The Influence of Temperature on the Formation of Platinum-carbonyl Sol.

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On passing carbon monoxide through a dilute aqueous solution of chloroplatinic acid at ordinary temperature, a colloidal solution of red colour is obtained in a short time, the general description of the formation and behaviour of the sol being given in the foregoing paper.[1] From various facts[1], [2] such as the oxidizing as well as decomposing action of air, oxygen and aqueous solution of bromine or hydrogen peroxide, the sol of red colour and the sol of black colour obtainable by dialyzing the red one or by letting it stand in the air, might be assumed to be composed of colloidal platinum-carbonyl and colloidal platinum respectively. The present paper deals with the influence of temperature together with concentration of the solution of chloroplatinic acid on the formation of the sol.

Experimental. Carbon monoxide was prepared by heating the mixture of formic acid and concentrated sulphuric acid and washed by bubbling it through alkaline hydroxide solutions. The aqueous solutions of

(1) I. Sano, this Bulletin, **9** (1934), 320.
(2) I. Sano, this Bulletin, **13** (1938), 118.

chloroplatinic acid were made by dissolving the acid ($H_2PtCl_6 \cdot 6H_2O$) from Takeda in ordinary distilled water. The reaction vessel used was cleaned, prior to use, with chromic acid mixture and, if necessary, with aqua regia and steamed with water vapour.

A 50 c.c. of the chloroplatinic acid solution of a definite concentration was taken in each run of the experiments. The gas was, by way of a pre-heating device constructed of glass-tube, introduced into it at the desired temperatures and at a rate of 3 litres per hour constant throughout the runs of experiment, from a capillary glass-tube having a diameter short of 1 mm.

Results and its discussion. The colour of the chloroplatinic acid solution turns, with the formation of colloidal solution, from pale yellow into red, brown as well as black according to the temperature and the concentration of the solution. The transitional change in colour of the solution was observed with the naked eye under day-light with simultaneous recording of time during the passage of carbon monoxide through the solution. Some of the results obtained are given in the following tables (Table 1 to Table 6 inclusive), where c stands for the concentration of the starting aqueous solution of the acid ($H_2PtCl_6 \cdot 6H_2O$) in per cent, θ the temperature of preparation in °C., t the time elapsed from the commencement in minutes and h the hue of the solution observed at time t.

As can be seen from the tables, the chloroplatinic acid solutions assume, through the stages as under stated, a variety of colours according to the temperature of reaction as well as the concentration of solution in consequence of the passage of carbon monoxide. The transitional change in colour of the solution in any run may be summarily outlined as follows: In the incipient stage, the solution will faintly assume a shade of a black tint in a short course of time from the start—this tendency will be perceived appreciably in concentrated solutions and promptly at high temperatures and may be supposed to be due to the transient formation of a lower salt like platinous chloride[1], [3] soluble in hydrochloric acid.[4] It will yield platinum carbonyl chloride in combination with carbon monoxide only to be so unstable in aqueous solution that it readily decomposes into platinum, carbon dioxide and hydrochloric acid—to be immediately followed by the colouration bearing brown as the predominant colour; this period being over, the solution will be of a tone of colour ranging from red to brown, and in the ultimate stage, will take, in accordance with the conditions concerned, a deep colour between purplish red and dark brown if observed in transmitted light, though tinged more or less deeply with black in reflected one. The colloidal solutions prepared from the acid solutions having larger concentrations such as 0.08 as well as 0.1% will be black in appearance and unstable, irrespective of the temperature of preparation, and settle in some measure presently after its formation. It was observed throughout the present experiment that

(3) F. C. Phillips, *Am. Chem. J.*, **16** (1894), 255.
(4) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 16, 251.

Table 1.

c: 0.02 θ: 20

t	h
0	pale yellow
16	faintly tinged with dark
20	faintly tinged with darkish red
23	light red with a mere dash of purple
30	red with a dash of purple
40	,,
60	,,

Table 2.

c: 0.02 θ: 50

t	h
0	pale yellow
9	faintly tinged with dark
11	light brown
17	brown with a dash of red
30	red having a tinge of brown
40	coloured more deeply
50	darkish red faintly tinged with brown
60	,,

Table 3.

c: 0.02 θ: 80

t	h
0	pale yellow
7	faintly tinged with dark
8	faintly tinged with darkish yellow slightly inclining to brown
10	light brown
25	tinged more deeply with dark
40	dark brown
60	,,

Table 4.

c: 0.08 θ: 20

t	h
0	light yellow
13	faintly tinged with dark
14	light yellow having a tinge of darkish red
16	brownish yellow with a mere dash of red
18	brown inclining to red
20	red with a tinge of brown
22	red with a dash of purple
60	,,

Table 5.

c: 0.08 θ: 50

t	h
0	light yellow
8	faintly tinged with dark
12	dark yellow
17	coloured more deeply
20	dark yellow with a dash of brown
40	dark brown slightly inclining to yellow
50	dark brown
60	,,

Table 6.

c: 0.1 θ: 20

t	h
0	light yellow
11	faintly tinged with dark
14	light brown slightly inclining to yellow
18	brown
19	brownish red faintly tinged with purple
21	red with a dash of purple
28	darkish red
40	darkish red with a tinge of brown
60	,,

the more dilute the starting acid solutions, the more stable were the sols obtained.

A summary of the hues, h, of colloidal solutions obtainable under sets of conditions concerning the concentration, c, of the chloroplatinic acid solution and the temperature, θ, at which the passage of carbon monoxide was performed is given in Table 7. The relations among them are plotted on a graph with the values of the temperature, θ, in °C. as ordinates and of the concentration, c, in % as abscissæ in Fig. 1.

Table 7.

c: 0.01

θ	h
5	red with a dash of purple
20	,,
35	,,
50	brownish red with a mere dash of purple
55	red slightly tinged with brown
60	brown with a tinge of red
65	brown
80	dark brown

c: 0.02

θ	h
5	red with a dash of purple
20	,,
35	,,
50	darkish red faintly tinged with brown
55	darkish red with a tinge of brown
60	brown
65	dark brown
80	,,

c: 0.05

θ	h
5	red with a dash of purple
20	,,
35	,,
50	brown with a tinge of red
55	brown
60	dark brown
65	,,

c: 0.08

θ	h
20	red with a dash of purple
25	brownish red faintly tinged with purple
35	brown slightly inclining to red
40	brown
50	dark brown

c: 0.1

θ	h
5	red with a dash of purple
15	,,
20	darkish red with a tinge of brown
30	brown with a mere dash of red
35	brown
45	,,
50	dark brown

It is no wonder that the boundaries between the domains of hue should be somewhat wanting in clearness, the lines of demarcation, a, b and c, though drawn well-definedly in the figure, only indicating the approximate positions of them. It can be seen from the figure that a colloidal solution assuming red with a dash of purple will be produced at ordinary

temperatures from the chloroplatinic acid solution of lower concentration; the domain of its formation is reduced with the increasing concentration of the starting solution and extinguished at a limiting concentration,

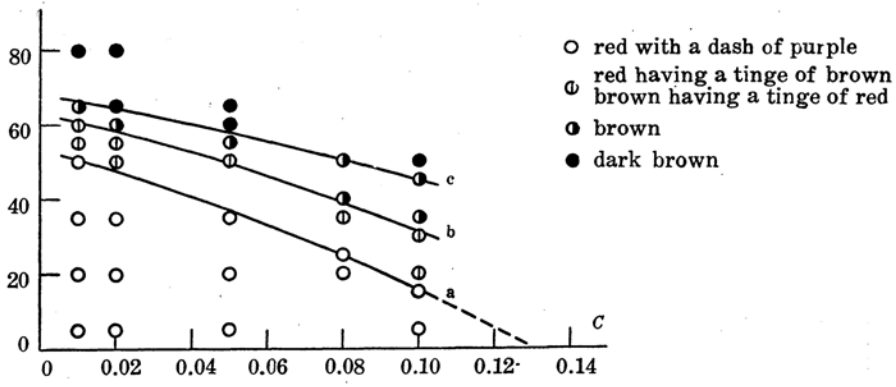

Fig. 1.

$c = 0.13$, as shown by the extension of the line a, and it points to the supposition, therefore, that there should be never produced stable sols of red inclining to purple beyond the limiting concentration at any temperature. F. C. Phillips[3] observed that aqueous solutions of platinum chloride were slightly tinged with black by the action of carbon monoxide, cold or at 100°C., to be subsequently followed by slow deposition of metallic platinum.

With the intention of acquiring further informations on the colouration effects above mentioned, the extinction coefficients of the sols were measured after they were left at room temperature out of contact with the air for the space of 2 hours from the close of preparation downward. The measurements were made with the Nutting's spectrophotometer at ordinary temperature, in that the extinction coefficient, ε, could be estimated with the aid of the formula

$$\varepsilon = -2 \log (\cos \alpha)/c.d,$$

where α denotes the angle of extinction for any visible ray to be determined through observation with the spectrophotometer, c the concentration and d the thickness of layer of the solution. The results obtained are diagrammatically depicted in Fig. 2, 3, 4, 5 and 6 in terms of the relationship between the extinction coefficient multiplied by the concentration, εc, per unit thickness in cm. of the sols concerned and the wavelength of the rays referred, λ, in mμ in company with the temperatures of preparation of the sols, θ, in °C. εc was taken in place of c on account of certain difficulties attending on the determination of concentration of the sols owing to their variability in the air. This will suffice to give informations on the extinction effects of the sols obtainable from the acid solution of one and the same concentration.

The dotted line in Fig. 6 represents the relation between εc and λ for a 0.1% solution of chloroplatinic acid; as compared with this, it is obvious for the colloidal solution to display a larger extinction effect.

The sols will turn black in due time, as already descibed,[1] by leaving it intact in the air owing to the disappearance of carbon monoxide or carbonyl group from colloidal particle due to volatilization towards as well as oxidation by the air. It might be considered for the extinction coefficient of the sol to exhibit a definite increase in magnitude as a consequence of the change in colour, this being manifestly indicated through the results given as the thick lines, full for the red sol as well as broken for the black one in Fig. 3.

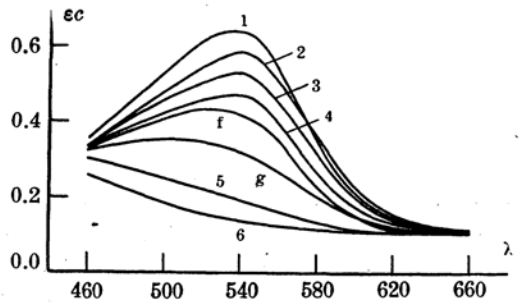

Fig. 2.

Curve	θ
1	5
a	15
2	20
b	25
c	30
3	35
d	40
e	45
4	50
f	55
g	60
5	65
6	80

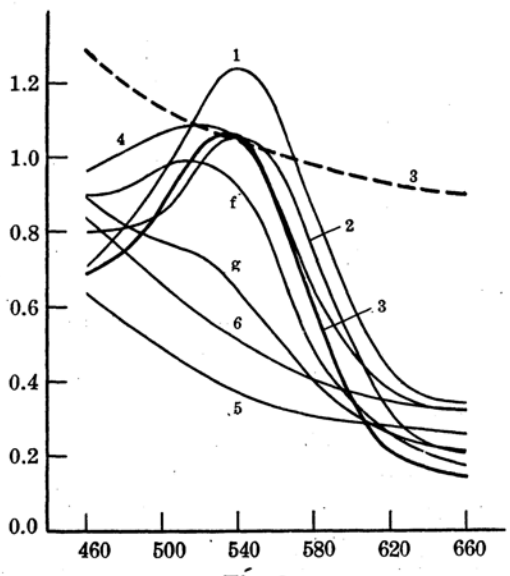

Fig. 3.

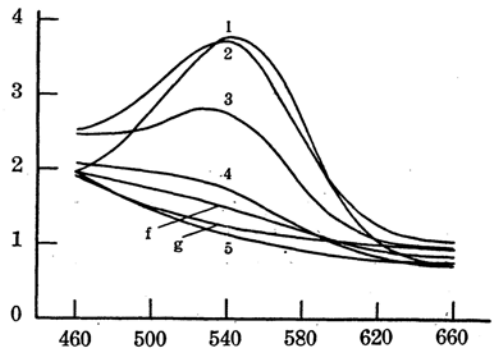

Fig. 4.

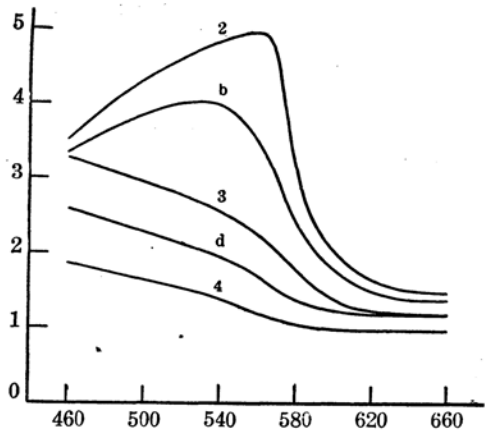

Fig. 5.

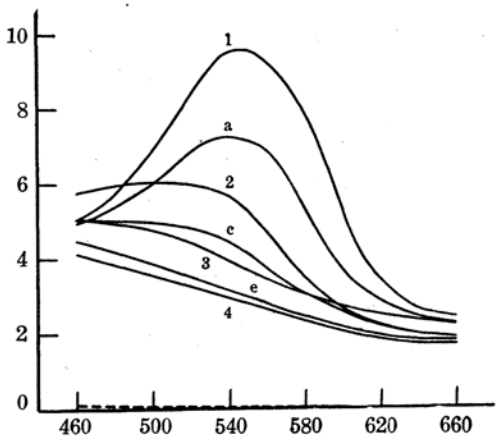

Fig. 6.

It can be distinctly seen from the figures that the extinction curves for the sols having a tinge of red reach a definite maximum at about 540 mμ; while the curves for those with a tinge ranging from brown to black show monotonously decreasing gradient with increasing wave-length. It would seem, therefore, that the extinction effect could be reduced as the temperature of formation of the sol is raised, although beyond a certain limiting temperature depending on the concentration of solution this should attain a noticeable magnitude for the second time as the chloroplatinic acid solution passes immediately into a sol tinged with black by the action of carbon monoxide at higher temperatures as indicated in Fig. 1.

It must be added that the run of the extinction curves was taken into consideration in discriminating the shade and tone of a colour of the sol produced and establishing the influence of the temperature of preparation and the concentration of chloroplatinic acid solution on the formation of it as represented in Fig. 1.

Summary.

(1) The influence of the temperature of preparation on the formation of platinum-carbonyl sol from the chloroplatinic acid solution by the action of carbon monoxide were investigated at various temperatures between 5° and 80°C., together with the influence of the concentration of solution ranging from 0.01 to 0.1% with respect to $H_2PtCl_6 \cdot 6H_2O$.

(2) Stable sols having a tinge of red with a dash of purple may be produced from the solutions of concentrations between 0.01 and 0.08% in a wide range of temperature; sols of various colours such as brownish red, brown as well as dark brown may be formed in the same limits of concentration as the above at the elevated temperatures.

(3) Sols tinged with red slightly inclining to purple may be obtained, though unstable, from the 0.1% acid solutions only at lower temperatures.

(4) The colouration effects above-mentioned were spectroscopically analyzed with the Nutting's spectrophotometer, and it was found that

the extinction curves for the sols tinged with red reach a maximum at about 540 mμ, while those for the sols with a tinge varying from brown to black decrease monotonously with the increasing wave-length.

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