Studies of the Stability of Cobalt Ferrocyanide Sol in Ultrasonic Field. The Ultrasonic Dispersion of Cobalt Ferrocyanide

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High frequency, inaudible sound waves can bring about various dispersion effects, such as the mutual emulsification of the liquid phase, the disintegration of certain solids, the peptization and liquefaction of gels, and the depolymerization of high molecular substances. Polotoskii[1] prepared hydrosol of camphor and iodine in water, and Sata and his co-workers[2] dispersed metallic hydroxide in water by means of ultrasonic waves. Prakash and Pandey[3] successfully utilized ultrasonic energy in the preparation of a colloidal cobalt hydroxide solution. The present authors have been able to obtain a very stable sol of cobalt ferrocyanide by using the ultrasonic dispersion method. The sol obtained was then stabilized by further irradiation. Our findings on the influence of ultrasonic waves on this sol in presence as well as in absence of oxygen and in presence of non-electrolytes, such as methanol, ethanol and acetone, will be reported in this paper.

Experimental

Materials.—B. D. H. (Analar) samples of potassium ferrocyanide, cobalt chloride, barium chloride, potassium chloride and hydrochloric acid and distilled methanol, ethanol and acetone (B. D. H., L. R.) were used.

Instruments, Procedures and Calculation.—*Electrical Conductance Measurements.*—The measurements of electrical conductance were carried out with a Leeds and Northrup Kohlrausch slidewire, with an audio-frequency oscillator. A dip-type cell was used. The temperature was kept constant (30±0.2°C).

pH Measurements.—The hydrogen ion concentration of the solution was measured with a Leeds and Northrup direct-reading pH indicator with a glass calomel electrode system. The instrument was standardised from time to time with a standard buffer of pH 6.8.

Transmission Measurements.—The transmission in percentage was determined with a Unicam SP 1400 prism absorptiometer, and the optical density was calculated by the equation:

$$\text{Optical density} = \log (1/T)$$

where T is the transmission.

Ultrasonic Generator.—The source of ultrasonic power was a Mullard high frequency ultrasonic generator, type E-7562, with a barium titanate transducer. The principal diagram of the electrical circuit is shown in Fig. 1. The frequency of the transducer was 1 Mc./sec.

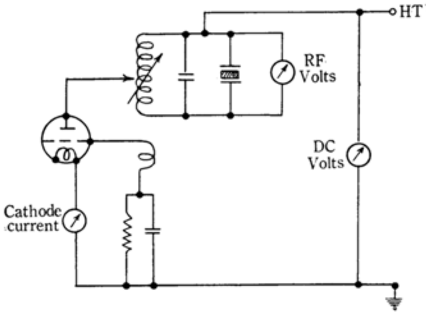

Fig. 1

Decinormal solutions of cobalt chloride and potassium ferrocyanide were mixed together, with more of the latter. The precipitate of cobalt ferrocyanide was filtered and washed. The precipitate was put into distilled water in a Jena glass bottle and exposed to ultrasonic waves. A cobalt ferrocyanide sol of a dirty brown colour was obtained within thirty minutes. In this way a sufficient amount of the sol was prepared and stored in a Jena bottle for detailed study. The sol was then purified by dialysis for three days. The concentration of the sol was determined by evaporating a known volume of the sol to dryness on a water bath. The sol concentration was found to be 19.3526 g./l.

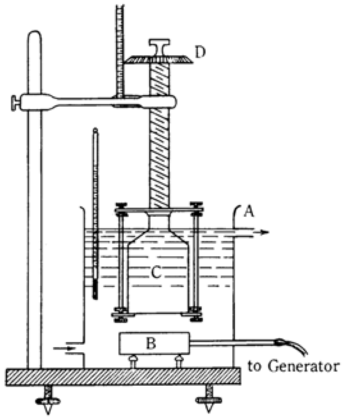

Fig. 2

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[1] G. G. Polotoskii, *Colloid. J.* (*U. S. S. R.*), **6**, 779 (1940).

[2] N. Sata and S. Watanabe, *Kolloid-Z.*, **73**, 50 (1935).

[3] S. Prakash and A. D. Pandey, ibid., **181**, 46 (1962).

The above sol, 30 ml., was then placed in a 250 ml. flat-bottomed Jena glass vessel with a ground glass stopper and exposed to the action of ultrasonic waves for various intervals of time. The ultrasonic bath (Fig. 2) was kept at a constant temperature (30±0.2°C) by circulating water into it. The Jena vessel was held vertically above the transducer, and the distance between the vessel and the crystal was so adjusted as to produce a maximum fountain inside the vessel. The distance was kept unchanged as much as possible during the course of the experiments.

The stability of the sol was determined after each exposure by noting the amount of potassium chloride and barium chloride required to coagulate the negatively-charged sol of cobalt ferrocyanide in a fixed time (30 min.). The variation in specific conductivity and hydrogen-ion concentration of the sol was also recorded every time. The change in optical density was thus observed.

The experiments were carried out in the absence of oxygen. The air was replaced with nitrogen by bubbling for thirty minutes. Nitrogen from a cylinder had previously been passed through solutions of vanadous sulphate and alkaline pyrogallol in order to remove the oxygen.

The influence of ultrasonic waves on this sol in the presence of methanol, ethanol and acetone was also studied. Measurements similar to those mentioned above were carried out after each exposure, and the results were compared with those when no non-electrolyte was present.

Results and Discussion

Figure 3 shows the amount of the dispersion of cobalt ferrocyanide when it is subjected to ultrasonic waves. As may be seen in the figure, the amount increases rapidly in the beginning. When the exposure time is further increased, the increment is slowed down and attains a maximum value.

The coagulation values of the sols under various conditions are shown in Tables I and II.

A perusal of these tables will show that, with the increase in the time of exposure to

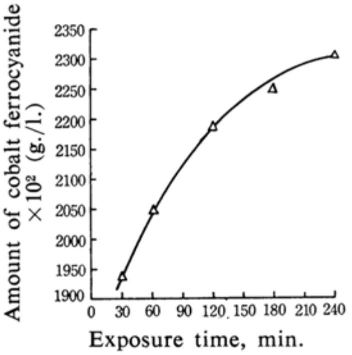

Fig. 3. Ultrasonic dispersion of cobalt ferrocyanide.

TABLE I. SOL A

Volume of sol taken, 2 ml.
Total volume, 8 ml.
Time allowed for coagulation, 30 min.
Temperature, 30±0.2°C
R. F. output voltage, 2.4 kV. (approx.)

Time of exposure min.	Coagulation values			
	In presence of air		In absence of oxygen	
	(M/100) $BaCl_2$	(M/10) KCl	(M/100) $BaCl_2$	(M/10) KCl
0	0.95	2.45	0.95	2.45
60	1.10	2.60	1.05	2.55
120	1.20	2.70	1.15	2.65
180	1.25	2.80	1.15	2.70
240	1.30	2.85	1.25	2.85
300	1.40	3.00	1.35	2.05

TABLE II. SOL A/2

Time of exposure min.	Coagulation values			
	In presence of air		In absence of oxygen	
	(M/100) $BaCl_2$	(M/10) KCl	(M/100) $BaCl_2$	(M/10) KCl
0	0.65	2.00	0.65	2.00
60	0.75	2.15	0.75	2.20
120	0.80	2.20	0.80	2.25
180	0.90	2.30	0.90	2.30
240	1.00	2.40	0.95	2.45
300	1.15	2.55	1.10	2055

TABLE III

Time of exposure min.	Coagulation values with M/5 HCl			
	25 ml. sol + 5 ml. water	25 ml. sol + 3 ml. water + 2 ml. methanol	25 ml. sol + 3 ml. water + 2 ml. ethanol	25 ml. sol + 3 ml. water + 2 ml. acetone
0	1.30	1.20	1.20	1.20
60	1.45	1.30	1.30	1.20
120	1.60	1.35	1.30	1.30
180	1.70	1.35	1.30	1.30
240	1.85	1.45	1.35	1.30

TABLE IV

Time of exposure min.	Coagulation values with M/5 HCl			
	25 ml. sol + 5 ml. water	25 ml. sol + 5 ml. methanol	25 ml. sol + 5 ml. ethanol	25 ml. sol + 5 ml. acetone
0	1.30	1.10	1.10	1.15
60	1.45	1.25	1.20	1.20
120	1.60	1.25	1.20	1.20
180	1.70	1.25	1.20	1.20
240	1.85	1.30	1.20	1.20

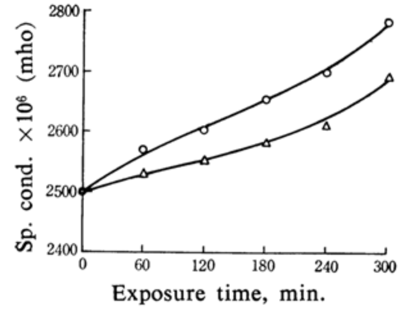

Fig. 4. Variation in sp. cond. in sol A.
○—○ In presence of air
△—△ In absence of oxygen

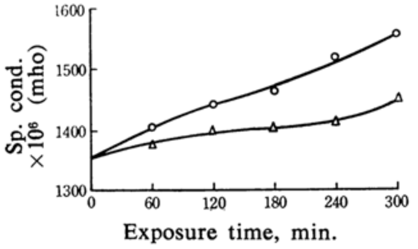

Fig. 5. Variation in sp. cond. in sol A/2.
○—○ In presence of air
△—△ In absence of oxygen

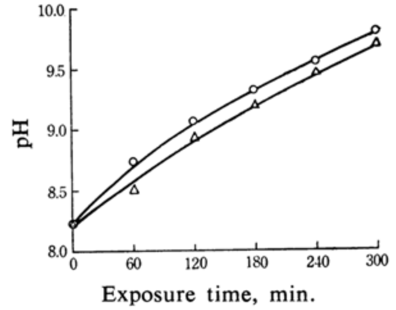

Fig. 6. pH variation in sol A.
○—○ In presence of air
△—△ In absence of oxygen

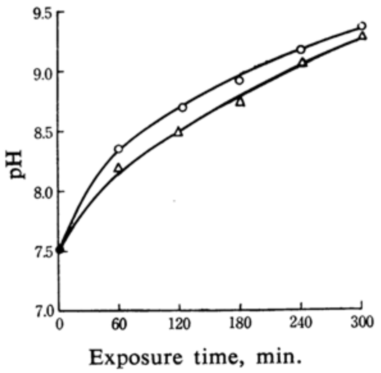

Fig. 7. pH variation in sol A/2.
○—○ In presence of air
△—△ In absence of oxygen

the ultrasonic waves, the stability of the sol increases in the presence as well as in the absence of oxygen. The small difference in the extent of stabilization under the two conditions shows that the presence or absence of oxygen in no way affects the ultrasonic action on this sol, as had previously been observed by the present authors in the case of the manganese dioxide sol.[4] As the sol is negatively charged, the enhanced stability may be attributed to the decrease in hydrogen ion concentration. The hydroxyl ions are increased in the system; they are adsorbed on the double layer, with the result that the sol attains more stability.

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[4] S. Prakash and O. Prakash, *Kolloid-Z.*, **188**, 136 (1963).

Dhar and his collaborator[5] have shown that ferrocyanide sols are appreciably hydrolysed in aqueous solutions and that this hydrolysis makes the sol more stable towards electrolytes. It is possible that, under the influence of ultrasonic waves, the sol of cobalt ferrocyanide becomes more hydrolysed and hence more stable to electrolytes. As Figs. 4 and 5 show, the specific conductivity of the sol also increases as the time of exposure is increased. A number of investigators[6-9] have found H_2O_2, HNO_2 and HNO_3 present in the sonolysis of water exposed to ultrasonic waves. The acid nature of these substances would increase the specific conductivity.

In spectroscopic studies (Figs. 8 and 9) of the unexposed and exposed sol, it is observed that an absorption maximum occurs at the same wavelength in both cases suggesting that no change in the basic characters of the substance has taken place. It seems that the ultrasonic waves have brought about a change in the physical character of the particles by their own cavitating action on larger aggregates, thus making them smaller. This theory is confirmed by the observation that, as the time of exposure increases, the turbidity in the unexposed sol continues to vanish and the sol becomes transparent.

The stability, specific conductivity and hydrogen ion concentration of the sol are very little affected by ultrasonic waves in the presence of methanol, ethanol and acetone, as Tables III and IV, and Figs. 10, 11 and 12 show. The great majority of the disruptive actions and the chemical reactions caused by ultrasonic

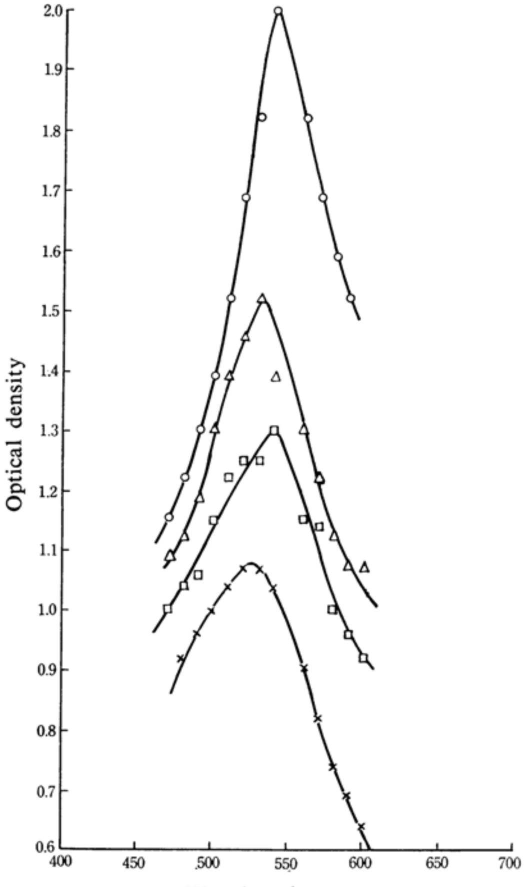

Fig. 8. Cobalt ferrocyanide sol A/4.

○ Unexposed
△ Exposed for 1/2 hr.
□ Exposed for 1 hr.
× Exposed for 2 hr.

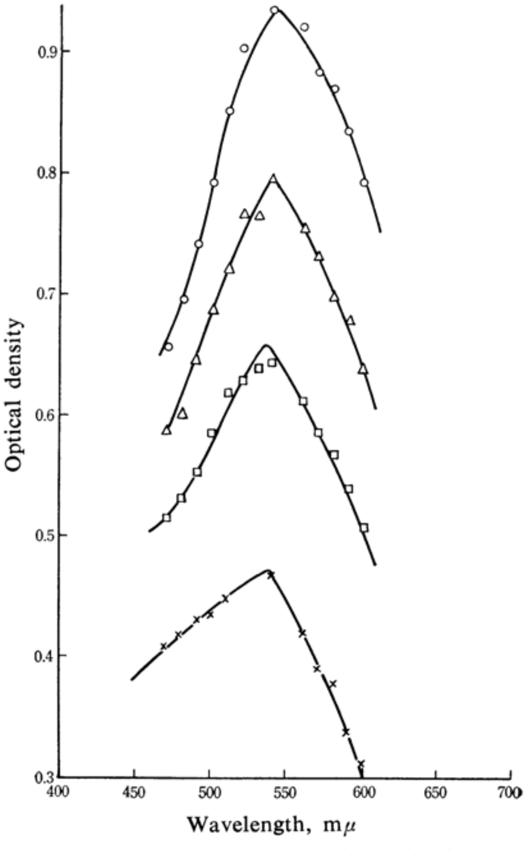

Fig. 9. Cobalt ferrocyanide sol A/8.

○ Unexposed
△ Exposed for 1/2 hr.
□ Exposed for 1 hr.
× Exposed for 2 hr.

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[5] S. Ghosh and N. R. Dhar, *J. Phys. Chem.*, **29**, 659 (1925) ; *Kolloid-Z.*, **39**, 349 (1926).

[6] I. G. Polotskii, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 649 (1947).

[7] H. Beuthe, *Z. Phys. Chem. Abt.*, **A163**, 161 (1933).

[8] S. Akiya and S. Okui, *J. Pharm. Soc. Japan*, **67**, 232 (1947).

[9] O. Nomoto and S. Okui, *J. Phys. Soc. Japan*, **3**, 47 (1948).

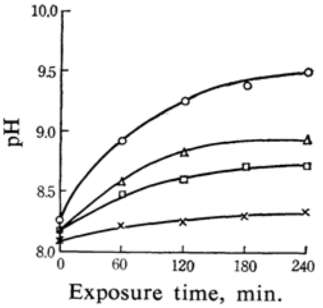

Fig. 10. pH variation in presence of non-electrolytes in sol A.

○—○ Without non-electrolyte
△—△ In presence of 2 ml. methanol
□—□ In presence of 2 ml. ethanol
×—× In presence of 2 ml. acetone

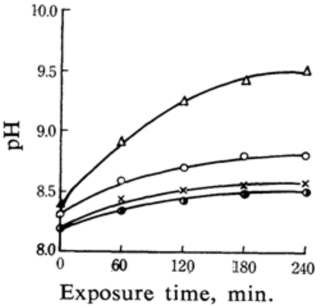

Fig. 11. pH variation in presence of non-electrolyte in sol A.

△—△ Without non-electrolyte
○—○ In presence of 5 ml. methanol
×—× In presence of 5 ml. ethanol
◑—◑ In presence of 5 ml. acetone

waves have been attributed to the phenomenon of cavitation. Because of a high dielectric constant, high surface tension and low vapour pressure values of water, the aqueous medium greatly favours the formation of cavitation bubbles, with the result that the ultrasonic activity observed in such a medium will be at a maximum. Thus, the inhibitive effect of non-electrolytes, e. g., methanol, ethanol and acetone, may be due to the suppression of this cavitation, because the presence of substances of a high vapour pressure(10) suppresses the breakdown of cavitation bubbles. Consequently, ultrasonic activity is very much lessened. Secondly, the energy released upon the collapse of the cavitation bubble is comparatively much less if the surface tension(11) and the internal pressure(12) of the medium are low, resulting in a decrease in the rate of ultrasonic action.

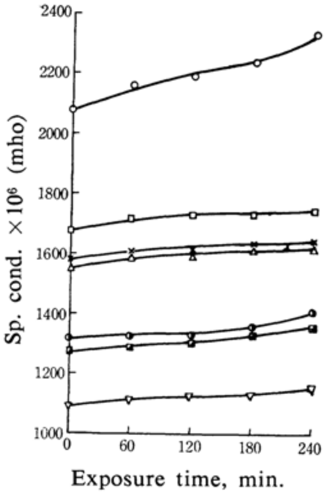

Fig. 12. Variation in sp. cond. in presence of non-electrolyte in sol A.

○—○ Without non-electrolyte
□—□ 2 ml. methanol
×—× 2 ml. acetone
△—△ 2 ml. ethanol
◑—◑ 5 ml. methanol
◪—◪ 5 ml. acetone
▽—▽ 5 ml. ethanol

Summary

A negatively-charged cobalt ferrocyanide sol has been prepared ultrasonically subjecting the washed precipitate of cobalt ferrocyanide and distilled water to ultrasonic waves. The amount of dispersion increases with the time of exposure. The sol is rendered more stable in an ultrasonic field in the presence as well as in the absence of oxygen. The enhanced stability has been attributed to the increase in hydroxyl ions in the medium as a result of the hydrolysis of cobalt ferrocyanide sol. The stability, pH and specific conductivity values are very little affected in the presence of methanol, ethanol and acetone. The inhibition is due to the suppression of cavitation and to a lesser energy release on the collapse of cavitational bubbles.

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11) T. F. Heuter and R. H. Bolt, "Sonics," John Wiley & Sons, New York (1955), p. 240.

12) S. C. Srivastava and N. Berkowitz, *Can. J. Chem.*, **41**, 1787 (1963).