

Effect of Number of Carboxyl Groups on Liquid Density of Esters of Alkylcarboxylic Acids

Joseph C. Phillips* and George J. Mattamal
National Bureau of Standards, Washington, D.C. 20234

Liquid-density data for esters covering a molecular weight range of 88–939 (monocarboxylics; dialkyl esters series; triglyceride esters series; and oligomeric ester series) and a temperature range of 0–242.8 °C have been empirically fitted to about 1% to an equation of the form $\rho = \lambda + K\lambda^2 + I'(T)$, where λ is a function of the absolute temperature, T , number of carboxyl groups, N_{COO} , and the molecular weight, M ; K is a function of T , N_{COO} , and N_2 (number of methylene groups). The equation in its limiting form may be used to estimate densities of poly(carboxylic esters) from a knowledge of the structure of the repeating unit. Data for the monocarboxylics were obtained from published values, those of the sebacate series and triglyceride series were measured dilatometrically and that of the oligomeric ester series was measured by a capillary method. The results show a rather strong dependence of the density on N_{COO} .

Liquid density is a very useful bulk property of a substance. Sometimes in practice, experimental difficulties such as stability and quantity of material reduce the accessibility of this property. Thus, for estimation purposes, correlations are available for compounds in general (2) and polymers specifically (2, 14). In this paper we present an empirical equation for the calculation of liquid density for carboxylic esters. The relation was derived from data on monocarboxylics, a sebacate series, triglyceride series, and an oligomeric series. Data for the monocarboxylics were obtained from published values (16), those for the sebacate and triglyceride series were measured dilatometrically, and those for the oligomer series were measured by a capillary method. The results presented here show that the density of an alkane molecule is affected rather strongly by carboxyl addition to the chain. Other properties of carboxylic esters, e.g., liquid heat capacity (11, 12), heats of vaporization (11), flexibility, and entropy of fusion (2, 8), show similar effects.

Analysis of Data

Liquid-density data used for this study are presented in Tables I–IV. Data for the monocarboxylic esters were obtained from the literature (16); data for the sebacate and triglyceride series were measured conventionally using a mercury-calibrated dilatometer (10) with uncertainties of less than 1%; and data for the oligomeric series were measured with a mercury-calibrated capillary tube (11, 13) with uncertainties of less than 1%.

The data in this study were treated according to a general equation used for polymer properties (1, 4), e.g., density, tensile strength, refractive index, etc. The form of the equation is given as

$$P = a/\bar{M}_n + b \quad (1)$$

where P is the property, a and b are parameters of the given system, and \bar{M}_n is the number-average molecular weight. As shown in Figure 1 in contrast to the n -alkanes, the homologous series of polar compounds (e.g., COOH, COO, OH) shows nonlinear effects with respect to density as a function of the reciprocal of the molecular weight. Such nonlinearity may be adequately taken into account for the carboxylic esters by a second-order expansion (4) of a term similar to the first term of the

right side of eq 1. Thus, the density in grams per cubic centimeter may be expressed as

$$\rho = \lambda + K\lambda^2 + I'(T) \quad (2)$$

where λ and K are empirically defined as

$$\lambda = (B(T)N_{\text{COO}} + A(T))/M \quad (3)$$

and

$$K = \left[\frac{C(T)N_2 + D(T)}{F(T, N_{\text{COO}})} \right] N_{\text{COO}} \quad (4)$$

The functions $I'(T)$, $A(T)$, $B(T)$, $C(T)$, $D(T)$, and $F(T, N_{\text{COO}})$ are linear functions of the absolute temperature, T , the latter being also a function of the number of carboxyl groups, N_{COO} . N_2 is the number of methylene groups, and M is the molecular weight. As indicated by eq 3, the slope of ρ vs. $1/M$ has been separated into an alkane portion, $A(T)$, and a portion depending on the number of carboxyl groups, $B(T)N_{\text{COO}}$. In eq 4, the function K is chosen such that $K = 0$ for the limits of $N_{\text{COO}} = 0$ and $N_{\text{COO}} = \infty$ (i.e., as $M \rightarrow \infty$).

Parameters from n -Alkane Data. For $N_{\text{COO}} = 0$, eq 3 and 4 reduce, respectively, to $\lambda = A(T)/M$ and $K = 0$. Thus, for the n -alkanes eq 2 yields

$$\rho = (A(T)/M) + I'(T) \quad (5)$$

The data in Table V were used to evaluate $A(T)$ and $I'(T)$ according to eq 5 by plotting ρ vs. $1/M$ at constant temperature; the slope and intercept were linearly least-squares fitted to temperature T to give

$$A(T) = -0.04639T - 2.453 \quad (6)$$

and

$$I'(T) = -0.0005281T + 1.0014 \quad (7)$$

The standard errors of estimate for eq 6 and 7 are, respectively, 0.37 and 0.0023.

Estimation of $B(T)$ from Oligomer Data. At infinite molecular weight, the coefficient $K = 0$ and from eq 3

$$\lim_{M \rightarrow \infty} \lambda = B(T)(N_{\text{COO}}/M)_0 \quad (8)$$

where $(N_{\text{COO}}/M)_0$ in eq 8 is the ratio of the number of carboxyl groups in the repeating unit to the molecular weight of the unit. By substituting eq 8 into eq 2, the density at infinite chain length becomes

$$\rho_{\infty} = B(T)(N_{\text{COO}}/M)_0 + I'(T) \quad (9)$$

From the oligomer data in Table IV, a plot of ρ vs. $1/M$ extrapolated to $1/M = 0$ at 30, 50, 72, and 100 °C yields ρ_{∞} at each respective temperature. By utilizing eq 9, the function, $B(T)$, was determined to be

$$B(T) = -0.04690T + 42.2 \quad (10)$$

where the standard error of estimate of eq 10 is 0.47.

Equation 9 may also be used to estimate the densities of other poly(carboxylic esters) at infinite chain length. In Table VI we show comparative calculations of three polymers. Structure uncertainty as a consequence of polymerization (3, 6, 9, 15)

Table I. Atmospheric Liquid Density, ρ , as a Function of Temperature for Carboxylic Esters; Data Were Taken from Ref 16

Compd	Mol wt	Liquid density, ρ , g/cm ³											
		273.15 K			288.15 K			293.15 K			303.15 K		
		Exptl	Calcd	% dev	Exptl	Calcd	% dev	Exptl	Calcd	% dev	Exptl	Calcd	% dev
Methyl propionate	88.1	0.9389	0.9312	0.820	0.9211	0.9106	1.14	0.9007	0.9046	-0.433	0.9034	0.8934	1.06
Ethyl acetate	88.1	0.9102	0.9144	-0.461	0.8938	0.8958	-0.223	0.8883	0.8905	-0.248	0.8946	0.8938	0.0894
<i>n</i> -Propyl acetate	102.1	0.9016	0.9031	-0.166	0.8865	0.8859	0.0676	0.8815	0.8811	0.0453	0.8772	0.8809	-0.422
<i>n</i> -Butyl acetate	116.1	0.9023	0.9031	-0.0886	0.8866	0.8859	0.0789	0.8794	0.8811	-0.193	0.8713	0.8723	-0.115
<i>n</i> -Propyl propionate	116.1	0.8896	0.8951	-0.618	0.8758	0.8791	-0.376	0.8770	0.8746	0.274	0.8708	0.8723	-0.172
Ethyl butyrate	130.2	0.8961	0.8951	0.111	0.8814	0.8791	0.260	0.8770	0.8746	0.274	0.8620	0.8664	-0.510
<i>n</i> -Butyl propionate	130.2	0.8914	0.8891	0.258	0.8774	0.8740	0.388	0.8680	0.8661	0.219	0.8666	0.8664	0.0230
Ethyl valerate	144.2	0.8700	0.8702	-0.0229	0.8700	0.8702	-0.0229	1.0402	1.0474	-0.692	0.8635	0.8620	0.174
<i>n</i> -Amyl propionate	158.2												
Butyl valerate	174.19												
Ethyl succinate ^a	174.19												
Butyl stearate ^a	340.58												

^a Data taken from "Handbook of Chemistry and Physics," 32nd ed, Chemical Rubber Publishing Co. Cleveland, Ohio, 1950. ^b Average error, 0.341%; standard error of estimate, 0.299.

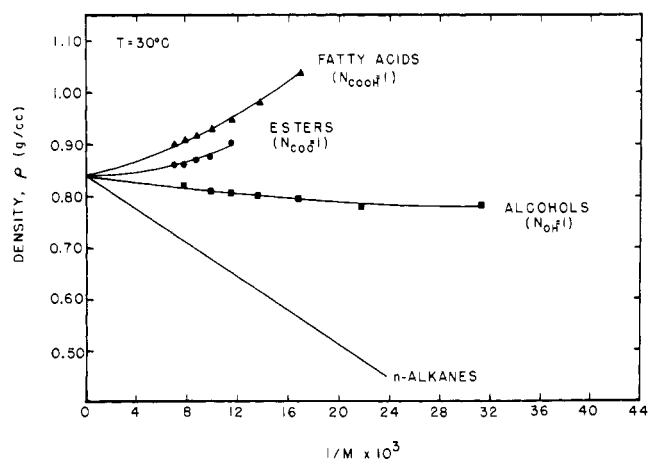


Figure 1. Liquid densities vs. the reciprocal molecular weight at 30 °C of various classes of compounds: *n*-fatty acids (\blacktriangle), carboxylic esters (\bullet); *n*-alcohols (\blacksquare); *n*-alkanes (solid line).

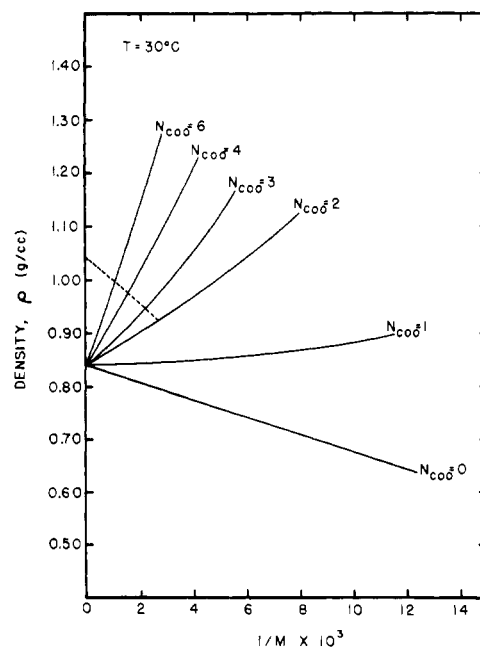


Figure 2. Liquid density calculated according to eq 2 at 30 °C of carboxylic esters vs. the reciprocal molecular weight and indicated carboxyl content. The dotted line connects the three points in the oligomeric, poly(hexamethylene sebacate) esters for $N_{\text{COO}} = 2, 4, 6, \dots$ and $N_{\text{COO}} = 0$ represents the *n*-alkanes.

renders the calculated result uncertain. For poly(decamethylene sebacate) and poly(decamethylene adipate), the oxygen atom and carbonyl group forming bonds with the end groups were taken as equivalent to a carboxyl group ($\text{O}=\text{CO}-$); the assumption here is used only as an aid in simplifying the calculation of ρ_{∞} . Thus, if ρ_{∞} data are known, one may utilize eq 9 to determine $(N_{\text{COO}}/M)_0$ which may aid structure assignment of the repeating units.

Evaluation of the Coefficient K . The parameters $C(T)$ and $D(T)$ were evaluated from eq 4 by assuming that for the monocarboxylic esters ($N_{\text{COO}} = 1$) the function $F(T, N_{\text{COO}}) = 1$, i.e.

$$K/N_{\text{COO}} = C(T)N_2 + D(T) \quad (11)$$

By calculating K from eq 2 [i.e., $K = (\rho - l'(T) - \lambda)/\lambda^2$], the slope and intercept of eq 11 at constant temperature, T , were found by fitting linearly K/N_{COO} vs. N_2 for data in Table I. Thus, the functions $C(T)$ and $D(T)$ were determined to be

$$C(T) = -0.01037T + 1.94 \quad (12)$$

Table II. Atmospheric Liquid Density, ρ , as a Function of Temperature for Linear Esters of Sebacic Series
$$\text{CH}_3(\text{CH}_2)_x\overset{\text{O}}{\parallel}\text{C}(\text{CH}_2)_8\overset{\text{O}}{\parallel}\text{C}(\text{CH}_2)_x\text{CH}_3 \quad (x = 3-17)$$

Compd	Empirical formula	Mol wt	Liquid density, ^a g/cm ³						
				301.25 K	331.05 K	371.25 K	420.35 K	468.25 K	515.95 K
Di- <i>n</i> -butyl sebacate	C ₁₈ H ₃₄ O ₄	314.45	Exptl	0.9382	0.9179	0.8901	0.8432	0.8047	0.7664
			Calcd	0.9437	0.9176	0.8832	0.8417	0.8002	0.7574
			% dev	-0.586	0.0326	0.775	0.178	0.559	1.17
Di- <i>n</i> -hexyl sebacate	C ₂₂ H ₄₂ O ₄	370.34	Exptl	0.9267	0.9267	0.8731	0.8365	0.7993	0.7655
			Calcd	0.9274	0.9029	0.8708	0.8318	0.7930	0.7530
			% dev	-0.0755	0.0332	0.263	0.562	0.788	1.63
Di- <i>n</i> -octyl sebacate	C ₂₆ H ₅₀ O ₄	426.00	Exptl	0.9132	0.8911	0.8639	0.8306	0.7945	0.7583
			Calcd	0.9156	0.8923	0.8618	0.8247	0.7877	0.7498
			% dev	-0.263	-0.135	0.243	0.710	0.856	1.12
Di- <i>n</i> -decyl sebacate	C ₃₀ H ₅₈ O ₄	482.79	Exptl		0.8827	0.8536	0.8180	0.7858	0.7458
			Calcd		0.8842	0.8548	0.8192	0.7837	0.7473
			% dev		-0.170	-0.140	-0.147	0.267	-0.201
Di- <i>n</i> -dodecyl sebacate	C ₃₄ H ₆₆ O ₄	539.00	Exptl		0.8713	0.8436	0.8103	0.7795	-0.7465
			Calcd		0.8779	0.8495	0.8149	0.7805	0.7454
			% dev		-0.757	-0.699	-0.568	-0.128	0.147
Di- <i>n</i> -tetradecyl sebacate	C ₃₈ H ₇₄ O ₄	595.00	Exptl			0.8394	0.8061	0.7739	0.7438
			Calcd			0.8451	0.8114	0.7780	0.7438
			% dev			-0.679	-0.657	-0.530	0.00
Di- <i>n</i> -hexadecyl sebacate	C ₄₂ H ₈₂ O ₄	651.36	Exptl			0.8367	0.8038	0.7726	0.7403
			Calcd			0.8416	0.8086	0.7759	0.7425
			% dev			-0.586	-0.597	-0.427	-0.297
Di- <i>n</i> -octadecyl sebacate	C ₄₆ H ₉₀ O ₄	707.36	Exptl			0.8319	0.8021	0.7706	0.7378
			Calcd			0.8386	0.8062	0.7741	0.7414
			% dev			-0.805	-0.511	-0.454	-0.488

^a Average error, 0.481%; standard error of estimate, 0.352.

and

$$D(T) = -0.0309T + 5.96 \quad (13)$$

where the standard errors of estimate of eq 12 and 13 are, respectively, 0.09 and 0.28.

For $N_{\text{COO}} = 2, 3, 4$, and 6 , the function $F(T, N_{\text{COO}})$ was determined from eq 4, 12, and 13, i.e.

$$F(T, N_{\text{COO}}) = (C(T)N_2 + D(T))/(K/N_{\text{COO}}) \quad (14)$$

or, $F(T, N_{\text{COO}})$ may be defined approximately as independent of N_2 and separated as

$$F(T, N_{\text{COO}}) = f(N_{\text{COO}})T + G(N_{\text{COO}}) \quad (15)$$

The coefficient K in eq 14 was again determined from eq 2. From the sebacate ($N_{\text{COO}} = 2$) and triglyceride ($N_{\text{COO}} = 3$) data, the function $F(T, N_{\text{COO}})$ calculated from eq 14 was averaged for each temperature, while only one value of the function could be calculated for the oligomer data ($N_{\text{COO}} = 2, 4, 6$). These results for the three series are summarized in Table VII with error estimates given for the averages. By utilizing eq 15, the functions $f(N_{\text{COO}})$ and $G(N_{\text{COO}})$ were determined from least-squares fits of $F(T, N_{\text{COO}})$ vs. T at each N_{COO} ; for $N_{\text{COO}} = 2$ the data for the sebacate and oligomer were used together to determine the functions $f(2)$ and $G(2)$; the other results for $N_{\text{COO}} = 3, 4$, and 6 , including error estimates and polynomial fits of the functions $f(N_{\text{COO}})$ and $G(N_{\text{COO}})$, are also included in Table VII.

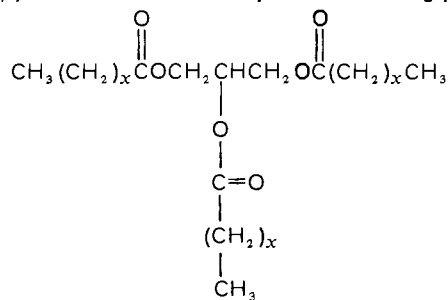
Determination of Liquid Density. The calculated values for the liquid densities of this study utilizing eq 2, 3, and 4 are given in Tables I-IV; the average error and the standard error of estimate of the average are also included in each table with the upper limit of the error being about 1%. Structural changes other than those considered here such as branching and odd- and even-numbered differences can produce fluctuations in the density, but these variations are generally within the 1% bound given by our density equation. In Figure 2 we show calculations utilizing eq 2, 3, and 4 at 30 °C. The results show a rather strong

and increasing dependence of density on the number of carboxyl groups, N_{COO} . Only at high carboxyl content and high molecular weight does the density become linear with N_{COO} and $1/M$, but the dotted line in Figure 2 for the oligomer series ($N_{\text{COO}} = 2, 4, 6, \dots$) shows an approximate linear dependence on $1/M$ over the range of molecular weights studied [extrapolate data for whole polymers of poly(hexamethylene sebacate) ($M_n = 623-3516$) show deviation of about 2% compared with values of the oligomer series (13)]. In contrast to the results shown in Figure 2, recent data show that other properties such as liquid heat capacity (11, 12) and heats of vaporization (11) decrease with increasing carboxyl content relative to the n -alkanes. Such property variations are not uncommon, for example, cycloparaffins and aromatic systems show similar kinds of differences for heats of sublimation (2).

The use of eq 2, 3, and 4 may be further clarified by showing a typical calculation. For example at $T = 515.95$ K, the results for Tristearin ($\text{C}_{57}\text{H}_{110}\text{O}_6$) are the following: $N_{\text{COO}} = 3$, $M = 890.50$, $N_2 = 50$, $A(T) = -26.39$, $B(T) = 18.00$, $I'(T) = 0.7289$, $\lambda = 0.03101$, $C(T) = -3.37$, $D(T) = -9.983$, $f(N_{\text{COO}}) = 0.5871$, $G(N_{\text{COO}}) = -129$, $F(T, N_{\text{COO}}) = 173.9$, $K = -3.079$; therefore, $\rho = 0.03101 - 3.079(0.03101)^2 + 0.7289 = 0.7564$ (deviation = -0.866%).

Conclusion

From the knowledge of the structure, the results presented here allow liquid density of carboxylic esters to be estimated to about 1% as a function of molecular weight and temperature over the experimental ranges shown. Density at infinite chain length may also be estimated for poly(carboxylic esters), if the structure of the repeating unit is known, but, if such is not the case and ρ_∞ data are available, then one may estimate (N_{COO}/M)₀.

Table III. Atmospheric Liquid Density, ρ , as a Function of Temperature for Triglyceride Series $(x = 2-16)$

Compd	Empirical formula	Mol wt	Liquid density, ^a g/cm ³						
				301.25 K	331.05 K	371.25 K	420.35 K	468.25 K	515.95 K
Tributylin	C ₁₅ H ₂₆ O ₆	302.37	Exptl	1.0263	0.9990	0.9620	0.9181	0.8740	0.8268
			Calcd	1.0266	1.001	0.9635	0.9148	0.8655	0.8149
			% dev	-0.0292	-0.200	-0.156	0.359	0.972	1.44
Tricaproin	C ₂₁ H ₃₈ O ₆	386.50	Exptl	0.9690	0.9451	0.9121	0.8741	0.8305	0.7934
			Calcd	0.9798	0.9580	0.9253	0.8829	0.8397	0.7953
			% dev	-1.11	-1.36	-1.45	-1.01	-1.11	-0.239
Trioctanoin	C ₂₇ H ₅₀ O ₆	470.69	Exptl	0.9453	0.9229	0.8923	0.8568	0.8244	0.7890
			Calcd	0.9517	0.9318	0.9018	0.8630	0.8235	0.7830
			% dev	-0.677	-0.964	-1.06	-0.724	0.109	0.760
Tridecanoin	C ₃₃ H ₆₂ O ₆	554.86	Exptl	0.9339	0.9025	0.8731	0.8384	0.8043	0.7711
			Calcd	-0.9330	0.9142	0.8860	0.8496	0.8125	0.7745
			% dev	0.0963	-1.30	-1.48	-1.34	-1.02	-0.441
Trilaurin	C ₃₉ H ₇₄ O ₆	639.02	Exptl		0.8963	0.8674	0.8327	0.8013	0.7673
			Calcd		0.9016	0.8746	0.8398	0.8045	0.7683
			% dev		-0.591	-0.830	-0.853	-0.399	-0.130
Trimyristin	C ₄₅ H ₈₆ O ₆	723.18	Exptl			0.8607	0.8275	0.7947	0.7656
			Calcd			0.8660	0.8325	0.7984	0.7636
			% dev			-0.616	-0.604	-0.466	0.261
Tripalmitin	C ₅₁ H ₉₈ O ₆	807.34	Exptl			0.8547	0.8209	0.7895	0.7614
			Calcd			0.8594	0.8267	0.7937	0.7599
			% dev			-0.550	-0.706	-0.532	0.197
Tristearin	C ₅₇ H ₁₁₀ O ₆	890.50	Exptl			0.8477	0.8145	0.7791	0.7504
			Calcd			0.8540	0.8221	0.7898	0.7569
			% dev			-0.743	-0.933	-1.37	-0.866

^a Average error, 0.733%; standard error of estimate, 0.429.Table IV. Atmospheric Liquid Density, ρ , as a Function of Temperature for Linear Oligomer Esters of Poly(hexamethylene sebacate)

X	Empirical formula	Mol wt	Liquid density, ^a g/cm ³						
				284.35 K	298.15 K	313.45 K	332.10 K	354.70 K	373.95 K
1	C ₂₂ H ₄₂ O ₄	370.34	Exptl	0.9359	0.9253	0.9129	0.9006	0.8836	0.8711
			Calcd	0.9418	0.9300	0.9172	0.9020	0.8840	0.8687
			% dev	-0.630	-0.508	-0.471	-0.471	-0.0450	0.276
2	C ₃₈ H ₇₀ O ₈	654.56	Exptl						
			Calcd						
			% dev						
3	C ₅₄ H ₉₈ O ₁₂	938.78	Exptl						
			Calcd						
			% dev						

^a Average error, 0.302%; standard error of estimate, 0.238.

Table V. Liquid Density Data for *n*-Alkanes Used for the Evaluation of $A(T)$ and $I'(T)$ According to Eq 5. Data Were Taken from Ref 16

Compd	Mol wt	Liquid density, g/cm ³						
		20 °C	50 °C	100 °C	150 °C	200 °C	250 °C	300 °C
C ₇ H ₁₆	100	0.6838						
C ₈ H ₁₈	114	0.7026	0.6782	0.6350				
C ₉ H ₂₀	128	0.7176	0.6942	0.6532	0.6086			
C ₁₀ H ₂₂	142	0.7379						
C ₁₁ H ₂₄	156	0.7402	0.7180	0.6800	0.6393	0.5947		
C ₁₂ H ₂₆	170	0.7490						
C ₁₃ H ₂₈	184	0.7563	0.7349	0.6985	0.6604	0.6201		
C ₁₄ H ₃₀	198	0.7628						
C ₁₅ H ₃₂	212	0.7683						
C ₁₆ H ₃₄	226	0.7736						
C ₂₀ H ₄₂	282			0.7358				
C ₂₈ H ₅₈	394			0.7555	0.7235	0.6910	0.6578	0.6226
C ₃₆ H ₇₄	506			0.7671	0.7357	0.7048	0.6730	0.6399

Table VI. Atmospheric Densities at Infinite Chain Length of Some Poly(carboxylic esters) Estimated According to Eq 9

Polymer	Repeating unit	$(N_{\text{COO}}/M)_0$	$T, ^\circ\text{K}$	$\rho_\infty, \text{g/cm}^3$		
				Exptl	Calcd	% dev
Poly(decamethylene sebacate)	$[\text{O}(\text{CH}_2)_{10}\text{OOC}(\text{CH}_2)_8\text{CO}]^a$	0.005882	382.15	0.9378 ^b	0.9424	-0.490
Poly(decamethylene adipate)	$[\text{O}(\text{CH}_2)_{10}\text{OOC}(\text{CH}_2)_4\text{CO}]^a$	0.0070422	382.15	0.9732 ^b	0.9706	0.267
Poly(hexamethylene sebacate)	$[(\text{CH}_2)_6\text{OOC}(\text{CH}_2)_8\text{COO}]^c$	0.00704722	345.15	1.0015 ^d	1.0023	0.0799

^a From ref 5. ^b From ref 7. ^c From Table IV. ^d Extrapolated from oligomer data in Table IV.

Table VII. Determination of the Functions $F(T, N_{\text{COO}})$, $f(N_{\text{COO}})$, and $G(N_{\text{COO}})$ According to Eq 14 and 15

T, K	$F(T, N_{\text{COO}})^a$					
	$N_{\text{COO}} = 2$	No. of values	$N_{\text{COO}} = 3$	No. of values	$N_{\text{COO}} = 4$ (1 value)	$N_{\text{COO}} = 6$ (1 value)
284.35	18.4	1				
298.15	21.3	1				
301.25	23.5 ± 2.1	3	45.1 ± 5.9	4		
312.65					299	
313.45	23.6	1				
327.85						1571
331.05	29.0 ± 3.9	5	55.0 ± 6.0	5		
332.1	29.6	1				
334.65					478	
345.15					322	
354.7	34.8	1				
357.75						2877
360.95					749	
371.25	36.5 ± 13.8	8	72.6 ± 9.1	8		
373.95	46.5	1				
377.15						19137
420.35	55.4 ± 42.2	8	95.2 ± 26.8	8		
468.25	14.7 ± 144	8	291 ± 511	8		
515.95	60.4 ± 136	8	79.8 ± 370	8		
$f(N_{\text{COO}})^b$	0.1219		0.5871		7.849	329.8
$G(N_{\text{COO}})^c$	-11.52		-129		-2194	-108,966
Std error	11.7		78.5		133	5356

^a For sebacate ($N_{\text{COO}} = 2$) and triglyceride ($N_{\text{COO}} = 3$), the function was averaged for the number of values given at temperature, T , with the standard error of estimate as the estimate of precision; for the oligomers ($N_{\text{COO}} = 2, 4, 6$), only one value of function was calculated at T . ^b Polynomial fitted equation: $f(N_{\text{COO}}) = 46.003 - 97.386N_{\text{COO}} + 69.8978N_{\text{COO}}^2 - 20.6906N_{\text{COO}}^3 + 2.17663N_{\text{COO}}^4$. ^c Polynomial fitted equation: $G(N_{\text{COO}}) = -16131.5 + 34023.1N_{\text{COO}} - 24289.9N_{\text{COO}}^2 + 7144.53N_{\text{COO}}^3 - 745.181N_{\text{COO}}^4$.

Glossary

$A(T)$	empirical linear function of absolute temperature
$B(T)$	empirical linear function of absolute temperature
$C(T)$	empirical linear function of absolute temperature
$D(T)$	empirical linear function of absolute temperature
$F(T, N_{\text{COO}})$	empirical function of the absolute temperature and the number of carboxyl groups.
$I'(T)$	empirical linear function of absolute temperature
K	$[C(T)N_2 + D(T)]/F(T, N_{\text{COO}})$, coefficient of λ^2
λ	$[B(T)N_{\text{COO}} + A(T)]/M$
M	molecular weight
N_2	number of methylene groups per molecule
N_{COO}	number of carboxyl groups per molecule
$(N_{\text{COO}}/M)_0$	ratio of number of carboxyl groups of the repeating unit to the molecular weight of the unit
ρ	density, g/cm ³
ρ_∞	density at infinite chain length, g/cm ³
T	absolute temperature, K

Literature Cited

- (1) Billmeyer, F. W., "Textbook of Polymer Science", Interscience, New York, N.Y., 1962, p 210.
- (2) Bondi, A., "Physical Properties of Molecular Crystals, Liquids and Glasses", Wiley, New York, N.Y., 1968.
- (3) Case, L. C., *J. Polym. Sci.*, **29**, 455 (1958).
- (4) D'Alelio, G. F., "Fundamental Principles of Polymerization", Wiley, New York, N.Y., 1952, p 103.
- (5) Flory, P. J., "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, p 573.
- (6) Flory, P. J., *J. Am. Chem. Soc.*, **58**, 1877 (1936).
- (7) Flory, P. J., *J. Am. Chem. Soc.*, **62**, 1057 (1940).
- (8) Hobbs, S. Y., Billmeyer, Jr., F. W., *J. Polym. Sci., Part A-2*, **8**, 1387, 1395 (1970).
- (9) Korshak, V. V., Vinogradova, S. V., Ravnovesnaya Polikondensatsiya (equilibrium polycondensation), Izd. "Nauka", 1968.
- (10) Mattamal, G. J., Ph.D. Thesis, The American University, Washington, D.C., 1970.
- (11) Phillips, J. C., Wall, L. A., Aldridge, M. A., *Polym. Eng. Sci.*, **15**, 73 (1975).
- (12) Phillips, J. C., Mattamal, M. M., *J. Chem. Eng. Data*, **21**, 228 (1976).
- (13) Phillips, J. C., M.S. Thesis, The American University, Washington, D.C., 1972.
- (14) Sewell, J. H., *J. Appl. Polym. Sci.*, **17**, 1741 (1973).
- (15) Sokolov, L. B., Sharikov, Yu V., Katlova, R. P., *Vysokomol. Soedin., Ser. A*, **12**, No. 9, 1934, 2190 (1970).
- (16) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", Vol. I and II, Elsevier, New York, N.Y., 1950, 1960, 1965.

Received for review October 20, 1976. Accepted July 14, 1977.

Vapor Pressure of Di-*tert*-butyl Peroxide

Doren Indritz,* Jack Stone, and Frederick Williams

Chemistry Division—Code 6180, Naval Research Laboratory, Washington, D.C. 20375

The vapor pressure of di-*tert*-butyl peroxide was determined and a predictive equation for its calculation is given. The molar heat of vaporization was calculated as 7.63 kcal.

Di-*tert*-butyl peroxide is quite useful as a source of free radicals in kinetic studies (2) and in high-temperature polymerizations (5). Di-*tert*-butyl peroxide, unlike the lower alkyl peroxides such as dimethyl, methyl ethyl, and diethyl, is rather stable to both heat and shock. It will decompose oxidatively and thermally at elevated temperatures but not with the severity associated with the lower alkyl peroxides. A cool flame, the emission of ¹A₂ H₂CO, from the oxidative decomposition of di-*tert*-butyl peroxide has been observed at approximately 550 K (6). At room temperature di-*tert*-butyl peroxide is quite stable and safe to handle (3). Dimethyl peroxide, however, is extremely shock sensitive and must be handled with utmost care.

In using di-*tert*-butyl peroxide as a radical source, it can be delivered by passing an inert gas stream through the liquid peroxide. The vapor concentration of peroxide is dictated by its vapor pressure. Therefore, the vapor pressure was measured and fitted to the integrated Clausius-Clapeyron equation. A value for the molar heat of vaporization of the peroxide was also calculated.

Experimental Section

The di-*tert*-butyl peroxide obtained from Matheson Coleman and Bell (Stock no. BX2020) was assayed by MCB at 99.7% purity with GC and IR spectra.

Table I. Vapor Pressure of Di-*tert*-Butyl Peroxide

Temp, °C	Pressure, Torr	Temp, °C	Pressure, Torr
-26.5	1.806	-4.0	7.695
-23.0	2.351	-3.0	7.709
-22.0	2.952	-3.0	8.660
-22.0	2.950	2.0	10.040
-22.0	2.825	4.0	11.324
-22.0	2.657	6.0	12.40
-22.0	2.459	10.0	15.08
-21.0	2.612	10.0	15.54
-20.5	2.925	14.0	19.08
-18.0	3.603	14.0	18.90
-17.5	3.491	16.0	20.29
-16.0	4.037	17.0	22.11
-16.0	3.933	20.0	27.24
-14.0	4.003	20.0	24.73
-12.0	5.371	24.0	30.40
-12.0	5.065	24.0	28.84
-10.0	5.350	25.0	31.34
-9.0	5.517	30.0	38.67
-7.0	7.192	31.0	39.65
-5.5	7.306	31.5	38.88
-5.0	7.936	33.0	39.16
-4.0	8.319	38.0	49.94
-4.0	7.740	40.0	48.14

Standard vapor pressure measurements were made by allowing an excess of liquid to equilibrate in an enclosed system resting in a Haake Model FK constant-temperature bath. Integral to the enclosed system was an MKS Model 144 Baratron for pressure measurements (± 0.001 Torr for less than 11.500 Torr