for eighteen months and have found no change which would justify an assumption of a change in degree of association on drying.

Summary

Carbon tetrachloride which has been in contact with pure phosphorus pentoxide in a sealed tube for five years at room temperature shows no change in boiling point or molecular weight, by the Victor Meyer vapor density method, which can be attributed to intensive drying and consequent change in degree of association.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE VISCOSITY OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES WITH SPECIAL REFERENCE TO BARIUM CHLORIDE

BY GRINNELL JONES AND MALCOLM DOLE

RECEIVED JUNE 12, 1929 PUBLISHED OCTOBER 5, 1929

Introduction

A number of related properties of barium chloride solutions have been determined with a high precision over a considerable range of concentration in the hope that a study of the data in the light of modern theories of solutions might reveal new relationships between the properties and new laws for the variation of the properties with the concentration. The first paper[1] of this series records the results of measurements of transference numbers by both the analytical- and electromotive-force methods which resulted in the discovery of a new and exact relationship between the transference number and the concentration. This, the second paper of the series, records measurements at 25° of the viscosity of barium chloride solutions relative to that of water, over the range 0.005 to 1.0 molal. This investigation has resulted in the discovery of a new exact relationship between the fluidity and the concentration. A later paper will give data on the conductivity of the same solutions.

Historical Review.—Poiseuille,[2] the great pioneer in research on viscosity, found that some salts increase the viscosity of water whereas others decrease the viscosity. Sprung[3] appears to have been the first to measure solutions of barium chloride and found that it increased the vis-

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[1] Grinnell Jones and Malcolm Dole, THIS JOURNAL, 51, 1073 (1929). We regret that in this paper we implied that Washburn found it necessary to filter his solutions during his work on transference numbers [THIS JOURNAL, 31, 322 (1909)]. This implication is, however, misleading as Washburn actually avoided the filtration of his solutions.

[2] Poiseuille, *Ann. chim. phys.*, [3] **21**, 76 (1847).

[3] Sprung, *Ann. Physik*, **159**, 1 (1876).

cosity of water. Arrhenius[4] made some viscosity measurements on solutions. He found that the change in viscosity caused by the addition of a salt was roughly proportional to the concentration at low concentrations but increased more rapidly than the concentration at moderate concentrations (1 normal). He proposed a new formula for the relationship between viscosity and concentration, namely, $\eta = A^c$, where η is the relative viscosity compared to that of water at the same temperature and A is a constant for any given salt and temperature. This equation has been tested by Reyher,[5] by Wagner[6] and by others and found to hold within a few tenths of 1 per cent. between $^1/_8$ and $^1/_2$ normal and within about 1% up to 1 normal.

Sutherland[7] suggests that the depolymerization of triple water molecules by the dissolved salt causes diminution in viscosity.

The next outstanding investigator on this subject was Grüneisen,[8] who made a careful and critical study of the experimental technique with the Ostwald form of viscometer and then made measurements, which are probably more precise than any previously made, on aqueous solutions of sixteen salts and of sucrose over a wide range of concentration. Grüneisen made measurements with more dilute solutions than his predecessors and thereby discovered that the viscosity–concentration curves, instead of becoming more nearly straight at the dilute end, exhibit a negative curvature. This behavior is not in accord with Arrhenius' equation which must, therefore, be regarded as invalid, even as a limiting law for low concentrations. Grüneisen found that both the salts which increase the viscosity and those which decrease the viscosity show a negative curvature of the viscosity–concentration curves at low concentrations. The viscosity–concentration curves for salts which increase the viscosity are so nearly straight lines that the deviations would not be readily apparent on the scale which could be printed on this page, but the deviations are clearly systematic and greater than the experimental error. For a salt which increases the viscosity of water, the curve starts at $\eta = 1.0000$ when $c = 0$ with a positive but diminishing slope, giving a negative curvature, then straightens out, passes through a point of inflection at moderate concentrations (about 0.3 molal), and then the curvature becomes slightly positive. These changes in the curve are more apparent if, following a suggestion of Grüneisen, we plot $(\eta - 1)/c$ against c (or some root of c for the sake of spreading out the points at the lower concentrations). $(\eta - 1)/c$ is strictly the slope of the chord connecting a point on the $\eta - c$ curve with the origin, but it is approximately the same as the slope of the $\eta - c$ curve at the same point.

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[4] S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

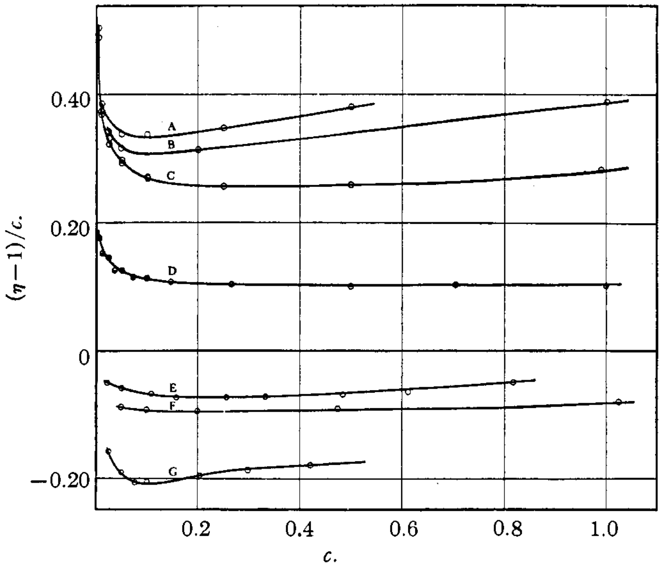
[5] R. Reyher, *ibid.*, **2**, 744 (1888).

[6] J. Wagner, *ibid.*, **5**, 31 (1890).

[7] W. Sutherland, *Phil. Mag.*, [5] **50**, 481 (1900).

[8] E. Grüneisen, *Wiss. Abh. Phys. Techn. Reichsanstalt*, **4**, 151, 237 (1905).

If the relationship between the viscosity and concentration were a linear one, $(\eta - 1)/c$ would be a constant and its plot would be a straight line parallel with the c axis. Figure 1 gives such curves for several salts (magnesium sulfate (A), lithium iodate (B), potassium iodide (F) from data by Grüneisen; lithium nitrate (D) from data by Grüneisen and by Applebey; cesium nitrate at 25° (E) and at 0° (G) from data by Merton; and the data on barium chloride (C) reported below in this paper). As will be seen, the values of $(\eta - 1)/c$ decrease rapidly with increase of concentration at low concentrations, pass through a minimum and then slowly rise. A downward slope in this curve corresponds to a negative curvature in the $\eta - c$ curve. Grüneisen's paper gives similar curves for many other salts. Grüneisen proposed the equation



Curve A, $MgSO_4$ at 18° after Grüneisen; B, $LiIO_3$ at 18° after Grüneisen; C, $BaCl_2$ at 25°, Jones and Dole; D, $LiNO_3$ at 18° ◒ Applebey, ● Grüneisen; E, $CsNO_3$ at 25° after Merton; F, KI at 18° after Grüneisen; G, $CsNO_3$ at 0° after Merton.

Fig. 1.—$(\eta-1)/c$ against c.

$$\eta = 1 + Aic + B(1 - i)c + Cc^2$$

where i is the degree of dissociation as computed from the conductivity and A, B and C are constants for any given salt and temperature. A is supposed to represent the effect of the friction of the ions on the water, B that of the un-ionized molecules on the water and C that of the ions and molecules on each other. Grüneisen was able to select values for the empirical constants to make the equation fit his data, although negative values of A

and B had to be selected in many cases. However, his equation is not a useful interpolation formula permitting the computation of the viscosity at any concentration owing to the presence of the parameter i, which is itself a function of the concentration. Grüneisen pointed out that the smaller the electrical mobility of an ion the greater is its influence in increasing the viscosity of solutions.

Schneider[9] has made measurements similar to Grüneisen's with many other salts, although with less precision, and obtained similar results, showing that Grüneisen's observation of negative curvature of the viscosity–concentration curves at low concentrations is a general one. He made no advance in the interpretation of the phenomena.

Among the many investigators of the viscosity of solutions the next who deserves mention in this brief review is Applebey,[10] who made careful measurements at 25, 18 and 0° on solutions of lithium nitrate, a salt which increases the viscosity of water. Applebey's work extended over a wide range of concentration, including solutions even more dilute ($c = 0.00724$) than those studied by Grüneisen. His results show that the negative curvature becomes more pronounced at very low concentrations (see Fig. 1, Curve D) and that the curvature in this region is much greater than would be predicted by Grüneisen's equation. He also showed that the negative curvature becomes greater as the temperature is lowered. Applebey made the suggestion that when a salt is dissolved in water there are two different effects on the viscosity: (1) a depolymerization of triple water molecules, $(H_2O)_3$, to form single molecules, which tends to diminish the viscosity; (2) an increase in viscosity due to the presence of the ions of the salt and the un-ionized molecules of the salt. It is assumed that the friction depends primarily on the size of the ion or molecule. In the case of salts composed of ions which are not greatly hydrated, such as the Cs^+, Rb^+, K^+, NH_4^+, I^-, Br^- or NO_3^- ions, the increase due to the friction of the ions on the water is less than the diminution of the viscosity due to depolymerization of the water, giving a net decrease in viscosity or a negative slope of the viscosity–concentration curve. Most ions, however, are sufficiently hydrated so that the increase in viscosity due to their presence more than offsets the decrease due to depolymerization, giving a net increase in viscosity with concentration. Applebey attempted to derive an equation connecting viscosity and concentration but the equation which he obtained contains the degree of dissociation of the salt computed from the conductivity, the association factor of water, and the hydration numbers of the ions (the number of molecules of water attached to each ion to form the hydrated ion). However, the exact form of the function connecting any of these variables with the concentration is unknown, and, therefore,

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[9] K. Schneider, "Dissertation," Rostock, 1910.

[10] M. P. Applebey, *J. Chem. Soc.*, 97, 2000 (1910).

Applebey's equation does not give even by implication the exact functional relationship connecting viscosity and concentration. In order to make his equation give any negative curvature at low concentrations, it was necessary for him to assume that the ions have a greater friction against the water than the un-ionized salt, which is hardly in accord with his assumptions that the volume of the particles is the important factor in the viscosity, or else that the ions are less effective than undissociated salt molecules in depolymerizing the water. But even with these assumptions, his equation cannot predict the rapid change in slope which actually occurs and, of course, the modern view that solutions of strong electrolytes are completely dissociated makes the attempt to account for the negative curvature in this manner entirely illusory. Applebey used his equation as a means of computing hydration numbers of the ions and obtained results for lithium nitrate which he regarded as plausible, but for cesium nitrate he obtained negative hydration numbers which are obviously absurd. Curve D in Fig. 1 shows the good agreement between Grüneisen's and Applebey's data on lithium nitrate at 18° and also the sharp curvature at low concentrations.

The viscosity–concentration curves for salts which diminish the viscosity of water are more complicated than for salts which increase the viscosity. The behavior at extreme dilutions has never been adequately investigated, but at the lowest concentrations for which data are available the curve has a slight negative curvature. These curves then pass through a point of inflection at moderate concentrations (about 0.1 to 0.2 molal), and have a positive curvature at all higher concentrations. The viscosity passes through a minimum in the neighborhood of one molal and has a positive slope at higher concentrations and at very high concentrations may again become greater than that of water.

The work of Merton[11] on cesium nitrate appears to be the most accurate and extensive study of a salt which diminishes the viscosity of water. His work confirms the observation of Applebey on lithium nitrate that at low temperatures negative slopes and negative curvatures are more pronounced than at higher temperatures. Merton made no theoretical advances. His data on cesium nitrate are shown in Fig. 1, Curves E and G.

The various hypotheses which have been suggested to account for "negative viscosity" are discussed at considerable length by Rabinovich.[12] He concludes that depolymerization of water molecules must be responsible for "negative viscosity."

It is apparent that although the general shape of the viscosity–concentration curves has been established, the phenomena at extreme dilutions have not been adequately investigated, and no one has yet found an exact general equation connecting viscosity and concentration.

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[11] T. R. Merton, *J. Chem. Soc.*, **97**, 2454 (1910).

[12] A. I. Rabinovich, THIS JOURNAL, **44**, 954 (1922).

Measurements of the viscosity of barium chloride solutions have been carried out by Sprung[3] at 18°, by Arrhenius[4] at 17.6°, by Wagner[6] at 25°, by Schneider[9] at 18° and by Herz[13] at 25°. Although the earlier work makes it clear that barium chloride increases the viscosity of water, the available data on this salt are lacking in precision and do not cover the lower range of concentration.

Experimental Part

The viscometer was of the Ostwald type made of quartz in accordance with the recommendations of Washburn and Williams,[14] except that a small bulb was blown between the lower mark on the upper reservoir and the capillary as suggested by Chadwell.[15] The capillary was 17.0 cm. long and its effective average radius was 0.026 cm. All measurements were made at 25°. The thermostat showed an extreme variation during the experiments of only 0.003°. The viscometer was permanently mounted in a stiff brass frame which was designed so that it could be attached to a rigid frame in a definite position inside the thermostat; but in spite of our efforts to ensure stability and reproducibility in the mounting, a major operation on the building produced an unavoidable disturbance in the mounting of the viscometer. During the first part of the work one end of the building (the Jefferson Physical Laboratory) was supported on jacks while repairs were being made on the foundations. During this period the time of flow of water in our viscometer was 342.54 seconds (see Table I). Then during the period beginning on August 30 and completed on September 2, the jacks were lowered, permitting one end of the building to move onto its new foundations. Following this event we found that the water value of our viscometer had changed to 342.33 seconds, or 0.21 second faster (see Table I). The data are therefore divided into two series, the first series including all measurements before September 2, which are computed with 342.54 as the water value, and the second series all made after this date which are computed with 342.33 seconds as the water value. The concentrations are expressed in gram molecules of barium chloride per liter. All of the data for a given concentration are grouped together in the table to facilitate comparison and averaging. In comparing the time of flow of an experiment in the first series with one in the second, proper allowance must be made for the change in the water value.

We found it advisable to fill the viscometer with sulfuric–chromic acid cleaning mixture and allow it to stand overnight at frequent intervals to ensure proper drainage. In order to avoid dust particles, everything that went into the viscometer—the water, the solutions, the cleaning mixtures and wash waters and the air used to dry the instrument between experiments—was passed through a sintered Jena glass filter. After this precaution was adopted only one experiment out of 39 had to be rejected on account of dust particles, which shows that this filtration was very helpful.

The so-called kinetic energy correction has been applied in accordance with the method recommended by Bingham,[16] but since there is some question as to the magnitude of this correction[17] we give our results both with and without the correction and have designed our viscometer so as to make the correction small. In our experiments this

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[13] W. Herz, *Z. anorg. Chem.*, **89**, 393 (1914).

[14] E. W. Washburn and G. T. Williams, THIS JOURNAL, **35**, 737 (1913).

[15] H. M. Chadwell, *ibid.*, **48**, 1915 (1926).

[16] See E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, **1922**, p. 18.

[17] N. E. Dorsey, *Phys. Rev.*, **28**, 833 (1926); W. Riemann III, THIS JOURNAL, **50**, 46 (1928).

correction has its maximum value of 0.14% with the molar solutions and falls off with dilution to 0.013% with 0.1 molar solution.

Measurement of Time of Flow.—The standard clock of the Jefferson Physical Laboratory, which has been proved by many tests to be sufficiently constant for our purpose, was used as our time standard. This clock has an attachment which gives a momentary electric impulse once every second. By means of a relay and induction coil the electric impulses from the clock produced a spark between two platinum points every second. This spark burned a hole in moving paper tape (stock market ticker tape) which passed at a constant velocity through the spark gap. The moment of passage of the meniscus past the marks was recorded on the same tape by touching a tapping key which also produced a spark. The motor which drove the paper tape was designed as a constant speed motor and a constant speed governor of the centrifugal type was added. The velocity of the tape was adjustable by means of the governor and in the final experiments was always within the limits of 9 to 12 cm. per second. Careful test indicated that this device recorded the moment of touching the tapping key within 0.01 second. There is, however, a psychological lag of unknown and variable amount between the observation of the passage of the meniscus past the mark and the tapping of the key with the finger. If this lag were equal at the beginning and the end of the time interval being measured, it would make no error. Therefore, the shape of the

TABLE I

RECORD OF EXPERIMENTAL DATA ON TIME OF FLOW OF WATER THROUGH VISCOMETER AT 25°

Series I

Time

	342.54	342.67	342.60	342.59	342.58	342.51
	342.44	342.70	342.56	342.61	342.57	342.52
	342.46	342.59	342.55	342.52	342.67	....
	342.48	342.65	342.52	342.47	342.59	....
	342.47	342.60	342.57	342.49	342.51	....
	342.48	342.49	342.58	342.49	342.64	....
	342.53	342.60	342.55	342.51	342.55	....
	342.50	342.62	342.59	342.57	342.53	....
	342.46	342.67	342.55	342.52	....	....
	342.51	342.57	....	342.49	....	....
	342.49	342.59	....	342.49	....	....
	342.54	342.62	....	342.49	....	....
	....	342.63	....	....	....	....
	....	342.63	....	....	....	....
Average	342.49	342.61	342.56	342.52	342.58	342.51

Mean for Series I, 342.54 seconds.

Series II

Time

	342.35	342.28	342.32	342.28	342.35	342.35	342.34	342.36	342.34
	342.35	342.25	342.26	342.28	342.30	342.34	342.38	342.40	342.34
	342.31	342.39	342.26	....	342.32	....	....	342.38	....
	342.31	342.30	....	....	....	....	....	....	....
	342.34	342.27	....	....	....	....	....	....	....
Average	342.33	342.30	342.28	342.28	342.32	342.35	342.36	342.38	342.34

Mean for Series II, 342.33 seconds.

viscometer at and immediately above the upper and lower marks was made as nearly identical as possible by an expert glass blower and care was taken to ensure that both marks were equally well illuminated in order that the two events being timed should be as nearly as possible identical. Much practice is also helpful in attaining precision, just as it is in many other endeavors which depend upon exact coördination of eye and hand. During the first series, the time of flow with water was measured 57 times on six different days with six independent fillings of the viscometer, giving an average of 342.54 seconds. The extreme variation between the highest and lowest of the 57 measurements was 0.26 second. The average was probably correct within 0.03 second or 0.01%. (The probable error of the mean when computed by Bessell's formula is 0.005 second.) During the second series with nine different fillings with water and 27 measurements, the average was 342.33 seconds and the extreme variation was 0.15 second. For the reasons explained above these averages are not comparable.

The experimental data on water are recorded in Table I and the solutions in Table II. The viscometer was cleaned, dried and refilled with water or barium chloride for each experiment. From 2 to 14 runs were made on

TABLE II

VISCOSITY OF BARIUM CHLORIDE SOLUTIONS AT 25°

Gram mole/ liter	Density, d_c	Av. time, sec., t_c	Water value, sec., t_0	$\frac{d_c t_c}{d_0 t_0}$	Kinetic corr.	Viscosity, η	Correction to round concn.	Viscosity, η at round concn.
0.004996	0.99823	342.76	342.33	1.00242	+0.0000$_2$	1.0024$_4$	+0	1.0024$_4$
.005000	.99819	342.80	342.33	1.00250	.0000$_2$	1.0025$_2$	+0	1.0025$_2$
						Mean η at c = 0.005,		1.0024$_8$
.010055	.99887	342.97	342.33	1.00368	.0000$_3$	1.0037$_1$	−0.00001	1.0037$_0$
.009990	.99881	343.00	342.33	1.00369	.0000$_3$	1.0037$_2$	+0	1.0037$_2$
						Mean η at c = 0.01,		1.0037$_1$
.024988	1.00161	343.51	342.33	1.00802	.0000$_5$	1.0080$_7$	+0	1.0080$_7$
.024995	1.00160	343.61	342.33	1.00830	.0000$_5$	1.0083$_5$	+0	1.0083$_5$
						Mean η at c = 0.025,		1.0082$_1$
.048598	1.00587	344.34	342.54	1.01413	.0000$_8$	1.0142$_1$	+0.0003$_5$	1.0145$_6$
.048598	1.00587	344.39	342.54	1.0142$_7$	.0000$_8$	1.0143$_5$	+ .0003$_5$	1.0147$_0$
.049960	1.00615	344.24	342.33	1.0147$_4$	.0000$_8$	1.0148$_2$	+ .0000$_1$	1.0148$_3$
.049960	1.00615	344.25	342.33	1.0147$_7$	.0000$_8$	1.0148$_5$	+ .0000$_1$	1.0148$_6$
						Mean η at c = 0.05,		1.0147$_4$
.09996	1.01520	345.30	342.33	1.0270$_2$	.0001$_3$	1.0271$_5$	+ .0000$_1$	1.0271$_6$
.09996	1.01520	345.28	342.33	1.0269$_6$	.0001$_3$	1.0270$_9$	+ .0000$_1$	1.0271$_0$
.09997	1.01497	345.25	342.33	1.0266$_4$	.0001$_3$	1.0267$_7$	+ .0000$_1$	1.0267$_8$
.09997	1.01497	345.35	342.33	1.0269$_3$	.0001$_3$	1.0270$_6$	+ .0000$_1$	1.0270$_7$
.09997	1.01497	345.33	342.33	1.0268$_7$	.0001$_3$	1.0270$_0$	+ .0000$_1$	1.0270$_1$
						Mean η at c = 0.10,		1.0270$_4$
.24990	1.04212	348.55	342.33	1.0641$_7$	.0002$_8$	1.0644$_5$	+ .0000$_3$	1.0644$_8$
.24990	1.04212	348.47	342.33	1.0639$_3$	.0002$_8$	1.0642$_1$	+ .0000$_3$	1.0642$_4$
.24948	1.04210	348.50	342.33	1.0640$_0$	.0002$_8$	1.0642$_8$	+ .0001$_3$	1.0644$_1$
						Mean η at c = 0.25,		1.0643$_8$
.4972	1.08663	354.61	342.54	1.1282$_2$	.0005$_6$	1.1287$_8$		
.4972	1.08663	354.65	342.54	1.1283$_5$	.0005$_6$	1.1289$_1$		
.4959	1.08640	354.46	342.33	1.1282$_0$	.0005$_6$	1.1287$_6$[a]		
				Mean η at c = 0.4972,		1.1289$_3$		
.9913	1.17358	372.26	342.54	1.2791$_5$	.0014$_4$	1.2805$_9$		
.9913	1.17358	372.20	342.54	1.2789$_5$	.0014$_4$	1.2803$_9$		
				Mean η at c = 0.9913,		1.2804$_9$		

[a] This figure is corrected to c = 0.4972 by adding +0.0003$_5$, giving 1.1291$_1$ and averaged with the two above, giving 1.1289$_3$.

each filling and the time of each is recorded in Table I to show the concordance of the data. The average time only is recorded for the solutions to save space.

Analysis and Interpretation of our Data on Barium Chloride.—The data recorded in Table II were then brought to round concentrations by applying very slight corrections and then averaged, except in the case of the two higher concentrations where the concentrations actually used were so far from the round concentrations that any attempt to correct them was thought to be inadvisable at this stage of the interpretation of the data. The viscosities thus obtained are shown in Col. 2 of Table III. Then we plotted the viscosity against the concentration and obtained a curve which is approximately straight but with a negative curvature at the dilute end, a point of inflection at a concentration of about 0.4 molal, and a slight positive curvature at the upper end. These deviations from linearity are apparent from Col. 3 of Table III, which gives the values of $(\eta - 1)/c$, which would be a constant if the line were straight. These values are plotted in Fig. 1, Curve C. We next tested the Arrhenius equation, $\eta = A^c$, or $\log \eta = c \log A$. If this equation holds, $(\log \eta)/c$ should be a constant, but it is evident from Col. 4 that $(\log \eta)/c$ is by no means a constant, especially at low concentrations, so that the Arrhenius equation must be rejected. Bingham[18] has pointed out that in the case of mixtures of organic liquids the relationships are simpler if the computation or curves, instead of being based on viscosity, are based on its reciprocal—the fluidity. This suggested that we try the fluidity in the case of aqueous solutions of electrolytes. Column 5 gives the fluidity, φ, at each concentration and Col. 6 the value of $(\varphi - 1)/c$. As will be seen, these values are by no means constant, showing that the fluidity is not a linear function of the concentration. Although the fluidity–concentration curve has a positive curvature at the dilute end (corresponding to the negative curvature of the viscosity–concentration curve) it has no point of inflection and no double curvature (up to 1 molal at least), and therefore evidently has a simpler form than the viscosity–concentration curve.

It was evident from our study of our data reinforced by data on other salts by Grüneisen, Applebey, and Merton that, although the principal effect of dissolved salts on viscosity or fluidity is proportional to the concentration, there must be some effect which is of relatively greater importance in dilute solutions and which is responsible for the curvature found in the dilute end of the viscosity–concentration and of the fluidity–concentration curves. Furthermore, this effect always tends to increase the viscosity regardless of whether the sum of all of the effects of adding the salt is an increase or decrease of the viscosity. The interionic attraction theory of

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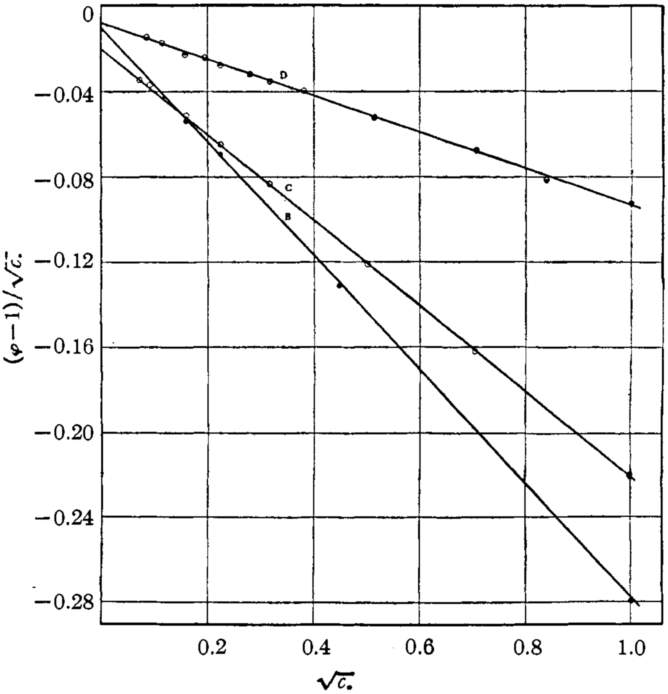
[18] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Company, Inc., New York, **1922**, Part II, Chapter I.

electrolytes gives a clue to the nature of this effect. According to this theory the ions tend to build and maintain a space lattice structure in the solution and any influence tending to disturb this space lattice arrangement whether by heat motion of the solvent molecules, the electrostatic force of charged electrodes in the solution, or any relative motion of parts of the liquid, will be opposed by the interionic forces. The forces which tend to maintain a space lattice structure of the ions, therefore, tend to stiffen the solution or increase its viscosity.[19] The effect of the interionic forces in opposing the motion of ions in an electric field has been shown by Debye and Hückel to be proportional to the square root of the concentration in very dilute solutions. It therefore occurred to us to try introducing a term proportional to the square root of the concentration into the equation for the fluidity, giving an equation of the form



Curve D, $LiNO_3$ at 18°, ◒ Applebey, ● Grüneisen; C, $BaCl_2$ at 25°, Jones and Dole; B, $LiIO_3$ at 18°, Grüneisen.

Fig. 2.—$(\varphi-1)/\sqrt{c}$ against $\sqrt{c}$.

$$\varphi = 1 + A\sqrt{c} + Bc$$

Since the interionic forces mentioned above tend to stiffen the solution or decrease its fluidity, it is to be expected that A will have a negative value

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[19] W. Sutherland, *Phil. Mag.*, [6] **14**, 1 (1907), suggests that interionic attraction should increase the viscosity.

for all strong electrolytes and the value 0 for non-electrolytes. Whether B will be positive or negative for any particular salt can only be determined at present by a study of the experimental data. Thus B will be positive for salts like potassium iodide or cesium nitrate which increase the fluidity and negative for salts which, like barium chloride, diminish the fluidity. This equation may readily be transformed to the form $(\varphi - 1)/\sqrt{c} = A + B\sqrt{c}$. Therefore, the simplest way to test the validity of this equation is to plot $(\varphi - 1)/\sqrt{c}$ against $\sqrt{c}$ and see if a straight line is obtained which does not pass through the origin. This was done with our data on barium chloride and gave a good straight line through the entire range from 0.005 to 1.0 molal. This curve (C) is reproduced on a much reduced scale in Fig. 2. It will be noticed that the intercept on the $(\varphi - 1)/\sqrt{c}$ axis, which gives the value of A, is negative, as was predicted, and that the slope, which gives the value of B, is also negative in this case. The numerical values of A and B were then determined with greater precision than is possible by plotting by the method of least squares, giving

$$\varphi = 1 - 0.02013\sqrt{c} - 0.20087c$$

The values of the fluidity as computed by this equation are shown in Col. 7 of Table III and the deviations between the computed and observed values in Col. 8. The greatest deviation is only 0.032% and the average deviation only 0.013% and there is no systematic trend. It may be concluded, therefore, that this equation is valid for barium chloride solutions at 25° within the limit of accuracy of the experiments over the entire range up to 1 molal. Table IV gives the values of φ and η at round concentrations computed from this equation.

TABLE III

VISCOSITY AND FLUIDITY OF BARIUM CHLORIDE SOLUTIONS AT 25°

c	η	$(\eta - 1)/c$	$(\log \eta)/c$	$\varphi_{\text{obs.}}$	$(\varphi - 1)/c$	$\varphi_{\text{comp.}}$	$\Delta\varphi$, obs.-comp.
0.005	1.00248	0.496	0.215	0.99753	−0.494	0.99757	−0.00004
.01	1.00371	.371	.161	.99630	− .370	.99598	+ .00032
.025	1.00821	.328	.140	.99186	− .326	.99180	+ .00006
.05	1.01474	.295	.127	.98547	− .291	.98546	+ .00001
.1	1.02704	.270	.116	.97367	− .263	.97355	+ .00012
.25	1.06438	.258	.108	.93951	− .242	.93973	− .00022
.4972	1.12893	.259	.105	.88579	− .230	.88594	− .00015
.9913	1.28049	.283	.108	.78095	− .221	.87084	+ .00011

TABLE IV

FLUIDITY AND VISCOSITY OF BARIUM CHLORIDE SOLUTIONS AT 25°

c	0.0005	0.001	0.0025	0.005	0.01	0.025
φ	0.99945	0.99916	0.99843	0.99757	0.99598	0.99180
η	1.00055	1.00084	1.00157	1.00244	1.00404	1.00827
c	0.05	0.10	0.25	0.50	1.0	
φ	0.98546	0.97355	0.93973	0.88533	0.77900	
η	1.01475	1.02717	1.06414	1.12952	1.28370	

Table V

Viscosity and Fluidity of Lithium Nitrate Solutions at 18° after Grüneisen (G) and Applebey (A)

	c	η	$(\eta - 1)/c$	$(\log \eta)/c$	$\varphi_{\text{obs.}}$	$(\varphi - 1)/c$	$\varphi_{\text{comp.}}$	$\Delta\varphi$, obs.-comp.
A	0.00724	1.0012_5	0.173	0.0749	0.99875	−0.173	0.99869	$+0.0000_6$
A	.01310	1.0020_1	.153	.0666	.99799	− .152	.99796	$+ .0000_3$
G	.02500	1.0036_4	.146	.0631	.99637	− .145	.99659	$- .0002_2$
A	.0379	1.0047	.124	.0537	.99532	− .123	.99520	$+ .0001_2$
G	.0500	1.0062_2	.124	.0538	.99382	− .123	.99394	$- .0000_8$
A	.0784	1.0090	.115	.0496	.99108	− .114	.99108	$+ .0000_0$
G	.1000	1.0112	.112	.0483	.98889	− .111	.98895	$- .0000_6$
A	.1446	1.0153_5	.106	.0457	.98488	− .104	.98466	$+ .0002_2$
A	.2653	1.0276	.104	.0446	.97314	− .101	.97335	$- .0002_1$
G	.5000	1.0503_2	.101	.0426	.95209	− .096	.95193	$+ .0001_6$
A	(.7034)	(1.0731)	(.104)	(.0434)	(.93188)	(− .097)	(.93365)	$(- .0017_7)$
G	1.000	1.1023	.102	.0423	.90719	− .093	.90724	$- .0000_5$
A	1.283	1.1429	.111	.0452	.87497	− .097	.88222	$- .0072_5$
A	1.471	1.1686_5	.115	.0460	.85569	− .098	.86566	$- .0099_7$
A	2.528	1.3472	.137	.0512	.74228	− .102	.77417	$- .0318_9$
A	2.550	1.3552	.139	.0517	.73790	− .103	.77126	$- .0333_6$
A	3.120	1.4869_5	.156	.0553	.67252	− .105	.72167	$- .0491_5$
A	3.279	1.5327	.162	.0565	.65244	− .106	.70785	$- .0554_1$
A	4.363	1.9274	.213	.0652	.51883	− .110	.61390	$- .0950_7$

Analysis and Interpretation of Other Data.—Most of the data in the literature are not well suited to test the generality of our new relationship because measurements on very dilute solutions are lacking. Most authors have apparently assumed that at low concentrations the curves become linear. The best available data for this purpose known to us are those of Grüneisen and of Applebey on lithium nitrate at 18° which cover the range from 0.00724 to 4.363 moles per liter. These data were first used to prepare a plot of $(\varphi - 1)/\sqrt{c}$ against $\sqrt{c}$ and gave a good straight line up to 1 molal, which is reproduced in Curve D of Fig. 2, giving negative values of A and B, as was expected. Then the equation of this line was determined by the method of least squares. (In this computation the data for Applebey's 0.7034 molal solution were omitted because the plotting indicated a serious error in this value.) The result was

$$\varphi = 1 - 0.00818\sqrt{c} - 0.08458c$$

The fundamental data and the derived values are shown in Table V. The conclusion that Arrhenius' equation is invalid is reinforced by a consideration of Col. 4. As will be seen by inspection of Col. 8, the values of the fluidity computed by our formula agree with the experimental results within 0.022% for all solutions measured up to 1 molal except for Applebey's 0.7034 molal solution, which is apparently in error experimentally. These data on lithium nitrate confirm in all respects the conclusions which we have drawn from our own data on barium chloride.

Grüneisen's data on lithium iodate have been used to prepare Curve B in Fig. 2. Lithium iodate solutions have an exceptionally high viscosity, but in spite of the magnitude of the effect, the equation

$$\varphi = 1 - 0.01076\sqrt{c} - 0.2689c$$

is in accord with the data up to 1 molal with a maximum deviation of only 0.03%. The equation, however, fails completely at 3 molal.

We have plotted the data on a number of other salts which increase the viscosity of water but forego to adduce other examples since in all other cases known to us the measurements lack precision or there are not sufficient measurements on solutions of low concentration to permit a sharp test of the validity of our general equation. The evidence of other cases studied, however, so far as it goes, supports the validity of our equation.

We next turn to salts which may decrease the viscosity of water within certain ranges of concentration and temperature. Such salts are sometimes said to exhibit a "negative viscosity" but this is not accurate phraseology since there is no such thing as a negative viscosity. Here the phenomena are more complicated than for salts which increase the viscosity. The data which are most suitable for testing our equation are the measurements of Merton[11] on cesium nitrate. Merton has made accurate measurements at 0° covering the range 0.025 to 0.42 molal, at 10° covering the range 0.029 to 0.7, at 18° covering the range 0.023 to 0.8, and at 25° covering the range 0.023 to 0.8. The values of $(\varphi - 1)/\sqrt{c}$ were plotted against $\sqrt{c}$. The resulting plots, which are omitted to save space, appear to be straight lines at the dilute end (below 0.2) but deviations are evident at higher concentrations; whereas for the salts which increase the viscosity, the straight lines were obtained up to 1 molal in the cases studied.

It is evident from these curves that the value of A is always negative, as is expected from our theoretical interpretation of the phenomena. Then by the method of least squares the coefficients were determined, giving at 18°

$$\varphi = 1 - 0.01029\sqrt{c} + 0.12456c$$

and at 0°

$$\varphi = 1 - 0.01488\sqrt{c} + 0.2587c$$

These data furnish further evidence as to the invalidity of Arrhenius' formula. There are several inferences which may be drawn tentatively from the variation of the constants with the temperature although we must be cautious because the available data do not extend to solutions as dilute as is desirable for the evaluation of the constant A. However, there are indications that the numerical value of A is greater at low temperatures than at high temperatures. Since A depends upon the stiffening effect of the space lattice, it is to be expected that this effect will be greater at low temperatures because the space lattice is less disturbed by heat vibration. This effect apparently exceeds the opposite effect of the change in dielectric constant with temperature. It is also to be observed that the value of B

is greater at low temperatures, which is in harmony with Applebey's suggestion that the increase in fluidity is due to depolymerization of triple water molecules. There are more triple molecules present at low temperatures and therefore more available to be depolymerized.

Grüneisen's data on potassium iodide and potassium nitrate at 18° have been computed and plotted and found to fit an equation of the same form with a negative value of A up to 0.2 molar.

If our hypothesis that the negative curvature at the lower end of the viscosity–concentration curves is due to a stiffening effect of the ionic space lattice is correct, there should be no such negative curvature manifested in solutions of non-electrolytes. Accurate measurements of the viscosity of such solutions at very low concentrations are very scarce in the literature. The best examples known to us are the data of Grüneisen on sucrose and of Washburn and Williams[20] on raffinose at three temperatures. Grüneisen's measurements extend down to 0.01 molal and according to Grüneisen may be accurately represented by the equation

$$\eta = 1 + 0.8816c + 0.7970c^2$$

and thus show no evidence of negative curvature at low concentrations or of any influence which is proportional to the square root of the concentration. The measurements of Washburn and Williams on raffinose extend down to 0.038 molal and also give no indication of a negative curvature at the dilute end of the viscosity–concentration curves. Further corroboration is given by the measurements of Chadwell[21] on aqueous solutions of methyl acetate, ethyl acetate and diethyl ether, which, although not extending to as great dilution as would be desirable to test this question, nevertheless show no indication of a negative curvature at the dilute end of the viscosity–concentration curves.

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 concentration will give an increase in viscosity at extreme dilutions is by Schneider,[9] who reports a relative viscosity of 1.0008 for 0.05 N potassium chlorate, and 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.

Grateful acknowledgment is made to Professor Theodore Lyman, Director of the Jefferson Physical Laboratory, for permission to work in that Laboratory and for making available to us its standard clock. We also wish to express our appreciation for a grant from the Milton Fund of Harvard University for the expenses of this research.

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[20] E. W. Washburn and G. T. Williams, THIS JOURNAL, **35**, 750 (1913).

[21] H. M. Chadwell, *ibid.*, **48**, 1912 (1926).

Summary

1. Measurements have been made on the viscosity of solutions of barium chloride at 25° covering the range 0.005 to 1.0 molal.

2. The fluidity (reciprocal of the viscosity) of these solutions can be computed within the limit of error of the data from the equation

$$\varphi = 1 - 0.02013\sqrt{c} - 0.20087c$$

3. It is shown that an equation of the form $\varphi = 1 + A\sqrt{c} + Bc$ can be made to fit the data by proper choice of the values of A and B in the case of many other salts for which precise data are available extending to low concentrations.

4. The value of A is negative for all strong electrolytes for which accurate data are available. This term probably represents the stiffening effect on the solution of the electric forces between the ions which tend to maintain a space lattice structure. The value of A is zero for non-electrolytes.

5. The value of B may be either positive or negative. Most salts resemble barium chloride in causing an increase in viscosity or a decrease in fluidity at all concentrations giving a negative value to B. In such cases the equation is apparently valid up to about 1 molal.

6. Some salts cause an increase in the fluidity or a decrease in the viscosity over a wide range of concentration, so that the value of B in our equation is positive. In such cases the equation is apparently valid up to nearly 0.2 molal.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, MICHIGAN AGRICULTURAL EXPERIMENT STATION]

THE DETERMINATION OF ALUMINUM IN PLANTS. II. ALUMINUM IN PLANT MATERIALS[1]

BY O. B. WINTER AND O. D. BIRD

RECEIVED JUNE 12, 1929 PUBLISHED OCTOBER 5, 1929

The biological significance of the use of aluminum in food materials, water purification, cooking utensils, etc., has been a live problem during the last one or two decades. Because of this, the aluminum content of plants has been considered of importance, even though the amount present may be small.

Langworthy and Austin,[2] Gonnerman,[3] Bertrand[4] and more recently

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[1] Published by permission of the Director of the Experiment Station as Journal Article No. 11 n.s. from the Station and No. 49 from the Chemical Laboratory.

[2] Langworthy and Austin, "The Occurrence of Aluminum in Vegetable Products, Animal Products and Natural Waters," New York, **1904**.

[3] Gonnerman, *Biochem. Z.*, **88**, 401 (1918).

[4] Bertrand, *Bull. soc. hyg. aliment.*, **8**, 49 (1920).