[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Solutions of Electrolytes as a Function of the Concentration. VII. Silver Nitrate, Potassium Sulfate and Potassium Chromate

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The earlier papers of this series[1] should be consulted for a discussion of the objectives and theoretical significance of the work and for a description of the experimental procedure.

Silver nitrate was purified[2] by solution in water, precipitation by the addition of freshly distilled nitric acid, and separation from the mother liquor by centrifugal drainage. This process was carried out three times in succession. It was then fused in a porcelain casserole, taking care to avoid overheating above the melting point, and then poured in small portions into a platinum dish to cool and solidify. Potassium chromate was recrystallized three times with centrifugal drainage, then dried and finally heated just below its melting point. The purified material gave a negative test for sodium, chloride and sulfate. Potassium sulfate was purified in the same manner as the chromate. It gave a negative test for sodium and chloride.

The results are summarized in Tables I to VI in which the concentrations, c, are expressed in gram molecular weights per liter, and viscosities, η, are given relative to that of water at the same temperature. A small kinetic energy correction has been applied to the data but no correction for the effect of surface tension has been made.[3] Figures in parentheses were not actually measured but were estimated by interpolation over a small range of concentration.

The densities of these solutions can be expressed by the equations given in the tables having the form suggested by Root,[4] throughout the entire range of concentration studied and with average deviation of less than 0.002%. It is remarkable that this equation should be valid for

TABLE I

DENSITY AND RELATIVE VISCOSITY OF SILVER NITRATE SOLUTIONS AT 25°

c	d^{25}_4	η	$(\eta - 1)/c$	Jones and Dole equation Simple $\Delta\eta \times 10^5$	Jones and Dole equation Extended $\Delta\eta \times 10^5$
0.002	0.99736	1.00036	0.18	−1	− 1
.005	.99778	1.00068	.136	+1	+ 1
.01	.99853	1.00110	.110	+2	+ 3
.015	.99919	1.00148	.099	+3	+ 5
.02	.99992	1.00177	.0885	−2	0
.05	1.00414	1.00364	.0728	−3	0
.10	1.01118	1.00652	.0652	+1	− 3
.20	1.02518	1.01224	.0612		− 5
.50	1.06709	1.03088	.06178		+ 6
.99719	1.13601	1.06783	.06802		+11
(1.0)	(1.13643)	(1.06806)			
2.0	1.27363	1.16788	.08394		− 2
(3.0)	(1.40942)	(1.29888)			
3.00425	1.41002	1.29951	.09970		
(4.0)	(1.54407)	(1.46261)			
4.0115	1.54565	1.46471	.11584		
4.99808	1.67745	1.66223	.13250		
5.000	(1.67775)	(1.66264)			

	Range of validity, M	Av. deviation, %
Root equation		
$d^{25}_4 = 0.997074 + 0.141956c - 0.002603c^{3/2}$	5	0.002
Jones and Dole equation		
$\eta = 1 + 0.0063\sqrt{c} + 0.04517c$	0.1	.002
$\eta = 1 + 0.0063\sqrt{c} + 0.043805c + 0.017845c^2$	2	.003

TABLE II

DENSITY AND RELATIVE VISCOSITY OF SILVER NITRATE SOLUTIONS AT 0°

c	d^{0}_4	η	$(\eta - 1)/c$	Jones and Dole equation Simple $\Delta\eta \times 10^5$	Jones and Dole equation Extended $\Delta\eta \times 10^5$
0.001	0.99991	1.00013	+0.130	0	0
.002	1.00016	1.00017	+ .085	+1	+1
.005	1.00059	1.00021	+ .042	+2	+3
.01	1.00132	1.00018	+ .018	+2	+3
.015	1.00204	1.00007	+ .005	−3	−2
.02	1.00278	1.00000	.000	−2	−2
.05	1.00714	0.99939	− .0122	+1	−6
.1	1.01438	0.99847	− .0153		0
.2	1.02880	0.99701	− .01495		+2
.5	1.07174	0.99782	− .0109		0
(1)	(1.14233)	(1.01373)			
1.00326	1.14293	1.01393	+ .01349		
(2)	(1.28164)	(1.08445)			
2.0157	1.28381	1.08576	+ .04255		
(3)	(1.41870)	(1.19439)			
3.03205	1.42306	1.19842	+ .06543		
(4)	(1.55418)	(1.33998)			
4.05174	1.56115	1.34860	+ .08604		
(5)	(1.6882)	(1.52342)			
5.05	1.69487	1.53375	+ .1057		

	Range of validity, M	Av. deviation, %
Root equation		
$d^{0}_4 = 0.999871 + 0.146431c - 0.003923c^{3/2}$	5	0.002
Jones and Dole equation		
$\eta = 1 + 0.00515\sqrt{c} - 0.03542c$	0.05	.002
$\eta = 1 + 0.00515\sqrt{c} - 0.03656c + 0.049844c^2$	.5	.002

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(1) The preceding paper, VI, THIS JOURNAL, **62**, 335 (1940), gives references to the earlier papers.

(2) T. W. Richards and G. S. Forbes, *ibid.*, **29**, 816 (1907); E. B. Rosa, G. W. Vinal and A. S. McDaniel, *Bull. Bur. Standards* **9**, 539 (1913).

(3) See footnote (7) of the previous paper for the method of applying this correction.

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

silver nitrate solutions even up to 5 molar, which contain more than 50% of salt by weight.

TABLE III

DENSITY AND RELATIVE VISCOSITY OF POTASSIUM SULFATE SOLUTIONS AT 25°

				Jones and Dole equation	
c	d^{25}_4	η	$(\eta - 1)/c$	Simple $\Delta\eta \times 10^5$	Extended $\Delta\eta \times 10^5$
0.0005	0.99715	1.00039	0.78	−2	− 1
.001	.99723	1.00062	.62	−2	− 1
.002	.99736	1.00103	.51	+1	+ 2
.005	.99779	1.00198	.396	+2	+ 4
.01	.99850	1.00334	.334	0	+ 4
.02	.99990	1.00586	.293	0	+ 7
.05	1.00407	1.01281	.256	−1	+11
.1	1.01094	1.02380	.238	0	+ 9
.2	1.02443	1.04535	.227		−16
.3	1.03774	1.06760	.225		$\underline{+6}$
.5	1.06386	1.11470	.229		

	Range of validity, M	Av. deviation, %
Root equation		
$d^{25}_4 = 0.997074 + 0.142388c - 0.012497c^{3/2}$	0.3	0.001
Jones and Dole equation		
$\eta = 1 + 0.01406\sqrt{c} + 0.19350c$	.1	.001
$\eta = 1 + 0.01406\sqrt{c} + 0.18951c + 0.033146c^2$	.3	.006

TABLE IV

DENSITY AND RELATIVE VISCOSITY OF POTASSIUM SULFATE SOLUTIONS AT 0°

				Jones and Dole equation	
c	d^0_4	η	$(\eta - 1)/c$	Simple $\Delta\eta \times 10^5$	Extended $\Delta\eta \times 10^5$
0.0005	0.99993	1.00028	0.56	−1	−1
.001	1.00001	1.00040	.40	−2	−1
.002	1.00015	1.00061	.30	0	+1
.005	1.00061	1.00101	.20	−2	+1
.01	1.00137	1.00157	.157	+1	+6
.02	1.00284	1.00241	.120	+1	+8
.05	1.00724	1.00441	.0882	$\underline{0}$	−2
(.1)	(1.01447)	(1.00787)			
.101044	1.01463	1.00795	.0787		−3
(.2)	(1.02851)	(1.01606)			
.20083	1.02876	1.01614	.0804		$\underline{0}$
(.3)	(1.04237)	(1.03020)			
.30138	1.04270	1.03040	.1009		

	Range of validity, M	Av. deviation, %
Root equation		
$d^0_4 = 0.999871 + 0.15149c - 0.01709c^{3/2}$	0.3	0.001
Jones and Dole equation		
$\eta = 1 + 0.01216\sqrt{c} + 0.03390c$	.05	.001
$\eta = 1 + 0.01216\sqrt{c} + 0.02798c + 0.12556c^2$	.2	.003

TABLE V

DENSITY AND RELATIVE VISCOSITY OF POTASSIUM CHROMATE SOLUTIONS AT 25°

				Jones and Dole equation	
c	d^{25}_4	η	$(\eta - 1)/c$	Simple $\Delta\eta \times 10^5$	Extended $\Delta\eta \times 10^5$
0.0005	0.99716	1.00036	0.72	−1	− 1
.001	.99723	1.00053	.53	−4	− 4
.002	.99739	1.00090	.45	0	+ 1
.005	.99786	1.00170	.34	0	+ 2
.01	.99863	1.00284	.284	−1	+ 2
.02	1.00018	1.00492	.246	0	+ 5
.05	1.00481	1.01062	.212	+4	+16
.1	1.01236	1.01940	.194	$\underline{-2}$	− 8
.2	1.02753	1.03732	.1866		− 2
(.5)	(1.07174)	(1.09446)			$\underline{0}$
.50178	1.07199	1.09457	.1885		
(1)	(1.14309)				
1.0005	1.14316	1.20946	.20936		
1.9992	1.27891	1.53171	.26596		
(2)	(1.27902)	(1.53204)			
(2.5)	(1.34424)	(1.7584)			
2.52209	1.34708	1.76931	.30503		

	Range of validity, M	Av. deviation, %
Root equation		
$d^{25}_0 = 0.997074 + 0.157186c - 0.01167c^{3/2}$	1	0.0014
Jones and Dole equation		
$\eta = 1 + 0.013305\sqrt{c} + 0.15210c$	0.1	.002
$\eta = 1 + 0.013305\sqrt{c} + 0.148502c + 0.042218c^2$	.5	.004

TABLE VI

DENSITY AND RELATIVE VISCOSITY OF POTASSIUM CHROMATE SOLUTIONS AT 0°

				Jones and Dole equation	
c	d^0_4	η	$(\eta - 1)/c$	Simple $\Delta\eta \times 10^5$	Extended $\Delta\eta \times 10^5$
0.0005	0.99995	1.00025	0.50	+1	+ 1
.001	1.00003	1.00032	.32	−1	− 1
.002	1.00019	1.00046	.23	0	+ 1
.005	1.00070	1.00070	+ .14	+1	+ 3
.01	1.00155	1.00090	.09	−2	+ 2
.02	1.00315	1.00122	.061	+2	+ 7
.05	1.00799	1.00157	.0314	$\underline{0}$	− 3
.1	1.01593	1.00223	.0223		−10
.2	1.03181	1.00496	.0248		+ 6
(.5)	(1.07745)	(1.0249)			$\underline{0}$
.504656	1.07814	1.02536	.05025		
(1)	(1.1503)	(1.0913)			
1.0078	1.15149	1.09270	.09198		
1.948675		1.32130	.16488		
(2)	(1.2878)	(1.3343)			
2.01707	1.28991	1.33989	.16851		
(2.5)	(1.3532)	(1.5224)			
2.54422	1.35890	1.54108	.21267		

	Range of validity, M	Av. deviation, %
Root equation		
$d^0_4 = 0.999871 + 0.166225c - 0.0157573c^{3/2}$	2.5	0.002
Jones and Dole equation		
$\eta = 1 + 0.01104\sqrt{c} - 0.01790c$	0.05	.001
$\eta = 1 + 0.01104\sqrt{c} - 0.023107c + 0.114591c^2$	.5	.003

Although silver nitrate solutions at 25° have a viscosity greater than that of water throughout the range of concentration studied, yet at 0° the viscosity is less than that of water in the range from 0.02 *M* to about 0.6 *M*, but greater than that of water in both the more dilute and more concentrated ranges.

Both potassium sulfate and potassium chromate solutions have viscosities greater than that of water at the same temperature throughout the concentration range, and as usual the relative viscosity at 25° for any given concentration is greater than for the same concentration at 0°.

The viscosities of these solutions relative to that of pure water at the same temperature can be expressed by the Jones and Dole equation: $\eta = 1 + A\sqrt{c} \pm Bc$ as follows:

Silver nitrate at 25°: $\eta = 1 + 0.0063\sqrt{c} + 0.04517c$ valid up to 0.1 M

at 0°: $\eta = 1 + 0.00515\sqrt{c} - 0.03542c$ valid up to 0.05 M

Potassium sulfate at 25°: $\eta = 1 + 0.01406\sqrt{c} + 0.19350c$ valid up to 0.1 M

at 0°: $\eta = 1 + 0.01216\sqrt{c} + 0.03390c$ valid up to 0.05 M

Potassium chromate at 25°:

$\eta = 1 + 0.013305\sqrt{c} + 0.1521c$ valid up to 0.1 M

at 0°: $\eta = 1 + 0.01104\sqrt{c} - 0.01790c$ valid up to 0.05 M

The following table gives a comparison of the values of the coefficients of the square root term (A) determined experimentally with that computed by the Falkenhagen and Vernon equation.

TABLE VII

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

	Equivalent conductance used in calcg.			
	cation	anion	A computed	A exptl.
$AgNO_3$ at 25°	61.92	71.44	0.0056	0.0063
$AgNO_3$ at 0°	32.9	40.4	.00505	.00515
K_2SO_4 at 25°	73.52	79.8	.0131	.0140$_6$
K_2SO_4 at 0°	40.4	41	.0122	.0121$_6$
K_2CrO_4 at 25°	73.52	79.3	.0131	.0133
K_2CrO_4 at 0°	40.4	42.6	.0119	.0110

These results confirm the conclusions drawn in the earlier papers in this series that the Falkenhagen and Vernon equation correctly gives the influence of both valence type and temperature on the values of the coefficient of the square root term.

Although earlier measurements[5] on solutions of these salts have been numerous, none of them extend to sufficiently dilute solutions to give a reliable determination of the A coefficient, or are as precise as our measurements.

Simon[6] has proposed a law, "the molecules of isomorphous substances modify equally the viscosity of water in which they are dissolved, at the same temperature and in certain ranges of concentration." He supports this thesis by his own data on potassium sulfate and potassium chromate. Our data show that Simon's rule is a rough approximation only at 25°, but fails grossly at 0°. Thus, for example, at 0° and at a concentration of 0.2 M the solution of potassium chromate has a viscosity of 0.5% greater than that of water, whereas the solution of potassium sulfate has a viscosity 1.6% greater than that of water. Indeed the coefficient of the linear term actually has a different sign for the two salts.

Summary

1. The absolute densities and the relative viscosities of many solutions of silver nitrate, potassium sulfate and of potassium chromate have been determined at 0° and at 25°.

2. These results confirm the Root equation for densities, the Jones and Dole equation for the viscosities, and the Falkenhagen and Vernon equation for the influence of interionic attraction on the viscosity.

3. These results do not confirm Simon's proposed law that isomorphous substances have the same influence on the viscosity.

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(5) For earlier measurements on $AgNO_3$ see: A. A. Blanchard, THIS JOURNAL, **26**, 1324 (1904); J. Wagner, *Z. physik. Chem.*, **5**, 40 (1889); A. Sachanov, *Z. Elektrochem.*, **19**, 588 (1913); J. W. Ingram, *J. Chem. Soc.*, 543 (1930).

For earlier measurements on K_2SO_4 see: A. Sprung, *Pogg. Ann. der Physik*, **159**, 1 (1876); S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887); B. E. Moore, *Phys. Rev.*, **3**, 321 (1896); J. Wagner, *Z. physik. Chem.*, **5**, 40 (1889); E. Grüneisen, *Wiss. Abhandl. physik.-tech. Reichsanstalt*, **4**, 237 (1905); G. Tigerstedt, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **1**, No. 5 (1922); M. Bobtelsky and Malkowa-Janowskaja, *Z. anorg. allgem. Chem.*, **166**, 249 (1927); W. J. Sulston, *Proc. Phys. Soc. London*, **47**, 657 (1935).

For earlier measurements on K_2CrO_4 see: A. Sprung, *Pogg. Ann. der Physik*, **159**, 1 (1876); K. F. Slotte, *Wied. Ann. der Physik*, **14**, 13 (1881); K. Schneider, Diss., Rostock, 1910; L. J. Simon, *Compt. rend.*, **178**, 1607 (1924).

(6) L. J. Simon, *Compt. rend.*, **178**, 1607 (1924).