P

80-

SPECTROPHOTOMETRIC STUDY OF MERCURIC CHLORIDE-DIPHENYLCARBAZONE COMPLEX BETWEEN 4000 ° and 7000 °A

NASIM MUFTI AND NAHEED FATIMA

Department of Physics, University of Sind, Hyderabad

Because the estimation of mercury in small amounts is important[1,2] in several chemical reactions, it was considered useful to study quantitatively the absorption spectrum of mercuric chloride complexes, using the simple spectrophotometric technique. Since the simple salt ($HgCl_2$) as such is transparent in the visible region of the spectrum, it was treated as usual with one of the reagents used to render it coloured, the departure being that disphenylcarbazone was used instead of diphenylcarbazide.[1]

Consider two solutions of a given substance of thicknesses t_1 and t_2, respectively, and concentrations C_1 and C_2, respectively. If light of the same intensity is incident on each and if intensities of transmitted beams are equal, i.e.

$I_{t_1} = I_{t_2}$, then from the Lambert-Beer law,

$$I_{t_1} = I_0\ 10^{-C_1 K t_1} = I_0\ 10^{-C_2 K t_2} = I_{t_2},$$

therefore $C_1 t_1 = C_2 t_2 = 1/K \log_{10} (I_0/I_t)$.

Hence if t_2 and either C_1, t_1 or K are known, C_2 may be determined. The extinction coefficient K depends on the wavelength and on the nature of the solution, and it can be obtained from the relation :

$$C = 1/K \log (I_0/I_1) = D/K$$

where $D = \log (I_0/I_1)$ is the optical density of 1 cm. thickness of the solution.

Experimental Details

A Hilger-Nutting polarizing photometer was used in conjunction with a constant deviation spectrometer. The light source used was a Pointolight 100 candle power lamp, kept in a housing, cooled by ventilators and cooling fins. The light from the source after being divided by the double system of glass rohmbs passes through two optically identical cells, one of which contains the test solution and the other the blank. Finally before entering the spectroscope (which allows light of the wavelength set on the drum to pass through the eyepieces) the two beams in juxtaposition pass through another Nicol, which can be rotated by a remote control so as simultaneously to increase the intensity of light in one beam and to reduce that in the other. The intensities of the two spectra are made equal by rotating the plate holding the Nicol prism, which acts as photometer, and the optical density for the particular wavelength set on the drum is then read directly from the scale. To map the whole spectrum in the visible region, this procedure was repeated generally at 10 millimicrons intervals with smaller 5 millimicrons intervals near the absorption maxima.

The solutions were prepared in ethyl alcohol, which was 99.9% pure, and were standardized by usual methods. The solutions were prepared in Pyrex B Class measuring flasks corrected for temperature, and it was observed that they remained quite stable for nearly two hours. In this appreciable period of stability, the whole absorption spectrum was scanned on the Hilger-Nutting spectrophotometer, special care being taken to avoid any impurity in the solution or specks of dirt sticking to the windows of absorption cell. All the vessels were placed in soap solution for nearly twelve hours, and then washed with chromic acid, distilled water, and finally several times with ethyl alcohol. Immediately before use, the cells were rinsed many times with the solutions to be placed in them.

Results and Discussion

The absorption curves of the test solution at various concentrations are drawn in Fig. 1, in which the optical density is taken along the ordinate and the abscissae represent the wavelengths in millimicrons. The molar extinction coefficients for λ_{max} have been calculated both with and without correction for background, and are indicated in Table 1.

From the curves and the table, one can conclude that the departure from Beer's law, when the

TABLE 1.—EXTINCTION COEFFICIENTS.

Concentration	$\frac{M}{500}$	$\frac{M}{750}$	$\frac{M}{1000}$	$\frac{M}{1250}$	$\frac{M}{1500}$	$\frac{M}{2000}$
Molar extinction coefficient at λ_{max} (570 ± 15mμ)/Without correction ..	348	339	309	284	302	260
With correction	225	240	235	250	260	250

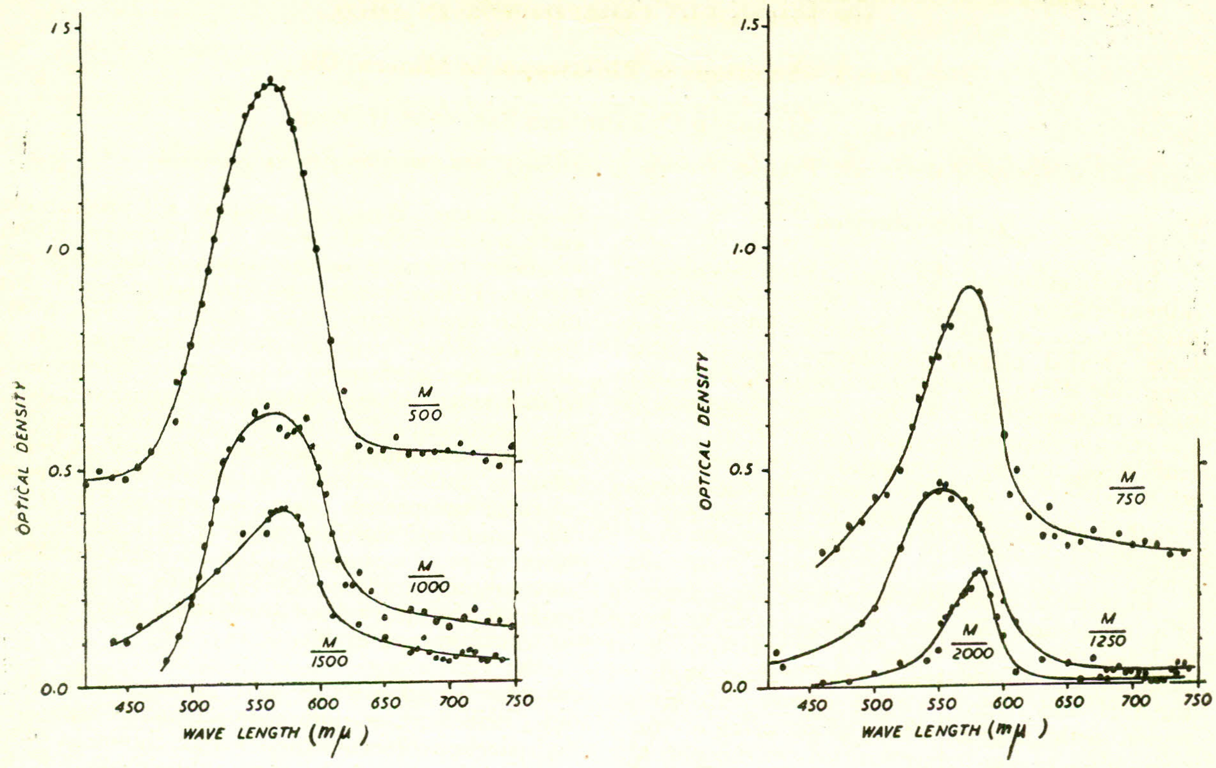

Fig. 1.—Absorption curves for different concentrations of mercuric chloride-diphenylcarbazone complex.

correction for background is made, is not very significant, and it can be seen that the optical density is proportional to the concentration to within ±5% upto as high a concentration as M/500. The absorption maxima at different concentrations lie pretty well over each other, although there is a noticeable shift towards greater wavelengths as the concentration is decreased. As should be expected, the half width of the absorption band is approximately independent of concentration, but with decreasing concentration a splitting of the primary maximum into two is suspected, perhaps indicating independent absorption by two states of the complex.

Since the accuracy of the results depends not only on the limits of the apparatus, but mostly on the observer himself, the data is expected to be accurate only to about 5%, and further work to investigate this complex will be taken in hand in the near future.

Acknowledgements

The authors wish to acknowledge the help extended to them by Dr. M.A. Kazi, Chairman, Department of Chemistry, University of Sind, and to thank Mr. Nasim Naqvi of the Chemistry Department for his valuable suggestions from time to time.

References

1. J. Cholak and D.M. Hubbard, Ind. Eng. Chem., Anal. Ed., **18**, 149 (1946).
2. F.W. Laird and A. Smith, ibid., **10**, 576 (1938).