[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Solutions of Salts in Methanol

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Introduction

Grüneisen[1] long ago showed experimentally that, although the viscosity–concentration curves for aqueous solutions of salts are approximately linear, nevertheless they exhibit systematic deviation from the simple linear relationship at low concentrations. The first plausible explanation of this "Grüneisen Effect" was offered by Jones and Dole,[2] who ascribed it to an increase in viscosity due to the electrical attraction between the ions. The increment of the viscosity due to this cause varies as the square root of the concentration and, therefore, becomes relatively more important at low concentrations in comparison with other effects which vary linearly with the concentration. Jones and Dole, Jones and Talley, and Wolfenden[3] and his associates have demonstrated that the equation $\eta = 1 + A\sqrt{c} \pm Bc$ is valid for aqueous solutions of many salts up to 0.2 N or above.

Falkenhagen and Dole, and Falkenhagen and Vernon[4] have deduced from the Debye theory of interionic attraction a complicated but explicit expression for the coefficient A of the square root term as a function of the mobilities and valences of the ions, the dielectric constant and viscosity of the solvent, the temperature and the usual universal constants which appear in the equations of the interionic attraction theory. Jones and Talley, and Wolfenden and his associates, have found a gratifying agreement between the values of A found experimentally for aqueous solutions of several salts and those computed by the equation of Falkenhagen and Vernon.

Finally Onsager and Fuoss[5] have proposed a generalized expression for the properties of solutions as a function of the concentration which in the case of viscosity would give the equation $\eta = 1 + A\sqrt{c} + Bc + Dc \log c + \ldots$ for the variation of the viscosity with the concentration, but without discussing the agreement of this equation with the available data.

The recent advances summarized above make it desirable to test the validity of these new relationships when applied to non-aqueous solutions. Methanol was chosen as the solvent to be studied because the dielectric constant is substantially lower than that of water and therefore the equation of Falkenhagen predicts a larger value of the coefficient A than for water solutions. This in turn means that the "Grüneisen Effect" should be more pronounced. Moreover, methanol has sufficient solvent power for many salts and gives solutions having a conductivity comparable with that of aqueous solutions and, therefore, the ionization must be substantial and the interionic attraction theory applicable.

Another object of this investigation was to obtain viscosity data to be used in the interpretation of conductance data on methanol solutions which were being determined simultaneously in this Laboratory.

Earlier investigations of the viscosity of solutions of salts in methanol have been made by Ewart and Raikes,[6] Tower,[7] and Harry C. Jones and E. C. Bingham.[8]

Experimental

Preliminary trials showed that the addition of water to methanol increases the viscosity at the rate of about 4% for each per cent. of water added. It was, therefore, evident that great care must be taken to purify the alcohol and to prevent the absorption of water from the air during the preparation and manipulation of the solutions.

The methanol used was a synthetic product made by the Commercial Solvents Company. A letter from the company stated that it contained no ethyl alcohol, less than 0.03% acetone and less than 0.2% water. It was purified by treatment with magnesium methylate in accordance with the method of Lund and Bjerrum,[9] followed by fractional distillation through a column 75 cm. long. The middle fraction consisting of about three liters of methanol boiling within about 0.04° of the true boiling point of

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(1) E. Grüneisen, *Wiss. Abh. phys.-techn. Reichsanstalt*, **4**, 151, 237 (1905).

(2) Grinnell Jones and Malcolm Dole, THIS JOURNAL, **51**, 2950 (1929).

(3) W. E. Joy and J. H. Wolfenden, *Nature*, **126**, 994 (1930); *Proc. Roy. Soc.* (London), **A134**, 413 (1931); Grinnell Jones and S. K. Talley, THIS JOURNAL, **55**, 624, 4124 (1933); W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc.* (London), **A145**, 475 (1934); V. D. Laurence and J. H. Wolfenden, *J. Chem. Soc.* 1144 (1934).

(4) 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).

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

(6) F. K. Ewart and H. R. Raikes, *J. Chem. Soc.*, 1907 (1926).

(7) O. F. Tower, THIS JOURNAL, **38**, 833 (1916).

(8) H. C. Jones and E. C. Bingham, *Am. Chem. J.*, **34**, 536 (1905)

(9) H. Lund and J. Bjerrum, *Ber.*, **64B**, 210 (1931).

64.65°, as given by Timmermans and Hennaut-Roland,[10] was collected in storage reservoirs with suitable protection from the moisture in the air. These reservoirs were provided with standardized interchangeable ground glass connections with the flasks used to make the solutions. During the progress of the work it was discovered that the methanol contained a trace of ammonia. Therefore, in the later part of this work the methanol after purification as described above was distilled again from solid anhydrous copper sulfate, as recommended by Hartley and Raikes,[11] although the results were not influenced significantly by the change in procedure. The average density at 25° of the seventeen batches whose density was determined was 0.786545 g. per milliliter. The maximum difference between the density of any batch and the mean was only 0.00001.

The four salts used in this investigation were the chloride, bromide, and iodide of potassium, and ammonium chloride. All were carefully purified and dried and are believed to have contained no impurity in significant amounts. The salts were weighed out and solutions of the desired concentration prepared with suitable precautions to prevent absorption of moisture from the air during the preparation of the solutions and subsequent transfer to the pycnometers and viscometers. All concentrations are expressed in gram molecules per liter of solution at 25°. The viscometric technique was the same as that already described in earlier papers from this Laboratory.[12] Kinetic energy corrections have been applied to the data. Two different quartz viscometers having periods of 623 and 539 seconds with water at 25° were used. Duplicate runs on the same filling rarely differed by more than 0.02 second. The variations caused by removing the viscometer from the thermostat, cleaning and drying it and replacing the solution did not exceed 0.05 second, and were usually less than this. The viscosities given in the tables are relative to that of pure methanol at the same temperature. The viscosity of the solution, η, was always compared with that of the same sample of methanol which was used to prepare the solution. The comparative measurements on the solution and on pure methanol were always made on the same day in the same instrument and with every care to maintain all conditions which might affect the results (temperature, mounting, timing mechanism, etc.) as nearly constant as possible. The relative viscosities given are, therefore, believed to have been determined more precisely than the absolute viscosity of methanol is known.

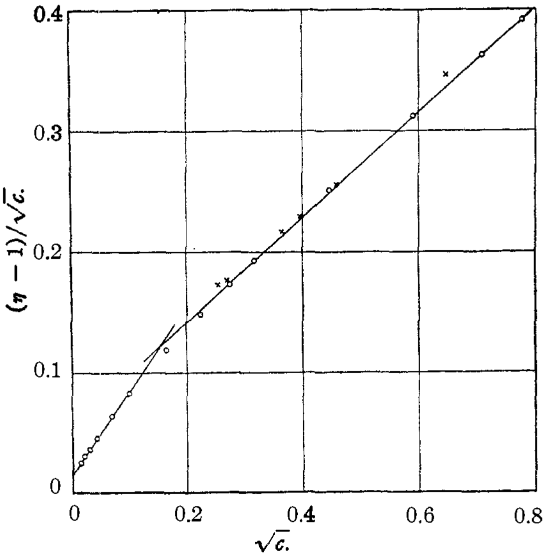

Fig. 1.—Test of the Jones and Dole equation: O, Jones and Fornwalt; X, Ewart and Raikes.

Potassium Iodide.—The results on potassium iodide solutions are shown in Table I and in Figs. 1 and 2. The density of potassium iodide solutions in methanol at 25° can be expressed by an equation of the form suggested by Root;[13] $d^{25}_4 = 0.786545 + 0.148096c - 0.007833c^{3/2}$; with an average deviation between our observed values and those computed by this equation of only 0.0021%.

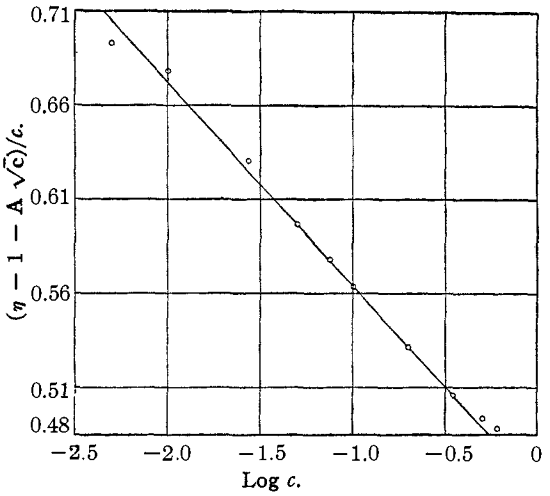

Fig. 2.—Test of the Onsager and Fuoss equation.

If the viscosity–concentration curves were linear the quantity $(\eta - 1)/c$ should be a constant, but column four shows that this quantity diminishes rapidly with increasing concentration at low concentrations but that, unlike most aqueous solutions, $(\eta - 1)/c$ does not pass through a minimum within the range of concentrations studied, which extends almost to saturation. The "Grüneisen Effect" is more pronounced in this case than for aqueous solutions. The Jones and Dole equation was then tested by plotting $(\eta - 1)/\sqrt{c}$ against $\sqrt{c}$ which gave a straight line up to and including $c = 0.01$. The coefficients A and B were then determined by the method of least squares using the data up to $c = 0.01$; giving η

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[10] J. Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 412 (1930).

[11] H. Hartley and H. R. Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

[12] Grinnell Jones and S. K. Talley, THIS JOURNAL, **55**, 624 (1933); *Physics*, **4**, 215 (1933).

[13] W. C. Root, THIS JOURNAL, **55**, 850 (1933).

$= 1 + 0.0159\sqrt{c} + 0.6747c$. As will be seen from Table I this equation agrees with the data up to $c = 0.01$ with an average deviation of only 0.002% but fails badly above this concentration. This same plot shows that the points from $c = 0.05$ to $c = 0.6$, inclusive, are also on a different straight line whose equation is $\eta = 1 + 0.05546\sqrt{c} + 0.43362c$ with an average deviation of 0.05%. The data were also used to test the Onsager and Fuoss equation: $\eta = 1 + A\sqrt{c} + Bc + Dc \log c$ by plotting $(\eta - 1 - A\sqrt{c})/c$ against $\log c$, which should give a straight line if the Onsager and Fuoss equation is valid and if the proper numerical value of A has already been chosen. Using the value $A = 0.0159$ already determined, an approximation to a straight line was found for the middle range of concentration (see Fig. 2). The two highest concentrations ($c = 0.5$ and $c = 0.6$) are clearly out of line. The deviations at the dilute end, although apparently large, are not significant because this method of plotting is extremely sensitive at the dilute end to experimental errors or to the value of A chosen. The method of least squares was then used to determine all of the coefficients in the Onsager and Fuoss equation using the data up to $c = 0.35$. The result was

TABLE I

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM IODIDE SOLUTIONS IN METHANOL AT 25°

Concentration c	Density d^{25}_4	Relative viscosity η observed	$(\eta - 1)/c$	Jones and Dole equation η Comp.	Jones and Dole equation $\Delta\eta \times 10^5$	Onsager and Fuoss equation η Comp.	Onsager and Fuoss equation $\Delta\eta \times 10^5$
0.0002504	0.78657_3	1.00040	1.60	1.00042	− 2	1.00044	− 4
.0005010	$.78662_1$	1.00069	1.38	1.00069	0	1.00076	− 7
.0010001	$.78668_7$	1.00115	1.15	1.00118	− 3	1.00128	− 13
.0020035	$.78684_6$	1.00206	1.03	1.00206	0	1.00220	− 14
.0050017	$.78728_1$	1.00457	0.91	1.00450	+ 7	1.00462	− 5
.0100232	$.78803_2$	1.00833	.83	1.00836	− 3	1.00828	+ 5
.0271490	$.79053_8$	1.01962	.722	1.02094	− 132	1.01947	+ 15
.0499222	$.79389_1$	1.03316	.664	1.03724	− 408	1.03312	+ 4
.0752514	$.79752_0$	1.04752	.632	1.05513	− 761	1.04749	+ 3
.100245	$.80119_8$	1.06107	.609	1.07267	− 1160	1.06113	− 6
.199325	$.81535_6$	1.11215	.563	1.14158	− 2943	1.11222	− 7
.348769	$.83653_0$	1.18420	.528	1.24470	− 6050	1.18417	+ 3
.501918	$.85810_8$	1.25651	.511	1.34991	− 9340	1.25420	+231
.603193	$.87221_4$	1.30385	.504	1.41932	−11547	1.29909	+476

Root equation: $d^{25}_4 = 0.786545 + 0.148096c - 0.007833c^{3/2}$.
Jones and Dole equation: $\eta = 1 + 0.0159\sqrt{c} + 0.6747c$.
Onsager and Fuoss equation: $\eta = 1 + 0.01575\sqrt{c} + 0.45174c - 0.10847c \log c$.

TABLE II

RELATIVE VISCOSITY AND DENSITY OF AMMONIUM CHLORIDE SOLUTIONS IN METHANOL AT 25°

Concentration c	Density d^{25}_4	Relative viscosity η observed	$(\eta - 1)/c$	Jones and Dole equation η Comp.	Jones and Dole equation $\Delta\eta \times 10^5$	Onsager and Fuoss equation η Comp.	Onsager and Fuoss equation $\Delta\eta \times 10^5$
0.0005015	0.786556	1.00078	1.56	1.00074	+ 4	1.00085	− 7
.0007966	$.78657_8$	1.00102	1.28	1.00104	− 2	1.00118	−16
.0009928	$.78659_8$	1.00113	1.14	1.00123	− 10	1.00138	−25
.0019827	$.78662_1$	1.00212	1.07	1.00213	− 1	1.00231	−19
.0049911	$.78673_8$	1.00467	0.936	1.00459	+ 8	1.00475	− 8
.0079583	$.78683_9$	1.00696	.875	1.00689	+ 7	1.00692	+ 4
.0099441	$.78695_0$	1.00832	.837	1.00840	− 8	1.00831	+ 1
.0149778	$.78712_2$	1.01166	.778	1.01214	− 48	1.01168	− 2
.0200046	$.78731_7$	1.01476	.738	1.01581	− 105	1.01490	−14
.0300215	$.78767_6$	1.02102	.700	1.02302	− 200	1.02105	− 3
.0400008	$.78806_4$	1.02707	.677	1.03010	− 303	1.02693	+14
.0499413	$.78840_5$	1.03298	.660	1.03710	− 412	1.03262	+36
.0700415	$.78912_6$	1.04386	.626	1.05114	− 728	1.04377	+ 9
.100215	$.79019_5$	1.05990	.598	1.07204	−1214	1.05986	+ 4
.199413	$.79358_9$	1.10932	.548	1.13998	−3066	1.10974	−42
.351163	$.79851_8$	1.18134	.516	1.24296	−6162	1.18118	+16

Root equation: $d^{25}_4 = 0.786545 + 0.039225c - 0.008672c^{3/2}$.
Jones and Dole equation: $\eta = 1 + 0.0183\sqrt{c} + 0.6610c$.
Onsager and Fuoss equation: $\eta = 1 + 0.02129\sqrt{c} + 0.43823c - 0.09196c \log c$.

TABLE III

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM BROMIDE SOLUTIONS IN METHANOL AT 25°

Concentration c	Density d^{25}_4	Relative viscosity η observed	$(\eta - 1)/c$	Jones and Dole equation		Onsager and Fuoss equation	
				η Comp.	$\Delta\eta \times 10^5$	η Comp.	$\Delta\eta \times 10^5$
0.0004104	(0.786589)	1.00058	1.41	1.00059	− 1	1.00064	− 6
.0005038	.786608	1.00067	1.33	1.00069	− 2	1.00075	− 8
.0010044	.786657	1.00116	1.15	1.00119	− 3	1.00129	−13
.0020020	.786775	1.00216	1.08	1.00212	+ 4	1.00224	− 8
.0050194	.787079	1.00473	0.942	1.00472	+ 1	1.00483	−10
.0100141	.787636	1.00882	.881	1.00883	− 1	1.00871	+11
.0149908	.788174	1.01257	.839	1.01283	− 26	1.01235	+22
.0300121	.789793	1.02265	.755	1.02466	− 201	1.02264	+ 1
.0500105	.791920	1.03548	.709	1.04017	− 469	1.03548	0
.0800065	.795098	1.05363	.670	1.06319	− 956	1.05373	−10
.100011	.797237	1.06527	.653	1.07846	−1319	1.06548	−21
.118905	.799295	1.07649	.643	1.09284	−1635	1.07630	+19

$d^{25}_4 = 0.786545 + 0.107068c$.

Jones and Dole equation: $\eta = 1 + 0.0142\sqrt{c} + 0.7396c$.

Onsager and Fuoss equation: $\eta = 1 + 0.01325\sqrt{c} + 0.48758c - 0.12504c \log c$.

TABLE IV

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM CHLORIDE SOLUTIONS IN METHANOL AT 25°

Concentration c	Density d^{25}_4	Relative viscosity η observed	$(\eta - 1)/c$	Jones and Dole equation		Onsager and Fuoss equation	
				η Comp.	$\Delta\eta \times 10^5$	η Comp.	$\Delta\eta \times 10^5$
0.0004786	0.786563	1.00068	1.42	1.00070	− 2	1.00064	+4
.0010431	.786615	1.00126	1.21	1.00128	− 2	1.00126	0
.0019996	.786676	1.00224	1.12	1.00220	+ 4	1.00222	+2
.0048375	.786884	1.00474	0.978	1.00475	+ 1	1.00482	−8
.0099940	.787233	1.00914	.915	1.00914	0	1.00912	+2
.0199816	.787914	1.01676	.839	1.01739	− 63	1.01671	+5
.0299878	.788589	1.02376	.792	1.02551	−175	1.02378	−2
.0350097	.788918	1.02716	.775	1.02956	−240	1.02719	−3
.0400159	.789246	1.03055	.763	1.03357	−302	1.03053	+2

$d^{25}_4 = 0.786545 + 0.067895c$.

Jones and Dole equation: $\eta = 1 + 0.0151\sqrt{c} + 0.7635c$.

Onsager and Fuoss equation: $\eta = 1 + 0.00367\sqrt{c} + 0.43974c - 0.21803c \log c$.

$\eta = 1 + 0.01575\sqrt{c} + 0.45174c - 0.10874c \log c$. The values computed from the equation are shown in the last two columns of Table I. As will be seen, this equation is better between $c = 0.027$ and $c = 0.35$ than any other equation known to us, but gives low results at $c = 0.5$ and $c = 0.6$ and is not as good as the Jones and Dole equation at $c = 0.01$ and below *if the constants are chosen to fit the data over the entire range up to* $c = 0.35$.

Ammonium Chloride.—Taking up the salts studied in order of decreasing solubility we find that ammonium chloride presents a picture very similar to potassium iodide. The density can be expressed by the Root equation with an average deviation of less than 0.001%; $d^{25}_4 = 0.786545 + 0.039225c - 0.008672c^{3/2}$. Again it was found that the Jones and Dole equation, $\eta = 1 + 0.0183\sqrt{c} + 0.6610c$ holds up to $c = 0.01$ but not above. The Onsager and Fuoss equation $\eta = 1 + 0.02129\sqrt{c} + 0.43823c - 0.09196c \log c$, is the best between $c = 0.01$ and $c = 0.35$, but not as good as the Jones and Dole equation for the more dilute solutions. The "Grüneisen Effect" is similar to potassium iodide solutions but slightly more pronounced.

Potassium Bromide and Potassium Chloride.—Owing to their limited solubility these salts do not give as severe and useful tests of the equations in which we are interested as the other salts studied. The densities of the solutions of both of these salts can be expressed as a linear function of the concentration (see Tables III and IV) with an average deviation of less than 0.002%. All four salts show the "Grüneisen Effect" in a similar degree. Again we find that the Jones and Dole equation is valid up to $c = 0.01$ but not above, and that the Onsager and Fuoss equation is better than the Jones and Dole equation for solutions more concentrated than $c = 0.01$.

General Discussion

Earlier investigations cited above have shown that the Jones and Dole equation is valid for aqueous solutions of salts which diminish the viscosity of water up to about 0.2 normal and to a considerably higher concentration for some salts which increase the viscosity. On the other hand, for these methanol solutions the Jones and Dole equation is valid only up to 0.01 normal.

All four of these salts give aqueous solutions which within certain ranges of concentration and of temperature, have a viscosity less than that of the pure solvent but none of them diminishes the viscosity of methanol at 25°. No salt has yet been found to have this effect in methanol solution. The B term in the Jones and Dole equation is positive for all methanol solutions that have yet been studied, but is negative for many salts in water solutions.

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

$$A = \frac{1.45}{\eta_0\sqrt{2DT}}\left[\frac{l_1 + l_2}{4l_1l_2} - \frac{(l_1 - l_2)^2}{(3 + 2\sqrt{2})l_1l_2(l_1 + l_2)}\right]$$

where η_0 and D are the absolute viscosity and dielectric constant of the solvent, T is the absolute temperature, and l_1 and l_2 are the equivalent conductances of the ions present; and the factor 1.45 is computed from universal constants. The values of A for the four salts have been computed by this equation using: $\eta_0 = 0.00542$ (a preliminary value from our own measurements, details to be published later); $D = 31.5$ (after Åkerlöf[14]); and the following values for the equivalent conductances of the ions; K^+, 53.8; Cl^-, 51.3; Br^-, 55.5; I^-, 61.0; NH_4^+, 59.0 (after Hartley and Raikes, and Ulich[15]).

The results are shown in Table V and compared with the values of A obtained directly from our experimental data by the use of the Jones and Dole equation and the Onsager and Fuoss equation. The agreement is sufficiently close to show that Falkenhagen's theory is correct in its fundamentals even if it may require some modification or elaboration in detail. Of special significance is the comparison of these results in methanol solutions with the investigations on aqueous solutions referred to above. For aqueous solutions A has a value of 0.005 (more or less for various salts), whereas an inspection of the Falkenhagen and Vernon equation shows that the lower value of η_0 and D for methanol in comparison with water should make A about threefold larger. This is confirmed by our experimental data.

TABLE V

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

Salt	Theoretical Falkenhagen	Experimental Jones and Dole	Onsager and Fuoss
KCl	0.0173	0.0151	0.0037
KBr	.0165	.0142	.0133
KI	.0158	.0159	.0158
NH_4Cl	.0165	.0183	.0213

Summary

1. The absolute density and relative viscosity at 25° of many solutions of potassium chloride, potassium bromide, potassium iodide and ammonium chloride in methanol have been measured covering a range of concentration from extreme dilution nearly to saturation.

2. The density of solutions of these salts in methanol may be expressed by an equation of the form suggested by Root for aqueous solutions.

3. Although all of these salts may cause a decrease in viscosity when dissolved in water, none of them shows this effect when dissolved in methanol.

4. All of these solutions show the "Grüneisen Effect" strongly.

5. The data are used to test the validity of several equations for the viscosity as a function of the concentration.

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[14] G. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

[15] H. Hartley and H. R. Raikes, *Trans. Faraday Soc.*, **23**, 394 (1927); H. Ulich, *ibid.*, **23**, 390 (1927).