A Structural Study of Complex Chromic-Ferrocyanide and -Ferricyanide by Means of Ultrasonic Waves

By Wahid U. MALIK and Jahan SINGH*

Chemical Laboratories, University of Roorkee, Roorkee, India

(Received January 11, 1966)

Sette¹⁾ has discussed and reviewed the use of ultrasonic velocities in the determination of molecular structures and the structure of liquids. Work on complex barium-citrate has been carried out by Prakash and Pandey,²⁾ and by Subrahmanyam.³⁾ These methods have, however, not been extensively employed to determine the composition and structure of coordination compounds. This is especially true for metal ferrocyanogen complexes, where, except for some preliminary studies on potassium ferrocyanide, nothing worth mentioning has so far been done. Investigations in this direction were, therefore, considered desirable.

The ultrasonic method cannot be applied to all the known metal ferro-cyanogen complexes, since most of them exist as insoluble compounds. Recently Malik,⁴,⁵⁾ during the course of his investigations into these compounds, came across a number of new ferrocyanogen complexes, like that of chromium, molybdenum, etc., which could exist in a soluble state. It was thought that some of these could be put to ultrasonic analysis and so ascertain their composition. In this communication the preliminary results on sono-metric study of chromic ferro- and ferricyanides have been reported.

Experimental

Standard solutions of chromium(III) chloride and potassium ferrocyanide and potassium ferricyanide were prepared by dissolving A. R. grade reagents in doubly-distilled water. A series of mixtures were then prepared according to Job's method⁶⁾ of continuous variation. These mixtures were allowed to stand for some time to attain equilibrium and to complete the reaction (as determined by the change in colour from light yellow to orange-red and by shifts in the absorption maximum). The velocity in each mixture was determined by the optical diffraction⁷,⁸⁾ method. An X-cut quartz crystal was suspended in a rectangular glass vessel containing the experimental mixture in such a manner that the crystal hung parallel to one side of the vessel. This crystal was then connected to a Hartley oscillator to produce ultrasonic waves. The stationary waves were formed in a liquid to give regions of compression and rarefraction, which act like a diffraction grating. The readings of the direct slit and diffraction orders were taken on the scale of the telescope. The velocity was calculated by the formula:

$$V=\frac{n\cdot f\cdot \lambda\cdot D}{x} \tag{1}$$

where f = the frequency of the Hartley oscillator for the impedance matching of crystal
n = the number of the diffraction order
λ = the wavelength of the source of light
D = the distance between the optical centre of the objective of the telescope and the scale
x = the distance between the nth order and the direct image of the slit.

The apparatus used was made by the Andhra Scientific Co., India. For this apparatus $D=100$ cm., and the least count of the scale is 0.01 cm. In our observations, $f=3$ mc./s., $\lambda=5893$ A. U. and $n=1$ (1st order). By putting these values into Eq. 1, we get:

$$V=\frac{176.79}{x}\ \text{m./sec.} \tag{2}$$

From Eq. 2 the velocity was calculated for different mixtures. These results are shown in Tables I and II.

Results and Discussion

From the graphs for Job's method it was found that the ultrasonic velocity gradually decreases, reaches a minimum, and then increases again. In graph No. 1 the minimum occurs at the point of 0.5 ratio $Cr^{3+}/(Cr^{3+}+Fe(CN)_6{}^{4-})$ at a composition

---

* Present address: Department of Physics, Regional Engineering, College Kurukshetra, India.

1) D. Setter, *Ric. Sci.*, **20**, 102 (1950).

2) S. Prakash and J. D. Pandey, *J. Phy. Chem.*, **68**, 3078 (1964).

3) S. V. Subrahmanyam and P. J. Reddy, *J. Phys. Soc. Japan*, **17**, 1061 (1962).

4) W. U. Malik, *J. Sci. Ind. Res.*, **20B**, 213 (1961).

5) W. U. Malik, *J. Ind. Chem. Soc.*, **38**, 293 (1961).

6) P. Job, *Ann. Chim.*, **9**, 113 (1928).

7) P. Debye and F. W. Sears, *Proc. Natl. Acad. Sci. U. S. A.*, **18**, 410 (1932).

8) E. C. Richardson, "Ultrasonic Physics," 2nd Ed., Elsevier Co., N. Y. (1962).

of 1 : 1. This indicates the maximum complex formation at that point. In graph 2 the minimum occurs at the point of 0.6 ratio $Cr^{3+}/(Cr^{3+}+Fe(CN)_6^{3-})$ at a composition of 3 : 2.

Had there been no interaction between the two solutions, the curve would be linear. When the complex formation is at a maximum, the ultrasonic velocity is at a minimum.

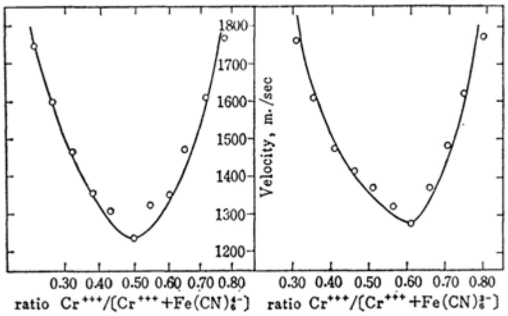

Fig. 1 Fig. 2

Graphs showing the variation of ultrasonic velocities of chromic ferrocyanide (Fig. 1) and chromic ferricyanide (Fig. 2) with different ratio of chromic (Cr^{3+}) to the complex ($Cr^{3+} + Fe(CN)_6^{4-}$ and $Cr^{3+} + Fe(CN)_6^{3-}$).

By a comparison of graphs 1 and 2, it may be seen that the velocity is more in the case of chromic-ferricyanide than in that of chromic-ferrocyanide. This difference may be attributed to the difference in the degree of hydration of chromic ferro- and ferricyanide particles, since both these compounds give colloidal precipitates. A confirmation of these results is found in the work of Malik[9] on the composition (using spectrophotometric and amperometric methods) and colloidal behaviour (sol-gel transformation) of chromic-ferro- and ferricyanides.

Tables I and II show the ultrasonic velocities of chromic-ferrocyanide and chromic-ferricyanide complexes respectively.

Table I

$0.1\,\text{M}\ CrCl_3 + 0.1\,\text{M}\ K_4Fe(CN)_6$

Total volume = 100 cc.

Sample No.	Vol. of $CrCl_3$ cc.	Vol. of $K_4Fe(CN)_6$ cc.	Ratio	x cm.	V m./s.
1	25	75	0.25	0.10	1767.9
2	30	70	0.30	0.11	1607.2
3	35	65	0.35	0.12	1473.3
4	40	60	0.40	0.13	1359.9
5	45	55	0.45	0.135	1309.6
6	50	50	0.50	0.14	1262.8
7	55	45	0.55	0.132	1339.3
8	60	40	0.60	0.13	1359.9
9	65	35	0.65	0.12	1473.3
10	70	30	0.70	0.11	1607.2
11	75	25	0.75	0.10	1767.9

Table II

$0.1\,\text{M}\ CrCl_3 + 0.1\,\text{M}\ K_3Fe(CN)_6$

Total volume = 100 cc.

Sample No.	Vol. of $CrCl_3$ cc.	Vol. of $K_3Fe(CN)_6$ cc.	Ratio	x cm.	V m./sec.
1	25	75	0.25	0.09	1964.3
2	30	70	0.30	0.10	1767.9
3	35	65	0.35	0.11	1607.2
4	40	60	0.40	0.12	1473.3
5	45	55	0.45	0.125	1414.3
6	50	50	0.50	0.13	1359.9
7	55	45	0.55	0.135	1309.5
8	60	40	0.60	0.14	1262.8
9	65	35	0.65	0.13	1359.9
10	70	30	0.70	0.12	1473.3
11	75	25	0.75	0.11	1607.2
12	80	20	0.80	0.10	1767.9

Thanks are due to the Head of the Physics Department, University of Roorkee, for allowing us to carry out some of this study in his laboratory.

---

[9] W. U. Malik, D. Sc. Thesis, Aligarh University, India (1960).