

# Enthalpies of Vaporization of Oligomers of Poly(hexamethylene sebacate) and Esters of Alkylcarboxylic Acids

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**ABSTRACT:** Enthalpies of vaporization for esters covering a molecular weight range of about 74–939 g/mol · [monocarboxylics; linear esters of sebacic series; branched esters of triglyceride series; and, oligomer esters of poly(hexamethylene sebacate)] and a temperature range of about 273.15–523.15 K have been empirically fitted to within about 5% to an equation of the following form:  $\Delta H_v(T, M) = S(T)f(M) + I_0(T)$ , where  $S(T) = C \ln(T) + K_0$ ,  $I_0(T) = aT + b_0$ , and  $f(M) = M/(1 + a_0M)$ ,  $M$  is the molecular weight (molar mass);  $T$  is in degrees Kelvin; and,  $C$ ,  $K_0$ ,  $a$ ,  $b_0$ , and  $a_0$  are constants. These results were used to determine the heat capacity difference,  $\Delta C_p = C_p(l) - C_p(g)$ , and compared to calculated values from functional relationships of  $C_p(l)$  and  $C_p(g)$ ,  $l$  is liquid  $g$  is gas. The heat capacity difference results in conjunction with  $C_p(l)$  were used to empirically calculate the heat capacity of the gas,  $C_p(g)$ , over the molecular weight and temperature ranges investigated and compared to a group contribution method. The functional forms for  $\Delta H_v(T, M)$ ,  $\Delta C_p(T, M)$ ,  $C_p(l)$ , and  $C_p(g)$  were also found to be applicable for  $n$ -alkanes. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 731–746, 1998

**Key words:** alkylcarboxylic; enthalpy; ester; molecular; oligomer; vaporization

## INTRODUCTION

Alkylcarboxylic esters are used extensively in industrial applications such as solvents and plasticizers.<sup>1–3</sup> Despite widespread usage of certain selected esters, few data of enthalpy of vaporization, liquid and gas heat capacity, and heat capacity difference measurements exist over extended temperature and molecular weight ranges. Estimation methods for enthalpy of vaporization and gas heat capacity may be found in the literature,<sup>4–7</sup> but estimations for liquid heat capacity are generally only available at or near 298.15 K and find limited use for higher temperatures. To address these limitations in this article, empirical

functions of temperature and molecular weight were used successfully to predict enthalpy changes within reasonable average error bounds ( $\approx \pm 5\%$ ). Liquid density of many of the compounds presented here over similar temperature and molecular weight ranges have previously been calculated to within average errors of  $\approx \pm 1\%$ .<sup>8</sup>

The molecular vaporization kinetics of esters, alkanes, and other classes of substances is often studied by vapor pressure<sup>9</sup> or weight loss techniques<sup>10,11</sup> to enhance the understanding of the decomposition of polyesters, hydrocarbon polymers, and other polymers. In theory, the rate of vaporization of high polymers is controlled by a mechanism involving the chemical breakage of bonds. In a high vacuum, the rate of vaporization is proportional to the weight of sample if the

**Table I** Some Characteristic Properties of Oligomers of Poly(hexamethylene sebacate)

General Formula	Molecular Weight (g/mol)		Melting Points (K)	Density (345.2 K, (g/cm <sup>3</sup> ))	Molar Refractivity	
	Found	Calc			Found	Calc
C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	371 ± 21	370.57	274	0.8915	107.18 ± 0.10	107.14
C <sub>38</sub> H <sub>70</sub> O <sub>8</sub>	659 ± 21	654.97	306	0.9386	184.28 ± 0.36	184.36
C <sub>54</sub> H <sub>98</sub> O <sub>12</sub>	922 ± 24	939.36	322	0.9577	261.78 ± 0.18	261.58

sample is of a certain thickness.<sup>10,11</sup> Most important is the size of molecules in the vaporization process. Below a critical limit of chain length, most molecules will vaporize molecularly with a rate that is dependent only on the surface area.<sup>10,11</sup> Assuming a random decomposition mechanism, the thermal decomposition of polyethylenes, polyamids, and polyesters were shown to occur in the temperature range of approximately 500–633 K. The sizes of the volatilizing fragments were about  $L \approx 72$  methylene units from the breaking of the C—C bond,  $L \approx 5$  peptide units from the breaking of the C—N bond, and  $L \approx 5$  carboxyl units from the breaking of the C—O bond.<sup>12–14</sup> The activation energies for these degradation processes depend on the number-average molecular weight and the rate of volatilization.<sup>12–14</sup>

## MOLECULAR VAPORIZATION

An exact treatment of the vaporization process of a simple molecular substance to a vapor consisting predominantly of single molecular species may be characterized thermodynamically by the pressure–temperature derivative of the Clapeyron and Clausius–Clapeyron equations.<sup>15–17</sup> Since the application of gas imperfection corrections to the enthalpy of vaporization,  $\Delta H_v$ , and the change in volume,  $\Delta V$ , from liquid to gas is often cumbersome, it is usually more convenient to consider vaporization as a reaction whose equilibrium constant is the ratio of the vapor fugacity,  $f_g$ , to the liquid activity,  $a_l$ , in which the free energy and enthalpy represent standard state changes; that is,  $\Delta G = \Delta G^0$  and  $\Delta H_v = \Delta H_v^0$ .

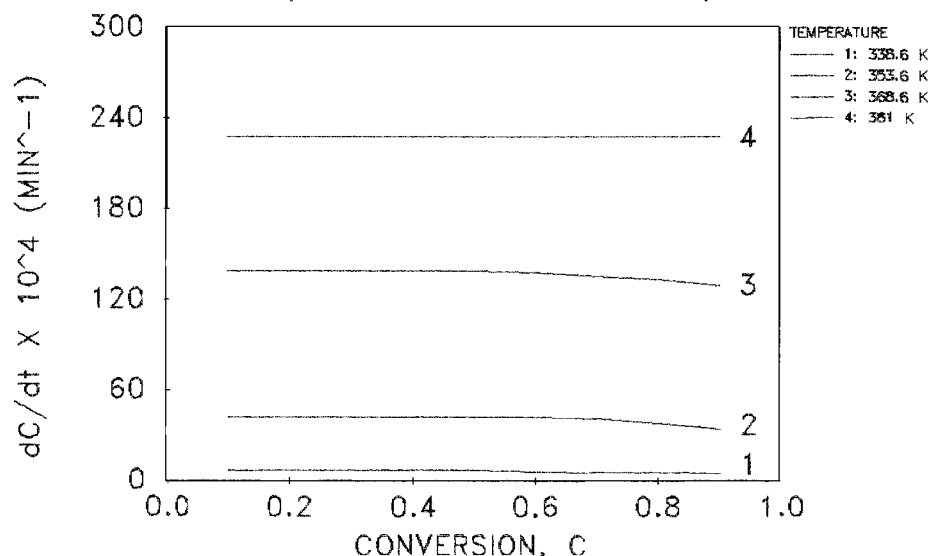
**Table II** Experimental Liquid Heat Capacity,  $C_{pe}(l)$ , Calculated Gas Values,  $C_p(g)$ , and Heat Capacity Difference,  $\Delta C_{pe} = C_{pe}(l) - C_p(g)$ , for Linear Oligomer Esters of Poly(hexamethylene sebacate)

Temperature (K)	Molecular Weight (g/mol)	$C_{pe}(l) \times 10^{-2}$ (J/mol K)	$C_p(g) \times 10^{-2}$ (J/mol K)	$\Delta C_{pe} \times 10^{-2}$ (J/mol K)
303.15	370.57	7.11	5.46	1.65
313.15	370.57	7.16	5.60	1.56
323.15	370.57	7.24	5.73	1.51
343.15	370.57	7.62	5.99	1.63
373.15	370.57	8.16	6.37	1.79
383.15	370.57	8.33	6.49	1.84
393.15	370.57	8.37	6.62	1.75
328.15	654.97	12.9	9.99	2.91
365.15	654.97	13.2	10.8	2.40
388.15	654.97	13.5	10.3	2.20
408.15	654.97	13.8	11.7	2.10
333.15	939.36	18.3	14.3	4.00
373.15	939.36	18.9	16.8	2.10
413.15	939.36	18.9	16.8	2.10
433.15	939.36	19.0	17.3	1.62

# RATES OF MOLECULAR VAPORIZATION

## OLIGOMER 1

### POLY(HEXAMETHYLENE SEBACATE)



**Figure 1** Rates of molecular vaporization,  $dC/dt$ , versus conversion,  $C$ , of oligomer 1 of poly(hexamethylene sebacate) at temperatures of: 338.6 K (1), 353.6 K (2), 368.6 K (3), and 381 K (4) ( $C = n/n_0$  = fraction of sample vaporized, where  $n$  = no. mol at time  $t$  and  $n_0$  = initial no. mol =  $10 \times 10^{-3}$  g/370.57 g/mol).

In many cases, the enthalpy of vaporization,  $\Delta H_v(T_1)$ , at a temperature  $T_1$  is experimentally measured, and the temperature dependence of  $\Delta H_v$  is determined from the heat capacity difference<sup>18,19</sup>; that is,

$$\Delta H_v(T) = \Delta H_v(T_1) + \int_{T_1}^T [C_p(l) - C_p(g)] dT \quad (1)$$

where  $\Delta C_p = C_p(l) - C_p(g)$  and  $C_p(l)$  and  $C_p(g)$  are the heat capacities of the liquid and gas, respectively, which were, estimated respectively, from published results of Phillips and Mat-tamal<sup>20</sup> and Rihani and Doraiswamy.<sup>21</sup>

In this article, the following determinations will be made:

1. the empirical temperature and molecular weight dependency of the enthalpy of vaporization,  $\Delta H_v(T, M)$ , from calculations based on equation (1) for the oligomeric esters of poly(hexamethylene sebacate)

and published values of 2 low-molecular-weight esters;

2. the empirical temperature and molecular weight dependency of the heat capacity difference,  $\Delta C_p(T, M)$ , from the temperature derivative of the empirical function of  $\Delta H_v(T, M)$ ; that is,

$$\Delta C_p(T, M) = -\delta \Delta H_v(T, M) / \delta T \quad (2)$$

3. comparative calculations of  $\Delta H_v(T, M)$  for the oligomeric series, linear esters of a sebacic series, branched esters of a triglyceride series, some selective alkane compounds, and other carboxylic esters; and
4. comparative calculations of  $C_p(g)$  from equation (2) and  $C_p(g)$  from Rihani et al.<sup>19</sup> for all of the alkylcarboxylic esters and alkane compounds reported in this article.

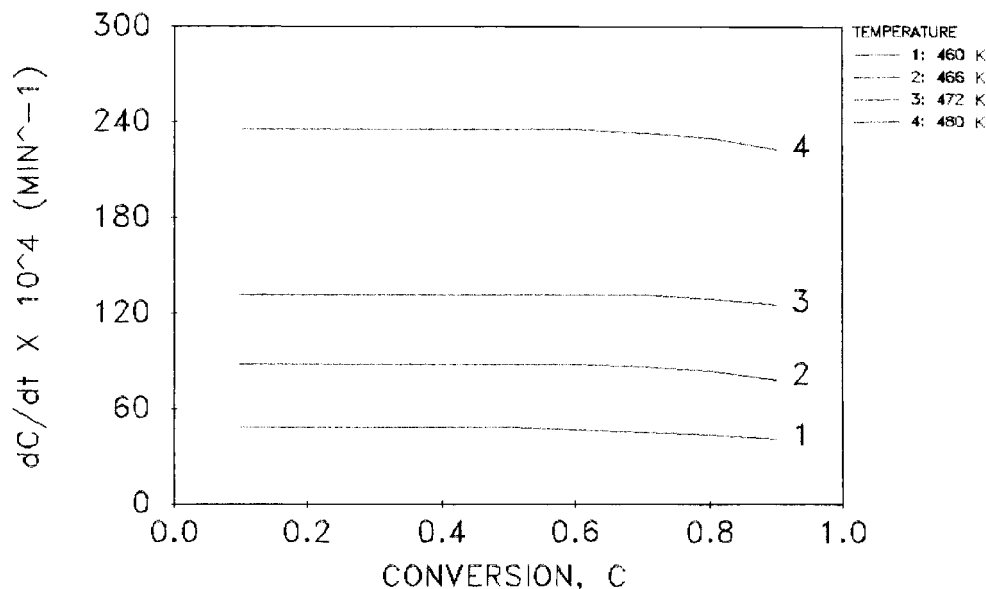
## EXPERIMENTAL

The oligomers of poly(hexamethylene sebacate) were prepared from an irreversible melt polycon-

# RATES OF MOLECULAR VAPORIZATION

## OLIGOMER 2

### POLY(HEXAMETHYLENE SEBACATE)



**Figure 2** Rates of molecular vaporization,  $dC/dt$ , versus conversion,  $C$ , of oligomer 2 of poly(hexamethylene sebacate) at temperatures of: 460 K (1), 466 K (2), 472 K (3), and 480 K (4) ( $C = n/n_0$  = fraction of sample vaporized, where  $n$  = no. mol at time,  $t$ , and  $n_0$  = initial no. mol =  $10 \times 10^{-3}$  g/654.97 g/mol).

densation technique, separated by adsorption chromatography, and characterized from infrared (IR) and nuclear magnetic resonance (NMR) spectra, molecular weights, molar refractivity, melting points, rates of vaporization, and density measurements.<sup>18-20</sup> Some of the characteristic properties of the oligomers are presented in Table I. The liquid heat capacities of the oligomers were determined within estimated errors of  $\pm 3\%$  (scans and calibration) with a differential scanning calorimeter (DSC-1B, Perkin-Elmer),\* and the technique and procedure are presented elsewhere.<sup>20-22</sup> The experimental liquid (melt) heat capacities of the oligomers are presented in Table II.

#### Rates of Molecular Vaporization

A thermogravimetric analysis (TGA) instrument was used to determine the rates of molecular va-

porization.<sup>22</sup> The experimental procedure consisted of suspending a quartz bucket ( $4 \times 10$  mm) containing a 10-mg sample by a  $76.2\text{-}\mu\text{m}$  tungsten wire hung from a weighing beam. All runs were reproducible to  $\pm 1.0\%$ . An all-glass vacuum chamber that enclosed the sample and furnace was evacuated to approximately  $1.33322 \times 10^{-1}$  Pa pressure. The loss in weight of the sample was monitored to within 2.0% by an electrobalance coupled with an electronic chart recorder.

An expression for the enthalpy of vaporization,  $\Delta H_v(T)$ , in terms of the vaporization rate,  $dn/dt$  (mol/s), is given as<sup>18,22</sup>:

$$\begin{aligned} \Delta H_v(T) &= \Delta E_v(T) + RT \\ &= -\frac{Rd \ln(dn/dt)}{d(1/T)} + (3/2)RT \quad (3) \end{aligned}$$

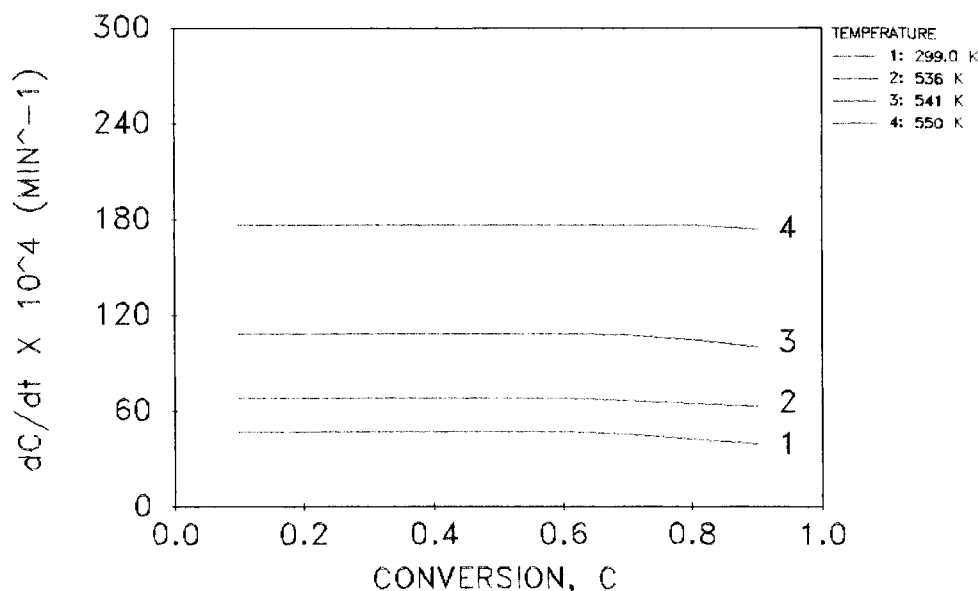
where  $\Delta E_v(T)$  is the internal energy of vaporization,  $R$  is gas constant,  $T$  is absolute temperature, and the quantity  $-Rd \ln(dn/dt)/d(1/T)$  is called the apparent Arrhenius activation energy,  $e_v$ . Hence, from a number of isothermal runs over a finite temperature interval, the enthalpy of vaporization,  $\Delta H_v(T_I)$ , may be determined at the mean temperature,  $T = \bar{T} = T_1$ , of the interval.

\* Certain commercial equipment, instruments, or materials are identified in this article in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards [presently, NIST], nor does it imply that the materials or equipment is the best available for the purpose.

# RATES OF MOLECULAR VAPORIZATION

## OLIGOMER 3

### POLY(HEXAMETHYLENE SEBACATE)

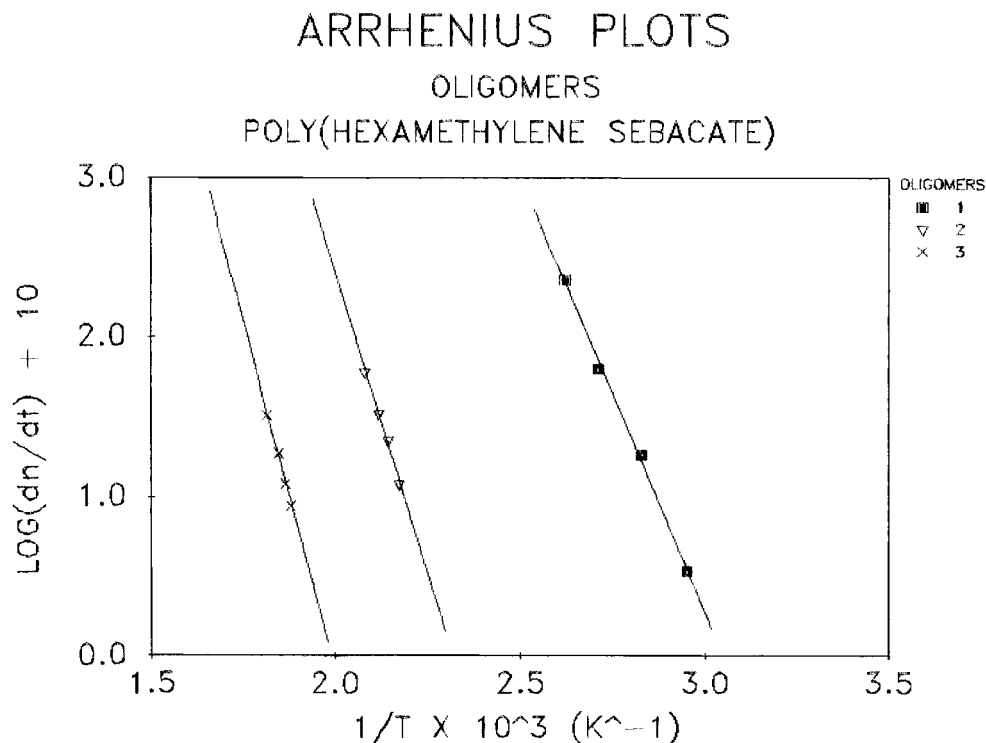


**Figure 3** Rates of molecular vaporization,  $dC/dt$ , versus conversion,  $C$ , of oligomer 3 of poly(hexamethylene sebacate) at temperatures of: 299.0 K (1), 536 K (2), 541 K (3), and 550 K (4) ( $C = n/n_0$  = fraction of sample vaporized, where  $n$  = no. mol at time,  $t$ , and  $n_0$  = initial no. mol =  $10 \times 10^{-3}$  g/939.36 g/mol).

The rate of vaporization,  $dC/dt$ , in reciprocal minutes ( $\text{min}^{-1}$ ) versus the conversion,  $C$  (fraction of initial sample volatilized), is given in Figures 1, 2, and 3, respectively, for oligomers 1, 2, and 3. In Figure 4, is shown a plot of  $\log(dn/dt)$  versus the reciprocal of the absolute temperature ( $1/T$ ) where  $dn/dt = n_0 \times dC/dt$  [ $C$  = fraction vaporized =  $n/n_0$ ;  $n$  = no. mol of sample = mass ( $t$ )/molar mass of sample;  $n_0$  = initial no. mol = the initial mass ( $t = 0$ )/molar mass of sample (the initial mass in this study was  $10 \times 10^{-3}$  g)]. From the slope of the diagonal lines, the activation energies,  $e_v$ , for oligomers 1, 2, and 3 were determined to be, respectively, 1.00, 1.34, and  $1.68 \times 10^2$  KJ/mol. The activation energies,  $e_v$ , in conjunction with equation (3) was used to calculate the enthalpies of vaporization,  $\Delta H_v(T) = \Delta H_{v0}(T, M)$  at  $T = T_1$ , and these values are shown in Table III ( $e$  = experimental). Small changes in the rate at high conversion, produced uncertainties in  $\Delta H_v(T_1)$  for oligomers 1, 2, and 3, respectively, of approximately 5, 8, and 10%. Errors due to sample size and bucket composition are discussed elsewhere.<sup>22</sup>

#### Calculated Gas Heat Capacity

In order to estimate the enthalpies of vaporization at temperature  $T$ , the heat capacity difference,  $\Delta C_p(T, M)$ , of liquid and gas heat capacities must be known over the temperature range of  $T$  and  $T_1$ ; that is,  $\Delta C_p(T, M) = C_p(l) - C_p(g)$ . The liquid heat capacity,  $C_p(l)$ , was obtained from previously published values.<sup>20</sup> Since experimental gas heat capacity,  $C_p(g)$ , for carboxylic esters were not easily available, the group contribution method of Rihani and Doraiswamy<sup>21</sup> was used to calculate these values. The group contribution method had been tested successfully on a number of hydrocarbons by Reid and Sherwood.<sup>4</sup> Gas values for polar compounds (*l*-eicosanol,  $M = 298.5$  g/mol; decanol,  $M = 156.3$  g/mol; *n*-butyl ether,  $M = 130.2$  g/mol) and higher-molecular-weight *n*-alkane compounds (tritricontane,  $M = 464.0$  g/mol; *n*-eicosane,  $M = 282.5$  g/mol) were calculated and found to be in agreement with measurements of Stull et al.<sup>23</sup> to within 5%. In order to further test the method for the gas values for the oligomers of poly(hexamethylene



**Figure 4** Arrhenius plots of  $\log(dn/dt)$  versus the reciprocal of the absolute temperature ( $1/T$ ) [ $dn/dt = n_0 \times dC/dt$ , where  $C = n/n_0 =$  the conversion = the fraction vaporized,  $n =$  no. mol, and  $n_0 =$  the initial no. mol = mass of sample ( $10 \times 10^{-3}$  g)/molar mass of sample (MW)]. The activation energies,  $e_v$ , determine for oligomers 1, 2, and 3, were found to be, respectively, 1.00, 1.34, and  $1.68 \times 10^2$  KJ/mol.

sebacate), the calculations of the empirical approach of Rihani were compared to the theoretical approach of Dobratz<sup>24</sup> and found to agree within 10%. The calculated gas values are presented in Table II.

#### Heat Capacity Difference

The correction integral in equation (1) was determined by 3 methods, as follows below.

$$I_j = \int_T^{T_1} \Delta C_{pj}(T, M) dT \quad (4)$$

where the values of  $\Delta C_{pj}(T, M)$  were determined from calculated gas heat capacity values<sup>17,18</sup> for  $j = e, n$ , and  $c$ ; for  $j = e$  and  $n$ , experimental liquid heat capacity values were used; for  $j = c$ , liquid heat capacity values were calculated from an empirical function.<sup>20</sup>

#### Method 1

In equation (4), the integral  $I_e$  was obtained from a graphical integration plot of  $\Delta C_{pe}(T, M)$  over the temperature range of  $T \rightarrow T_1$  using experimental liquid heat capacity and calculated gas heat capacity. The graphical areas were determined with a planimeter having an accuracy better than 1%. These values, along with the enthalpies of vaporization,  $\Delta H_{ve}(T)$ , are tabulated in Table III.

#### Method 2

In the second method, the heat capacity difference,  $\Delta C_{pn}(T, M)$ , was calculated from a correlation model for flexible  $n$ -alkanes<sup>7,25</sup>; that is,

$$\Delta C_{pn}(T, M) = A(M)/T + 2R \quad (5)$$

where  $A(M) = kM$  is a function of molecular weight, and  $R$  is the gas constant. The constant  $k$  may be obtained as follows: (1) from the flexible

**Table III** The Correction Integrals (KJ/mol),  $I_j$ , Heats of Vaporization (KJ/mol),  $\Delta H_{vj}(T)$ , and Heat Capacity Difference (KJ/mol K),  $\Delta C_{pj}$ , Determined According to Method 1 [ $j = e$  (Experimental Liquid Heat Capacity/Group Contribution Method for gas)], Method 2 [ $j = n$  (Flexible Model for  $n$ -Alkanes)], and Method 3 [ $j = c$  (Empirical Liquid Heat Capacity/Group Contribution Method for Gas)]

Temperature (K)	$j$	$M = 370.57 \text{ g/mol}$			$M = 654.97 \text{ g/mol}$			$M = 939.36 \text{ g/mol}$		
		KJ/mol		KJ/mol <sup>-1</sup> K <sup>-1</sup>	KJ/mol		KJ/mol <sup>-1</sup> K <sup>-1</sup>	KJ/mol		KJ/mol <sup>-1</sup> K <sup>-1</sup>
		$I_j$	$\Delta H_{vj}(T)$	$\Delta C_{pj}$	$I_j$	$\Delta H_{vj}(T)$	$\Delta C_{pj}$	$I_j$	$\Delta H_{vj}(T)$	$\Delta C_{pj}$
298.15	e:	10.0	114.4	0.165						
	n:	8.1	112.5	0.141	33.6	173.4	0.237	59.8	234.8	0.332
	c:	11.3	115.7	0.197	41.5	181.3	0.308	58.1	233.1	0.383
323.15	e:	6.2	110.6	0.151						
	n:	4.7	109.1	0.132	27.9	167.7	0.220	51.8	226.8	0.308
	c:	6.5	110.9	0.184	34.2	174.0	0.285	49.1	224.1	0.348
348.15	e:	2.1	106.5	0.172	26.3	166.1	0.263	30.3	205.3	0.316
	n:	1.5	106.0	0.123	22.6	162.4	0.205	44.4	219.4	0.287
	c:	2.1	106.5	0.172	27.4	167.2	0.263	40.9	215.9	0.316
[360.55] <sup>a</sup>		0.0	104.4							
393.15	e:	-5.9	98.5	0.175	15.1	154.9	0.228	16.3	191.2	0.263
	n:	-3.8	100.6	0.111	13.9	153.7	0.184	32.2	207.2	0.256
	c:	-5.2	99.2	0.152	16.4	156.2	0.228	28.1	200.1	0.263
423.15	e:	-11.9	92.5	0.140	8.8	148.6	0.207	9.8	184.8	0.232
	n:	-7.0	97.4	0.104	8.6	148.4	0.172	24.8	199.8	0.239
	c:	-9.5	94.9	0.140	10.0	149.8	0.207	20.8	195.8	0.232
473.15	e:	-20.1	84.4	0.124	0.3	140.1	0.178	2.3	177.3	0.189
	n:	-12.0	92.4	0.095	0.4	140.2	0.155	13.4	188.4	0.216
	c:	-16.1	88.3	0.124	0.4	140.2	0.178	10.6	185.6	0.189
[475.65] <sup>a</sup>					0.0	139.8				
523.15	e:			0.112	-4.8	135.4	0.156	0.4	175.4	0.154
	n:	-16.5	87.9	0.088	-7.0	132.8	0.142	3.1	178.1	0.197
	c:	-22.0	82.4	0.112	-7.8	132.0	0.156	2.3	177.3	0.154
[539.35] <sup>a</sup>								0.0	175.0	

<sup>a</sup> Experimental heats of vaporization  $\Delta H_v(T_1)$ , at mean temperature,  $T_1$ .

$n$ -alkane model, the constant  $k = Tf(\rho^*)$ , where  $T$  is the absolute temperature and  $f(\rho^*)$  is a function of the reduced density,  $\rho^*$ ; or, (2) use  $\Delta C_p = \Delta C_{pe}$  to calculate  $A(M) = kM$  from a plot of  $\Delta C_p$  versus  $1/T$  ( $T = \text{deg K}$ ); that is,  $k = \text{slope}/M$  with intercept  $2R$ ; empirically,  $k$  was found to be  $k = 0.1002 \pm 0.0185$ . From equation (5), the correction integral,  $I_n$ , was obtained as follows:

$$I_n = [A(M)\ln(T_1/T)] + 2R(T_1 - T) \quad (6)$$

The integral values calculated from equation (6), along with values of the heat capacity difference,  $\Delta C_{pn}$ , from equation (5), and the enthalpies of vaporization,  $\Delta H_{vn}(T)$ , from equation (1) for the oligomers of poly(hexamethylene sebacate) are tabulated in Table III.

### Method 3

In the third method, the correction integral,  $I_c$ , was determined from the heat capacity difference,  $\Delta C_{pc} = C_{pc}(l) - C_p(g)$ , where the liquid heat capacity,  $C_{pc}(l)$ , was empirically calculated from Phillips et al.<sup>20</sup> and the gas heat capacity,  $C_p(g)$ , was calculated from the group contribution method of Rihani and Doraiswamy.<sup>21</sup> These values, along with the heats of vaporization,  $\Delta H_{vc}(T)$ , are also tabulated in Table III.

**Table IV** Estimated Values for Constant Ratios,  $K_{12}$ , for  $i = 1, 2, 3$ , and  $4$  from Phillips and Mattamal.<sup>20</sup>

$i$	$K_{i2}$	Estimated Value
1	$K_{12}$	1.03
2	$K_{22}$	1.00
3	$K_{32}$	0.80
4	$K_{42}$	0.97

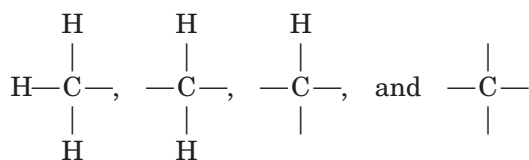
**Table V** Group Contribution Constants,  $a_{ij}$ , for Gas Heat Capacities for Group,  $i$ , and Term,  $j$  [for  $i = 1, 2, 3$ , and 4; and  $j = 1, 2, 3$ , and 4 for a Given  $i$ ] According to Equations (14)–(16) Taken from Rihani et al.<sup>21</sup>

$i$	Group	$a_{ij}$			
		$j =$			
		1	2 ( $\times 10^2$ )	3 ( $\times 10^4$ )	4 ( $\times 10^6$ )
1	—CH <sub>3</sub>	0.6087	2.1433	−0.0852	0.001135
2	—CH <sub>2</sub> —	0.3945	2.1363	−.01197	0.002596
3	—CH— 	−3.5232	3.4158	−0.2816	0.008015
4	—C— 	−5.8307	4.4541	−0.4208	0.012630
$i = (\text{COO})$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—O—} \end{array}$	2.7350	1.0751	0.0667	−0.009230

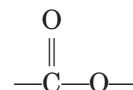
## RESULTS

### Liquid Heat Capacity

Linear and branched carboxylic esters are composed of alkane groups,  $N_i$ , and ester groups,  $N_{\text{COO}}$  [symbols and notations are those used by Somayajulu and Zwolinski]. For  $i = 1, 2, 3$ , and 4, the alkane groups are



and the ester group is represented as



The molecular weight of the ester molecule is given as

$$M = \left[ \sum_{i=1}^4 W_i N_i \right] + W_{\text{COO}} N_{\text{COO}} \quad (7)$$

where  $W_1$  and  $W_{\text{COO}}$  are the respective molar weights of the alkane groups and carboxyl group

**Table VI** Atmospheric Heats of Vaporization,  $\Delta H_v(T_b, M)$ , at Experimental Temperature,  $T_b$ , for the Linear Oligomer Esters of Poly(hexamethylene sebacate) Compared to Calculated Values According to Equation (24). Heat Capacity Difference,  $\Delta C_p(T_b, M)$ , and Comparative Gas Heat Capacities,  $C_p(g)$ , According, Respectively, to Equations (26), (28), and (14).<sup>a</sup>

$x$	Empirical Formula	MW, $M$ (g/mol)	Temp [ $T = T_1$ ] (K)	Calculations					
				$\Delta H_v(T_1, M)^b$ (KJ/mol)			$\Delta C_p(T_1, M)$ (J/mol K)		$C_p(g)$ (J/mol K)
				Exptl	Calcd	% Dev	Eq. (26)	Eq. (28)	Eq. (14)
1	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	370.57	360.55	104.4	97.3	−6.8	109.1	678.2	621.7
2	C <sub>38</sub> H <sub>70</sub> O <sub>8</sub>	654.97	475.65	139.8	137.8	−1.4	134.4	1343.9	1303.4
3	C <sub>54</sub> H <sub>98</sub> O <sub>12</sub>	939.36	539.35	175.0	171.1	−1.1	158.3	1991.7	2010.9

<sup>a</sup> CH<sub>3</sub>—(CH<sub>2</sub>)<sub>5</sub>—OOC—(CH<sub>2</sub>)<sub>8</sub>—COO—[(CH<sub>2</sub>)<sub>6</sub>—OOC—(CH<sub>2</sub>)<sub>8</sub>—COO] <sub>$x-1$</sub> —(CH<sub>2</sub>)<sub>5</sub>—CH<sub>3</sub> where  $x = 1, 2, 3, \dots$

<sup>b</sup> Average error =  $\pm 3.1\%$ .



**Table VII Atmospheric Heats of Vaporization,  $\Delta H_v(T_p, M)$ , at Experimental Temperature,  $T_p$ , for the Linear Esters of Sebacic Series Compared to Calculated Values According to Equation (24). Heat Capacity Difference,  $\Delta C_p(T_p, M)$ , and Comparative Gas Heat Capacities,  $C_p(g)$ , According, Respectively, to Equations (26), (28), and (14).<sup>a</sup>**

Empirical Formula	MW, $M$ (g/mol)	Temp $T = T_p$ (K)	Calculation					
			$\Delta H_v(T_1, M)^b$ (KJ/mol)			$\Delta C_p(T_1, M)$ (J/mol K)	$C_p(g)$ (J/mol K)	
			Exptl. <sup>c</sup>	Calcd.	% Dev.	Eq. (26)	Eq. (28)	Eq. (14)
C <sub>18</sub> H <sub>34</sub> O <sub>4</sub> (di- <i>n</i> -Butyl sebacate)	314.47	327.15	88.2	88.4	0.20	104.0	535.2	474.8
C <sub>22</sub> H <sub>42</sub> O <sub>4</sub> (di- <i>n</i> -Hexyl sebacate)	370.57	344.15	99.9	99.2	-0.74	113.7	660.3	600.7
C <sub>26</sub> H <sub>50</sub> O <sub>4</sub> (di- <i>n</i> -Octyl sebacate)	426.68	368.15	109.7	108.4	-1.2	120.1	799.8	744.5
C <sub>30</sub> H <sub>58</sub> O <sub>4</sub> (di- <i>n</i> -Decyl sebacate)	482.79	405.45	120.5	115.3	-4.3	121.8	964.6	920.0
C <sub>34</sub> H <sub>66</sub> O <sub>4</sub> (di- <i>n</i> -Dodecyl sebacate)	539.00	420.15	132.0	124.3	-5.8	128.9	1107.1	1068.5
C <sub>38</sub> H <sub>74</sub> O <sub>4</sub> (di- <i>n</i> -Tetradecyl sebacate)	595.00	439.85	142.8	132.1	-7.5	133.8	1261.9	1232.5
C <sub>42</sub> H <sub>82</sub> O <sub>4</sub> (di- <i>n</i> -Hexadecyl sebacate)	651.11	460.25	149.8	139.3	-7.0	137.9	1424.0	1405.1
C <sub>46</sub> H <sub>90</sub> O <sub>4</sub> (di- <i>n</i> -Octadecyl sebacate)	707.22	480.15	157.5	146.0	-7.3	141.6	1592.1	1583.6

<sup>a</sup> CH<sub>3</sub>—(CH<sub>2</sub>)<sub>*x*</sub>—OOC—(CH<sub>2</sub>)<sub>8</sub>—COO—(CH<sub>2</sub>)<sub>*x*</sub>CH<sub>3</sub> where *x* = 3 - 17.

<sup>b</sup> Average error = ±4.3%.

<sup>c</sup> Taken from Mattamal.<sup>28</sup>

$W_1 = 15.034$  g/mol;  $W_2 = 14.027$  g/mol;  $W_3 = 13.019$  g/mol;  $W_4 = 12.011$  g/mol;  $W_{\text{COO}} = 44.010$  g/mol.

The liquid heat capacity of an ester molecule may be considered linear<sup>4,20,26</sup> in the number of alkane groups,  $N_1$ , and in the number of ester groups,  $N_{\text{COO}}$ ; that is,

$$C_p(l) = \left[ \sum_{i=1}^4 G_i(T)N_i \right] + G_{\text{COO}}(T, N_2)N_{\text{COO}} \quad (8)$$

where the sum in equation (8) represents the contributions due to the alkane portion and  $G_{\text{COO}}(T, N_2)N_{\text{COO}}$  that due to the carboxyl groups. By utilizing equation (7) and solving for  $N_2$ , the molecular weight dependence of equation (8) after inserting  $N_2$  and simplifying becomes

$$C_p(l) = [G_2(T)/W_2]M + \Delta_1 N_1 + \Delta_3 N_3 + \Delta_4 N_4 + \Delta_{\text{COO}} N_{\text{COO}} \quad (9)$$

where for the alkanes,  $\Delta_1 = G_1(T) - \{[G_2(T)/W_2]W_1\}$ ,  $i = 1, 3$ , and  $4$ ; and, for the carboxyl group,  $\Delta_{\text{COO}} = G_{\text{COO}}(T, N_2) - \{[G_2(T)/W_2]W_{\text{COO}}\}$ .

### Temperature-Dependent Coefficients

The coefficients,  $G_1(T)$ , for the alkane groups may be represented as

$$G_i(T) = k_i T + b_i = K_{i2} G_2(T) \quad (10)$$

where  $k_i$ ,  $b_i$ , and  $k_{i2}$  are constants; the constant  $k_i = k_2 \times k_{i2}$  and  $b_i = b_2 \times k_{i2}$ . The constants,  $k_{i2}$ , have been estimated and are tabulated in Table IV. The coefficient,  $G_2(T)$ , for the group, —CH<sub>2</sub>—, has been determined empirically by Broadhurst<sup>27</sup> and is given as

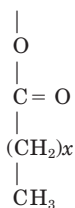
$$G_2(T) = k_2 T + b_2 \quad (11)$$

where  $k_2 = 0.0342$  J/mol K<sup>2</sup> and  $b_2 = 20.9$  J/mol K.

**Table VIII Atmospheric Heats of Vaporization,  $\Delta H_v(T_b, M)$ , at Experimental Temperature,  $T_l$ , for Separate Branched Esters of Triglyceride Series Compared to Calculated Values According to Equation (24). Heat Capacity Difference,  $\Delta C_p(T_b, M)$ , and Comparative Gas heat Capacities,  $C_p(g)$ , According, Respectively, to Equations (26), (28), and (14).<sup>a</sup>**

Empirical Formula	MW, <i>M</i> (g/mol)	Temp $T = T_l$ (K)	$\Delta H_v(T_1, M)^b$ (KJ/mol)			Calculation		
			Exptl <sup>c</sup>	Calcd	% Dev	$\Delta C_p(T_1, M)$ (J/mol K) Eq. (26)	$C_p(g)$ (J/mol K) Eq. (28)	Eq. (14)
C <sub>15</sub> H <sub>26</sub> O <sub>6</sub> (Tributyrin)	302.37	308.55	83.5	87.5	4.8	106.0	465.6	344.9
C <sub>21</sub> H <sub>38</sub> O <sub>6</sub> (Tricaproin)	386.53	349.35	99.9	102.1	2.2	116.1	661.4	542.4
C <sub>27</sub> H <sub>50</sub> O <sub>6</sub> (Trioctanoin)	470.69	386.15	118.7	115.2	-2.9	124.6	870.0	760.4
C <sub>33</sub> H <sub>62</sub> O <sub>6</sub> (Tridecanoin)	554.85	411.45	130.5	128.4	-1.6	134.4	1077.8	980.8
C <sub>39</sub> H <sub>74</sub> O <sub>6</sub> (Trilaurin)	639.01	437.95	147.1	140.2	-4.7	142.1	1299.6	1218.4
C <sub>45</sub> H <sub>86</sub> O <sub>6</sub> (Trimyristin)	723.17	468.75	155.8	150.3	-3.5	147.3	1541.9	1480.2
C <sub>51</sub> H <sub>98</sub> O <sub>6</sub> (Tripalmitin)	807.34	483.15	166.3	161.9	-2.6	156.0	1765.0	1717.8
C <sub>57</sub> H <sub>110</sub> O <sub>6</sub> (Tristearin)	891.50	505.85	174.9	171.4	-2.0	161.4	2014.7	1985.3

<sup>a</sup> CH<sub>3</sub>-(CH<sub>2</sub>)<sub>x</sub>-COO-CH<sub>2</sub>-CH-CH<sub>2</sub>-OOC-(CH<sub>2</sub>)<sub>x</sub>-CH<sub>3</sub> where  $x = 2 - 16$ .



<sup>b</sup> Average error =  $\pm 3.0\%$ .

<sup>c</sup> Taken from Mattamal.<sup>28</sup>

The coefficient,  $G_{\text{COO}}(T, N_2)$ , for the carboxyl group has been determined empirically by Phillips and Mattamal<sup>20</sup> and is given as

$$G_{\text{COO}}(T, N_2) = K_{\text{COO}} G_2(T) \quad (12)$$

where  $K_{\text{COO}}$  is expressed as

$$\begin{aligned}
 K_{\text{COO}} &= F(N_2) + c \\
 &= \left\{ \frac{[-0.025N_2 + 1.40]}{[1 + 0.0015(N_2)^2]} \right\} + 0.90 \quad (13)
 \end{aligned}$$

where the first term on the right is the function,  $F(N_2)$ , and the second term is the constant,  $c = 0.90$ .

### Gas Heat Capacity

The calculated values for the gas heat capacity were determined from the group contribution method of Rihani and Doraiswamy<sup>21</sup> and may be summarized as follows:

$$C_p(g) = \left[ \sum_{i=1}^4 R_i(T) \right] + R_{\text{COO}}(T) \quad (14)$$

where,

$$R_i(T) = \left\{ \sum_{j=1}^4 [a_{ij} T^{j-1}] \right\} N_i \quad (15)$$

**Table IX Atmospheric Heats of Vaporization,  $\Delta H_v(T, M)$ , at Experimental Temperature,  $T_b$ , for  $n$ -Alkanes Compared to Calculated Values According to Equation (24). Heat Capacity Difference,  $\Delta C_p(T, M)$ , and Comparative Gas Heat Capacities,  $C_p(g)$ , According, Respectively, to Equations (26), (28), and (14).**

Empirical Formula	MW, $M$ (g/mol)	Temp $T = T_1$ (K)	Calculation					
			$\Delta H_v(T_1, M)^b$ (KJ/mol)			$\Delta C_p(T_1, M)$ (J/mol K)	$C_p(g)$ (J/mol K)	
			Exptl	Calcd	% Dev	Eq. (26)	Eq. (28)	Eq. (14)
$C_{10}H_{22}^c$ ( $n$ -Decane)	142.28	433	35.8	41.9	17.0	45.1	314.5	324.9
$C_{19}H_{40}^d$ ( $n$ -Pristine)	268.53	308.15	79.1	79.1	0.0	96.3	503.5	474.7
$C_{24}H_{50}^d$ ( $n$ -Tetracosane)	338.66	348.15	92.1	91.7	-0.48	104.6	685.4	656.8
$C_{36}H_{74}^d$ ( $n$ -Hexatricosane)	506.98	418.15	126.4	118.4	-6.3	123.2	1147.2	1124.5
$C_{94}H_{190}^d$ ( $n$ -Tetranonacontane)	1320.54	618.15	200.0	209.3	4.6	179.2	3778.5	3801.4

<sup>a</sup>  $CH_3-(CH_2)_x-CH_3 = C_nH_{2n+2}$  where  $x = 8 - 92$  and  $n = x + 2$ .

<sup>b</sup> Average error = 5.7%.

<sup>c</sup> Taken from the literature.<sup>29</sup>

<sup>d</sup> Taken from Wall et al.<sup>22</sup>

and,

$$R_{COO}(T) = \left\{ \sum_{j=1}^4 [a_{(COO)_j} T^{j-1}] \right\} \quad (16)$$

where  $a_{ij}$  and  $a_{(COO)_j}$  are constants, respectively, for alkane groups,  $i$ , and ester group, COO;  $j$  represents the term in the sum of equations (14)–(16). These constants are given in Table V.

### Heat Capacity Difference and Heat of Vaporization

The results of equation (8) and equations (10)–(16) were used to determine the heat capacity difference, as follows:

$$\Delta C_p = \Delta C_p(T, M) = \left\{ \sum_{i=1}^4 [G_i(T) - R_i(T)] \right\} N_i + \{ [G_{COO}(T, N_2) - R_{COO}(T)] \} N_{COO} \quad (17)$$

By defining  $D_i(T) = G_i(T) - R_i(T)$  and  $D_{COO}(T) = G_{COO}(T, N_2) - R_{COO}(T)$  and solving for  $N_2$  from equation (7), the molecular weight dependence of equation (16) may be given as

$$\Delta C_p = \{ [D_2(T)/W_2] M \} + \Delta'_1 N_1 + \Delta'_3 N_3 + \Delta'_4 N_4 + \Delta'_{COO} N_{COO} \quad (18)$$

where  $\Delta'_i = D_i(T) - \{ [D_2(T)/W_2] W_i \}$  for  $i = 1, 3$ , and 4, and  $\Delta_{COO} = D_{COO} - \{ [D_2(T)/W_2] W_{COO} \}$ .

The correction integral,  $I_c$ , may be defined from equation (4) as

$$I_c = \int_T^{T_i} \Delta C_p dT = \left[ \sum_{i=1}^4 I_{ci} \right] + I_{c(COO)} \quad (19)$$

and where the integral,  $I_{ci}$ , is expressed as

$$I_{ci} = N_i \left\{ \sum_{j=1}^2 [(1/j) \{ (k_{i2} k_{22}) - a_{ij} \} (T^j - (T_1)^j)] \right\} - \left\{ \sum_{j=3}^4 [(1/j) b_{i(j-1)} (T^j - (T_1)^j)] \right\} \quad (20)$$

and

$$I_{c(COO)} = N_{COO} \left\{ \sum_{j=1}^2 [(1/j) \times \{ (K_{COO} k_{22}) - a_{(COO)(j-1)} \} (T^j - (T_1)^j)] \right\} - \left\{ \sum_{j=3}^4 [(1/j) b_{(COO)(j-1)} (T^j - (T_1)^j)] \right\} \quad (21)$$

where  $G_{COO}(T, N_2)$  and  $K_{COO}$  are, respectively, given in equations (12) and (13).

**Table X Atmospheric Heats of Vaporization,  $\Delta H_v(T_b, M)$ , at Experimental Temperature,  $T_b$ , for Carboxylic Esters Compared to Calculated Values According to Equation (24). Heat Capacity Difference,  $\Delta C_p(T_b, M)$ , and Comparative Gas Heat Capacities,  $C_p(g)$ , are According, Respectively, to Equations (26), (28), and (14).**

Empirical Formula	MW, $M$ (g/mol)	Temp $T = T_b$ (K)	Calculation					
			$\Delta H_v(T_1, M)^{a,b}$ (KJ/mol)			$\Delta C_p(T_1, M)$ (J/mol K)	$C_p(g)$ (J/mol K)	
			Exptl. <sup>b</sup>	Calcd.	% Dev.	Eq. (26)	Eq. (28)	Eq. (14)
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> (methyl acetate)	74.08	273	35.4	32.0	-9.7	39.8	92.2	74.0
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> (methyl propionate)	88.11	352	29.5	32.6	10.4	37.6	138.2	116.2
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> (ethyl acetate)	88.11	273	37.6	35.8	-4.7	44.9	116.6	96.5
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> ( <i>n</i> -Propylacetate)	102.13	373.6	32.4	35.2	8.5	39.9	172.8	150.0
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> (methyl Isobutyrate)	102.13	364.2	33.4	35.5	6.4	40.6	170.1	147.2
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> (methyl <i>n</i> -butyrate)	102.13	375.8	34.1	35.1	2.9	39.7	173.4	150.7
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> (ethyl Propionate)	102.13	372.8	34.2	35.3	3.1	40.1	172.0	149.2
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub> (iso-butyl <i>n</i> -Valerate)	158.24	442	38.2	45.0	17.8	47.8	315.8	254.8
C <sub>10</sub> H <sub>20</sub> O <sub>2</sub> (ethyl caprylate)	172.27	480	43.5	46.2	6.1	47.8	369.6	350.5
C <sub>11</sub> H <sub>22</sub> O <sub>2</sub> (ethyl nonylate)	186.29	500	45.2	48.1	6.4	49.1	413.0	395.6

<sup>a</sup> Average error =  $\pm 7.6\%$ .

<sup>b</sup> Data taken from the literature.<sup>29</sup>

The molecular weight dependence of  $I_c$  in equation (19) may be derived by solving equation (7) for  $N_2$  and inserting the results into equations (19) and (20) to give

$$I_c = [(I_2/W_2)M] + \Delta_1''N_1 + \Delta_3''N_3 + \Delta_4''N_4 + \Delta_{\text{COO}}''N_{\text{COO}} \quad (22)$$

where  $\Delta_i'' = I_{ci} - [(I_{c2}/W_2)W_i]$  for  $i = 1, 3$ , and  $4$  and  $\Delta_{\text{COO}}'' = I_{c(\text{COO})} - [(I_{c2}/W_2)W_{\text{COO}}]$ . From the results of equation (22), the heat of vaporization may be expressed as

$$\Delta H_{vc}(T, M) = \Delta H_v(T_1, M) + I_c \quad (23)$$

The results calculated from equations (17) or (18), (19) or (22) and (23) (method 3;  $j = c$ ) are tabulated in Table III.

## EMPIRICAL RELATIONS

### Enthalpy of Vaporization and Heat Capacity Difference

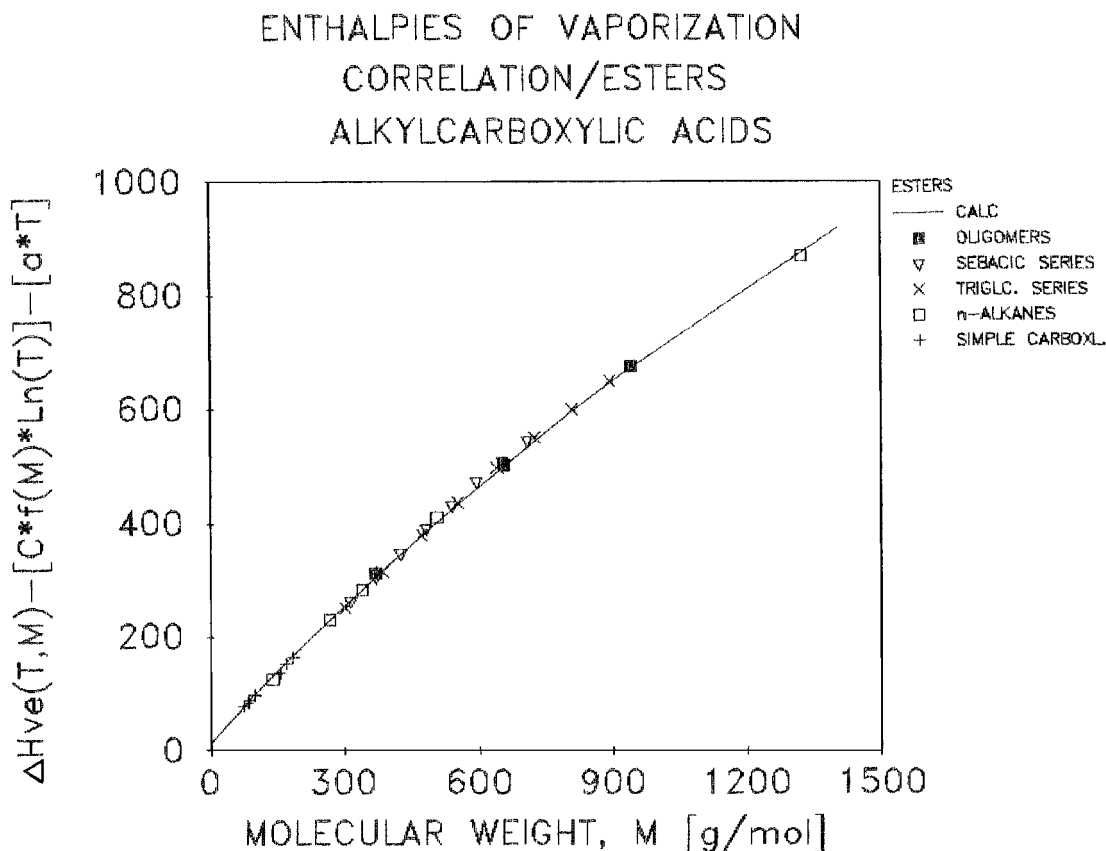
The enthalpy of vaporization results for the oligomers of poly(hexamethylene sebacate) in Table III [ $\Delta H_{ve}(T)$ ] along with published values for isobutyl acetate and ethyl caprylate,<sup>26</sup> were used to derive the empirical molecular weight and temperature dependent enthalpy of vaporization in KJ/mol; that is,

$$\Delta H_v(T, M) = S(T)f(M) + I_0(T) \quad (24)$$

where

$$S(T) = C \ln(T) + K_0 = -0.102 \ln(T) + 0.856 \quad (25a)$$

$$f(M) = M/(1 + a_0M) = M/[1 + (0.0002335M)] \quad (25b)$$



**Figure 5** Correlation of enthalpies of vaporization of esters of alkylcarboxylic acids and *n*-alkanes: (—) calculated according to equation (27); (■) linear oligomer esters of poly(hexamethylene sebacate) ( $N_{\text{COO}} = 2, 4, 6, \dots$  Table VI); (▽), linear esters of sebacic series ( $N_{\text{COO}} = 2$ ; Table VII); (×), branched esters of triglyceride series ( $N_{\text{COO}} = 3$ ; Table VIII); (□), *n*-alkanes ( $N_{\text{COO}} = 0$ ; Table IX); (+) simple carboxylic esters ( $N_{\text{COO}} = 1$ ; Table X).

$$I_0(T) = aT + b_0 = -0.01263T + 14.76 \quad (25c)$$

By taking the derivative of equation (30)  $\{-[d\Delta H_v(T, M)/dT]\}$  and using the results of equations (25a)–(25c), the heat capacity difference may be expressed in J/mol K as

$$\Delta C_p(T, M) = \{(102 \times M) / [1 + (0.0002335 \times M)] / T\} + 12.63 \quad (26)$$

Equations (24) and (26) were used to calculate the results ( $j = c$ ) in Tables VI–X, respectively, for the oligomers of poly(hexamethylene sebacate), linear esters of sebacic series, branched esters of triglyceride series, selected *n*-alkanes ( $N_{\text{COO}} = 0$ ), and other carboxylic esters. The average percentage of deviation for each group of compounds were, respectively,  $\pm 3.1$ ,  $\pm 4.3$ ,  $\pm 3.0$ ,  $\pm 5.6$ , and

$\pm 7.6\%$ ; the overall average percentage of deviation for the empirical calculation for the compounds in this study is  $\approx \pm 5\%$ .

In order to compare the experimental enthalpies of vaporization,  $\Delta H_{ve}(T, M)$ , for all of the substances presented in this article, a temperature–molecular weight correlation from equations (24)–(25) was determined as follows:

$$\Delta H_{ve}(T, M) - [C \cdot f(M) \cdot \ln(T)] - [a \cdot T] = [K_0 / (1 + a_0 M)] M + b_0 \quad (27)$$

where the parameters  $C$ ,  $f(M)$ ,  $a$ ,  $K_0$ , and  $b_0$  have been defined previously. The experimental enthalpies of vaporization in Tables VI–X were used in equation (27) to determine the values for the substances shown in Figure 5. The results clearly indicate that *n*-alkanes and various

classes of alkylcarboxylic esters ( $N_{\text{COO}} = 1, 2, 3, \dots$ ) and the oligomeric series ( $N_{\text{COO}} = 2, 4, 6, \dots$ ) may be represented as a unique function of the molecular weight at a given temperature over the ranges studied in this article to within an average deviation of  $\approx \pm 5\%$ . This deviation is rather similar to the results for reduced liquid heat capacities that have been presented previously for alkylcarboxylic esters.<sup>20</sup>

### Gas Heat Capacity

The gas heat capacity,  $C_p(g)$ , was determined from the empirical liquid heat capacity,  $C_p(l)$ , from Phillips and Mattamal<sup>20</sup> and the heat capacity difference,  $\Delta C_p(T, M)$ , of equation (26) to yield

$$C_p(g) = C_p(l) - \Delta C_p(T, M) \quad (28)$$

Using the results of equations (9) and (26), equation (28) may be expressed as

$$C_p(g) = \{[G_2(T)/W_2] - [C/(1 + a_0M)]\} + [\Delta_1 N_1 + \Delta_3 N_3 + \Delta_{\text{COO}} N_{\text{COO}}] - b_0 \quad (29)$$

where the parameters in equation (29) have been defined previously. Equation (29) was used to calculate the gas heat capacity for the compounds given in Tables VI–X; the results seem to be in reasonable agreement with the group contribution method of Rihani and Doraiswamy.<sup>21</sup>

### CONCLUSION

The results presented in this investigation seem to suggest that enthalpies of vaporization for alkyl carboxylic esters (including linear, branched, and oligomeric) may be reasonably correlated to within estimated errors of  $\pm 10\%$ . The data also suggests that the molecules over the temperature and molecular weight ranges studied will vaporize instead of decomposing, as have been demonstrated by previously published results.

The 3 methods presented for calculating the correction integrals,  $I_{ci}$ , for the temperature dependence of  $\Delta H_v(T)$  were shown not to be too sensitive to variations of the temperature dependence of  $\Delta C_p(T)$ . For example, a deviation of 10% in  $I_{ci}$  produces a deviation of less than 2% deviation in  $\Delta H_v(T)$ . These results also tend to further suggest that methods 2 and 3 may be used to reasonably determine  $\Delta H_v(T)$  to within 10%. If a

very high degree of accuracy is desired, it is suggested that experimental values of  $C_p(l)$  and  $C_p(g)$  be determined over the temperature range of interest.

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### NOMENCLATURE

- $a$  = empirical constant
- $a_1$  = gas activity
- $a_0$  = empirical constant
- $a_{ij}$  = constants for groups  $i$  for  $R_i(T)$  (Alkane:  $i = 1, 2, 3$ , and 4, and  $j = 1, 2, 3$ , and 4. Carboxyl:  $i = \text{COO}$ , and  $j = 1, 2, 3$ , and 4), and for  $I_{ci}$ : (alkane:  $i = 1, 2, 3$ , and 4, and  $j = 1$  and 2).
- $A(M) = kM$  = molecular weight function for the determination of  $\Delta C_{pn}$  [ $k$  = constant =  $T(\rho^*)$ ;  $T$  = temperature (K);  $\rho^*$  = reduced density]
- $b_0$  = empirical constant
- $b_i = b_2 \times K_{i2}$  = empirical constants for alkane groups  $i = 1, 2, 3$ , and 4) in  $G_i(T)$
- $b_{i(j-1)}$  = constants for groups  $i$  (Alkane:  $i = 1, 2, 3$ , and 4. Carboxyl:  $i = \text{COO}$ , and  $j = 3$  and 4 for  $I_{ci}$  and  $I_{c(\text{COO})}$ )
- $C$  = empirical constant
- $c$  = empirical constant
- $C_p(l) = C_{pj}$  = liquid heat capacity [ $j = e$  (experimental);  $j = c$  (calculated)]
- $C_p(g)$  = gas heat capacity
- $\rho$  = density
- $\rho^*$  = reduced or packing density =  $V_w/V_m = \rho V_w/M$
- $\Delta C_p = \Delta C_p(T, M) = \Delta C_{pj}$  = heat capacity difference [ $j = e$  (experimental for liquid and calculated for gas);  $j = n$  (determined from flexible model of  $n$ -alkanes);  $j = c$  (calculated from empirical liquid heat capacity and group-contribution for gas heat capacity);  $T$  = temperature (Kelvin);  $M$  = molecular weight]

- $\Delta_{\text{COO}} = G_{\text{COO}}(T, N_2) - \{[G_2(T)/W_2]W_{\text{COO}}\}$   
 $\Delta G$  = change in Gibb's free energy  
 $\Delta H = \Delta H_v(T) = \Delta H_v(T, M) = \Delta H_{vj}(T)$  = heat of vaporization  
 $\{j = e$  (determined from  $I_e$  using experimental  $\Delta C_{pe}$ );  $n$  (determined from  $I_n$  using  $\Delta C_{pn}$ );  $c$  [determined from  $I_c$  using empirical  $C_p(l)$  and  $C_p(g)$ ]  
 $D_i(T) = G_i(T) - R_i(T)$  (alkane:  $i = 1, 2, 3,$  and  $4$ ; carboxyl:  $i = \text{COO}$ )  
 $\Delta_i = G_i(T) - \{[G_2(T)/W_2]W_i\}$ ;  $i = 1, 3,$  and  $4$   
 $\Delta'_i = D_i(T) - \{[D_2(T)/W_2]W_i\}$ ;  $l = 1, 3,$  and  $4$   
 $\Delta''_i = I_{ci} - [(I_{c2}/W_2)W_i]$ ;  $i = 1, 3,$  and  $4$   
 $\Delta V$  = increase of volume from liquid to real vapor  
 $dn/dt$  = the vaporization rate ( $n$  = no. mol)  
 $e_v$  = Arrhenius activation energy determined from the vaporization rate,  $dn/dt$   
 $f(\rho^*)$  = Function of reduced or packing density,  $\rho^*$   
 $f_g$  = gas fugacity  
 $f(M) = M/[1 + \alpha_0 M]$  = empirical function of molecular weight  
 $F(N_2)$  = empirical function of number of methylene groups  
 $G_{\text{COO}}(T, N_2)$  = temperature-dependent coefficient of the carboxyl group (as a function of  $N_2$ )  
 $G$  = Gibb's free energy  
 $G_i(T) = k_i T + b_i$  = temperature-dependent coefficient of alkane groups;  $i = 1, 2, 3,$  and  $4$   
 $I_0(T) = aT + b_0$  = empirical temperature function for the empirical calculation of  $\Delta H_v(T, M)$   
 $i$  = alkane groups ( $1 = \text{CH}_3$ ;  $2 = \text{CH}_2$ ;  $3 = \text{CH}$ ;  $4 = \text{C}$ )  
 $I_{ci}$  = integrals determined for groups  $i$  (alkane:  $i = 1, 2, 3,$  and  $4$ ; carboxyl:  $i = \text{COO}$ ) used to calculate the correction integral,  $I_c$   
 $j$  = terms for  $a_{ij}$  and  $b_{i(j-1)}$  (alkane:  $i = 1, 2, 3,$  and  $4$ ; carboxyl:  $i = \text{COO}$ );  $j = 1, 2, 3,$  and  $4$   
 $K_0$  = empirical constant  
 $K_{\text{COO}} = G_{\text{COO}}(T, N_2)/G_2(T) = F(N_2) + c$   
 $c$  = ratio of coefficient of carboxyl group to that of the coefficient of methylene group  
 $K_{i2} = G_i(T)/G_2(T)$  = ratio of coefficient of  $i$  group to that of coefficient of methylene group;  $1 = 1, 2, 3,$  and  $4$  ( $k_{22} = 1.00$ )  
 $k_i = k_2 \times k_{i2}$  = constants for alkane groups ( $i = 1, 2, 3,$  and  $4$ ) in  $G_i(T)$   
 $M$  = molar mass = molecular weight (g/mol)  
 $n_0$  = initial no. mol = initial mass at  $t = 0$ /molar mass  
 $n$  = no. mol = mass at time,  $t$ /molar mass (molar mass = molecular weight)  
 $N_{\text{COO}}$  = number of carboxyl groups per molecule ( $1, 2, 3, \dots$ )  
 $N_i$  = number of alkane groups per molecule;  $i = 1, 2, 3,$  and  $4$   
 $R$  = gas constant  
 $R_i(T)$  = temperature-dependent sum of terms,  $a_{ij} T^{j-1}$ , for groups  $i$  (alkane:  $i = 1, 2, 3,$  and  $4$ ; carboxyl:  $i = \text{COO}$ )  
 $S(T) = C \ln(T) + k_0$  = empirical temperature function for the empirical calculation of  $\Delta H_v(T, M)$   
 $T$  = absolute temperature (degree Kelvin, K)  
 $T_i$  = experimental (K) for measurement of heat of vaporization  
 $V$  = volume ( $\text{cm}^3$  or mL)  
 $V_m$  = molar volume =  $V/\text{mol} = M/\rho$   
 $V_w$  = van der Waals volume (volume/mol)  
 $W_{\text{COO}}$  = molecular weight of carboxyl group (g/mol)  
 $W_i$  = molecular weight of alkane groups (g/mol);  $i = 1, 2, 3,$  and  $4$

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