Spectrophotometric Studies on V(iv)-I,8Dihydroxy Naphthalene 3:6 Disulphonic Acid (D. N. S.) Chelate

By S. M. Fazlur Rehman and Aneesuddin Malik

With 4 Figures

Summary

1,8-Dihydroxy naphthalene 3:6 di sulphonic acid is known to form coloured complexes with a number of metal ions. A few of the references worth mentioning are those on Ti(iv)[1], Fe(iii)[2], Cu(ii)[3], Cr(vi)[4], Uo_2^{++}[5] etc. The formation of a brown coloured product by the interaction of vanadium with the reagent has also been mentioned by some authors[6] but details about its behaviour and composition are lacking. It was, therefore, thought worthwhile to determine spectrophotometrically the composition of a vanadyl complex which in our case was pink in colour.

Vanadyl sulphate $VOSO_4$ $2 H_2O$ (Riedel, extra pure) was used for the experiments. It was estimated[7] by reducing the vanadyl sulphate solution through a Jone reductor where it got converted into the bivalent state, the latter was taken in excess of an acidified solution of A. R. iron alum and the ferrous iron thus formed was titrated against standard $KMnO_4$ solution. Chromotropic acid (Na salt) (E. Merck) was dissolved in double distilled water and kept in amber coloured bottles.

Preliminary experiments showed that the reaction between vanadyl sulphate and DNS was a slow one. In the case of fairly concentrated solutions $(2.5 \cdot 10^{-3}$ M to $1 \cdot 10^{-3}$ M) it took about six hours for completion while with dilute solutions $(1 \cdot 10^{-3}$ M to $2 \cdot 10^{-4}$ M) the time interval was more than

[1] A. Okac and L. Sommer, Z. analyt. Chem. 143, 52 (1954).

[2] J. Heller and G. Schwarzenbach, Helv. chim. Acta 34, 1876 (1951).

[3] Calvin and Martell, "Chemistry of the metal Chelate Compounds" Prantice Hall; New York. p. 503 (1952).

[4] F. Garret, J. Ind. Engng. Chem. 5, 298 (1913).

[5] A. K. Dey and A. K. Mukerji, J. Ind. chem. Soc. 35, 113 (1958).

[6] E. B. Sandell, "Colour Detn of Traces of Metals", Interscience Publications III Edition 1959 page 3988.

[7] A. I. Vogel, "Quantitative Inorganic Analysis", Longmans, Green & Co., II Edition 1955, page 319.

twelve hours. Equimolar solutions $(2.5 \cdot 10^{-3}\,M)$ of vanadyl sulphate and DNS were mixed in the ratios of $2:8$, $3:7$, $4:6$, $5:5$, $6:4$ etc. and were kept for about six hours to ensure complete reaction; their optical densities in
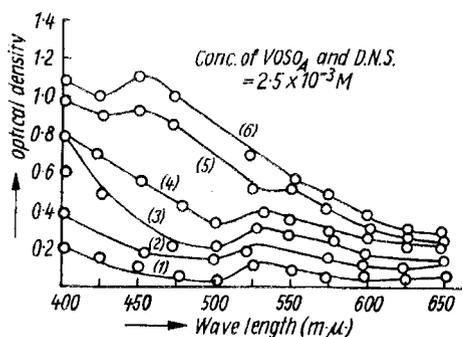

Fig. 1. Reactants mixed in the ratios of: —
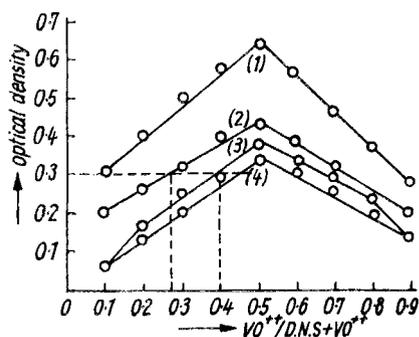(1) $2:8$; (2) $3:7$; (3) $4:6$; (4) $5:5$; (5) $6:4$; (6) $7:3$

Fig. 2. Conc. of the reactants: —
(1) $2.5 \cdot 10^{-3}\,M$; (2) $2.0 \cdot 10^{-3}\,M$;
(3) $1.66 \cdot 10^{-3}\,M$; (4) $1.25 \cdot 10^{-3}\,M$

1 Cm Corex cells were measured at different wave lengths ($400\,m\mu$ to $600\,m\mu$) with a BECKMAN DU Spectrometer (tungston lamp as the source of light). The maximum absorption for all mixtures was found at $525\,m\mu$, indicating the formation of only one complex[8]).
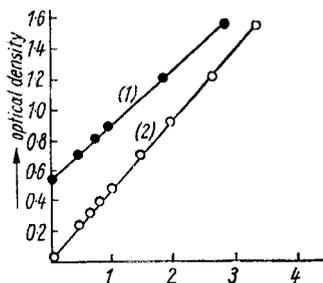

Fig. 3. (1) Conc. of D. N. S. $=$
$2 \cdot 10^{-3}\,M$ and strength of $VOSO_4$
added in cc's. $= 5 \cdot 10^{-3}\,M$; (2)
Conc. of $VOSO_4 = 2 \cdot 10^{-3}\,M$ and
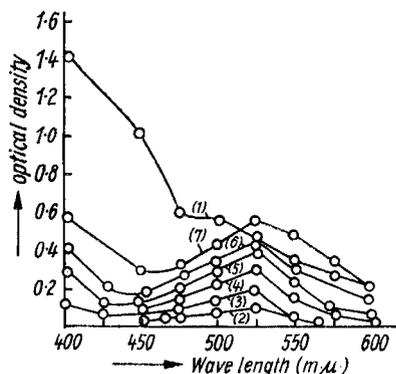strength of D. N. S. added in
cc's. $= 5 \cdot 10^{-3}\,M$

Fig. 4. Total conc. of the complex $=$
$1.0 \cdot 10^{-3}\,M$. (1) pH $= 5.0$; (2) pH $= 5.6$;
(3) pH $= 7.1$; (4) pH $= 8.3$; (5) pH $= 9.1$;
(6) pH $= 9.8$; (7) pH $= 11.0$

The composition of the complex was determined by JOB's[9]) method of continuous variation and the slope ratio method[10]). For the method of

8) W. C. VOSBURGH and G. R. COOPER, J. Amer. chem. Soc. 63, 437 (1941).

9) P. JOB, Ann. Chim. 9, (10), 113 (1928).

10) E. HARVEY and D. L. MANNING, J. Amer. chem. Soc. 72, 4488 (1950).

continuous variation, three sets of mixtures of equimolecular concentration $(2.5 \cdot 10^{-3}$ M, $1.66 \cdot 10^{-3}$ M and $1.25 \cdot 10^{-3}$ M) were prepared and O.D. was determined a 525 mμ. Since the absorption of vanadyl sulphate and DNS were negligible at this wave length the O.D. of the mixtures were plotted against the ratio $\dfrac{VO^{++}}{VO^{++} + DNS}$ (Fig. 2). In the case of slope ratio method, the concentration of DNS $(2 \cdot 10^{-3}$ M) was kept constant and the concentration of vanadyl sulphate varied $(2 \cdot 10^{-4}$ M to $2.5 \cdot 10^{-3}$ M) in one set while in the other the concentration of DNS $(2 \cdot 10^{-4}$ M to $2.5 \cdot 10^{-3}$ M), keeping the concentration of VO^{++} $(2 \cdot 10^{-3}$ M) constant. The slopes over the strauight line portion of the curces were used for determining the combining ratio (Fig. 3).

The influence of pH on the formation of the complex was investigated by using equimolar solutions $(1.0 \cdot 10^{-2}$ M) of the reactants in the ratio of 1:1 and then diluting them ten times by the buffers[11]) (Walpole acetate buffers pH 4 to 6,5, $Na_2HPO_4 - NaH_2PO_4$ for pH 6.5 to 9.0 and $Na_2HPO_4 - NaOH$ for pH 9.5 to 12.0) prepared from A. R. products. Mixtures in the pH range 4 to 11.0 were thus obtained. The absorbances of these solutions were noted, max at $= 525$ mμ only was realised in the pH range 6.7 to 11.0.

Discussion

The combining ratio as indicated by Job's and the slope ratio method was 1:1, the composition of the complex could therefore, be depicted as $VO^{++}(DNS)$ and its structure as
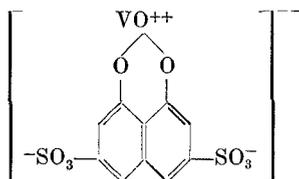
The complex was stable in the pH range of 6.7 to 11.0.

If two concentrations $(a_1 + b_1)$ and $(a_2 + b_2)$ have the same O.D. (that is the same value of x, the concentration of the complex) then the equilibrium constant is given by the expression[12]).

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)}$$

or

$$x = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1) - (a_2 + b_2)}.$$

[11]) H. T. S. Britton, "Hydrogen Ion", page 223 Chapman & Hall, I Edn.
[12]) A. K. Mukerji and A. K. Dey, Proc. Nat. Acad. Sci., India 26, 20 (1957).

For two mixtures having the same optical density (0.30) the value of x was found to be $4 \cdot 10^{-4}$ M. From this, the value of formation constant was found to be $3.99 \cdot 10^3$ and the free energy of the reaction came out to be $-\Delta F = 2.67$ K Cals at 20 °C.

Aligarh, (India), Department of Chemistry, Aligarh Muslim University.