A NEW TECHNIQUE FOR RUBIN NUMBERS

By K. S. G. Doss, F.A.Sc., and A. Kalyanasundaram

(*Indian Institute of Sugar Technology, Kanpur*)

Received August 16, 1950

Introduction

'Gold Number' originated by Zsigmondy[1] gives a measure of the protective action of a hydrophilic colloid. In view of the difficulties in the preparation of the Zsigmondy red gold sol and also the elaborate methods of standardisation necessary with other gold sols, Ostwald's[2] 'Rubin Numbers' can be used with advantage in the place of gold number. Subramhanya and others[3] have studied in detail the technique of rubin numbers and have found that a pH of 5·1 to 5·3 gives best results. Though their technique employing the pH colorimeter is a distinct improvement over the original procedure of Ostwald with regard to precision, careful study of the method has revealed certain defects. The new technique presented in this paper has been developed by overcoming these defects.

Experimental

1. *Materials used.*—(i) Congo rubin: congo rubin of purity 99·5% is obtained by purifying the Kahlbaum product by the method employed by Doss[4] for benzopurpurin 10B. The purity has been determined by finding out the percentage of sulphated ash.

(ii) The buffer solution of pH 5·1 is prepared[5] from sodium acetate and acetic acid, the pH being determined by the quinhydrone electrode.

(iii) Starch and albumin are pure products of Kahlbaum and Merck respectively.

(iv) Casein: The Kahlbaum product is dissolved in 0·1 N NaOH and the solution made up after exactly neutralising the alkali with acid.

2. *Procedure.*—5 c.c. of 0·004% aqueous solution of congo rubin is mixed with 0·5 c.c. of the buffer of pH 5·1 and the required quantity of the protective colloid. The mixture is made up to 10 c.c. with water and allowed to stand for 3 minutes. 1 c.c. of 10% sodium chloride in water is then added and the mixture heated to a temperature of 60° C. for 10 minutes and cooled to room temperature. The solution is then centrifuged to remove the blue dye in suspension and the red colour of the centrifugate is measured by the

Lovibond Tintometer, using a 0·6″ cell. In actual practice, double the quantities have been used for the determination.

The results are given in Tables I, II, III and IV and Figs. 1, 2 and 3. The method of calculating the rubin numbers from the above data is discussed in the next section.

TABLE I. *Casein*

Mg. of casein in 10 c.c. of solution	Colour of centrifugate : Red in Lovibond units
0·0	2·9
0·2	3·7
0·3	4·4
0·4	5·1
0·5	6·2
0·6	6·7
0·7	7·5
0·8	8·6
1·0	12·8
2·0	13·4
2·5	14·0
3·0	14·3
Colloid and no salt	15·0

TABLE II. *Albumin*

Mg. of albumin in 10 c.c. of solution	Colour of centrifugate : Red in Lovibond units
0·0	2·9
0·5	3·1
1·0	3·7
1·5	5·6
2·0	8·9
2·5	9·4
3·0	9·6
4·0	9·8
Colloid and no salt	9·8

TABLE III. *Starch*

Mg. of starch in 10 c.c. of solution	Colour of centrifugate : Red in Lovibond units
0	2·9
5	3·4
20	4·8
30	5·2
40	5·7
50	7·2
70	8·0
90	8·9
100	9·7
140	12·0
Colloid and no salt	15·0

TABLE IV

Colloid	Rubin Nnmber by the new method	Rubin Number Subramhanya, Doss & Rao	Gold Number[7]
Starch ..	91	31	25
Casein ..	0·82	0·66	0·01
Albumiu ..	2·1	2·5	0·09

of the protective colloid the colour is X units and with infinite concentration the colour should be Y units, then the rubin number can be defined as the number of milligrams of colloid necessary for obtaining a residual colour of $\frac{X+Y}{2}$ units, *i.e.*, $\frac{2{\cdot}9+15{\cdot}0}{2}$ or 9·0 units. The rubin number for starch on this basis works out to be 91. It can be seen from Fig. 1, that the curve rises more or less linearly with the concentration of starch.

The rubin number of casein worked out on the above basis is 0·82. It is interesting to note that the curve in Fig. 2 rises steeply at the region corresponding to 9 units which incidentally enables an accurate determination of the rubin number.

The rubin number for albumin, corresponding to 9 tintometric units of red colour in the centrifugate comes out to be 2·1. In this case however, there is a complication arising from denaturation of albumin, in spite of the care taken not to allow the temperature of the solution to go above 50° C. The residue on centrifuging is not pure blue as in the other cases but has a reddish tinge, its intensity depending upon the amount of the albumin used. With larger amounts of albumin, the precipitate settled in the centrifuge tubes is red in colour. (It may be pointed out that with large amounts of other protective colloids there would be no sediment on centrifuging.) Owing to this, the maximum residual colour obtained with albumin is only 9·8 units, as compared with the theoretical 15·0 units.

An examination of Table IV shows that the rubin numbers determined as herein described show the same trend as those obtained by the earlier methods.

4. *Mechanism of interaction between the hydrophilic colloids and rubin.*— The interaction equilibrium between the protective colloid P and rubin R may be provisionally formulated as follows:—

$$P + nR \rightleftharpoons PR_n.$$

Applying Law of Mass Action (using concentrations instead of activities) we get

$$\frac{[PR_n]}{[P]\,[R]^n} = k_1.$$

Since solid rubin would be present at equilibrium one can put [R] constant,

$$\therefore \quad [PR_n] = k_2[P]$$

Thus the amount of solubilisation of rubin brought about by the hydrophilic colloid would be proportional to the concentration of the free protective colloid. But since only a small fraction of the latter would be present as complex the solubilisation would be proportional to the total concentration of the protective colloid. Thus the intensity of red colour in the centrifugate would be a rectilinear function of the concentration of the colloid. This explains very well the behaviour of starch as seen from Fig. 1. A departure from linearity can, however, be expected at very high concentrations of starch, at which the solubilisation may be very high and the solid rubin phase may disappear.

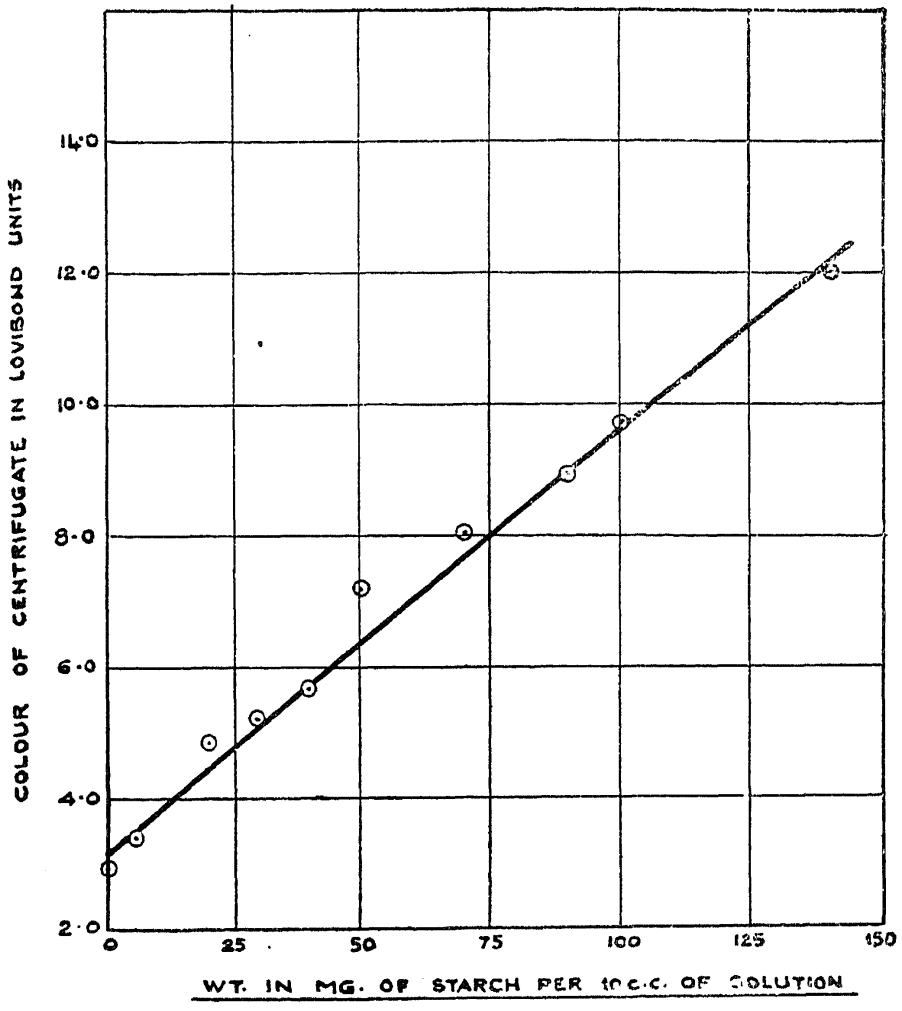

FIG. 1. Starch

With casein and albumin, however, it is seen that the curve is of S shape (Figs. 2 and 3). But, the above simple formulation ignores the effects due to factors such as electric charge and micelle formation. It is a matter of great interest from the point of view of the mechanism of interaction between hydrophilic colloids and the dye to investigate the cause of the great dissimilarity in the curves obtained with the different protective colloids.

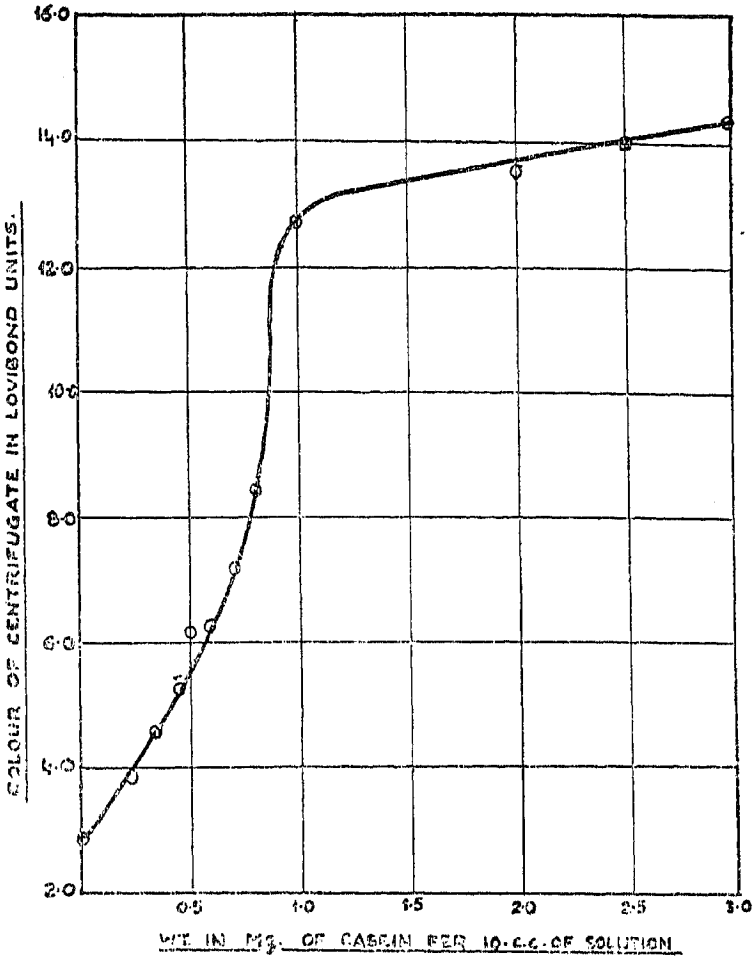

FIG. 2. Casein

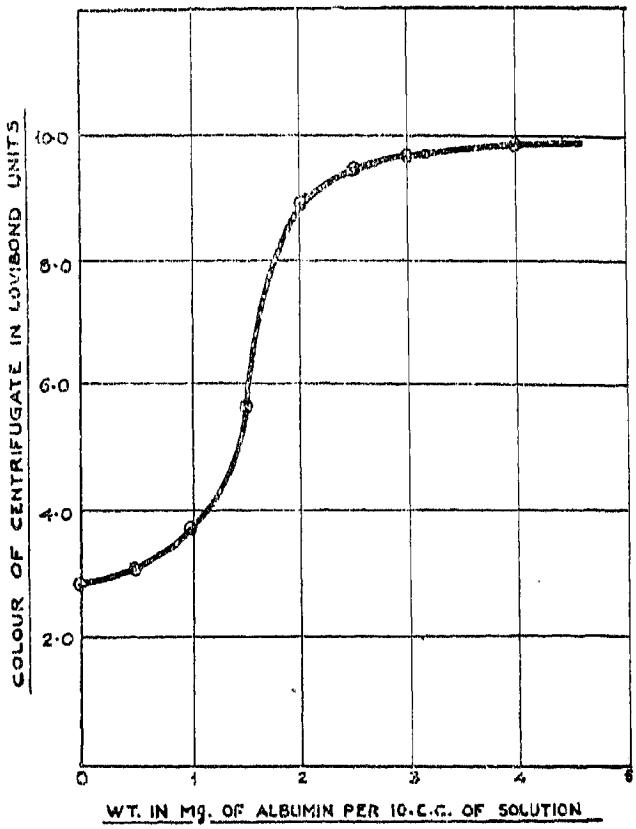

FIG. 3. Albumin

The authors wish to thank Prof. J. M. Saha, Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest.

Summary

A new method for the determination of rubin numbers has been advanced. The previous method based on the measurement of the blue colour was discarded as the blue dye was found to be in suspension. The rubin number of a protective colloid is defined as the number of milligrams of that colloid which when present in 10 c.c. of 0·002% congo rubin solution of pH 5·1 produces 9·0 Lovibond units of red colour in a 0·6″ cell on addition of 1 c.c. of 10% sodium chloride and centrifuging. The results obtained by this method in the case of starch, casein and albumin show the same trend as the results of the earlier methods.

References

1. Zsigmondy .. *Anal. Chem.*, 1901, **40**, 698.
2. Ostwald .. *Kolloid Chem. Beihefte*, 1919, **10**, 234.
3. Subramhanya, Doss and Rao .. *Proc. Ind. Acad. Sci.*, 1947, **24**, 197.
4. Doss .. *Kolloid Z.*, 1938, **84**, 138.
5. Clark .. *Determination of Hydrogen Ions*, p. 21.
6. Ostwald .. *Kolloid Beihefte*, 1919, **10**, 179.
7. Holmes .. *Introductory Colloid Chemistry*, 1934, p. 45.