

STUDIES ON GUM JEOL (*LANNEA GRANDIS*, SUPER). PART V.
DEPENDENCE OF VISCOUS AND ELECTROCHEMICAL
PROPERTIES OF THE AQUEOUS SOLUTION
ON ITS CONCENTRATION

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Variation of physical and electrochemical properties with concentration of gum solution has been studied. Curves showing such variations with concentration all show breaks, but the regions in which these breaks appear are not identical in all cases. Gum particles can be thrown out of solution by centrifuging at a moderate speed (4000–6000 r. p. m.). These particles also have the property of taking up hydrogen ions from HCl solution, and increase its p_H when added in increasing proportions.

Gum jeol has been shown to be a mixture of Ca, Mg and K salts of a carboxylic acid to which quite a large number of sugar molecules, principally *l*-arabinose and *d*-galactose, remain attached. These sugar molecules become liberated when the gum is hydrolysed in different stages on treatment with acids (*cf.* Parts I-III of this series, this *Journal*, 1948, 25, 59, 63, 113).

Although no work on this particular gum as to its physical and electrochemical properties is recorded in the literature, previous work done on gum arabic solution presents conflicting views regarding the fundamental nature of the aqueous solution itself. One group of workers (Thomas and Murray, *J. Phys. Chem.*, 1928, 32, 677; Taft and Malm, *ibid.*, 1931, 35, 874) has inferred from their observations that these systems behave exactly as true electrolytes in aqueous solutions (*cf.* also Hammersten, *Biochem. Z.*, 1924, 144, 383). Other workers have, however, regarded this as colloidal solution having considerable electrolytic conductance (Hatschek, "Physics and Chemistry of Colloids", 1927, p. 24; Freundlich, "Colloid and Capillary Chemistry", 1922, p. 596). Kruyt and Tendeloo (*Kol.-Chem. Beih.*, 1929, 29, 396) have emphasised the lyophilic character of gum arabic from their study on the viscosity of aqueous solutions of gum arabic.

Workers belonging to the latter group are again divided amongst themselves into two sections in point of application of the classical or modern concepts of electrochemistry. Some of these hold that all the facts observed so far can be explained on the basis of Arrhenius's theory of partial dissociation (Briggs, *J. Phys. Chem.*, 1934, 38, 83; McBain, *J. Amer. Chem. Soc.*, 1928, 50, 1636; Linderström-Lang, *Compt. rend. Trav. lab. Carlsberg*, 1926, 16, No. 16). The opposite section relies upon the Debye-Hückel theory of interionic attraction for explanation of the observed facts (van Rysselberghe, *J. Phys. Chem.*, 1934, 38, 645; Pauli *et al.*, *Kolloid Z.*, 1933, 62, 162; 1937, 79, 63; "Electrochemie der Kolloide," 1929). Some again (Pauli and Valko, *loc. cit.*) are of opinion that the modern theory of interionic attraction together with the assumption of a suitable association factor would be sufficient for explaining the observed facts,

The object of the present investigation is to reopen the same question in the case of gum jeol. The first point of attack has been the question as to how the physical and electrochemical properties of the aqueous solution of this gum change with progressive dilution of the system. The scope of this study extends to the examination of the variation of hydrogen ion activity, equivalent conductance, cataphoretic velocity, relative viscosity and turbidity at different dilutions.

EXPERIMENTAL

Preparation of the Solution.—The gum samples used in this investigation were all procured directly from plants and therefore contained impurities in the form of bark and leaves of the plant, dust, etc. The gum was therefore dissolved by keeping in contact with water for about 6 to 10 hours. As decantation and/or filtration was not possible, the impurities were removed by centrifuging at a rate of 6000 r. p. m. for about 10 minutes after filtering it once through a single-fold linen. Higher speed or longer time was carefully avoided as both of these separated the dissolved gum from the solvent leaving only a dilute solution in the tube. This fact strongly suggests that the gum actually does not dissolve in water to form a true solution but only a colloidal solution (or rather a mere suspension) is formed from which it is possible to separate the gum by centrifuging at a moderate speed. The suspended impurities settling at the bottom were removed by decantation. The supernatant solution was found to contain suspended matter of finer size still. The solution, so obtained, was then treated with rectified spirit (3 volumes of the spirit to 1 volume of the solution). The gum precipitated out as a white flocculent mass and it was separated from the solution by centrifuging the mass once again at the above speed for about 10 minutes. The solid gum thus obtained was lighter in colour than the crude sample. This was again dissolved in water, precipitated by alcohol and centrifuged when a purer stuff was obtained. The process was sometimes repeated even thrice when the pure specimen of gum became almost a white mass free from insoluble impurities. In the final stage, before preparation of the experimental solution, the alcohol was driven out from the solid mass by drying in air and finally *in vacuo*. The solution was then prepared by dissolving a weighed amount of the substance in water.

The colourless solution of the gum, so obtained, was then preserved under a thin layer of toluene in a Jena glass bottle, previously cleaned and sterilised by steaming. Purity of the specimen was examined by testing for sulphates (by BaCl_2), phosphate (by Am. molybdate) and nitrogen (by Kjeldahl's method), all of which were found absent.

Methods of Measurements.—Measurements were all carried out at the room temperature (30°). Each datum is the mean of at least two determinations. All the chemicals used in this connection were of Merck's reagent or B. D. H. 'Analar' quality.

Potentiometric measurements were carried out in a (L. & N.) K-type potentiometer matched with a R-type galvanometer together with a certified Weston standard cell. In measuring hydrogen-ion activity both Pt- H_2 and quinhydrone electrodes were used according to convenience together with a saturated calomel half-element (potential

0.237 volt at 35°). Hydrogen gas was generated in the pure state by electrolysis of a 15% solution of NaOH between two nickel electrodes. Special precautions were taken with regard to the platinised platinum electrode (cf. Mukherjee and co-workers, *J. Agric. Sci.*, 1936, **6**, 517) which was replatinised every alternate day. A clean, bright, stout Pt wire was used for measurements with quinhydrone which was usually accomplished in 5 minutes' time after mixing the quinhydrone with the solution. No special measures were taken to eliminate the liquid junction potential except using a saturated KCl bridge.

Conductance was measured in a Leeds-Northrup bridge. The specific conductance of water used was as much as 1.6×10^{-6} mhos at 35° with an induction coil giving a frequency of about 500 cycles per sec.

Cataphoretic speeds were measured by the microscopic method. The apparatus and the principle of measurement have been the same as described by Mukherjee and Sarkar (*J. Indian Chem. Soc.*, 1947, **24**, 67). The current passing through the cell was 0.002 to 0.02 amp at 220 volts. The dimension of the cell used was 8.0 cm. long, 0.95 cm. broad and 0.088 cm. thick. Readings were always taken at 0.21 cm. depth from the top. The optical arrangement was a Zeiss microscope with a 28X ocular fitted with a micrometer scale and a 20X achromatic objective. The distance between the ocular and objective was fixed. Normally the particles were not visible or visible with difficulty. But when they moved in a potential field their movement could be followed with lesser difficulty with a little practice.

Relative viscosity was measured in an Ostwald viscometer, the time of flow of water through which was 60 seconds. Time of flow was noted up to $\frac{1}{10}$ th of a second.

Turbidity (relative) was measured in the Stufu colorimeter illuminated by a Nitralamp and fitted with the nephelometric outfit. Solutions were taken in cells having stratum thickness of exactly 1 cm. Relative turbidity was determined by comparison with turbidity disc No. 1.

Reproducibility of Measurement.—In the present investigation it was necessary to prepare a number of different gum solutions since the same solution (once prepared) could not be kept for sufficient length of time. Hence arises the necessity of checking the reproducibility of the different specimens prepared by purification of the gum on different occasions so far as the properties studied herein are concerned. Results appear in Table I.

TABLE I

*Conc. of soln.	η_{sp}	Sp. conduc. $\times 10^4$.	c. v. $\times 10^5$.	Relative viscosity.	Turbidity
2.446%	4.57	7.595 mho	10.52	3.720	50.5
	4.55	7.986	9.87	3.800	51.0
	4.57	7.856	9.90	3.770	51.2
2.936%	4.72	7.680	11.51	3.869	52.3
	4.68	7.840	10.23	3.758	50.7
	4.75	7.755	10.95	3.801	52.0

* Conc. has been expressed in percentage which signifies the no. of g. of the substance in 100 c. c. of the solution.

For approximately equal concentrations the data appear to be reproducible within the limits of experimental error. Repetitions of the same measurement in the same solution are also reproducible as will be evident from the concordance of the three figures in each column.

The influence of the effect of mechanical treatment on some of the physical properties was also examined. For this reason the solution was vigorously stirred in a mechanical shaker for more than an hour and the properties were measured before and after shaking. Results are shown in Table II.

TABLE II

Mechanical treatment.

Conc. of the soln. = 2.446%. Temp. = 35° ± 0.1.

Properties studied.	Before shaking.	After shaking.
Relative viscosity	3.720	3.680
p_H	4.57	4.57
Sp. conductance	7.986×10^{-4}	8.017×10^{-4}

Thus the previous history of gum jeol solutions, so far as the mechanical treatment goes, has no effect on their relative viscosity, p_H and specific conductance.

DISCUSSION

Hydrogen-ion Activity.— p_H values at four different concentrations have been shown in column 2 of Table III. Hydrogen-ion activity (a_H) appears in column 3.

TABLE III

Conc. (in g. %).	p_H .	$a_H \times 10^5 N.$	a_H/c ratio.
0.49	4.398	3.990	8.0×10^{-6}
0.82	4.390	4.074	5.0
1.22	4.350	4.470	3.5
2.45	4.22	6.100	2.7

Neither p_H nor a_H appears to change very much, although the concentration change has been as much as 500%. This is very suggestive of the fact that probably the gum has an inherent buffering property. This point was further examined by the addition of increasing quantities of the gum to a fixed quantity of HCl solution and noting the changes in p_H produced. For this reason 10 c. c. of an HCl solution ($N/50$ approx.) were taken and increasing volumes of the gum solution added to it and the final volume of the mixture was made up to 20 c. c. with water. A control experiment was performed by mixing 10 c. c. of HCl solution with 10 c. c. of water. The control was observed to have a p_H of 2.3. The results of this series of experiments have been graphically represented in Fig. 1, from which it will be evident that the p_H of the HCl

solution gradually increases with addition of increasing quantities of the gum. Such large changes in the activity of H-ions cannot be wholly attributed to the changes in ionic strength of the solution brought about by increasing the concentration of the gum as envisaged in Debye-Hückel interionic attraction theory. The buffering properties of the gum can therefore be understood in the light of the H-ion reserve which it sets up as the concentration increases. These H-ions are released on dilution as will be evident from column 4 of Table III which shows the a_m/c ratio *i.e.*, the amount of active hydrogen ions per g. of the gum increases roughly three times when the solution is diluted five times. Regarding the mechanism as to how and where these hydrogen-ions are retained by the gum molecules, the problem appears to await further experimentation.

FIG. 1

Buffering properties.

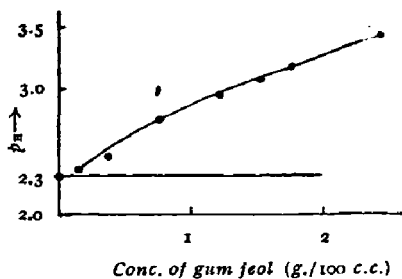
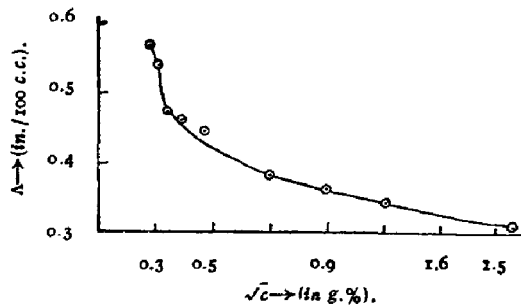


FIG. 2

 $\Lambda - \sqrt{c}$ curve.

Electrolytic Conductance.—Results of the measurements appear in Table IV. Values of specific conductance appear in row 3.

TABLE IV

*Conc.	0.079	0.094	0.116	0.153	0.224	0.489	0.855	1.223	2.446
\sqrt{c}	0.28	0.31	0.34	0.39	0.47	0.70	0.90	1.11	1.56
Sp. conduc. (R) $\times 10^4$ mho	0.448	0.509	0.552	0.710	0.992	1.882	2.971	4.209	7.595
‡Equiv. conduc (Λ)	0.570	0.542	0.476	0.464	0.447	0.385	0.365	0.344	0.311

* In g./100 c. c. sol.

‡ For 1g./100 c. c.

Since the equivalent weight of the gum is not known, the equivalent conductance in the usual sense could not be calculated. We can, however, define a quantity (Λ) which is the conductance of that volume of solution (in c. c.) which contains 1 g. of the gum, placed between two electrodes 1 cm. apart. This quantity will be strictly proportional to the actual equivalent conductance of the gum solution.

If the gum solution were a true electrolytic solution we would expect Onsager relation to hold good :

$$\Delta_0 = \Delta_0 - k \sqrt{c}$$

and Δ plotted against \sqrt{c} would give a straight line. The relation as shown in Fig. 2 presents the following features :

(i) The $\Delta - \sqrt{c}$ curve appears to show a break at a concentration of 0.094 g./100 c. c. from where the curve exhibits steeper downward slope with concentration. This point can be compared to the critical concentration observed by McBain in soap solutions (McBain *et al.*, *loc. cit.*).

(ii) The curve does not reach a minimum within the concentration range studied.

This break in the $\Delta - \sqrt{c}$ curve at the critical concentration and the subsequent steep course may be the outcome of an aggregation of the gum molecules into bigger micelles. This aspect will be clear from the study of viscosity and turbidity presented in subsequent sections.

Cataphoretic Velocity.—Results have been presented in Table V and graphically shown in Fig. 3.

TABLE V

Conc. of gum (g./100 c. c.)	0.048	0.094	0.153	0.242	0.489	0.815	1.223	1.834	2.446
C. v. $\times 10^5$ (cm./sec./volt/cm.)	9.59	14.64	15.73	—	13.58	10.52	9.65	9.47	8.43
Relative turbidity	—	—	0.172	0.176	0.304	0.326	0.417	0.515	1.00

From the figure it is evident that the curve shows a steep rise at lower concentrations, reaches a maximum and then shows an almost equally steep descent at higher concentrations. At still higher concentrations (0.98/100 c. c. solution) the rate of decrease diminishes considerably and the curve runs almost flat. The maximum occurs at a concentration of 0.28%.

FIG. 3

C.v. — c curve.

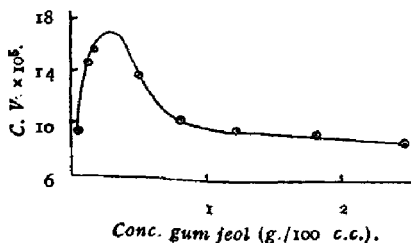
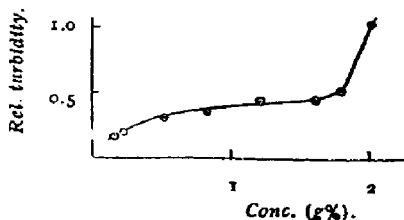


FIG. 4

Turbidity-conc. curve.



Increase in cataphoretic velocity with concentration indicates an increase in equivalent conductance of the micelle. Hartley (*Kolloid Z.*, 1939, **88**, 22) observed a rise of equivalent conductance and McBain, Bowden and Laing (vide Pauli and Valko, "Elektrochemie der Kolloide", 1929, p. 584) reported a rise of transport number above unity with concentration in their system which they explained as due to the aggregation of particles into larger micelles. Mukherjee and Sen-Gupta (*Nature*, 1940, **145**, 971) observed a rise of cataphoretic velocity with concentration in bentonite suspensions which they explained as due to the formation of bigger particles at higher concentration.

In the light of these observations, the increase in cataphoretic velocity may be regarded as an outcome of the progressive aggregate formation in the present system. With the progress of aggregate formation, the micelles, if they are to be stable, must arrest more and more counter-ions round them and thus diminish the effective charge density on their surface which would otherwise bring about disintegration of the micelles due to a strong electrical repulsion arising out of high charge density on the surface. The decrease in the effective charge density on the surface of each micelle may be the cause for a lowering of cataphoretic velocity at higher concentrations. The behaviour of the concentrated gum solution on centrifuging at moderate speeds, which can separate the major part of the gum leaving only a dilute solution behind, also suggests the formation of bigger and heavier micelles which remain sufficiently stable. It appears that the flat portion of the *c. v.*—*c* curve occurring at still higher concentrations may be due to the stoppage of arrest of more counter-ions round each micelle and/or due to the stoppage of the growth of micelle size. Results on turbidity measurements are expected to throw light on this aspect (*vide infra*).

Turbidity (relative).—Relevant data appear in Table V (row 3) with reference to the most concentrated solution (containing 2.446 g./100 c. c. of the solution) as the standard (turbidity = 1). Graphical representation appears in Fig. 4. It is evident from the figure that at low concentrations the turbidity tends to increase a little with increasing concentration of the gum, but afterwards it remains almost constant over a certain range of concentration beyond which the curve tends to shoot up.

Normally an increase of concentration should have a tendency to increase the turbidity of suspensions but such increase should be smooth, if not linear. Any abrupt change appears to be the outcome of some change in the state of aggregation of the particles in the solution. In the light of these considerations there appear to be two inflexion points, one at a concentration of 0.5 g./100 c. c. and the second at 1.82 g./100 c. c. If we assume an aggregate formation it is possible to explain the first inflexion at 0.5 g% as the outcome of the influence of two opposing tendencies; the first being a decrease in the total number of particles owing to aggregate formation which will have a diminishing tendency and the second one being an increase in the size of the micelles which will tend to increase turbidity.

Beyond the first inflexion it appears that both these factors act with equal intensity as a result of which the curve is flat indicating an almost constant turbidity over a certain region. At the second inflexion it is quite likely that the growth of size stops and the particles increase in number gradually. Results of *c. v.* measurements, referred to in the

previous section, are also in agreement with the conclusion that at a concentration in the neighbourhood of 1.8 g./100 c.c., the aggregation reaches its limit and the particle size becomes maximum.

Relative Viscosity.—Results of measurements have been presented in the following table and the graphical representation in Fig. 5.

TABLE VI

 $t = 30^\circ$.

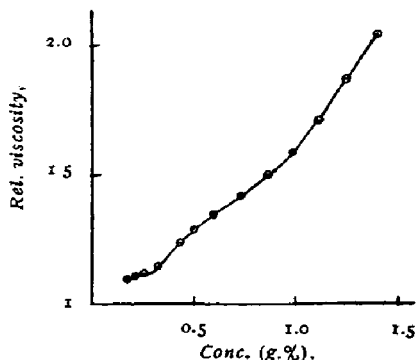
Conc. (g./100 c.c.)...	0.18	0.21	0.24	0.33	0.37	0.42	0.49	0.59	0.73	0.98	1.468	2.936
Rel. viscosity ...	1.089	1.090	1.123	1.132	1.160	1.227	1.272	1.338	1.406	1.569	2.038	3.869
Absolute η (Cp) ...	0.839	0.839	0.865	0.872	0.893	0.945	0.979	1.030	1.083	1.208	1.569	2.979

The curve for gum jeol shows that the relationship is not linear. At about a concentration of 0.33 g./100 c.c. there is a break indicating a sudden increase of slope. Again at a concentration of 0.42% there is another break where the slope tends to decrease again. At higher concentrations the curve runs convex towards the concentration axis, which signifies that the viscosity increases much more rapidly than the concentration.

The mode of increase of relative viscosity at higher concentrations, as observed here, has been regarded by Kruyt and Tendeloo (*Koll.-Chem. Beih.*, 1929, 29, 396) and Taft and Malm (*loc. cit.*) as a characteristic feature of all lyophilic colloids. The behaviour exhibited by this gum stands intermediate between those of cane sugar, which is a true solution, and of gelatin, which forms a colloid. Mere analogy with a lyophilic colloid is, however, of little avail if we cannot have an insight into the mechanism which works within and which is responsible for such a rapid rise of viscosity.

To get an insight into this aspect the responsibility of hydration should be taken into consideration along with the effect of aggregation proceeding at higher concentrations. Aggregate formation with increasing concentration increases the size of the particle for which the viscosity of the solution is expected to increase. With increasing concentration again, water taken up by the micelle by way of solvation becomes considerable and the concentration of the solution becomes greater due to removal of water than what is expected from the percentage concentration. It is of course true that with increasing concentration, water available for hydration of each micelle is far less than in a dilute solution where the degree of hydration is much greater (*cf.* Hatschek,

FIG. 5
Rel. viscosity—conc. curve.



"Physics and Chemistry of Colloids," 1927). Molecules with smaller number of water molecules bound to them at higher concentrations will necessarily have smaller dimensions and will tend to decrease the viscosity; but the net effect is determined by all the simultaneously influencing factors, viz., aggregation and hydration of the micelles.

If a break in the curve signifies starting of aggregate formation, it may be concluded that the starting point is either at 0.33% or 0.42% concentration.

A study of the influence of concentration of the gum jeol solution on the properties thereof thus reveals certain peculiar features. The graphs representing the variation of such properties with concentration do not run smooth but show one or two breaks within the concentration range studied (Table VII).

TABLE VII

Nature of curves.	No. of inflexions.	Concentration at	
		1st inflexion.	2nd inflexion.
$\Lambda - \sqrt{c}$ (Fig. 2)	1	0.094%	...
\bar{c} v. $-c$ (Fig. 3)	2	0.28	0.81
Turbidity-conc. (Fig. 4)	2	0.50*	1.84
Relative viscosity-conc. (Fig. 5)	2	0.22	0.42*

Experience gathered from centrifuging a gum solution shows that the more concentrated the solution, the less are the time and the speed at which the gum is thrown out. At higher concentrations the gum molecules therefore become bigger and heavier. Thus formation of aggregate undoubtedly proceeds with increasing concentration in the gum jeol. The concentration from which this aggregation starts is, however, not clear since different properties show inflexions in different regions and some show two inflexions (cf. the case of yeast nucleic acid, Mukherjee and Sarkar, *loc. cit.*).

Diminution of equivalent conductance with increasing concentration of gum is also quite in accordance with the observation that increasing addition of gum increases the p_H of a hydrochloric acid solution. Disappearance of H^+ -ions as more and more gum is added (Fig. 1) shows that the gum takes up the H^+ -ions which may either go to intensify the ionic atmosphere (according to Debye-Hückel interionic attraction theory) or become bound in the double layer surrounding each micelle. Mukherjee (*Kolloid Z.*, 1933, 62, 257, *et. seq.*), however, drew attention to the inadequacy of the treatment of colloidal solutions from the view point of Debye-Hückel theory or of any classical concept of electrochemistry. Although there is a certain amount of similarity, as brought out by the work of Duclaux (*J. chim. phys.*, 1907, 5, 36; 1909, 7, 413), Pauli (*loc. cit.*), Zsigmondy, McBain (*loc. cit.*) and others between the behaviour of colloidal electrolytes and ordinary electrolytes, there is, however, little justification for treating these two systems as exactly alike, because according to Mukherjee, the similarity observed is more apparent than real and there are essential differences which characterise the behaviour of colloidal electrolytes. He regards the colloids as a polyphase system whose electrochemical behaviours are governed by adsorption and surface energy. He suggests that

any theory attempting to explain the electrochemical properties of a colloidal solution should take into account not only the electrolytic ions associated with the colloidal particles but also the equilibrium which exists between these ions and those in the bulk of the solution. The application of Debye-Hückel concept or any other classical concepts in electrochemistry tacitly assumes a definite solubility, molar concentration, activity, valency and thermodynamic equilibrium amongst the various species of electrical carriers. But in a colloidal solution it is almost absurd to apply these ideas to the case of a micelle or to speak of the "solubility or activity of a coagulum" obtained by coagulation of a colloid or to regard this system as a molecular one in the sense of the phase rule.

In the light of these observations, it appears that a gum solution should be treated as composed of particles which are colloidal micelles surrounded by a double layer of counter-ions rather than a polyvalent ion under the influence of the ionic atmosphere. Further evidence in support of this will form the subject matter of a separate communication.

C O N C L U S I O N S

Molecules of gum jeol form bigger aggregates in concentrated solution, so much so, that the gum is thrown out of solution by centrifuging at a moderate speed.

The gum molecules can take up hydrogen ions from an HCl solution and increase the p_H . Most probably these hydrogen-ions are retained in the double layer surrounding the colloidal micelles.

Variation of physical and electrochemical properties indicate an aggregate formation on the part of the micelles but the critical concentration is not definite.

In the variations of relative viscosity, hydration also appears to play an important role.

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