transference numbers, it is evident that the movement of the boundary past a graduation mark must have been read, at least in the case of the positive ion, to the nearest second and, also, that the current must have been constant in this interval, within the range of error of the measurements, which was about 0.02%. The sum of the average values of the two transference numbers is 0.5122 + 0.4872 = 0.9994, or within 0.06% of unity. The only previously recorded value for a transference number of potassium nitrate (0.501 for the positive ion) is given by Denison and Steele;[5] this is evidently in error. A series of measurements on transference numbers of a series of nitrates, which present peculiarities which are interesting in the light of the modern theories of electrolytic dissociation, is now in progress.

Summary

An apparatus involving a photo-electric relay system is described. This device maintains a constant current, within 0.02–0.03%, through a moving-boundary apparatus, the resistance of which steadily increases during a determination. Data are given on the moving-boundary measurements on potassium nitrate solutions which indicate that regulation to that precision has been attained in practice.

CAMBRIDGE, MASSACHUSETTS

THE VISCOSITIES OF SEVERAL AQUEOUS SOLUTIONS OF ORGANIC SUBSTANCES AND THE POLYMERIZATION OF WATER

BY HARRIS MARSHALL CHADWELL

This investigation is a continuation of the study of aqueous solutions of non-polar materials from the point of view of the polymerization of water. In a recent paper[1] in collaboration with T. W. Richards it was shown that the changes in volume and in compressibility on solution of various organic materials could be explained adequately by consideration of (1) the cohesive affinities concerned, (2) the effect of polymerization of one or both liquids (and the possible formation of complex solvated molecules), and (3) the effect of the several compressibilities of the cohering substances. The present paper reports the determination of another property of the solutions and an attempt to explain the data by the same considerations.

[5] Denison and Steele, *Trans. Roy. Soc. London.*, **205A**, 449 (1906).

[1] Richards and Chadwell, THIS JOURNAL, **47**, 2283 (1925).

The property of viscosity has been interpreted by many investigators[2] to reflect changes in molecular constitution, particularly the formation of complex molecules between the two components of the solution. The generally accepted explanation for the fact that aqueous solutions of such materials as the alcohols and acetic acid have a greater viscosity than water (even though the solute may have a smaller viscosity) is the formation of more or less definitely solvated molecules.[3] The existence of such definite hydrates would be more conclusive if the exact relationship between viscosity and concentration for an "ideal" solution[4] were known with certainty.

However, the property of viscosity should throw some light on the nature of the solutions previously studied. If water is depolymerized by the addition of a second substance, and the resulting water has a smaller viscosity (analogous to the effect of an increase in temperature) then the viscosity would tend to be less than for pure water. Such a result is found in dilute solutions of certain inorganic salts and has been called "negative viscosity."[5]

This paper records the viscosity determinations of solutions of methyl and ethyl acetates, ethyl ether and benzene in water, water in the esters, and methyl acetate in ethyl acetate.

The most striking outcome of the investigation is that aqueous solutions of organic materials seem to have a greater viscosity than pure water despite the fact that the pure solutes have a smaller viscosity.

Purification of Materials

Water.—Thrice distilled water (free from oil, organic matter, ammonia and carbon dioxide) was used.

Ethyl Acetate.—Commercial "anhydrous" ethyl acetate, neutral to litmus, was freed from alcohol after a preliminary drying with phosphorus pentoxide, by distilling with a trace of water according to the method of Wade and Merriman[6] using a 20-disk distilling head recommended by Young.[7] The ester was then dried by successive addi-

[2] Reviewed in (a) Dunstan and Thole, "The Viscosity of Liquids," Longmans, Green and Co., London, 1914 (Monographs of Inorganic and Physical Chemistry, edited by Findlay); (b) Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922; a very complete bibliography is included.

[3] Evidence of definite hydrate formation in aqueous solutions of H_2SO_4 and $FeCl_3$ from viscosity measurements is given by Smits, Lande and Bouman, Proc. Acad. Sci. Amsterdam, 23, 969 (1921). For criticism and review, see Jorissen, Rec. trav. chim., 40, 281 (1921).

[4] (a) Kendall, THIS JOURNAL, 36, 1069 (1914). (b) Kendall and Brakeley, ibid., 43, 1826 (1921). (c) Kendall and Monroe, ibid., 39, 1787 (1917); (d) 43, 115 (1921). (e) Kendall and Wright, ibid., 42, 1776 (1920). See also Ref. 2 b, p. 84 and following pages.

[5] Discussed very completely from this same point of view by Rabinovich, THIS JOURNAL, 44, 954 (1922).

[6] Wade and Merriman, J. Chem. Soc., 101, 2429 (1912).

[7] Young, ibid., 75, 679 (1899).

tions of phosphorus pentoxide over a period of six days, and finally fractionated from a Richards and Barry[8] flask and all-glass apparatus. In all distillations the greatest precautions were taken to protect the materials from moisture. All of the material distilled at the temperature of 77.15° (760 mm.), within the accuracy of reading the thermometer. All boiling points were measured with Anschütz thermometers graduated in 0.2° and standardized with an accuracy of $\pm 0.05°$. Portions of each of the three fractions had the same viscosity within the accuracy of measurement (0.05%). The density[9] (d_4^{25} vac.) was 0.89451.

To confirm the belief that the ester was dry, about 250 ml. was shaken with approximately 35 g. of phosphorus pentoxide and the mixture allowed to stand for six hours. It formed a gel[10] rigid enough not to break when the flask was inverted. On being heated, the ester distilled at the same temperature and the distillate had the same viscosity as before.

Methyl Acetate.—Commercial "anhydrous" methyl acetate, neutral to litmus, and shown to be free from acetone by the salicyl aldehyde test,[11] was treated thrice with phosphorus pentoxide, as recommended by Young and Thomas[12] and then fractionated with the Young disk column. It was again treated with phosphorus pentoxide and distilled in the Richards flask, all of the material passing over at 57.2° (760 mm.) within 0.1°. Its purity was confirmed in the same way as was that of the ethyl acetate. Its density (d_4^{25}) was 0.92740, in good agreement with the determination of 0.92704 (interpolated) of Young and Thomas.[13]

Ethyl Ether.—One of the purest commercial preparations of "absolute" diethyl ether was treated with five successive portions of phosphorus pentoxide over a period of a week as recommended by Wade and Finnemore.[14] On fractionation in the Richards flask all of the material except the forerun distilled at 34.6°. Its density (d_4^{25}) was 0.70792, in good agreement with the determination of 0.70788 by Squibb.[15]

Benzene.—The benzene had been purified for molecular weight determinations by the method suggested by Richards and Shipley,[16] followed by six crystallizations.

Apparatus and Technique of Viscosity Determinations.—The measurements of viscosity were made with the modified Ostwald viscometer, developed by Washburn and Williams[17] but constructed of Pyrex glass instead of quartz. Although not adapted to such diversified uses as the viscometer of Bingham,[18] it can be used with greater ease for aqueous solutions.

[8] Richards and Barry, THIS JOURNAL, **36**, 1787 (1914).

[9] Others have obtained the following values (d_4^{25}): Kendall and Walden, 0.8938 [*Z. physik. Chem.*, **65**, 134 (1909)]; Hubbard, 0.89422 [*ibid.*, **74**, 217 (1910)]; Tyrer, 0.89450 [*J. Chem. Soc.*, **97**, 2624 (1910)]; Wade and Merriman, 0.89446 [*ibid.*, **101**, 2429 (1912)]; Willard and Smith, 0.8945 [THIS JOURNAL, **45**, 289 (1923)].

[10] Williams [THIS JOURNAL, **47**, 2649 (1925)] reports a similar gel with nitromethane, phosphorus pentoxide and a trace of water.

[11] Allen, "Commercial Organic Analysis," Blakiston, Philadelphia, 1912, Vol. 1, p. 105.

[12] Young and Thomas, *J. Chem. Soc.*, **63**, 1191 (1893).

[13] Ref. 12, p. 1207.

[14] Wade and Finnemore, *J. Chem. Soc.*, **95**, 1842 (1909).

[15] Squibb, *Chem. News*, **51**, 66, 76 (1885).

[16] Richards and Shipley, THIS JOURNAL, **36**, 1825 (1914).

[17] Washburn and Williams, *ibid.*, **35**, 739 (1913).

[18] Described completely in Bingham, Ref. 2 b, p. 295. Its use in a series of very careful investigations by Kendall and co-workers is there reported.

The instrument was modified slightly by blowing a bulb of about 0.2 ml. capacity at the top of the capillary, the lower of the two scratches being between this bulb and the higher reservoir. The constrictions beneath the scratches had a radius at least ten times that of the capillary according to the specifications of Bingham. The distance between the two scratches was 5.79 cm., the volume of liquid contained between them, 9.37 ml. The capillary was about 18.1 cm. in length, having a diameter of 0.0453 cm. In other details and dimensions the viscometer was essentially the same as that of Washburn and Williams. The three-way stopcock by which the arms of the viscometer could be connected together or opened to the atmosphere was found to be very convenient.

The viscometer was mounted in a brass frame of such construction that the capillary was held in the same vertical position when placed in the thermostat. This thermostat was of glass with a window in the heat-insulating material so that the viscometer could be seen easily. The temperature was maintained at $25.00°$ ($\pm 0.002°$, corrected) by the usual automatic electric device.

The time of flow was measured by a stopwatch having an excellent Swiss movement of the sort that continued to run independently of the hands. It recorded the time to $^1/_5$ second. It was verified frequently by an horologist and during its use was kept at a constant state as regards winding and position.

The densities of the various materials were determined in 10-ml. Ostwald pycnometers and were calculated to the vacuum standard by the method proposed by Richards and Chadwell.[1] The density of water at $25°$ was taken as 0.99707.

The solutions of known composition by weight were prepared in glass-stoppered flasks of such size that very little gas space was left above the liquid. The more volatile constituent was added last. A constant volume (62 ml.) of liquid was transferred to the large bulb of the viscometer by means of a pipet, the pipet being filled quickly by the application of a pressure of dry, clean air on the liquid in the flask. By a similar method the small bulb was filled by forcing liquid from the larger bulb. After the viscometer and its contents had come to the temperature of the thermostat, and the stopcock had been opened momentarily to the atmospheric pressure, then turned to connect the two tubes of the viscometer, the time of flow was measured. After the time of flow had been taken, liquid was forced again into the smaller bulb by a pressure of clean, dry air and another run made. It would seem that this method of transferring liquid would change the concentration of the solution less than by applying suction to the other side of the viscometer. The time of flow as reported is a mean of several determinations, enough so that the time was certain within the accuracy of the stopwatch ($^1/_5$ sec.). There must have been a slight change in con-

centration of the solutions as the number of runs increased, but no trend in the times of flow was observed.

There must also have been a change in concentration due to the saturation of the air with the vapors from the solution. In the experiments with water solutions of ether and benzene, the viscometer was filled with air, previously dried and then bubbled through a large volume of a solution of the same concentration. This treatment would partially obviate the change in concentration due to evaporation.

After each run the viscometer was washed with chromic acid cleaning solution, dust-free water, alcohol and ether, and then dried with air previously passed through sulfuric acid and a long tube of absorbent cotton. Frequent runs were made with water to detect any change in the capillary or irregularity in technique. At no time did this time of flow vary from the mean result by more than the experimental error.

Calculation of the Results

The values of viscosity are calculated from Poiseuille's law with and without the application of the kinetic energy correction. Without the correction the relative viscosity is given by the well-known expression

$$\eta/\eta_0 = \frac{(d - D) t}{(d_0 - D) t_0} = \frac{\rho t}{\rho_0 t_0} \tag{1}$$

where the subscript zero refers to the data for water, d the density of the liquid in air, D the density of the air, ρ the density in vacuum and t the time.

When the vacuum correction is applied, the formula becomes, using the nomenclature of Bingham $\eta = Cpt - C'\rho/t$; $C = 384.8\ r^4/vl$; $C' = 0.0446$ v/l, where η is the viscosity in poises, p is the "true average pressure" (g. per sq. cm.), r the radius (cm.) of the capillary, l its length (in cm.) and v the volume (ml.) of liquid. The constant in the expression for C is based on the value of 980 for the acceleration due to gravity. This expression can be modified to make it applicable to the Ostwald viscometer by substituting for Cp the term $K\rho$, the expression becoming

$$\eta = K\rho t - C'\rho/t \tag{2}$$

where K is a new constant and determined by a run with water, after C' has been calculated from the dimensions of the viscometer. This formula is slightly different from that used by Lewis,[19] in that the latter does not include the kinetic energy correction for water; and is also different from that suggested by Bingham and his collaborators[20] in which an attempt

[19] Lewis, THIS JOURNAL, **47**, 626 (1925).

[20] Bingham, Schlesinger and Coleman, *ibid.*, **38**, 27 (1916). This paper reports the use of the Washburn and Williams viscometer without the application of any correction to the simple formula. The importance of the consideration of this pressure correction, when the Bingham viscometer is used, has been emphasized by Kendall and Monroe, *ibid.*, Ref. 4c, p. 1787.

is made to correct for the "true average pressure." It is identical with the formula developed by Martin.[21]

In these calculations of viscosity no attempt has been made to correct for surface-tension effects.

The invariant factors used in the calculations are as follows: $\rho_0 = 0.99707$, $t_1 = 706.6$ sec., $\eta_0 = 0.008949$ poises,[22] $K = 0.000012748$, $C' = 0.0231$. The results are summarized by Table I, the data for solutions in
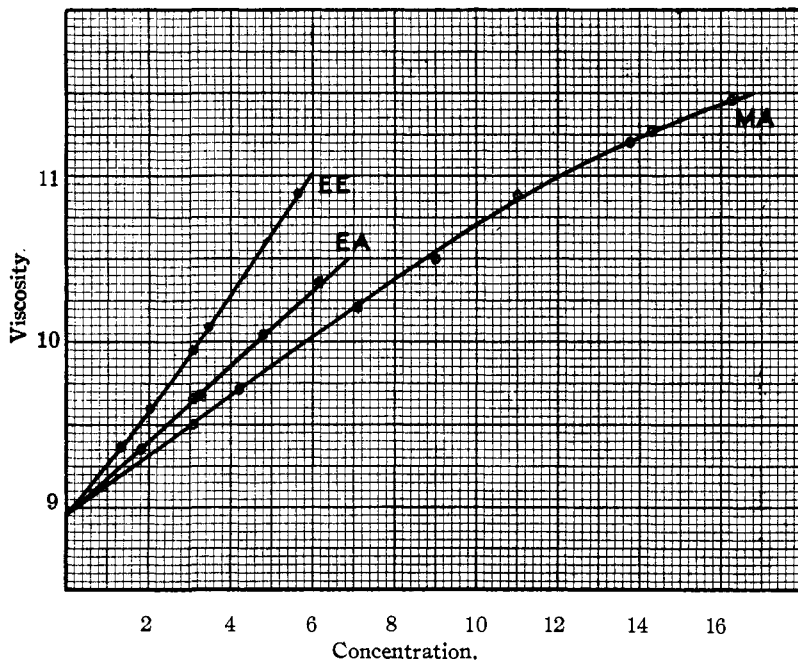

Fig. 1.—The change of viscosity of aqueous solutions at 25°; viscosity in millipoises are plotted as ordinates, and concentrations as weight percentages as abscissas.

Curve EE represents viscosities of aqueous solutions of diethyl ether, Curve EA represents viscosities of aqueous solutions of ethyl acetate, Curve MA represents viscosities of aqueous solutions of methyl acetate.

water being shown in Fig. 1. In the first column are recorded the percentages by weight of the solute (the first substance given in the titles), in the second the time in seconds, in the third the densities in a vacuum, in the fourth the viscosity as calculated by Formula 1, in the fifth the viscosity as calculated by Formula 2. The viscosities are recorded in the table in units of millipoises (the values calculated from the above constants multiplied by 1000).

[21] Martin, *Bull. soc. chim. Belg.*, **34**, 81 (1925).

[22] The value accepted by the International Critical Tables.

TABLE I
RESULTS OF VISCOSITY DETERMINATIONS AT 25°

	Time t sec.	Density (ρ) $\left(d_4^{25} \text{ vac.}\right)$	Viscosity Millipoises η_I	η_{II}
Water	706.6	(0.99707)	(8.949)	(8.949)
Methyl acetate	309.8	.92740	3.649	3.594
Ethyl acetate	377.0	.89451	4.283	4.244
Ethyl ether	252.8	.70792	2.273	2.216

%	t	ρ	η_I	η_{II}
		ETHYL ACETATE IN METHYL ACETATE		
0.000	309.8	0.92740	3.649	3.594
9.159	314.6	.92399	3.692	3.638
21.698	322.4	.91962	3.766	3.713
36.562	331.5	.91456	3.851	3.801
48.840	339.3	.91045	3.924	3.876
59.560	346.3	.90695[a]	3.990	3.943
81.855	362.2	.90000[a]	4.140	4.098
89.295	368.4	.89774	4.201	4.158
100.000	377.0	.89451	4.283	4.244
		METHYL ACETATE IN WATER		
0.000	706.6	0.99707	8.949	8.949
3.122	749.6	.99792	9.501	9.505
4.215	765.5	.99824	9.706	9.711
7.113	803.5	.99901[a]	10.196	10.214
9.010	826.6	.99947	10.494	10.504
11.077	854.7	.99997[a]	10.856	10.869
13.793	878.8	1.00038	11.166	11.181
14.295	886.0	1.00045	11.260	11.274
16.259	900.3	1.00060	11.442	11.458
		WATER IN METHYL ACETATE		
0.000	309.8	0.92740	3.649	3.594
1.730	319.4	.93004	3.773	3.720
3.248	331.8	.93250	3.930	3.879
5.025	347.7	.93532[a]	4.131	4.084
6.671	365.4	.93823	4.354	4.311
		ETHYL ACETATE IN WATER		
0.000	706.6	0.99707	8.949	8.949
.676	718.1	.99704[a]	9.094	9.095
.892	720.8	.99702	9.128	9.129
1.815	738.4	.99698	9.351	9.354
3.041	761.8	.99692	9.646	9.652
3.284	763.8	.99690[a]	9.671	9.678
4.809	792.5	.99682	10.034	10.043
6.170	817.1	.99675	10.346	10.357
		WATER IN ETHYL ACETATE		
0.000	377.0	0.89451	4.283	4.244
.890	382.2	.89610	4.349	4.312
1.658	388.8	.89745[a]	4.432	4.395
2.459	396.8	.89891	4.530	4.495

TABLE I   (*Concluded*)

%	t	ρ	η_{I}	η_{II}
		ETHYL ETHER IN WATER		
0.000	706.6	0.99707	8.949	8.949
1.360	741.5	.99413	9.363	9.366
2.060	760.5	.99301ᵃ	9.592	9.597
3.089	790.2	.99164	9.953	9.959
3.485	801.5	.99106ᵃ	10.090	10.099
5.848	864.0	.98791	10.841	10.883

ᵃ Values were obtained by interpolation.

The viscosities of the pure materials may be compared with those obtained at this same temperature by other investigators. The result for ethyl acetate (4.244) is in very good agreement with the value of 4.239 reported by Kendall and Wright.[4e] Their result is calculated from the value of 8.946 for water. When changed to the same value for water (8.949) as used above, the result is 4.241. The value of 2.216 for ethyl ether is slightly lower than 2.233 found by Kendall and Wright and 2.231 by J. R. Lewis.[23]

It was found that the viscosity of water saturated with benzene differed appreciably from that of water. Two saturated solutions were prepared in the thermostat at 25°. They gave times of flow of 709.3 and 709.4 seconds, a density of 0.9968 and values of η of 8.981 and 8.982, respectively. The concentration of this saturated solution is not known exactly. As has been pointed out recently by A. E. Hill,[24] Hantzsch[25] gives the value of 0.113% by weight of benzene at 25°; Herz[26] 0.08% at 22°; Moore and Roaf[27] 0.15% at 15°; and Hill[24] 0.15% at 0°.[28]

Discussion of Results

According to the present conception of solutions[29] the system, methyl acetate-ethyl acetate, should be nearly ideal, and so it is of interest to ascertain which of the various formulas that have been proposed for ideal solutions represent these experimental results. The two most satisfactory formulas are those of Kendall[30] and of Bingham. They are, respectively: $\eta^{1/3} = x\eta_1^{1/3} + (1-x)\eta_2^{1/3}$; and $1/\eta = x/\eta_1 + (1-x)/\eta_2$,

[23] Lewis, THIS JOURNAL, **47**, 626 (1925).

[24] Hill, *ibid.*, **45**, 1155 (1923).

[25] Hantzsch, *Z. physik. Chem.*, **30**, 295 (1899).

[26] Herz, *Berl. Ber.*, **31**, 2669 (1898).

[27] Moore and Roaf, *Proc. Roy. Soc.*, **77B**, 96 (1905).

[28] Arrhenius [*Z. physik. Chem.*, **1**, 285 (1887)] reports the following data for relative viscosities at 24.7°: (% by vol.) methyl acetate: 5%, 1.092, 2%, 1.035; ethyl acetate: 5%, 1.114, 2%, 1.044; ether: 7.5%, 1.224, 5%, 1.146.

[29] Hildebrand, "Solubility," Chemical Catalog Co., New York, **1924**, pp. 23, 86.

[30] Kendall and Wright, Ref. 4 e, record the application of these formulas to systems of other esters.

where η is the viscosity of the solution, η_1 and η_2 are the viscosities of the pure materials and x is the mole fraction of the component whose viscosity is η_1. The comparison between calculated and experimental results is given in Table II.

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF VISCOSITIES OF SOLUTIONS OF METHYL AND ETHYL ACETATE

Viscosities expressed in millipoises at 25°

η Ethyl acetate = 4.244 η Methyl acetate = 3.594

% (by wt.) Et. Ac.	Mole fraction Et. Ac.	η calculated by equation of		Observed η
		Kendall	Bingham	
9.16	0.0782	3.645	3.639	3.638
21.70	.1892	3.709	3.701	3.713
36.56	.3264	3.804	3.783	3.801
48.84	.4454	3.877	3.856	3.876
59.56	.5533	3.944	3.926	3.943
81.86	.7915	4.104	4.090	4.098
89.30	.8753	4.158	4.151	4.158

Average deviation from Kendall's formula = 0.003
Average deviation from Bingham's formula = 0.012

It would seem that Kendall's formula is more satisfactory than the second since it represents the viscosities within the experimental error— a deviation of 0.001 millipoise in viscosity corresponding to 0.15% in composition and 0.1 second of time. However, the viscosities of the pure substances are too nearly alike to afford a conclusive test for any formula. Bingham has shown that the rule of additive fluidities does not hold when there is a volume change, that the observed viscosity is greater than the calculated when there is a contraction. This does not explain the divergence of the rule above, for there is a slight expansion (never greater than 0.8 ml. per liter as in the case of the solution containing 48.8% ethyl acetate), and the observed values are consistently higher than the calculated. It seems that Kendall and Wright[31] are correct in stating that the perfect solution equation has not yet been satisfactorily developed and must await the advent of an adequately developed theory of liquids.

The results for the solutions containing water are the most interesting. They show very conclusively that the decrease in viscosity resulting from a depolymerization of water[32] is more than balanced, at least at this temperature, by one or more tendencies that cause an increase. It is to be remembered that changes in polymerization were reflected in the properties of density and compressibility. The viscosity would be decreased by the breaking up of bulky polymerized solvent molecules. All of the solutes used possess viscosities very much lower than that of water.

[31] Ref. 4 e, p. 1783.
[32] See, for example, Röntgen, *Wied. Ann.*, **52**, 510 (1884). Sutherland, *Phil. Mag.*, [V] **50**, 460 (1901). Richards and Palitzsch, THIS JOURNAL, **41**, 59 (1919).

The data confirm a generalization pointed out long ago by Arrhenius[33] but not emphasized recently, that aqueous solutions in general have a viscosity greater than that of water, even though the viscosity of the solute may be very low. Practically all aqueous solutions of organic materials possess a greater viscosity than water, for example,[34] the alcohols, the acids, acetone, and various amines. To this list may now be added with assurance two esters, an ether and a hydrocarbon. The only materials so far investigated at this temperature which produce aqueous solutions of lower viscosity seem to be those inorganic salts showing "negative viscosity." This latter phenomenon has been adequately explained[35] by the theory of the dissociation

TABLE III

CONTRACTION AND SMOOTHED VALUES OF VISCOSITY

Solute %	Concentration, moles per liter	Contraction, ml. per liter	Increase in η_{II} (mp.)
	METHYL ACETATE IN WATER		
1	0.14	1.1	0.180
2	.27	2.1	.360
3	.40	3.2	.540
4	.54	4.2	.720
5	.68	5.2	.895
6	.81	6.1	1.074
10	1.35	10.2	1.750
15	2.01	14.8	2.385
	ETHYL ACETATE IN WATER		
1	0.11	1.1	0.218
2	.23	2.2	.446
3	.34	3.3	.678
4	.45	4.3	.908
5	.57	5.4	1.140
6	.68	6.5	1.368
	ETHYL ETHER IN WATER		
1	0.14	1.9	0.305
2	.27	4.1	.630
3	.40	6.8	.969
4	.53	9.3	1.312
5	.67	12.0	1.650
6[a]	.80	14.8	1.992

	WATER IN METHYL ACETATE						WATER IN ETHYL ACETATE		
Solute, %	1	2	3	4	5	6	1	2	3
Contraction, ml. per l.	1.1	2.2	3.3	4.4	5.5	6.6	1.0	2.3	4.3
Increase in η_{II} (mp.)	0.066	0.152	0.258	0.372	0.495	0.624	0.079	0.182	0.309

[a] Extrapolated.

---

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

[34] For many cases, see Landolt-Börnstein-Roth-Scheel, "Tabellen," 5th Ed., **1923**, Vol. 1, p. 137 and following pages.

[35] Rabinovich, Ref. 5.

of polymerized water. At lower temperatures, urea[36] composed of relatively small molecules produces aqueous solutions of smaller viscosity than water.

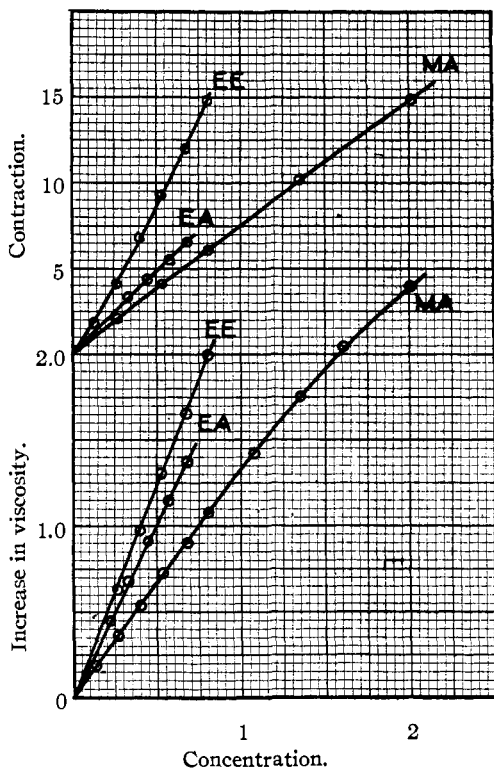The commonly accepted explanation[37] for such data showing increasing viscosity, and possibly a maximum, is the formation of solvated molecules. Such hydrates very probably exist in many cases,[38] but the general occurrence of increased viscosity, as pointed out above, with such a diversification of solutes possessing very different affinities for water suggests the search for other explanations.[39]

That there is often a close connection between contraction in volume and increase in viscosity has been emphasized by many investigators (reviewed by Bingham). The increase in viscosity of these particular solutions is also accompanied by a contraction, as shown in Table III. In the first column is given the concentration of solute expressed as per cent. by weight; in the second, as moles per liter of solution; the third gives the contraction in milliliters resulting in the formation of one liter of solution, and the fourth gives the difference in viscosity between the solution and solvent, expressed as millipoises.

The data for aqueous solutions given above are depicted in Fig. 2, where contraction and increase in viscosity are plotted as ordinates and concentrations as moles per liter as abscissas. The close similarity between the change in these two proper-

Fig. 2.—The parallelism between increase of viscosity and contraction of aqueous solutions at 25°. The increases of viscosity in millipoises and contractions in ml. per liter are plotted as ordinates and the molal concentrations per liter as abscissas.

Curve EE refers to aqueous solutions of diethyl ether, EA to aqueous solutions of ethyl acetate and MA to aqueous solutions of methyl acetate.

[36] Mützel, through Bingham, Ref. 2 b, p. 179.

[37] Dunstan and Thole, J. Chem. Soc., 95, 1556 (1909). Thole, Mussell and Dunstan, ibid., 103, 1108 (1913).

[38] See, for example, Scatchard, THIS JOURNAL, 43, 2406 (1921).

[39] See Frank, Z. physik. Chem., 114, 257 (1924).

ties is very evident and perhaps this volume change may be the chief explanation for the change in viscosity. MacLeod,[40] for instance, has suggested that both the contraction and the increase in viscosity are due to a decrease in "free space" in the liquids.

It has been suggested by Tammann[41] that the materials in solution behave as if they were under pressure. The magnitude of the change in viscosity given above is in the same order as the change in viscosity of the various solutes caused by external pressure. Bridgman[42] has shown recently that for pure liquids the volume and viscosity changes are not parallel, that with an increase in pressure the viscosity increases the most with substances having complex molecules. With a change of a given external pressure (2000 kg./sq. cm.) the viscosity of ether is greater than that of ethyl acetate, which in turn is greater than that of methyl acetate (Bridg-

TABLE IV

THE RELATIVE VISCOSITIES OF AQUEOUS SOLUTIONS OF 5% (BY WEIGHT) OF NON-ELECTROLYTES COMPARED TO THE MOLECULAR VOLUMES OF THE SOLUTE AT 25°

Substance	Relative viscosity (water = 1)	Molecular volume	Absolute viscosity (mp.) (water = 8.95)
Urea[a]	1.05	45.4	
Acetone[b]	1.07	73.9	3.46
Methyl acetate	1.100	79.8	3.65
Urethan[c]	1.13 (20°)	82.1	
Pyridine[d]	1.12	91.1	8.8
Ethyl acetate	1.128	98.6	4.28
Benzene	(1.16)	89.6	6.05
Ethyl ether	1.185	104.7	2.27
Methyl alcohol[e]	1.138	40.7	5.53
Ethyl alcohol[e]	1.254	58.5	11.15 (99.2%)
n-Propyl alcohol[e]	1.260	75.0	19.36
Acetic acid[e]	1.098	57.4	12.23 (99.1%)
Nicotine[f]	1.544 (20°)	161.0	45.36

[a] Mützel, through Bingham, Ref. 2 b, p. 181.
[b] Jones and collaborators, Carnegie Inst. Pub., 180, 119 (1913).
[c] Richards and Palitzsch, THIS JOURNAL, 41, 59 (1919).
[d] Faust, Z. physik. Chem., 79, 97 (1912).
[e] Ref. 37.
[f] Tsakalotos, Bull. soc. chim., 5, 397 (1909).

The relative viscosities are interpolated, assuming linearity from zero concentration to the first reported determination. The viscosity for the benzene solution is an extrapolated value, assuming that the saturated solution had a concentration of 0.113%. The densities used in calculating molecular volume are those reported by the several investigators.

[40] MacLeod, Preprints Faraday Soc., 1923, 1925; Trans. Faraday Soc., 20, 348 (1924); through C. A., 17, 2211; 19, 1361, 2152.

[41] Tammann, "Über die Beziehungen zwischen der inneren Kräften und Eigenschaften der Lösungen," Leopold Voss, Hamburg and Leipzig, 1907.

[42] Bridgman, Proc. Nat. Acad. Sci., 11, 603 (1925).

man does not record data for methyl acetate but the relative magnitude is evident from his table and conclusions).

Another very important consideration in determining the viscosity of an aqueous solution of a non-electrolyte seems to be the molecular volume of the solute.[43]   This is confirmed by Table IV in which is shown the relative viscosity (water = 1) of aqueous solutions having the arbitrarily chosen concentration of 5% by weight.[44]

This table seems to show that when the solute is normal[45] the larger the molecular volume, the larger is the relative viscosity, the viscosity of the pure solute playing a less important role.   As would be expected, the alcohols and acetic acid do not behave normally.

That the bulky solute molecules contribute to an increase in viscosity is only logical, for the internal pressures[46] under which the solutes exist in the water are probably approximately the same, and the viscosity is then influenced by the bulk (and possibly the shape) of the particles.   The viscosities of the pure liquids, on the other hand, are less significant because the internal pressures and cohesive forces are different in the different liquids.   As a consequence it is logical to suppose that the properties of the molecules would be different in a solution than when these molecules exist under the influence of similar molecules in the pure liquid.   This effect of the volume of the solute molecules is probably one of the most important of the tendencies which overbalance the effect of the depolymerization of the water.

I wish to express my indebtedness and gratitude to the Elizabeth Thompson Science Fund for providing mechanical aid in the calculations.

Summary

This paper gives results of viscosity determinations at 25° with a Washburn and Williams viscometer of the following solutions: methyl acetate in ethyl acetate, methyl acetate in water, water in methyl acetate, ethyl acetate in water, water in ethyl acetate, ethyl ether in water, and a saturated water solution of benzene.   The densities are also recorded.

The general phenomenon is emphasized that aqueous solutions of non-polar material possess a greater viscosity than water even though the solute possesses a smaller viscosity.

The parallelism between contraction on solution and increase in viscosity (with these particular substances) is indicated.

[43] Very kindly suggested by Professor T. W. Richards.

[44] If the ideal solution equation were known with certainty, it would be more illuminating to compare the divergence of various aqueous solutions containing the same molal concentration, with the molecular volume of the solute.

[45] See Turner, "Molecular Association," Longmans, Green and Co., London, 1915, p. 164.

[46] For a review and bibliography, see Richards, *Chem. Rev.*, 2, 315 (1925).

The data are discussed from the point of view of the polymerization of water and the internal pressures concerned.

TUFTS COLLEGE, MASSACHUSETTS

NOTE

A Non-Spattering, Continuous-Stream Wash Bottle.— The equivalent of two Bunsen valves serves to combine in one bottle in a way which is apparently novel two useful features, to wit —

First, the tip is kept full at all times, preventing spattering.

Second, it is not necessary to blow while using the bottle, as one breath expels 50 to 75 cc. of water.

Short sections of rubber tubing slipped over the glass tubes act as valves, a slight lateral pressure serving to open them. A liter flask about one-third full provides sufficient air capacity. If warm water is desired, the bottle may be kept on a warming oven. It is then unnecessary to provide for blowing as the combined pressure of air and water vapor suffices.

This bottle was designed and used at Northwestern University in 1924.

H. E. BENT
G. A. HUNT