peroxide and bromine under the influence of blue light gives quantum yields considerably in excess of unity. A recalculation of Livingston and Schoeld's data gives quantum yields greater than unity for green light also. A chain mechanism is indicated, contrary to the conclusion of Livingston and Schoeld.

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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. IV. Potassium Ferrocyanide

BY GRINNELL JONES AND ROBERT ELIOT STAUFFER

Introduction

This paper describes a continuation of the earlier researches[1] carried out in this Laboratory on the viscosity of solutions of electrolytes. An historical introduction and a discussion of the general objects of the investigation and the progress already made will be found in the earlier papers of this series and is therefore omitted here. In this paper the investigation is extended to a salt of a higher valence type and measurements are made at both 25 and 0° on the same solution in order to permit the study of the influence of temperature on the phenomena. Potassium ferrocyanide was selected as the most suitable unitetravalent salt since it is sufficiently soluble and stable and is only slightly hydrolyzed. Moreover, measurements on viscosity were needed for use in the interpretation of data on the conductance of this salt which were being obtained in this Laboratory (see the following paper).

Experimental

The apparatus and experimental procedure was the same as that described in the earlier papers with some modifications and improvements in detail. The most important innovation was the construction of an ice thermostat permitting the viscometer to be placed in succession in the 25 and 0° thermostats so that measurements could be made in succession on the same solution.

The ice thermostat consisted of a tank of about 180-liter capacity firmly supported on a three-point support of Monel metal and surrounded on all sides except the top with diatomaceous earth at least 8 cm. thick. The top had insulating covers built in sections permitting temporary removal in parts when necessary to insert the viscometers or to add fresh ice. The tank had small double windows of plate glass in front and rear to permit observation and operation of the optical system necessary for the automatic timing described in the earlier papers. The thermostat when in use was filled with a well-stirred mixture of ice and water. Wire screens of 14-mesh were arranged as near to the viscometer as possible to protect the fragile instrument from fracture by the moving ice and also to keep open narrow paths for the beam of light needed for operation of the automatic timing system and for inspection of the upper bulb of the viscometer. Water was kept circulating vigorously through the ice and around the viscometer by three motor-driven stirrers. A very good thermometer having an open scale 6 cm. long per degree was mounted totally immersed near the viscometer and read through the window to thousandths of a degree by a telescope. The readings of the thermometer and the consistency of the viscometric data prove that our thermostat can maintain a temperature safely within 0.003 of 0°. It requires about 50 pounds (25 kg.) of ice per day in hot summer weather.

Our old instrument has an inconveniently long period at 0° and therefore a new viscometer of vitreous silica was constructed with a slightly wider capillary (0.052 cm. diameter and 17.9 cm. long) and therefore a shorter period (428.7 sec. for water at 25° and 862.9 sec. for water at 0°). The ice thermostat had its own optical system, photoelectric cell and amplifiers but the same chronograph and clocks served both thermostats. Three different viscometers could be used interchangeably in either thermostat and measurements with different instruments could be going on simultaneously in both thermostats if desired.

The best potassium ferrocyanide available by purchase was twice recrystallized by dissolving in water at 60°, cooling and adding ethyl alcohol, followed by centrifugal drainage. It was dried by heating to 90° in nitrogen at low pressure for several hours. The solutions were made up by weight.

The experimental data at 25 and at 0° are recorded in Tables I and II, respectively. The values for the density given in parentheses were not actually measured but were computed by the formula given below. The third column gives the relative viscosity before applying the kinetic energy correction, which is shown in column 4. The relative viscosity after applying the kinetic energy correction is given in column 5. In some cases a small correction was necessary to bring the data to a round concentration. The results after applying this correction are shown in the last column.

Interpretation of the Data.—The experimental data given below on the density of potassium

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[1] Grinnell Jones and M. Dole, THIS JOURNAL, 51, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, 55, 624, 4124 (1933); *Physics*, 4, 215 (1933); Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, 57, 2041 (1935); 58, 619 (1936).

TABLE I

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM FERROCYANIDE SOLUTIONS IN WATER AT 25°

Concn., c	Density, d^{25}_4	$d_c t_c / d_0 t_0$	K. E.	Relative η obsd.	η at round concn.
0.000200	(0.99712)	1.00053	0	1.00053	1.00053
		1.00053	0	1.00053	1.00053
.000350	(.99716)	1.00082	+1	1.00083	1.00083
.000349	(.99716)	1.00070	1	1.00071	1.00071
		1.00081	1	1.00082	1.00082
.000500	(.99720)	1.00102	1	1.00103	1.00103
		1.00102	1	1.00103	1.00103
.000749	(.99726)	1.00133	2	1.00135	1.00135
		1.00140	2	1.00142	1.00142
.000997	.997376	1.00161	2	1.00163	1.00163
		1.00161	2	1.00163	1.00163
.001995	.997562	1.00238	3	1.00241	1.00241
		1.00243	3	1.00246	1.00246
.004991	.998317	1.00455	4	1.00459	1.00459
.004963	.998304	1.00442	4	1.00446	1.00447
		1.00442	4	1.00446	1.00447
.009938	.999556	1.00736	6	1.00742	1.00744
		1.00736	6	1.00742	1.00744
.019768	1.001979	1.01231	10	1.01241	1.01252
.019975	1.002079	1.01249	10	1.01259	1.01259
.049935	1.009326	1.02615	18	1.02633	1.02634
.049916	1.009308	1.02610	18	1.02628	1.02630
.099212	1.021107	1.04778	30	1.04808	1.04839
.099822	1.021248	1.04804	30	1.04834	1.04840
.199543	1.044628	1.09339	58	1.09397	1.09412
.199588	1.044675	1.09353	58	1.09411	1.09416
.198806	1.044321	1.09272	58	1.09330	1.09414
		1.09272	58	1.09330	1.09414
.499582	1.112550	1.26143	178	1.26321	1.26350
		1.26138	178	1.26315	1.26344

ferrocyanide solutions may be expressed with an average deviation of 0.003% by the equations

$$d^{25}_4 = 0.99707 + 0.25074c - 0.02776c^{3/2}$$
$$d^{0}_4 = .99987 + .26836c - .04313c^{3/2}$$

The agreement with the Root equation is not quite so good as has been found for other salts of simpler valence type in previous work in this Laboratory. The deviations although small are apparently systematic in this case and greater than the experimental error.

Column 4 of Tables III and IV shows that the "Grüneisen Effect" is more pronounced than for the salts of lower valence type which have been studied in this Laboratory.

The results at 25° can be expressed in terms of relative fluidity by the equation having the form proposed by Jones and Dole, namely

$$\varphi = 1/\eta = 1 - 0.03995\sqrt{c} - 0.33518c$$

up to 0.1 molar (or 0.4 N) with an average deviation of only 0.004% as is shown in column 5 of Table III. The extended form of the equation $\varphi = 1/\eta = 1 - 0.03995\sqrt{c} - 0.32859c - 0.0639c^2$ fits the data over the entire range up to and including 0.5 molar (or 2 N) with an average deviation of only 0.006% as is shown in column 6

TABLE II

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM FERROCYANIDE SOLUTIONS AT 0°

Concn., c	Density, d^{0}_4	$d_c t_c / d_0 t_0$	K. E.	Relative η obsd.	η at round concn.
0.000200	(0.99992)	1.00054	0	1.00054	1.00054
		1.00052	0	1.00052	1.00052
.000351	(.99996)	1.00061	0	1.00061	1.00061
.000350	(.99996)	1.00056	0	1.00056	1.00056
		1.00062	0	1.00062	1.00062
.000502	(1.00000)	1.00091	0	1.00091	1.00091
		1.00089	0	1.00089	1.00089
.000751	(1.00007)	1.00098	0	1.00098	1.00098
.000751	(1.00007)	1.00092	0	1.00092	1.00092
.001000	1.000200	1.00120	0	1.00120	1.00120
		1.00120	0	1.00120	1.00120
.002002	1.000405	1.00165	0	1.00165	1.00165
		1.00163	0	1.00163	1.00163
.004978	1.001225	1.00260	0	1.00260	1.00260
		1.00245	0	1.00245	1.00245
.005005	1.001199	1.00255	0	1.00255	1.00255
.009968	1.002520	1.00374	0	1.00374	1.00375
		1.00376	0	1.00376	1.00377
.019830	1.005108	1.00554	0	1.00554	1.00557
.020037	1.005165	1.00550	0	1.00550	1.00550
.050110	1.012846	1.01018	−1	1.01017	1.01016
.050091	1.012846	1.01006	−1	1.01005	1.01004
.099610	1.025199	1.01800	−2	1.01798	1.01801
.100224	1.025353	1.01807	−2	1.01805	1.01804
.200532	1.049802	1.03918	−4	1.03914	1.03902
.200578	1.049856	1.03921	−4	1.03917	1.03904

TABLE III

RELATIVE VISCOSITY AND RELATIVE FLUIDITY OF POTASSIUM FERROCYANIDE SOLUTIONS AT 25°

				Jones and Dole equation	
c	η	φ	$\frac{\eta - 1}{c}$	Simple $\Delta\varphi \times 10^5$	Extended $\Delta\varphi \times 10^5$
0.00020	1.00053	0.99947	2.65	+ 10	+10
.00035	1.00079	.99921	2.26	+ 7	+ 7
.00050	1.00103	.99897	2.06	+ 3	+ 2
.00075	1.00138	.99862	1.84	− 3	− 4
.001	1.00163	.99837	1.63	− 3	− 1
.002	1.00244	.99757	1.22	+ 3	+ 1
.005	1.00451	.99551	0.90	+ 1	− 2
.01	1.00744	.99261	.744	− 4	−10
.02	1.01255	.98761	.628	− 4	−14
.05	1.02632	.97435	.526	+ 4	−13
.1	1.04839	.95384	.484	− 1	− 3
.2	1.09414	.91396	.471	− 114	+10
.5	1.26347	.79147	.527	−1270	− 1

Jones and Dole equations	Range of validity	Average % deviation
$\varphi = 1 - 0.03995\sqrt{c} - 0.33518c$	0.1	0.004
$\varphi = 1 - .03995\sqrt{c} - .32859c - 0.0639c^2$	.5	.006
$\eta = 1 + .03695\sqrt{c} + .3660c$	.1	.008
$\eta = 1 + .03695\sqrt{c} + .33538c + 0.27832c^2$	.5	.023

of Table III. If the results are expressed in terms of relative viscosity instead of relative fluidity the agreement is not quite so good. The equation $\eta = 1 + 0.03695\sqrt{c} + 0.3660c$ fits the data up to 0.1 molar with an average deviation of 0.008% and the equation $\eta = 1 + 0.03695\sqrt{c} + 0.33538c + 0.27832c^2$ fits the data up to 0.5 molar with an average deviation of 0.023%.

After our experimental work was completed Hood and Williams[2] published measurements of the viscosity of solutions of potassium ferrocyanide at 18 and 25°. Their results for the viscosity at 25° are slightly lower than ours. They state that their results at 25° are in agreement with the equation $\varphi = 1 - 0.0245\sqrt{c} - 0.3720c$.

Our results show that as usual the relative viscosity at 0° is lower than at 25°, the difference being mainly in the effect responsible for the linear term. At 0° both the simple and extended forms of the Jones and Dole equation seem to be equally good whether expressed in terms of viscosity or of fluidity. At 0° the simple form only holds up to 0.02 molar, whereas at 25° the simple form holds up to 0.1 molar. These equations are given below Table IV.

TABLE IV

RELATIVE VISCOSITY AND RELATIVE FLUIDITY OF POTASSIUM FERROCYANIDE SOLUTIONS AT 0°

c	η	φ	$\frac{\eta - 1}{c}$	Jones and Dole equation Simple $\Delta\varphi \times 10^5$	Jones and Dole equation Extended $\Delta\varphi \times 10^5$
0.0002	1.00053	0.99947	2.6	− 3	− 3
.00035	1.00060	.99940	1.7	+ 6	+ 6
.0005	1.00090	.99910	1.8	− 10	−11
.00075	1.00096	.99904	1.28	+ 2	+ 2
.001	1.00120	.99880	1.20	− 7	− 7
.002	1.00164	.99836	0.82	− 2	− 3
.005	1.00255	.99746	.508	+ 7	+ 6
.01	1.00376	.99625	.375	+ 2	+ 2
.02	1.00554	.99449	.275	− 2	+ 7
.05	1.01010	.99000	.202	− 82	+ 5
.1	1.01803	.98229	.180	− 414	− 3
.2	1.03903	.96244	.195	−1651	+ 1

Jones and Dole equations	Range of validity	Average % deviation
$\varphi = 1 - 0.03502\sqrt{c} - 0.02679c$	0.02	0.005
$\varphi = 1 - .03502\sqrt{c} - .02266c - 0.4340c^2$	.2	.005
$\eta = 1 + .03508\sqrt{c} + .02768c$	.02	.005
$\eta = 1 + .03508\sqrt{c} + .02123c + 0.4778c^2$	.2	.004

An attempt was made to fit an equation of the form suggested by Onsager and Fuoss[3] to the data without success. In previous papers of this series it has been shown that the Onsager–Fuoss equation is useful for solutions of several salts in methanol but that it failed for aqueous solutions of potassium permanganate and of cesium iodide.

It now remains to compare the values of the coefficient of the square root term (A) determined by experiment with that computed by the Falkenhagen and Vernon equation.[4] Although we can probably estimate the equivalent conductance of the ferrocyanide ion at infinite dilution more accurately than that of any other tetravalent ion, nevertheless the difficulty of extrapolating the conductance of a 1–4 salt is so great that this equivalent conductance is not known as well as for ions of lower valence (see the following paper). If the equivalent conductance of the ferrocyanide ion at 25° is assumed to be 117, the value of A computed by Falkenhagen and Vernon's equation is 0.033. If the equivalent conductance is assumed to be 122 (which is probably too high), then the computed value comes out to be 0.032. The experimentally determined value is 0.037. At 0° the computed value of A (based on the equivalent conductance of the ferrocyanide ion of 64) is 0.030, whereas the experimental value is 0.035. Although the agreement is not perfect, nevertheless the experimental results do harmonize with the prediction of the theory that increasing the valence of the ions involved should increase greatly the value of A and that raising the temperature should cause a moderate increase in A.

Summary

1. The absolute density and relative viscosity of many solutions of potassium ferrocyanide have been determined at 0 and 25°, covering a range of concentration from extreme dilution nearly to saturation.

2. The "Grüneisen Effect" is especially pronounced in this salt of high valence type.

3. The Jones and Dole equation is found to fit our data.

4. The results confirm approximately the equation of Falkenhagen for the computation of the influence of interionic attraction on the viscosity.

CAMBRIDGE, MASS.

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(2) G. R. Hood and J. C. Williams, *Ohio J. Sci.*, **35**, 415 (1935).

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

(4) H. Falkenhagen and E. L. Vernon, *Physik. Z.*, **33**, 140 (1932).