

Duplicate cells with nearly pure acetic acid as the solvent could be reproduced to within 0.1 mv. and were constant in electromotive force for several months at least.

A cell containing two solid phases in equilibrium with the saturated solution was prepared.

The heat of formation of the compound $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{H}_2\text{O}$ was determined.

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The Viscosity of Aqueous Solutions as a Function of the Concentration

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It has long been known that the viscosity of aqueous solutions is approximately a linear function of the concentration. In 1876 Sprung¹ published measurements on many salts at many temperatures. His viscosity-concentration curves are approximately linear but have an upward trend at higher concentrations which indicates an increasing deviation from a linear limiting law. Arrhenius² also found that the linear relationship holds approximately over the lower part of the concentration range but that the viscosity increases more rapidly than the concentration at high concentrations. He proposed an equation which is reducible to the form $\eta = A^c$, η is the relative viscosity compared to that of water at the same temperature and A is an empirical constant for any salt and temperature. This equation has been much used by later experimenters although it is only a rough approximation.

Most salts give solutions with viscosity greater than that of water at all concentrations. Some salts (including most but not all of the iodides, bromides, chlorides, bromates, chlorates, nitrates and thiocyanides, of cesium, rubidium, potassium, ammonium, thallium and hydrogen) give solutions having a viscosity less than that of water.³ In such cases it is usual for the viscosity-concentration curve to go through a minimum and for some salts at sufficiently high concentrations the viscosity may become greater than that of water. This type of curve cannot be reproduced by the Arrhenius equation.

(1) A. Sprung, *Pogg. Ann. Phys. Chem.*, **159**, 1 (1876).

(2) S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

(3) A. I. Rabinovich, *THIS JOURNAL*, **44**, 954 (1922), discusses the hypotheses which have been suggested to account for this phenomenon. An interesting suggestion has recently been made by Z. W. Wolkowa and W. S. Titow [*Z. physik. Chem.*, **A155**, 53 (1931)], who say "We may therefore suspect (vermuten) that an aqueous solution can only have a greater fluidity than water if the heat of dilution is negative."

Einstein⁴ in 1906 deduced from the principles of hydrodynamics that if the solute could be regarded as made up of spherical incompressible uncharged particles which are large in comparison with the molecules of the water the viscosity of the solution would be $\eta = 1 + 2.5 \Theta$, where Θ is the total volume of the solute particles per unit volume of solution. This equation obviously connotes a linear relationship between viscosity and concentration.

Finkelstein⁵ extended Einstein's treatment to solutions of binary electrolytes in polar solvents. He investigated mathematically the effect on the viscosity of the relaxation time of the solvent dipoles and concluded that the electric influence of the ions on the polar solvent will increase the viscosity proportionally to the concentration. Neither Einstein nor Finkelstein account for the fact that some solutes diminish the viscosity of water.

Grüneisen,⁶ who improved the experimental technique and extended his measurements to greater dilution than his predecessors, found that for sucrose the linear relationship is valid; but that for salts, deviations from the linear law became more pronounced at low concentrations instead of disappearing. Grüneisen made the deviation from linearity evident by plotting $(\eta - 1)/c$ against c (or some root of c for the sake of spreading out the points at the lower concentrations). This method of plotting would give a horizontal straight line if the linear relationship held. His curves, however, show a pronounced negative slope at low concentrations, pass through a minimum at about 0.2 normal and then have a slight positive slope and positive curvature at higher concentrations. We shall call the departure of the viscosity-concentration curves from linearity at high dilutions the Grüneisen effect. However, Grüneisen's attempts to give a theoretical explanation of the failure of the linear law at high dilutions, on the basis of Arrhenius' theory of electrolytic dissociation, and to derive an equation expressing the viscosity as a function of the concentration were unsuccessful.

Later workers, especially Schneider, Applebey and Merton,⁷ found the Grüneisen effect with other salts, but they did not give a satisfactory interpretation or derive a valid equation for the variation of the viscosity with the concentration.

Measurements of the viscosity of solutions of barium chloride were undertaken in this Laboratory by the senior author and Malcolm Dole⁸ on account of their interest in these data in connection with the phenomena

(4) A. Einstein, *Ann. Physik*, [4] **19**, 289 (1906); [4] **34**, 591 (1911).

(5) B. N. Finkelstein, *Physik. Z.*, **31**, 130, 165 (1930).

(6) E. Grüneisen, *Wiss. Abhandl. physik. tech. Reichsanstalt*, **4**, 151, 237 (1905).

(7) K. Schneider, "Dissertation," Rostock, 1910; M. P. Applebey, *J. Chem. Soc.*, **97**, 2000 (1910); T. R. Merton, *ibid.*, **97**, 2454 (1910).

(8) Grinnell Jones and Malcolm Dole, *THIS JOURNAL*, **51**, 2950 (1929). This paper contains a more detailed discussion of the Grüneisen effect.

of electrolytic conductance and for this purpose were carried to a high dilution (0.005 molal). These measurements showed that the Grüneisen effect is magnified at great dilution. Analysis showed that in this case the fluidity-concentration curve has a simpler form than the viscosity-concentration curve. It was pointed out that, although the principal effect of the dissolved salts on viscosity is proportional to the concentration, the curvature (discovered by Grüneisen) in the dilute end of the viscosity-concentration (or fluidity-concentration) curves proves that there is another effect of the dissolved salt which is of relatively greater importance in dilute solutions. The Grüneisen effect always tends to increase the viscosity regardless of whether the sum of all of the effects of the salts is to increase or decrease the viscosity.

It then occurred to Jones and Dole that the Debye-Hückel theory of interionic attraction might be extended by applying it to this problem. The electric forces between the ions tend to establish and maintain a preferred arrangement of the ions and resist any distortion of the preferred arrangement and thus stiffen the solution or increase its viscosity. Although they did not succeed in deriving an equation for the viscosity as a function of the concentration which makes adequate allowance for the Grüneisen effect by rigid deduction from fundamental postulates of the Debye-Hückel theory, they inferred that the effect would be proportional to the square root of the concentration. This idea together with the knowledge that, for salts which increase the viscosity of water, the fluidity is approximately a linear function of the concentration suggested an equation of the form $\varphi = 1 + A\sqrt{c} + Bc$; where φ is the fluidity (*i. e.*, the reciprocal of the relative viscosity) and A would be expected to be negative for all electrolytes but zero for non-electrolytes. The value of B may be either positive or negative in different cases. The equation $\varphi = 1 - 0.02013 \sqrt{c} - 0.20087 c$, was found to fit their data for barium chloride over the whole range from 0.005 to 1 molal. It was furthermore found that the equation is consistent with the best data on other salts available in the literature, although the scarcity of precise measurements at low concentrations hindered a rigid test of the general validity of the equation.

The manuscript of the paper by Jones and Dole was then taken to Debye by Dole during the summer of 1929. Debye suggested that the problem could be attacked by modifying the fundamental differential equation of Onsager to allow for the viscous flow. With the inspiration of Debye's interest and suggestions, Falkenhagen and Dole⁹ then attacked the problem deductively and found a partial solution. In order to simplify the problem it was at first assumed that only a binary salt is present and that the anion and the cation have the same mobility. The result was an equation,

(9) H. Falkenhagen and M. Dole, *Z. physik. Chem.*, [B] **6**, 159 (1929); *Physik. Z.*, **30**, 611 (1929).

$\eta = 1 + A\sqrt{c}$, which was, however, regarded only as a limiting law for extreme dilution. It is obvious that A in this equation is the same as the A in the Jones and Dole fluidity equation with a reversed sign. Later the mathematical difficulties of a more general treatment were overcome by Falkenhagen,¹⁰ who derived an equation of the same form, but with a more explicit evaluation of the coefficient A , applicable to any salt with ions of any valence and any mobility.

The deductive treatment of Falkenhagen is a substantial advance over the inductive treatment of Jones and Dole in that the coefficient A is given as a complicated but explicit function of the mobilities and valences of the ions, the temperature, and the universal constants which commonly appear in the equations derived from the Debye-Hückel theory. Falkenhagen and Vernon have computed the value of A for a number of salts. However, the deductive reasoning of Falkenhagen did not give the linear term, which is numerically greater than the square root term except at extreme dilutions. On the other hand, the inductive reasoning of Jones and Dole has given a new law for the relationship of viscosity to concentration which appears to be valid over a substantial range of concentration.

The original paper of Jones and Dole contains the following statement: "It may be predicted from our equation that at very low concentrations the viscosity of solutions of all strong electrolytes will be greater than that of water, including salts which at moderate concentrations show diminished viscosity. So far as we are aware, the only published measurement which shows that even those salts which cause diminished viscosity at moderate concentrations will give an increase in viscosity at extreme dilutions is by Schneider, who reports a relative viscosity of 1.0008 for 0.05 N potassium chlorate, and a viscosity of less than 1 for solutions of 0.1 to 0.5 N potassium chlorate. We expect to test this prediction experimentally in the near future."

Schneider makes no comment on the significance of his recorded observation that 0.05 N potassium chlorate has a viscosity greater than 1 whereas stronger solutions have a viscosity less than that of water.

Since the publication of the prediction by Jones and Dole quoted above, Joy and Wolfenden¹¹ have tested this prediction by means of new data on potassium chloride, rubidium nitrate, potassium chlorate, and nitric acid at both 18° and 35°. They have confirmed the prediction for the three salts at 18° and for rubidium nitrate at 35°, but have found that nitric acid increases the viscosity at all concentrations at both of these temperatures, and potassium chloride and chlorate behave likewise at 35°. Incidentally they found that Schneider's figure of 1.0008 for the viscosity

(10) H. Falkenhagen, *Physik. Z.*, **32**, 365, 745 (1931); H. Falkenhagen and E. L. Vernon, *ibid.*, **33**, 140 (1932); *Phil. Mag.*, [7] **14**, 537 (1932).

(11) W. E. Joy and J. H. Wolfenden, *Nature*, **126**, 994 (1930); *Proc. Roy. Soc.*, **A134**, 413 (1931); H. G. Smith, J. H. Wolfenden and Hartley, *J. Chem. Soc.*, 403 (1931); G. R. Hood, *J. Rheology*, **3**, 326 (1932).

of 0.05 *N* potassium chlorate at 18° is an experimental error. Their measurements show that at this concentration and temperature the viscosity is really less than that of water and that a viscosity greater than that of water is only found at concentrations less than 0.008 *N*.

The primary object of the present investigation was to test the validity of the prediction of Jones and Dole that all salts will give solutions which have a viscosity greater than that of water if measured at sufficiently great dilution, even including those salts whose solutions exhibit diminished viscosity at moderate concentrations. Secondary objects were to collect additional data to test the general validity of the Jones and Dole equation, to compare the values of *A* found experimentally with the value computed by the formula of Falkenhagen and Vernon, and to test more rigorously the conclusion drawn from existing data that the square root term is absent for non-electrolytes.

In order to accomplish our primary object it was evidently necessary to measure the relative viscosity of extremely dilute solutions with high precision. The analysis of the meager existing data on salts which give solutions having a viscosity less than that of water indicated that the maximum in the viscosity-concentration curves would probably be less than 0.1% greater than that of water. Therefore data reliable to 0.01% or better are needed.

The earlier measurements on viscosity in this Laboratory had been carried out by observing the movement of a meniscus past a mark on the viscometer and tapping a key with the hand to record the instant of transit on the moving tape of a chronograph. Our experience with this method made it clear that the greatest source of error was that due to an inexact coördination of the eye and hand. We therefore undertook to eliminate this psychological error entirely by substituting a photoelectric cell and its amplifier and other accessories for the human eye, brain, nerves and hand, in the hope that a more precise record of the time of transit of the meniscus in the viscometer could be obtained.

Experimental

A new viscometer of quartz of the Ostwald type was made for this investigation at the Lynn Works of the General Electric Company. The workmanship is extraordinarily good and our exacting specifications were met with astonishing precision. It is shown in Fig. 1.

In order to avoid any surface irregularities which might cause irregular drainage the tube from which the bulb, B, was made was ground and polished internally before being drawn down and sealed to the tubes C₁ and C₂. Care was taken that the end portions of the bulb connecting the side walls of the bulb and the constriction should have sufficiently steep slopes at all points to give good drainage over the entire surface.

The time of flow was determined by timing the transit of the meniscus past fixed points in the upper and lower constrictions C₁ and C₂. The diameter of these tubes is an important detail. By making them narrow the rate of motion of the meniscus is increased and therefore the event to be timed is made more definite. On the other hand,

if the tube C_1 is made too narrow the liquid draining from the upper wall after the passage of the meniscus will bridge across the tube and will obstruct the entrance of air into the bulb. Of course this obstruction will soon be broken by the suction of the receding liquid, but the drop of liquid will immediately be drawn back into the capillary tube by its surface tension. This process repeats itself indefinitely. The result is an extra irregular back pressure which gives erratic and erroneous results. The tube C_1 must, therefore, be wide enough to remain free of drops after the meniscus has passed. After some preliminary trials with tubes of various diameters we specified a diameter of 1.0 mm. for this tube with satisfactory results. The lower tube C_2 should be of the same diameter so that the two transits which are to be timed shall be as nearly identical as possible. The tubes C_1 and C_2 were therefore made from the same piece of tubing. The ground joints connecting the upper Pyrex cross piece with the viscometer were placed on the outside of the viscometer because this construction minimizes the danger that ground glass or grease will get into the viscometer. The more important dimensions are the average hydrostatic head, 22.8 cm.; the volume of the upper bulb, 10.063 ml.; the length of the capillary, 18.5 cm.; the diameter of the capillary, 0.0476 cm. The period with water at 25° is approximately 618 seconds.

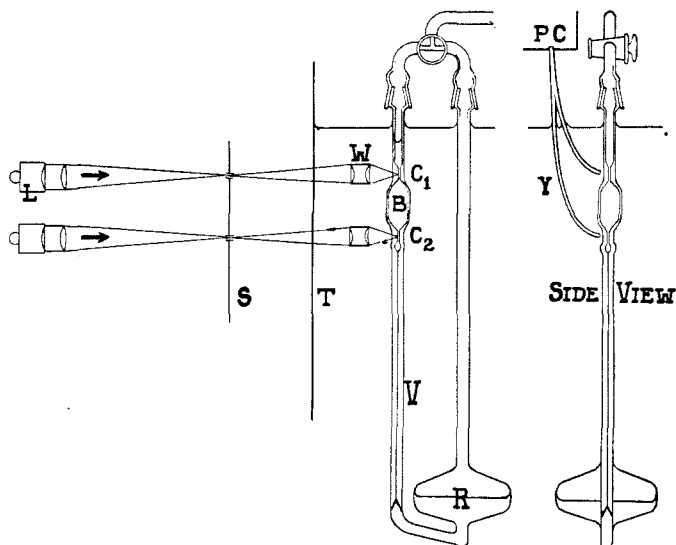


Fig. 1.—Viscometer and optical system.

The viscometer was mounted permanently in a stout brass frame and was always handled in its frame. It is important that after the instrument is removed from the thermostat for cleaning and refilling it shall always be put back in a definite reproducible position so that the hydrostatic head shall be constant. The frame was therefore held at only three points against a strong well-braced support which was designed to give mechanical stability with minimum of interference with the circulation of the water of the thermostat.

Since the viscosity of water changes about 2% per degree, the thermostat used must be of high quality. Our thermostat apparently maintained its temperature within 0.001° but the means used to obtain this constancy need not be described in detail since they are not novel. Our thermostat was set at 25.00° for all of the measurements recorded in this paper. Since the temperature coefficient of a dilute solution will not vary

greatly from that of water the absolute value of the temperature does not have to be known with great precision.

The most novel feature of our viscometric procedure was the development and use of automatic timing of the transit of the meniscus by means of a photoelectric cell. The method of timing finally adopted was based on the total internal reflection of a beam of light at the quartz-air interface which is formed in the constriction at the instant of the transit of the meniscus. This method requires a beam of light which is as narrow as possible vertically but broad enough horizontally to cover at least half of the tube C_1 and which can be focused at a definite reproducible height on the tube C_1 . The source of light was an automobile head-light bulb (6 candle power, 6 volts) with a straight tungsten filament which was mounted so that the filament would be horizontal. In order to secure more intense illumination the bulb was operated with 10 volts instead of its rated 6 volts. The light passed through a condensing-projecting lens, L (a Bausch and Lomb, series II Cinephor with an effective focal length of five inches and a relative aperture of 3.5) and was brought to a primary focus outside the thermostat, as shown in Fig. 1. A screen with a horizontal slit was placed at this focus. This helped greatly in obtaining a beam which was narrow vertically at the viscometer. The diverging beam from the slit passed through a plate glass window in the side of the thermostat and then through a double lens, W , which brought the beam to a focus on the viscometer at C_1 . In order to increase the relative aperture without increasing the aberrations the parts of the final double lens were mounted in a water-tight cell so that their more refractive inner surfaces were in contact with the enclosed air and the outer surfaces were in contact with the water of the thermostat. This lens when mounted as described in water had an effective focal length of 75 millimeters and a relative aperture of 2.5. A single lamp and projecting lens, L , served for both the upper and lower meniscus by mounting them in an elevator provided with suitable stops. The final double lenses, W , and slit in the screen, S , were duplicated so that each constriction C_1 and C_2 had its own lens and slit which remained in a fixed position. The double lenses were especially made for us by the firm of Pinkham and Smith of Boston. We wish to thank Mr. John A. Seaverns of this firm for his help in the construction of this optical system.

The optical effect which forms the basis of our new method of timing is shown diagrammatically in Fig. 2.

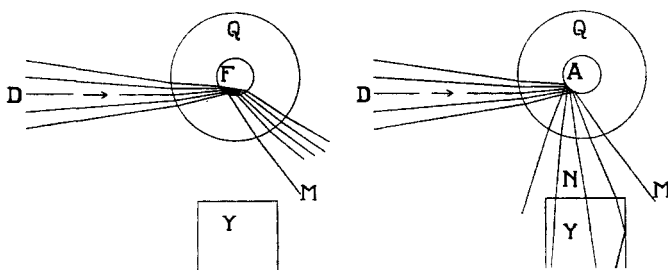


Fig. 2.—Principle of optical effect at meniscus transit.

When the narrow horizontal beam of light, D , strikes the quartz-water interface at the capillary tube inside C_1 most of the light will pass into the water, F , inside the capillary and finally emerge into the water of the thermostat nearly opposite where it entered the quartz. A small portion of the light beam which strikes the interface at a sufficiently acute angle will suffer total internal reflection as shown (M) but will miss the collecting rod of quartz, Y . However, as soon as the meniscus has passed below the light beam the water inside the capillary will be replaced by air, A , and as a consequence the critical angle for total internal reflection will be greatly changed, and therefore a

much larger portion of the beam will suffer a total internal reflection to the side as shown at N in Fig. 2 and will emerge from the quartz tube into the water of the thermostat at an angle from the entering beam. The light thus diverted sideways enters the end of a quartz collecting rod, Y, which is suitably mounted near C_1 and C_2 , and passes through the rod lengthwise to the photoelectric cell. The light cannot emerge into the water of the thermostat owing to total internal reflection provided the curves in the rod are not too sharp.

The two quartz collecting rods from the two constrictions were joined together in the form of a Y as shown in Fig. 1. The upper end of the quartz rod entered a light-tight box where the photoelectric cell was mounted. The invention of this method of producing a side-wise reflection of the light at the moment of transit of the meniscus and the device of leading this reflected light out of the water of the thermostat to the photoelectric cell by means of a quartz rod are the essential novel features of our method of timing. It was developed only after patient experimentation and adopted after critical comparison with other procedures which proved to be less satisfactory. The development of the rest of the apparatus to record the time accurately, although laborious and expensive, was comparatively speaking a routine matter. We used the photoelectric cell made by the General Electric Company and designated by them as type PJ-23. It is more sensitive than any other cell which we tried. Dr. R. F. Field and Mr. Horatio Lanson of the General Radio Company kindly brought their new type of stretched wire oscillograph to our laboratory and made some measurements on the current given by the photoelectric cell both when using the optical effect described above and when using other effects which proved to be less useful and are therefore not described here. These oscillographic tests showed that, when operating as described above, about 0.05 second was required from the time when the current from the photoelectric cell could be first detected until it reached its maximum value. This presumably measured the total time of transit of the meniscus through the height of the beam of light. This does not mean, however, that there is an error or uncertainty of this magnitude in our final results because the electromagnetic recording device operated when the current attained a definite value less than the maximum. We are measuring the difference in time between two very similar transits and the recording device operated at the corresponding stage of the two transits and thus gave the interval correctly. Moreover, we always compared the time of flow of a dilute solution with that of water so that any constant errors would be canceled out of the results.

The power output from a photoelectric cell is too small to operate the chronograph needle directly and must therefore be amplified. There are difficulties in amplifying a current which takes 0.05 second to build up from zero to its maximum, which corresponds to a frequency of 5 cycles per second, but they can be overcome. The amplifier finally built uses three audion tubes with resistance-capacitance coupling and a minimum of inductance. It is shown diagrammatically in Fig. 3. The types of tubes and the voltages used are shown in the figure. The best values for the resistances and capacitances indicated in the diagram will depend to some extent on the individual tubes. In our apparatus R_1 was 20 megohms, R_2 and R_4 were each 2 megohms, and R_3 and R_5 were 1 megohm each, C_1 and C_2 were 2 microfarads. When the meniscus transit occurs the electric impulse from the amplifier through the chronograph was about 20 milliamperes. The photoelectric cell and entire amplifier, except the batteries, was contained in an electrostatically shielded box mounted immediately over the thermostat. We do not claim that this amplifier is the best possible design but merely that it worked satisfactorily. Figure 3 also shows a switch, CK, which when closed connected the clock to the chronograph and recorded seconds on the tape; and a tapping key, IK, which permitted the operator to make a mark on the tape at will to identify or call attention to any particular signal from the clock or photoelectric cell.

Our timing depended on a pendulum clock of good quality made by the Gaertner Scientific Company of Chicago and described in their catalog under Number L1013. The invar pendulum carried a platinum tip which swung through a small trough of mercury, thus closing, once every second, an electric circuit including a battery and the chronograph. It seems improbable that the rate of this clock varied sufficiently during any day to cause an error of 0.01 second in 618 seconds.

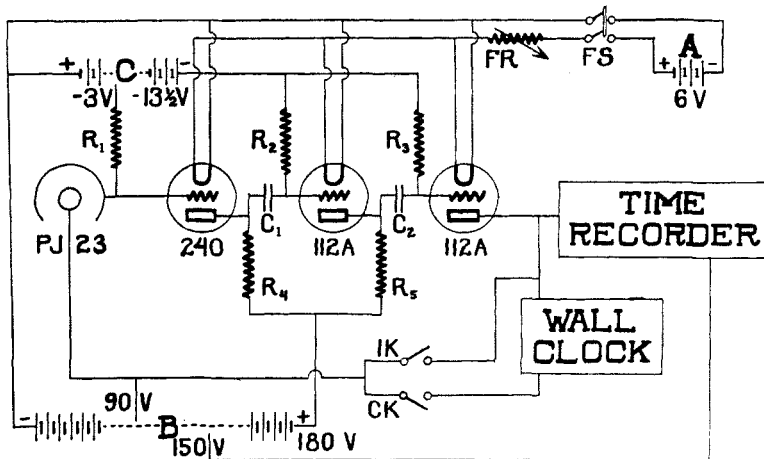


Fig. 3.—Photoelectric cell, amplifier and electrical connections.

The chronograph used was a Duplex Syphon Recorder made by the General Radio Company of Cambridge and designated by them as type 456. It had a moving paper tape (stock market ticker tape) which had an idling speed of 2.5 cm. per second and a recording speed of 30 cm. per second. It had two independent siphon pens operated by electromagnets which required about 5 milliamperes more or less dependent on the adjustment of the spring of the armature. It is estimated that the lag in these pens was not more than 0.001 second. One pen recorded the transits of the meniscus, the seconds given by the pendulum clock, and the marks manually impressed by the key, IK, to identify the seconds of the clock. The other pen recorded the seconds and tenths of seconds given by another clock driven by a synchronous electric motor. This electric clock was made by the General Radio Company and is their type 511S. The rate of this clock depended on the frequency of alternations of the power supplied by the Cambridge Electric Light Company. The records of this clock were only used to subdivide the full seconds given by the pendulum clock. Unless the rate of this electric clock varied by more than 1% within the second in which the transit of the meniscus occurred, its records are reliable to within 0.01 second for the purpose of subdividing the full seconds. With this arrangement the velocity of the paper tape would have to vary by 10% within the 0.1 second in which the transit occurred to cause an error of 0.01 second. It seems probable that the timing mechanism was reliable to within 0.01 second.

After many months of apparently fruitless effort and disappointments following changes in the equipment, the eventful day arrived when seven successive runs with water gave results for the time of flow which differed by only 0.01 second between the highest and lowest of the seven, out of a total of 618 seconds. This demonstrated that the optical effect of the passage of the meniscus was sufficiently definite and that the timing mechanism and temperature control were adequate. But these observations were made on one filling of the viscometer. The problem of cleaning and refilling the

viscometer without changing the period still gave us much trouble and indeed has not yet been completely solved. Absolute cleanliness is essential as a trace of grease or dust will give erratic results. Cleansing reagents can make as much trouble as the more obvious forms of dirt. Indeed on one occasion the period increased from one filling to the next by nearly a second and the new high value for the period persisted for about two months in spite of drastic cleaning and then suddenly and inexplicably returned to its old value. The most plausible hypothesis to account for such a large change is that a speck of dust had become lodged in the capillary although it was not revealed by careful inspection. We have found it essential that every thing which enters the viscometer (water, solutions, cleansing reagents, and the air used to dry the instrument) should be filtered through a sintered glass filter or a platinum sponge filter. The sintered glass filter was made for us of Pyrex glass by H. E. Bent.¹²

If the volume of the working liquid is varied the hydrostatic head will change and this will influence the period. Therefore we filled the viscometer by means of a special pipet with a goose-neck delivery tube designed to deliver as definite a volume as possible each time and yet permit the actual volume delivered in each experiment to be determined by weighing the pipet to milligrams before and after filling the viscometer. If the amount actually delivered differed by a significant amount from the standard volume (about 60 ml.) a correction to the measured time was applied, based on the results of special experiments showing that a surplus of 0.013 ml. caused the time of flow to be increased by 0.01 second. After skill in the manipulation of the pipet had been acquired by practice the volume correction averaged less than 0.01 second. The delivery tube was broken accidentally twice during the experiments and after being repaired delivered a slightly different standard volume which caused a corresponding difference in the water value. The water value was also changed by slight but significant amounts in the course of the work by adjustments in the optical system, by remounting the viscometer in its frame, and by a redetermination of the 25° mark on the Beckmann thermometer after it had been lost by overheating. All of these changes, however, affect the solutions to the same extent as the water. Since we could not be sure that the water value would remain unaltered it was our invariable practice to measure water and a solution alternately and always measure the water at least once on the same day that the solutions were measured. After the technique had been perfected successive measurements of the time of flow without refilling rarely differed by more than 0.02 second and different fillings made on different days usually agreed within 0.03 second although occasionally much greater variations occurred for the reasons explained above. The viscosity of the solutions is computed with a water value determined within four hours of the time of measuring the solution instead of an average (or standard value) and the results for the relative viscosity of the solutions thus obtained are more consistent than can be obtained by assuming the water value to be unchanged.

The kinetic energy correction was applied to the results in all cases in which it amounted to 0.001% or more, in accordance with a method suggested by Bingham.¹³ The greatest correction which needed to be applied was only 0.00013 in the case of 0.02 molal sucrose solution.

The density of the solutions enters into the calculations of the relative viscosity as a direct factor and therefore needs to be known with the same precision as the time of flow. For this reason the density of all of the solutions was determined by the use of pycnometers of about 50 cc. capacity. The densities were determined with greater precision than the time of flow could be determined.

Materials.—The water used both for making up the solutions and to determine the period of the viscometer was conductivity water, collected in contact with the laboratory

(12) W. E. Bruce and H. E. Bent, *THIS JOURNAL*, **53**, 990 (1931).

(13) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, 1922, p. 18.

air and kept in large Non-Sol bottles. Its conductivity was determined before it was used and if the conductivity was found to be abnormally high the water was rejected. The average conductivity was 1.0×10^{-6} at 25° . All of the materials used are believed to have contained no impurities in sufficient amounts to affect the results measurably. The most dangerous impurity would be specks of dust. The purest salts available by purchase were dissolved, filtered through sintered glass filters, crystallized, drained and washed in platinum Gooch crucibles in a centrifuge. This entire process was repeated several times for some salts, but not in all cases, depending on the purity of the salts as judged by the color in the flame or other tests. Potassium chloride was fused and the other salts subjected to prolonged drying in vacuum desiccators. The cesium nitrate was kindly prepared for us from the mineral pollucite by Professor Brainerd Mears of Williams College. Spectroscopic and chemical tests showed that this material was of the highest quality.

Two non-electrolytes, sucrose and urea, were studied in order to test the theoretical prediction that the viscosity-concentration curves for electrolytes and for non-electrolytes would have an essentially different shape at low concentrations. It was, therefore, especially important to ensure that these materials should be as free as possible from electrolytes. This was, of course, easily tested by measuring the conductivity of the solutions. The sample of sucrose was estimated by conductimetric analysis to contain about 0.001% of electrolytes which could not influence the viscosity measurably. Since dilute sucrose solutions are liable to change by inversion or fermentation, the solutions were measured as promptly as possible after they were prepared. A special experiment showed no measurable change in viscosity after standing for forty-eight hours.

Sterling's c. p. urea was treated twice by the procedure described above for salts. Solutions of urea may be slowly hydrolyzed to form ammonium carbonate, and this change was easily detected by a slow change in the conductivity.

The conductivity of our freshly prepared solution indicated that it had hydrolyzed to the extent of nearly 0.002%, which increased to nearly 0.02% after standing for twenty-four hours in the conductance cell (in contact with the platinum electrodes which may have catalyzed the reaction). The strongest urea solution measured was 0.2 molal and even assuming 0.02% hydrolysis, which is probably an overestimate since the viscosity measurements were made promptly after preparing the solution, the concentration of the ammonium carbonate would have been only 0.00004 molal and therefore could not have influenced the viscosity measurably.

The solutions were prepared by weighing out the solute and making up the solution to 1 liter in a volumetric flask at 25° .

The data on the solution of 0.1 *N* potassium chlorate are given in considerable detail in Table I in order to show the concordance of the data obtainable with our new procedure.

The first line gives the concentration, *c*, of the solution in moles per liter at 25° and the date of the experiment; the second line gives the density at 25° , based on 0.997074 for the density of water at the same temperature with the letters B, C, D designating the different pycnometers used and *av.* the average. The numbers 1, 2, 3, designate the successive measurements of the time of flow on the same filling of the viscometer. The viscometer was filled with solution giving the results shown in the second column, then washed and dried and filled with water giving the results shown in the third column and again filled with another portion of the same solution giving the results shown in the fourth column. The figures designated by

wt. are the weights of water or solution delivered by the filling pipet. The next line gives the volume correction (v. c.) in seconds to correct for the influence on the measured time of the variations in average hydrostatic head. The next line gives the average time of transit, t , with the volume correction applied. The next line gives the apparent viscosity, $d_c t_c / d_0 t_0$, before the kinetic energy correction has been applied, and the last line gives the corrected relative viscosity, η , after applying the kinetic energy correction.

TABLE I
DETAILED EXAMPLE OF DATA

Potassium chlorate $c = 0.100000$		11/25/31	
d B 1.004691	C 1.004689	D 1.004684	av. 1.004688
Liq.	Soln.	Water	Soln.
1	612.77	618.32	612.77
2	612.78	618.33	612.77
3	612.77	618.32	612.75
av.	612.77	618.32	612.76
wt.	61.090	60.635	61.094
v. c.	0.00	0.00	0.00
t	612.77	618.32	612.76
$d_c t_c / d_0 t_0$		0.99859	0.99858
Kinetic energy corr.		-0.00008	-0.00008
η		0.99851	0.99850

The data on the other solutions are given in a more abbreviated form in Table II to save space in printing. The column headings have the following significance: c , concentration in gram moles per liter, d_c is the density based on water at $25^\circ 0.997074$; t_c is the average time of flow for the solution; t_0 is the average time of flow for water; $d_c t_c / d_0 t_0$ is the apparent relative viscosity with no kinetic energy correction applied; K. E. corr. is the kinetic energy correction; η obs. is the measured viscosity relative to that of water at the same temperature; η comp. is the viscosity computed by the equations given below.

for KClO_3	$\eta = 1 + 0.0050 \sqrt{c} - 0.0309 c$
KCl	$\eta = 1 + .0052 \sqrt{c} - .0140 c$
KNO_3	$\eta = 1 + .0050 \sqrt{c} - .0531 c$
KBrO_3	$\eta = 1 + .0058 \sqrt{c} - .0008 c$
CsNO_3	$\eta = 1 + .0043 \sqrt{c} - .092 c$
NH_4Cl	$\eta = 1 + .00566 \sqrt{c} - .01439 c$
Sucrose	$\eta = 1 + .8786 c$
Urea	$\eta = 1 + .03784 c$

$\Delta\eta = \eta$ obs. - η comp. is the difference between the observed and computed viscosity.

Interpretation of the Results

In Figs. 4, 5 and 6 plots of the results are shown with relative viscosity as ordinate and concentration as abscissa. These curves and the data on

TABLE II
RELATIVE VISCOSITY OF SALT SOLUTIONS AT 25°
Potassium Chlorate

c	d_c	t_c	t_0	d_{ct_0}/d_0t_0	K. E. corr.	η obs.	η comp.	$\Delta\eta$ obs. - comp.
0.002001	0.997230	618.21	618.20	1.00017	0.00000	1.00017	1.00016	+0.00001
.005000	.997448	618.11	618.21	1.00021	.00000	1.00021	1.00020	+ .00001
.010000	.997830	617.86	618.22	1.00018	- .00001	1.00017	1.00019	- .00002
.020001	.998596	617.39	618.26	1.00012	- .00001	1.00011	1.00009	+ .00002
.050000	1.000892	615.68	618.28	0.99961	- .00004	0.99957	0.99957	- .00000
.100000	1.004688	612.76	618.32	.99858	- .00008	.99850	.99849	+ .00001
Potassium Chloride at 25°								
0.002004	0.997160	618.20	618.14	1.00019	0.00000	1.00019	1.00021	-0.00002
.005011	.997312	618.27	618.23	1.00030	.00000	1.00030	1.00030	+ .00000
.010020	.997550	618.08	619.11	1.00040	.00000	1.00040	1.00038	+ .00002
.020041	.998023	618.71	619.02	1.00045	- .00001	1.00044	1.00046	- .00002
.035072	.998730	618.24	618.96	1.00050	- .00001	1.00049	1.00048	+ .00001
.050103	.999443	617.79	618.99	1.00043	- .00002	1.00045	1.00046	- .00001
		616.88	618.03	1.00051	- .00002			
.075154	1.000625	616.15	618.08	1.00042	- .00003	1.00039	1.00037	+ .00002
.100205	1.001790	615.85	618.08	1.00029	- .00004	1.00025	1.00024	+ .00001
.150309	1.004128	613.71	618.05	1.00000	- .00006	0.99994	0.99991	+ .00003
.200411	1.006463	612.14	618.15	0.99960	- .00009	.99951	.99952	- .00001
Potassium Nitrate at 25°								
0.001000	0.997134	618.86	618.82	1.00012	-0.00000	1.00012	1.00010	+0.00002
.002000	.997200	618.82	618.82	1.00013	- .00000	1.00013	1.00012	+ .00001
.005000	.997390	618.67	618.79	1.00012	- .00000	1.00012	1.00009	+ .00003
.010004	.997709	618.39	618.81	0.99996	- .00001	0.99995	0.99997	- .00002
.020000	.998336	617.82	618.81	.99966	- .00002	.99964	.99964	- .00000
.050001	1.000192	615.92	618.78	.99849	- .00004	.99845	.99846	- .00001
.100000	1.003283	612.77	618.83	.99637	- .00009	.99628	.99627	+ .00001
Potassium Bromate at 25°								
0.002001	0.997315	618.80	618.79	1.00026	0.00000	1.00026	1.00026	+0.00000
.005000	.997698	618.70	618.81	1.00045	.00000	1.00045	1.00040	+ .00005
.010000	.998294	618.38	618.77	1.00059	- .00000	1.00059	1.00057	+ .00002
.020000	.999519	617.72	618.75	1.00078	- .00001	1.00077	1.00080	- .00003
.052994	1.003556	615.59	618.79	1.00130	- .00005	1.00125	1.00129	- .00004
.099999	1.009284	612.40	618.75	1.00186	- .00009	1.00176	1.00175	+ .00001
Cesium Nitrate at 25°								
0.000500	0.997140	618.19	618.20	1.00005 ₀	0.00000	1.00003	1.00005	-0.00002
.000500		618.83	618.86	1.00000 ₂	.00000			
.001000	.997205	618.20	618.28	1.00001 ₆	.00000	1.00003	1.00004	- .00001
.001000		618.82	618.88	1.00003 ₄				
.002000	.997350	618.07	618.24	1.00000 ₂	.00000	1.00000	1.00001	- .00001
		618.73	618.90	1.00000 ₂				
.005000	.997788	617.72	618.25	0.99985 ₈	- .00001	0.99986	0.99984	+ .00002
		618.28	618.80	0.99987 ₅				
.010000	.998517	617.66	618.84	0.99953 ₇	- .00002	.99952	.99951	+ .00001
.020000	.999953	616.43	618.93	0.99883 ₆	- .00004	.99876	.99877	- .00001
		616.29	618.83	0.99877 ₁				
Ammonium Chloride at 25°								
0.002000	0.997115	618.89	618.79	1.00020	0.00000	1.00020	1.00022	-0.00002
.005000	.997162	618.74	618.60	1.00031	.00000	1.00031	1.00033	- .00002
.009999	.997248	618.91	618.74	1.00045	.00000	1.00045	1.00042	+ .00003
.020000	.997423	618.81	618.71	1.00051	.00000	1.00051	1.00051	+ .00000
.050000	.997940	618.60	618.70	1.00054	- .00000	1.00054	1.00055	- .00001
.100005	.998789	617.87	618.70	1.00037	- .00001	1.00036	1.00035	+ .00001
.200000	1.000473	616.44	618.74	0.99968	- .00003	0.99965	0.99965	- .00000

TABLE III
RELATIVE VISCOSITY OF SOLUTIONS OF NON-ELECTROLYTES AT 25°
Sucrose

c	d_0	t_0	t_0	$d_{\text{obs}}/d_{\text{obs}0}$	K. E. corr.	η obs.	η comp.	$\Delta\eta$ obs. - comp.
0.000200	0.997094	618.34	618.23 ₅	1.00019	+0.00000	1.00009	1.00018	+0.00001
.000500	.997137	618.45	618.22	1.00043	+ .00001	1.00044	1.00044	+ .00000
.001000	.997194	618.75	618.27	1.00090	+ .00001	1.00091	1.00088	+ .00003
.002000	.997332	619.15	618.25	1.00172	+ .00001	1.00173	1.00176	- .00003
.005000	.997714	620.50	618.21	1.00435	+ .00003	1.00438	1.00439	- .00001
.010000	.998391	622.83	618.29	1.00867	+ .00007	1.00874	1.00879	- .00005
.020001	.999699	627.36	618.21	1.01747	+ .00013	1.01760	1.01757	+ .00003

Urea

0.002000	0.997106	618.32	618.30	1.00006	+0.00000	1.00006	1.00008	-0.00002
.005000	.997152	618.35	618.28	1.00019	.00000	1.00019	1.00019	+ .00000
.010001	.997230	618.42	618.30	1.00035	.00000	1.00035	1.00038	- .00003
.020000	.997390	618.54	618.27	1.00076	.00000	1.00076	1.00076	+ .00000
.050033	.997867	618.97	618.32	1.00185	+ .00001	1.00186	1.00189	- .00003
.099994	.998666	619.61	618.30	1.00372	+ .00002	1.00374	1.00378	- .00004
.199632	1.000252	620.98	618.29	1.00755	+ .00004	1.00759	1.00755	+ .00004

which they are based show that the prediction of Jones and Dole that even those salts which decrease the viscosity of water at moderate concentration

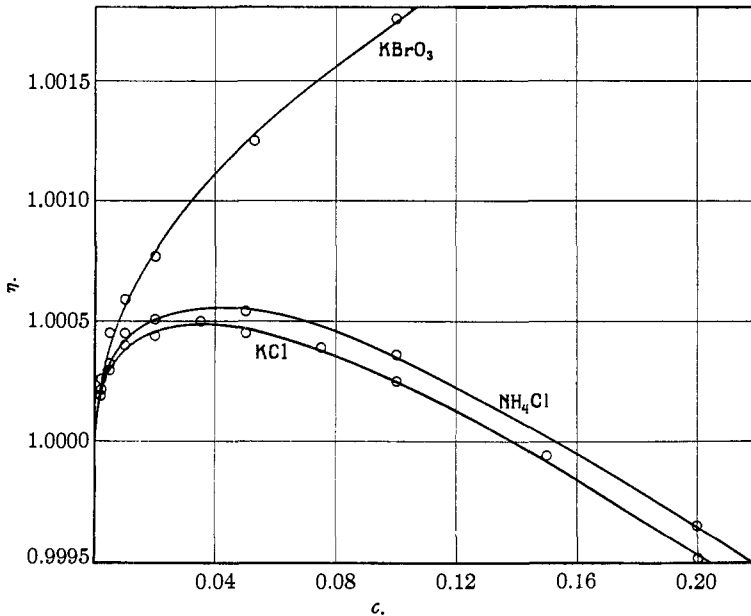


Fig. 4.—Relative viscosity-concentration curve for potassium bromide, ammonium chloride and potassium chloride.

will give an increased viscosity at sufficiently low concentration has been confirmed experimentally at 25° for five salts, potassium chlorate, potassium chloride, ammonium chloride, potassium nitrate and cesium nitrate.

In addition, the prediction has been confirmed by Joy and Wolfenden for potassium chloride, potassium chlorate, and rubidium nitrate at 18° and for rubidium nitrate at 35°. In the case of potassium bromate the viscosity remains greater than that of water throughout the range of concentration covered by our experiments (up to 0.1 molal).

Jones and Dole demonstrated that for barium chloride, which is presumably typical of the salts which increase the viscosity of water, the fluidity-concentration curves have a simpler form than the viscosity-concentration curves and that the equation $\varphi = 1 + A\sqrt{c} + Bc$ is valid up to 1 molal.

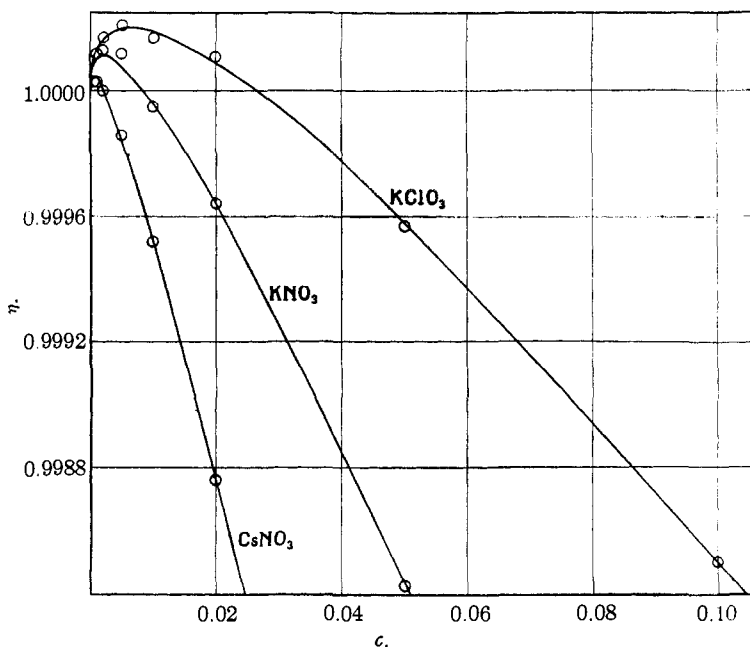


Fig. 5.—Relative viscosity-concentration curve for potassium chlorate, potassium nitrate and cesium nitrate.

In this equation A is expected to have a negative value for all salts and B may be either positive or negative, depending on the salt and temperature. On the other hand, for salts which diminish the viscosity of water this equation is probably not generally valid beyond 0.2 molal. For such salts it will probably be better to use an equation of similar form in terms of viscosity, namely, $\eta = 1 + A\sqrt{c} + Bc$, where the A is the same as the A in the fluidity equation except for a reversed sign, and the B will also be reversed in sign and identical in value within the limit of error to which B has yet been determined. The substantial equivalency of the two forms for dilute solutions ($c \ll 1$) will be apparent by replacing φ by $1/\eta$ and taking the reciprocal of both sides of the equation, making due allowance for

the fact that A and B are much smaller than unity for all salts yet studied. When the equation is stated in terms of viscosity A is expected to be positive for all salts and zero for non-electrolytes. B may have either a positive or negative value depending on the salt and the temperature.

The equation $\eta = 1 + A\sqrt{c} \pm Bc$ may be readily transformed into $(\eta - 1)/\sqrt{c} = A \pm B\sqrt{c}$. This equation may therefore be most conveniently tested by plotting $(\eta - 1)/\sqrt{c}$ against \sqrt{c} which should give a straight line whose intercept on the vertical axis is A and whose slope is B .

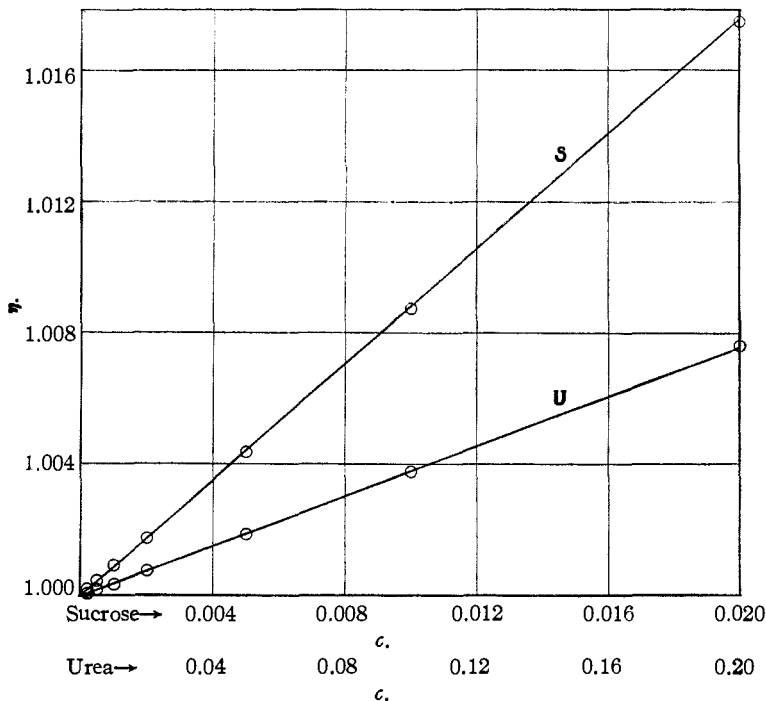


Fig. 6.—Relative viscosity-concentration curves for sucrose and urea.

As will be seen from Figs. 7 and 8 the plotted data lie on a straight line and the value for A is positive for all the salts and zero for sucrose and urea. The values for A and B were selected by the use of the method of least squares instead of by plotting because the algebraic procedure is more precise and entirely objective. In the last column of Table III are given the differences between the observed viscosity and the viscosity computed by this equation with the values of coefficients A and B given in Table IV below. The average deviation, disregarding the sign, is 0.0015% which corresponds to an error in the time of flow of only 0.01 second. The maximum deviation for any of the forty-two solutions measured is 0.005% which corresponds to an error in the time of flow of 0.03 second.

This maximum deviation is probably accounted for by the fact that this particular measurement was made during a period of hot weather when the temperature of the room was above 25° which makes the control of the temperature less satisfactory than during cooler weather. The Jones and Dole equation is therefore confirmed for these six salts within the limit of error of the experiments.

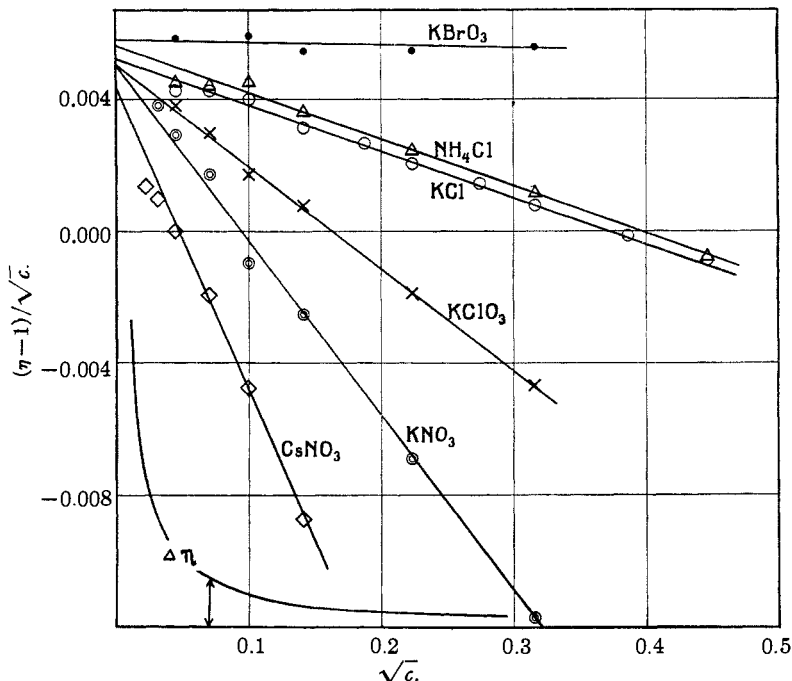


Fig. 7.— $(\eta - 1)/\sqrt{c}$ against \sqrt{c} for electrolytes: the curve $\Delta\eta$ shows graphically how a variation of 0.01% in η affects the data as plotted above.

The experimental values of A and B , computed by the method of least squares from the data above to fit the Jones and Dole equation, are shown in the following table and compared with the theoretical values of A computed by the Falkenhagen and Vernon equation. This equation reduces to the following form for the case of a uni-univalent salt

$$A = \frac{1.45}{\eta_0 \sqrt{2D_0T}} \left[\frac{l_1 + l_2}{4l_1 l_2} - \frac{(l_1 - l_2)^2}{(3 + \sqrt{2})l_1 l_2 (l_1 + l_2)} \right]$$

where η_0 and D_0 are the absolute viscosity and dielectric constant of water at the temperature T and l_1 and l_2 are the equivalent conductances of the two ions at zero concentration.

The coefficient of the linear term (B) varies much more from salt to salt and has a greater temperature coefficient than the coefficient of the square root term (A). For most salts the sign of B will be positive in the viscosity

TABLE IV
VALUES OF THE CONSTANTS IN THE EQUATION $\eta = 1 + A\sqrt{c} + Bc$

Solute	B	A	A
	J. & D. experimental	J. & D. experimental	F. & V. theoretical
KCl	-0.0140	0.0052	0.0050
KClO ₃	- .0309	.0050	.0055
KBrO ₃	- .0008	.0058	.0058
KNO ₃	- .0531	.0050	.0052
NH ₄ Cl	- .01439	.0057	.0050
CsNO ₃	- .092	.0043	.0051
Sucrose	+ .8786	0	0
Urea	+ .03784	0	0

equation (or negative in the fluidity equation). Little is known as yet in regard to the factors which influence the sign and value of this coefficient.

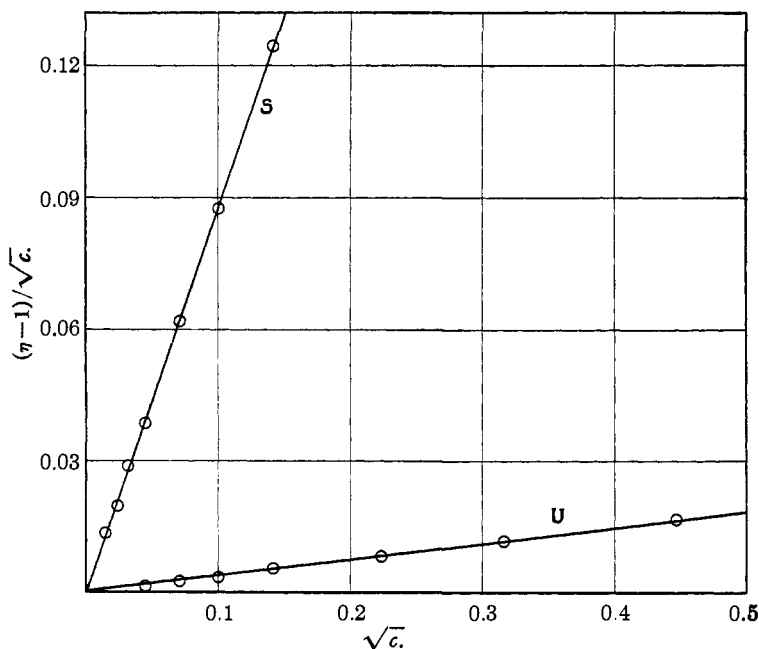


Fig. 8.— $(\eta-1)/\sqrt{c}$ against \sqrt{c} for the non-electrolytes sucrose and urea.

The agreement between the observed and computed values is good and supports the Falkenhagen and Vernon equation for A . According to the Falkenhagen and Vernon equation the value of A for any given salt, solvent, and temperature will depend mainly on the valence type of the salt and to a less extent on the mobilities of the ions concerned. The results obtained up to the present time are in harmony with these conclusions as far as they go.

The results on extremely dilute solutions of sucrose and urea confirm

the theoretical prediction that square root term will be absent for non-electrolytes.

It is planned to continue the work in this Laboratory by measurements on other salts, at other temperatures, and in other solvents.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for the expenses of this investigation.

Summary

1. A new method for the automatic measurement of the time of flow of the liquid in a viscometer of the Ostwald type by means of a photoelectric cell is described. The elimination of the psychological errors inherent in the older technique permits greater precision.

2. The viscosities of dilute aqueous solutions of six salts and two non-electrolytes have been measured at 25°.

3. The results confirm the prediction made by Jones and Dole based on the Debye theory of interionic attraction that all salts will increase the viscosity of water if measured at sufficiently low concentration, including those salts which give a diminished viscosity at moderate concentrations.

4. The results confirm the Jones and Dole equation for the viscosity of solutions of electrolytes.

5. The results also confirm the Falkenhagen and Vernon equation for the computation of the influence of interionic attraction on the viscosity.

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The Solubility of Nitrates in Anhydrous Acetic Acid

BY ARTHUR W. DAVIDSON AND HARRIET A. GEER

Introduction

Although several investigations have recently been carried out upon various properties of solutions of salts in anhydrous acetic acid, quantitative solubility data for such solutions are still very meager. Aside from some early work on halides of mercury,¹ calcium and magnesium,² and antimony,³ and the studies of acetates (bases in this solvent) reported from this Laboratory,⁴ the only accurate solubility measurements have been those of Seward and Hamblet⁵ on potassium perchlorate and potassium nitrate, at a single temperature, in the presence of varying amounts of added salts.

(1) Étard, *Ann. chim. phys.*, [7] **2**, 555 (1894).

(2) Menshutkin, *Z. anorg. Chem.*, **54**, 89 (1907).

(3) Menshutkin, *J. Russ. Phys.-Chem. Soc.*, **43**, 1785 (1911); *Chem. Abstracts*, **6**, 1280 (1912).

(4) (a) Davidson and McAllister, *THIS JOURNAL*, **52**, 507, 519 (1930); (b) Davidson and Griswold, *ibid.*, **53**, 1341 (1931).

(5) Seward and Hamblet, *ibid.*, **54**, 554 (1932).