

## Structural Effects on the Vaporization of High Molecular Weight Esters

K. Kishore,\* H. K. Shobha,

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

and G. J. Mattamal

Scientific & Engineering Section, Headquarters U.S. Army Material Command, 5001 Eisenhower Avenue, Alexandria, Virginia 22333-0001 (Received: April 1, 1987; In Final Form: July 21, 1989)

To understand the effect of molecular weight and branching on the heats of vaporization ( $\Delta H_v$ ) and their flow behavior,  $\Delta H_v$  and viscosity ( $\eta$ ) were measured at different temperatures in the high molecular weight ester series: linear flexible di-*n*-alkyl sebacates and compact branched triglycerides with molecular weight ranging from 300 to 900.  $\Delta H_v^\circ$  values ( $\Delta H_v$  corrected to 298 K) have been obtained with experimental  $\Delta H_v$  and also computed according to the group additivity method; a smaller  $-\text{CH}_2-$  group value of 3.8 kJ mol<sup>-1</sup> compared to the normal value of 5.0 kJ mol<sup>-1</sup> is found to give good agreement with the experimental data (within 2–5% error). Both ester series have the same  $\Delta H_v^\circ$  irrespective of their molecular features, namely, shape, flexibility, and polarity, suggesting the coiling of the molecules during vaporization. The segmental motion of these ester series during their flow and its dependence on their molecular features unlike  $\Delta H_v^\circ$  are demonstrated by the correlation of the enthalpy of activation for viscous flow ( $\Delta H^*$ ) and the ratio  $\Delta E_v/\Delta H^* = n$  ( $\Delta E_v$  is the energy of vaporization) with molecular weight.

### Introduction

High molecular weight esters are commonly used as plasticizers in polymers.<sup>1</sup> The viscous flow behavior of these esters is believed to be the main contributing factor in the plasticizing mechanism.<sup>2</sup> Since plasticizers considerably influence the ultimate physico-mechanical properties of polymers,<sup>1</sup> it is necessary to understand the structure–property relationship in these esters and ultimately to quantify their behavior, if possible. Unfortunately, there is no information available, particularly on the effect of molecular weight and branching on the thermodynamic and transport properties of the long-chain esters. However, limited information is available for long-chain *n*-alkanes<sup>3–5</sup> up to a molecular weight of about 400 and for simple compounds<sup>6–8</sup> including esters. In the present paper, an attempt has been made to determine the influence of structure and molecular weight of high molecular weight esters (molecular weight above 300), where no data are available, on their macroscopic thermodynamic properties such as heats of vaporization and flow behavior. The selected liquids varying in molecular weight from 300 to 900 comprise two homologous series of esters, namely, di-*n*-alkyl sebacates, which are polar flexible linear molecules, and triglycerides, which are polar compact molecules having branches at the center.

### Experimental Section

AnalaR grade esters, di-*n*-butyl sebacate (DBS), di-*n*-octyl sebacate (DOS), di-*n*-decyl sebacate (DDS), di-*n*-dodecyl sebacate (DDoS), tributyrin (TB), tricaproin (TC), trioctanoin (TO), tridecanoin (TD), trilaurin (TL), trimyrustin (TM), tripalmitin (TP), and tristearin (TS), with approximately 99% purity were obtained from Eastman Kodak Co. and used as such.

The esters di-*n*-hexyl sebacate (DHS), di-*n*-tetradecyl sebacate (DTeS), di-*n*-hexadecyl sebacate (DHeS), and di-*n*-octadecyl

sebacate (DOcS) were prepared by reacting sebacyl chloride with respective alcohols in toluene using pyridine for removing HCl. The esters were separated from the reaction mixture by fractional distillation. DHS was purified by vacuum distillation while DTeS, DHeS, and DOcS were purified by recrystallization. They were characterized by IR and <sup>1</sup>H NMR spectroscopy using a Perkin-Elmer Model 715 IR spectrometer and a Varian T-60 spectrometer and found to be pure within the sensitivity of these measurements.

Absolute viscosity ( $\eta$ ) measurements were made with a Cannon-Fenske viscometer having kinematic viscosity in the ranges (cSt) 0.4–1.6, 0.8–3.2, 3–15, and 7–35. These were calibrated according to NBS standards. To obtain  $\eta$ , kinematic viscosity ( $\nu$ ) of the esters, determined in the temperature range 301.1–515.8 K (ASTM D445-64 method),<sup>9</sup> was used. Both viscosity and density measurements involve silicone oil bath, whose temperature was kept constant up to  $\pm 0.1$  °C.  $\eta$  is obtained from the equation

$$\eta = \nu \rho$$

where the density ( $\rho$ ) was experimentally measured by use of a dilatometer.<sup>10</sup> The error in density measurements was  $\pm 0.5\%$ . Since the flow was considered as Newtonian under the experimental conditions, no correction for the shear viscosity was made. The error due to kinetic energy was minimized by keeping high efflux times (above 200 s). The accuracy of viscosity data was about  $\pm 2.5\%$ .

Use of thermal analysis techniques like thermogravimetric (TG) and differential thermal analysis (DTA) for determining vapor pressure and heats of vaporization ( $\Delta H_v$ ) is well-known.<sup>11–15</sup> The  $\Delta H_v$  values of the esters in the present investigation have been measured by isothermal TG. The instrumentation and the experimental details in measuring the  $\Delta H_v$  are the same as that used by Wall and co-workers.<sup>16</sup> The vaporization was found to occur without decomposition.<sup>16–19</sup> Isothermal rates of vaporization

(1) Sears, J. K.; Touchette, N. W. Plasticizers. In *Encyclopedia of Chemical Technology*, 3rd ed.; Kirk, R., Othmer, D., Eds.; Wiley: New York, 1982; Vol. 18, p 111.

(2) Darby, J. R.; Sears, J. Plasticizers. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Gaylord, N. G., Eds.; Wiley: New York, 1969; Vol. 10, p 228.

(3) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941; Chapter 9.

(4) Wake, W. C. *Trans. Faraday Soc.* **1947**, *43*, 708.

(5) Moore, R. J.; Gibbs, P.; Eyring, H. *J. Phys. Chem.* **1953**, *57*, 172.

(6) Sharma, B. K. *Ind. J. Pure Appl. Phys.* **1976**, *14*, 992.

(7) Thomas, L. H. *Trans. Faraday Soc.* **1966**, *62*, 328.

(8) Brice, T. J.; Coon, R. I. *J. Am. Chem. Soc.* **1953**, *75*, 2921.

(9) ASTM D 445. *Annual Book of ASTM Standards*; American Society for Testing Materials: Philadelphia, 1976; Part 23, p 231.

(10) Phillips, J. C.; Mattamal, G. J. *J. Chem. Eng. Data* **1978**, *23*, 1.

(11) Kubaschewski, O.; Chart, T. G. *J. Chem. Thermodyn.* **1974**, *6*, 467.

(12) Pfefferkorh, J.; Wiedmann, H. C. *Prog. Vac. Microbalance Tech.* **1973**, *2*, 221.

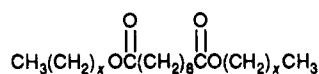
(13) Seyler, R. J. *Thermochim. Acta* **1976**, *17*, 129.

(14) Charles, R. G. *Thermochim. Acta* **1980**, *38*, 315.

(15) Nikolic, D.; Minic, D. *Naucno-Teh. Pregl.* **1981**, *31*, 46.

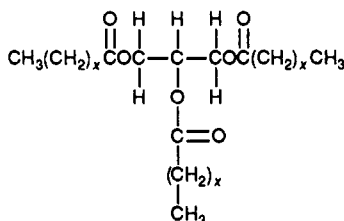
(16) Wall, L. A.; Flynn, J. H.; Straus, S. *J. Phys. Chem.* **1970**, *74*, 3237.

(17) Wall, L. A. Pyrolysis. In *Analytical Chemistry of Polymers*; Kline, G. M., Ed.; Interscience: New York, 1962; Vol. 2.

TABLE I: Thermodynamic Data on the Dialkyl Sebacate Ester Series<sup>a</sup>

x	compd	molecular weight	mean T, K	$E_v$ , kJ mol <sup>-1</sup>	$\Delta E_v$ , kJ mol <sup>-1</sup>	$\Delta H_v$ , kJ mol <sup>-1</sup>	$\Delta H_v^\circ$ , kJ mol <sup>-1</sup>	$\Delta E_v^\circ$ , kJ mol <sup>-1</sup>
3	DBS	314	327.1	84.1 ± 1.4	85.4 ± 2.6	88.1 ± 3.1	91.8 ± 3.2	89.3 ± 2.7
5	DHS	370	344.1	95.6 ± 1.6	97.0 ± 2.9	99.9 ± 3.5	106.4 ± 3.7	103.9 ± 3.1
7	DOS	426	368.1	105.1 ± 1.8	106.7 ± 3.2	109.7 ± 3.8	120.8 ± 4.2	118.3 ± 3.5
9	DDS	482	405.4	115.5 ± 1.9	117.2 ± 3.5	120.5 ± 4.2	138.7 ± 4.9	136.2 ± 4.1
11	DDoS	539	420.1	126.7 ± 2.2	128.5 ± 3.9	131.9 ± 4.6	154.5 ± 5.4	152.0 ± 4.6
13	DTeS	595	439.8	137.3 ± 2.3	139.1 ± 4.2	142.8 ± 5.0	170.6 ± 5.9	168.1 ± 5.0
15	DHeS	651	460.2	147.0 ± 2.5	149.0 ± 4.5	149.8 ± 5.2	183.8 ± 6.4	181.3 ± 5.4
17	DOcS	707	480.1	151.5 ± 2.6	153.5 ± 4.6	157.5 ± 5.5	197.7 ± 6.9	195.2 ± 5.9

<sup>a</sup>The maximum error involved in  $E_v$  is 1.7%; in  $\Delta E_v$  and  $\Delta E_v^\circ$  it is 3% and in  $\Delta H_v$  and  $\Delta H_v^\circ$  it is 3.5%.

TABLE II: Thermodynamic Data on the Triglyceride Ester Series<sup>a</sup>

x	compd	molecular weight	mean T, K	$E_v$ , kJ mol <sup>-1</sup>	$\Delta E_v$ , kJ mol <sup>-1</sup>	$\Delta H_v$ , kJ mol <sup>-1</sup>	$\Delta H_v^\circ$ , kJ mol <sup>-1</sup>	$\Delta E_v^\circ$ , kJ mol <sup>-1</sup>
2	TB	302	308.5	79.6 ± 1.4	80.9 ± 2.4	83.5 ± 2.9	84.9 ± 2.5	82.4 ± 2.5
4	TC	386	349.3	95.6 ± 1.6	97.0 ± 2.9	99.9 ± 3.5	108.3 ± 3.8	105.9 ± 3.2
6	TO	470	386.1	113.9 ± 1.9	115.5 ± 3.5	118.7 ± 4.2	135.4 ± 4.7	132.9 ± 3.9
8	TD	554	411.4	125.3 ± 2.1	127.0 ± 3.8	130.5 ± 4.6	154.6 ± 5.4	152.1 ± 4.6
10	TL	639	437.9	141.6 ± 2.4	143.4 ± 4.3	147.1 ± 5.1	180.0 ± 6.3	177.5 ± 5.3
12	TM	723	468.7	149.9 ± 2.5	151.9 ± 4.6	155.8 ± 5.5	199.2 ± 6.9	196.7 ± 5.9
14	TP	807	483.1	160.6 ± 2.7	162.6 ± 4.9	166.3 ± 5.8	217.1 ± 7.6	214.6 ± 6.4
16	TS	890	505.8	168.6 ± 2.9	170.7 ± 5.1	174.9 ± 6.1	236.2 ± 8.3	233.8 ± 7.0

<sup>a</sup>The maximum error involved in  $E_v$  is 1.7%; in  $\Delta E_v$  and  $\Delta E_v^\circ$  it is 3% and in  $\Delta H_v$  and  $\Delta H_v^\circ$  it is 3.5%.

( $dw/dt$ ) were measured at various temperatures: the activation energy ( $E_v$ ) at the mean temperature of experiments was determined from the slope of the plot of  $\ln(dw/dt)$  vs  $1/T$  and was precise to within ±1.7%.

## Results and Discussion

$E_v$  obtained from the slope of the plot of  $\ln(dw/dt)$  vs  $1/T$  is related to the energy of vaporization ( $\Delta E_v$ ) according to eq 1, which considers the kinetics of condensation-vaporization equilibrium:<sup>16</sup>

$$\Delta E_v = E_v + (1/2)RT \quad (1)$$

where  $R$  is the gas constant and  $T$  is the mean temperature. Since  $\Delta H_v = \Delta E_v + RT$ , eq 1 can be written as

$$\Delta H_v = E_v + (3/2)RT \quad (2)$$

$\Delta H_v$  values at the corresponding mean temperatures, obtained from eq 2 for the two ester series, were precise to within ±3.5%. The  $\Delta H_v$  values were corrected to the standard reference temperature of 298 K ( $\Delta H_v^\circ$ ) according to a group additivity method<sup>20-28</sup>

TABLE III: Calculated Heat of Vaporization of the Dialkyl Sebacate Ester Series by the Group Additivity Method Using Different  $-\text{CH}_2-$  Group Values of 3.3, 3.8, and 5.0 kJ mol<sup>-1</sup><sup>a</sup>

compd	calcd $\Delta H_v^\circ$ , kJ mol <sup>-1</sup> , at			exptl $\Delta H_v^\circ$ , kJ mol <sup>-1</sup>
	5.0 kJ mol <sup>-1</sup>	3.8 kJ mol <sup>-1</sup>	3.3 kJ mol <sup>-1</sup>	
DBS	100.4 ± 5.0	88.3 ± 4.4	84.1 ± 4.2	91.8 ± 3.2
DHS	119.5 ± 5.9	103.3 ± 5.2	97.5 ± 4.9	106.4 ± 3.7
DOS	138.6 ± 6.9	118.4 ± 5.9	110.9 ± 5.5	120.8 ± 4.2
DDS	157.6 ± 7.9	133.5 ± 6.7	124.3 ± 6.2	138.7 ± 4.9
DDoS	176.7 ± 8.8	148.5 ± 7.4	137.7 ± 6.9	154.5 ± 5.4
DTeS	195.8 ± 9.8	163.6 ± 8.2	151.0 ± 7.6	170.6 ± 5.9
DHeS	214.9 ± 10.7	178.7 ± 8.9	164.4 ± 8.2	183.8 ± 6.4
DOcS	233.9 ± 11.7	193.7 ± 9.7	177.8 ± 8.9	197.7 ± 6.9

<sup>a</sup>In calculated and experimental  $\Delta H_v^\circ$ , the maximum errors are 5% and 3.5%, respectively.

TABLE IV: Calculated Heat of Vaporization of the Triglyceride Ester Series by the Group Additivity Method Using Different  $-\text{CH}_2-$  Group Values at 3.3, 3.8, and 5.0 kJ mol<sup>-1</sup><sup>a</sup>

compd	calcd $\Delta H_v^\circ$ , kJ mol <sup>-1</sup> , at			exptl $\Delta H_v^\circ$ , kJ mol <sup>-1</sup>
	5.0 kJ mol <sup>-1</sup>	3.8 kJ mol <sup>-1</sup>	3.3 kJ mol <sup>-1</sup>	
TB	92.6 ± 4.6	88.9 ± 4.4	87.7 ± 4.4	84.9 ± 2.9
TC	121.3 ± 6.1	111.6 ± 5.6	107.8 ± 5.4	108.3 ± 3.8
TO	149.9 ± 7.5	134.2 ± 6.7	127.9 ± 6.4	135.4 ± 4.7
TD	178.5 ± 8.9	156.6 ± 7.8	147.9 ± 7.4	154.6 ± 5.4
TL	207.1 ± 10.3	179.4 ± 8.9	168.1 ± 8.4	180.0 ± 6.3
TM	235.7 ± 11.8	201.9 ± 10.1	188.2 ± 9.4	199.2 ± 6.9
TP	264.3 ± 13.2	224.6 ± 11.2	208.2 ± 10.4	217.1 ± 7.6
TS	292.9 ± 14.6	247.1 ± 12.4	228.3 ± 11.4	236.2 ± 8.3

<sup>a</sup>In calculated and experimental  $\Delta H_v^\circ$ , the maximum errors are 5% and 3.5%, respectively.

(18) Flynn, J. H.; Wall, L. A. *J. Res. Natl. Bur. Stand., Sect. A* **1966**, *70*, 487.

(19) Wall, L. A.; Flynn, J. H.; Straus, S. *Polym. Eng. Sci.* **1970**, *10*, 19.

(20) Reid, R. C.; Sherwood, T. K. *Properties of Gases and Liquids: Their Estimation and Correlation*, 2nd ed.; McGraw-Hill: New York, 1966; *Ibid.*, 3rd ed.; 1977.

(21) Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958**, *29*, 546.

(22) Janz, G. J. *Estimation of Thermodynamic Properties; Properties of Organic Compounds*, 2nd ed.; Academic Press: New York, 1976.

(23) Johnson, A. I.; Huang, G. J. *Can. J. Technol.* **1957**, *34*, 405.

(24) Rihani, D. N.; Doraiswamy, L. K. *Ind. Eng. Chem. Fundam.* **1965**, *4*, 17.

TABLE V: Absolute Viscosities of the Dialkyl Sebacate Ester Series at Various Temperatures<sup>a</sup>

compd	$\eta$ , cP, at					
	301.1 K	330.9 K	371.1 K	420.2 K	468.1 K	515.8 K
DBS	7.22 ± 0.18	3.63 ± 0.09	1.81 ± 0.05	0.99 ± 0.03	0.57 ± 0.01	0.38 ± 0.01
DHS	11.19 ± 0.28	5.02 ± 0.13	2.40 ± 0.06	1.23 ± 0.03	0.76 ± 0.02	0.46 ± 0.01
DOS	15.91 ± 0.40	6.45 ± 0.16	2.85 ± 0.07	1.40 ± 0.04	0.85 ± 0.02	0.58 ± 0.01
DDS		8.12 ± 0.20	3.53 ± 0.09	1.75 ± 0.04	1.05 ± 0.03	0.71 ± 0.02
DDoS		11.37 ± 0.28	4.73 ± 0.12	2.26 ± 0.06	1.33 ± 0.03	0.89 ± 0.02
DTeS			5.65 ± 0.14	2.63 ± 0.07	1.50 ± 0.04	0.97 ± 0.02
DHeS			7.12 ± 0.18	3.21 ± 0.08	1.79 ± 0.05	1.15 ± 0.03
DOcS			7.96 ± 0.20	3.56 ± 0.09	2.01 ± 0.05	1.24 ± 0.03

<sup>a</sup>The maximum error in  $\eta$  is 2.5%.

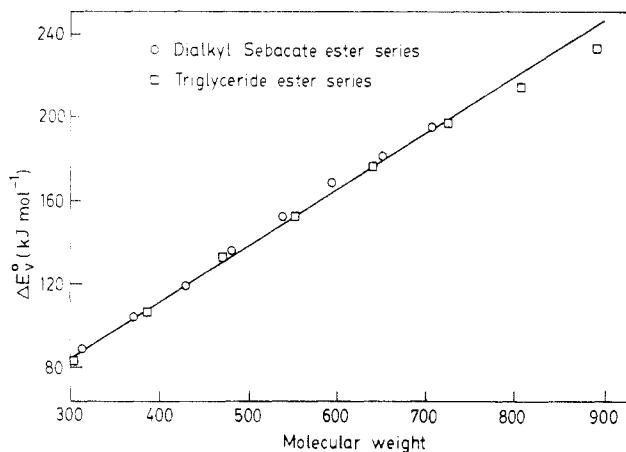


Figure 1. Energy of vaporization at 298 K ( $\Delta E_v^0$ ) as a function of molecular weight.

(Appendix). Since  $\Delta H_v^0 = \Delta E_v^0 + RT$ ,  $\Delta E_v^0$  ( $\Delta E_v$  at 298 K) has also been calculated from  $\Delta H_v^0$ , and data are given in Tables I and II. The  $\Delta H_v^0$  values were also computed according to a group additivity method<sup>29-36</sup> (Appendix) and are presented in Tables III and IV.

To analyze the influence of molecular weight on the rate of vaporization,  $\Delta E_v^0$  values of the esters are plotted (Figure 1) as a function of molecular weight: a linear dependence is obtained. Surprisingly, both the linear and the branched ester series show almost identical  $\Delta E_v^0$  values despite the variation in shape, flexibility, and polarity of the molecules. The experimental  $\Delta H_v^0$  values were compared with those calculated from the group additivity method (Tables III and IV). Figure 2 shows that  $\Delta H_v^0$  values, calculated by group additivity, give concordant results with the experimental values.

A noticeable feature in Figure 2 is that, as the molecular weight increases, regardless of the shape, flexibility, and polarity, both linear and branched esters of similar molecular weights exhibit almost identical  $\Delta H_v^0$ . This behavior can happen only when molecules of both ester series acquire similar shapes during vaporization. From Figure 3, the plot of  $\Delta H_v^0$  vs (molecular weight)<sup>2/3</sup> is a straight line, showing the "coiled spherical nature" of the molecules during vaporization.<sup>16</sup> A polymer molecule in

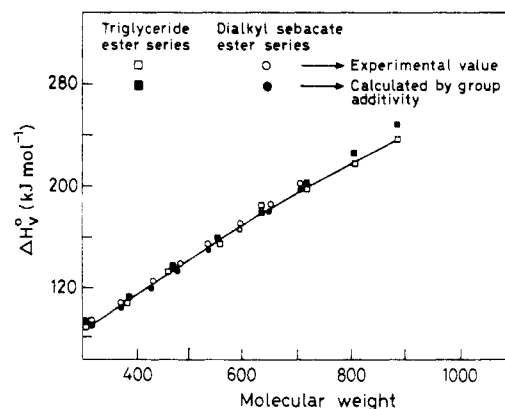


Figure 2. Heat of vaporization corrected to 298 K ( $\Delta H_v^0$ ) as a function of molecular weight.

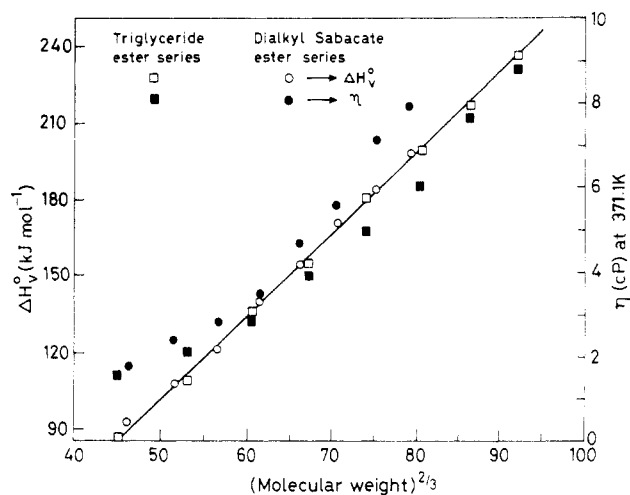


Figure 3. Heat of vaporization ( $\Delta H_v^0$ ) and viscosity ( $\eta$ ) as a function of (molecular weight)<sup>2/3</sup>.

the bulk, situated in a medium of its own molecules, will have a configuration similar to that in a  $\theta$  solvent.<sup>37,38</sup> Hence the ester molecules will exist in an unperturbed extended configuration in the liquid state. Since vacuum is considered to be a poor solvent, the molecules, as they begin to vaporize from the surface, start curling up and assume a tightly coiled spherical form in the vapor state. The molecular segments on the surface of this coiled configuration, presumably methylene and methyl groups, encounter the surrounding differently from the bulk fluid and hence the interactions involving these will contribute to the enthalpy of vaporization. The number of molecular segments so affected will be approximately proportional to the surface area of this structure, and hence it would be proportional to the 2/3 power of the molecular weight, which in turn is proportional to the volume. This

(25) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968.

(26) Shaw, R. J. *Chem. Eng. Data* **1969**, *14*, 461.

(27) Lauria, M.; Benson, S. W. *J. Chem. Eng. Data* **1977**, *22*, 90.

(28) Broadhurst, M. G. *J. Res. Natl. Bur. Stand.* **1963**, *67A*, 233.

(29) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(30) Stein, S. E. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1457.

(31) Ducros, M.; Gruson, J. F.; Sannier, H. *Thermochim. Acta* **1980**, *36*, 39.

(32) Guthrie, J. P.; Taylor, K. F. *Can. J. Chem.* **1983**, *61*, 602.

(33) Stein, S. E.; Fahr, A. *J. Phys. Chem.* **1985**, *89*, 3714.

(34) Omar, M. M. *J. Chem. Soc. C* **1967**, *20*, 2038.

(35) Abramzon, A. A. *Zh. Prikl. Khim.* **1967**, *40*(11), 2598.

(36) Ducros, M.; Gruson, G. F.; Sannier, H. *Thermochim. Acta* **1981**, *44*, 131.

(37) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.

(38) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J.; Janinik, G.; Ober, R.; Picot, C.; des Cloizeaux, J. *Macromolecules* **1974**, *7*, 863.

TABLE VI: Absolute Viscosities of the Triglyceride Ester Series at Various Temperatures<sup>a</sup>

compd	$\eta$ , cP, at					
	301.1 K	330.9 K	371.1 K	420.2 K	468.1 K	515.8 K
TB	8.10 ± 0.20	3.56 ± 0.09	1.63 ± 0.04	0.85 ± 0.02	0.55 ± 0.01	0.39 ± 0.01
TC	11.09 ± 0.28	4.68 ± 0.12	2.12 ± 0.05	1.08 ± 0.03	0.66 ± 0.02	0.48 ± 0.01
TO	17.60 ± 0.44	6.79 ± 0.17	2.85 ± 0.07	1.42 ± 0.04	0.85 ± 0.02	0.57 ± 0.01
TD	28.00 ± 0.70	10.79 ± 0.27	3.89 ± 0.10	1.76 ± 0.04	1.05 ± 0.03	0.69 ± 0.02
TL		13.18 ± 0.33	4.95 ± 0.12	2.24 ± 0.06	1.30 ± 0.03	0.85 ± 0.02
TM			6.00 ± 0.15	2.64 ± 0.07	1.50 ± 0.04	0.98 ± 0.02
TP			7.65 ± 0.19	3.25 ± 0.08	1.79 ± 0.04	1.17 ± 0.03
TS			8.82 ± 0.22	3.59 ± 0.09	1.93 ± 0.05	1.23 ± 0.03

<sup>a</sup>The maximum error in  $\eta$  is 2.5%.

TABLE VII: Kinetic Data on the Dialkyl Sebacate Ester Series<sup>a</sup>

compd	$\Delta G^\ddagger$ , kJ mol <sup>-1</sup> , at						$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	$n^b$
	301.1 K	330.9 K	371.1 K	420.2 K	468.1 K	515.8 K		
DBS	44.9 ± 1.8	47.5 ± 1.9	51.2 ± 2.1	56.1 ± 2.2	60.5 ± 2.4	65.1 ± 2.6	16.2 ± 1.3	5.27
DHS	46.4 ± 1.9	48.9 ± 2.0	52.6 ± 2.1	57.4 ± 2.3	62.3 ± 2.5	66.6 ± 2.7	17.2 ± 1.4	5.63
DOS	47.7 ± 1.9	50.0 ± 2.0	53.6 ± 2.1	58.4 ± 2.3	63.3 ± 2.5	68.2 ± 2.7	18.4 ± 1.5	5.80
DDS		51.0 ± 2.0	54.7 ± 2.2	59.7 ± 2.4	64.6 ± 2.6	69.7 ± 2.8	19.1 ± 1.5	6.14
DDoS		52.3 ± 2.1	56.0 ± 2.2	60.9 ± 2.4	66.0 ± 2.6	71.2 ± 2.9	19.7 ± 1.6	6.53
DTeS			56.9 ± 2.3	61.8 ± 2.5	66.9 ± 2.7	72.0 ± 2.9	20.0 ± 1.6	6.94
DHeS			57.9 ± 2.3	62.9 ± 2.5	68.0 ± 2.7	73.1 ± 2.9	20.2 ± 1.6	7.39
DOcS			58.5 ± 2.3	63.6 ± 2.5	68.7 ± 2.8	73.8 ± 3.0	20.2 ± 1.6	7.61

<sup>a</sup>The maximum error involved in  $\Delta G^\ddagger$  is 4%, and in  $\Delta H^\ddagger$  it is 8%. <sup>b</sup> $\Delta E_v/\Delta H^\ddagger = n$ .

TABLE VIII: Kinetic Data on the Triglyceride Ester Series<sup>a</sup>

compd	$\Delta G^\ddagger$ , kJ mol <sup>-1</sup> , at						$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	$n^b$
	301.1 K	330.9 K	371.1 K	420.2 K	468.1 K	515.8 K		
TB	44.9 ± 1.8	47.1 ± 1.9	50.5 ± 2.0	55.1 ± 2.2	58.2 ± 2.3	61.6 ± 2.5	17.7 ± 1.4	4.58
TC	46.4 ± 1.9	48.7 ± 1.9	52.3 ± 2.1	56.9 ± 2.3	61.7 ± 2.5	66.9 ± 2.7	18.7 ± 1.5	5.18
TO	48.1 ± 1.9	50.3 ± 2.0	53.9 ± 2.2	58.7 ± 2.4	63.5 ± 2.5	68.5 ± 2.7	20.1 ± 1.6	5.75
TD	49.7 ± 2.0	52.1 ± 2.1	55.4 ± 2.2	60.1 ± 2.4	65.1 ± 2.6	70.1 ± 2.8	20.4 ± 1.6	6.23
TL		53.1 ± 2.1	56.4 ± 2.3	61.4 ± 2.5	66.4 ± 2.7	71.6 ± 2.9	20.5 ± 1.6	6.98
TM			57.6 ± 2.3	62.5 ± 2.5	67.5 ± 2.7	72.7 ± 2.9	20.8 ± 1.7	7.29
TP			58.7 ± 2.4	63.6 ± 2.5	68.7 ± 2.8	73.9 ± 3.0	20.9 ± 1.7	7.77
TS			59.5 ± 2.4	64.3 ± 2.6	69.4 ± 2.8	74.7 ± 3.0	20.9 ± 1.7	8.16

<sup>a</sup>The maximum error involved in  $\Delta G^\ddagger$  is 4%, and in  $\Delta H^\ddagger$  it is 8%. <sup>b</sup> $\Delta E_v/\Delta H^\ddagger = n$ .

TABLE IX: Entropy of Activation for Viscous Flow of Dialkyl Sebacate Ester Series at Various Temperatures<sup>a</sup>

compd	$\Delta S^\ddagger$ , J deg <sup>-1</sup> mol <sup>-1</sup> , at					
	301.1 K	330.9 K	371.1 K	420.2 K	468.1 K	515.8 K
DBS	-95.3 ± 11.4	-94.6 ± 11.4	-94.4 ± 11.3	-94.9 ± 11.4	-94.6 ± 11.4	-94.9 ± 11.4
DHS	-96.8 ± 11.6	-95.6 ± 11.5	-95.4 ± 11.4	-95.6 ± 11.5	-96.2 ± 11.5	-96.6 ± 11.5
DOS	-97.4 ± 11.7	-95.6 ± 11.5	-95.0 ± 11.4	-95.2 ± 11.4	-95.2 ± 11.4	-96.0 ± 11.5
DDS		-96.4 ± 11.6	-96.0 ± 11.5	-96.6 ± 11.6	-97.3 ± 11.7	-98.2 ± 11.8
DDoS		-98.5 ± 11.8	-97.8 ± 11.7	-98.1 ± 11.8	-98.9 ± 11.9	-99.8 ± 12.0
DTeS			-99.2 ± 11.9	-99.5 ± 11.9	-100.0 ± 12.0	-100.6 ± 12.1
DHeS			-101.6 ± 12.2	-101.6 ± 12.2	-101.9 ± 12.2	-102.5 ± 12.3
DOcS			-103.3 ± 12.4	-103.2 ± 12.4	-103.7 ± 12.4	-103.9 ± 12.5

<sup>a</sup>The maximum error involved in  $\Delta S^\ddagger$  is 12%.

empirically encountered relationship is consistent with the notion that these molecules, on the average, are spherical with an interior that is like the bulk fluid.

The above discussion clearly suggests that molecules coil up and evaporate in the form of a compact sphere,<sup>39</sup> lest they will differ in size, too. A similar dependence in *n*-alkanes has also been reported where the vaporization in a coiled spherical form has been suggested.<sup>40</sup> The coiled spherical form is acquired due to intramolecular van der Waals forces, which also entails the rupturing of a minimum amount of van der Waals bonding during the vaporization process.<sup>16</sup> Furthermore, the presence of branching (especially at the center, for instance, as in glycerides) leads to a more closely packed arrangement due to intramolecular forces which favor coiling.

The absolute viscosity ( $\eta$ ) data of the two ester series at different temperatures are given in Tables V and VI.  $\eta$  at a given temperature *T* is related to the free energy of activation for viscous flow ( $\Delta G^\ddagger$ ) according to the equation<sup>3</sup>

$$\Delta G^\ddagger = RT \ln (V_m \eta / Nh) \quad (3)$$

where *N* is Avogadro's number, *h* is Planck's constant, and *V<sub>m</sub>* is the molar volume ( $V_m = M/\rho$ ; *M* = molecular weight and  $\rho$  = density) which has been obtained from the density<sup>10</sup> and molecular weight.  $\Delta G^\ddagger$  data at different temperatures for the two ester series are given in Tables VII and VIII. Since  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ , the plot of  $\Delta G^\ddagger/T$  vs  $1/T$  is a straight line, and the slope from a least-squares fit gives the enthalpy of activation ( $\Delta H^\ddagger$ ) for the viscous flow; data are given in Tables VII and VIII. The entropy of activation for viscous flow ( $\Delta S^\ddagger$ ) is then calculated at each temperature by use of the relation  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ ; data are given in Tables IX and X. The maximum estimated errors

(39) Aten, A. H. W. *J. Chem. Phys.* 1937, 5, 264.

(40) Huggins, M. L. *J. Phys. Chem.* 1939, 43, 1083.

TABLE X: Entropy of Activation for Viscous Flow of Triglyceride Ester Series at Various Temperatures<sup>a</sup>

compd	$\Delta S^*$ , J deg <sup>-1</sup> mol <sup>-1</sup> , at					
	301.1 K	330.9 K	371.1 K	420.2 K	468.1 K	515.8 K
TB	-90.3 ± 10.8	-89.1 ± 10.7	-88.5 ± 10.6	-89.1 ± 10.7	-86.5 ± 10.4	-85.1 ± 10.2
TC	-91.8 ± 11.0	-90.4 ± 10.8	-90.3 ± 10.8	-90.9 ± 10.9	-91.8 ± 11.0	-93.3 ± 11.2
TO	-93.1 ± 11.2	-91.3 ± 10.9	-91.0 ± 10.9	-91.8 ± 11.0	-92.8 ± 11.1	-93.8 ± 11.3
TD	-97.4 ± 11.7	-95.8 ± 11.5	-94.2 ± 11.3	-94.5 ± 11.3	-95.4 ± 11.5	-96.4 ± 11.6
TL		-98.2 ± 11.8	-96.7 ± 11.6	-97.3 ± 11.7	-98.0 ± 11.8	-99.0 ± 11.9
TM			-99.0 ± 11.9	-99.0 ± 11.9	-99.8 ± 12.0	-100.6 ± 12.1
TP			-101.8 ± 12.2	-101.5 ± 12.2	-102.1 ± 12.3	-102.8 ± 12.3
TS			-103.7 ± 12.5	-103.2 ± 12.4	-103.6 ± 12.4	-104.2 ± 12.5

<sup>a</sup>The maximum error involved in  $\Delta S^*$  is 12%.

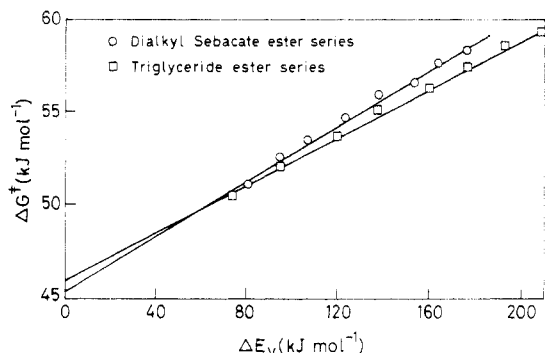


Figure 4. Free energy of activation for viscous flow ( $\Delta G^*$ ) as a function of energy of vaporization ( $\Delta E_v$ ) at 371.1 K.

in  $\Delta G^*$ ,  $\Delta H^*$ , and  $\Delta S^*$  were found to be 4%, 8%, and 12%, respectively.

When  $\Delta G^*$  is compared with  $\Delta E_v$  at the corresponding states, i.e., at their boiling points, in a number of systems (e.g., *n*-paraffins, moderately branched paraffins, and aromatics), a straight line is obtained<sup>5</sup> with an empirical equation (in SI units, kJ)

$$\Delta G^* = 0.53\Delta E_v + 1.88 \quad (4)$$

In the present case,  $\Delta G^*$  and  $\Delta E_v$  cannot be compared at their boiling points because of the unavailability of the data at the boiling temperatures (the esters studied presently may decompose at their boiling temperatures owing to their very high molecular weight and hence the data on the values of  $\Delta E_v$  and  $\Delta G^*$  cannot be obtained at these temperatures). Hence  $\Delta G^*$  and  $\Delta E_v$  were compared at one temperature, namely, 371.1 K (Table XI). Experimental  $\Delta E_v$  values were converted to this temperature by the group additivity method. The plot of  $\Delta G^*$  vs  $\Delta E_v$  (Figure 4) shows two distinct lines for the two ester series satisfying the empirical relationships

dialkyl sebacate ester series

$$\Delta G^* = 0.075\Delta E_v + 45.35 \quad (5)$$

triglyceride ester series

$$\Delta G^* = 0.066\Delta E_v + 46.00 \quad (6)$$

Though there is some similarity in terms of slope and intercept in eq 5 and 6, they are very different from eq 4. Equations 5 and 6 cannot be readily compared with eq 4 because it involves data at the boiling temperature; the significant difference may be due to the difference in vaporization and flow behavior of long chain ester molecules from other systems.<sup>5</sup> Within the two ester series, it is observed that  $\Delta E_v$  is same at a given molecular weight; the observed difference in eq 5 and 6 may be attributed to the difference in the flow behavior of linear and branched esters.

A liquid may be considered as made up of "holes" moving about in the matter.<sup>41</sup> For a molecule to flow, a "hole" is required; this "hole", however, may not necessarily be of the full size of the molecule. Therefore,  $\Delta H^*$ , which denotes the energy required to form this "hole", should be some fraction of  $\Delta E_v$ , which rep-

TABLE XI: Free Energy of Activation for Viscous Flow and Energy of Vaporization at 371.1 K for Dialkyl Sebacate and Triglyceride Ester Series<sup>a</sup>

compd	$\Delta E_v$ , kJ mol <sup>-1</sup>	$\Delta G^*$ , kJ mol <sup>-1</sup>
DBS	80.3 ± 2.4	51.2 ± 2.1
DHS	93.4 ± 2.8	52.6 ± 2.1
DOS	106.2 ± 3.2	53.6 ± 2.2
DDS	122.5 ± 3.7	54.7 ± 2.2
DDoS	136.8 ± 4.1	55.9 ± 2.2
DTeS	151.4 ± 4.5	56.9 ± 2.3
DHeS	163.0 ± 4.9	57.9 ± 2.3
DOcS	175.3 ± 5.3	58.5 ± 2.3
TB	72.8 ± 2.2	50.5 ± 2.0
TC	93.9 ± 2.8	52.3 ± 2.1
TO	118.7 ± 3.6	53.9 ± 2.2
TD	135.6 ± 4.1	55.4 ± 2.2
TL	158.6 ± 4.8	56.4 ± 2.3
TM	175.1 ± 5.3	57.6 ± 2.3
TP	191.0 ± 5.7	58.7 ± 2.4
TS	207.9 ± 6.2	59.5 ± 2.4

<sup>a</sup>The maximum error involved in  $\Delta E_v$  is 3%, and in  $\Delta G^*$  it is 4%.

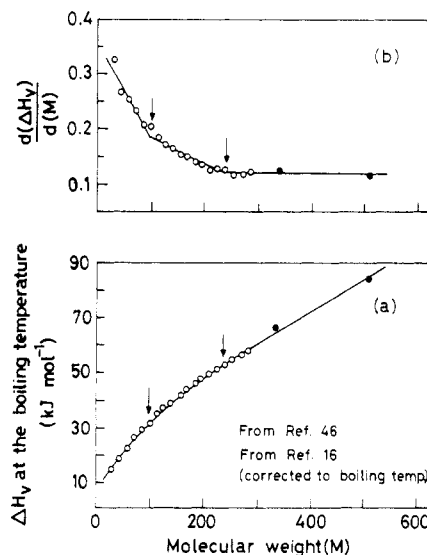


Figure 5. (a) Heat of vaporization (at the boiling temperature) of *n*-alkanes as a function of molecular weight. (b) Derivative of a plotted against molecular weight.

resents the energy required to create a "hole" of the molecular size in the liquid. Thus  $\Delta E_v/\Delta H^* = n$ , where *n* is a factor indicating the rough size of the "hole" necessary for viscous flow or, more precisely, of the unit of flow.<sup>6</sup> From data on a large number of liquids, it was found that,<sup>3</sup> for spherical molecules, *n* at the boiling temperature is about 3, whereas for polar molecules and others that are nonspherical, such as long-chain hydrocarbons, *n* is about 4. Generally *n* lies between 3 and 4 for various liquids,<sup>6-8,42-44</sup> when the molecule as a whole moves. The value of

(41) (a) Eyring, H. *J. Chem. Phys.* **1936**, *4*, 283. (b) Hirschfelder, J. O.; Stevenson, D. P.; Eyring, H. *Ibid.* **1937**, *5*, 896.

(42) Erdey-Gruz, T. *Transport Phenomenon in Aqueous Solutions*; Adam Hilger: London, 1974; p 104.

TABLE XII: Estimation of Liquid and Vapor Heat Capacities ( $\text{J deg}^{-1} \text{mol}^{-1}$ ) of the Dialkyl Sebacate Ester Series<sup>a</sup>

compd	mean $T$ , K	$C_p(l)$		$C_p(g)$	
		298 K	mean $T$ , K	298 K	mean $T$ , K
DBS	327.1	571.6 $\pm$ 11.4	591.9 $\pm$ 11.8	443.0 $\pm$ 13.3	474.8 $\pm$ 14.2
DHS	344.1	693.5 $\pm$ 13.9	731.2 $\pm$ 14.6	539.5 $\pm$ 16.2	600.7 $\pm$ 18.0
DOS	368.1	815.0 $\pm$ 16.3	882.1 $\pm$ 17.6	636.1 $\pm$ 19.1	744.5 $\pm$ 22.3
DDS	405.4	936.5 $\pm$ 18.7	1054.1 $\pm$ 21.1	732.6 $\pm$ 21.9	920.0 $\pm$ 27.6
DDoS	420.1	1058.0 $\pm$ 21.2	1208.4 $\pm$ 24.2	829.1 $\pm$ 24.9	1068.5 $\pm$ 32.1
DTeS	439.8	1179.6 $\pm$ 23.6	1373.5 $\pm$ 27.5	925.6 $\pm$ 27.8	1232.5 $\pm$ 36.9
DHeS	460.2	1301.1 $\pm$ 26.0	1545.2 $\pm$ 30.9	1022.2 $\pm$ 30.1	1405.1 $\pm$ 42.2
DOcS	480.1	1422.6 $\pm$ 28.4	1721.5 $\pm$ 34.4	1118.3 $\pm$ 33.5	1583.6 $\pm$ 47.5

<sup>a</sup>The maximum error involved in  $C_p(l)$  is 2%, and in  $C_p(g)$  it is 3%.

TABLE XIII: Estimation of Liquid and Vapor Heat Capacities ( $\text{J deg}^{-1} \text{mol}^{-1}$ ) of the Triglyceride Ester Series<sup>a</sup>

compd	mean $T$ , K	$C_p(l)$		$C_p(g)$	
		298 K	mean $T$ , K	298 K	mean $T$ , K
TB	308.5	498.9 $\pm$ 9.9	505.4 $\pm$ 10.1	361.6 $\pm$ 10.8	370.8 $\pm$ 11.1
TC	349.3	681.2 $\pm$ 13.6	723.3 $\pm$ 14.5	506.4 $\pm$ 15.2	569.1 $\pm$ 17.1
TO	386.1	863.5 $\pm$ 17.3	953.9 $\pm$ 19.1	651.2 $\pm$ 19.5	787.4 $\pm$ 23.6
TD	411.4	1045.7 $\pm$ 20.9	1185.3 $\pm$ 23.7	796.0 $\pm$ 23.9	1007.9 $\pm$ 30.2
TL	437.9	1228.0 $\pm$ 24.6	1429.0 $\pm$ 28.6	940.8 $\pm$ 28.2	1245.3 $\pm$ 37.4
TM	468.7	1410.3 $\pm$ 28.2	1690.5 $\pm$ 33.8	1073.1 $\pm$ 32.2	1506.5 $\pm$ 45.2
TP	483.1	1592.5 $\pm$ 31.9	1934.4 $\pm$ 38.7	1230.4 $\pm$ 36.9	1743.8 $\pm$ 52.3
TS	505.8	1691.1 $\pm$ 33.8	2201.3 $\pm$ 44.0	1375.2 $\pm$ 41.3	2010.5 $\pm$ 60.3

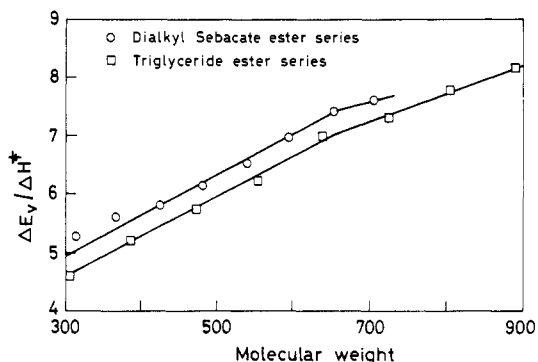
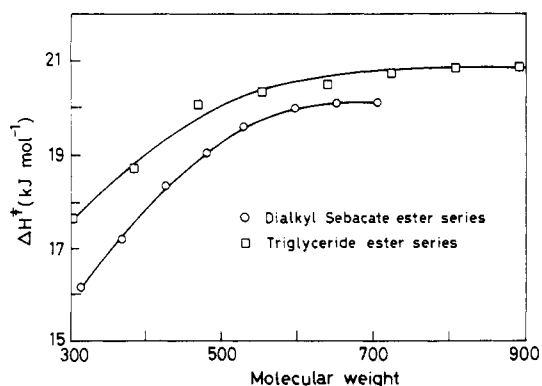
<sup>a</sup>The maximum error involved in  $C_p(l)$  is 2%, and in  $C_p(g)$  it is 3%.

$n$  greater than 4 shows<sup>45</sup> that the unit of flow is less than the unit of vaporization thus, suggesting the segmental motion.

A different aspect of the  $n$  value concept in understanding the spherical nature of the molecule during vaporization has been attempted. A plot of  $\Delta H_v$  for the  $n$ -alkanes<sup>16,46</sup> at the boiling temperature with respect to their molecular weights is shown in Figure 5a. From the plot, it is found that there are three linear portions with a difference in slope, and knees are observed at a molecular weight around 100 and 250. The derivative graph (Figure 5b) of Figure 5a distinctly emphasizes the knee formation. Figure 5b has been obtained from a standard computer program using Newton interpolation for the function and its first derivative. Below molecular weight of 100,  $n$  is less than 4 ( $\Delta H$  data from ref 5 and  $\Delta E_v$  from  $\Delta H_v$  data of ref 16 and 46); between molecular weights of 100 and 250, the value of  $n$  is approximately equal to 4. The first knee in Figure 5 occurring at a molecular weight of about 100 has been attributed to the tendency of longer chains to become coiled.<sup>3,16</sup> This situation prevails up to a molecular weight of about 250, above which ( $n > 4$ ) the molecules become sufficiently longer and extensive coiling forces the whole molecule into a rigid sphere. For a long-chain polar molecule with its strong secondary forces, a more rigid sphere may be formed. It may then be said that higher  $n$  values represent the vaporization of the long-chain molecules in a rigid coiled spherical form; this "coiled spherical symmetry" however, may be distinguished from the spherical symmetry of smaller molecules (where  $n < 4$ ), which is a result of their inherent spherical structure.

When the above arguments are extended to the present case of esters, it is evident that they vaporize in a spherically coiled form because all of them have a molecular weight above 300 and  $n > 4$  (Tables VII and VIII). This comports our earlier discussion based on Figures 2 and 3, that esters vaporize in a coiled spherical form.

Since  $n > 4$  (Tables VII and VIII), the flow behavior of the two ester series is apparently in the form of segmental motion. We draw attention to the fact that  $n$  is temperature dependent and it is necessary to compare  $\Delta E_v$  and  $\eta$ , at their corresponding

Figure 6. Ratio of  $\Delta E_v/\Delta H^*$  or  $n$  as a function of molecular weight.Figure 7. Enthalpy of activation for viscous flow ( $\Delta H^*$ ) as a function of molecular weight.

states.<sup>47</sup> In the present investigation, because of the unavailability of the  $\eta$  value at the boiling temperature (due to the previously mentioned reasons), comparison of  $\Delta E_v$  and  $\eta$  is made at temperatures in the range 298–523 K which is less than the boiling temperature. Since the  $\Delta E_v$  values obtained in this range are anticipated to be larger than the values at the boiling temperature, the corresponding  $n$  value will obviously be higher than what it would have been at the boiling temperature; this difference, however, should not be very significant.

(43) Saleh, M. A.; Omar, A. J. *Bangladesh Acad. Sci.* 1984, 8(2), 35.  
 (44) Grunberg, L.; Nissan, A. H. *Trans. Faraday Soc.* 1949, 49, 125.  
 (45) Ewell, R. H.; Eyring, H. *J. Chem. Phys.* 1937, 5, 726.  
 (46) Zwolinski, B. J.; Wilhoit, R. C. *Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons & Related Compounds*; API 44, TRC Publication 101; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1971.

(47) Eirich, F.; Simha, R. *J. Chem. Phys.* 1939, 7, 116.

Comparison of  $n$  values of both ester series (Figure 6) shows a regular rise in the  $n$  values with increase in the molecular weight. A marked difference in the flow mechanism of these ester series is manifested by the significantly different  $n$  values even at the same molecular weight. From the plot of  $\Delta H^*$  vs molecular weight (Figure 7) the same inference may be drawn. It is observed that  $\Delta H^*$  is different for both ester series. This difference may be attributed to the polarity and stiffness of the independently moving segment. It is vividly seen in the case of branched esters that the addition of the  $-\text{C}(\text{O})\text{O}-$  group, having a high rotational barrier<sup>48</sup> (71 128 J mol<sup>-1</sup>) and greater spherical symmetry due to additional branching, leads to an increase in the chain stiffness. From Figure 7,  $\Delta H^*$  initially increases with molecular weight and levels off at a later stage in both ester series. This means that the "hole" required for the molecule to move becomes smaller relative to the size of the molecule as the chain length increases. That is, as the molecule becomes longer, it commences to move in a segment rather than in single whole molecule;<sup>49</sup>  $\Delta H^*$  therefore requires only a smaller and smaller fraction of  $\Delta E_v$ , with successive increase in the chain length. When a chain becomes sufficiently large, it appears to move in units of fixed size which are independent of molecular weight. However, the magnitude of  $\Delta H^*$  still remains different for both ester series, suggesting that it is still sensitive to the structure of the molecules.

From Figure 7, the point from where the  $\Delta H^*$  becomes independent of molecular weight could be taken as the approximate segment size that corresponds to a molecular weight of around 650 in both ester series. Incidentally, in Figure 6 also, a knee is observed at a molecular weight of around 650. The apparent similarity of the segment size in terms of molecular weight in the two ester series is elusive. In triglycerides, the actual length of the segment will be reduced approximately to two-thirds due to branching. Wake<sup>4</sup> has determined the segment size in  $n$ -paraffins from  $\Delta H^*$  and  $\Delta H^*_{\text{total}}$  (a hypothetical  $\Delta H^*$  when the whole molecule is activated at the same time) data and found that it varies with molecular weight in the range 100–450. Kauzmann and Eyring<sup>49</sup> found that, in long-chain hydrocarbons, there is a tendency for  $\Delta H^*$  to level off as the chain length increases to 30 carbon atoms. From Figure 7, the semiquantitative approach of obtaining the segment size is found to be more direct although the estimated value is approximate. It may be pointed out that segmental mobility in the elementary flow process remains an intriguing but an elusive goal. Figure 3 shows that  $\eta$  vs (molecular weight)<sup>2/3</sup> does not give a linear fit, suggesting that molecules do not flow in coiled spherical form though vaporization in a coiled spherical form is operative. This result lends support to a flow mechanism involving segmental motion, in contrast to the mechanism for vaporization.

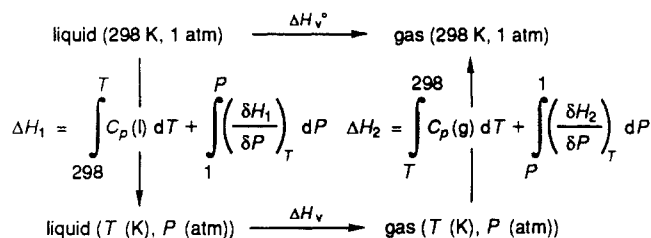
Finally, it is evident from the foregoing discussion that, in long-chain esters, a macroscopic thermodynamic property such as heat of vaporization is sensitive to the molecular weight and insensitive to the structure (branching, flexibility, and polarity). The flow behavior, on the other hand, is sensitive to both the structure and the molecular weight but is independent of molecular weight as the chain length increases. The large negative entropy of activation for viscous flow  $\Delta S^*$  (Tables IX and X), may be attributed not only to the higher order required in the molecules surrounding the hole formed for the segmental flow but also to the hindrance of the segmental flow by the successive attached segments.

**Acknowledgment.** We are thankful to the Department of Science and Technology, New Delhi, India, for financial support.

(48) Hobbs, S. Y.; Billmeyer, F. W., Jr. *J. Polym. Sci. A-2* **1970**, *8*, 1395.  
 (49) Kauzmann, W.; Eyring, H. *J. Am. Chem. Soc.* **1940**, *62*, 3113.

### Appendix: Correction of Heat of Vaporization to 298 K and Calculation of $\Delta H_v^\circ$ by Group Additivity Method

$\Delta H_v$  measured at temperature  $T$  were converted to  $\Delta H_v^\circ$  at 298 K from the following Hess's cycle.



From the above scheme

$$\begin{aligned}
 \Delta H_v^\circ &= \Delta H_v + \Delta H_1 + \Delta H_2 \\
 &= \Delta H_v + \int_{298}^T C_p(l) dT + \int_1^P \left(\frac{\delta H_1}{\delta P}\right)_T dP + \\
 &\quad \int_T^{298} C_p(g) dT + \int_P^1 \left(\frac{\delta H_2}{\delta P}\right)_T dP \quad (\text{A1})
 \end{aligned}$$

$(\delta H_1/\delta P)_T$  is negligible for liquids and solids. Considering the vapors to behave ideally,  $(\delta H_2/\delta P)_T$  is also negligible. Equation A1 becomes

$$\Delta H_v^\circ = \Delta H_v + \int_{298}^T C_p(l) dT - \int_{298}^T C_p(g) dT \quad (\text{A2})$$

Heat capacities of liquids  $C_p(l)$  and gases  $C_p(g)$  were estimated from the group contribution method<sup>20-28</sup> using the equations

$$C_p(g) = \sum a + T \sum b + T^2 \sum c + T^3 \sum d \quad (\text{A3})$$

$$C_p(l) = C_p^{298 \text{ K}}(l) + n(T - 298)(0.00818) \quad (\text{A4})$$

where  $a$ ,  $b$ ,  $c$ , and  $d$  are characteristic of that particular group and  $n$  is the number of  $-\text{CH}_2-$  units in the molecule under consideration.  $C_p^{298 \text{ K}}(l)$  was obtained by the group additivity method.<sup>26</sup> The calculated  $C_p(g)$  and  $C_p(l)$  values at temperatures  $T$  and 298 K are given in Tables XII and XIII. The maximum error involved in  $C_p(g)$  and  $C_p(l)$  computations are 3% and 2%, respectively. Substituting the above  $C_p(g)$  and  $C_p(l)$  values in eq A2,  $\Delta H_v^\circ$  was obtained (Tables I and II).

The group additivity method is widely used to estimate thermodynamic properties,<sup>29-33</sup> so far it has been applied to various organic compounds up to a molecular weight of 250 to estimate  $\Delta H_v^\circ$ . For applying to high molecular weight compounds, we have estimated the error in the  $\Delta H_v^\circ$ , from the extrapolation of the plot of error vs molecular weight. An error within the acceptable limits of 3–5% was found for the calculated value of  $\Delta H_v^\circ$  for esters in the molecular weight range 200–1000.

The commonly used  $\Delta H_v^\circ$  group value for the methylene group<sup>31,32</sup> is 5.0 kJ mol<sup>-1</sup>; lower values of 3.3 and 3.8 kJ mol<sup>-1</sup> have also been used.<sup>34,35</sup> We have calculated  $\Delta H_v^\circ$  for esters using  $-\text{CH}_2-$  group values of 3.3, 3.8, and 5.0 kJ mol<sup>-1</sup>. The  $-\text{CH}_2-$  group value of 3.8 kJ mol<sup>-1</sup> gives good agreement (within 95–98%) with the experimental value (Tables III and IV). The agreeable lower  $-\text{CH}_2-$  group value may be attributed to the rigid carbonyl group in esters, which leads to poorer alignment of the chains causing a lower interactions among the chains. The other group values of  $\Delta H_v^\circ$  calculation were taken from ref 31, and suitable corrections were applied.<sup>36</sup>

**Registry No.** DBS, 109-43-3; DHS, 2449-10-7; DOS, 2432-87-3; DPS, 2432-89-5; DDoS, 2432-88-4; DTeS, 26719-47-1; DHeS, 26719-48-2; DOcS, 3072-03-5; TB, 60-01-5; TC, 621-70-5; TO, 538-23-8; TD, 621-71-6; TL, 538-24-9; TM, 555-45-3; TP, 555-44-2; TS, 555-43-1.