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Polargroaphic Estimation of Gum Arabic

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A polarographic method for the estimation of gum arabic has been presented. The gum appears to form a complex with the supporting electrolyte. This complex suffers reduction at the Hg-dropping cathode, the number of electrons involved in the process being unity.

In course of our investigations on solutions of gum arabic, it was felt that a quick and convenient method should be worked out for the rapid routine estimation of gums. The conventional method till now is principally a chemical one in which it would be necessary to separate the gum from solution, either by evaporation of the solution to dryness very carefully, avoiding charring of the gum, or by precipitation of the gum by addition of sufficient quantity of ethanol, by desiccation of the precipitated gum in vacuum, and then estimating the elements present in a definite amount of the precipitated gum. The process is not only tedious but also inconvenient for a quick result which is so often necessary.

In order to devise some quick physico-chemical method for routine work, various properties, such as, specific rotation, refractive index, etc. of the gum were looked into. Determination of optical rotation of the gum was found possible in dilute solutions only (0.1% or less), but the angle of rotation was observed to differ very little from that of water. With concentrated solutions the transmission of light was seriously affected by scattering, etc. and the field became too dark for any reliable result. Refractometric estimation was more successful and refractive indices exhibited linear variations within narrow ranges of concentrations, but the line of separation produced by total internal reflection being not quite sharp, the method was far from satisfactory (*vide infra*).

Potentiometric and conductometric titrations were tried by electrodialysis of the gum or by treatment of the gum with HCl and subsequent dialysis; the total acidity for the acid was found different with different bases[1]. This presented peculiar difficulties in the way of choosing which of these results would present the true concentration. Moreover, these methods are time-consuming.

The difficulties enumerated above ultimately led us to apply the polarographic method in this case. In the present investigation, it has been our object to study the polarographic waves of gum solutions, using different supporting electrolytes like the chlorides, nitrates, sulphates, etc. of sodium, potassium, lithium, and barium.

Gum arabic is known to be composed of (—)-arabinose, (+)-galactose, (—)-rhamnose, and (+)-glycuronic acid. The (+)-glycuronic acid residue confers acidic character to the

1. Mukherjee and Ghosh, this *Journal*, 1949, 26, 81.

macromolecules. Moderately concentrated solutions show *p*H between 2.2 and 2.7. Polarographic studies of these constituents have been reported in the literature. (—)-Arabinose and (+)-galactose in phosphate buffer (*p*H 7) show half-wave potentials of −1.58 V and 1.59 V respectively[2]. (—)-Rhamnose is a ketose. It has been identified polarographically, using 0.2 *M*-$CaCl_2$ as a supporting electrolyte. Studies on (+)-glycuronic acid have been made by Ishidate and Shimozawa[3], but the polarographic study of the whole gum has not been reported so far.

EXPERIMENTAL

Gum arabic samples used in these experiments were of Stafford Allen & Sons' pure quality. This was purified by repeated (thrice) precipitation with dry ethanol and its removal with dry ether. The sample thus prepared was next exposed to air at room temperature (about 30°) to remove ether.

Polarographs of this purified samples of the gum were taken at concentrations of 0.5, 1,2, and 3% of the gum in aqueous solutions. Supporting electrolytes were taken at a concentration of 0.1 *M* (final conc.) with 0.07% dextrin[4] as a suppressor. Reagents used were all of G.R. quality of E. Merck.

The instrument was the Cambridge pen-writing polarograph. Sensitivity of the apparatus was adjusted to read 3 in the third place of decimals for the half-wave potential and 13.3 mm and 26.6 mm for 1 μA for the diffusion currents. Drop time was 3.5 secs. approximately. The mass value per unit time was 2.55 mg./sec.

The same solutions were used for refractometric and polarimetric measurements. Refractometric measurements could not, however, be carried out with an ordinary Abbe refractometer as the differences were too small to be confidently relied upon. So these measurements were conducted in a differential refractometer (Phoenix type) in the blue light 4369Å of the Hg-spectrum.

DISCUSSION

Polarograms of the gum at different concentrations appear in Fig. 1. The graphs refer to 0.1 *M*-$BaCl_2$ as the supporting electrolyte. Only one specimen with $BaCl_2$ has been graphically presented.

Curves obtained with other electrolytes, viz., (0.1 *M*) KCl, NaCl, LiCl, KNO_3, K_2SO_4, are exactly similar in shape, appearance, and half-wave potentials.

The value of $E_{\frac{1}{2}}$ against saturated calomel electrode was observed to be −1.50 volts. The values of i_d were found to be proportional to the concentration in each case; passing

2. Carpenter and Kodicek, *Biochem. J.*, 1948, **43**, 11.
3. *J. Pharm. Soc. Japan*, 1944, **64**, 53; *Chem. Abst.*, 1951, **45**, 3293.
4. Wawzonek, *Anal. Chem.*, 1958, **30**, 661.

through the origin on extrapolation. The i_d values could not, however, be calculated from Ilkovic's equation:

$$i_d = 607\, nD^{\frac{1}{2}}\, m^{2/3}\, b^{1/6}\, C$$

primarily because of the uncertainty of the value of D and n.

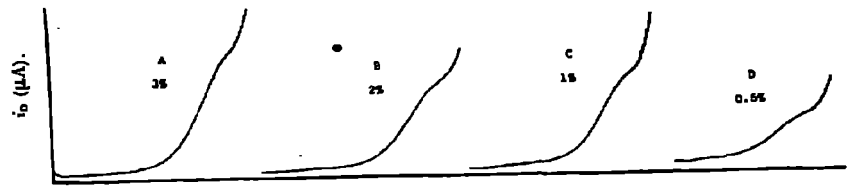

FIG. 1

(a) Curves A, B, C, and D represent 3.0, 2.0, 1.0, and 0.5% of gum respectively.
(b) Starting potential in all case equals — 1.0 volt excepting curve D where the starting potential is — 1.1 volt.
(c) 10 div. on the X-axis represent 0.1 volt.
(d) For curves A and B 13.3 mm represents 1 μA and for C and D, 26.6 mm represents 1μA.

An attempt to calculate the value of n has been made in the light of the following considerations. The gum is known to be the K, Mg, and Ca-salt of a complex acid usually termed the arabic acid (according to the name of the gum from which it is derived). The principal ion of the gum is therefore anionic in character with a negative charge. That anions had little effect was confirmed by changing the anions which produced almost no effect on $E_{\frac{1}{2}}$ of the wave with the same cation. The values of the valency number (n) was calculated from any point on the wave where the current was i by the help of the equation:

$$E = E_{\frac{1}{2}} - \frac{0.0591}{n} \log \frac{i}{i_d - i}$$

where E and i are the potential and the current at any point and $E_{\frac{1}{2}}$ and i_d, the half-wave potential and the diffusion current of the wave[5]. The value of n was calculated to be near about 0.74 from the slope of the above equation. The valency number, n, thus approximates to unity.

With electrolytes (like KCl, KNO_3, NaCl, LiCl, etc.) the value of i_d for the same concentration of the gum was almost constant, but it varied slightly with $BaCl_2$ and K_2SO_4. Results are shown in Table I, where slightly higher values of i_d have been observed.

TABLE I

Temp. = 35°. Conc. of electrolyte = 0.1 M.

Conc. of gum.	Average diffusion current (in μA) with					
	KCl.	NaCl.	LiCl.	$BaCl_2$	KNO_3.	K_2SO_4.
0.5%	0.403	0.403	0.413	0.488	0.413	0.488
1.0	0.815	0.806	0.854	1.013	0.825	1.013
2.0	1.575	1.575	1.650	2.016	1.575	2.200
3.0	2.326	2.326	2.400	2.850	2.362	3.375

5. Meites, "Polarographic Techniqne", Interscience Publishers, p. 104.

The average value of i_d was calculated from three determinations in each case. The relationship obviously appears to be linear with concentration.

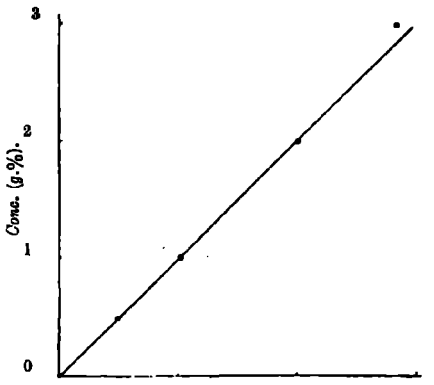

FIG. 2

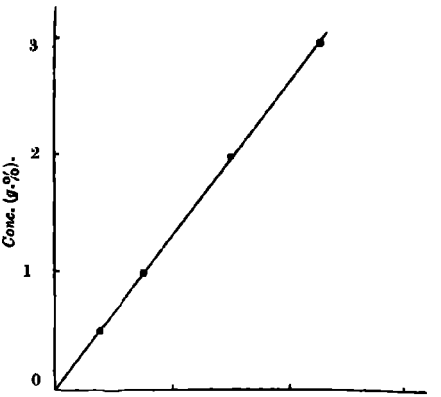

FIG. 3

This evidently shows that if we can determine the value of i_d for a unit concentration of the gum, which we shall term the specific i_d-value when the concentration is exactly 1%, we can, by the help of this, estimate the concentration of a specimen of unknown concentration from its i_d value. It is worthwhile to point out in this connection that more dilute solutions of gum than 0.25% do not produce good polarographic waves, calculation of i_d from which does not appear to be sufficiently warranted. The method therefore appears to hold for comparatively concentrated solutions.

This work is but a preliminary one. Other gums and other electrolytes with various concentrations are being tested, results of which will appear later.

Results of refractometric measurements appear in Fig. 3. The graph is obviously linear, but although the variations of refractive indices occur in the third place of decimals (Table II), these cannot be reliably determined in ordinary Abbe refractometers due to the boundary line between the dark and the bright fields being blurred. Results relate to the differential refractometer referred to above.

TABLE II

Temp. = 30°.

Conc. (%)	0.5	1.0	2.0	3.0
Ref. index	1.332421	1.333159	1.334615	1.336176

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