

On the Viscosity of dilute Alcoholic Solutions.

By

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ARRHENIUS¹⁾ has shown first that the viscosity of an aqueous solution containing any two indifferent dissolved substances can be expressed with good results by the following exponential formula,

$$z = A^x B^y, \dots\dots\dots(1)$$

where A and B are two constants characteristic of the substances dissolved at a constant temperature, x and y being their respective volume percentages. Since $z=1$, when $x=y=0$, the viscosity thus expressed is the specific viscosity of the solution, where the viscosity of the solvent is made unity. When only one substance is dissolved the formula reduces to the simpler one,

$$z = A^x. \dots\dots\dots(2)$$

ARRHENIUS has further shown that the formula can be applied to aqueous solutions of electrolytes and non-electrolytes up to 1.5 normal and 10 vol. per cent. solutions respectively, in which the resulting error rarely exceeds one per cent.

The correctness of the above results in the case of aqueous solutions has since been confirmed by the works of REYHER,²⁾ WAGNER³⁾ and others.

1) Zeit. physik. Chem., 1887, I, 285.
2) " " " 1888, II, 744.
3) " " " 1890, V, 40.

Believing it to be of some interest to determine whether such regularities exist in other solvents than water, I undertook some experiments on the viscosities of alcoholic solutions.

The following experiments were made using ethyl alcohol as the solvent, which was obtained by dehydrating commercial "absolute alcohol" with freshly burnt lime; all the dissolved substances used, were tested for the impurities frequently contained in them and freed from these; their densities, boiling points and, when easily observable, their melting points, were compared with those given for the pure substances and found quite satisfactory.

The experimental method was as follows:—A glass tube, like an ordinary test tube closed at one end, and furnished with a glass stopper at the other, was taken. The tube was graduated in cubic centimeter from the bottom up to 20 c.c. Into this tube the required volume of the liquid to be dissolved was poured and the solvent alcohol gradually added, with frequent shakings, until it filled 20 c.c. The dissolved substance and the solvent, before mixing, were kept in a thermostat whose temperature was 25°C. The solution thus made was kept in the thermostat for a sufficient length of time before its viscosity was measured.

Solutions containing only one dissolved substance were made as follows, and the measurements made on each: At first, 5 c.c. of the substance to be dissolved was taken and diluted to 20 c.c. with the alcohol; then the half, i. e. 10 c.c., of the solution, was taken and diluted again to 20 c.c.; in this way, 25, 12.5, 6.25, 3.125, 1.5625 and 0.7813 vol. per cent. solutions were made.

The viscosimeter used in the experiment was that of OSTWALD (Fig. 1) and had the following dimensions: Length of the

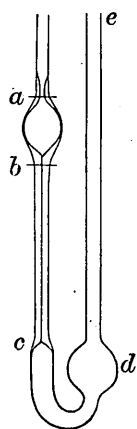


Fig. 1.

capillary tube bc , 12 cm.; diameter of the capillary, 0.0544 cm.; volume of the upper bulb between the marks a and b , 6.51 c.c. The total volume of liquid used was 9 c.c.

After the fixed volume (=9 c.c.) of the solution had been poured in at e by means of a pipette, the apparatus was sunk vertically under the water of the thermostat until the mark a was a sufficient distance below the surface. The liquid in the bulb d was pushed up, by pressing in some dry air at e , and when its head reached the mark a , the pressure was removed and the liquid was left to flow down the capillary by its own weight. The time required to flow down from a to b was then read.

The time was measured by means of a watch, capable of being read to one fifth of a second.

As is well known, when t and t' are the times of flow from a to b , and s and s' are the densities of any two liquids respectively, then the ratio of their absolute viscosities η and η' is,

$$\frac{\eta'}{\eta} = \frac{s' \cdot t'}{s \cdot t}$$

Hence if we know the time of flow and the density of a liquid we can readily calculate the specific viscosity of that liquid. I measured the specific gravity of a liquid with a SPRENGEL'S U-shaped pycnometer whose capacity was about 3 c.c.

At first, I made the determinations with solutions having only one dissolved substance.

I found that the formula (2) gives good results, in a wide range of concentrations, with the dissolved substances I had taken, except in the case of water; the following table gives

the constant A and the specific viscosities z (the viscosity of ethyl alcohol at 25°C. being unity) of the substances dissolved and the upper limits of concentrations expressed in vol. %, below which the calculation from (2) gives differences less than one per cent from the direct observations.

Dissolved substance.	A	z	Limit.
Acetone	0.9786	0.2946	12.5
Ethyl ether... ..	0.9840	0.2292	25
Ethyl acetate	0.9865	0.4189	25
Carbon bisulphide	0.9888	0.3583	25
Ethyl bromide	0.9888	0.3815	25
Ethyl iodide	0.9918	0.5611	25
Methyl alcohol	0.9922	0.5270	25
Benzene	0.9924	0.5608	25
Chlorobenzene	0.9970	0.6989	25
Nitrobenzene	1.001	1.687	25
Ethyl benzoate	1.001	1.7918	25
Propyl alcohol	1.0053	1.841	25
Aniline	1.007	4.306	25
Amyl alcohol	1.0085	3.455	12.5
Glycerine	1.055	—	12.5

In the above table the dissolved substances are arranged according to their constants A . We see from the table that, *in general*, the substances of greater viscosity give greater constants and we can not find the remarkable fact that ARRHENIUS observed in aqueous solutions, viz., that the constant A of glycerine is less than that of ether.

We further noticed, when compared with aqueous solutions at 25°C., that while in the aqueous solutions the constants A of all non-electrolytes are greater than unity, many of the constants found in the alcoholic solutions are less than unity.

The following tables show the differences between the observed viscosities and those calculated from the above constants.

Acetone.

$$A=0.9786.$$

x	z	A^x	Diff.
25	0.6137	0.5823	-0.0314
12.5	0.7653	0.7631	-0.0022
6.25	0.8695	0.8735	+0.0040
3.125	0.9355	0.9346	-0.0009
1.5625	0.9689	0.9668	-0.0021
0.78125	0.9905	0.9832	-0.0073

Ethyl ether.

$$A=0.9840.$$

x	z	A^x	Diff.
25	0.6620	0.6682	+0.0062
12.5	0.8187	0.8174	-0.0013
6.25	0.9069	0.9041	-0.0028
3.125	0.9575	0.9508	-0.0067
1.5625	0.9823	0.9751	-0.0072
0.78125	0.9949	0.9875	-0.0074

Ethyl acetate.

$$A=0.9865.$$

x	z	A^x	Diff.
25	0.7163	0.7119	-0.0044
12.5	0.8424	0.8438	+0.0014
6.25	0.9137	0.9186	+0.0049
3.125	0.9614	0.9584	-0.0030
1.5625	0.9845	0.9790	-0.0055
0.78125	0.9963	0.9894	-0.0069

Carbon bisulphide.

$$A=0.9888.$$

x	z	A^x	Diff.
25	0.7491	0.7546	-0.0055
12.5	0.8656	0.8687	+0.0031
6.25	0.9326	0.9320	-0.0006
3.125	0.9666	0.9654	-0.0012
1.5625	0.9910	0.9826	-0.0084
0.78125	0.9971	0.9912	-0.0059

Ethyl bromide.

$$A=0.9888.$$

x	z	A^x	Diff.
25	0.7488	0.7546	+0.0058
12.5	0.8687	0.8687	± 0
6.25	0.9324	0.9320	-0.0004
3.125	0.9682	0.9654	-0.0028
1.5625	0.9857	0.9826	-0.0031
0.78125	0.9940	0.9912	-0.0028

Ethyl iodide.

$$A=0.9918.$$

x	z	A^x	Diff.
25	0.8078	0.8140	+0.0062
12.5	0.9029	0.9022	-0.0007
6.25	0.9514	0.9498	-0.0016
3.125	0.9815	0.9746	-0.0069
1.5625	0.9912	0.9872	-0.0040
0.78125	0.9950	0.9936	-0.0014

Methyl alcohol.

$$A=0.9922.$$

x	z	A^x	Diff.
25	0.8218	0.8222	+0.0004
12.5	0.9062	0.9068	+0.0006
6.25	0.9500	0.9522	+0.0022
3.125	0.9744	0.9758	+0.0014
1.5625	0.9870	0.9878	+0.0008

Benzene.

$$A=0.9924.$$

x	z	A^x	Diff.
25	0.8267	0.8264	-0.0003
12.5	0.9090	0.9090	± 0
6.25	0.9548	0.9534	-0.0014
3.125	0.9827	0.9764	-0.0063
1.5625	0.9955	0.9882	-0.0073
0.78125	0.9959	0.9941	-0.0018

Chlorobenzene.

$$A=0.9970.$$

x	z	A^x	Diff.
25	0.9189	0.9276	+0.0087
12.5	0.9674	0.9631	-0.0043
6.25	0.9894	0.9814	-0.0080
3.125	0.9972	0.9907	-0.0065
1.5625	1.0012	0.9953	-0.0059
0.78125	1.0029	0.9977	-0.0052

Nitrobenzene.

$$A=1.001.$$

x	z	A^z	Diff.
25	1.0230	1.0253	+0.0023
12.5	1.0078	1.0126	+0.0048
6.25	1.0062	1.0063	+0.0001
3.125	1.0074	1.0031	-0.0043
1.5625	1.0058	1.0016	-0.0042
0.78125	1.0074	1.0008	-0.0066

Ethyl benzoate.

$$A=1.001.$$

x	z	A^z	Diff.
25	1.0324	1.0253	-0.0071
12.5	1.0126	1.0126	± 0
6.25	1.0066	1.0063	-0.0003
3.125	1.0080	1.0031	--0.0049
1.5625	1.0075	1.0016	--0.0059
0.78125	1.0079	1.0008	-0.0071

Propyl alcohol (normal).

$$A=1.0053.$$

x	z	A^z	Diff.
25	1.1406	1.1413	+0.0007
12.5	1.0684	1.0683	-0.0001
6.25	1.0353	1.0336	-0.0017
3.125	1.0185	1.0167	-0.0018
1.5625	1.0088	1.0083	-0.0005
0.78125	1.0045	1.0041	-0.0004

Aniline.

$$A=1.007.$$

x	z	A^z	Diff.
25	1.2081	1.1905	-0.0176
12.5	1.0864	1.0911	+0.0047
6.25	1.0439	1.0446	+0.0007
3.125	1.0279	1.0220	-0.0059
1.5625	1.0176	1.0110	-0.0066
0.78125	1.0103	1.0055	-0.0048

Amyl alcohol (isobutyl carbinol).

$$A=1.0085.$$

x	z	A^z	Diff.
25	1.2401	1.2357	-0.0044
12.5	1.1074	1.1116	+0.0042
6.25	1.0508	1.0543	+0.0035
3.125	1.0258	1.0268	+0.0010
1.5625	1.0127	1.0133	+0.0006

Glycerine.

$$A=1.055.$$

x	z	A^z	Diff.
25	4.1224	3.8134	-0.3090
12.5	1.9600	1.9528	-0.0072
6.25	1.3958	1.3974	+0.0016
3.125	1.1746	1.1821	+0.0075
1.5625	1.0814	1.0873	+0.0059
0.78125	1.0492	1.0427	-0.0065

As is seen from the tables, most of the dissolved substances above mentioned are calculable with the formula (2) with differences less than one per cent up to 25 vol. % solutions and a few, i. e. three out of the fifteen, up to 12.5 vol. % solutions. But when water is the dissolved substance the formula does not apply in the same manner unless the concentrations of the solutions are less than 3 vol. % as the following tables show :

Water.

x	z	$A^z (A=1.032)$	Diff.	$A^z (A=1.040)$	Diff.
25	1.8300	2.1978	-0.3680	—	—
12.5	1.4715	1.4825	-0.0110	1.6327	-0.1612
6.25	1.2575	1.2176	+0.0399	1.2778	-0.0203
3.125	1.1407	1.1034	+0.0373	1.1304	+0.0103
1.5625	1.0808	1.0505	+0.0303	1.0632	+0.0176
0.78125	1.0412	1.0249	+0.0163	1.0311	+0.0101

$A^z (A=1.043)$	Diff.	$A^z (A=1.045)$	Diff.
—	—	—	—
—	—	—	—
—	—	—	—
1.1406	+0.0001	1.1475	-0.0068
1.0680	+0.0128	1.0712	+0.0096
1.0334	+0.0078	1.0350	+0.0062

This is also clear from the shape of the viscosity curve of the water solutions, the dotted line in the figure (Fig. 2) is that calculated from $A=1.032$.

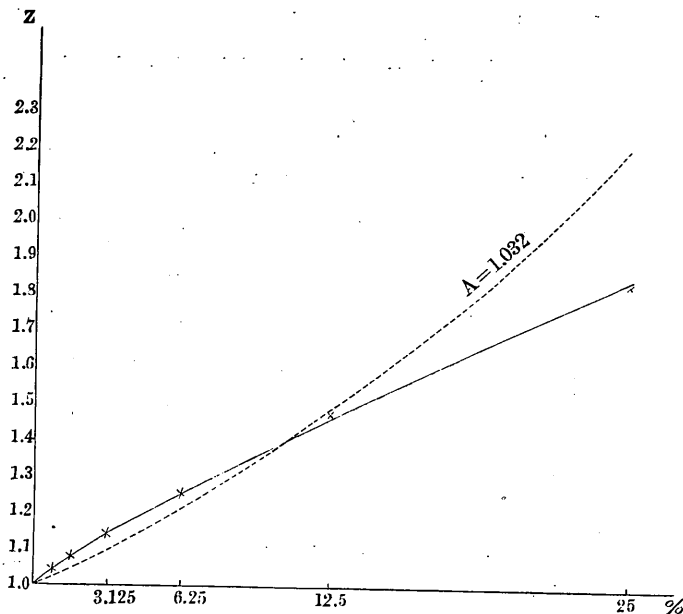


Fig. 2.

Next, I tried the application of formula (1) to solutions containing two dissolved substances. The results were that, so far as my experiment went, the formula gave good results at least to 10 vol. % solutions.

The pairs of the dissolved substances I have taken are as follows :

Dissolved substances.	Limit.
Carbon bisulphide and ethyl ether	20 vol. %
Nitrobenzene and ethyl ether	20 "
Acetone and nitrobenzene	20 "
Benzene and nitrobenzene	10 "
Benzene and carbon bisulphide	10 "
Aniline and carbon bisulphide	10 "
Benzene and propyl alcohol	20 "
Benzene and ethyl benzoate	20 "

I found in this case, that when the constants A and B were calculated from the observed viscosities by the formula,

$$z = A^x \cdot B^y,$$

the values of A and B thus obtained were nearly equal to the constants which we had found when only one substance was used; and on calculating z using the latter constants, it was found that the observed and the calculated values did not differ by more than one per cent. This is shown in the following tables; the constants used are all those found before. The limits, within which the above relations hold good, and noted in the right hand column of the above table, are the maximum concentrations of the two dissolved substances taken together and expressed in volume percentage. The maximum volume percentage of each of the two dissolved substances is one-half of the above limits.

Carbon bisulphide and Ethyl ether.

Carbon bisulphide: $A=0.9888$.

Ethyl ether: $B=0.9840$.

x	y	z	$A^x \cdot B^y$	Diff.
10	10	0.7600	0.7604	+0.0004
5	5	0.8704	0.8720	+0.0016
2.5	2.5	0.9347	0.9338	-0.0009
5	10	0.8024	0.8044	+0.0020
2.5	5	0.8976	0.8969	-0.0007
10	5	0.8255	0.8243	-0.0012

Nitrobenzene and Ethyl ether.Nitrobenzene: $A=1.001$.Ethyl ether: $B=0.9840$.

x	y	z	$Ax.By$	Diff.
10	10	0.8635	0.8596	-0.0039
5	5	0.9288	0.9271	-0.0017
2.5	2.5	0.9637	0.9629	-0.0008
5	10	0.8592	0.8553	-0.0039
2.5	5	0.9295	0.9248	-0.0047
10	5	0.9315	0.9318	+0.0003

Acetone and Nitrobenzene.Acetone: $A=0.9786$.Nitrobenzene: $B=1.001$.

x	y	z	$Ax.By$	Diff.
10	10	0.8195	0.8136	-0.0059
5	5	0.8997	0.9020	+0.0023
2.5	2.5	0.9476	0.9497	+0.0021
5	10	0.8997	0.9065	+0.0068
10	5	0.8092	0.8095	+0.0003

Benzene and Nitrobenzene.Benzene: $A=0.9924$.Nitrobenzene: $B=1.001$.

x	y	z	$Ax.By$	Diff.
10	10	0.9205	0.9359	+0.0154
5	5	0.9597	0.9674	+0.0077
2.5	2.5	0.9818	0.9836	+0.0018
5	10	0.9600	0.9722	+0.0122
2.5	5	0.9816	0.9860	+0.0044
10	5	0.9250	0.9312	+0.0062
5	2.5	0.9618	0.9650	+0.0037

Benzene and Carbon bisulphide.Benzene: $A=0.9924$.Carbon bisulphide: $B=0.9888$.

x	y	z	Ax, By	Diff.
10	10	0.8119	0.8279	+0.0160
5	5	0.9035	0.9099	+0.0064
2.5	2.5	0.9498	0.9539	+0.0041
10	5	0.8636	0.8758	+0.0122
5	2.5	0.9325	0.9359	+0.0034
5	10	0.8463	0.8600	+0.0137
2.5	5	0.9191	0.9274	+0.0083

Aniline and Carbon bisulphide.Aniline: $A=1.007$.Carbon bisulphide: $B=0.9888$.

x	y	z	Ax, By	Diff.
10	10	0.9296	0.9580	+0.0284
5	5	0.9690	0.9788	+0.0098
2.5	2.5	0.9862	0.9893	+0.0031
10	5	0.9989	1.0135	+0.0146
5	2.5	1.0061	1.0067	+0.0006
5	10	0.9078	0.9252	+0.0174
2.5	5	0.9589	0.9619	+0.0030

Benzene and Propyl alcohol.Benzene: $A=0.9924$.Propyl alcohol: $B=1.0053$.

x	y	z	Ax, By	Diff.
10	10	0.9711	0.9768	+0.0057
5	5	0.9895	0.9884	-0.0011
2.5	2.5	0.9945	0.9942	-0.0003
10	5	0.9476	0.9514	+0.0038
5	10	1.0103	1.0148	+0.0045

Benzene and Ethyl benzoate.Benzene: $A=0.9924$.Ethyl benzoate: $B=1.001$.

x	y	z	$A^x \cdot B^y$	Diff.
10	10	0.9266	0.9359	+0.0093
5	5	0.9619	0.9674	+0.0055
2.5	2.5	0.9785	0.9836	+0.0051
5	10	0.9672	0.9722	+0.0050
10	5	0.9232	0.9312	+0.0080

SUMMARY.

1. It is shown that **ARRHENIUS'** formula, $z=A^x \cdot B^y$, which gives good results in dilute aqueous solutions also holds good when ethyl alcohol is used as the solvent.

2. The formula can be applied to the solution of all the substances that I have examined with an error of less than one per cent, at least to 10 volume percentage concentration. Water forms an exception.

3. When water is the dissolved substance the formula can be applied only to very dilute solutions. When the concentration exceeds 3 volume percentage the error amounts to more than one per cent.