

of this correction was between +0.06 and +0.08 mg., all as silver bromide.

Results

When making the corrections necessary for reducing the observed weights of silver, silver bromide and rubidium bromide to the vacuum standard, the specific gravity of silver was taken

TABLE I
NEPHELOMETRIC ANALYSES

Expt.	Rubidium bromide	Rubidium bromide in vac., g.	Silver in vac., g.	At. wt. of rubidium
1	I	3.67283	2.39554	85.485
2	I	3.27067	2.13320	85.488
3	II	4.04039	2.63537	85.479
4	II	3.20309	2.08916	85.485
5	II	4.00547	2.61245	85.488
6	II	6.66951	4.35022	85.480
7	II	4.69377	3.06150	85.481
8	II	3.33389	2.17458	85.477
9	III	3.62456	2.36409	85.483
				Average 85.483

TABLE II
GRAVIMETRIC ANALYSES

Expt.	Rubidium bromide in vac., g.	Silver bromide in vac., g.	At. wt. of rubidium
6	6.66951	7.57272	85.481
7	4.69377	5.32945	85.480
9	3.62456	4.11561	85.473
			Average 85.478

as 10.49, of silver bromide as 6.473 and that of rubidium bromide as 3.282.

The equivalents used in making the calculations for the tables were Ag = 107.880 and Br = 79.916.

These values agree well with the value found from the study of the chloride. We then have three values as follows:

From Rubidium Chloride-Silver	85.482
From Rubidium Bromide-Silver	85.483
From Rubidium Bromide-Silver Bromide	85.478
Average 85.481	

The atomic weight of rubidium cannot therefore be far from 85.481.

This research was greatly aided by an award to one of us in the form of a scholarship from Dr. Francis J. Nicholson.

Summary

The nephelometric determination of the rubidium bromide-silver ratios gave a value 85.483 for the atomic weight of rubidium and the gravimetric estimation of the ratios rubidium bromide-silver bromide gave the figure 85.478. When these values are combined with that obtained from the rubidium chloride analyses the average value 85.481 is obtained for the atomic weight in question.

VANCOUVER, B. C.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions of Electrolytes as a Function of the Concentration. III. Cesium Iodide and Potassium Permanganate

BY GRINNELL JONES AND HOLMES J. FORNWALT

This paper describes a continuation of the earlier researches¹ carried out in this Laboratory on the viscosity of solutions for the purpose of testing further the general validity of the following: (1) the law for the variation of the viscosity with the concentration, $\eta = 1 + A\sqrt{c} \pm Bc$, proposed by Jones and Dole; (2) the Falkenhagen and Vernon² equation for the coefficient of the square root term A ; (3) the suggestion of Cox and

Wolfenden³ that the coefficient of the linear term ($\pm B$) is made up additively of parts characteristic of each ion; (4) the extension of the Jones and Dole equation proposed by Onsager and Fuoss,⁴ $\eta = 1 + A\sqrt{c} - Bc + Dc \log c + \dots$; (5) the Root⁵ equation for the variation of the density of solutions with the concentration.

Cesium iodide was selected for study because the available data on other salts indicated that the cesium ion exceeds all other cations and the iodide ion all other anions, in their tendency to cause a decrease in the viscosity of water. It is,

(1) Grinnell Jones and M. Dole, *THIS JOURNAL*, **51**, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933); *Physica*, **4**, 215 (1933); Grinnell Jones and H. J. Fornwalt, *THIS JOURNAL*, **57**, 2041 (1935).

(2) H. Falkenhagen and M. Dole, *Z. physik. Chem.*, **B6**, 159 (1929); *Physik. Z.*, **30**, 611 (1929); H. Falkenhagen, *ibid.*, **32**, 365, 745 (1931); H. Falkenhagen and E. L. Vernon, *ibid.*, **33**, 140 (1932); *Phil. Mag.*, [7] **14**, 537 (1932).

(3) W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc. London*, **A145**, 475 (1934).

(4) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(5) W. C. Root, *THIS JOURNAL*, **55**, 850 (1933).

therefore, to be expected, if the ionic effects are additive as suggested by Cox and Wolfenden, that cesium iodide will give a lower viscosity than any other known salt at corresponding concentrations, and therefore give an especially severe test of the Jones and Dole equation.

There are no published data known to us on the viscosity of solutions of any permanganate. Potassium permanganate was selected for study because the data would be as useful as those of any other salt for the general purposes outlined above and in addition might lead to the discovery of another ion having the property of causing a diminution of the viscosity of water. It was also of interest to determine whether our new technique of timing by means of a photoelectric cell would be applicable to such highly colored almost opaque solutions as nearly saturated solutions of potassium permanganate.

By measuring all solutions at both 25 and 0° we have made a beginning in the study of the temperature coefficient of viscosity of solutions.

Experimental

The viscometric apparatus and technique were the same as that devised by Jones and Talley and used by them and others in this Laboratory. The viscometer, which was of the Ostwald type, was built entirely of quartz and had an efflux volume of 10 cc. and a working volume of 65.2 cc. The capillary was 16.5 cm. long and 0.048 cm. in diameter. The period of efflux with water was about 539 seconds at 25° and 1082 seconds at 0°. The ice thermostat was designed and constructed by Mr. R. E. Stauffer and will be described in a later paper. The viscosity of a solution was first measured at 25° and then the viscometer transferred to the ice thermostat without removing the solution and measurements made at 0°. The viscometer was then rinsed, dried and filled with water and the period of efflux determined at both temperatures. Finally a second sample of the solution was placed in the viscometer and the viscosity determined at both temperatures. As usual in this type of work, a few erratic results were obtained which are believed to be due to traces of dust or grease since the difficulty could be eliminated by removing the solution, cleaning the viscometer and adding a fresh filtered solution. The figures given in the tables are the average of results obtained with two independent fillings of the viscometer which did not differ by more than

0.01% in any case. These differences were only 0.005% on the average.

Materials.—The cesium iodide was kindly prepared for us from the mineral pollucite by Professor Brainerd Mears of Williams College. The pollucite was first converted into the cesium alum which was purified by recrystallization and converted in turn into the nitrate and the sulfate. A solution of the latter was treated with a solution of carefully purified barium iodide (free from chloride and bromide), and after filtration from barium sulfate the cesium iodide was twice crystallized with centrifugal drainage. Photographs of the spectra, kindly made for us by Professor G. P. Baxter, showed the absence of any significant amounts of sodium, potassium, rubidium, barium or aluminum. Qualitative tests for sulfate gave negative results. The salt was placed in a platinum boat in a quartz tube and heated for two hours at 150° in a stream of oxygen-free nitrogen. The solutions were neutral to phenolphthalein.

The potassium permanganate was made from Mallinckrodt analytical reagent. It was twice dissolved in water, boiled, filtered, crystallized and centrifuged. The salt was dried in platinum boats in a vacuum at 100°. No manganese dioxide was ever observed to have deposited in the capillary or walls of the viscometer. The water used for calibrating the instrument and making up the solutions was conductivity water. The solutions were made up by weight. All liquids were filtered through sintered Pyrex disks to remove dust before they were placed in the viscometer for measurement.

Interpretation and Discussion of the Results.—The first three columns of Tables I to IV give: (1) the concentration of the solutions, c , in moles per liter; (2) the observed absolute density, d^{25}_4 or d^0_4 , in grams per milliliter; (3) the observed viscosity, η , relative to that of water at the same temperature.

The density of these solutions can be expressed by the equations given at the bottom of each table. These equations have the form suggested by Root and are valid over the entire range of concentration studied with an average deviation of only two parts per hundred thousand in the cases of cesium iodide at 25 and 0° and three parts per hundred thousand in the case of potassium permanganate at 25°. For the latter salt at 0° a linear equation suffices with an average deviation of two parts per hundred thousand.

The fourth column in these tables gives the values of $(\eta - 1)/c$ which would be a constant if there

TABLE I
RELATIVE VISCOSITY AND DENSITY OF CESIUM IODIDE SOLUTIONS IN WATER AT 0°

Concn., <i>c</i>	Density <i>d</i> ₄	Rel. η obs.	$(\eta - 1)/c$	Rel. ϕ obs.	Jones and Dole Equations	
					Simple $\Delta\phi$ $\times 10^5$	Ex- tended $\Delta\phi$ $\times 10^5$
0.000200	0.99992	1.00001	+0.05	0.99999	- 2	- 2
.000500	1.00002	0.99998	-.04	1.00002	- 5	- 5
.001000	1.00011	.99985	-.15	1.00015	- 2	- 3
.002000	1.00036	.99962	-.19	1.00038	- 2	- 3
.005000	1.00091	.99881	-.238	1.00119	+ 10	+ 8
.009998	1.00195	.99773	-.227	1.00228	- 1	- 5
.010000	1.00193	.99771	-.229	1.00230	+ 1	- 3
.019977	1.00401	.99535	-.233	1.00467	- 4	-11
.029950	1.00607	.99289	-.237	1.00716	0	- 9
.049993	1.01021	.98802	-.240	1.01213	+ 2	-11
.074995	1.01538	.98205	-.239	1.01828	- 5	-19
.078389	1.01605	.98117	-.240	1.01919	+ 1	-12
.099989	1.02052	.97600	-.240	1.02459	+ 2	- 9
.150018	1.03077	.96441	-.237	1.03690	- 18	-12
.200017	1.04108	.95329	-.234	1.04900	- 61	-23
.285023	1.05849	.93480	-.229	1.06975	-120	+ 5
.385037	1.07896	.91467	-.222	1.09329	-282	+ 1
.496900	1.10182	.89346	-.214	1.11924	-503	+25
.750096	1.15341	.85166	-.198	1.17418	-1391	-33
1.00007	1.20415	.81561	-.184	1.22608	-2509	+39
1.43997	1.29307	.76524	-.163	1.30677	-5548	-11

Root equation:
 $d_4 = 0.99987 + 0.20739c - 0.00314c^{3/2}$ 1.44 0.002

Jones and Dole equations:
 $\phi = 1 - 0.00253\sqrt{c} + 0.25368c$ 0.1 .003
 $\phi = 1 - 0.00253\sqrt{c} + 0.25769c - 0.02949c^2$ 1.44 .012

TABLE II
RELATIVE VISCOSITY AND DENSITY OF CESIUM IODIDE SOLUTIONS IN WATER AT 25°

Concn., <i>c</i>	Density <i>d</i> ₂₅	Rel. η obs.	$(\eta - 1)/c$	Rel. ϕ obs.	Jones and Dole Equations	
					Simple $\Delta\phi$ $\times 10^5$	Ex- tended $\Delta\phi$ $\times 10^5$
0.000199	0.99710	1.00009	+0.45	0.99991	- 6	- 7
.000498	.99714	0.99997	-.06	1.00003	+ 6	+ 6
.000997	.99726	1.00003	+.03	0.99997	- 3	- 4
.001994	.99746	0.99983	-.085	1.00017	+ 10	+ 9
.004985	.99806	.99963	-.074	1.00037	+ 3	+ 1
.009971	.99908	.99911	-.089	1.00089	+ 6	+ 2
.019919	1.00108	.99815	-.093	1.00185	- 4	- 10
.029862	1.00309	.99709	-.097	1.00292	- 7	- 15
.049888	1.00713	.99478	-.104	1.00525	0	- 13
.074758	1.01216	.99192	-.108	1.00815	+ 5	- 10
.078141	1.01284	.99160	-.108	1.00847	- 2	- 18
.099661	1.01717	.98910	-.109	1.01102	+ 3	- 12
.149505	1.02724	.98344	-.111	1.01684	+ 3	- 7
.199281	1.03725	.97785	-.111	1.02265	- 3	+ 4
.283884	1.05425	.96897	-.109	1.03202	- 70	- 13
.383349	1.07422	.95866	-.108	1.04312	- 144	+ 8
.494697	1.09656	.94799	-.105	1.05486	-302	+ 2
.745855	1.14680	.92618	-.099	1.07973	-830	- 3
.993688	1.19645	.90726	-.093	1.10222	-1585	+ 21
1.42912	1.28333	.88080	-.083	1.13533	-3511	- 8
1.99969	1.39696	.85818	-.071	1.16526	-7423	-280

Root equation:
 $d_{25} = 0.99707 + 0.20225c - 0.00162c^{3/2}$ 2.0 0.002

Jones and Dole equations:
 $\phi = 1 - 0.00387\sqrt{c} + 0.12250c$ 0.2 .004
 $\phi = 1 - 0.00387\sqrt{c} + 0.12607c - 0.01965c^2$ 1.44 .009

TABLE III
RELATIVE VISCOSITY AND DENSITY OF POTASSIUM PERMANGANATE SOLUTIONS IN WATER AT 0°

Concn., <i>c</i>	Density <i>d</i> ₄	Rel. η obs.	$(\eta - 1)/c$	Rel. ϕ obs.	Jones and Dole Equations	
					Simple $\Delta\phi$ $\times 10^5$	Ex- tended $\Delta\phi$ $\times 10^5$
0.000511	0.99993	1.00000	0.000	1.00000	+ 2	+ 2
.001031	0.99999	0.99995	-.05	1.00005	+ 1	+ 1
.005080	1.00047	.99952	-.095	1.00048	- 9	-11
.010079	1.00100	.99847	-.152	1.00153	+ 19	+17
.019994	1.00213	.99709	-.146	1.00292	0	- 3
.020105	1.00214	.99710	-.144	1.00291	- 3	- 6
.030096	1.00329	.99555	-.148	1.00447	- 12	-15
.050375	1.00557	.99201	-.159	1.00805	+ 6	+ 9
.075239	1.00836	.98815	-.158	1.01199	- 24	- 6
.100314	1.01118	.98403	-.159	1.01623	- 30	+10
.125493	1.01398	.98047	-.156	1.01992	- 96	-22
.150518	1.01675	.97625	-.158	1.02433	- 89	+27
.180744	1.02014	.97221	-.154	1.02858	-189	-11

Range of validity Av. % dev.
Density equation: $d_4 = 0.99987 + 0.11233c$ 0.18 0.002

Jones and Dole equations:
 $\phi = 1 - 0.00472\sqrt{c} + 0.17968c$.05 .006
 $\phi = 1 - 0.00472\sqrt{c} + 0.18268c - 0.07094c^2$.18 .011

TABLE IV
RELATIVE VISCOSITY AND DENSITY OF POTASSIUM PERMANGANATE SOLUTIONS IN WATER AT 25°

Concn., <i>c</i>	Density <i>d</i> ₂₅	Rel. η obs.	$(\eta - 1)/c$	Rel. ϕ obs.	Jones and Dole Equations	
					Simple $\Delta\phi$ $\times 10^5$	Ex- tended $\Delta\phi$ $\times 10^5$
0.000509	0.99712	1.00012	+0.24	0.99988	- 2	- 3
.001028	.99714	1.00017	+ .17	.99983	- 5	- 6
.005065	.99763	1.00012	+.024	.99988	- 4	- 6
.010050	.99809	0.99978	-.022	1.00022	+ 14	+10
.019934	.99913	.99950	-.025	1.00050	- 1	- 6
.030004	1.00024	.99905	-.032	1.00095	- 3	- 10
.050215	1.00236	.99800	-.040	1.00200	- 2	-10
.074986	1.00496	.99673	-.044	1.00238	- 9	-12
.099961	1.00762	.99511	-.049	1.00491	+ 13	+19
.125028	1.01022	.99388	-.049	1.00616	- 5	+18
.149938	1.01283	.99261	-.049	1.00745	- 22	+22
.180015	1.01602	.99127	-.048	1.00881	- 62	+14
.250256	1.02336	.98868	-.045	1.01145	-218	-33
.351500	1.03379	.98483	-.043	1.01540	-438	-21
.450368	1.04397	.98165	-.041	1.01869	-716	+16

Range of validity Av. % dev.
Root equation:
 $d_{25} = 0.99707 + 0.10664c - 0.00367c^{3/2}$ 0.45 0.003

Jones and Dole equations:
 $\phi = 1 - 0.00577\sqrt{c} + 0.06800c$.125 .006
 $\phi = 1 - 0.00577\sqrt{c} + 0.06978c - 0.04451c^2$.45 .013

were a linear relationship between the viscosity and the concentration. The results, however, show that with increasing concentration the value of $(\eta - 1)/c$ decreases sharply in the dilute range. This effect is due to interionic forces. If the solubility is sufficient, $(\eta - 1)/c$ passes through a flat minimum at moderate concentrations and rises gently at high concentrations. This behavior, which was first observed by Grüneisen,⁶ is typical

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

of all electrolytes which have been studied with precision.

These data are in accord with the observation of earlier experimenters that lowering the temperature tends to cause a decrease in the relative viscosity of aqueous solutions.

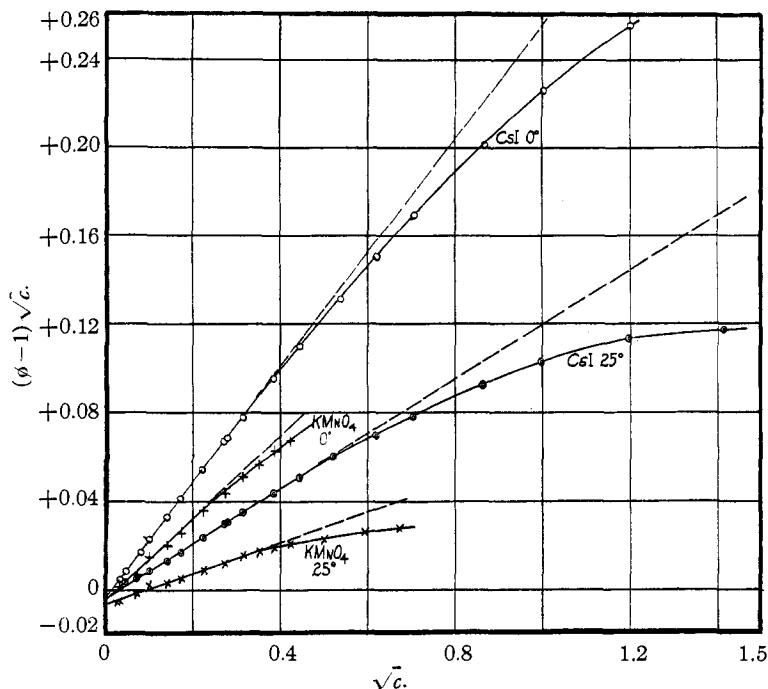


Fig. 1.—Test of the simple Jones and Dole equation.

The Jones and Dole equation may be written either in terms of viscosity $\eta = 1 + A\sqrt{c} + Bc$, or in terms of fluidity $\phi = 1 - A\sqrt{c} - B'c$, which are almost but not quite identical when applied to dilute solutions. The two forms have the same numerical value for the coefficient of the square root term, although the sign is opposite; and nearly the same value (although opposite sign) for the coefficient of the linear term. There is little practical difference between the usefulness of the two forms provided the concentrations are sufficiently low so that terms of a higher order are negligible. But for concentrated solutions this is by no means true.

Jones and Dole found that for barium chloride the equation $\phi = 1 - 0.02013\sqrt{c} - 0.20087c$ is valid up to 1 molal, whereas an equation of the same simple form in terms of viscosity is valid up to 0.1 molal. The reciprocal of the above equation may be obtained by division giving

$$\eta = 1/\phi = 1 + 0.02013\sqrt{c} + 0.20128c + 0.00809c^{3/2} + 0.04059c^2 + \dots$$

It is thus apparent that an equally simple form of the equation in terms of η will be valid only at concentrations sufficiently low so that the terms of higher order than linear will be negligible. In this particular case if the simple fluidity equation is valid up to 1 molal the simple viscosity equation

can only be valid up to about 0.1 molal. On the other hand, it has been shown by Jones and Fornwalt that solutions of several salts in methyl alcohol which increase the viscosity give simpler equations in terms of viscosity. Jones and Talley found it slightly better to use the viscosity equation for several salts which diminish the viscosity of water. But although both cesium iodide and potassium permanganate decrease the viscosity, we have found that the results can be expressed better in terms of fluidity than in terms of viscosity although the advantage is not great. For the sake of brevity the equations will be given in terms of fluidity only. The reasons for these subtle and puzzling anomalies are not clear, but it is hoped that when sufficient additional cases

have been studied the explanation will be found.

Figure 1 gives a plot of $(\phi - 1)/\sqrt{c}$ against \sqrt{c} which gives straight lines in the dilute range in all four cases. These straight lines all have a negative intercept on the vertical axis and a positive slope which proves that an equation of the form $\phi = 1 - A\sqrt{c} + Bc$ holds. By the use of the method of least squares the numerical values of the coefficients were found to be as follows.

$$\begin{aligned} \phi &= 1 - 0.00253\sqrt{c} + 0.2537c \text{ valid up to } c = 0.1 N \\ \phi &= 1 - .00387\sqrt{c} + .1225c \text{ valid up to } c = .2 N \\ \phi &= 1 - .00472\sqrt{c} + .1797c \text{ valid up to } c = .05 N \\ \phi &= 1 - .00577\sqrt{c} + .0660c \text{ valid up to } c = .12 N \end{aligned}$$

The deviations between the observed results and values computed by these equations are shown in the sixth column of Tables I to IV.

It now becomes of interest to find an equation which will be valid over a higher range of concentration. Jones and Talley have found that the addition of a term proportional to c^2 in the viscosity equation gave an equation which is useful up to 3 *N* for potassium chloride at 25° and up to 2 *N* for potassium bromide at 25°. For cesium

iodide and potassium permanganate we have found that the extended fluidity equation is better than the extended viscosity equation. If an equation of the form $\phi = 1 - A\sqrt{c} + Bc + Dc^2$ is valid and if we assume that the numerical value of A has been determined from the results with dilute solutions as explained above, then a plot of $(\phi - 1 + A\sqrt{c})/c$ against c should give a straight line. Plots of this kind are shown in Fig. 2 and were used to determine the useful range of the extended form of the equation. Erratic points in the dilute range are not significant in this plot

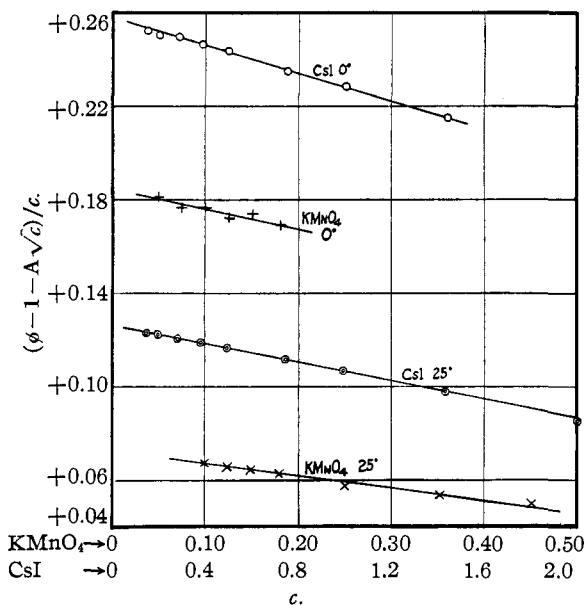


Fig. 2.—Test of the extended Jones and Dole equation.

because the plot is extremely sensitive to experimental errors for dilute solutions. These plots show that the extended equation holds for potassium permanganate throughout the range studied which extends nearly to saturation and for cesium iodide up to and including 1.44 N but not at 2 N . The numerical values for B and D were then determined by the method of least squares (omitting the data for cesium iodide at 2 N) with the following results.

CsI at 0°	$\phi = 1 - 0.00253\sqrt{c} + 0.25759c - 0.02949c^2$
CsI at 25°	$\phi = 1 - .00387\sqrt{c} + .12607c - 0.01965c^2$
KMnO ₄ at 0°	$\phi = 1 - .00472\sqrt{c} + .18268c - 0.07034c^2$
KMnO ₄ at 25°	$\phi = 1 - .00577\sqrt{c} + .06978c - 0.04451c^2$

The deviations between the observed results and values computed by these equations are also given in the seventh column of Tables I to IV.

The Onsager and Fuoss equation $\eta = 1 + A\sqrt{c} + Bc + Dc \log c + \dots$ has been tested in Fig. 3 by plotting $(\eta - 1 - A\sqrt{c})/c$ against $\log c$ which should give a straight line if the equation is valid.

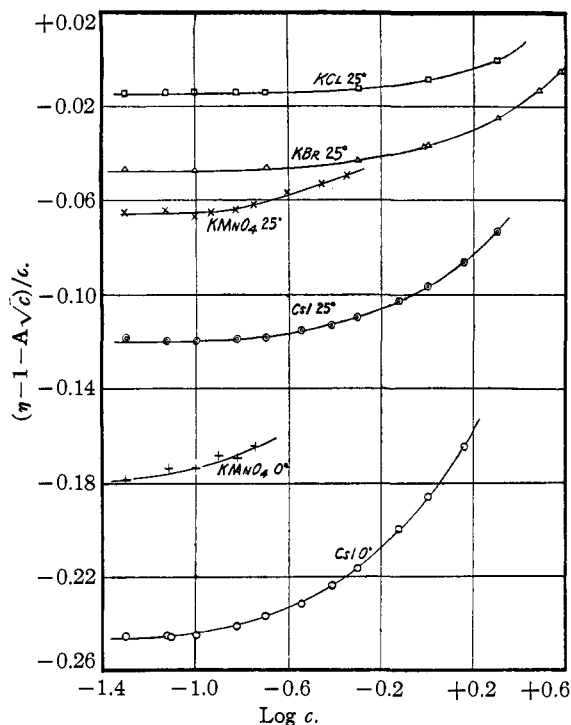


Fig. 3.—Test of the Onsager and Fuoss equation.

The A was assigned the value found from the data for dilute solutions by the simple Jones and Dole equation. None of the data below $c = 0.05 N$ are plotted on the graph because this method of plotting is very sensitive to experimental errors in the dilute range. The data for potassium chloride and potassium bromide at 25° from the paper of Jones and Talley have been added to the plot. It is evident from the graph that it is impossible to draw a straight line through the points over any appreciable part of the curves and it therefore follows that this equation is not useful. Similar plots in terms of fluidity have been prepared but are no better. This conclusion is rather surprising in view of the fact that the Onsager and Fuoss equation has been found to be valid for solutions of potassium chloride, bromide, iodide and ammonium chloride in methanol up to $c = 0.35 N$ in some cases.

Falkenhagen and Vernon have used the Debye theory of interionic attraction to derive an expression for the coefficient A of the square root term which for the case of uni-univalent salts reduces to

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

where η_0 and D are the absolute viscosity and the dielectric constant of the solvent, T is the absolute temperature and l_1 and l_2 are the equivalent conductances of the ions. The factor 1.45 is computed from the universal constants common to the equations based on the Debye theory. The values of A have been computed from this equation for both salts at both temperatures using the values of the constants shown in Table V.

TABLE V

VALUES USED IN COMPUTING A BY THE FALKENHAGEN AND VERNON EQUATION

Temp., °C.	η	D	Equivalent ionic conductances			
			Cs	I	K	MnO ₄
0	0.017921 ^a	88.0 ^b	44.4 ^c	43.4 ^c	40.4 ^f	31.0 ^h
25	.008937 ^a	78.8 ⁱ	78.1 ^d	76.7 ^e	73.5 ^g	61.7 ^e

^a E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York City, 1922, p. 340. ^b "International Critical Tables," Vol. VI, p. 78. ^c Landolt and Börnstein, "Phys. chem. Tabellen," 5th edition, 1st supplement, Part I, p. 619, 620. ^d H. Hartley and H. R. Raikes, *Trans. Faraday Soc.*, **23**, 394 (1927). ^e Grinnell Jones and M. L. Hartmann, *THIS JOURNAL*, **37**, 258 (1915). ^f J. Johnston, *ibid.*, **31**, 1015 (1909). ^g D. A. MacInnes, T. Shedlovsky and L. G. Longworth, *ibid.*, **54**, 2762 (1932). ^h Estimated from the 25° value, assuming ionic conductance proportional to the fluidity of the solvent. ⁱ H. Falkenhagen, *Physik. Z.*, **32**, 763 (1931).

The values for the ionic conductances are not strictly comparable since they are obtained from many different authors who have used different standards of absolute conductance and various methods for extrapolation of their conductance data to infinite dilution, and different values of transference numbers. However, the inconsistencies in these figures probably will not influence the computed values of A by more than one or two units in the second significant figure.

TABLE VI

COMPARISON OF THE THEORETICAL AND EXPERIMENTAL VALUES OF THE COEFFICIENT OF THE SQUARE ROOT TERM,

Salt	Temp., °C.	A	
		Theoretical Falkenhagen	Experimental
CsI	0	0.0042	0.0025
CsI	25	.0048	.0039
KMnO ₄	0	.0052	.0047
KMnO ₄	25	.0056	.0058

The agreement for potassium permanganate is gratifying. For cesium iodide the agreement is poor, especially at 0°. It should, however, be pointed out that the experimental determination

of A is more difficult for cesium iodide than for any other salt yet studied, especially at 0°, because the coefficient of the linear term is larger than for any other known salt so that the linear term tends to mask the square root term.

Our data demonstrate that cesium iodide is more effective both at 25 and 0°, in lowering the viscosity of water than any other known salt at corresponding concentrations. This was anticipated from the postulate of Cox and Wolfenden that the values of B for salts are made up additively of parts characteristic of each ion. According to these authors the cesium ion at 25° contributes -0.046 to the B and the iodide ion -0.079 giving a value of B for cesium iodide of -0.125 . Our data on cesium iodide at 25° up to $c = 0.2 N$ can be expressed by the equation $\eta = 1 + 0.0306 \sqrt{c} - 0.1184c$. Our experimental value of B is therefore -0.118 which indicates that the ionic effects are approximately additive in determining the value of B . It may also be inferred from the Jones and Dole equation that for a salt having such a large negative value of B the positive maximum in the viscosity curve will occur at such an extreme dilution that it cannot be realized experimentally. This accords with our experience.

Our data show for the first time that the permanganate ion must be added to the list of ions which tend to cause a diminution in the viscosity of water. At 25° the value of the B coefficient is -0.066 . Cox and Wolfenden assign a value -0.008 to the potassium ion so that on this basis the value for the permanganate ion is -0.058 . So far as is now known the iodide ion ($B = -0.079$) is the only ion which has a greater effect in lowering the viscosity of water. The positive maximum in the viscosity curve is, however, clearly demonstrated experimentally for potassium permanganate at 25°.

Summary

1. The absolute density and relative viscosity of many solutions of cesium iodide and potassium permanganate in water have been measured at 0 and 25°, covering a range of concentration from extreme dilution nearly to saturation.

2. The density of these solutions can be expressed as a function of the concentration by Root's equation.

3. Cesium iodide is more effective in lowering the viscosity of water than any other known salt.

Cox and Wolfenden's suggestion that this effect is approximately an additive property of the ions has been confirmed.

4. It is shown for the first time that permanganates have the property of diminishing the viscosity of water.

5. The extended Jones and Dole equation is

found to fit our data better and over a greater range of concentration than any other known equation.

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

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE C. F. KETTERING FOUNDATION FOR THE STUDY OF CHLOROPHYLL AND PHOTOSYNTHESIS]

A New Porphyrin Synthesis. The Synthesis of Porphin¹

BY PAUL ROTHEMUND

Recently we reported on the formation of porphyrins from pyrrole and aldehydes (formaldehyde, acetaldehyde and furaldehyde),² and we announced further studies to ascertain the applicability of the reaction to other aldehydes. It was found that the reaction can be used for the synthesis of a large number of porphyrins, when pyrrole is used as one component and a substance with aldehydic function as the other component. In this paper the reaction between pyrrole and formaldehyde will be described, as the reaction product, porphin³ (Fig. 1), is of interest as the fundamental ring system in all the porphyrins, and hence also in the important pigments hemin and chlorophyll.

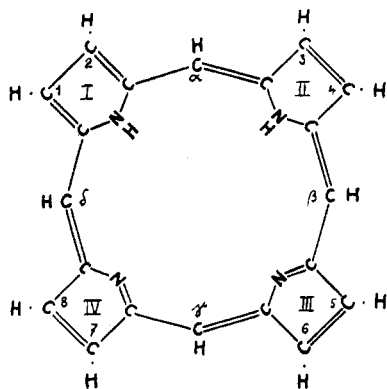


Fig. 1.—Porphin.

Attempts to prepare this ring system had been made by different investigators in the field,^{4,5}

(1) This investigation was carried out with the experimental cooperation of T. Londergan in partial fulfilment of the requirements for his Bachelor's degree under the Antioch Coöperative Plan.

(2) Rothemund, *THIS JOURNAL*, **57**, 2010 (1935).

(3) Fischer and Halbig, *Ann.*, **448**, 193 (1926); Fischer, Halbig, and Walach, *ibid.*, **452**, 268 (1927).

(4) Chelintzev and Maksorov, *J. Russ. Phys.-Chem. Soc.*, **48**, 748 (1916); quoted from *C. A.*, **11**, 782 (1917).

(5) Godnew and Naryschkin, *Ber.*, **58**, 2703 (1925); *ibid.*, **59**, 2897 (1926).

but the reaction products obtained did not exhibit the characteristic properties of porphyrins. Very recently Fischer⁶ reported a synthesis of porphin, brought about by adding pyrrole- α -aldehyde to boiling formic acid; his spectroscopic data for porphin checked with those published from this Laboratory.²

Our porphin synthesis may be represented by the scheme shown in Fig. 2. When formaldehyde and pyrrole were used, porphin (Fig. 1) was obtained; with pyrrole and another aldehyde a porphin with substitution in the positions α , β , γ and δ resulted.

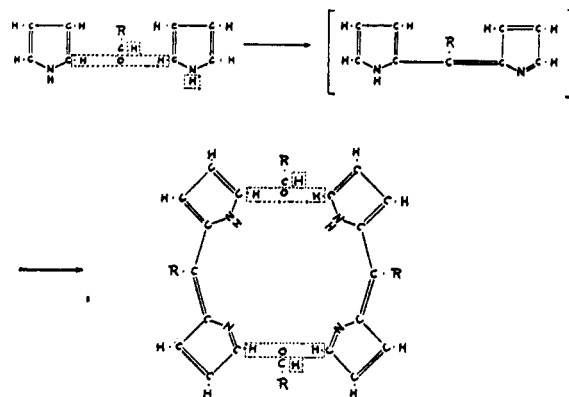


Fig. 2.

If the synthesis with formaldehyde and pyrrole was performed at a temperature of 145–155° instead of 90–95° as described for porphin in the experimental part, a porphyrin resulted which differed from porphin spectroscopically in the positions of the two main absorption bands: these bands were shifted approximately 100 Å. toward the red region of the spectrum. The hydrochloric acid number was much lower than that of porphin. Studies are now in progress to deter-

(6) Fischer and Gleim, *Ann.*, **521**, 157 (1935).