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Received for review November 6, 1964. Accepted May 1, 1965. 148th Meeting, ACS, Chicago, Ill., September 1964. This research was sponsored by the USAF Aero Propulsion Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, under Delivery Order **33(657)-63-37**, Task 304801. Reference to specific trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

Thermodynamics of Liquid Surfaces

Surface Tension of a Homologous Series of α,ω-Alkane Dinitrate Esters

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The influence of temperature and number of methylene groups on surface tension and density has been investigated in a study of the physical and chemical properties of nitrate esters. The esters investigated were the α,ω-dinitroxy compounds of ethane through decane. The densities and surface tensions were measured at several temperatures, and thermodynamic quantities such as temperature coefficient and surface energy have been calculated.

THE POSSIBLE utilization of the dinitrate esters as fuel additives, propellants, and explosives indicates the value of data concerning their thermodynamic properties. Because of the lack of experimental data, it has been necessary to resort to estimations to obtain certain information involving these dinitrate esters. This investigation was undertaken to study the influence of the nitrate ester groups and the number of carbon atoms in the molecule on the surface tension.

EXPERIMENTAL

Materials. The α,ω-dinitroxy alkanes from ethane through decane were prepared by nitration of the corresponding diols (2). The esters were isolated by means of a Hickman Still, redistilled (under vacuum) and run through a Beckman Megachrom (20% paraplex on 40- to 60-mesh chromosorb W). The purity of the compound was better than 99%. No change in surface tension was measured between the twice distilled samples and those additionally run through the megachrom. Also no changes in the IR spectrophotometer curves were detected. Any remaining impurity in the nitrate esters will most likely come from the starting material, the diols. To study the effect of impurity on surface tension, trimethylene glycol was gradually added to a triply distilled propane dinitrate ester sample, and the surface tensions were measured. An addition of 1% trimethylene glycol caused a change in surface tension of approximately −0.14 dyne per cm.

Procedure. The densities were measured in a 1-ml. pycnometer which was calibrated at 25° C. Correction was applied for the variation of the pycnometer volume with the temperature (7). Surface tensions were measured by the maximum bubble pressure method using a Cassel surface tensiometer from the National Instrument Co. (*3, 6*). The apparatus, which is simple in operation, consists essentially of a thick-walled glass nozzle mounted in vertical position and a screw-operated piston to apply pressure. The glass nozzle has a conical-shaped aperture in the top, with the smallest diameter in the center of the nozzle tip. The exterior surface of the nozzle is flat and polished. The maximum pressure inside the bubble formed at the orifice is recorded by a manometer. Figure 1

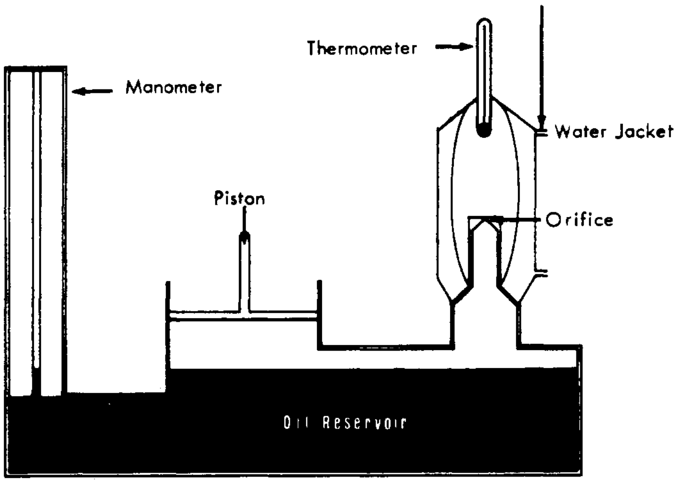

Figure 1. Schematic diagram of Cassel surface tensiometer

Table I. Densities and Molar Volumes of α, ω-Alkane Nitrate Series as a Function of Temperature and C-Atom Number

	Temperature, ° C.							
C-Number	−20	−10	±0	+10	+20	+25	+35	+45
2	1.545[a]	1.532	1.518	1.502	1.491	1.485	1.472	1.456
	98.4[b]	99.2	100.1	101.2	101.9	102.4	103.3	104.4
3	1.446	1.434	1.421	1.408	1.395	1.388	1.376	1.363
	114.8	115.8	116.8	117.9	119.1	119.6	120.7	121.8
4	1.374	1.363	1.350	1.338	1.326	1.320	1.309	1.298
	131.1	132.1	133.4	134.6	135.8	136.4	137.6	138.7
5	1.318	1.306	1.293	1.282	1.270	1.264	1.254	1.244
	147.3	148.6	150.1	151.4	152.8	153.6	154.8	156.1
6	1.269	1.259	1.249	1.238	1.228	1.223	1.214	1.204
	164.0	164.3	166.6	168.1	169.5	170.2	171.4	172.9
7	1.220	1.210	1.205	1.189	1.179	1.174	1.164	1.153
	182.1	183.6	184.4	186.8	188.4	189.2	190.8	192.7
8	1.182	1.171	1.165	1.155	1.144	1.139	1.130	1.120
	199.8	201.7	202.7	204.5	206.4	207.4	209.0	210.9
9	1.153	1.145	1.136	1.128	1.122	1.116	1.109	1.100
	217.0	218.5	220.3	221.8	223.0	224.2	225.6	227.5
10	1.136	1.125	1.116	1.105	1.096	1.090	1.081	1.071
	232.6	234.9	236.8	239.1	241.1	242.4	244.4	246.7

[a] Top figures denote density in grams per cc. [b] Bottom figures denote molar volumes in cc. per mole.

shows a schematic diagram of the apparatus. The temperature is controlled (±0.01° C.) by circulating a liquid from a thermostated bath through the heating jacket in which the nozzle is placed. Only a small sample is required (0.1 ml.) involving a small hydrostatic head. The rupture of the bubble is noted with a stethescope. The hydrostatic head and the density were neglected, the error was only of the order of 0.05%, which is less than the error in reading the bursting pressure on the manometer. The physical condition of the glass nozzle orifice was such that it was very difficult to measure precisely the minimum radius, which would be the effective radius, in determining the maximum bubble pressure. Therefore, the minimum capillary radius was calculated using Equation 1:

$$\gamma = \frac{grH_bD}{2} \tag{1}$$

where

g = 980.099 cm. per sec.^{2}
r = minimum radius of curvature of the bubble at its apex
H_b = height of the manometer fluid at bursting pressure
D = density of manometer fluid
$(g\,r)/2$ = C_n, constant for a given nozzle
$H_b\,D$ = P_b, bursting pressure

The nature of C_n will be constant for a given nozzle, provided the minimum radii of curvature of the bubbles formed at that nozzle are constant over the range of the surface tension investigated.

The nature of γ calculated from Equation 1 differed slightly from the true surface tension by a corrective term A. Equation 1 was corrected for this deviation by Equation 2:

$$\gamma = C_nP_b + A \tag{2}$$

The corrective term A was determined for a number of surface tensions using highly purified (gas chromatography and distillation) standard liquids. The standard liquids were:

Nitromethane	γ 20° C. = 36.8 dynes per cm.
Cyclohexane	γ 13° C. = 25.5 dynes per cm.
Benzenaldehyde	γ 20° C. = 40.0 dynes per cm.
Glycerin	γ 20° C. = 63.4 dynes per cm.

The surface tensions were taken from the literature. The precision of the method was ±0.1 dyne per cm. or better,

Table II. Surface Tension, $T(d\gamma/dT)$, Total Surface Energy, of α,ω-Alkane Nitrate Esters at Several Temperatures

Compound	Temp., ° C.	S. T., Dynes Per Cm.	T(d/dT), Erg Per Cm.^{2}	Total S. E.,[a] $E_s = -T$(d/dT), Erg Per Cm.^{2}	
1,2 -Dinitroxy ethane	0	49.1	. . .	. . .	
	45	46.7	. . .	. . .	
1,3 -Dinitroxy propane	0	48.8	−42.3	91.1	
	10	47.2	−43.8	91.1	91.0
	25	44.8	−46.2	91.0	
	35	43.1	−47.7	90.8	
	45	41.8	−49.3	91.1	
1,4 -Dinitroxy butane	0	46.2	−35.5	81.5	
	10	44.9	−37.7	82.8	82.1
	25	43.2	−38.7	82.0	
	35	41.9	−40.1	82.1	
	45	40.8	−41.4	82.3	
1,5 -Dinitroxy pentane	0	45.2	−31.4	76.7	
	10	45.0	−32.5	77.6	76.8
	25	42.3	−34.2	76.6	
	35	41.1	−35.4	76.5	
	45	39.9	−36.5	76.5	
1,6 -Dinitroxy hexane	0	43.0	−27.3	70.3	
	10	42.2	−28.3	70.5	70.4
	25	40.6	−29.8	70.4	
	35	39.7	−30.8	70.5	
	45	38.8	−31.5	70.5	
1,7 -Dinitroxy heptane	0	42.0	−25.9	67.9	
	10	41.1	−26.9	68.0	67.9
	25	39.7	−28.3	68.0	
	35	38.6	−29.2	67.9	
	45	37.7	−30.2	67.9	
1,8 -Dinitroxy octane	0	40.8	−23.7	64.6	
	10	39.5	−24.6	64.1	64.5
	25	38.7	−25.9	64.6	
	35	37.9	−26.8	64.7	
	45	37.0	−27.6	64.7	
1,9 -Dinitroxy nonane	0	40.4	−21.3	61.7	
	10	39.5	−22.0	61.6	61.6
	35	38.4	−23.2	61.6	
	35	37.5	−24.0	61.5	
	45	36.7	−24.8	61.5	
1,10-Dinitroxy decane	0	39.6	−20.4	60.1	
	10	39.0	−21.2	60.2	60.3
	25	37.9	−22.8	60.2	
	35	37.3	−23.1	60.4	
	45	36.6	−23.8	60.4	

[a] Total surface energy.

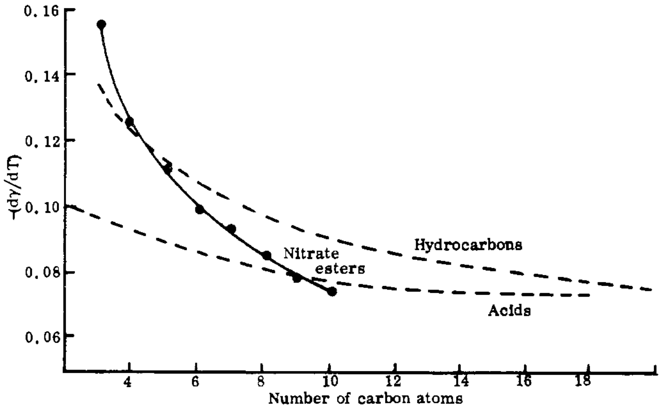

Figure 2. $-(d\gamma/dT)$ of α,ω-alkane nitrate esters as a function of the chain length compared to *n*-paraffins and carboxylic acids (*1*)

and the average deviation of the measured values was ± 0.15 dyne per cm.

The corrective term A varied somewhat with the bursting pressure, but this has been accounted for by calibration curves of known materials. A few compounds of known surface tensions which were measured with this apparatus over the range of temperature encountered in this investigation are listed as follows:

	Water				Benzene	
T, ° C.	20	30	40	50	25	40
γ, dynes per cm.	72.8	71.1	69.6	67.9	28.4	26.4
γ, dynes per cm. (*5*)	72.75	71.18	69.56	67.91	28.35	26.30

The surface tensions of the nitrate esters were measured at the following temperatures: 0°, 10°, 25°, 35°, and 45° C. The reported data are the averages of 15 measurements.

RESULTS

The densities and molar volumes of the α,ω-dinitroxy alkanes from ethane to decane as a function of temperature and carbon atom numbers (n) are listed in Table I. The surface thermodynamic quantities are given in Table II. These values were calculated from the surface tension and its temperature dependence (*4*). The surface energy remained constant within the experimental error over the measured temperature range, and it decreased with increasing chain length. The values of the surface tension alternate slightly as n changes between odd and even values. The alternation of the surface tension caused by the change of n decreased when the temperature increased from 0° to 45° C.

In Figure 2, the temperature coefficient ($-d\gamma/dT$, entropy) of the surface tension for each compound of the homologous series is given as a function of n. The slope $-d\gamma/dT$ for each compound was determined by the method of least squares. The temperature coefficient $-d\gamma/dT$ has high values for the shorter chain compounds and falls gradually as the n increases. The limiting value for the hydrocarbons and acids, which is about 0.07, (*1*), seems to be reached gradually also by this homologous series. In all three series (acids, hydrocarbons, and nitrate esters), the limiting value is practically reached when the chains are about 10 carbon atoms long.

ACKNOWLEDGMENT

This investigation was supported by the Bureau of Naval Weapons, Department of the Navy, through Task Assignment RMMP-22-153/286-1/R001-06-01. The authors wish to thank J. Tuono and B. Bartocha for their support during the course of the investigation and Robert Robb for performing some of the measurements.

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RECEIVED for review September 4, 1964. Accepted April 26, 1965.

Specific Conductance of Aqueous Sodium Chromate at 25° C.

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THE CONDUCTANCES of comparatively dilute aqueous solutions of sodium chromate have been measured by Watkins and Jones (*5*), Heydweiller (*3*, p. 251), and Clausen (*3*, p. 251).

This present work extends the conductance data to aqueous sodium chromate solutions of concentrations ranging from 5% to near saturation, and it was done in answer to questions on the instrumental control of concentration. Although this information was obtained on a weight basis, density measurements at 25.0° C. were made to permit values to be interpreted on a volume basis.

PREPARATION OF CHROMATE SOLUTIONS

The sodium chromate solutions were prepared by accurately weighing quantities of purposely analyzed, reagent grade $Na_2CrO_4 \cdot 4H_2O$, and deionized water, to give nine