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Viscosity–Temperature Relations

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Perhaps the most frequently suggested relationship for expressing the variation of the viscosity of liquids with temperature is the general equation

$$\eta = KT^{-n} e^{(C/T + DT)} \qquad (1)$$

which is derived from thermodynamic[2] and kinetic[3] considerations. Since an equation involving four constants is rather cumbersome; most investigators have used the simplified form of equation 1 in which the constants n and D are each equal to zero

$$\eta = Ke^{C/T} \qquad (2)$$

Andrade[4] has developed a modification of equation 2, which correlates with experimental data more acceptably than does equation 2, *i. e.*

$$\eta = Kd^{1/3} e^{cd/T} \qquad (3)$$

Kinematic Viscosity Equation

If the effect of temperature on the frequency of vibration of the liquid molecule is ignored and it is assumed that a transfer of momentum involves molecules which possess a mutual potential energy ($-E$), the viscosity will be proportional to the number of molecules possessing this energy.[4] The ratio of the number of molecules in a given mass which have energy $-E$ at temperature T to the number which have the same energy at temperature T_0 is represented by the Boltzmann distribution formula. The ratio of the number of molecules in unit volume at temperatures T and T_0 is the ratio of the densities. Thus the viscosity–temperature relationship may be expressed as

$$\eta_T/\eta_{T_0} = d_T/d_{T_0}e^{E/K\,(1/T + 1/T_0)} \text{ or } \eta_T = bd_Te^{a/T} \qquad (4)$$

Equation 4 may be written more conveniently in the linear logarithmic form

$$\log_{10}(\eta_T/d_T) = A/T - B \qquad (4a)$$

in which η_T is viscosity in millipoises; d_T is density in grams per cc.; T is absolute temperature in degrees Kelvin; A is $0.4343a$; and B is $-\log_{10}b$.

Correlation with Data

Equation 4a has been fitted to the viscosity–temperature data of forty-seven organic liquids as shown in Table I. Mitsukuri and Tonomura[5] provide the viscosities at low temperatures for the alcohols. Viscosities and densities of the hexadecyl alcohols and acetates are those of Bingham and Stephens.[6] Other viscosity data are from Thorpe and Rodger[7] and Bingham and Spooner.[8] Liquid densities are from Sidney Young[9] and the "International Critical Tables."[10]

Andrade[4] has published a comparison between the observed viscosities of a number of liquids and the viscosities calculated by means of equation 3. From a comparison of Table I with Andrade's results, it may be seen that equation 4a correlates with the observed viscosities at least as satisfactorily as equation 3 and is considerably easier to use.

Table I summarizes the application of equation 4a to forty-seven organic liquids, giving for each compound the constants A and B (for viscosity in millipoises and density in grams per cc.), the temperature range covered, the viscosity range expressed as the ratio of the largest and smallest absolute viscosities, and the percentage error in the calculated viscosities at a number of different temperatures. The constants A and B were obtained by plotting the logarithm of the observed kinematic viscosity (η/d) against the reciprocal of the absolute temperature and fitting graphically what appeared to be the best straight line over the range of the data. For an accurate fit of equation 4a, a plot of the observed $\log_{10} \eta/d$ against the reciprocal of the absolute temperature should represent a straight line. Any regular curvature in such a plot is indicated by the progression of the percentage errors. For example, *n*-undecane, *m*-xylene and iodobenzene are slightly convex toward the reciprocal-temperature axis.

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(1) Sterling Fellow in Chemical Engineering.

(2) Guzman, *Anales soc. españ. fís. quím.*, **11**, 353 (1913); Drucker, *Z. physik. Chem.*, **92**, 287 (1918); Raman, *Nature*, **111**, 532 (1923); Dunn, *Trans. Faraday Soc.*, **22**, 401 (1926).

(3) Kendall and Monroe, THIS JOURNAL, **39**, 1799 (1917); Iyer, *Ind. J. Phys.*, **5**, 14, 371 (1930); Andrade, *Nature*, **125**, 489 (1931); Lederer, *Kolloid Beiheft*, **34**, 270 (1931); Sheppard, *J. Rheol.*, **1**, 349 (1931).

(4) Andrade, *Phil. Mag.*, **17**, 698 (1934).

(5) Mitsukuri and Tonomura, *Proc. Imp. Acad. Japan*, **3**, 155 (1927); **5**, 23 (1929).

(6) Bingham and Stephens, *Physics*, **4**, 207 (1933).

(7) Thorpe and Rodger, *Trans. Roy. Soc.* (London), **A185**, 397 (1895); **A189**, 71 (1897).

(8) Bingham and Spooner, *Physics*, **4**, 387 (1933)

(9) Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1909–10).

(10) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, 1926, p. 27.

TABLE I

Compound	A	B	Range		Per cent. error in calcd. η at temp., °C.						
			Temp., °C.	Rel. vis.	0	20	40	60	80	100	120
n-Pentane	291.5	0.4246	0–30	1.34	0.0	0.0					
Isopentane	291.3	.4359	–30	1.34	.0	+ .5					
n-Hexane	328	.4321	–60	1.79	.0	.0	0.0	0.0			
Isohexane	328	.4564	–60	1.80		.0					
Diisopropyl	392	.5736	–30	1.45	.0	.0					
n-Heptane	365.4	.4669	–80	2.24	− .1	− .1	− .2	.0	+0.3		
Isoheptane	364	.4957	–80	2.21	.0	− .3					
n-Octane	414.4	.5283	–122	3.45	− .2	+ .1	− .2	.1	− .1	0.0	+0.2
n-Nonane	465	.5891	–100	3.24	−1.5	+ .5	+1.0	+ .6	− .6	−0.5	
n-Decane	510	.6422	–100	3.57	−2.2	+ .7	+1.5	+1.1	− .1	−1.1	
n-Undecane	559	.7028	–100	3.96	−3.0	+1.5	+1.9	+1.6	+ .4	−2.0	
Cyclohexane	621	1.0231	17–35	1.37		+1.3					
Benzene	502	.8403	0–60	2.29	−0.8	+0.7	+0.7	−1.7			
Toluene	410	.5657	–100	2.86	−1.0	+ .4	+ .4	+0.4	− .1	−0.4	
m-Xylene	401	.5127	–120	3.21	−1.0	+ .2	+ .8	+ .7	+ .1	− .1	− .7
Chloroform	332	.5535	–60	1.79	+0.1	− .1	.0	0.0			
Carbon tetrachloride	510	.9505	–60	2.31	+ .2	+1.3	+ .3	−1.2			
Ethylene chloride	454	.7231	–80	2.64	−1.0	+0.6	+ .1	+0.2	.0		
Tetrachloroethylene	371	.5211	–120	2.97	−0.6	+ .2	+ .4	− .1	− .1	.0	+ .1
Fluorobenzene	404	.6307	10–80	2.09		− .4	− .7	− .2	+ .8		
Chlorobenzene	429	.6039	0–120	3.45	− .7	+ .3	+ .4	+ .3	+ .4	− .1	+ .1
Bromobenzene	473	.7250	–120	4.44	−3.1	+ .9	+ .7	+1.8	+ .5	−1.6	−2.3
Iodobenzene	528	.8329	–140	5.04	−2.5	− .6	+2.1	+2.1	− .7	−1.3	−2.2
Acetone	305	.4293	–40	1.47	+0.1	.0	+0.2				
Methyl ethyl ketone	369	.5383	–76	2.18	− .3	+ .2	+ .1	0.0			
Ethyl ether	287.6	.4637	–30	1.43	+ .2	.0					
Methyl alcohol	498	.8255	–60	2.31	− .2	+ .1	− .3	+ .7			
Ethyl alcohol	678	1.1362	–60	3.00	+1.0	− .7	− .5	+1.2			
	653	1.0519	−98 to +61	75.7	Max. error		−3.0	+3.4			
n-Propyl alcohol	909	1.6520	0–80	6.19	+0.1	+0.2	0.0	−0.3	.0		
	882	1.5704	−60 to +96	67.0	Max. error		−2.7	+2.9			
Isopropyl alcohol	1096	2.2589	0–80	8.75	−0.4	0.0	+1.0	+0.5	−1.5		
n-Butyl alcohol	969	1.7459	–100	9.83	− .4	.0	+0.3	.0	+0.2	−0.3	
Isobutyl alcohol	1155	2.2524	–100	15.2	−2.1	+ .4	+1.7	+1.6	+ .7	−2.2	
2-Heptylnonanol	1715	3.1836	20–100	18.8		−4.0	+2.3	+5.0	+1.8	−6.5	
2-Ethyltetradecanol	1619	2.9038	20–100	16.6		−7.5	+3.0	+5.0	+1.6	−6.3	
Methyl formate	311	0.5073	0–30	1.36	−0.1	+0.2					
Ethyl formate	349	.5510	–40	1.54	.0	− .1	−0.1				
Propyl formate	398	.6010	–80	2.39	.0	.0	.0	0.0	−0.2		
Methyl acetate	344	.5617	–40	1.53	− .1	.0	.0				
Ethyl acetate	386	.6176	–60	1.95	− .2	+ .2	+ .1	− .4			
n-Propyl acetate	433	.6600	–97	2.95	− .7	+ .3	+ .4	+ .1	− .2	+0.1	
Methyl propionate	374	.5777	–60	1.91	− .2	+ .3	+ .1	− .2			
Ethyl propionate	406	.6072	–80	2.42	− .2	+ .1	+ .3	− .1	− .1		
Methyl *n*-butyrate	420	.6250	–100	2.97	− .9	+ .3	+ .6	+ .2	.0	− .1	
Methyl isobutyrate	400	.5978	–80	2.40	+ .3	+ .3	+ .1	− .1	.0		
2-Heptyl nonyl acetate	1044	1.6313	10–100	8.48		+ .4	+7.2	+5.9	+ .9	−6.4	
2-Ethyl tetradecyl acetate	1099	1.4972	0–100	10.9	−8.3	+1.8	+7.2	+6.0	+1.0	−6.5	
Acetic acid	524	0.7274	20–100	2.65		−1.0	+0.7	+0.5	+0.1	−0.5	

Limitations of Equations

Equation 4a is based on the assumption of constant pressure and since the constants A and B of Table I are based on data at substantially atmospheric pressure, they are not valid for calculating viscosities at high pressures.

Inspection of the precentage errors given in Table I shows that the error in the viscosity calculated by means of equation 4a (as well as equations 2 and 3) increases with the higher members of each homologous series. This observation indicates that the increase in the error is correlated either with the increase in molecular weight and complexity of the molecule, or with increase in the absolute viscosity. That the error is probably related to the magnitude of the molecular weight rather than the viscosity is indicated by inspection of the results with ethyl, *n*-propyl, and the hexadecyl alcohols. The data on ethyl alcohol below 0°, and *n*-propyl alcohol below 22° cover viscosities similar in range and magnitude to those of the hexadecyl alcohols between 20 and 100°. The errors in the application of equation 4a to these data on ethyl and *n*-propyl alcohols show no general regularity, whereas the errors with the hexadecyl alcohols show a pronounced curvature in the plot of log viscosity against reciprocal temperature.

Application of equations 2, 3, and 4a to materials of much greater molecular weight, such as petroleum oils, is wholly unsatisfactory except over short ranges of temperature.

Summary

1. The kinematic viscosity–temperature equation, $\log_{10} \eta/d = A/T - B$, has been fitted to the data on forty-seven organic liquids with errors in most cases of less then 1%. The constants A and B and the errors at various temperatures for each compound are reported.

2. This equation appears to be at least as accurate as the equation of Andrade[4] and is more convenient to use.

3. The error increases with increase in molecular weight rather than with increase in viscosity.

4. The equation is not suited for materials of high molecular weight such as petroleum oils.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

Mixing Device for Thermochemical Calorimeters[1]

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In thermochemistry, as precision has increased, it has become more and more common to have material which is to be added to the calorimeter liquid immersed in that liquid (but not touching it) before the beginning of the calorimetric observations, the container of the material being opened at the proper time. This ensures that the temperature of the material shall be most accurately equal to that of the calorimeter, and that every bit of it shall be added to the solution. Where the added material is liquid, cells closed by rubber stoppers and similar arrangements in great variety have been used. Fairhall and Lamb (unpublished paper) used a glass cell to which was cemented by paraffin a thin glass cover which was smashed by a glass rod. When the material was powder, thin-walled glass bulbs have been used, and Frederick Barry[2] showed ingenuity and skill in making the bulbs so that when broken they should fly to pieces, leaving no cups to hold small masses of powder out of the circulating liquid.

In our case the liquid was hydrofluoric acid, so glass was out of the question. The chemical conditions made it imperative to pour the loose powder very quickly into the liquid and to do this well below the surface.

This was accomplished by means of a Redmanol[3] boat with a deck of sheet material sealed on with wax. To liberate the powder the deck was rolled up by pulling a platinum wire attached to its far end. The boat was vertical in the calorimeter, and the pull was upward against the calorimeter cover. The cover can be braced by a rod, as of hard rubber, which may be removed if desired, immediately after the pull. In our case the cover was clamped to the calorimeter whose weight, 1.5 kg., was enough to withstand the necessary pull. In placing the boat the wire must of course be thrust up through the cover. Since several successive charges of material were used on one calorimeter filling, a small lid was used over a hole in the cover, through which the boat was inserted. The wire was easily pushed through this before it was put on the calorimeter. The wire, with the wax seal, can support the weight of the boat before the pull, but it was thought best to do everything possible toward freeing the wax from mechanical strain, hence each boat was screwed to its own lid, which held it firmly in exact position and made it easy to handle.

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[1] Original manuscript received March 9, 1936.

[2] Frederick Barry, THIS JOURNAL, **44**, 1917 (1922).

[3] Probably practically the same as Bakelite.