Vapor Pressures and Enthalpies of Vaporization of a Series of the Symmetric Linear n-Alkyl Esters of Dicarboxylic Acids

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Ⓢ *Supporting Information*

ABSTRACT: Vapor pressures and the molar enthalpies of vaporization of the linear aliphatic alkyl esters of dicarboxylic acids R—CO_2—$(CH_2)_n$—CO_2—R with n = (0 to 4) with R = C_2H_5, n-C_3H_7, and n-C_4H_9 have been determined using the transpiration method. A linear correlation of enthalpies of vaporization (at T = 298.15 K) of the esters with the number n and with Kovat's indices has been found, proving the internal consistency of measured data.

■ INTRODUCTION

Linear alkyl esters of dicarboxylic acids can be used as green solvents to extract carboxylic acids, as plasticizers in polymers, as an additive in fragrance formulation, and even as an additive for biodiesel.[1] In addition, esters are intermediates in the polymer production, for example, polybutylene succinate polymers.[2] The reliable data on vapor pressures and enthalpies of vaporization are required for the optimization of technological processes and for the assessment of the environmental fate of chemicals. Thermodynamic properties of dimethyl esters of dicarboxylic acids have been studied recently.[3] Vapor pressure and vaporization enthalpy data of esters of dicarboxylic acid with a longer alkyl chain are scarce and contradicting. This paper extends our previous[3−9] studies on the esters with the systematic study of the linear aliphatic n-alkyl esters of dicarboxylic acids C_mH_{2m+1}—CO_2—$(CH_2)_n$—CO_2—C_mH_{2m+1} with n = (0 to 4) and m = (2 to 4). The enthalpies of vaporization, $\Delta_l^g H_m$, have been obtained from the temperature dependence of the vapor pressures measured by the transpiration method. These data together with those available from the literature were used to establish the general regularities in the $\Delta_l^g H_m$ and the vapor pressures within this homologous series.

■ EXPERIMENTAL SECTION

Materials. The sample of diethyl ester of oxalic acid was of commercial origin (Aldrich). Other samples of alkyl esters of dicarboxylic acids were synthesized by the esterification of an appropriate dicarboxylic acid with the alcohol of the desired alkyl chain length.[10] Phosphoric acid was used as a catalyst. Samples were purified by repeated vacuum distillation. The degree of purity of the samples was determined using a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 $cm^3 \cdot s^{-1}$. A capillary column HP-5 (stationary phase cross-linked 5 % phenyl methyl silicone)

was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was T = 333.15 K for 180 s followed by a heating rate of 0.167 $K \cdot s^{-1}$ to T = 523.15 K. No total impurities (greater than mass fraction 0.003) could be detected in the samples used for the vapor pressure measurements.

Measurements of the Enthalpies of Vaporization Using the Transpiration Method. Vapor pressures were determined using the method of transpiration in a saturated nitrogen stream,[11,12] and enthalpies of dialkyl esters of dicarboxylic acids were obtained applying the Clausius—Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provided a surface which was sufficient for the vapor—liquid equilibration. At constant temperature (± 0.1 K), a nitrogen stream was passed through the U-tube, and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and optimized to reach the saturation equilibrium of the transporting gas at each temperature under study. On one hand, the flow rate of the nitrogen stream in the saturation tube should be not too slow to avoid the transport of material from the U-tube due to diffusion. On the other hand, the flow rate should be not too fast to reach the saturation of the nitrogen stream with a compound. We tested our apparatus at different flow rates of the carrier gas to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus, the contribution due to diffusion was negligible at a flow rate up to 0.11 $cm^3 \cdot s^{-1}$. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration

Table 1. Vapor Pressures, p, and Vaporization Enthalpy, $\Delta_l^g H_m$, Obtained by the Transpiration Method

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
K	mg	dm³	dm³·h⁻¹	Pa	Pa	kJ·mol⁻¹	K	mg	dm³	dm³·h⁻¹	Pa	Pa	kJ·mol⁻¹

diethyl oxalate; $\Delta_f^g H_m(298.15\,\text{K}) = (57.80 \pm 0.36)\,\text{kJ·mol}^{-1}$

$$\ln(p/\text{Pa}) = \frac{305.6}{R} - \frac{81119.36}{R(T/K)} - \frac{78.2}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T	m	V	gas flow	p	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$	T	m	V	gas flow	p	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$
283.6	5.75	6.07	5.09	16.4	−0.4	58.95	313.5	7.42	0.711	2.84	175.0	1.1	56.61
288.5	5.58	3.74	5.16	25.6	0.0	58.56	316.4	8.80	0.711	2.84	207.5	−4.7	56.38
293.4	5.71	2.48	2.78	39.2	0.8	58.18	318.3	10.33	0.711	2.84	243.4	2.3	56.23
298.3	5.73	1.70	2.80	57.1	0.3	57.80	321.4	5.58	0.319	1.13	297.2	1.4	55.99
303.3	4.82	1.00	2.80	81.4	−1.9	57.41	325.4	6.41	0.284	1.10	383.4	0.9	55.68
308.4	5.31	0.711	2.84	125.4	4.1	57.01	329.5	6.51	0.229	1.10	483.2	−10.6	55.36
311.3	6.30	0.704	2.82	150.9	1.7	56.78	333.5	6.77	0.183	1.10	627.5	−1.3	55.04

diethyl malonate; $\Delta_f^g H_m(298.15\,\text{K}) = (61.70 \pm 0.25)\,\text{kJ·mol}^{-1}$

$$\ln(p/\text{Pa}) = \frac{320.15}{R} - \frac{87489.79}{R(T/K)} - \frac{86.5}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T	m	V	gas flow	p	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$	T	m	V	gas flow	p	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$
283.8	1.26	2.85	3.14	6.89	−0.04	62.95	304.2	2.66	1.01	3.57	40.5	0.0	61.18
286.2	1.46	2.65	3.57	8.58	−0.1	62.74	304.7	4.87	1.75	3.14	42.8	0.6	61.14
289.2	1.85	2.50	3.57	11.5	0.1	62.48	307.3	2.58	0.774	3.57	51.3	−0.4	60.91
292.3	2.20	2.26	3.57	15.0	0.0	62.21	310.2	2.63	0.625	3.57	64.6	0.1	60.66
295.2	1.49	1.19	3.57	19.3	0.0	61.96	313.3	2.36	0.446	3.57	81.4	0.0	60.39
298.2	3.00	1.85	3.57	25.1	0.2	61.70	316.3	2.33	0.357	3.57	100.5	−0.9	60.13
301.3	2.61	1.25	3.57	32.1	0.1	61.43							

diethyl succinate; $\Delta_f^g H_m(298.15\,\text{K}) = (65.07 \pm 0.25)\,\text{kJ·mol}^{-1}$

$$\ln(p/\text{Pa}) = \frac{332.36}{R} - \frac{93334.78}{R(T/K)} - \frac{94.8}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T	m	V	gas flow	p	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$	T	m	V	gas flow	p	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$
290.2	9.22	26.6	8.65	4.95	0.02	65.83	323.5	3.92	0.708	2.83	77.7	1.0	62.67
290.5	1.77	4.99	8.56	5.04	−0.03	65.80	326.5	4.65	0.695	2.78	94.1	−0.8	62.39
293.5	3.78	7.99	8.56	6.78	0.1	65.52	326.5	4.16	0.608	1.46	96.3	1.3	62.39
296.4	3.61	5.98	8.54	8.61	−0.1	65.24	328.5	5.56	0.695	2.78	112.5	3.4	62.20
301.4	4.05	4.27	8.54	13.4	0.0	64.77	331.4	4.25	0.450	1.46	133.0	−0.2	61.92
306.4	4.26	2.90	8.70	20.8	0.3	64.29	331.6	6.90	0.718	2.78	135.1	0.1	61.90
311.4	4.81	2.18	8.70	31.3	0.6	63.82	333.6	7.50	0.695	2.78	151.7	−2.7	61.71
313.4	1.77	0.708	2.83	35.0	−0.9	63.63	336.5	4.81	0.364	1.46	186.4	−0.6	61.44
316.4	4.30	1.34	2.67	45.5	0.2	63.34	339.4	5.73	0.364	1.46	222.1	−3.3	61.16
318.4	2.54	0.708	2.83	50.3	−2.4	63.16	342.4	6.86	0.364	1.46	265.8	−6.7	60.88
321.4	4.28	0.914	2.74	66.1	0.3	62.87	345.5	8.69	0.359	1.44	342.5	12.5	60.59

diethyl glutarate; $\Delta_f^g H_m(298.15\,\text{K}) = (69.76 \pm 0.38)\,\text{kJ·mol}^{-1}$

$$\ln(p/\text{Pa}) = \frac{347.220}{R} - \frac{100503.36}{R(T/K)} - \frac{103.1}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T	m	V	gas flow	p	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$	T	m	V	gas flow	p	$(p_{exp}-p_{calc})$	$\Delta_l^g H_m$
298.3	3.52	13.06	8.29	3.52	0.1	69.75	322.2	2.63	1.35	4.05	25.4	−1.1	67.29
303.4	3.90	8.84	8.29	5.75	0.3	69.23	323.3	8.00	3.73	8.29	27.7	−1.2	67.18
308.6	4.27	6.29	8.29	8.77	0.1	68.69	328.2	3.15	1.01	4.05	40.5	−1.4	66.67
311.2	2.90	3.52	7.81	10.8	−0.1	68.42	333.2	5.29	1.15	4.05	60.1	−0.4	66.16
313.5	3.37	3.30	7.91	13.4	0.2	68.19	338.2	6.79	1.01	4.05	87.4	1.5	65.64
316.2	4.58	3.68	8.18	16.1	−0.4	67.91	343.2	10.24	1.08	4.05	123.6	3.0	65.12
318.2	2.78	1.95	7.82	18.5	−0.8	67.70	347.9	98.33	7.36	8.18	172.5	8.6	64.64
318.5	9.06	5.86	8.18	20.0	0.2	67.67							

diethyl adipate; $\Delta_f^g H_m(298.15\,\text{K}) = (74.03 \pm 0.27)\,\text{kJ·mol}^{-1}$

$$\ln(p/\text{Pa}) = \frac{361.74}{R} - \frac{107240.52}{R(T/K)} - \frac{111.4}{R}\ln\left(\frac{T/K}{298.15}\right)$$

Table 1. Continued

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$	K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$
303.5	2.63	14.58	8.18	2.20	0.04	73.44	335.2	3.00	1.13	2.06	32.3	0.6	69.90
308.2	2.07	7.36	8.18	3.43	0.1	72.91	338.2	7.43	2.32	8.18	39.0	−0.5	69.57
313.3	1.82	4.22	8.18	5.23	−0.1	72.34	340.2	2.60	0.685	2.06	46.2	0.5	69.35
318.2	1.33	2.04	8.18	7.93	−0.2	71.80	343.2	3.48	0.754	2.06	56.1	−0.5	69.01
323.1	3.05	3.13	8.18	11.8	−0.4	71.25	346.2	4.32	0.754	2.06	69.8	0.0	68.68
328.2	3.72	2.45	8.18	18.5	0.0	70.68	349.1	3.83	0.548	2.06	85.1	0.0	68.36
329.6	3.05	1.78	2.11	20.9	0.3	70.53	352.2	4.48	0.514	2.06	106.1	1.5	68.01
333.2	4.59	2.04	8.18	27.3	0.1	70.13							

dipropyl oxalate; $\Delta_l^g H_m (298.15\ K) = (61.40 \pm 0.49)\ kJ \cdot mol^{-1}$

$$\ln(p/Pa) = \frac{322.28}{R} - \frac{89666.99}{R(T/K)} - \frac{94.8}{R} \ln\left(\frac{T/K}{298.15}\right)$$

293.6	5.01	7.58	7.58	9.43	0.4	61.84	318.6	3.40	0.771	3.08	62.6	−1.0	59.47
298.5	5.01	5.12	7.58	13.9	0.3	61.37	321.4	4.02	0.771	3.08	74.1	−3.1	59.20
301.4	4.65	3.79	7.58	17.5	0.1	61.10	323.3	4.90	0.771	3.08	90.3	2.3	59.02
306.4	4.65	2.59	7.58	25.5	−0.2	60.63	326.3	5.89	0.771	3.08	108.5	0.8	58.74
308.4	1.60	0.746	2.99	30.4	0.3	60.44	328.3	6.79	0.771	3.08	124.8	2.2	58.55
311.4	4.83	1.90	7.58	36.2	−1.5	60.15	330.4	7.73	0.771	3.08	142.3	1.6	58.35
313.4	2.18	0.746	2.99	41.3	−2.4	59.96	333.5	9.78	0.771	3.08	180.1	8.8	58.06
316.3	2.82	0.771	3.08	52.0	−2.0	59.69							

dipropyl malonate; $\Delta_l^g H_m (298.15\ K) = (66.18 \pm 0.40)\ kJ \cdot mol^{-1}$

$$\ln(p/Pa) = \frac{339.6}{R} - \frac{96922.69}{R(T/K)} - \frac{103.1}{R} \ln\left(\frac{T/K}{298.15}\right)$$

293.3	2.63	9.88	9.26	3.56	−0.1	66.69	315.3	4.06	2.21	9.47	24.5	0.5	64.42
298.3	2.69	6.16	9.36	5.82	0.03	66.17	318.5	2.30	1.03	3.00	29.6	−1.1	64.09
299.4	3.03	6.20	7.59	6.52	0.1	66.06	319.4	5.51	2.21	9.47	33.2	0.4	64.00
303.2	3.25	4.81	9.47	8.97	0.1	65.67	323.4	3.23	1.00	3.00	42.6	−1.5	63.59
307.3	3.13	3.24	9.47	12.9	0.3	65.25	328.5	3.54	0.75	3.00	62.2	−1.5	63.06
308.2	0.77	0.75	3.00	13.5	0.0	65.15	333.5	5.07	0.75	3.00	89.0	−0.8	62.54
311.3	3.28	2.45	9.47	17.8	0.4	64.83	336.4	6.23	0.75	3.00	109.5	0.5	62.25
313.3	1.13	0.75	3.00	19.9	−0.5	64.63	338.5	7.40	0.75	3.00	130.0	4.8	62.03

dipropyl succinate; $\Delta_l^g H_m (298.15\ K) = (70.98 \pm 0.32)\ kJ \cdot mol^{-1}$

$$\ln(p/Pa) = \frac{354.66}{R} - \frac{104193.73}{R(T/K)} - \frac{111.4}{R} \ln\left(\frac{T/K}{298.15}\right)$$

308.3	6.17	15.50	7.78	4.87	0.1	69.85	328.6	2.90	1.38	4.15	25.2	0.3	67.59
312.4	3.80	6.73	7.34	6.85	0.1	69.40	331.3	3.48	1.38	4.14	30.3	−0.1	67.29
316.4	4.89	6.30	7.34	9.36	−0.1	68.95	333.4	3.13	1.04	4.15	36.2	0.8	67.06
318.5	0.96	1.04	4.15	11.1	−0.1	68.72	336.5	3.82	1.04	4.14	44.3	0.1	66.71
321.5	2.38	2.06	4.05	13.9	−0.4	68.38	338.5	4.40	1.04	4.15	50.9	0.0	66.49
323.5	1.41	1.04	4.15	16.3	−0.5	68.16	341.5	5.33	1.03	4.11	62.5	−0.2	66.16
326.4	3.60	2.07	4.14	20.9	−0.1	67.84	343.5	6.17	1.03	4.11	72.3	0.6	65.93

dipropyl glutarate; $\Delta_l^g H_m (298.15\ K) = (75.48 \pm 0.31)\ kJ \cdot mol^{-1}$

$$\ln(p/Pa) = \frac{369.20}{R} - \frac{111167.48}{R(T/K)} - \frac{119.7}{R} \ln\left(\frac{T/K}{298.15}\right)$$

313.3	3.41	14.09	8.80	2.76	0.01	73.67	333.6	2.66	2.00	4.00	14.9	−0.1	71.24
316.4	3.13	9.86	8.83	3.59	−0.03	73.30	336.4	2.80	1.72	6.87	18.4	−0.1	70.91
318.5	0.53	1.33	4.00	4.44	0.1	73.05	338.5	2.60	1.33	3.99	22.0	0.4	70.66
319.4	2.53	6.02	8.80	4.78	0.1	72.94	341.4	2.37	0.986	3.95	27.1	0.3	70.31
322.5	2.42	4.46	8.92	6.09	−0.09	72.57	343.6	2.75	0.997	3.99	31.0	−0.4	70.04
323.5	0.78	1.37	4.00	6.37	−0.3	72.45	346.4	3.37	0.986	3.95	38.5	0.3	69.71

Table 1. Continued

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$
K	mg	dm³	dm³·h⁻¹	Pa	Pa	kJ·mol⁻¹	K	mg	dm³	dm³·h⁻¹	Pa	Pa	kJ·mol⁻¹
325.4	2.63	3.79	8.92	7.78	−0.01	72.22	348.4	3.83	0.997	3.99	43.2	−0.7	69.47
328.5	1.19	1.33	4.00	10.0	0.0	71.85	350.5	4.56	1.02	3.95	50.4	−0.3	69.22
329.5	2.93	3.01	8.81	10.9	0.1	71.73	353.5	5.57	0.997	3.99	62.8	0.8	68.86
331.4	2.58	2.29	6.87	12.8	0.2	71.50							

dipropyl adipate; $\Delta_f^g H_m(298.15\ \mathrm{K}) = (80.97 \pm 0.31)\ \mathrm{kJ \cdot mol^{-1}}$

$$\ln(p/\mathrm{Pa}) = \frac{386.62}{R} - \frac{1191102.74}{R(T/\mathrm{K})} - \frac{127.9}{R} \ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$
318.8	1.33	8.30	8.89	1.73	0.03	78.33	345.5	4.26	3.00	8.77	15.2	−0.7	74.92
321.7	1.73	8.41	8.77	2.22	0.00	77.96	348.3	4.03	2.19	8.77	19.6	0.0	74.56
323.5	0.64	2.63	8.78	2.60	−0.01	77.73	351.5	2.94	1.24	2.01	25.3	0.5	74.15
327.4	2.25	6.54	8.72	3.67	−0.01	77.23	354.2	2.93	1.02	2.04	30.6	0.5	73.81
333.2	2.79	4.94	8.72	6.02	0.01	76.49	357.1	2.42	0.698	2.04	37.3	0.4	73.44
336.1	2.24	3.13	8.72	7.65	0.02	76.12	361.2	2.46	0.545	2.04	48.5	0.2	72.91
339.1	1.98	2.18	8.72	9.72	0.02	75.74	365.3	3.14	0.528	2.04	63.9	0.0	72.39
342.1	2.49	2.18	8.72	12.2	−0.1	75.35							

dibutyl oxalate; $\Delta_f^g H_m(298.15\ \mathrm{K}) = (71.37 \pm 0.21)\ \mathrm{kJ \cdot mol^{-1}}$

$$\ln(p/\mathrm{Pa}) = \frac{355.36}{R} - \frac{104587.61}{R(T/\mathrm{K})} - \frac{111.4}{R} \ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$
291.4	1.54	21.91	7.83	0.87	−0.01	72.13	325.3	2.47	1.67	4.00	18.0	−0.2	68.35
293.4	1.66	18.65	7.83	1.10	0.02	71.91	326.4	2.12	1.34	4.01	19.3	−0.4	68.23
295.7	2.04	17.61	7.83	1.43	0.1	71.65	327.5	1.55	0.879	1.82	21.5	0.0	68.11
298.8	1.64	11.09	7.83	1.82	−0.02	71.31	328.2	3.89	2.12	3.17	22.3	−0.5	68.03
300.4	1.66	9.78	7.83	2.09	−0.1	71.13	328.5	2.50	1.35	4.03	22.6	−0.7	68.00
302.3	2.26	11.13	9.41	2.49	−0.1	70.92	330.3	2.09	1.00	4.00	25.4	−1.2	67.80
302.8	1.76	7.83	7.83	2.76	0.1	70.86	331.1	2.01	0.848	1.81	28.9	0.7	67.71
303.3	2.17	9.33	8.00	2.83	0.02	70.81	331.4	2.41	1.00	4.01	29.2	0.4	67.68
305.2	2.72	9.78	7.82	3.40	0.1	70.59	333.2	4.80	1.75	3.17	33.9	0.3	67.47
305.3	2.13	7.84	9.40	3.34	−0.03	70.58	333.5	3.27	1.15	1.81	34.6	0.9	67.44
308.2	2.19	6.00	7.82	4.46	0.1	70.26	333.5	3.69	1.35	4.03	33.3	−0.4	67.44
308.3	2.05	5.73	8.00	4.33	−0.1	70.25	335.2	3.10	1.00	4.00	37.5	−0.6	67.25
308.4	2.29	6.27	9.40	4.48	0.02	70.24	336.3	3.41	1.00	4.01	41.4	0.2	67.13
311.3	2.17	4.70	9.40	5.65	−0.1	69.91	337.0	1.73	0.485	1.81	43.4	0.0	67.05
312.3	1.70	3.32	7.96	6.24	−0.03	69.80	338.1	4.15	1.06	3.17	47.5	0.6	66.93
313.2	2.26	4.13	8.00	6.60	−0.2	69.70	338.6	3.94	1.01	4.03	47.5	−1.1	66.87
314.3	2.41	4.00	9.40	7.37	−0.1	69.58	340.2	4.48	1.00	4.00	54.3	0.0	66.69
315.5	4.30	6.13	7.82	8.55	0.3	69.45	340.8	3.69	0.766	1.91	58.6	2.0	66.63
317.4	2.44	3.14	9.40	9.37	−0.3	69.23	341.4	4.68	1.00	4.01	56.8	−2.1	66.56
317.8	1.79	2.09	7.82	10.5	0.5	69.19	343.2	4.27	0.794	3.17	65.1	−1.5	66.36
318.2	2.32	2.67	8.00	10.5	0.2	69.15	343.4	2.72	0.479	1.91	69.3	1.7	66.34
319.9	1.52	1.50	5.62	12.4	0.5	68.96	343.5	5.54	1.04	4.03	64.5	−3.5	66.33
320.2	2.24	2.35	9.40	11.5	−0.7	68.92	345.2	3.34	0.545	1.63	74.1	−2.1	66.14
322.5	2.09	1.71	3.95	14.9	0.3	68.67	348.3	8.40	1.06	3.17	96.2	2.6	65.79
323.2	2.64	2.00	8.00	15.9	0.5	68.59	351.2	3.84	0.409	1.63	113.7	0.9	65.47
323.4	1.667	1.35	4.03	15.1	−0.6	68.57	353.1	11.06	1.01	3.17	133.2	6.0	65.26
325.3	1.46	1.01	4.04	17.6	−0.6	68.35	358.2	6.11	0.409	1.63	181.1	6.8	64.69

dibutyl malonate; $\Delta_f^g H_m(298.15\ \mathrm{K}) = (75.28 \pm 0.39)\ \mathrm{kJ \cdot mol^{-1}}$

$$\ln(p/\mathrm{Pa}) = \frac{370.83}{R} - \frac{110964.14}{R(T/\mathrm{K})} - \frac{119.7}{R} \ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$
303.2	0.96	7.97	8.69	1.38	−0.02	74.68	338.2	2.88	1.23	4.92	26.7	−1.0	70.49
308.3	1.41	7.24	8.69	2.23	−0.1	74.07	340.2	2.78	0.976	2.93	32.5	0.4	70.25

Table 1. Continued

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$	K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$
313.3	2.08	6.52	8.69	3.66	0.04	73.47	343.2	2.98	0.839	3.35	40.7	0.8	69.89
318.3	2.11	4.35	8.69	5.57	−0.1	72.87	345.2	3.20	0.805	2.93	45.4	−0.5	69.65
323.2	1.90	2.46	4.92	8.78	0.3	72.28	349.1	1.33	0.259	1.04	58.6	−1.6	69.18
325.1	1.93	2.20	2.93	10.1	0.1	72.06	353.1	1.84	0.267	1.04	78.8	0.1	68.70
328.2	2.83	2.46	4.92	13.1	0.3	71.68	357.2	2.62	0.293	1.04	102.2	−0.7	68.21
330.2	2.28	1.71	2.93	15.2	0.2	71.45	361.2	3.04	0.259	1.04	134.3	1.7	67.73
333.2	3.20	1.88	4.92	19.3	0.4	71.09	365.2	3.79	0.259	1.04	167.2	−2.4	67.26
335.2	2.31	1.22	2.93	21.7	−0.4	70.85	369.2	4.92	0.259	1.04	217.4	2.0	66.78

dibutyl succinate; $\Delta_l^g H_m(298.15\ \mathrm{K}) = (79.11 \pm 0.38)\ kJ \cdot mol^{-1}$

$$\ln(p/\mathrm{Pa}) = \frac{382.77}{R} - \frac{117236.9}{R(T/\mathrm{K})} - \frac{127.9}{R} \ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
313.3	0.83	6.73	8.78	1.32	0.02	77.17	335.4	1.71	2.08	8.31	8.77	−0.1	74.35
316.2	1.33	8.31	8.31	1.70	0.00	76.80	338.2	2.40	2.35	5.03	11.0	−0.1	73.99
318.3	0.96	5.03	5.03	2.05	−0.02	76.54	340.1	2.54	2.23	8.93	12.1	−0.6	73.75
320.2	1.77	7.62	8.31	2.48	0.03	76.29	343.2	1.92	1.26	5.03	16.4	0.2	73.35
323.2	0.76	2.52	5.03	3.25	0.1	75.91	346.2	1.53	0.830	1.92	19.7	−0.5	72.97
325.2	2.24	6.23	8.31	3.83	0.03	75.65	349.2	1.48	0.638	1.92	24.7	−0.4	72.58
328.2	1.72	3.78	5.03	4.89	−0.02	75.27	352.1	1.43	0.479	1.92	31.9	1.1	72.21
330.2	2.02	3.74	8.31	5.77	−0.04	75.01	355.1	2.02	0.559	1.92	38.7	0.8	71.83
333.2	2.03	2.94	5.03	7.43	0.01	74.63	358.2	2.12	0.479	1.92	47.3	0.6	71.43

dibutyl glutarate; $\Delta_l^g H_m(298.15\ \mathrm{K}) = (83.07 \pm 0.21)\ kJ \cdot mol^{-1}$

$$\ln(p/\mathrm{Pa}) = \frac{394.44}{R} - \frac{123673.84}{R(T/\mathrm{K})} - \frac{136.2}{R} \ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
317.5	1.36	21.26	7.97	0.64	0.00	80.44	337.6	1.33	3.58	8.60	3.75	−0.1	77.70
318.3	2.18	31.32	8.47	0.70	0.01	80.33	338.6	1.80	4.50	8.43	4.04	−0.1	77.56
322.4	1.43	14.00	7.96	1.03	0.01	79.77	340.5	1.02	2.15	8.61	4.75	−0.1	77.30
323.4	1.28	11.24	8.43	1.14	0.03	79.63	343.3	1.20	2.02	2.02	6.00	−0.04	76.92
323.4	1.89	16.93	8.47	1.13	0.01	79.63	346.6	1.41	1.82	2.02	7.82	0.02	76.47
325.4	1.21	9.26	7.93	1.32	−0.02	79.36	349.6	1.30	1.35	2.02	9.73	−0.1	76.07
326.5	1.34	9.28	7.96	1.45	−0.02	79.21	350.3	1.54	1.51	2.02	10.3	0.1	75.97
328.4	0.62	3.51	8.43	1.79	0.04	78.95	352.5	1.21	1.01	2.02	12.1	0.0	75.67
328.4	1.48	8.60	8.60	1.73	−0.02	78.95	354.7	1.46	1.02	2.03	14.5	0.3	75.37
330.6	1.38	6.63	7.95	2.10	−0.02	78.65	357.5	1.48	0.845	2.03	17.7	0.3	74.99
331.5	1.46	6.45	8.60	2.29	0.00	78.53	360.6	1.43	0.676	2.03	21.3	−0.3	74.57
333.5	1.37	5.06	8.43	2.73	0.02	78.26	363.4	1.31	0.507	2.03	26.0	−0.2	74.19
334.6	1.52	5.02	8.60	3.06	0.1	78.11	366.4	1.59	0.504	2.02	31.8	−0.1	73.78
334.7	2.38	8.03	7.90	2.98	−0.02	78.09	369.5	2.02	0.504	2.02	40.3	1.2	73.35

dibutyl adipate; $\Delta_l^g H_m(298.15\ \mathrm{K}) = (88.51 \pm 0.51)\ kJ \cdot mol^{-1}$

$$\ln(p/\mathrm{Pa}) = \frac{413.05}{R} - \frac{131594.6}{R(T/\mathrm{K})} - \frac{144.5}{R} \ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$	T^a	m^b	$V_{(N2)}{}^c$	gas flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
313.2	2.58	135.7	8.61	0.18	0.00	86.34	348.2	1.92	3.9	8.65	4.67	0.1	81.29
318.2	0.55	17.2	8.61	0.30	0.00	85.62	353.2	2.15	2.9	8.65	7.05	0.2	80.56
323.2	1.08	21.7	8.61	0.48	−0.02	84.90	358.2	2.26	2.1	4.50	10.2	0.2	79.84
328.2	1.07	13.1	8.61	0.79	−0.02	84.18	363.2	2.44	1.6	4.50	14.3	−0.1	79.12
333.3	1.20	9.0	8.61	1.27	−0.01	83.44	368.2	2.79	1.3	4.50	20.1	−0.4	78.40
338.4	1.07	5.0	8.61	2.02	0.00	82.70	373.2	3.39	1.1	4.50	28.5	−0.4	77.67
343.1	0.97	3.0	8.65	3.04	0.03	82.02							

[a] Temperature of saturation. [b] Mass of transferred sample condensed at $T = 243.15$ K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at the cooling temperature $T = 243.15$ K.

was at a flow rate of 10 $cm^3 \cdot s^{-1}$. Thus, we carried out the experiments in the flow rate interval of (1 to 9) $cm^3 \cdot s^{-1}$ which has ensured that transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The mass of the compound collected within a certain time interval was determined by dissolving it in a suitable solvent with a certain amount of external standard (n-decane, n-undecane, n-dodecane). This solution was analyzed using a gas chromatograph equipped with an autosampler. The peak area of the compound related to the peak of the external standard (hydrocarbon $n\text{-}C_nH_{2n+2}$) is a direct measure of the mass of the compound condensed into the cooling trap, provided that a calibration of the system has been made. The saturation vapor pressure p_i^{sat} at each temperature T_i (maintained and measured $\pm$ 0.1 K) was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated

$$p_i^{sat} = m_i RT_a/VM_i; \quad V = V_{N2} + V_i; \quad (V_{N2} \gg V_i) \quad (1)$$

where R = 8.314472 $J \cdot K^{-1} \cdot mol^{-1}$; m_i is the mass of transported compound; M_i is the molar mass of the compound; and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. The volume of transporting gas V_{N2} was determined from the flow rate and time measurements. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using the following equation[11]

$$R \ln p_i^{sat} = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \quad (2)$$

where a and b are adjustable parameters and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase, respectively. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2 the expression for the vaporization enthalpy at temperature T is derived

$$\Delta_l^g H_m(T)/J \cdot mol^{-1} = -b + (\Delta_l^g C_p/J \cdot mol^{-1} \cdot K^{-1})T \quad (3)$$

Values of $\Delta_l^g C_p$ have been calculated according to a procedure developed by Chickos.[13-15] Our own experimental results and parameters a and b are listed in Table 1. The errors in the enthalpies of vaporization are calculated from eq 2 by using the method of least-squares, and uncertainties in values of $\Delta_l^g C_p$ are not taken into account. We have checked the experimental and calculation procedure with measurements of vapor pressures of n-alcohols.[12] The uncertainty of the GC analysis of transported mass of the material, δm_i = (1 to 3) %, was the main contributor to the total experimental error of vapor pressure data, δp_i = (1 to 3) %, measured by the transpiration method.

■ RESULTS AND DISCUSSION

Vapor Pressures and Enthalpies of Vaporization. Vapor pressures and vaporization enthalpies of the dimethyl esters of dicarboxylic acids were studied in our lab recently.[3] Compilation of the molar vaporization enthalpies is given in Table S1, Supporting Information. In this work, we have investigated dialkyl esters of dicarboxylic acids with the longer alkyl chain length. A compilation of vaporization enthalpies of alkyl esters of dicarboxylic acids available from the literature and our new own values is presented in Table 2. We treated the original

experimental $p-T$ data available from the literature[8,16-25] using eq 2 and eq 3, in the same way as our own results, and calculated $\Delta_l^g H_m(298.15$ K) for the sake of comparison. The handbook by Stephenson and Malanowski[16] as well as a review article by Stull[18] contain vapor pressure data for some alkyl esters of dicarboxylic acids. The origin of the data presented there is unclear, and methods of measurements, errors of measurements, and purities of compounds are unknown. However, we also treated the results from Stephenson and Malanowski[16] using eq 2 and eq 3 and calculated $\Delta_l^g H_m(298.15$ K), but the agreement or disagreement with other data in each case should be questionable[3] (see Table 2). Antoine equation coefficients for some alkyl esters of dicarboxylic acid were found in the compilation by Dikyi et al.,[19] and we also used this data for estimation of $\Delta_l^g H_m(298.15$ K) using eq 2 and eq 3 (see Table 2). Vapor pressures of some diethyl esters were measured by Heiber et al.[17] using the static method in 1940; however, the purities of esters were not reported. Their results are generally in agreement with the available data (see Figure 1 to 3), but the vaporization enthalpies derived from their data are systematically lower than those measured in this work.

Diethyl Oxalate. Vapor pressures of diethyl oxalate available from the literature are very consistent (see Figure 1) except for data from Stull[18] and some of the lower points by by Heiber et al.[17] Enthalpies of vaporization calculated from the vapor pressures measured using ebulliometry[20,21] are about 1 $kJ \cdot mol^{-1}$ higher than value measured in the current work. Such a difference could be explained due long extrapolation of data in refs 20 and 21 to 298.15 K.

Diethyl Malonate. Vapor pressures (Figure 2) and enthalpies of vaporization of diethyl malonate (Table 2) are in disarray. The vapor pressures measured close to the boiling point agree well, but the lower temperatures reported by Stull[18] and Heiber et al.[17] are in disagreement with the trend obtained in this temperature range by our new result. Vapor pressures reported in our earlier work[8] most probably were affected by water traces, and these data should be disregarded. In this study, we used a sample of impeccable quality (purity 99.99 % and water content 100 ppm according to the Karl Fisher titration). The spread of vaporization enthalpies listed in the Table 2 for diethyl malonate ranges from (60.5 to 71.0) $kJ \cdot mol^{-1}$, but our new value $\Delta_l^g H_m(298.15$ K) = (61.7 $\pm$ 0.3) $kJ \cdot mol^{-1}$ measured in this work around the reference temperature is not affected by extrapolation as another data set.

Diethyl Succinate. In contrast to diethyl malonate, vapor pressures of diethyl succinate are remarkably consistent (Figure S1, Supporting Information), and as a consequence, vaporization enthalpies derived from these vapor pressures are generally close to $\Delta_l^g H_m(298.15$ K) = (65.1 $\pm$ 0.3) $kJ \cdot mol^{-1}$ measured in this work.

Diethyl Glutarate. Vapor pressures (Figure S2, Supporting Information) and enthalpies of vaporization of diethyl glutarate (Table 2) are generally consistent (again, except for data from Stull[18] and some of the lower points by Heiber et al.[17]). However, our value $\Delta_l^g H_m(298.15$ K) = (69.8 $\pm$ 0.4) $kJ \cdot mol^{-1}$ is noticeably (2 to 3) $kJ \cdot mol^{-1}$ higher in comparison with the literature data.

Diethyl Adipate. Vapor pressures (Figure 3) for this compound are in agreement (except for ref 25), but the spread of vaporization enthalpies inspected is large, from (65 to 74) $kJ \cdot mol^{-1}$. Our new value $\Delta_l^g H_m(298.15$ K) = (74.0 $\pm$ 0.3) $kJ \cdot mol^{-1}$ is again the highest one in comparison with other results.

Table 2. Compilation of Data on Enthalpies of Vaporization $\Delta_f^g H_m$(298.15 K) of the Linear Symmetric Alkyl Esters of Dicarboxylic Acids R$-$CO$_2$$-$(CH$_2$)$_n$$-CO_2$$-$R with n = (0 to 4)

compounds	n^a	technique[b]	T-range K	C_p^l $(\Delta_f^g C_p)^c$ J·mol^{-1}·K^{-1}	$\Delta_f^g H_m$ (T_{av}) kJ·mol^{-1}	$\Delta_f^g H_m$(298.15 K)^d kJ·mol^{-1}	ref
diethyl oxalate	0	E	320.5 to 458.8	260.0 (−78.2)	58.6	65.2	18
95-92-1			343.0 to 457.0		53.9	61.9	16
			320.0 to 459.0		62.3	69.4	16
		S	303.8 to 447.5		49.5	55.3 ± 0.2	17
		E	339.0 to 392.2		54.1	59.3	20
		E	353.5 to 499.4		49.2	58.6 ± 0.3	21
		T	283.6 to 333.5		57.1	**57.8 ± 0.4**	this work
diethyl malonate	1	E	386.2 to 491.0	291.9 (−86.5)	56.9	67.2 ± 0.5	22
105-53-3		T	288.2 to 318.3		64.7	65.1 ± 0.2	8
		E	313.0 to 472.0		51.2	60.5	18
		S	314.7 to 463.8		51.2	58.7 ± 0.2	17
		GC	298.2			58.4 ± 0.6	23
			293.0 to 318.0		63.3	63.9	16
			384.0 to 468.0		59.9	71.0	16
			313.0 to 472.0		51.2	59.4	16
		T	283.8 to 316.3		61.6	**61.7 ± 0.3**	this work
diethyl succinate	2	E	356.6 to 488.0	323.8 (−94.8)	56.8	67.0 ± 0.3	24
123-25-1		E	327.7 to 489.6		54.7	64.5	18
		GC	298.2			60.6 ± 0.6	23
		S	335.2 to 465.1		54.7	63.8 ± 0.1	17
			298.2			60.1	16
			327.0 to 490.0		55.1	64.5	16
		E	378.0 to 533.7		52.6	66.9 ± 0.3	21
		T	290.2 to 345.5		63.5	**65.1 ± 0.3**	this work
diethyl glutarate	3	E	338.7 to 510.0	355.7 (−103.0)	55.5	67.6	18
818-38-2			338.0 to 510.0		55.3	67.0	16
		S	339.7 to 473.0		54.9	65.9 ± 0.1	17
		T	298.3 to 347.9		67.3	**69.8 ± 0.4**	this work
diethyl adipate	4	TE	299.6 to 334.5	387.6 (−111.4)	56.0	58.0 ± 1.2	25
141-28-6		GC	298.2			64.7 ± 0.7	23
		E	350.6 to 523.9		58.4	73.0	18
		S	350.8 to 469.9		58.4	70.5 ± 0.3	17
			298.2			64.6	16
		T	303.5 to 352.5		70.8	**74.0 ± 0.3**	this work
dipropyl oxalate	0		326.0 to 487.0	323.8 (−94.8)	55.1	64.4	16
615-98-5		E	326.5 to 486.6		54.6	64.0	18
		T	293.6 to 333.5		60.0	**61.4 ± 0.5**	this work
dipropyl malonate	1	T	293.3 to 338.5	355.7 (−103.1)	64.4	**66.2 ± 0.4**	this work
1117-19-7							
dipropyl succinate	2		350.0 to 524.0	387.6 (−111.4)	58.1	72.4	16
925-15-5		E	350.6 to 523.9		58.4	73.0	18
		T	308.3 to 343.5		67.9	**71.0 ± 0.3**	this work
dipropyl glutarate	3	T	313.3 to 353.5	419.5 (−119.7)	71.3	**75.5 ± 0.3**	this work
1724-48-7							
dipropyl adipate	4		413 to 540	451.4 (−127.9)	63.6	85.8	19
106-19-4			413.0 to 540.0			85.7	16
		T	318.8 to 365.3		75.5	**81.0 ± 0.3**	this work
dibutyl oxalate	0	T	291.4 to 358.2	387.6 (−111.4)	68.8	**71.4 ± 0.2**	this work
2050-60-4							
dibutyl malonate	1	T	303.2 to 369.2	419.5 (−119.7)	70.9	**75.3 ± 0.4**	this work
1190-39-2							

Table 2. Continued

compounds	n^a	technique[b]	T-range	C_p^l $(\Delta_f^g C_p)^c$	$\Delta_l^g H_m$ (T_{av})	$\Delta_l^g H_m$(298.15 K)[d]	ref
			K	J·mol^{-1}·K^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	
dibutyl succinate	2	E		451.4 (−127.9)		67.4	18
141-03-07		E	397.8 to 475.5		69.1	86.3 ± 0.2	25
		T	313.2 to 358.2		74.4	**79.1 ± 0.3**	this work
dibutyl glutarate	3	T	317.5 to 369.5	483.3 (−136.2)	77.2	**83.1 ± 0.2**	this work
6624-57-3							
dibutyl adipate	4		435.2 to 563.2	515.2 (−144.5)	68.7	96.9	19
105-99-7		T	313.2 to 373.2		84.2	**88.5 ± 0.5**	this work

[a] n is the number of CH_2 groups in the linear aliphatic esters of dicarboxylic acids $R-CO_2-(CH_2)_n-CO_2-R$ with n = 0 to 4. [b] Techniques: E = ebulliometry; S = static method; T = transpiration; TE = torsion-effusion method; GC = gas−liquid chromatographic correlation method. [c] Values of $\Delta_f^g C_p$ have been derived from the isobaric molar heat capacity of the liquid esters C_p^l according to the procedure developed by Chickos et al.[13−15] [d] Vapor pressure data available in the literature were treated using eq 2 and eq 3 to evaluate enthalpy of vaporization at T = 298.15 K in the same way as our own results in Table 1.

Figure 1. Plot of vapor pressure against reciprocal temperature for diethyl oxalate. ○, ref 17; ■, ref 18; ∗, ref 20; ◇, ref 21; ▲, this work.

Figure 2. Plot of vapor pressure against reciprocal temperature for diethyl malonate. ○, ref 18; ◇, ref 22; ∗, ref 8; ▲, ref 17; △, this work.

Available vapor pressure data for dipropyl oxalate (Figure S3, Supporting Information), dipropyl succinate (Figure S4, Supporting Information), dipropyl adipate (Figure S5, Supporting Information), dibutyl succinate (Figure S6, Supporting Information), and dibutyl adipate (Figure S7, Supporting Information) seem to be consistent, and they are presented graphically in figures given in the Supporting Information.

Enthalpies of vaporization of some alkyl esters of dicarboxylic acid were assessed by Chickos et al.[24] using correlation gas chromatography. Their vaporization enthalpies for the diethyl malonate, succinate, and adipate are (3 to 9) kJ·mol^{-1} lower than our results (Table 2). As a matter of fact, for the correlation gas chromatography method, Chicoks et al.[24] considered a system of reference vaporization enthalpies based on data compiled in the handbook by Stephenson and Malanowski,[16] which according to Table 2 were not always reliable. However, it is possible to recalculate the data reported by Chicoks et al.[24] using their primary retention data and the reliable vaporization enthalpies from Table 2.

Correlation of Enthalpies of Vaporization with the Number of C-Atoms in Esters. The correlation of enthalpies of
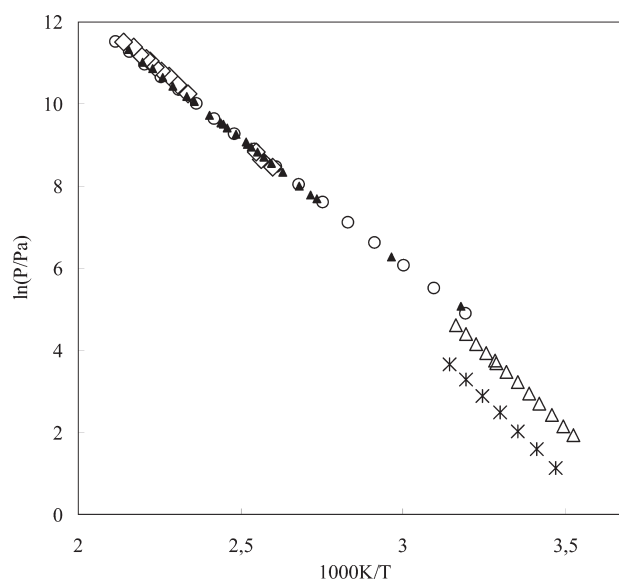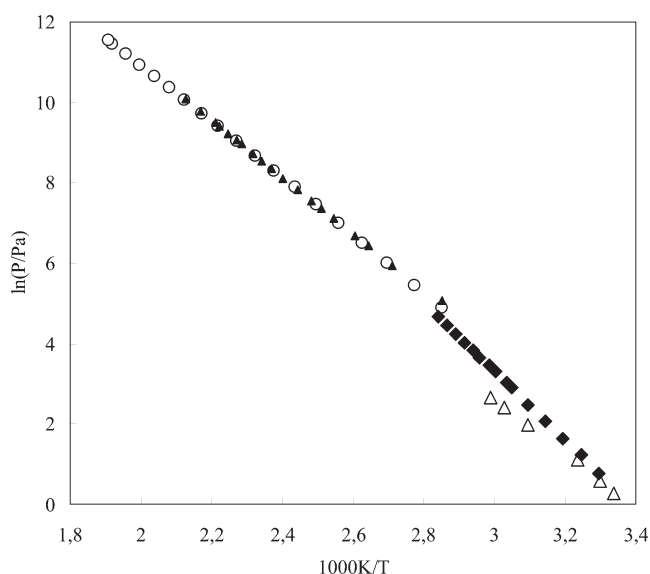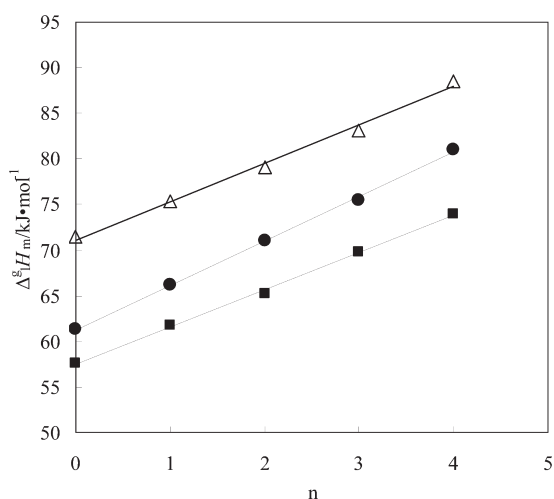
vaporization with the number of C-atoms in the series of homologues is a valuable test to check the internal consistency of the experimental results. Vaporization enthalpies, $\Delta_l^g H_m$, linearly depended on the number of carbon atoms of the methyl ester of dicarboxylic acid.[3] The plot of $\Delta_l^g H_m$(298.15 K) against the number of C-atoms in the linear aliphatic alkyl esters of dicarboxylic acids $R-CO_2-(CH_2)_n-CO_2-R$ with n = (0 to 4) is presented in Figure 4. The dependence of vaporization enthalpy on the number of C-atoms is described by the following equations for diethyl, dipropyl, and dibutyl esters correspondingly

$$\Delta_l^g H_m(298.15 \text{ K})/\text{kJ·mol}^{-1}$$
$$= (57.5 \pm 0.2) + (4.09 \pm 0.08)n$$
$$(R^2 = 0.9989) \tag{4}$$

$$\Delta_l^g H_m(298.15 \text{ K})/\text{kJ·mol}^{-1}$$
$$= (61.3 \pm 0.2) + (4.87 \pm 0.08)n$$
$$(R^2 = 0.9991) \tag{5}$$

Figure 3. Plot of vapor pressure against reciprocal temperature for diethyl adipate. O, ref 18; △, ref 25; ▲, ref 17; ◆, this work.

Figure 4. Plot of experimental vaporization enthalpies $\Delta_l^g H_m$(298.15 K) against the number of CH_2 groups in the linear aliphatic esters of dicarboxylic acids $R-CO_2-(CH_2)_n-CO_2-R$ ($R = CH_3-$, C_2H_5-, C_3H_7-, C_4H_9-): ◆, ethyl; ●, propyl; △, butyl.

$$\Delta_l^g H_m(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1}$$

$$= (71.1 \pm 0.4) + (4.20 \pm 0.18)n$$

$$(R^2 = 0.9946) \tag{6}$$

from which enthalpy of vaporization $\Delta_l^g H_m$(298.15 K) for other representatives of this series with $n > 4$ can be calculated.

Correlation of Enthalpies of Vaporization with Kovat's Indices. The correlation of the enthalpies of vaporization with Kovat's indices of the organic compounds is another valuable method to study the systematic behavior in homologous series. Kovat's index is the retention characteristics acknowledged among analytic chemists for the identification of the individual compounds in diverse mixtures. In Kovat's index, n-alkanes serve as the

standards, and logarithmic interpolation is utilized defined by

$$J_x = \frac{\lg(t_x) - \lg(t_N)}{\lg(t_{N+1}) - \lg(t_N)} \cdot 100 + 100 \cdot N \tag{7}$$

where x refers to the adjusted retention time; N is the number of carbon atoms of the n-alkane eluting before; and $(N + 1)$ is the number of carbon atoms of the n-alkane eluting after the peak of interest. According to the established GC procedure, all retention times are corrected for the "dead" retention time adjusted from the retention times of the homologous n-hydrocarbons.[26,27] There are some comprehensive libraries containing J_x values available from the literature, which are generally standardized for the common stationary phases. In this work, we used the data for stationary phases OV-101.[10]

The vaporization enthalpy $\Delta_l^g H_m$ appears to be a linear function of Kovat's indices in homologous series of methyl esters
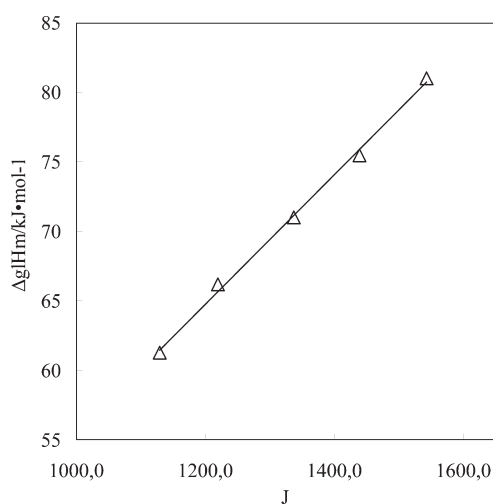
Figure 5. Plot of experimental vaporization enthalpies $\Delta_l^g H_m$(298.15 K) against Kovat's index J (OV-101 at 423.15 K) for dipropyl esters of dicarboxylic acids $(Pr-CO_2-(CH_2)_n-CO_2-Pr)$ with $n = 0, 1, 2, 3,$ and 4.
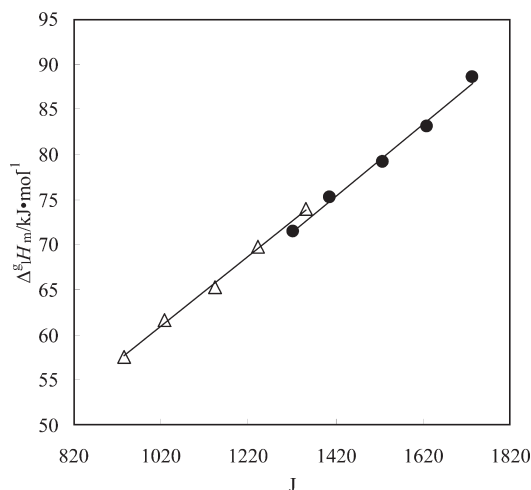
Figure 6. Plot of experimental vaporization enthalpies $\Delta_l^g H_m$(298.15 K) against Kovat's index (OV-101 at 423.15 K) for diethyl and dibutyl esters of dicarboxylic acids: $R-CO_2-(CH_2)_n-CO_2-R$ with $n = 0, 1, 2, 3,$ and 4. △, ethyl; ●, butyl.

Table 3. Vapor Pressure Coefficients of Equation 2 for Dialkyl Esters of Dicarboxylic Acids

compounds	temperature range, K	a	b	$\Delta_l^g C_p$
diethyl oxalate	283.5 to 458.8	307.57	−81385.52	78.2
diethyl malonate	283.7 to 472.0	321.86	−87949.79	86.5
diethyl succinate	290.1 to 489.6	333.19	−93562.27	94.8
diethyl glutarate	298.3 to 510.0	348.03	−100716.15	103.1
diethyl adipate	303.4 to 523.9	364.39	−108100.31	111.4
dipropyl oxalate	293.5 to 486.6	332.37	−92817.18	94.8
dipropyl succinate	308.2 to 523.9	359.27	−105719.28	111.4
dipropyl adipate	318.7 to 540.0	400.00	−123641.37	127.9
dibutyl succinate	313.2 to 457.7	389.01	−119340.17	127.9
dibutyl adipate	313.1 to 563.1	430.12	−137398.93	144.5

of dicarboxylic acids.[3] We have used Kovat's indices obtained in our previous work[10] and own results for $\Delta_l^g H_m(298.15 \text{ K})$ for alkyl esters of dicarboxylic acids (see Table 2) to test how the results fit into a systematic dependence on Kovat's indices. Experimental J_x values for alkyl esters of dicarboxylic acids with $n = 0$ to 4, used in this work, are given in Table S2, Supporting Information. It is apparently from Figures 5 and 6 that the data for $\Delta_l^g H_m(298.15 \text{ K})$ fit very well in the linear correlation. This fact could serve as evidence of the internal consistency of our experimental results for vaporization enthalpies.

Vapor Pressure Correlations for Dialkyl Esters of Dicarboxylic Acids. Taking the generally good agreement between vapor pressure data reported in this work and the literature into account, the experimental data (if it has been possible) were regressed together to develop correlations accurately describing the vapor pressure of dialkyl esters of dicarboxylic acids over a temperature range from ambient to the normal boiling point. Table 3 summarizes coefficients of the vapor pressure correlation (eq 3) for dialkyl esters of dicarboxylic acids, which could be used for thermochemical and technical calculations.

ASSOCIATED CONTENT

S **Supporting Information.** Experimental data on enthalpies of vaporization of the methyl esters of dicarboxylic acids (Table S1); Kovat's indices on the OV-101 phase at 423.15 K of the linear symmetric alkyl esters of dicarboxylic acids (Table S2); comparison of the vapor pressures available for alkyl esters of dicarboxylic acids (Figures S1 to S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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