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Viscosity of Glycerol and Its Aqueous Solutions

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Viscosity data for aqueous glycerol solutions in the range of 0° to 100° C. and 0 to 100% concentration have been reported by various authors, each working within limited temperature or concentration ranges. Different types of viscometers were used. As a result there are gaps and inconsistencies in the data.

The viscosity data reported here were obtained with a single type of viscometer over the entire range of 0° to 100° C. and 0 to 100% glycerol concentration.

The data will be useful in the design and use of glycerol-handling equipment. They also make it possible to use aqueous glycerol solutions as viscosity standards over a wide range of viscosity and at temperatures from 0° to 100° C.

THERE have been several studies of glycerol viscosity for limited ranges of concentrations and temperatures. However, there has been no extensive study of aqueous glycerol solutions over 0° to 100° C. temperature range using a single type of viscometer. Herz and Wegner (12) measured the viscosity of glycerol solutions of 10 to 92% concentration at temperatures from 10° to 80° C. Their results were published in terms of both relative and absolute viscosity. Archbutt and Deeley (2) made careful viscosity measurements of glycerol solutions at 20° C. The capillary of their viscometer had a diameter of 0.6180 mm. and a length of 21.991 cm., with square ends. The hydrostatic head was increased by a supplementary tube attached to the capillary when the more viscous solutions were used. Darke and Lewis (10) measured the relative viscosity of glycerol solutions of 10 to 92% concentration at 1° C. They did not record the specific gravities of their solutions, nor did they state how the viscosity measurements were made. They published their data together with the relative viscosity data of Herz and Wegner to make a comprehensive tabulation. Cocks (9) combined other published data with those published by Darke and Lewis and added some original data obtained with a standard Redwood viscometer to make a compilation covering most of the points from 1° to 100° C., and from 0 to 99% of glycerol. The data are given in terms of poises. There are a number of inconsistencies in the above data, particularly in the region of temperatures above 70°

C. Sheely (16), using a viscometer of the type described by Bingham and Jackson (4), in which pressure on the liquid was controlled by a regulated air supply, made very careful measurements of the viscosity of glycerol solutions of 0 to 100% concentrations and at the temperatures of 20°, 22.5°, 25°, 27.5°, and 30° C. Müller (14) published viscosity values for water and five concentrations of glycerol at temperatures from 17° to 90° C.

Vand (18), using Ostwald viscometers, determined the viscosity of glycerol solutions of 98.4 and 99.6% concentrations at ten temperatures from 80° to 167° C. Green and Parke (11) measured the viscosities of glycerol solutions at temperatures from 0° to -40° C., within the limits of the freezing points of the solutions. Tammann and Hesse (17) measured the viscosity of 99.5% glycerol at temperatures from -42° to -4.2° C. The viscosity of pure glycerol at pressures up to 12,000 kg. per sq. cm., at 30° C., was measured by Bridgman (6).

The present work was done to correct some inaccuracies in the previous data, to provide data where none were available, and to provide a series of consistent viscosity data all obtained with the same type of viscometer, within the limits of 0° to 100° C., and 0 to 100% glycerol concentration.

GLYCEROL AND GLYCEROL SOLUTIONS

A selected sample of c.p. glycerol was distilled from a 5-liter flask through a 25-cm. Vigreux column. The column was connected to the flask with a standard-taper ground-glass joint. The middle portion of the distillate, boiling point 140° C. at 1 mm., weighing 4330 grams, was taken for use. Its specific gravity at 25/25° C. was 1.26192, which corresponds to 99.97% of glycerol by weight.

The glycerol-water solutions were prepared by mixing calculated weights of glycerol and of distilled water which had been recently boiled and cooled. The actual concentrations were determined from their specific gravities at 25/25° C. Two Geissler 25-ml. pycnometers were used. Duplicate tests were made with each solution, one test with each pycnometer. The equivalent glycerol concentrations were obtained from the data of Bosart and Snoddy (5). The maximum difference between duplicate determinations was equivalent to 0.08% glycerol. The average difference was 0.04%. The concentrations of the solutions were

TABLE I. CALIBRATION OF VISCOMETERS AT 20° C.

Solution	Vis-cometer No.	Time, Sec.	Solution Density	Absolute Viscosity	Kinematic Viscosity	Viscometer Constant
Water	50	209.5	0.99824	1.0050	1.0068	0.00481
Glycerol, %						
60.02	50	1946.3	1.15406	10.795	9.3539	
60.02	100	622.3	1.15406	10.795	9.3539	0.01503
85.07	100	5990.0	1.22223	110.04	90.036	
85.07	200	936.4	1.22223	110.04	90.036	0.0962
85.07	300	349.4	1.22223	110.04	90.036	0.2577
96.00	300	1934.0	1.25109	623.50	498.37	
96.00	400	396.1	1.25109	623.50	498.37	1.258

0.00, 10.20, 20.04, 29.96, 40.01, 49.93, 60.02, 66.97, 74.97, 79.99, 85.07, 90.03, 92.09, 92.97, 94.96, 96.00, 96.99, 97.89, 98.86, and 99.97%. The solutions with 50% or less of glycerol were stored at 5° to 10° C. to prevent mold growth.

APPARATUS

The viscometers used were the No. 50, 100, 200, 300, and 400 sizes of the modified Ostwald viscometers described by Cannon and Fenske (7, 8). Specifications and directions for use are also given by the American Society for Testing Materials (ASTM) (1). The viscometer to be used for a test was selected so that the efflux time of the liquid would be at least 200 seconds, and for convenience, not over about 800 seconds. At temperatures above 60° or 70° C. evaporation of water from the solution in the viscometer became appreciable. To reduce such evaporation an inverted U-tube was attached to the two ends of the viscometer with short pieces of rubber tubing. Connected to the U-tube were stopcocks arranged so that the solution could be blown into the upper bulb of the viscometer preparatory to a test. Except when the solution was being transferred to the upper bulb, the system was kept closed. The internal pressure was the same as the atmospheric pressure, and the passage between the ends of the viscometer was open. Even with these precautions there was some slight loss of water from the solutions as vapor condensed in the cooler parts of the tube above the thermostat bath. The amount of condensate varied from a trace to perhaps two drops when the more dilute solutions were heated to the higher temperatures. Because of this progressive loss of water, only five individual readings were taken to obtain an average value in such cases. For other solutions, ten readings were taken.

The thermostat could hold four viscometers, and it was frequently convenient to have several viscometers in operation at one time. The temperature was constant to $\pm 0.05^\circ$ below 60° C. Above 60° C. the constancy decreased, and at 90° to 100° C. was $\pm 0.1^\circ$.

The thermometers used were calibrated by the U. S. Bureau of Standards. One, used from 0° to 60° C., had scale divisions of 0.1°. The other, used from 60° to 100° C., had scale divisions of 0.5°.

The stop watches used were compared with an accurate pocket watch (which had been checked against a chronometer) and the necessary corrections applied to the average observed times.

CALIBRATION OF THE VISCOMETERS

Water was taken as the standard of reference, its absolute viscosity at 20° C. being 1.0050 centipoises (4) and its density 0.99824. Using boiled, distilled water, the viscometer constant of the No. 50 viscometer was determined with Equation 3.

$$v = kd \text{ or } v = ctd \quad (1)$$

$$k = ct \text{ or } c = k/t \quad (2)$$

$$c = v/dt \quad (3)$$

where v = absolute viscosity in centipoises at 20° C.
 k = kinematic viscosity in centistokes at 20° C.
 t = efflux time in seconds at 20° C.
 d = density of the liquid at 20° C.
 c = viscometer constant at 20° C.

Since the flow of water through the No. 100 viscometer was too rapid for accuracy, it was calibrated with a glycerol solution, the viscosity of which had been measured in the No. 50 viscometer, calculations being made with Equation 2. In a similar manner

the remaining viscometers were calibrated with more viscous glycerol solutions. The data are given in Table I.

In order to confirm the calibrations of the viscometers, they were recalibrated with solutions of sucrose and with American Petroleum Institute (A.P.I.) oil standards. The sucrose solutions were prepared with c.p. sucrose and distilled water. Their viscosities and densities as given by Bates (3) are

34.07% sucrose at 20° C.: $v = 4.098$ centipoises, $d = 1.14669$

65.87% sucrose at 20° C.: $v = 178.6$ centipoises, $d = 1.32174$

Data for the kinematic viscosities of the A.P.I. oil standards as supplied with the samples were

Alpha oil: kinematic viscosity = 66.44 centistokes at 100° F.

Beta oil: kinematic viscosity = 417.9 centistokes at 100° F.

The viscometers were calibrated at 20° C. with the sucrose solutions and at 100° F. with the oils. The latter data were then calculated to 20° C. in the manner described below. The recalibrations are shown in Tables II and III. The No. 400 viscometer was not calibrated with sucrose solution because even a saturated solution was not viscous enough to give a satisfactory reading.

The value of the viscometer constant, c , decreases as the temperature is increased, the amount of change depending upon the capacity of the viscometer, the expansion of the liquid, and the radius of the lower bulb of the viscometer; the viscometer being filled at 20° C. and then used at a different temperature. The temperature correction for c was calculated by the method of Cannon and Fenske (8):

Av. height of liquid in viscometer, cm.	10.0
Inside radius of lower bulb, cm.	1.55
Vol. of liquid, ml.	3.5
Coefficient of expansion of the liquid (use 50% glycerol) from 20° to 100° C.	0.04545

Therefore, the value of c is decreased or increased by a factor of 0.000263 for each increase or decrease of 10° from the calibration and filling temperature of 20° C.

TABLE II. CALIBRATION OF VISCOMETERS WITH SUCROSE SOLUTIONS AT 20° C.

Sucrose Concn., %	Vis-cometer No.	Time, Sec.	Solution Density	Absolute Viscosity	Vis-cometer Constant
34.07	50	745.0	1.14669	4.0975	0.00480
34.07	100	237.5	1.14669	4.0975	0.01505
65.87	200	1391.9	1.32174	178.6	0.0971
65.87	300	522.4	1.32174	178.6	0.2587

TABLE III. CALIBRATION OF VISCOMETERS WITH A.P.I. OIL STANDARDS AT 100° F.

Oil	Viscometer No.	Time, Sec.	Kinematic Viscosity	Viscometer Constant	
				100° F.	20° C.
Alpha	50	13627	65.64	0.00482	0.00482
Alpha	100	4341	65.64	0.01512	0.01513
Alpha	200	676.4	65.64	0.0970	0.0971
Beta	200	4339	417.9	0.0963	0.0964
Alpha	300	252.9	65.64	0.2595	0.2597
Alpha	300	1617	417.9	0.2584	0.2585
Beta	400	336.7	417.9	1.241	1.242

TABLE IV. CORRECTION OF EFFLUX TIME WITH CHANGE IN TEMPERATURE

Viscometer No.	Correction for 0.1° C., Sec./1000 Sec. of Observed Time
50	3.0
100	4.0
200	5.6
300	6.4
400	9.8

TABLE V. VISCOSITY OF AQUEOUS GLYCEROL SOLUTIONS

Glycerol, % Wt.	Temperature, ° C.										
	0	10	20	30	40	50	60	70	80	90	100
	Viscosity, Centipoises										
0 ^a	1.792	1.308	1.005	0.8007	0.6560	0.5494	0.4688	0.4061	0.3565	0.3165	0.2838
10	2.44	1.74	1.31	1.03	0.826	0.680	0.575	0.500
20	3.44	2.41	1.76	1.35	1.07	0.879	0.731	0.635
30	5.14	3.49	2.50	1.87	1.46	1.16	0.956	0.816	0.690
40	8.25	5.37	3.72	2.72	2.07	1.62	1.30	1.09	0.918	0.763	0.668
50	14.6	9.01	6.00	4.21	3.10	2.37	1.86	1.53	1.25	1.05	0.910
60	29.9	17.4	10.8	7.19	5.08	3.76	2.85	2.29	1.84	1.52	1.28
65	45.7	25.3	15.2	9.85	6.80	4.89	3.66	2.91	2.28	1.86	1.55
67	55.5	29.9	17.7	11.3	7.73	5.50	4.09	3.23	2.50	2.03	1.68
70	76.0	38.8	22.5	14.1	9.40	6.61	4.86	3.78	2.90	2.34	1.93
75	132	65.2	35.5	21.2	13.6	9.25	6.61	5.01	3.80	3.00	2.43
80	255	116	60.1	33.9	20.8	13.6	9.42	6.94	5.13	4.03	3.18
85	540	223	109	58.0	33.5	21.2	14.2	10.0	7.28	5.52	4.24
90	1310	498	219	109	60.0	35.5	22.5	15.5	11.0	7.93	6.00
91	1590	592	259	126	68.1	39.8	25.1	17.1	11.9	8.62	6.40
92	1950	729	310	147	78.3	44.8	28.0	19.0	13.1	9.46	6.82
93	2400	860	367	172	89.0	51.5	31.6	21.2	14.4	10.3	7.54
94	2930	1040	437	202	105	58.4	35.4	23.6	15.8	11.2	8.19
95	3690	1270	523	237	121	67.0	39.9	26.4	17.5	12.4	9.08
96	4600	1585	624	281	142	77.8	45.4	29.7	19.6	13.6	10.1
97	5770	1950	765	340	166	88.9	51.9	33.6	21.9	15.1	10.9
98	7370	2460	939	409	195	104	59.8	38.5	24.8	17.0	12.2
99	9420	3090	1150	500	235	122	69.1	43.6	27.8	19.0	13.2
100	12070	3900	1412	612	284	142	81.3	50.6	31.9	21.3	14.8

^a Viscosity of water taken from Bingham and Jackson (4).

TABLE VI. COMPARISON OF VISCOSITY DATA

Glycerol, %	Viscosity, Centipoises						Archbutt and Deeley (2)		
	Authors		Sheely (16)						
	20° C.	30° C.	20° C.	% diff.	30° C.	% diff.	20° C.	% diff.	
0	1.005	0.8007	1.005	0.00	0.800	0.088	1.005	0.00	
10	1.31	1.03	1.311	0.076	1.024	-0.058	1.328	1.37	
20	1.76	1.35	1.769	0.51	1.360	0.74	1.798	2.16	
30	2.50	1.87	2.501	0.04	1.876	0.32	2.529	1.16	
40	3.72	2.72	3.750	0.81	2.731	0.40	3.718	-0.05	
50	6.00	4.21	6.050	0.83	4.247	0.88	5.994	-0.10	
60	10.8	7.19	10.96	1.48	7.312	1.70	10.791	-0.08	
65	15.2	9.85	15.54	2.24	10.02	1.73	15.26	0.39	
70	22.5	14.1	22.94	1.95	14.32	1.56	22.63	0.58	
75	35.5	21.2	36.46	2.71	21.68	2.26	36.63	3.18	
80	60.1	33.9	62.00	3.16	34.92	3.01	61.27	1.94	
85	109	58.0	112.9	3.58	60.05	3.54	112.1	2.84	
90	219	109	234.6	7.12	115.3	5.77	233.1	6.45	
91	259	127	278.4	7.50	134.4	5.82	275.9	6.54	
92	310	147	328.4	5.93	156.5	6.46	326.2	5.23	
93	367	172	387.7	5.65	182.8	6.28	386.6	5.35	
94	437	202	457.7	4.74	212.0	4.95	457.8	4.76	
95	523	237	545	4.40	248.8	4.98	548.0	4.79	
96	624	281	661	5.93	296.7	5.59	659.3	5.67	
97	765	340	805	5.23	354.0	4.12	804.1	5.11	
98	939	409	974	3.73	424.0	3.67	977.4	6.22	
99	1150	500	1197	4.09	511.0	2.20	
100	1412	612	1499	6.32	624.0	1.96	

MEASUREMENT OF VISCOSITY

When measuring the viscosities of the glycerol solutions, the viscometer to be used was selected so that the efflux time would be at least 200 seconds. By this means the correction to be applied for the loss of kinetic energy was kept so low that it could be omitted. The calculation of results was thereby simplified and made as described in ASTM D 445-46T (1), and also by Ruh, Walker, and Dean (15), using Equation 1, given above. The viscosities of the most dilute solutions at the higher temperatures were too low to be measured accurately.

The densities of glycerol solutions at 20° C. were calculated from their specific gravities at 20/20° C. and the density of water at 20° C. Densities of the glycerol solutions at other than 20° C. were calculated with the aid of the thermal expansion data of Gerlach as given by Lawrie (13).

When adjusting the thermostat to obtain a given temperature, it was not practical to set it precisely at the desired temperature, due to the design of the regulator. Divergence from desired temperature did not exceed 0.1°. The observed times of efflux were adjusted to correspond to the desired even temperature. By plotting observed time for a given solution on a logarithmic scale against temperature on an arithmetic scale it was found that the resulting curve for each viscometer was nearly a straight line over

temperature intervals of 10° C. Therefore, interpolated corrections for temperature changes of 0.1° or less would be correct within the limits of experimental accuracy. A number of corrections were calculated for each of the viscometers. Average values were then used in making all corrections. These average values are given in Table IV. The correction is added with decreased temperature, subtracted with increased temperature.

The viscosities of solutions of even per cent concentration were calculated from the experimental data by interpolation, assuming logarithmic increase of viscosity with concentration. The rate of change is actually greater than a logarithmic function. Therefore, if interpolation is to be made over more than about 1% of glycerol concentration, it is preferable to plot accurately the known points on semilogarithmic coordinate paper which can be read to three significant figures and read the viscosities from smoothly drawn curves. This latter procedure was used to obtain the viscosities of glycerol

solutions of 65, 70, 91, and 94% concentrations. Similarly, the viscosities of 10% glycerol at 50°, 60°, and 70° C., of 20% glycerol at 70° C., of 30% glycerol at 80° C., and 40% glycerol at 90° and 100° C. were obtained by extrapolation of the curves. Complete data are given in Table V.

The viscosity values obtained in this work are believed to be accurate to at least ±1% at temperatures of 60° C. and lower. Above 60° C. the accuracy of temperature control and temperature recording was less satisfactory. The evaporation of water from the solutions introduced an error that increased with the temperature. Therefore, the accuracy of the data for the higher temperatures varies from ±1.5 to ±3.0%, the greater errors being with the most dilute solutions at the highest temperatures.

A comparison of the viscosity values for 20° and 30° C. with those of Sheely (16) for the same temperatures and concentrations (see Table VI) shows the latter data to be consistently higher. The differences range from a few tenths of a per cent in the dilute solutions to a maximum of 7.5%. Although there are minor variations, there is nevertheless a consistent difference between the two sets of data which is probably to be accounted for by the different types of viscometers used and the attendant corrections and calculations.

The viscosity data of Archbutt and Deeley (2) also are in general higher than those reported in this paper, the greater differences being found with the more concentrated solutions. As with Sheely's data, the type of viscometer used may explain the major differences. Interpolated values to correspond with the glycerol concentrations used in this paper are shown in Table VI.

Compared to the present data, the viscosities of glycerol solutions at 1° C. as determined by Darke and Lewis (10) are much too low. The differences are greater at the higher glycerol concentrations, being 1.3% for 10% glycerol, and reaching a maximum of 37.8% for 88% glycerol. Since Darke and Lewis published their data in conjunction with data of Herz and Wegner, it is assumed that the specific gravity tables of the latter authors were used. Glycerol concentrations were recalculated with the Bosart and Snoddy specific gravity tables when comparing the Darke and Lewis data with those of the present authors.

The viscosity data of Herz and Wegner (12), with the glycerol concentrations recalculated from the Bosart and Snoddy specific gravity tables, are in fair agreement with the present data at the lower solution concentrations and lower temperatures but otherwise show considerable irregularity, for the most part being too low.

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Limits of Flammability of Paraffin Hydrocarbons in Air

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A FLAMMABLE gaseous mixture is a mixture of gases through which flame can propagate. The flame is initiated in the gaseous mixture by means of an external source that delivers energy to the system, composed of the gaseous mixture and its surroundings. A flammable gaseous mixture may apparently or actually be rendered nonflammable by a change in one or more of the following items associated with the mixture or its surroundings:

- (a) Temperature
- (b) Pressure
- (c) Ratio of combustible to oxygen
- (d) Ratio of inert or other foreign gas to oxygen
- (e) Characteristics of the ignition source
- (f) Geometry and size of the confining vessel
- (g) Physical state and surroundings of the gaseous mixture

Although a suitable change in one or more of the above items may render a flammable mixture nonflammable, the converse is not necessarily true.

As in general only gaseous mixtures composed of one combustible and air are considered in this investigation, item *d* is constant and will not be considered further. Furthermore, if all the above items are kept constant except *c*, which is varied by adding air, the combustible content of the flammable mixture eventually becomes too low to propagate flame. If then a number of similar tests are made in which *e*, *f*, and *g* are also varied (although the gaseous mixture should remain homogeneous and quiescent

during the period of application of the ignition source as well as the subsequent period of observation), the lowest concentration of combustible in air that is capable of propagating flame through a homogeneous quiescent mixture of the combustible and air being tested may be taken to be:

$$L = 1/2 [C_{e_1} + C_{n_0}] \quad (1)$$

L = lower limit of flammability at a specified temperature and pressure
 C_{e_1} = least concentration of combustible in air which is still flammable
 C_{n_0} = greatest concentration of combustible in air which is non-flammable

where $C_{n_0} < C_{e_1}$ and $|C_{e_1} - C_{n_0}|$ is of the order of the limit of accuracy of the measuring apparatus. Thus L , the lower limit of flammability of a combustible in air, is a quantity that depends only on the temperature, pressure, and combustible used in the gaseous mixture.

A similar definition may be given for U , the upper limit of flammability in air, except that in this case a flammable mixture is rendered nonflammable by the addition of combustible.

STATEMENT OF THE PROBLEM

According to the definition of L , at a particular temperature and pressure in an "appropriate" apparatus, a concentration of