

XV.—The Viscosity of Solutions. By C. Ranken, B.Sc., Carnegie Research Scholar, and Dr W. W. Taylor. Part I. *Communicated by Professor CRUM BROWN.*

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In a recent paper * published by the authors, some measurements of the viscosity of aqueous solutions indicated that it would be of interest to investigate more fully the viscosity of solutions, especially those which exhibit what is now generally known as "negative viscosity," over a wider range of temperature.

This has now been done to a certain extent, and to enable a comparison to be made between electrolytes and non-electrolytes in aqueous solution, some other substances have been included in the investigation. They are:—potassium chloride, potassium chlorate, ammonium iodide, potassium ferri-cyanide, potassium ferrocyanide; mercuric chloride, mercuric cyanide; carbamide.

METHOD AND APPARATUS.

In the determination of relative viscosity by OSTWALD'S method (OSTWALD-LUTHER, *Phys. chem. Messungen*, p. 260) there are two, if not three, points which require special attention, in addition to the usual precautions to ensure constant temperatures, etc. These special features are:—the cleaning of the capillary tube, the constancy of the volume of liquid introduced into the viscosity tube, and the measurement of the time interval which the liquid takes in flowing from the one mark to the other. The last is the most difficult to deal with, and, in order to minimise the error, the dimensions of the tube are often so adjusted by means of a very fine capillary, or of a bulb containing a comparatively large volume of liquid, that the time of flow is very long. Each of these devices is open to serious objections, and, as our previous experience had convinced us of the inherent unreliability of ordinary stop-watches, and especially of the impossibility of starting or stopping them at the precise instant, we adopted a different method of time measurement which has been found to be convenient and accurate to a high degree.

An electromagnetic clock with half-second pendulum electrically records seconds, or other intervals of time up to one minute, on a band of smoked paper. This band of paper is about 3 metres in length, and runs over two drums, one large and one small, the large one being driven at an approximately constant speed by an electric motor; the speed is reduced and adjusted by means of a worm reducing-gear. An electromagnetic time-marker records the experimental times on the paper immediately

* *Proc. Roy. Soc. Edin.*, 25, p. 231, 1904.

below the clock record. In most of our experiments the speed of the paper was so adjusted that 15–20 millimetres corresponded to an interval of one second.*

As the determinations of the corresponding times of flow for the solvent and the solution were always made on the same day, errors due to variation of the rate of the clock were to a large extent eliminated.

The following consecutive determinations of the time of flow of a volume of liquid will give some idea of the accuracy attained:—

- (1) Water, 166·95, 166·93, 166·96 seconds.
- (2) Solution of carbamide, 157·77, 157·84, 157·78 seconds.
- (3) Water (30°), 206·50, 206·55, 206·30, 206·42, 206·43 seconds; mean, 206·45 seconds.

No. (3) is given as an example of the extreme variation observed. In such cases the experimenter is often aware that he has missed the precise moment; but, as in the above set, exclusion of the lowest, or of the two extremes, has practically no effect on the mean value. •

Before each experiment the viscosity tubes were cleaned with chromic acid mixture and thoroughly washed with distilled water. In order to avoid the use of alcohol and ether, the tubes were dried by connecting them with an electrically-driven Geryk pump, the air being passed through cylinders with calcium chloride, phosphoric anhydride, and cotton wool before being admitted to the tube. If, on repetition, the results were not found to be concordant, it was generally found that the discrepancy disappeared after the tube had been recleaned.

The degree of accuracy attainable in introducing the same volume of liquid into the viscosity tube was also carefully inquired into. This was necessary, for it seemed probable that the volume of liquid delivered by the same pipette might be different for the solvent and the solution, and for different concentrations of the solution, owing to the differences in viscosity of the liquids.

In the test experiments the viscosity tube was weighed before and after the addition of the solvent and of the solution, and the weights of liquid were compared with their densities as determined in the usual manner.

- (1) 15° C. H_2O , (a) 2·1412 gm.; (b) 2·1416 gm.; (c) 2·1410 gm.
- (2) 25° C. H_2O , (a) 2·7215 gm.; (b) 2·7201 gm.
 ·05 m. KCl, (a) 2·7247 gm.; (b) 2·7262 gm.
 $d_{25^\circ/4^\circ} = 0·9988$, instead of 0·9993.
- (3) 15° C. H_2O , (a) 2·7239 gm.; (b) 2·7222 gm.
 ·25 m. KCl, (a) 2·7560 gm.; (b) 2·7568 gm.
 $d_{15^\circ/4^\circ} = 1·0114$, instead of 1·0112.

It may be taken that the volume delivered was constant to within 1 in 2000.

In conclusion, a few actual experiments are appended, which were made on totally

* [This form of electric chronograph, which is commonly used in physiological laboratories, is very convenient for physico-chemical purposes; for, if required, it can make a large number of independent experimental records simultaneously, without alteration of the apparatus beyond an additional number of electromagnetic time-markers, which are small and inexpensive. The apparatus was made for us by J. EDNIE, mechanic in the Physiology Department, Edinburgh University.]

independent solutions of the same substance; and from them the limits of variation in the value of the viscosity may be ascertained.

(1) 25° C. .1 m. KCl.

(a) Nov. 22, 1905.

Water	.	.	97.50 sec.	$\eta/\eta_0 = 1.0002.$
Solution	.	.	97.05 „	

(b) Jan. 31, 1906.

Water	.	.	206.06 sec.	$\eta/\eta_0 = 0.9996.$
Solution	.	.	204.96 „	

Two different viscosity tubes were used in this case.

(2) 8° C. .03125 m. carbamide.

(a) June 14, 1906.

Water	.	.	152.84 sec.	$\eta/\eta_0 = 0.9987.$
Solution	.	.	152.57 „	

(b) June 18, 1906.

Water	.	.	152.84 sec.	
Solution	.	.	152.55 „	$\eta/\eta_0 = 0.9985.$

The tubes employed by us, up to the present, are all of the Ostwald pattern (as figured in OSTWALD-LUTHER'S *Phys. chem. Messungen*, p. 260). The difference of time of outflow is not caused to any considerable extent by differences in length or diameter of the capillary, but is due to the fact that the bulbs immediately above the capillary were of different capacities, and, indeed, were generally adjusted so as to give a suitable time of outflow.

The diameters of the two capillary tubes were measured, and were found to be as follows :—

(1) Greatest diameter, 0.56 mm. ; least diameter, 0.50 mm.

(2) „ „ 0.60 mm. ; „ „ 0.52 mm.

The pycnometers with which the density determinations were made were of about 13 c.cm. capacity. The solutions and the water were carefully freed from air, and the temperatures at which the adjustments of the volumes in the pycnometer were made were extremely constant. The densities of the solutions may be taken to be accurate to 1 in 10,000. The densities of water at the different temperatures were the values given in the table of THIESEN, SCHEEL, and DIESSELHORST (in OSTWALD-LUTHER'S *Phys. chem. Messungen*, p. 128). The relative viscosity was calculated by means of the formula

$$\eta/\eta' = dt/d't',$$

and not from the more accurate formula

$$\eta/\eta_1 = (d - \lambda)t / (d' - \lambda)t',$$

as the density of the air (λ) would not introduce an error greater than 1 in 10,000, and may therefore be neglected.

EXPERIMENTAL RESULTS.

In the following tables

η_0 is the viscosity, expressed in absolute units, of water at the given temperature.

The values of η_0 are taken from THORPE and RODGER's determinations.*

m is the concentration of the solution in mols per litre.

d is the density of the solution referred to water at 4°.

η/η_0 is the ratio of the viscosity of the solution to that of the solvent at the given temperature, as directly determined by experiment.

η is the viscosity of the solutions in absolute units, and is obtained from the ratio given in the third column by multiplication with the value of η_0 given at the head of the table.

POTASSIUM CHLORIDE.

15° C.				30° C.			
$\eta_0 = \cdot 011335.$				$\eta_0 = \cdot 007975.$			
m	d	η/η_0	η	m	d	η/η_0	η
1	1·0456	·9695	·01099	1	1·0411	1·0057	·00802
·5	1·0227	·9822	·01113	·5	1·0187	1·0008	·00798
·25	1·0112	·9890	·01121	·25	1·0073	1·0005	·007978
·2	1·0087	·9925	·01125				
·125	1·0052	·9953	·01128				
·1	1·0040	·9965	·011295				
·0625	1·0022	·9970	·01130				
·0500	1·0014	·9982	·011315				

25° C.				35° C.			
$\eta_0 = \cdot 00891.$				$\eta_0 = \cdot 00720.$			
m	d	η/η_0	η	m	d	η/η_0	η
1	1·0428	0·9935	·00885	1	1·0393	1·0160	·007315
·5	1·0201	·9940	·00886	·5	1·0170	1·0082	·00726
·25	1·0087	·9967	·00888	·25	1·0057	1·0048	·007235
·2	1·0064	·9985	·008895				
·125	1·0029	·9989	·00890				
·1	1·0017	1·0000	·00891				
·0625	1·0000	·9990	·00890				
·05	0·9993	·9995	·008905				

45° C.			
$\eta_0 = \cdot 00597.$			
m	d	η/η_0	η
1	1·0357	1·0312	·006155
·5	1·0127	1·0150	·006059
·25	1·0021	1·0080	·006018
·1	·9950	1·0032	·005989

* *Phil. Trans.*, 185, p. 449, 1894.

MERCURIC CYANIDE.

15° C.

 $\eta_0 = \cdot 011335$.

m	d	η/η_0	η
$\cdot 25$	1·0479	1·0361	$\cdot 01174$
$\cdot 125$	1·0234	1·0178	$\cdot 01154$
$\cdot 0625$	1·0112	1·0103	$\cdot 01145$

35° C.

 $\eta_0 = \cdot 00720$.

m	d	η/η_0	η
$\cdot 25$	1·0433	1·0330	$\cdot 00744$
$\cdot 125$	1·0181	1·0167	$\cdot 00732$
$\cdot 0625$	1·0061	1·0089	$\cdot 00726$

25° C.

 $\eta_0 = \cdot 00891$.

m	d	η/η_0	η
$\cdot 25$	1·0454	1·0345	$\cdot 00922$
$\cdot 125$	1·0213	1·0175	$\cdot 00907$
$\cdot 0625$	1·0092	1·0092	$\cdot 00899$

45° C.

 $\eta_0 = \cdot 00597$.

m	d	η/η_0	η
$\cdot 25$	1·0384	1·0310	$\cdot 006155$
$\cdot 125$	1·0146	1·0150	$\cdot 006069$
$\cdot 0625$	1·0024	1·0076	$\cdot 006015$

MERCURIC CHLORIDE.

15° C.

 $\eta_0 = \cdot 011335$.

m	d	η/η_0	η
$\cdot 125$	1·0286	1·0142	$\cdot 01152$
$\cdot 0625$	1·0137	1·0095	$\cdot 01146$
$\cdot 03125$	1·0063	1·0042	$\cdot 011395$

25° C.

 $\eta_0 = \cdot 00891$.

m	d	η/η_0	η
$\cdot 125$	1·0263	1·0165	$\cdot 00906$
$\cdot 0625$	1·0118	1·0107	$\cdot 009005$
$\cdot 03125$	1·0043	1·0053	$\cdot 00896$

POTASSIUM FERRICYANIDE.

1·6° C.

 $\eta_0 = \cdot 01683$.

m	d	η/η_0	η
$\cdot 25$	1·0458	$\cdot 9905$	$\cdot 01667$
$\cdot 125$	1·0231	$\cdot 9868$	$\cdot 01661$
$\cdot 0625$	1·0117	$\cdot 9918$	$\cdot 01668$

15° C.

 $\eta_0 = \cdot 011335$.

m	d	η/η_0	η
$\cdot 5$	1·0854	1·0703	$\cdot 01213$
$\cdot 25$	1·0428	1·0227	$\cdot 01159$
$\cdot 125$	1·0214	1·0100	$\cdot 01145$

25° C.

 $\eta_0 = \cdot 00891$.

m	d	η/η_0	η
$\cdot 5$	1·0827	1·1085	$\cdot 00988$
$\cdot 25$	1·0407	1·0465	$\cdot 00932$
$\cdot 125$	1·0190	1·0208	$\cdot 009095$

POTASSIUM FERROCYANIDE.

15° C.

 $\eta_0 = \cdot 011335$.

m	d	η/η_0	η
·5	1·1164	1·2206	·01384
·25	1·0595	1·0947	·01241
·125	1·0299	1·0470	·01187

25° C.

 $\eta_0 = \cdot 00891$.

m	d	η/η_0	η
·5	1·1128	1·2575	·01120
·25	1·0564	1·1173	·00996
·125	1·0273	1·0593	·00944

POTASSIUM CHLORATE.

15° C.

 $\eta_0 = \cdot 011335$.

m	d	η/η_0	η
·25	1·0184	·9880	·01120
·125	1·0088	·9923	·01125
·0625	1·0039	·9958	·01129

30° C.

 $\eta_0 = \cdot 007975$.

m	d	η/η_0	η
·333	1·0208	1·0000	·007975
·25	1·0146	·9980	·00796
·125	1·0052	·9985	·007965
·0625	1·0006	·9995	·00797

25° C.

 $\eta_0 = \cdot 00891$.

m	d	η/η_0	η
·333	1·0223	·9937	·00885
·25	1·0160	·9980	·00889
·125	1·0065	·9990	·00890
·0625	1·0017	1·0005	·008915

35° C.

 $\eta_0 = \cdot 00720$.

m	d	η/η_0	η
·333	1·0189	1·0010	·00721
·25	1·0128	1·0002	·00720
·125	1·0035	·9989	·00719
·0625	·9988	1·0000	·00720

45° C.

 $\eta_0 = \cdot 00597$.

m	d	η/η_0	η
·25	1·0088	1·0045	·005997
·125	0·9998	1·0023	·005985
·0625	0·9952	1·0018	·00598

AMMONIUM IODIDE.

30° C.

 $\eta_0 = \cdot 007975$.

m	d	η/η_0	η
6	1·5285	1·0315	·00823
4	1·3513	·9137	·00729
1	1·0944	·9446	·00753
·5	1·0401	·9705	·00774
·25	1·0181	·9860	·00786
·125	1·0071	·9930	·00792

45° C.

 $\eta_0 = \cdot 00597$.

m	d	η/η_0	η
1	1·0853	·9682	·005780
·5	1·0380	·9810	·005855
·25	1·0145	·9925	·005925
·125	1·0026	·9968	·005950

CARBAMIDE.

8° C.

$\eta_0 = \cdot 013895.$

m	d	η/η_0	η
0.125	1.0020	1.0012	·01391
·03125	1.0004	·9985	·01387

30° C.

$\eta_0 = \cdot 007975.$

m	d	η/η_0	η
1	1.0115	1.0443	·00833
·5	1.0037	1.0210	·00814
·25	·9999	1.0113	·008065

15° C.

$\eta_0 = \cdot 011335.$

m	d	η/η_0	η
1	1.0156	1.0325	·01170
·5	1.0074	1.0150	·011505
·25	1.0032	1.0085	·01143

35° C.

$\eta_0 = \cdot 00720.$

m	d	η/η_0	η
1	1.0094	1.0448	·00752
·5	1.0019	1.0232	·00737
·25	·9991	1.0120	·00729

25° C.

$\eta_0 = \cdot 00891.$

m	d	η/η_0	η
·125	·99906	1.0050	·008955
·03125	·99754	1.0020	·00893

45° C.

$\eta_0 = \cdot 00597.$

m	d	η/η_0	η
1	1.0054	1.0488	·00626
·5	·9978	1.0241	·00611
·25	·9942	1.0124	·00604

AMMONIUM IODIDE

in a solution of KClO_3 , for which $\eta/\eta_0 = 1$ at 30° C.

30° C.

$\eta_0 = \cdot 007975.$

$m(\text{NH}_4\text{I})$	η/η_0	η
1	·9464	·00755
·5	·9710	·00774
·25	·9853	·00786
·125	·9935	·00792

CARBAMIDE

in a solution of KClO_3 , for which $\eta/\eta_0 = 1$ at 30° C.

30° C.

$m(\text{CO}(\text{NH}_2)_2)$	η/η_0	η
1	1.0462	·00834
·5	1.0218	·00815
·25	1.0113	·008065

DISCUSSION OF THE RESULTS.

1. *The relation between concentration and relative viscosity.*—The previous determinations of the relative viscosity of potassium chloride solutions were insufficient to show conclusively the nature of the curves below concentrations of 1 mol per litre. It was obvious, however, that below that concentration the curves which were practically straight lines must change their character, since the line did not pass through the origin at zero concentration. Whether the viscosity of the solution at some finite concentration became the same as that of water below which concentration it was less than that of water (so-called "negative viscosity"), finally at infinite dilution to again become the same as that of the solvent, could not be settled. Our present results indicate that the course of the curve is somewhat complicated. At 25° C. at concentrations between 1 mol and 2 mols per litre, the value of η/η_0 is greater than 1, at 1 mol per litre it is less than 1, but steadily increases with increasing dilution until at 0.1 mol per litre the ratio is again = 1; after which it is probably a little less than 1, the observed values being .9990 and .9995.

2. The results obtained for potassium chloride were recalculated and curves drawn to show the relation of the ratio η/η_0 to the concentration of the solution expressed in mols per kilogram of solution, to the number of mols of solvent to one mol of solute, and to the number of mols of solution to one mol of solute, but none of these methods of representation introduced any simplification of the curve.

3. In all the solutions examined, with the one exception of mercuric cyanide, increase of temperature increases the ratio η/η_0 . For electrolytes the rate of increase is very much greater than for non-electrolytes; mercuric chloride, which is very little ionised, ranges itself with the non-electrolytes in this respect also.

At high temperatures solutions of mercuric cyanide might be expected to exhibit "negative viscosity," but at 45° C. the ratio η/η_0 is still distinctly greater than unity, the temperature-coefficient being very nearly the same as for water.

4. Our measurements give further support to the view that the relative viscosity of all solutions passes through at least one minimum, the position of the minimum being determined by the nature of the substance and the temperature. The minimum value may be smaller than the corresponding value for the solvent. Whether this occurs or not depends on some factor yet unrecognised.

5. *Carbamide.*—RUDORF* found that, at 25° C., the relative viscosity of aqueous solutions of carbamide decreased with dilution, and at concentrations below .234 mol per litre became less than that of water; the values are—

m	η/η_0
0.937	1.010
.469	1.002
.234	.996
.117	.993
.058	.995

* *Zeit. f. Phys. Chem.*, 43, p. 257, 1903.

FAWSITT* was unable to confirm these results of RUDOLF, and did not obtain any evidence of "negative viscosity" at any concentration. Our measurements, while not in close agreement with FAWSITT's results, also give no indication of "negative viscosity" at 25° C., the values of η/η_0 being 1.005 for 0.125 m. solutions, and 1.002 for 0.03125 m. solutions.

When determinations were made at 8° C., the ratio became slightly less than 1, but only in the case of the most dilute solution. The ratio η/η_0 for a concentration of 0.03125 mol per litre is 0.9985. This value, and also all the other data for carbamide solutions, have been repeatedly determined with independent solutions, and with two different samples of carbamide, and though it is so nearly equal to 1, it is certainly less than 1. The "negative viscosity" would probably be more pronounced at lower temperatures.

Hitherto the only exception to the general rule that aqueous solutions of electrolytes alone exhibit "negative viscosity" has been the fact, established by MÜHLENBEIN and WAGNER,† that some organic substances in organic solvents, *e.g.* cyanobenzol in ethyl alcohol, also exhibit it. Aqueous solutions of carbamide have now been shown to do the same. Other substances may also do so at low temperatures, whilst, as already mentioned, mercuric cyanide may be expected to do so at high temperatures.

6. It seemed probable that a comparison of the viscosity-effect of adding equivalent quantities of an electrolyte, and of a non-electrolyte, to water on the one hand, and to an aqueous solution which at the temperature of experiment has the same relative viscosity as water ($\eta/\eta_0 = 1$), might yield interesting results.

Accordingly, a large quantity of solution of potassium chlorate was made up (approximate concentration .3 mol per litre) which at 30° C. had the relative viscosity 0.998. This substance was chosen because slight variation in the concentration has very little effect on η , nor does η/η_0 change to any great extent with change of temperature; the necessary concentration, also, is not great.

It was necessary to select a salt which has no ion in common with potassium chlorate, so as to avoid alterations in ionisation, etc.; ammonium iodide fulfils this condition; carbamide was used as a non-electrolyte which does not react with the chlorate.

The results obtained show that when the amount of solute added is small there is no recognisable difference between the pure water and the chlorate solution. When the amount of solute added reaches 1 mol per litre there is a slight but distinct difference in both cases; this is probably mainly due to the fact that the ratio of the number of molecules of water to those of ammonium iodide or carbamide becomes more widely different when the number of molecules of the solute is great.

This difference is in the same direction and approximately to the same extent with both solutes. These experiments do not throw much light on the question of the

* *Proc. Roy. Soc. Edin.*, 25, p. 52, 1904.

† *Zeit. f. Phys. Chem.*, 46, p. 872, 1903.

combination of solvent with solute, but, if such combination takes place, one might expect that the viscosity of water and of a solution of potassium chlorate would be altered to an appreciably different extent by addition of an indifferent solute, which also enters into combination with the solvent.

We are at present engaged in an investigation of the comparative effect of certain solutes on the viscosity of different solvents, the comparison being made on the basis of the number of molecules of the solute per volume of solution, and of the number of molecules of the solute to molecules of solvent. In this way it is hoped some light may be thrown on the nature of the effect of solute on solvent, and the alteration of the effect with the nature of the solvent.

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