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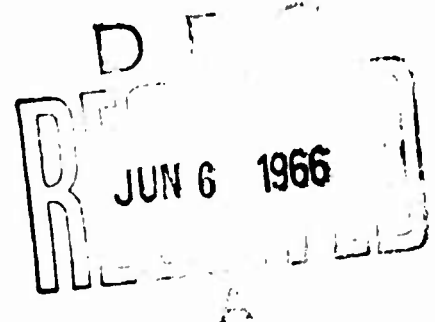
SOME THERMODYNAMIC PROPERTIES OF
CASTOR OIL VS TEMPERATURE AND
PRESSURE

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UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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SOME THERMODYNAMIC PROPERTIES OF
CASTOR OIL VS TEMPERATURE AND PRESSURE

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ABSTRACT: Specific volume, isothermal compressibility, and thermal expansion of Baker db-grade castor oil have been computed from an empirical equation fitted to data obtained by the differential transformer densitometer technique. Data is presented over a temperature range of 0-40°C and a pressure range of 1-1000 bars.

PHYSICS RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

NOLTR 66-68

14 April 1966

This report provides high precision data on some thermodynamic properties of a fluid which is widely used in filling Navy transducers, namely Baker db-grade castor oil. The measurements were requested by the Underwater Sound Reference Laboratory, Orlando, Florida and funded under Castor Oil Characteristics, Task No. NOL-855/USRL. The report will be of interest to anyone concerned with the use of pressure transmitting fluids in underwater sound transducers.

J. A. DARE
Captain, USN
Commander


T. F. JOHNSTON
By direction

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INTRODUCTION

Castor oil is used as a coupling liquid between transducers and the sea in various acoustic devices. Some specific volume data as a function of temperature at atmospheric pressure⁽¹⁾⁽²⁾, and some data as a function of pressure at 40°C⁽²⁾ are available, but a more complete reference for specific volume as a function of both temperature and pressure is not available. The wide use of castor oil in acoustic devices indicates that a more thorough knowledge of the thermodynamic properties of this liquid will be of value. When coupled with sound velocity data, this data can be used to determine acoustic impedance of castor oil as a function of temperature and pressure.

EQUIPMENT

The differential transformer densitometer used for specific volume measurements is described in detail in reference (3). However, since that report was written the calibration equation has been changed from a parabolic in temperature, T , to a cubic in T . The new calibration equation is discussed in the Theory section of this report.

The instrumentation required for monitoring and controlling the physical environment of the densitometer is described in reference (4). Since that report the pressure measuring instrumentation has been improved. A pressure sensitive manganin cell constitutes one arm of a Mueller resistance bridge. The output of the bridge is amplified by a photo-electric galvanometer and then monitored by a spotlight galvanometer. This equipment provides measurement of pressure to 1/4 of 1 psi over the pressure range of 14.7 to 15000 psia.

PROCEDURE

The bath surrounding the differential transformer densitometer was brought to the desired temperature and allowed to remain overnight. The system was then pumped to the desired pressure and allowed to stand for thirty minutes so that the densitometer and contents could return to bath temperature. The data for that particular temperature and pressure was then recorded. In this manner, measurements at a particular temperature were taken over the pressure range 14.7 - 14000 psia in 1000 psia increments. The procedure was repeated at 5°C intervals from 0 to 40°C.

THEORY

The differential transformer densitometer has been calibrated to relate specific volume to a length measurement. The secondary of the transformer is wound on a shaft which is spring loaded against a bellows that contains the test liquid. As pressure and/or temperature change(s), the liquid in the bellows expands or contracts, causing the secondary to move relative to the primary, and a change in output from the transformer occurs. An exact replica of the differential transformer is contained in a separate housing and its secondary is moved by means of a micrometer screw. The outputs of the transformers feed opposite arms of a diode bridge. Thus a movement of the bellows can be measured quite precisely by adjusting the micrometer screw for a null in the bridge detector.

Specific volume data for distilled water^{(5) (6) (7) (8) (9)} was used in the calibration of the densitometer. The relation between the specific volume of distilled water and the length measurement determined by the position of the bellows was represented by

$$v = f(T,P) + B_1 L \quad (1)$$

where v is the specific volume of distilled water in cm^3/g , $f(T,P)$ is a function of temperature and pressure, B_1 is a constant and L is the micrometer reading in inches. A series of measurements were made using distilled water in the densitometer, and values for L were recorded for temperatures and pressures within the specified range. The method of least squares was used to fit the observed data to equation (1). The best fit was found for

$$f(T,P) = B_0 + B_2 T + B_3 T^2 + B_4 T^3 + B_5 P \quad (2)$$

where T is the temperature in $^{\circ}\text{C}$, P is the pressure in bars, and B_0 , B_2 , B_3 , B_4 and B_5 are constants. Combining equations (1) and (2),

$$v = B_0 + B_1 L + B_2 T + B_3 T^2 + B_4 T^3 + B_5 P \quad (1')$$

Values for the B_n 's are given in Table I.

The total volume of the densitometer was then determined by the equation

$$V = B'_0 + B'_1 L + B'_2 T + B'_3 T^2 + B'_4 T^3 + B'_5 P \quad (3)$$

where $B'_0 = M B_0$, V is the total volume of the densitometer in cm^3 and M is the mass in grams of distilled water in the densitometer. The volume of the densitometer is thus known as a function of temperature, pressure, and micrometer reading.

Measurements were then taken for castor oil over the specified temperature and pressure range. The values for specific volume of castor oil were calculated using the equation

$$v_{\text{co}} = \frac{V}{M_{\text{co}}} \quad (4)$$

where v_{co} is the specific volume of castor oil and M_{co} is the mass of the castor oil contained in the densitometer. Rearranging terms,

$$\begin{aligned} v_{\text{co}} &= \frac{1}{M_{\text{co}}} (B'_0 + B'_1 L + B'_2 T + B'_3 T^2 + B'_4 T^3 + B'_5 P) \\ &= \frac{M}{M_{\text{co}}} (B_0 + B_1 L + B_2 T + B_3 T^2 + B_4 T^3 + B_5 P) \\ &= R (B_0 + B_1 L + B_2 T + B_3 T^2 + B_4 T^3 + B_5 P) \end{aligned} \quad (4')$$

where R is the ratio $\frac{M}{M_{\text{co}}}$.

Obtaining R by direct methods proved unsatisfactory, due to the relatively large mass of the densitometer (~ 500 g). A heavier, less precise balance had to be used, so that the difference between the full and empty weighings, i.e., the mass of the liquid in the densitometer, was not known to the desired precision. It was decided to obtain R by the pycnometer method. The specific volume of castor oil was determined by this method (10) and found to be

$$v_{co} = 1.04845 \pm 0.00003 \text{ cm}^3/\text{g}$$

at 29.12°C and one atmosphere pressure. The micrometer reading from the densitometer measurements at this temperature and pressure was put into equation (4') along with the above value of v_{co} , and R was determined to be

$$R = 1.04036 .$$

For the purpose of obtaining values of the specific volume of castor oil at even temperatures and pressures, and to smooth the data, the observed values were fitted to the equation

$$v = A_1 + A_2 T + A_3 T^2 + A_4 T^3 + A_5 P + A_6 P T + A_7 P T^2 + A_8 P T^3 \\ + A_9 P^2 + A_{10} P^2 T + A_{11} P^2 T^2 + A_{12} P^3 + A_{13} P^3 T \quad (5)$$

by the method of least squares, where the A_n 's are constants. Table II contains values for the A_n 's.

The thermal expansion is given by

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \quad (6)$$

and the isothermal compressibility is given by

$$K_T = - \frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T . \quad (7)$$

Thus thermal expansion and isothermal compressibility were obtained by differentiating equation (5).

DISCUSSION

The castor oil used in this experiment, Baker's db oil, is manufactured by the Baker Castor Oil Company, Bayonne, New Jersey. Their brochure⁽¹¹⁾ lists the chemical composition as being "approximately 85% Triglyceride of Ricinoleic Acid". The International Critical Tables⁽²⁾ lists data on a castor oil

consisting "largely (of) glycerides of ricinoleic and isoricinoleic acids, with small amount saturated acids". Del Grosso⁽¹⁾ lists data for "Baker castor oil" whose properties are close to those in the brochure mentioned above. The present data will be compared to these two references. It is to be emphasized however that such terms as "85%" and "largely" do not specify the composition of the castor oil to a close enough degree to expect agreement to within the precision of the measurements taken.

Specific volume, thermal expansion and isothermal compressibility data are given in Tables III, IV and V respectively. Specific volume vs temperature and specific volume vs pressure are given in Figures 1 and 2 respectively.

Comparisons with other data are given in Tables VI and VII. Table VI compares the densitometer data with that of Hübl from the Critical Tables⁽²⁾ and Del Grosso⁽¹⁾ at atmospheric pressure. Table VII compares the densitometer data with that of Kahlbaum and Räber⁽²⁾ as a function of pressure at 40°C.

As can be seen in Table VI, the densitometer data agrees quite closely with Critical Tables data, differing on the average by 3 parts in 10,000. Del Grosso's data is, on the average, some 7 parts in 1000 higher over the range.

In Table VII, comparison with Critical Tables data shows a nearly constant difference of 6 parts in 1000 for data over the pressure range. A comparison of the value from the Critical Tables at 40°C, 1 atm, given in Table VI to that in Table VII shows the two values differing by 5 parts in 1000. These values from the Critical Tables are from reports by different experimenters, supposedly on the same type of castor oil and serve to illustrate the scatter in available specific volume data.

The accuracy of the densitometer method used is, of course, limited ultimately by the data⁽⁵⁾⁽⁶⁾⁽⁷⁾⁽⁸⁾⁽⁹⁾ used to calibrate the instrument. Even so, it is difficult to estimate the accuracy of the densitometer castor oil data due to the fact that there is a considerable spread in values from the literature and the belief that the present data and earlier data could very well be from different types of castor oil.

The ability of the instrumentation to measure temperature, pressure and bellows position warrants a claim of precision of 1 part in 10,000. One should be careful, however, in applying precision data to a given castor oil, due to the differences among types.

ACKNOWLEDGEMENTS

The author would like to thank D. L. Bradley and W. D. Wilson for their frequent aid during this project.

The castor oil sample was supplied by the U. S. Navy Underwater Sound Reference Laboratory, Orlando, Florida.

This work was performed in the Acoustics Division of the Physics Research Department of the U. S. Naval Ordnance Laboratory.

TABLE I

COEFFICIENTS FOR EQUATION (1')

<u>Coefficient</u>	<u>Value</u>
B_0	0.782948
B_1	0.43132
B_2	3.30459×10^{-5}
B_3	-7.54645×10^{-9}
B_4	4.10121×10^{-9}
B_5	-3.133×10^{-7}

TABLE II

COEFFICIENTS FOR EQUATION (5) FITTED
TO SPECIFIC VOLUME DATA

<u>Coefficient</u>	<u>Value</u>
A_1	+1.02714
A_2	$+7.03806 \times 10^{-4}$
A_3	$+9.65911 \times 10^{-7}$
A_4	$+3.04471 \times 10^{-9}$
A_5	-4.90916×10^{-5}
A_6	-2.63300×10^{-7}
A_7	-4.04224×10^{-10}
A_8	-8.77192×10^{-12}
A_9	$+1.47088 \times 10^{-8}$
A_{10}	$+9.18117 \times 10^{-11}$
A_{11}	$+3.59139 \times 10^{-13}$
A_{12}	-3.63370×10^{-12}
A_{13}	-1.65674×10^{-14}

TABLE III
SPECIFIC VOLUME - BAKER DB-GRADE CASTOR OIL

P (Bars) T (°C)		P (Bars)										
		1	100	200	300	400	500	600	700	800	900	1000
0		1.0271	1.0224	1.0179	1.0136	1.0096	1.0058	1.0022	0.9987	0.9954	0.9922	0.9891
5		1.0306	1.0258	1.0212	1.0168	1.0127	1.0088	1.0051	1.0015	0.9982	0.9949	0.9917
10		1.0342	1.0292	1.0245	1.0200	1.0158	1.0118	1.0080	1.0044	1.0009	0.9976	0.9944
15		1.0379	1.0328	1.0279	1.0233	1.0190	1.0149	1.0110	1.0073	1.0038	1.0003	0.9970
20		1.0416	1.0363	1.0313	1.0266	1.0222	1.0180	1.0140	1.0102	1.0066	1.0031	0.9998
25		1.0453	1.0399	1.0348	1.0300	1.0255	1.0212	1.0171	1.0132	1.0095	1.0059	1.0025
30		1.0491	1.0436	1.0384	1.0334	1.0287	1.0243	1.0202	1.0162	1.0124	1.0088	1.0053
35		1.0530	1.0473	1.0419	1.0369	1.0321	1.0276	1.0233	1.0192	1.0153	1.0116	1.0081
40		1.0570	1.0511	1.0456	1.0404	1.0355	1.0308	1.0264	1.0223	1.0183	1.0145	1.0109

TABLE IV
THERMAL EXPANSION - BAKER DB-GRADE CASTOR OIL

T (°C)	P (Bars)										
	1	100	200	300	400	500	600	700	800	900	1000
0	+6.85	+6.64	+6.43	+6.24	+6.06	+5.90	+5.74	5.60	+5.46	+5.33	+5.21
5	6.92	6.71	6.50	6.31	6.13	5.96	5.81	5.66	5.53	5.40	5.30
10	7.00	6.78	6.57	6.38	6.19	6.03	5.87	5.73	5.59	5.47	5.35
15	7.08	6.85	6.64	6.44	6.26	6.09	5.93	5.78	5.65	5.52	5.41
20	7.16	6.93	6.71	6.51	6.32	6.15	5.98	5.83	5.70	5.57	5.46
25	7.25	7.01	6.78	6.58	6.38	6.20	6.03	5.88	5.74	5.61	5.50
30	7.34	7.09	6.86	6.64	6.44	6.25	6.08	5.92	5.78	5.65	5.53
35	7.43	7.17	6.93	6.71	6.50	6.30	6.13	5.96	5.81	5.67	5.55
40	7.52	7.26	7.01	6.77	6.56	6.35	6.17	5.99	5.83	5.69	5.56

Units of Thermal Expansion: $^{\circ}\text{C}^{-1} \times 10^{-4}$

TABLE V
COMPRESSIBILITY - BAKER DB-GRADE CASTOR OIL

T (°C)	P (Bars)										
	1	100	200	300	400	500	600	700	800	900	1000
0	+47.8	+45.2	+42.9	+40.7	+38.7	+36.9	+35.3	+33.9	+32.7	+31.7	+30.9
5	48.9	46.3	43.9	41.6	39.6	37.7	36.0	34.6	33.3	32.3	31.5
10	50.0	47.4	44.9	42.5	40.4	38.5	36.8	35.3	34.0		32.0
15	51.2	48.5	45.9	43.5	41.3	39.3	37.5	36.0	34.6		32.6
20	52.4	49.6	46.9	44.5	42.2	40.2	38.3	36.7	35.3	34.1	33.1
25	53.6	50.7	48.0	45.5	43.1	41.0	39.1	37.4	35.9	34.7	33.7
30	54.9	51.9	49.1	46.5	44.1	41.9	39.9	38.1	36.6		34.2
35	56.2	53.1	50.2	47.5	45.1	42.8	40.7	38.9	37.3	35.8	34.8
40	57.5	54.4	51.4	48.7	46.1	43.8	41.6	39.7	38.1	36.6	

Units of Compressibility: Bars⁻¹ x 10⁻⁶

TABLE VI

COMPARISON WITH OTHER DATA AT ONE ATMOSPHERE

T, °C	$\underline{v_1}$ cm ³ /g	$\underline{v_2}$	$\underline{v_3}$ cm ³ /g	$\underline{\Delta_1}$	$\underline{\Delta_2}$ cm ³ /g
0	1.0271	-----	1.031	-----	-0.004
5	1.0306	1.0302	1.036	.0004	-0.005
10	1.0342	1.0339	1.042	.0003	-0.008
15	1.0379	1.0376	1.046	.0003	-0.008
20	1.0416	1.0413	1.050	.0003	-0.008
25	1.0453	1.0450	1.054	.0003	-0.009
30	1.0491	1.0489	1.057	.0002	-0.008
35	1.0530	1.0527	1.060	.0003	-0.007
40	1.0570	1.0566	1.063	.0004	-0.006

 v_1 = Specific volume by densitometer method v_2 = Specific volume from Critical Tables⁽²⁾ v_3 = Specific volume from Del Grosso⁽¹⁾ Δ_1 = $v_1 - v_2$ Δ_2 = $v_1 - v_3$

TABLE VII
COMPARISON WITH CRITICAL TABLES AT 40°C

<u>P</u>	<u>v₁</u>	<u>v₂</u>	<u>Δ</u>
1 Bar	1.0570cm ³ /g	1.0621cm ³ /g	-0.0051cm ³ /g
100	1.0511	1.0569	-0.0058
200	1.0456	1.0517	-0.0061
300	1.0404	1.0466	-0.0062
400	1.0355	1.0420	-0.0065
500	1.0308	1.0374	-0.0066
600	1.0264	1.0332	-0.0068
700	1.0223	1.0289	-0.0066
800	1.0183	1.0248	-0.0065
900	1.0145	1.0207	-0.0062
1000	1.0109	1.0171	-0.0062

v_1 = Specific volume by densitometer method

v_2 = Specific volume from Critical Tables⁽²⁾

$$\Delta = v_1 - v_2$$

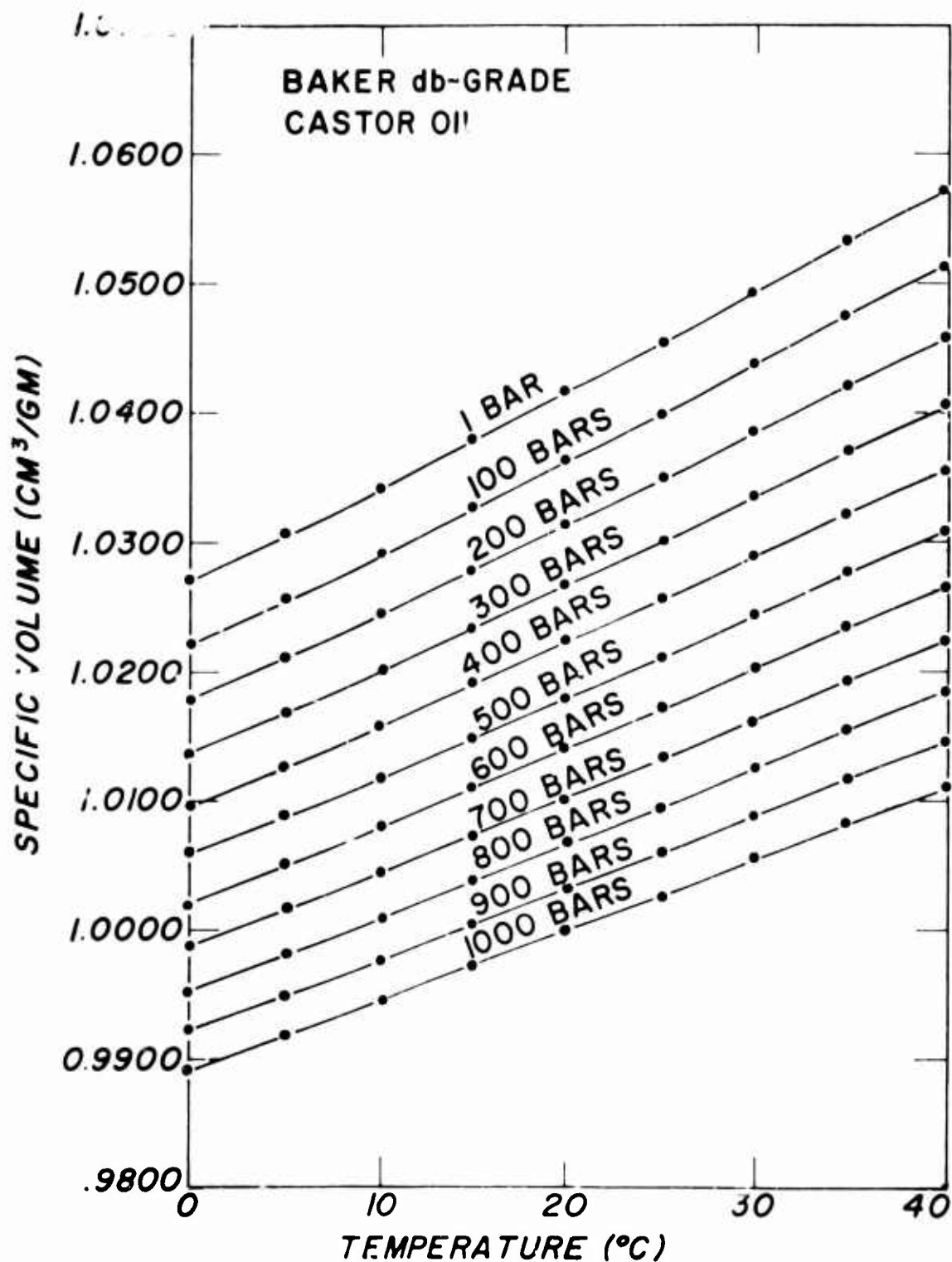
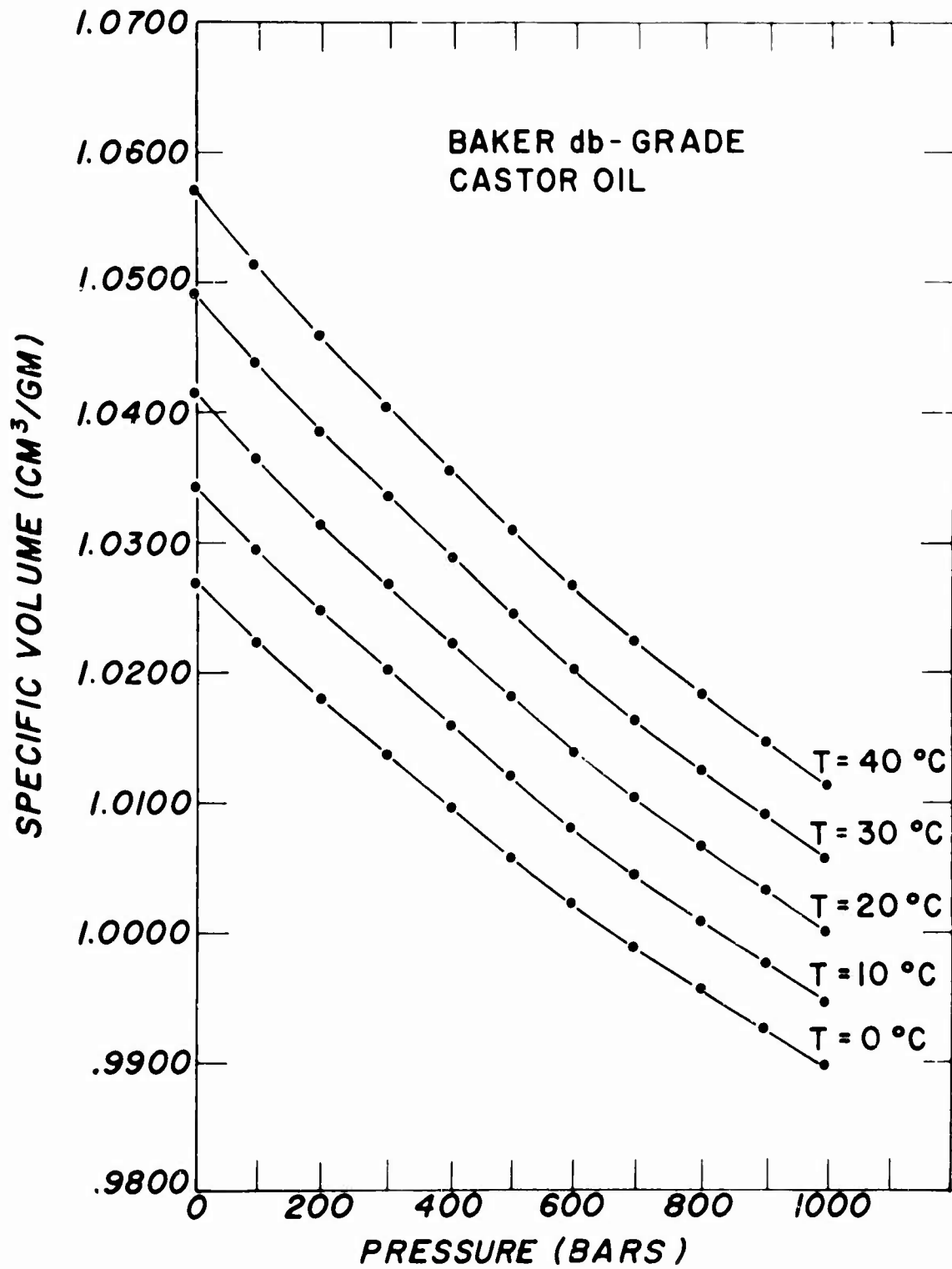


FIGURE 1. SPECIFIC VOLUME VS TEMPERATURE



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Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1 ORIGINATING ACTIVITY (Corporate author)		2a REPORT SECURITY CLASSIFICATION
U. S. Naval Ordnance Laboratory, White Oak		Unclassified
		2b GROUP

3 REPORT TITLE		
Some Thermodynamic Properties of Castor Oil vs Temperature and Pressure		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5 AUTHOR(S) (Last name, first name, initial)		
Stallard, John M.		
6 REPORT DATE	7a TOTAL NO. OF PAGES	7b NO. OF REFS
	19	11
8a CONTRACT OR GRANT NO		9a ORIGINATOR'S REPORT NUMBER(S)
b PROJECT NO 855/JSRL		NOLTR 66-68
c		9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d		
10 AVAILABILITY/LIMITATION NOTICES		
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14. KEY WORDS	LINK A		LINK B		LINK C	
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Castor Oil Specific Volume Isothermal Compressibility Thermal Expansion Baker db Oil Differential Transformer Densitometer Acoustic Coupling Liquid						

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