it is seen that the cat. speed, conductivity and stability as determined by F.V. with KCl continuously decrease on ageing of both the short period and long period dialysed sols.

The results are similar to those obtained with V_2O_5 sol and can be similarly interpreted.[1, 6]

Section E: Changes on exposure to sunlight of sols dialysed for different periods.—In Table V are given the results of these experiments.

TABLE V

Exposure to sunlight in hours	Sol dialysed for 8 days			Sol dialysed for 22 days		
	Cat. speed × 10^5	Sp. conductivity × 10^6	F.V. with KCl	Cat. speed × 10^5	Sp. conductivity × 10^6	F.V. with KCl
0	23·56	440·2	0·44	28·12	152·3	0·30
1	20·96	417·8	0·41	26·54	106·0	0·26
2	..	..	0·35	..	..	..
3	19·50	376·0	..	..	..	0·20
5	..	..	0·27	23·30	97·4	..
6	18·30	323·1	..	..	..	0·13
8	..	..	0·20	21·00	83·8	..
10	16·80	286·3	0·17	..	..	0·08
13	..	..	..	20·56	68·0	..
15	..	..	..	..	..	0·06
17	..	..	..	20·10	64·1	..

As in the case of ageing, the cat. speed, conductivity and stability decrease continuously on increasing exposure to sunlight of both the short period as well as the long period dialysed sols and these changes can be explained in the same manner. One additional factor has also to be considered in this case. It has been observed by Matuschek[9] that potassium ferrocyanide, which is the peptising agent in this case, decomposes into ferric hydroxide, potassium cyanide and hydrocyanic acid on exposure to light. This will decrease the cat. speed appreciably as the univalent peptising ions will not be as strongly preferentially adsorbable as the tetravalent peptising ions. It is also found that the sol dialysed for 8 days shows a tendency for precipitation on exposure of 10 hours, while that dialysed for 22 days does not show the same tendency even after 15 hours exposure; the short period dialysed sol contains more of $K_4Fe(CN)_6$ than the long period dialysed sol and hence the greater effect of light in the former than in the latter case.

Summary

The changes in the cataphoretic speed, stability and conductivity of colloidal zinc ferrocyanide dialysed, diluted, allowed to age and exposed to sunlight for different periods have been studied.

With the progress of dialysis the cataphoretic speed first increases and then decreases, while the stability and conductivity continuously decrease.

In the case of sols dialysed for periods shorter than the maximum in the cataphoretic speed-dialysis curve, the cataphoretic speed first increases and then decreases on dilution, while for sols dialysed for longer periods the cataphoretic speed continuously decreases. The stability and conductivity, however, continuously decrease on dilution in all the cases.

It is found that for short period dialysed sols, the cataphoretic speed first increases and then decreases on adding small increasing amounts of KCl, K_2SO_4, $K_4Fe(CN)_6$, $MgCl_2$ and $MgSO_4$; for long period dialysed sols the cataphoretic speed continuously decreases with all the electrolytes except $K_4Fe(CN)_6$ where it first increases and then decreases. The idea of critical potential is not supported.

On allowing both the short period and long period dialysed sols to age or exposing them to sunlight, the cataphoretic speed, stability and conductivity continuously decrease.

The results are interpreted by means of assumptions similar to those employed in the case of the other colloidal solutions investigated in this laboratory.

REFERENCES

1. Desai, Barve and Paranjpe   *Proc. R. S. E.*, 1939, **59**, 30.
2. Desai and Borkar   .. *Trans. Faraday Soc.*, 1933, **29**, 1269.
3. ——— and Desai   .. *Ibid.*, 1933, **30**, 265.
4. Mankodi, Barve and Desai   *Proc. Ind. Acad. Sci.*, 1936, **4**, 480
5. Desai, Barve and Paranjpe   *Proc. R. S. E.*, 1939, **59**, 22.
6. ——— and Barve   *Trans. Nat. Inst. Sci.* (India), 1939, **2**, 39.
7. Chaudhury   .. *J. India Chem. Soc.*, 1933, **10**, 431.
8. Powis   .. *Zeit. physik. Chem.*, 1915, **89**, 186.
9. Matuschek   .. *Chem. Zeit.*, 1901, **25**, 565.