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THE VISCOSITIES OF GLYCEROL TRINITRATE AND CERTAIN RELATED GLYCOL NITRIC ESTERS[1]

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Introduction

During a general study of glycerol trinitrate and certain glycol dinitrates need arose for data on the viscosities of these substances. A search of the literature revealed only a small amount of data and the values which were reported covered a very limited temperature range. It was then necessary to undertake the task of determining these viscosities and determinations were made at five-degree intervals over the temperature range 10 to 60°, inclusive, on highly purified samples of the following esters: propylene glycol dinitrate, ethylene glycol dinitrate, trimethylene glycol dinitrate, diethylene glycol dinitrate and glycerol trinitrate.

Naoúm[2] tabulates viscosities at 20° for four of the esters included in the present investigation. The data are given in seconds required to run 5 cc. out of a 10-cc. pipet, as follows: propylene glycol dinitrate, 5.0 seconds; ethylene glycol dinitrate, 5.0 seconds; trimethylene glycol dinitrate, 5.5 seconds, and glycerol trinitrate, 12.5 seconds. A calibration of the pipet with water required 4.5 seconds for the time of flow. The results indicate that the viscosities of the esters are only slightly greater than the viscosity of water, with the exception of glycerol trinitrate, which appears to be about 2.5 times as viscous. More reliable values were determined by Rinkenbach[3] for glycerol trinitrate and diethylene glycol dinitrate between 15 and 27°. In an earlier communication[4] he gives values for the viscosities of ethylene glycol dinitrate and glycerol trinitrate at 23.6°. These values are included for comparative purposes in the tables of viscosities for the present work.

Materials.—The nitric esters were prepared from the corresponding glycols by nitration with a mixture of nitric and sulfuric acids as described by Crater.[5] After neutralization, washing and thorough drying, determinations of the specific gravity and nitrogen content were made for each compound. The results given in Table I indicate compounds of a high degree of purity.

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[1] Presented before the Division of Inorganic and Physical Chemistry at the 76th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 9 to 13, 1929.

[2] Naoúm, "Nitroglycerin und Nitroglycerin Sprengstoffe," Julius Springer, Berlin, **1924**, p. 234. Also Lawrie, "Glycerol and the Glycols," The Chemical Catalog Company, Inc., New York, **1928**, p. 340.

[3] Rinkenbach, *Ind. Eng. Chem.*, 19, 925 (1927).

[4] Rinkenbach, *ibid.*, **18**, 1195 (1926).

[5] Crater, *Ind. Eng. Chem.*, **21**, 674 (1929).

TABLE I

SPECIFIC GRAVITY AND NITROGEN CONTENT OF ESTERS

Material	Formula	Specific gravity 15°/15° Found	Specific gravity 15°/15° Literature	Nitrogen, % Found	Nitrogen, % Calcd.
Propylene glycol dinitrate	$C_3H_6(NO_3)_2$	1.3939	1.368 (20°)[a]	16.85	16.87
Ethylene glycol dinitrate	$C_2H_4(NO_3)_2$	1.4956	1.4963[a]	18.31	18.42
Trimethylene glycol dinitrate	$C_3H_6(NO_3)_2$	1.4708	1.393 (20°)[a]	16.81	16.87
Diethylene glycol dinitrate	$C_4H_8O(NO_3)_2$	1.3901	1.3908[b]	14.24	14.29
Glycerol trinitrate	$C_3H_5(NO_3)_3$	1.5978	1.599[a]	18.42	18.51

[a] Naoúm. [b] Rinkenbach.

Method.—A Bingham and Jackson[6] viscometer was used to determine the viscosities of the esters. While this instrument is of the pipet type, it eliminates most of the objections so common to many of the pipet methods and is capable of giving absolute values for viscosity in c. g. s. units. A correction may be applied when necessary for the kinetic energy of the liquid measured, a correction which is too often overlooked or neglected in viscosity determinations.

The method consists essentially in measuring the time of flow of a given volume of liquid (about 4 cc.) at a specified temperature and under a known constant pressure, through a capillary tube which has been previously calibrated. Details of the instrument and method may be found by referring to the original paper.

Temperature was held automatically to ±0.1° of that desired by means of a large, well-stirred water thermostat controlled by a mercury regulator in conjunction with a relay and knife type lagless heater. Pressure was supplied from a tank filled to any desired pressure directly from the compressed air line and was measured by an open-end mercury manometer. Corrections were made to reduce the manometer readings to mm. of mercury at 0°. The tank was of sufficient size so that there was no perceptible drop in pressure resulting from the small quantity of air removed during a determination. Time measurements were made with a stop watch accurate to 0.2 second.

Calibration and Calculations.—The viscosities were calculated by the formula

$$\eta = Cpt - \frac{C'\rho}{t} \qquad (1)$$

where η is viscosity of the substance in c. g. s. units (poises), C and C' are constants of the individual instrument, t is time in seconds, p is pressure in grams per square centimeter and ρ is density of sample in grams per cubic centimeter.

The second term of the right-hand member of the above equation is the

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[6] Bingham and Jackson, Sci. Papers of the Bureau of Standards, No. 298 (1917).

kinetic energy correction, which is kept small by keeping t comparatively large. For this reason C' and ρ need not be known with great accuracy. The density of the ester used in this correction was calculated from the specific gravity values given in Table I.

The value of the constant C' was determined from the dimensions of the instrument as outlined by Bingham.[7] The value of the constant C was obtained by filling the viscometer with freshly distilled, dust-free water and determining the time of flow at 20°. The value used for the viscosity of water at 20° was 1.005 centipoises. Table II lists the constants of the two instruments used.

TABLE II

CONSTANTS OF VISCOMETERS

Viscometer	Capillary length, mm.	Radius, mm.	Volume of bulb, cc. (20°)	C	C'
Instrument 1	121.0	0.169	4.08	6.416×10^{-7}	0.01504
Instrument 2	120.0	0.244	4.02	2.851×10^{-6}	0.01494

Data.—In Tables III, IV, V, VI and VII are tabulated summaries of the viscosity data obtained. Four to six determinations were made at each temperature for each substance; the number in each case is given in the first column of each table. The temperature of the liquid at the time of the determination is given in Col. 2, the average of the values for the separate viscosity determinations is tabulated in Col. 3 and the maximum deviation of the individual determinations from the average viscosity is recorded in Col. 4. The fluidity in rhes (reciprocal viscosity in poises) was calculated and is given in Col. 5. The values for the viscosities of the esters at the corresponding temperatures as reported by previous investigators, Rinkenbach (indicated by **R**) and Naoúm (indicated by N),

TABLE III

VISCOSITIES OF PROPYLENE GLYCOL DINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported η, poises
6	10.0	0.0556	0.0001	18.0	
5	15.0	.0476	.0001	21.0	
4	20.0	.0407	.0002	24.6	0.0155 (N)
5	25.0	.0355	.0000	28.2	
4	30.0	.0314	.0000	31.9	
4	35.0	.0278	.0001	36.0	
4	40.0	.0246	.0000	40.7	
4	45.0	.0221	.0000	45.3	
4	50.0	.0203	.0000	49.3	
4	55.0	.0183	.0000	54.6	
4	60.0	.0171	.0000	58.5	

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[7] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Company, Inc., New York, **1922**, p. 295.

TABLE IV

VISCOSITIES OF ETHYLENE GLYCOL DINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported η, poises
4	10.0	0.0573	0.0002	17.5	
4	15.0	.0487	.0001	20.5	
4	20.0	.0421	.0001	23.8	
	23.6				0.0166 (N) 0.0363 (R)
4	25.0	.0369	.0001	27.1	
4	30.0	.0329	.0001	30.4	
4	35.0	.0292	.0000	34.3	
4	40.0	.0260	.0001	38.5	
4	45.0	.0236	.0001	42.5	
4	50.0	.0214	.0001	46.7	
4	55.0	.0195	.0001	51.3	
4	60.0	.0182	.0001	54.9	

TABLE V

VISCOSITIES OF TRIMETHYLENE GLYCOL DINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported η, poises
4	10.0	0.0851	0.0001	11.8	
4	15.0	.0706	.0002	14.2	
4	20.0	.0597	.0002	16.8	0.0179 (N)
4	25.0	.0501	.0002	20.0	
4	30.0	.0436	.0002	22.9	
4	35.0	.0388	.0002	25.8	
4	40.0	.0344	.0001	29.1	
4	45.0	.0310	.0001	32.3	
4	50.0	.0282	.0001	35.5	
4	55.0	.0258	.0001	38.8	
4	60.0	.0233	.0001	42.9	

TABLE VI

VISCOSITIES OF DIETHYLENEGLYCOL DINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported η, poises
4	10	0.119	0.000	8.40	
5	15	.0970	.0002	10.3	0.099 (R)
	17.5				.085 (R)
5	20.0	.0808	.0002	12.4	.078 (R)
	22.5				.073 (R)
4	25.0	.0673	.0001	14.9	.070 (R)
	27.0				.066 (R)
4	30.0	.0573	.0000	17.5	
4	35.0	.0496	.0001	20.1	
4	40.0	.0437	.0000	22.9	
5	45.0	.0383	.0001	26.1	
4	50.0	.0351	.0001	28.6	
4	55.0	.0306	.0001	32.7	
4	60.0	.0275	.0001	36.4	

TABLE VII

VISCOSITIES OF GLYCEROL TRINITRATE[*]

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported η, poises	
4	10	0.692	0.002	1.45		
4	15	.491	.000	2.04	0.511 (R)	
	17.5				.423 (R)	
4	20.0	.360	.000	2.78	.355 (R)	0.043 (N)
	22.5				.303 (R)	
	23.6				.288 (R)	
5	25.0	.270	.000	3.70	.283 (R)	
	27				.258 (R)	
4	30	.210	.000	4.76		
5	35	.168	.001	5.95		
4	40	.136	.000	7.35		
4	45	.112	.000	8.93		
6	50	.0938	.0002	10.7		
4	55	.0792	.0001	12.6		
4	60	.0680	.0000	14.7		

are given in the last column. Naoúm's values were converted to c. g. s units, for comparative purposes, by the equation

$$\eta = \eta_0 \frac{\rho\, t}{\rho_0\, t_0} \tag{2}$$

where η, ρ and t represent the viscosity, density and time of flow, respectively, for the unknown and η_0, ρ_0 and t_0 represent similar quantities for the standard substance (water). η_0 was taken as 0.0100 poises at 20° and ρ_0 was taken as 1.0.

Discussion of Results

Pressure measurements ranged from 10.04 to 163.23 cm. of mercury. The maximum error was probably not greater than 0.2 mm., which would result in an error of not more than 0.2% in the calculated viscosities even at the lower pressures. The times of flow varied from 490.6 to 45.6 seconds. Except in the case of ethylene glycol dinitrate, however, the times of flow were over 200 seconds. An error of 0.2 second in the time measurements would cause an error of not more than 0.1% in the calculated values, except with ethylene glycol dinitrate, where the error may reach 0.4%. By using an accurately controlled thermostat and waiting several minutes for temperature equilibrium of the sample to be reached after each change in the thermostat temperature, the error from this source was negligible. The total error in the final results is thought to be not greater than 0.25% for the individual determinations and this appears to be justified by an examination of the maxium deviation from the mean as given in the tables.

The average viscosities when plotted against temperatures give smooth curves, as shown in Fig. 1. Considering the fact that the plotted viscosities are the mean of four to six closely agreeing, duplicate values, the resulting curves should be in error by not more than 0.1%. This is within the limitations associated with the purification of the compounds studied.

It is interesting to note that the values are almost the same for propylene glycol dinitrate and ethylene glycol dinitrate, while the values for the two isomers, propylene glycol dinitrate and trimethylene glycol dinitrate differ considerably. Such a marked increase in the viscosity of glycerol trinitrate might not have been expected. Because of its large coefficient of viscosity with temperature in this temperature range, the upper part of the viscosity curve, Fig. 1, was cut off. The unplotted values, however, fall upon as smooth a curve as do the plotted values.

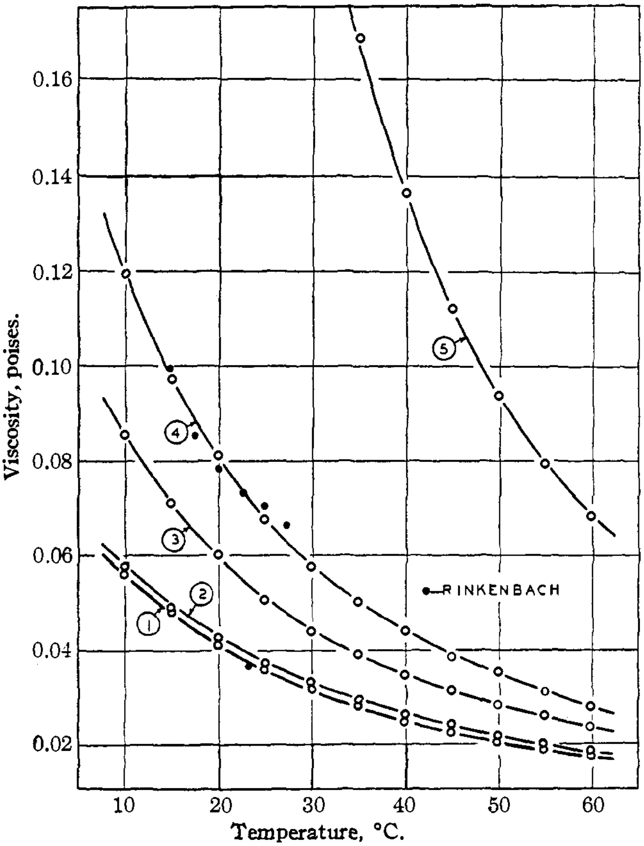

Fig. 1.—Viscosity–temperature curves of esters: 1, propylene glycol dinitrate; 2, ethylene glycol dinitrate; 3, trimethylene glycol dinitrate; 4, diethylene glycol dinitrate; 5, glycerol trinitrate.

The results herein reported agree quite satisfactorily with those reported by Rinkenbach. The values given by Naoúm are worthy of special attention. They are quite typical of many values reported in the literature obtained by arbitrary methods where the viscometer used is calibrated by a substance which differs greatly from the unknown substance, and no kinetic energy corrections are made for rapid rates of flow. While such results are usually intended only for relative values, they are often decidedly misleading. In the present case it would be assumed from the times of flow that glycerol trinitrate is approximately 2.5 times as viscous as water at 20°, or four times as viscous if the viscosity is calculated by Equation 2. The results obtained during this investigation show the ratio to be about 36 to 1.

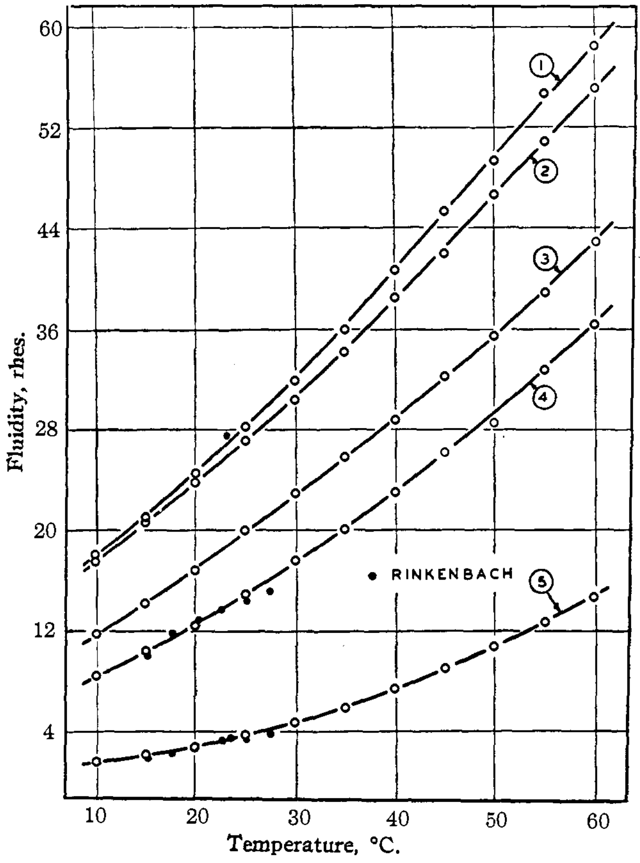

Fig. 2.—Fluidity–temperature curves of esters: 1, propylene glycol dinitrate; 2, ethylene glycol dinitrate; 3, trimethylene glycol dinitrate; 4, diethylene glycol dinitrate; 5, glycerol trinitrate.

Since fluidities (reciprocal viscosities) are more convenient to use in certain cases than viscosities, they are included in the tables and are plotted in Fig. 2. The resulting curves deviate somewhat from straight lines, a slight sag being noted in each case.

Plotting log viscosities against temperatures resulted in curves which deviated from straight lines to about the same extent as did the fluidity curves.

The fluidity curves, however, approach straight lines nearly enough so that they may be easily extended to temperatures beyond those actually determined, at least to those temperatures of importance in the commercial application of the esters.

Acknowledgment.—The author wishes to express his appreciation of the assistance of W. deC. Crater, who kindly prepared the samples used in this investigation.

Summary

The viscosities of highly purified samples of propylene glycol dinitrate, ethylene glycol dinitrate, trimethylene glycol dinitrate, diethylene glycol dinitrate and glycerol trinitrate were measured in c. g. s. units (poises) at five-degree intervals over the temperature range 10 to 60°, inclusive, and the results compared with previously reported values. The corresponding fluidities were calculated and reported.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON HYDANTOINS. XLIX. A NEW REARRANGEMENT LEADING TO THE FORMATION OF 4-AMINOHYDANTOIN DERIVATIVES

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In the course of an investigation dealing with the synthesis of 5,5-dialkylated hydantoins from ketones, the authors had occasion to study the applicability of a series of reactions suggested for the preparation of 1,5,5-trialkyl-hydantoins. Tiemann and Piest[2] first showed that the Strecker synthesis of α-amino acids could be modified to include N-alkylamino acids if an amine is used in place of ammonia in the reaction with aldehyde or ketone cyanhydrins. Biltz and Slotta[3] applied this phase of the Strecker–Tiemann reaction to the synthesis of 1-alkyl-hydantoins. We have now employed the same series of reactions described by Biltz and Slotta under modified experimental conditions for the preparation of 1,5,5-trialkyl-

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[1] Eli Lilly Company Graduate Scholar, 1928–1929.

[2] Tiemann and Piest, *Ber.*, **14**, 1982 (1881); **15**, 2028 (1882).

[3] Biltz and Slotta, *J. prakt. Chem.*, **113**, 233 (1926).