[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Viscosity of Aqueous Solutions as a Function of the Concentration. II. Potassium Bromide and Potassium Chloride

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Recent papers from this Laboratory<sup>1</sup> have pointed out the significance of viscosities in the development of the modern theory of electrolytic solutions and have recorded data obtained by an improved technique. The present paper contains new data on aqueous solutions of potassium bromide over a wide range of concentration (0.001 to 3.75 N) and an extension of the data already published for potassium chloride up to 3 N.

Our new method of timing by means of a photoelectric cell which has been described in detail in the third paper referred to was used. The salts were carefully purified and are believed to have contained no impurities in significant amounts. The data are recorded in Table I in which the headings have the same significance as in our earlier paper, except that instead of giving the absolute densities of the solutions, the relative apparent densities in air (*i. e.*, the weight of the solution divided by the weight of an equal volume of water at the same temperature with no vacuum corrections applied) are given because this is the figure needed for the present

## TABLE I

Relative Viscosity at 25°

								Δπ
C	$d_{\rm c}/d_0$	tc	t <sub>0</sub>	$d_0 t_c/d_0 t_0$	K. E. corr.	η obs.	η comp.	obs comp.
Potassium Bromide								
0.001000	1.000089	618,55	618.54	1.00010	0.00000	1.00010	1.00010	0.00000
.002000	1.000160	618.60	618.64	1.00010	,00000	1.00010	1.00011	00001
,005000	1.000417	618.39	618.59	1.00009	.00000	1.00009	1.00009	.00000
.010005	1.000841	618.26	618.79	0.99998	.00000	0.99998	0.99998	+.00000
.020001	1.001695	617.51	618.72	99974	- ,00002	.99972	.99969	+ .00003
.050001	1.004256	615.12	618.49	.99879	00005	.99874	.99864	+ .00010
.099899	1.008492	611.34	618.46	.99688	00010	.99678	.99672	+ .00006
.199882	1,016955	603.98	618.50	. 99308	00021	.99287	.99281	+ .00006
.499927	1.042194	582.87	618.38	.98235	00055	.98180	.98189	00009
.959172	1.080449	555.29	618.59	.96989	00104	.96885	.96884	+ .00001
.998357	1.083718	553.06	618.50	.96906	00108	.96798	.96795	+ .00003
1,999826	1.166031	509.04	618.63	.95959	00203	.95756	.95747	+ .00009
2.003090	1.166167	508,96	618,53	.95947	00203	.95744	.95747	00003
3.030933	1.249592	481.41	618.68	.97234	00281	.96953	. 97181	00228
3.749274	1.307264	470.81	618.58	.99498	- ,00321	.99177	. 99695	00518
Potassium Chloride								
0 409450	1 002002	802 02	410 KQ	0.00793	0.000022	0 00780	0 00764	0.0004
0.490430	1.026225	500 00	010.00 A19 A7	0.99760	-0.00023	0.70700	0.33704	-0.00004
0.011510	1 000801	579 10	618 77	1 00940	00044	1 00773	1 00785	⊥ 00014
2.011010	1 121070	585 85	A10 45	1 03309	- 00001	1 03211	1 02221	- 00010
2.702070	1.101272	000.00	010.10	1.03302	00091	1.00211	1.03221	

(1) Grinnell Jones and Malcolm Dole, THIS JOURNAL, 51, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, 55, 624 (1933); Grinnell Jones and S. K. Talley, *Physics*, 4, 213 (1933).

purpose. For the dilute solutions reported in the earlier paper the difference is insignificant. All measurements were made at  $25.00^{\circ}$ .

It will be noted that although all solutions of potassium bromide within the range of 0.01 to 3.75 normal have a viscosity less than that of water, nevertheless the 0.001, 0.002 and 0.005 normal solutions have a viscosity greater than that of water. This furnishes another case supporting the prediction of Jones and Dole that "At very low concentrations the viscosities of solutions of all strong electrolytes will be greater than that of water, including salts which at moderate concentrations show diminished viscosity."

The data recorded in this paper show that an equation of the form  $\eta = 1 + A \sqrt{c} - Bc$ , is only valid up to about 0.1 N for solutions of potassium bromide and up to about 0.2 N for solutions of potassium chloride. Both of these salts have a minimum viscosity (at about 0.8 normal for potassium chloride and at about 1.9 normal for potassium bromide). Other data in the literature indicate that salts which give solutions having a viscosity less than that of water will commonly have a minimum in their viscosity–concentration curves and again have a viscosity greater than that of water at high concentrations if they are sufficiently soluble. A more detailed discussion of the laws for the viscosity of concentrated solutions will be postponed until more extensive data are available. The results so far obtained, however, indicate that another term proportional to the square of the concentration must be added.

The viscosity of solutions of potassium bromide up to 2 N can be expressed approximately by the equation

 $\eta = 1 + 0.00474 \sqrt{c} - 0.04904 c + 0.01221 c^2$ 

The values computed by this equation are given in the table in the next to the last column. The greatest deviation up to 2 N is only 0.01%. The value of the coefficient of the square root term computed from the formula of Falkenhagen and Vernon<sup>2</sup> is 0.0049 which agrees satisfactorily with the value 0.00474 obtained from our experiments. For potassium chloride the equation

 $\eta = 1 + 0.0052 \sqrt{c} - 0.01612 c + 0.00808 c^2$ 

holds approximately up to 3 N. The greatest deviation between our experimental data and the values computed by this equation is only 0.016%.

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 <sup>(2)</sup> H. Falkenhagen, Physik. Z., 32, 365, 745 (1931); H. Falkenhagen and E. L. Vernon, *ibid.*, 33, 140 (1932); Phil. Mag., [7] 14, 537 (1932); L. Onsager and R. M. Fuoss, J. Phys. Chem. 36, 2689 (1933).