[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions of Electrolytes as a Function of the Concentration. VIII. Potassium Ferricyanide

BY GRINNELL JONES AND SCHUYLER M. CHRISTIAN

This paper is an extension of the work on the viscosity of solutions of electrolytes which has been reported in a series of earlier papers.[1]

Potassium ferricyanide was selected because it gives a good example of a salt of the 1–3 valence type. Measurements of the viscosity of solutions of this salt have been carried out by Wagner,[2] by Abegg,[3] and by Rankin and Taylor,[4] but the available data do not cover as wide a range of concentration or have as great precision as is desired for our purposes. It is of interest that Rankin and Taylor found that although at 25° the solutions of this salt are more viscous than water, yet at 1.6° the solutions are less viscous than water with a minimum in the viscosity–concentration curve.

The best grade of salt available by purchase was further purified by crystallization and carefully dried. The viscometer, thermostats, timing apparatus and experimental procedure were the same as those used by Jones and Stauffer. Two minor changes were made in the calculation of the corrections to the experimental data. In the previous papers of this series the kinetic energy correction has been calculated by the method recommended by Bingham, using the value $m = 1.12$ for the coefficient of the correction term. The value for this coefficient has recently been determined experimentally for this particular instrument by T. W. Dakin[5] and found to be $m = 0.98$, and this new value was used in the computation of the correction. For a nearly saturated solution (3.5 N) at 25° the kinetic energy correction computed by the old value of m is $+0.00297$, which is reduced to $+0.00266$ by the use of the new value of m, or a change of less than 0.03% of the viscosity. However, the correction decreases rapidly with dilution. Thus for the 1 N solution at 25° the correction is only $+0.00011$ with the old value of m and $+0.00010$ with the new value. At 0° the kinetic energy correction itself is much smaller than at 25° owing to the fact that the efflux time is approximately doubled and furthermore the viscosity of the solutions is much closer to that of water, so that for relative measurements the effect is substantially reduced. The kinetic energy correction for the strongest solution studied at 0° (2 N) was only -0.00025 and the difference in the correction caused by the change in the value of m is only 0.004%. We have not yet recomputed the correction for the data on other salts which have been determined in this Laboratory by the use of this instrument but these examples indicate that the error in this correction due to the use of $m = 1.12$ will not be significant except perhaps in a few of the most concentrated solutions studied. The situation is even more favorable in the cases of the measurements made with another viscometer designated as the T Instrument because (1) the kinetic energy correction is smaller because of a greater efflux time; and (2) Dakin's determination of the value of m for this instrument gave a value of 1.16 which is nearer to the assumed value of 1.12 used in the computation of the published data obtained with this instrument.

A surface tension correction is applied to the data by the use of a correcting factor computed by the formula $f = 1 + 0.0076\left(1 - \frac{\sigma_c\rho_0}{\sigma_0\rho_c}\right)$ given by Jones and Fornwalt.[1] The surface tension data for 25° are taken from the paper by Jones and Ray.[6] Jones and Ray did not make any measurements at 0° but some approximate measurements made at 0° with a DuNouy tensometer gave results for the relative surface tension which agree well with those at 25°. In contrast to the kinetic energy correction this surface tension correction is nearly independent of the temperature and is approximately linear with respect to the concentration. It amounts to +0.027% for a 1 N solution.

In a few cases a correction not exceeding 0.003% has been applied to the viscosity data and density data to bring the results to a round concentration. In all cases where the correction exceeded 0.003% the data as obtained are published and the estimated values at a round concentration are given in parentheses.

Interpretation of the Results

The experimental data on the density of potassium ferricyanide solutions may be expressed by equations having the form suggested by Root[7] with an average deviation of only 0.0023%.

$$d^{25}_4 = 0.99707_4 + 0.181448c - 0.0204495c^{3/2}$$

$$d^{0}_4 = 0.99987_0 + 0.193367c - 0.0204495c^{3/2}$$

The viscosity and fluidity of these solutions can be expressed by equations of the form suggested by Jones and Dole, as is shown in Table III. It is interesting that the viscosity–concentration curve at 0° has both a maximum (at $c = 0.0034$; $N \doteq$

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(1) Grinnell Jones and Associates, VII, THIS JOURNAL, **62**, 338 (1940). For references to earlier articles see *ibid.*, **62**, 335 (1940).

(2) J. Wagner, *Z. physik. Chem.*, **5**, 31 (1889).

(3) R. Abegg, *ibid.*, **11**, 248 (1893).

(4) C. Rankin and W. W. Taylor, *Trans. Roy. Soc. Edin.*, **45**, 401 (1905).

(5) T. W. Dakin, Harvard University Dissertation, 1940 (not yet published).

(6) Grinnell Jones and W. A. Ray, THIS JOURNAL, **63**, 288 (1941).

(7) W. C. Root, *ibid.*, **55**, 850 (1933).

TABLE I

VISCOSITY OF POTASSIUM FERRICYANIDE SOLUTIONS AT 25°

c	N	Density	$\frac{d_ct_c}{d_0t_0}$	KE Correction $\times 10^6$	Surface tension correction $\times 10^6$	$\frac{\eta_6}{\eta_0} = \eta$	$\varphi = 1/\eta$	$(\eta - 1)/c$
0.000333	0.001	0.99714	1.000461	+ 5	0	1.00047	0.99953	+1.41
.000667	.002	.99721	1.000648	+ 6	0	1.00065	.99935	+ .97
.001667	.005	.99739	1.001196	+ 10	+ 1	1.00121	.99879	+ .726
.003333	.010	.99768	1.001774	+ 13	+ 3	1.00179	.99821	+ .537
.006667	.020	.99830	1.002777	+ 17	+ 5	1.00280	.99721	+ .420
.016667	.050	1.00009	1.004992	+ 22	+ 13	1.00503	.99500	+ .301
.03333	.100	1.00305	1.008232	+ 25	+ 26	1.00828	.99179	+ .248
.097772	.29332	1.01439	1.019284	+ 22	+ 84	1.01939	.98098	+ .198
(.100)	.300	(1.01478)				(1.01978)	(.98060)	.1978
.16667	.500	1.02632	1.031468	+ 24	+ 149	1.03164	.96933	.1898
.33333	1.000	(1.05472)				(1.06678)	(.93740)	.2003
.33349	1.00048	1.05474	1.066429	+ 96	+ 300	1.06682	.93737	.2004
.66604	1.99814	1.11002	1.169455	+ 619	+ 597	1.17067	.85421	.2562
.6667	2.000	(1.11012)				1.1709	(.85403)	.2563
.9996	2.99883	1.16399	1.333798	+1763	+ 920	1.33648	.74823	.3356
1.000	3.000	(1.16405)				(1.3367)	(.7481)	.3367
1.166666	3.500	(1.19038)				(1.4489)	(.6902)	.3848
1.1677	3.50321	1.19055	1.445938	+2600	+1102	1.44964	.68983	.3851

TABLE II

VISCOSITY OF POTASSIUM FERRICYANIDE SOLUTIONS AT 0°

c	N	Density	$\frac{d_st_s}{d_0t_0}$	KE correction $\times 10^6$	Surface tension correction $\times 10^6$	η	$\varphi = \frac{1}{\eta}$	$\eta = \frac{1}{c}$
0.000333	0.001	0.99998	1.000376	+ 1		1.00038	0.99962	+1.14
.000667	.002	1.00006	1.000447	+ 1	+ 1	1.00045	.99955	+0.67
.001667	.005	1.00021	1.000588	+ 1	+ 2	1.00059	.99941	+ .35
.003333	.010	1.00053	1.000681		+ 5	1.00069	.99931	+ .21
.006667	.020	1.00111	1.000540	− 2	+ 10	1.00055	.99945	+ .082
.016667	.050	1.00305	0.999839	− 10	+ 20	0.99985	1.00015	− .009
.033333	.100	1.00616	.999178	− 23	+ 41	.99820	1.00180	− .054
.098143	.29443	1.01823	.992206	− 76	+115	.99224	1.00782	− .079
.100	.300	(1.01857)				(.99210)	1.00796	− .079
.16667	.500	(1.03074)				(.98818)	1.01196	− .0715
.167383	.50215	1.03088	.988148	−124	+182	.98820	1.01194	− .0705
.33333	1.00	(1.06036)				(.98879)	1.01134	− .0336
.33538	1.00615	1.06071	.988822	−212	+318	.98891	1.01121	− .0331
.66667	2.000	1.11763	1.032548	−251	+607	1.03289	0.96816	+ .0498

TABLE III

EQUATIONS FOR VISCOSITY AND FLUIDITY OF AQUEOUS SOLUTIONS OF POTASSIUM FERRICYANIDE

25°C.	Range of validity	Average deviation
$\eta = 1 + 0.0244\sqrt{c} + 0.1141c$	$c \longrightarrow 0.0333\ (N = 0.1)$	0.000025
$\eta = 1 + .0244\sqrt{c} + .10785c + 0.13262c^2$	$c \longrightarrow .1667\ (N = .5)$	.000043
$\varphi = 1 - .0245\sqrt{c} - .1114c$	$c \longrightarrow .033\ (N = .1)$	.000026
$\varphi = 1 - .0245\sqrt{c} - .102371c - .129818c^2$	$c \longrightarrow .666\ (N = 2.0)$	.000066
0°C.		
$\eta = 1 + 0.02113\sqrt{c} - 0.1701c$	$c \longrightarrow .033\ (N = .1)$	.00003
$\eta = 1 + .02113\sqrt{c} - .18133c + 0.35368c^2$	$c \longrightarrow .1667\ (N = .5)$	.00003
$\varphi = 1 - .02113\sqrt{c} + .1701c$	$c \longrightarrow .033\ (N = .1)$	.00003
$\varphi = 1 - .02113\sqrt{c} + .18151c - .34973c$	$c \longrightarrow .1667\ (N = .5)$	.00003
$\varphi = 1 - .02113\sqrt{c} + .17736c - .31959c^2$	$c \longrightarrow .33\ (N = 1.0)$	.000056

0.01) and a minimum (at $c = 0.17$; $N = 0.5$). This behavior is unusual but has been obtained at 0° for solutions of potassium chloride (Jones and Talley) and of silver nitrate (Jones and Colvin).

In order to compute the coefficient of the square root term (A) in the viscosity equation by the use of the Falkenhagen and Vernon equation,[8] reliable values for the equivalent conductance of the potassium and ferricyanide ions at 25 and 0°

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

are needed. For 25° we shall use the values 73.52 for the potassium ion and 101.0 for the ferricyanide ion given by MacInnes,[9] based on measurements of the conductance of potassium ferricyanide solutions by Hartley and Donaldson.[10] These measurements were evidently well done and cover a very low range of concentration; N = 0.00004 to 0.0002. The results are supported by the measurement of Hölzl[11] which cover the range from N = 0.001 N to 0.03 N but when plotted appear to be consistent with those of Hartley and Donaldson. On the other hand, the earlier measurements of Harry C. Jones and C. Watkins[12] are inconsistent with the others by nearly 7%, and deserve no further consideration.

Unfortunately, the available information as to the mobility of the ferricyanide at 0° is far less satisfactory. The only measurements of the conductance of a ferricyanide solution at 0° which we have found in the literature are those of Harry Jones and Watkins which, as explained above, are grossly in error at 25°. There is a strong presumption that an error of this magnitude is due to a wrong choice of the reference standard used in the determination of their cell constants. This is supported by the values for potassium chloride given by Harry C. Jones[13] which are also substantially below the correct values at both 25 and 0°. It is necessary to multiply his values for potassium chloride by a factor 1.067 to obtain the correct values. We have, therefore, applied this factor to his data on potassium ferricyanide and plotted the results against $\sqrt{c}$. Extrapolation gives a value of 94.4 for the limiting conductance at infinite dilution. The values thus obtained are consistent with the values given in the "International Critical Tables" which are stated to be based on Jones and Watkins and, therefore, the process of adjustment described above must have been used in preparing the "International Critical Tables." Subtracting the mobility of the potassium ion at 0°, 40.4, gives 54 for the ferricyanide ion.

TABLE IV

	25°C.	0°C.
T	298.18	278.18
D	78.8	88.0
η	0.008949	0.01792
$l_1(K^+)$	73.52	40.4
$l_2(\mathrm{Fe(CN)_6}^{---})$	101.0	54
A computed	0.0222	0.020
A experimental	.0244	.0211

The other parameters used in the calculation and in the results are shown in Table IV. The agreement between the computed and experimental results is about as close as usual[14] and shows that the formula of Falkenhagen and Vernon correctly evaluates the influence of valence type and of the temperature.

Summary

1. Data are given for the density and viscosity of potassium ferricyanide solutions at 25 and 0° covering the range up to saturation.

2. Equations expressing the density, viscosity and fluidity as functions of the concentration are given.

3. The predictions of the Falkenhagen and Vernon equation are verified for this case.

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[9] D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Company, N. Y., 1939, p. 342.

[10] G. H. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, **33**, 465 (1937).

[11] F. Hölzl, *Monatsh.*, **55**, 137 (1930).

[12] Harry C. Jones and C. Watkins, THIS JOURNAL, **37**, 2631 (1915).

[13] H. C. Jones, Carnegie Institute at Washington, Pub. 130, p. 20.

[14] See H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Company, New York, N. Y., 1943, p. 177, for a tabulation of the available data in other cases.

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The Characterization of Capillaries Used for Dropping Mercury Electrodes in Polarographic Studies

BY OTTO H. MÜLLER

The best identifying characteristics of a capillary are its length and internal diameter, provided that it has a truly uniform bore. While some factory made capillaries fulfill this condition, all laboratory made capillaries do not, because they are drawn from wider stock and are consequently more or less tapered. Even if capillaries of uniform bore were used exclusively, the means for measuring with sufficient accuracy diameters varying from 10–50 μ, or for determining the uniformity of the bore are not available to most chemists. The present study was therefore undertaken to find certain characteristics which would (a) be peculiar to *all* kinds of capillaries, (b) be determinable without special apparatus, (c) permit comparison of straight and tapered capillaries and a prediction of their performance, and (d) give enough information for the duplication of any given capillary. It was found that the capillary constant, κ, and the radius of the capillary orifice, ρ, are two factors which meet all of these requirements. Some simple techniques for their precise determination and some incidental observations made during this study will be discussed in this