Thesis.

AN EQUIPMENT FOR DETERMINING THE RELATIVE VISCOSITY OF AQUEOUS SOLUTIONS.

by

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Introduction.

In order to calculate accurately the degree of ionization of many electrolytes in solution, it is necessary to take into account the relative viscosity of their solutions. The viscosity of the medium undoubtedly has an effect upon the mobility of the ions, and hence, a correction must be applied to the simple formula usually employed for calculating the degree of ionization from conductance data. Washburn[1], Noyes[2], Kraus[3], and others, have discussed the nature of this correction. There is some doubt as to its exact form, but the relation

$$\gamma = \frac{\Lambda\eta}{\Lambda_0\eta_0}$$

probably gives the degree of ionization as accurately as the conductance data is known. This correction for normal solutions, in some instances, amounts to as much as seven or eight per cent.

1. Jour. Am. Chem. Soc. 33, 1464, (1911).
2. Ibid. 34, 457, (1912).
3. Ibid. 36, 35-65, (1914).

Although many investigators have determined the viscosity of aqueous solutions, but few have made extensive and careful investigations in the range where the data is most valuable for the purpose of calculating the degree of ionization. As a rule the investigators had other purposes in view, and, until quite recently, the attention paid to certain details in the experimental determination was insufficient to yield results comparable in accuracy with good conductivity data.

A viscosimeter as ordinarily constructed does not obey Poiseuille's law of flow, and hence, a considerable correction factor should often be applied to the relative viscosity as given by the simple formula

$$\eta/\eta_0 = \frac{dT}{dT_0}$$

where η and η_0 are the viscosities of the solution and pure water respectively, d and d_0 the corresponding densities and t and t_0 the corresponding kinds of flow. But few investigators determined whether Poiseuille's law was obeyed by their viscosimeters. In many cases the time of flow was not accurately determined; a stop watch which reads fifths of a second only, has been usually employed.

Hence it follows, that although there has been

accumulated a considerable amount of data upon the viscosity of aqueous solutions of electrolytes, but little reliable data is available. Greneisen[1] is the only investigator who has made an extensive series of careful measurements, and all of his determinations were made at 18°C. More complete data at 18°C should be known, and the relative viscosity at 25°C of nearly all salts remains to be determined accurately.

It is planned to undertake such an investigation in this laboratory, so that there may be available fairly complete viscosity data for solutions, normal and more dilute, of the common electrolytes. It will not be necessary to determine the data for all salts at 25°C, yet very few investigations conducted at this temperature can be said, a priori, to be of high accuracy; for while the viscosimeters of many may have obeyed Poiseuille's law, but few took the trouble to investigate this point. By redetermining the relative viscosity of a few salts which a given investigator used in a viscosimeter which obeys Poiseuille's law, it will be possible to form an opinion as to the accuracy of his work. If it is accurate, then it will not be necessary to repeat the determinations

1. Gruneisen. Wiss. Abhandl. Phys. Tech. Reichsanstalt. 4, 159, 241, (1914).

for other salts that he may have used.

APPARATUS.

The viscosimeter used in this work was of the Ostwald type (Fig. 1.) and was made of fused quartz. It was almost identical with the one used by E. W. Washburn and G. Y. Williams.[1] As noted in their paper, the advantages of a quartz viscosimeter are:- first, its dimensions do not change with the temperature, as do those of glass apparatus, and as a result there is no hysteresis when it is brought from one temperature to another; and second, water and other solutions used in cleaning do not have as great a solvent action on quartz as on glass, and thus there is not as much danger of the diameter of the capillary being changed.

The overall length of the viscosimeter was 35.5 cm. (without the three way stop cock). The capillary was about 19 cm. long and 0.5 mm. in diameter. The tube was marked on both sides of the small bulb by a fine wire fastened around it with kotinsky cement. The viscosimeter was constructed according to the relations recommended by Gruneisen so that there would be a minimum deviation from Poiseuille's law.

1. Jour. Am. Chem. Soc. 35, 737, June 1913.

The center of the large bulb was 20 cm. below the center of the small bulb; this was the mean head of flow during a determination, because the amount of solution for each run was taken so that the large bulb which was 80 mm. wide would be filled to the center when the small bulb was filled to the center.

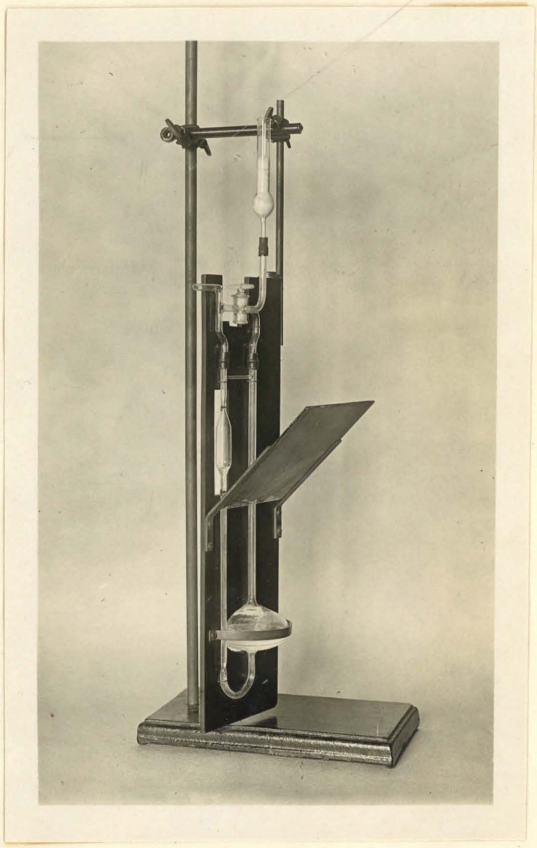

Fig. 1.

The viscosimeter was mounted on a sheet of bakelite 6 mm. thick, places being cut out for the two bulbs. A mirror placed in brackets at an angle of 45° to the bakelite so that the two marks on the opposite sides of the small bulb would be reflected up and could be observed on looking down into the thermostat. A rod fastened to the bakelite served as a means of rigidly supporting the apparatus in the thermostat. In order that the viscosimeter would always be placed in the same perpendicular position for each determination, a small spirit level (similar to those used on kodaks) was fastened to the top of the bakelite.

FILLING THE VISCOSIMETER.

In filling the viscosimeter it was necessary to remove it from the thermostat and also to disconnect the three way stop cock. The same amount of solution (50 cc.) measured by a pipette was put in the viscosimeter each time.

By means of the three way stop cock, (See Fig. 1.) it was possible to make any number of determinations with a given solution without removing the viscosimeter from the thermostat. Thus after the completion of a determination the three way stop cock was turned so that upon applying suction to the side arm, the solution was drawn

up into the small bulb; the air entering the other arm of the viscosimeter was filtered through a cotton wool plug. During a determination the stop cock was turned so that the two arms of the viscosimeter were connected. In this way the air passed directly from one side of the viscosimeter to the other.

TEMPERATURE CONTROL.

The viscosity of water changes about 2% per degree centigrade and it is therefore very necessary to have good temperature control. A porcelain-lined thermostat was used, the water was kept in continual motion by means of a turbin stirrer. The temperature was regulated by an improved automatic regulator and heating lamp. The temperature was observed by a thermometer graduated to tenths of a degree and was often checked with a thermometer (#11154) which had been calibrated and standardized by the National Bureau of Standards. The change in temperature during a determination, which was only two or three thousandths of a degree, was observed by a Beckman thermometer which was kept in the thermostat continually. For this work it is necessary that the temperature shall not vary from one run to another, but it is not so necessary to know it exactly because the relative

viscosity changes but slightly with the temperature.

MEASUREMENT OF TIME.

The measurement of time is, of course, a most important factor in viscosity determinations. Stop watches have been used for most of the previous work and with them time can never be measured closer than one-fifth of a second. For the measurement of time in this work the main clock which was accurate to a few seconds per week was used and a chronograph (Fig. 2.) which was constructed in the chemistry department's instrument shop was employed for measuring and recording the time of flow.

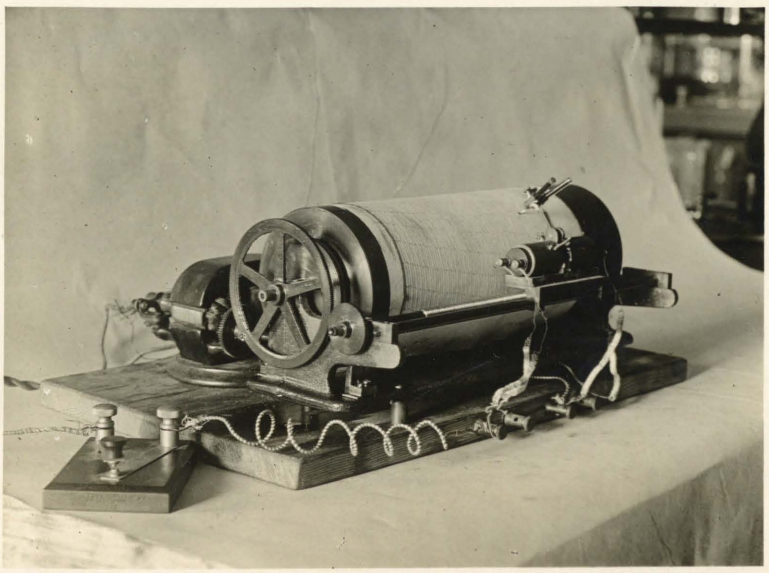

Fig. 2.

The drum of the chronograph was 11¾ in. long and 4½ in. in diameter, it was driven through a set of gears by means of a small motor; the motor also drove a worm on which was a small carriage carrying two magnets with pens attached. The magnet actuating one of the pens was placed in the clock circuit and it made a gog every second on the paper which was fastened to the revolving drum. A small resistance was placed in the motor circuit so that the speed of the drum could be varied. Thus the distance between jogs could be changed and this distance was usually about 6 mm.

The other magnet and pen on the carriage was connected in a circuit which the operator could close by means of a key, and the pen which was beside the magnet operated by the clock made a jog whenever the circuit was closed. By measuring the distance from the nearest second recorded and finding the number of intervening seconds, the time could be accurately measured to at least two hundredths of a second.

RESULTS.

At 25°C the time of flow of water through the viscosimeter was over ten minutes, and sometimes a series of determinations would check very well as shown by the following data for water. The Beckman reading -3.899 corresponded to 25°C on the standardized thermometer.

The arrangement of the entire apparatus is shown in (Fig. 3.)

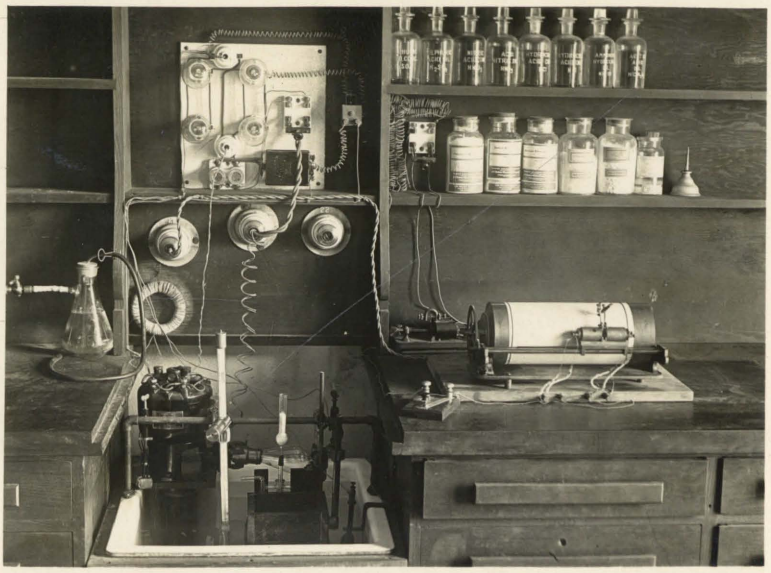

Fig. 3.

Beckman Reading	Time of Flow
3.898-3.902	633.96 sec.
3.897-3.900	633.92 "
3.897-3.900	634.17 "
3.902-3.900	634.05 "
3.900-3.902	634.13 "

The time of flow of consecutive runs would sometimes

suddenly change by several seconds and the only explanation which could be found for this discrepency was that small particles of dust had become lodged in the capillary.

Several weeks after the first determinations with water were made it was found that a constant value for the time of flow of water was obtained which was about eight seconds higher than the value previously found and at this time the viscosimeter was cleaned by filling with chromic acid and immersing the apparatus in a bucket of boiling water for three hours. Nitric acid containing alcohol was also used but the values could not be reduced to those obtained at the beginning. No satisfactory explanation of this behaviour can be offered.

A great number of determinations were made with a normal solution of hydrochloric acid and the following results were obtained at the time when the water constant of the viscosimeter was as given in the above table.

Beckman Reading	Time of Flow
3.898-3.907	662.36 sec.
3.907-3.911	662.15 "
3.889-3.898	662.53 "
3.898-3.910	662.36 "

From the above data the relative viscosity was calculated and found to be 1.063 assuming the density

of the 0.9777 normal hydrochloric acid to be 1.0146.

Green[1] gives for the relative viscosity of 0.9955 normal hydrochloric acid solution 1.0602 and uses as the density of the solution the above value.

Reyher[2] gives for the relative viscosity of a chloric acid normal solution 1.0520, using 1.0485 as the density of his solution. When his data is recalculated employing 1.0146 as the density of the solution the relative viscosity becomes 1.067.

A great deal of trouble was encountered with the hydrochloric acid solutions, however, because they were found to contain small particles of dust, though the utmost care was taken in making up the solutions, and filtering them through hardened filters; even after this treatment they wer still found to contain small fiber like particles.

SUMMARY.

An arrangement of apparatus is escribed by which the relative viscosity of solutions can be accurately determined, provided that the solutions can be made up in such a way as to be absolutely free from all dust particles.

1. Jour. of Chem. Soc. Trans. 93, 2023, (1908).
2. Zeit. Phys. Chem. 2, 744, (1888).