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Vapor Pressures, Enthalpies of Vaporization, and Critical Parameters of a Series of Linear Aliphatic Dimethyl Esters of Dicarboxylic Acids

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Vapor pressures and the molar enthalpies of vaporization of the linear aliphatic dimethyl esters of dicarboxylic acids CH_3-CO_2-$(CH_2)_n$-CO_2-CH_3 with n = (0 to 8) have been determined by the transpiration method. A linear correlation of enthalpies of vaporization (at T = 298.15 K) of the esters studied with the number n and with the Kovat's indices and has been found. The critical temperatures and pressures of the esters with n = (0 to 6) and n = 8 have been measured by the pulse-heating method with the residence times ranging from (0.03 to 1) ms. Experimental data on the critical properties are compared with the estimations by group contribution methods by Constantinou and Gani and by Marrero and Gani. Both methods considerably underestimate the critical temperatures of the esters studied; however, the method by Marrero and Gani provides the prediction of the critical pressures of the esters with an average absolute error approximately equal to the uncertainty of the measurements.

Introduction

Esters are commonly used as plasticizers in polymers. The vapor pressure of a compound will determine, in part, the rate of evaporation of a plasticizer from polymer. Vapor pressure and enthalpy of vaporization are also among of the key thermophysical properties determining the environmental fate of chemicals. We have contributed to this series of required thermophysical data in the past by determining vapor pressures and enthalpies of vaporization investigations on some branched aliphatic esters,[1,2] linear aliphatic esters,[3] aliphatic dialkyl esters of dicarboxylic acids,[4,5] and trialkyl esters of tricarboxylic acids.[6] This paper extends our previous[1−6] studies on the esters with the systematic study of the linear aliphatic dimethyl esters of dicarboxylic acids CH_3-CO_2-$(CH_2)_n$-CO_2-CH_3 with n = (0 to 8). 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 document the general regularities in the $\Delta_l^g H_m$ and the vapor pressures within the homologous series.

The critical point defines the upper limit of the two-phase behavior of fluids. Knowledge of the critical temperature and pressure allows vapor pressure data to be extrapolated to the critical point. In addition, the critical constants are used in many thermodynamic and transport property predictions. However, in the homologous series of dimethyl esters of dicarboxylic acids, the critical properties have been measured only for dimethyl oxalate.[7] Information about the thermal stability of dimethyl esters of dicarboxylic acids is scanty. Stern and Kay[8] reported that dimethyl oxalate decomposed above 473 K. Probably, all other members of this homological series are also thermally unstable at their critical points, so the pulse-heating method with ultra-low residence times has been applied in this work.

Experimental Section

Materials. Samples of dimethyl esters of dicarboxylic acids were of commercial origin (Aldrich, Fluka). The degree of purity was determined using a Hewlett-Packard gas chromatograph (GC) 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 i.d. of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was T = 333 K for 180 s followed by a heating rate of 0.167 $K \cdot s^{-1}$ to T = 523 K. No total impurities (greater than mass fraction 0.003) could be detected in the samples used for the vapor pressure measurements.

Before and after the critical properties measurements, the purities of the samples were determined by gas chromatography (Shimadzu GS-Ha) and proton magnetic spectroscopy (Bruker DRX). The mass fraction of impurities was found not to exceed the value of 0.003 both for the samples before and after measuring the critical constants. It may seem to be strange because according to the data by Stern and Kay[8] dimethyl

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oxalate decomposes above 473 K, whereas the critical temperature determined by us was equal to 639 K. However, in the course the pulse-heating experiments only the volume V_1 of the order of 10^{-11} m^{-3} of the substance under study was heated while the volume of the whole sample was 10^{-6} m^{-3}. Since $V_1 \ll V_2$, the mass fraction of decomposition products in the volume of the whole sample was negligible.

Measurement of the Enthalpies of Vaporization Using the Transpiration Method. Vapor pressures were determined using the method of transpiration in a saturated nitrogen stream,[9,10] and enthalpies of dimethyl 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 thermostated U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide a surface that 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 flowmeter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. On one hand, flow rate of nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of material from U-tube due to diffusion. On the other hand, the flow rate should be not too fast in order to reach the saturation of the nitrogen stream with a compound. We tested our apparatus at different flow rates of the carrier gas in order 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 was at a flow rate of 1.5 $cm^3 \cdot s^{-1}$. Thus, we carried out the experiments in the flow rate interval of (0.28 to 0.52) $cm^3 \cdot s^{-1}$, which has ensured that transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The mass of compound collected within a certain time interval was determined by dissolving it in a suitable solvent with certain amount of internal standard (hydrocarbon). This solution was analyzed using a GC equipped with autosampler. Uncertainty of the sample amount determined by GC analysis was assessed to be within (1 to 3) %. The peak area of the compound related to the peak of the external standard (hydrocarbon n-C_nH_{2n+2}) is a direct measure of the mass of the compound condensed into the cooling trap provided a calibration run has been made. From this information, the vapor pressure of the compound under study can be determined (i.e., the ideal gas law can be applied provided that the vapor pressure of the substance is low enough). Real gas corrections arising from interactions of the vapor with the carrier gas were negligible. The saturation vapor pressure p_i^{sat} at each temperature T_i 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:

$$p_i^{\text{sat}} = m_i R T_a / V M_i \quad V = V_{N_2} + V_i \quad (V_{N_2} \gg V_i) \tag{1}$$

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_{N_2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. The volume of transporting gas V_{N_2} 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 following equation:[10]

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

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:

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \tag{3}$$

Values of $\Delta_l^g C_p$ have been calculated according to a procedure developed by Chickos and co-workers.[11−13] 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 experimental and calculation procedures with measurements of vapor pressures of n-alcohols.[10] It turned out that vapor pressures derived from the transpiration method were reliable within (1 to 3) % and that their accuracy was governed by reproducibility of the GC analysis. To assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{\text{sat}}) = f(T^{-1})$ using the method of least squares. The uncertainty in the enthalpy of vaporization was assumed to be identical with the average deviation of experimental $\ln(p_i^{\text{sat}})$ values from this linear correlation.

Measurement of the Critical Temperatures and Pressures Using the Pulse-Heating Method. The critical temperatures and pressures of the esters were experimentally determined by the pulse-heating method. Only a brief outline of this technique is given below. Additional details are available in several publications.[14−16] A liquid under study filled a Teflon cup with thin walls; the pressure outside the cup was created by a press and measured by a dial gauge. A platinum wire probe, 2×10^{-3} cm in diameter and (1 to 3) cm in length, was placed in the liquid. The probe was heated by pulses of electric current. By the end of a pulse, the probe and the thin liquid layer near it were heated to the temperature of spontaneous boiling-up (attainable superheat). The time from the start of a pulse to the moment of boiling-up was from (0.03 to 1.0) ms. At the moment of boiling-up a probe temperature perturbation arises from an abrupt change of the conditions of heat transfer from the probe to the liquid. The probe temperature was determined from its resistance at this moment. The probe temperature perturbation may be both positive and negative. The pressure in the liquid increased until the negative temperature perturbation dropped to the level of the apparatus sensitivity (1×10^{-3} K). This pressure is taken to be equal to the measured value of the critical pressure p_c^m, and the temperature of the attainable superheat at this pressure is taken to be equal to the measured value of the critical temperature T_c^m.

The values of the critical pressure p_c^m and the critical temperature T_c^m determined in such a way are always lesser than the true ones. It is an inherent feature of the pulse-heating method. The true critical constants p_c and T_c of a stable compound are calculated by the following equations:

$$p_c = p_c^m / \pi_0 \quad T_c = T_c^m / \tau_0 \tag{4}$$

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

T	m	$V(N_2)$	N_2 flow	p	$p_{exp} - p_{calc}$	$\Delta_l^g H_m$	T	m	$V(N_2)$	N_2 flow	p	$p_{exp} - p_{calc}$	$\Delta_l^g H_m$
K^a	mg^b	dm^3 ^{c}	cm^3·s^{-1}	Pa^d	Pa	kJ·mol^{-1}	K^a	mg^b	dm^3 ^{c}	cm^3·s^{-1}	Pa^d	Pa	kJ·mol^{-1}
Dimethyl Oxalate(l), $\Delta_l^g H_m(298.15\ K) = (54.65 \pm 0.30)$ kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = \frac{287.5}{R} - \frac{73013.0}{R(T/\mathrm{K})} - \frac{61.6}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
330.4	19.62	0.293	1.17	1399.3	10.5	52.66	350.4	58.26	0.293	1.17	4141.1	43.4	51.43
333.2	22.61	0.293	1.17	1612.0	−19.2	52.49	352.2	62.86	0.293	1.17	4478.5	−5.8	51.32
335.2	27.21	0.313	1.17	1818.7	−7.5	52.37	355.5	99.66	0.390	1.17	5324.8	49.8	51.12
337.2	28.36	0.293	1.17	2021.5	−19.9	52.24	357.2	80.11	0.293	1.17	5706.9	−20.2	51.01
340.3	35.84	0.313	1.17	2394.7	−23.8	52.05	359.2	88.16	0.293	1.17	6280.2	−21.1	50.89
343.2	39.86	0.293	1.17	2840.5	15.9	51.87	360.6	91.61	0.293	1.17	6525.9	−206.1	50.80
345.3	44.23	0.293	1.17	3144.3	−10.2	51.75	362.2	100.81	0.293	1.17	7181.1	−73.8	50.70
346.2	45.61	0.293	1.17	3250.0	−55.7	51.69	365.2	126.12	0.312	1.17	8421.6	92.3	50.52
349.2	54.81	0.293	1.17	3905.2	48.9	51.51							
Dimethyl Oxalate(cr), $\Delta_{cr}^g H_m(298.15\ K) = (75.8 \pm 0.53)$ kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = \frac{312.1}{R} - \frac{82178.4}{R(T/\mathrm{K})} - \frac{23.8}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
293.3	3.66	1.52	1.19	49.95	1.5	75.20	311.2	5.46	0.395	1.19	287.26	3.1	74.77
296.3	4.92	1.50	1.19	68.01	1.8	75.13	313.2	46.71	2.88	5.76	337.16	−4.6	74.73
298.2	4.56	1.19	1.19	79.59	−0.8	75.08	316.2	6.80	0.316	1.19	446.64	−2.0	74.65
301.2	4.47	0.890	1.19	104.57	−4.1	75.01	318.3	8.35	0.313	1.17	554.51	13.4	74.60
303.2	3.82	0.613	1.19	129.77	−2.6	74.96	319.2	8.53	0.297	1.19	600.61	14.8	74.58
306.2	5.25	0.613	1.19	178.03	0.9	74.89	321.2	10.15	0.293	1.17	719.12	21.3	74.54
308.2	4.02	0.395	1.19	210.35	−4.1	74.84	325.3	15.44	0.332	1.17	965.67	−26.3	74.44
Dimethyl Malonate, $\Delta_l^g H_m(298.15\ K) = (57.53 \pm 0.33)$ kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = \frac{297.3}{R} - \frac{78366.8}{R(T/\mathrm{K})} - \frac{69.9}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
278.2	1.86	3.04	2.72	11.70	0.1	58.92	299.4	3.97	1.06	2.72	69.74	0.5	57.44
281.2	2.62	3.31	2.72	15.07	−0.2	58.71	302.2	3.92	0.839	2.72	87.29	1.6	57.25
284.3	2.64	2.54	2.72	19.69	−0.4	58.50	303.3	3.48	0.690	2.76	94.23	1.1	57.17
287.2	3.50	2.54	2.72	25.93	0.1	58.30	305.3	4.77	0.839	2.72	106.3	−1.7	57.03
290.8	1.53	0.814	2.76	35.23	0.4	58.04	308.4	3.83	0.544	2.72	131.3	−4.0	56.81
293.2	3.02	1.33	2.76	42.53	0.1	57.88	311.2	3.61	0.408	2.72	165.0	−0.2	56.62
296.1	3.23	1.13	2.72	53.30	−0.2	57.67	314.3	4.23	0.385	2.72	204.6	−0.3	56.40
298.0	3.15	0.924	2.76	63.86	1.7	57.54							
Dimethyl Succinate, $\Delta_l^g H_m(298.15\ K) = (61.01 \pm 0.28)$ kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = \frac{311.0}{R} - \frac{84321.1}{R(T/\mathrm{K})} - \frac{78.2}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
286.4	2.50	3.99	2.63	10.62	−0.1	62.09	316.2	3.07	0.433	1.04	118.70	−0.5	59.57
289.4	3.24	3.95	2.63	13.89	−0.1	61.83	319.2	3.02	0.346	1.04	146.21	−1.2	59.32
292.3	2.01	1.89	2.63	17.93	−0.2	61.59	322.3	3.24	0.294	1.04	184.57	1.8	59.06
295.2	2.02	1.45	2.73	23.39	0.2	61.34	325.3	3.42	0.260	1.04	220.57	−3.3	58.80
298.1	1.58	0.910	2.73	29.20	−0.4	61.10	328.3	4.31	0.268	1.04	268.63	−4.3	58.55
301.1	2.57	1.137	2.73	37.98	0.2	60.85	331.4	5.01	0.260	1.04	323.20	−10.3	58.29
304.2	2.70	0.910	2.73	49.88	1.5	60.59	334.5	6.61	0.280	1.05	395.04	−10.5	58.03
307.2	3.39	0.910	2.73	62.42	1.3	60.33	337.5	7.67	0.263	1.05	489.08	1.1	57.77
310.2	3.01	0.658	2.63	76.85	0.1	60.08	340.6	9.97	0.271	1.05	615.14	26.8	57.51
313.2	5.30	0.910	2.73	97.59	1.7	59.83							
Dimethyl Glutarate, $\Delta_l^g H_m(298.15\ K) = (65.74 \pm 0.36)$ kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = \frac{327.5}{R} - \frac{91529.5}{R(T/\mathrm{K})} - \frac{86.5}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
283.7	2.13	11.97	7.98	2.75	−0.25	66.99	319.2	3.87	0.891	2.14	66.40	0.51	63.92
286.3	2.16	9.31	7.98	3.57	−0.31	66.77	320.2	4.66	0.982	3.93	73.43	2.40	63.84
288.4	1.86	6.65	7.98	4.30	−0.45	66.59	320.3	3.23	0.706	2.12	69.68	−1.88	63.83
290.5	1.50	4.11	4.93	5.64	−0.17	66.41	321.4	2.95	0.586	2.13	76.92	−0.76	63.73
293.2	4.03	8.13	8.00	7.58	0.10	66.17	323.2	3.17	0.533	2.13	90.72	2.01	63.58
293.3	1.82	3.78	4.93	7.47	−0.08	66.16	323.3	4.57	0.817	2.23	85.42	−3.94	63.57
295.6	1.70	2.75	4.93	9.58	0.25	65.96	323.3	15.25	2.51	4.93	93.98	4.62	63.57
296.2	5.22	8.13	8.00	9.84	−0.01	65.91	325.2	4.55	0.682	1.64	103.3	0.76	63.40
298.2	5.27	6.67	8.00	12.14	0.36	65.74	325.2	4.05	0.606	2.14	102.1	−0.45	63.40
298.4	2.11	2.71	4.93	12.04	0.05	65.72	327.1	4.39	0.530	2.12	126.29	8.75	63.24
300.3	3.86	4.00	8.00	14.79	0.61	65.56	328.3	5.87	0.705	2.23	127.58	−0.38	63.14
303.2	3.27	2.67	8.00	18.81	0.59	65.31	329.2	6.05	0.624	2.14	148.03	11.72	63.06
303.3	5.71	4.67	8.00	19.30	0.92	65.30	330.2	5.04	0.545	1.64	142.80	−3.35	62.97
305.4	4.00	2.67	8.00	23.01	1.05	65.12	331.3	5.71	0.530	2.12	164.55	6.83	62.88
306.2	3.11	2.00	8.00	23.88	0.40	65.05	333.1	12.30	1.08	2.23	175.25	−3.15	62.72
308.2	6.64	3.60	8.00	29.04	1.34	64.87	333.2	6.29	0.535	2.14	179.81	0.20	62.71
309.2	4.17	2.07	8.00	31.02	0.96	64.79	335.3	5.32	0.409	1.64	197.71	−9.23	62.53
310.2	4.43	2.00	8.00	33.48	0.87	64.70	335.3	3.78	0.281	1.12	205.13	−1.81	62.53

Table 1. (Continued)

T	m	$V(N_2)$	N_2 flow	p	$p_{exp} - p_{calc}$	$\Delta_l^g H_m$	T	m	$V(N_2)$	N_2 flow	p	$p_{exp} - p_{calc}$	$\Delta_l^g H_m$
K[a]	mg[b]	dm^3 [c]	$cm^3 \cdot s^{-1}$	Pa[d]	Pa	$kJ \cdot mol^{-1}$	K[a]	mg[b]	dm^3 [c]	$cm^3 \cdot s^{-1}$	Pa[d]	Pa	$kJ \cdot mol^{-1}$
Dimethyl Glutarate, $\Delta_l^g H_m(298.15\ K) = (65.74 \pm 0.36)\ kJ \cdot mol^{-1}$													
312.1	3.32	1.28	2.14	39.95	1.96	64.54	338.3	13.14	0.817	2.23	247.39	−5.00	62.27
313.2	4.01	1.47	4.41	41.46	0.01	64.44	338.3	4.78	0.281	1.12	259.8	7.38	62.27
313.5	4.60	1.64	4.93	43.23	0.78	64.42	340.2	6.83	0.382	1.64	271.9	−13.70	62.11
315.2	4.25	1.31	3.93	50.31	1.82	64.27	341.3	5.55	0.281	1.12	301.73	−4.78	62.01
315.5	3.58	1.070	2.14	51.26	1.62	64.24	343.1	12.25	0.557	2.23	338.19	−5.51	61.86
316.2	3.66	1.07	2.14	52.85	0.45	64.18	343.2	6.30	0.281	1.12	342.48	−3.40	61.85
318.1	3.52	0.891	2.14	60.49	−0.13	64.02	345.2	11.00	0.464	1.64	365.12	−26.98	61.67
318.3	4.51	1.10	4.41	62.76	1.21	64.00	348.1	11.89	0.419	1.67	436.82	−32.01	61.42
Dimethyl Adipate, $\Delta_l^g H_m(298.15\ K) = (69.01 \pm 0.18)\ kJ \cdot mol^{-1}$													
$\ln(p/Pa) = \frac{337.7}{R} - \frac{97276.2}{R(T/K)} - \frac{94.8}{R}\ln\left(\frac{T/K}{298.15}\right)$													
294.2	2.94	14.92	9.95	2.84	0.1	69.39	333.2	4.28	0.852	2.84	71.35	2.2	65.69
297.1	5.29	21.23	6.76	3.56	0.0	69.12	334.3	2.76	0.546	2.05	72.03	−2.7	65.59
297.4	3.21	12.27	9.95	3.77	0.1	69.09	337.4	4.02	0.649	2.05	88.19	−4.6	65.30
298.1	4.61	16.67	6.76	3.91	0.0	69.02	338.5	5.08	0.710	2.84	101.30	1.0	65.19
300.6	2.91	8.14	5.82	5.05	0.1	68.78	338.5	4.53	0.619	1.12	103.85	3.7	65.19
303.1	5.02	11.5	6.76	6.19	0.0	68.54	340.2	5.34	0.683	2.05	111.42	−0.9	65.03
303.3	3.16	6.88	5.82	6.49	0.2	68.53	343.5	6.98	0.710	2.84	139.34	−1.1	64.71
305.4	2.82	5.14	5.82	7.75	0.1	68.33	343.5	4.91	0.511	2.04	136.87	−3.2	64.72
308.1	4.53	6.76	6.76	9.48	−0.2	68.07	348.5	4.50	0.336	1.22	189.25	−5.5	64.23
308.1	2.01	3.01	5.82	9.46	−0.2	68.07	348.6	4.76	0.337	1.12	200.40	5.3	64.23
311.6	2.69	2.91	5.82	13.08	0.1	67.74	351.7	4.87	0.289	1.08	240.55	3.2	63.94
313.2	5.51	5.18	6.76	15.01	0.1	67.59	353.6	5.63	0.306	1.22	260.42	−6.0	63.76
314.4	3.39	2.91	5.82	16.48	0.1	67.48	358.6	8.19	0.326	1.22	355.14	−6.7	63.28
317.2	2.94	2.04	5.82	20.59	0.0	67.21	358.6	7.37	0.281	1.12	373.23	11.6	63.28
318.2	5.60	3.50	6.75	22.54	0.1	67.11	361.7	8.68	0.276	1.08	445.97	13.4	62.99
318.5	2.87	1.86	2.05	21.98	−0.9	67.09	363.7	10.57	0.316	1.22	473.05	−12.8	62.80
320.2	3.46	1.94	5.82	25.43	−0.7	66.93	368.7	13.94	0.312	1.22	631.23	−13.0	62.32
323.3	3.53	1.55	5.82	32.44	−0.8	66.63	368.7	12.86	0.271	1.08	675.95	32.1	62.32
323.4	4.14	1.72	6.87	34.34	0.8	66.62	369.7	13.16	0.271	1.08	686.32	5.7	62.22
326.2	3.93	1.40	2.05	39.96	−1.5	66.36	373.8	18.20	0.308	1.22	834.69	−10.4	61.84
328.3	6.05	1.72	6.87	50.27	1.7	66.15	373.8	17.44	0.280	1.08	887.59	41.6	61.84
332.2	3.21	0.751	2.05	60.88	−3.5	65.79							
Dimethyl Pimelate, $\Delta_l^g H_m(298.15\ K) = (73.48 \pm 0.37)\ kJ \cdot mol^{-1}$													
$\ln(p/Pa) = \frac{357.6}{R} - \frac{104221.6}{R(T/K)} - \frac{103.1}{R}\ln\left(\frac{T/K}{298.15}\right)$													
291.3	5.82	108.12	8.05	1.30	0.00	74.19	323.2	5.37	5.08	7.81	25.58	0.53	70.90
293.3	2.69	40.42	8.05	1.61	0.01	73.99	328.2	6.13	3.91	7.81	37.78	0.39	70.39
298.3	2.44	22.27	8.05	2.64	−0.02	73.47	333.1	4.44	1.95	7.81	54.70	−0.10	69.88
303.2	3.09	17.44	8.05	4.23	−0.07	72.96	338.2	6.41	1.97	7.81	78.40	−1.65	69.35
308.2	3.20	11.13	8.09	6.93	0.10	72.45	343.2	9.79	2.10	7.81	112.28	−1.82	68.84
313.2	2.70	6.07	8.09	10.73	−0.04	71.93	348.1	13.14	1.95	7.81	161.77	1.16	68.33
318.2	4.69	6.47	8.09	17.34	0.82	71.42	353.1	18.89	2.02	7.81	225.12	1.76	67.82
Dimethyl Suberate, $\Delta_l^g H_m(298.15\ K) = (78.08 \pm 0.19)\ kJ \cdot mol^{-1}$													
$\ln(p/Pa) = \frac{373.4}{R} - \frac{111295.2}{R(T/K)} - \frac{111.4}{R}\ln\left(\frac{T/K}{298.15}\right)$													
293.3	2.34	90.4	7.93	0.62	0.02	78.63	323.1	3.96	8.55	8.25	11.07	0.00	75.30
295.3	3.11	97.9	7.93	0.77	0.03	78.40	328.1	3.41	4.83	7.81	16.84	−0.09	74.74
298.3	2.33	53.9	7.93	1.05	0.02	78.07	333.1	3.78	3.58	7.81	25.24	−0.17	74.19
303.2	2.31	32.7	7.93	1.69	−0.02	77.52	338.1	6.20	3.78	7.81	39.23	1.37	73.63
308.3	2.12	18.7	8.25	2.73	−0.09	76.96	343.0	4.58	1.97	7.81	55.66	0.70	73.09
313.2	3.40	18.0	8.25	4.51	0.00	76.41	348.1	6.88	2.02	7.81	81.23	1.63	72.52
318.1	3.61	12.4	8.25	6.98	−0.10	75.86	352.1	9.18	2.02	7.81	108.28	2.55	72.08
Dimethyl Azelate, $\Delta_l^g H_m(298.15\ K) = (82.26 \pm 0.35)\ kJ \cdot mol^{-1}$													
$\ln(p/Pa) = \frac{381.2}{R} - \frac{117948.2}{R(T/K)} - \frac{119.7}{R}\ln\left(\frac{T/K}{298.15}\right)$													
298.1	3.21	194.3	7.32	0.19	0.01	82.27	343.4	2.68	2.60	7.32	11.71	−0.52	76.84
303.1	2.91	119.1	7.31	0.28	−0.03	81.67	343.8	2.85	2.47	7.79	13.11	0.51	76.79
308.1	6.61	137.6	7.37	0.54	0.03	81.07	348.5	2.72	1.78	7.12	17.57	−0.55	76.23
313.2	2.37	33.74	7.31	0.80	−0.06	80.46	348.6	2.80	1.71	3.31	18.50	0.30	76.22
313.2	1.10	15.02	8.50	0.84	−0.02	80.46	351.1	2.74	1.44	2.16	21.69	−0.22	75.93
318.2	2.69	22.20	7.32	1.38	−0.01	79.86	353.6	2.93	1.32	5.29	25.48	−0.86	75.62
318.2	2.06	17.71	8.50	1.31	−0.08	79.86	353.6	2.51	1.16	1.88	24.36	−1.92	75.63
320.2	1.17	7.85	7.47	1.67	0.00	79.63	353.6	2.47	1.10	3.31	25.18	−1.10	75.63
320.2	1.23	8.54	8.50	1.64	−0.02	79.63	358.6	2.81	0.875	2.02	36.63	−1.15	75.02
323.3	3.89	19.58	7.32	2.26	0.02	79.24	358.7	4.18	1.323	5.29	36.35	−1.51	75.02
323.4	2.23	11.08	7.73	2.28	0.03	79.24	360.2	2.81	0.775	2.38	41.23	−0.78	74.84

Table 1. (Continued)

T K[a]	m mg[b]	$V(N_2)$ dm^3 [c]	N_2 flow cm^3·s^{-1}	p Pa[d]	$p_{\mathrm{exp}} - p_{\mathrm{calc}}$ Pa	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ kJ·mol^{-1}	T K[a]	m mg[b]	$V(N_2)$ dm^3 [c]	N_2 flow cm^3·s^{-1}	p Pa[d]	$p_{\mathrm{exp}} - p_{\mathrm{calc}}$ Pa	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ kJ·mol^{-1}
Dimethyl Azelate, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) = (82.26 ± 0.35) kJ·mol^{-1}													
325.3	2.61	10.71	7.98	2.78	0.11	79.01	363.7	2.52	0.536	2.13	53.91	0.34	74.41
328.3	2.83	9.64	7.32	3.35	−0.14	78.65	363.7	2.47	0.515	2.06	54.51	1.08	74.42
328.3	2.46	7.68	7.78	3.62	0.13	78.65	366.2	3.02	0.526	1.43	65.60	2.20	74.11
330.8	1.33	3.26	7.54	4.66	0.32	78.35	368.9	3.77	0.570	2.13	76.01	0.33	73.79
333.4	3.40	7.07	7.32	5.49	0.10	78.05	368.9	3.70	0.525	2.07	80.31	4.63	73.79
333.4	2.41	4.85	7.65	5.61	0.22	78.05	371.3	2.88	0.363	1.66	89.18	1.02	73.51
335.9	1.39	2.23	7.45	7.11	0.47	77.75	371.3	2.40	0.310	1.66	86.95	−1.15	73.51
338.4	2.98	4.39	7.32	7.71	−0.46	77.44	373.8	2.63	0.297	0.98	101.57	−1.78	73.21
338.4	2.62	3.47	7.70	8.58	0.39	77.44	373.8	2.88	0.307	1.65	106.48	2.87	73.20
341.0	2.59	2.90	7.81	10.11	0.05	77.14							
Dimethyl Sebacate, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) = (86.38 ± 0.47) kJ·mol^{-1}													
$\ln(p/\mathrm{Pa}) = \frac{395.4}{R} - \frac{124511.0}{R(T/\mathrm{K})} - \frac{127.9}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
304.1	1.49	112.6	7.73	0.14	0.00	85.62	343.5	1.87	3.37	7.43	5.94	0.01	80.58
308.1	1.31	69.72	7.43	0.20	−0.01	85.10	348.2	1.46	1.86	7.43	8.39	−0.24	79.98
313.2	1.46	43.12	7.43	0.36	0.00	84.46	353.6	3.18	2.41	7.43	14.05	0.91	79.29
318.2	1.38	25.08	7.43	0.59	−0.01	83.81	355.6	3.16	2.25	7.73	14.86	−0.46	79.03
323.4	1.67	17.79	7.43	1.01	0.01	83.15	358.6	3.06	1.76	6.44	18.49	−0.68	78.65
328.3	1.40	9.29	7.43	1.62	0.04	82.52	363.7	4.42	1.67	6.44	28.08	0.40	78.00
333.4	1.91	8.19	7.43	2.50	0.00	81.87	368.8	7.13	1.93	7.73	39.65	0.22	77.35
338.4	1.77	4.85	7.43	3.88	0.01	81.23	373.8	9.88	1.93	7.73	54.73	−0.45	76.71

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at $T = 243$ 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 $T = 243$ K.

where $1/\pi_0$ and $1/\tau_0$ are correction factors.[14] For calculating these correction factors, the thermophysical properties of the substance under study near the critical point are required. They are estimated using the formulas based on the principle of corresponding states and given in the previous paper.[17] The formulas contain the similarity parameter of a substance: the acentric factor or the Filippov parameter A:[18]

$$A = 100\frac{p(T/T_c = 0.625)}{p_c} \tag{5}$$

where p is the vapor pressure. The Filippov parameters and the critical properties of the esters studied were calculated using an iteration method. For the first iteration, p_c^m and T_c^m were taken as the critical constants. The vapor pressures at high temperatures of esters with n from (0 to 4) at a reduced temperature $T/T_c = 0.625$ are known from the literature.[25,27,28,30,38] For esters with $n = 5$, 6, and 8, the vapor pressures at this temperature were estimated by us using the equation

$$\ln p = B - \frac{C}{T} \tag{6}$$

The parameters B and C were calculated from the values of p_c^m and T_c^m and normal or reduced pressure boiling points taken in accordance with the NIST Chemistry WebBook.[19] Then the values of π_0 and τ_0 and, with the help of eq 4, p_c and T_c were calculated. The second iteration was made using the values of the critical properties obtained after the first iteration. We restricted ourselves to two iterations because the corrections factors were very sensitive to the variations of the Filippov parameter.

The values of the correction factors depend on the thermophysical properties of a compound under investigation, mainly in the following way: the greater is the acentric factor or the lower is the Filippov parameter of a substance, the greater are the correction factors. For the dimethyl esters of dicarboxylic acids studied, the correction factors vary from $1/\tau_0 = 1.002$ and $1/\pi_0 = 1.027$ (dimethyl oxalate) to $1/\tau_0 = 1.004$ and $1/\pi_0 1.070$ (dimethyl sebacate).

To calculate the correction factors, two quantities are also needed: the ideal gas heat capacity of a substance under investigation and the factor $G_T \equiv \partial \ln J/\partial T$, where J is the rate of bubble nucleation in a superheated liquid. The ideal gas heat capacity was estimated by the method of Rihani and Doraiswamy as presented by Reid et al.[20] The factor G_T was measured in one experiment with the critical constants as described in our paper[14] and estimated at 1.5 K^{-1}.

The apparent critical constants of a thermally unstable compound measured as described above may depend on the time from the beginning of the heating pulse to the moment of boiling-up t^* due to decomposition. The critical properties of dimethyl esters of dicarboxylic acids were measured at heating times $t^* =$ (0.035, 0.06, 0.11, 0.22, 0.45, and 1.0) ms. The critical constants were determined by averaging the apparent critical constants over the heating times from (0.035 to 0.45) ms. In this interval, the apparent critical temperatures and pressures did not depend on the heating time. The uncertainties in the critical temperatures and pressures measured by the pulse-heating method were discussed in our previous paper.[21] We estimate the uncertainties for esters studied at 0.01 T_c and 0.03 p_c.

Results and Discussion

Vapor Pressures and Enthalpies of Vaporization. A summary of vaporization enthalpy measurements of dimethyl esters dicarboxylic acids available from the literature is presented in Table 2. We treated original experimental results available from the literature[22−29] using eq 2 and eq 3 and calculated $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) for the sake of comparison with our results. The comprehensive compilation by Stephenson and Malanowski[28] contains vapor pressure data for some nitriles over a wide range of temperatures. The origin of the data presented there is unclear; the methods of measurements are unknown as well as are errors of measurements and purities of com-

Table 2. Compilation of Data on Enthalpies of Vaporization $\Delta_l^g H_m$(298.15 K) of the Linear Aliphatic Dimethyl Esters of Dicarboxylic Acids CH_3-CO_2-$(CH_2)_n$-CO_2-CH_3 with n = (0 to 8)

	n^a	technique^b	temp range K	$C_p^l(\Delta_l^g C_p)^c$ J·mol^{-1}·K^{-1}	$\Delta_l^g H_m(T_{av})$ kJ·mol^{-1}	$\Delta_l^g H_m(298\ K)^d$ kJ·mol^{-1}	ref
dimethyl oxalate(cr)	0	S	289.2−306.9	153.8(23.8)	47.4 ± 0.5	47.4 ± 0.5	22
		C	298.15			74.5 ± 0.7	23
		HS	268.4−298.4		75.6 ± 1.6	75.3 ± 1.6	23
		T	293.3−325.3		74.8 ± 0.5	75.1 ± 0.5	this work
dimethyl oxalate(l)	0	E	329−436	196.2(61.6)	48.0	52.9	24
		GC	298			53.6 ± 0.5	23
		E	347.0−528.5		47.3 ± 0.3	55.2 ± 0.3	25
			328−443			52.5	29
		T	330.4−365.2		51.6 ± 0.3	54.7 ± 0.3	this work
dimethyl malonate	1	E	308−454	228.1(69.9)	52.5	57.5	24
		E	374.1−619.6		50.2 ± 0.2	63.0 ± 0.2	25
		T	277.9−308.0		61.9 ± 0.8	61.5 ± 0.8	5
		E	351.0−441.3		50.6 ± 0.3	58.1 ± 0.3	26
		T	278.2−314.3		57.7 ± 0.3	57.5 ± 0.3	this work
dimethyl succinate	2	E	398−468	260.0(78.2)	51.9	62.4	27
			349−470		49.3	57.6	28
		E	366.7−459.9		51.8 ± 0.4	60.9 ± 0.4	38
		S	342.2−468.7		54.6 ± 0.4	61.7 ± 0.4	30
		T	286.4−340.6		59.9 ± 0.3	61.0 ± 0.3	this work
dimethyl glutarate	3	E	388−483	291.9(86.5)	54.2	66.1	27
			366−483			65.2	28
		T	283.7−348.1		64.3 ± 0.4	65.7 ± 0.4	this work
dimethyl adipate	4	E	428−498	323.8(94.8)	57.8	73.4	27
			382−500			71.8	28
			418−501			72.9	28
		TE	293.3−323.2		55.1 ± 2.0	55.9 ± 2.0	31
		T	293.2−334.2		65.8 ± 0.3	67.1 ± 0.3	32
		T	294.2−373.8		65.9 ± 0.2	69.0 ± 0.2	this work
dimethyl pimelate	5	T	291.3−353.1	355.7(103.1)	71.3 ± 0.4	73.5 ± 0.4	this work
dimethyl suberate	6	T	293.3−352.1	387.6(111.4)	75.6 ± 0.2	78.1 ± 0.2	this work
dimethyl azelate	7	T	298.1−373.8	419.5(119.7)	77.6 ± 0.4	82.3 ± 0.4	this work
			413−540			84.2	28
dimethyl sebacate	8	T	304.1−373.8	451.4(127.9)	81.5 ± 0.5	86.4 ± 0.5	this work

[a] n is the number of CH_2 groups in the linear aliphatic dimethyl esters of dicarboxylic acids CH_3-CO_2-$(CH_2)_n$-CO_2-CH_3 with n = (0 to 8). [b] E, ebulliometry; T, transpiration; S, static method; TE, torsion-effusion method; HS, headspace method; GC, gas−liquid chromatographic correlation method. [c] Values of $\Delta_l^g C_p$ have been derived from the isobaric molar heat capacity of the liquid, C_p^l, and solid, C_p^{cr}, esters according to procedure developed by Chickos and co-workers.[11−13] [d] Vapor pressure data available in the literature were treated using eq 2 and eq 3 in order to evaluate enthalpy of vaporization at T = 298.15 K in the same way as our own results in Table 1.

pounds. Despite this fact, we also treated the results from Stephenson and Malanowski[28] using eq 2 and eq 3 and calculated $\Delta_l^g H_m$(298.15 K) for the sake of comparison with our results. However, the agreement or disagreement with other data in each case should be questionable.[33]

Askonas and Daubert[25] reported vapor pressures of dimethyl oxalate. An ebulliometer was the central piece of apparatus used in obtaining subatmospheric vapor pressure data while superatmospheric measurements were obtained in a capillary apparatus by observing the meniscus. Our results are in close agreement with those from ebulliometry within the boundaries of the experimental uncertainties (see Table 2 and Figures 1 and 2).

A careful ebulliometric study of the dimethyl malonate was reported by Steele et al.[26] Extended discussion of the available vapor pressure data on this compound was also performed in that work. They stated that the absolute vapor-pressure values measured in earlier work[5] are in good agreement with the available results;[25,26] however, the value of the vaporization enthalpy[5] is in poor agreement (see Table 2). This report gave us an opportunity to check our previous results[5] for dimethyl malonate. We have repeated vapor pressures on this compound (see Table 1), and we have obtained excellent agreement with our previous results[5] except for two experimental points at 277.9 K and 308.0 K. It is now apparent that these two experimental points have caused the deviation of vaporization enthalpy reported in ref 5.

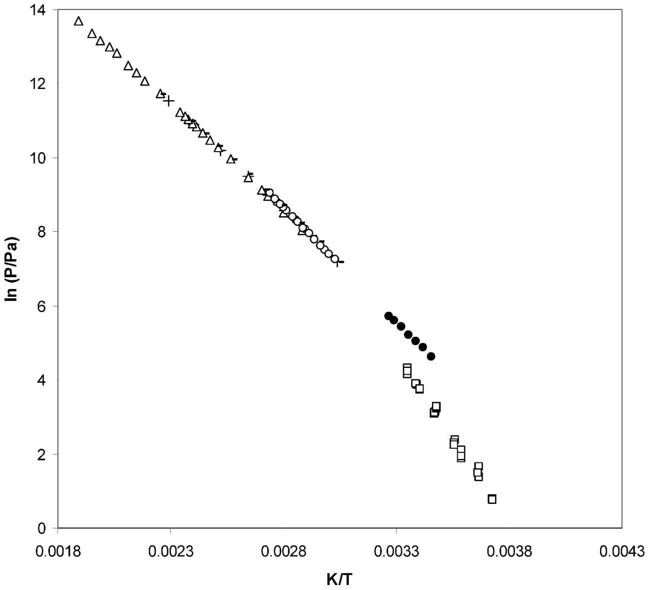

Figure 1. Plot of vapor pressure against reciprocal temperature for dimethyl oxalate: ●, ref 22; □, ref 23; +, ref 24; △, ref 25; −, ref 29; ○, this work.

Askonas et al.[25] also reported vapor pressures of dimethyl malonate from ebulliometry in the very broad temperature range of (374.1 to 619.6) K. Treatment of these data using eq 2 and eq 3 in the full temperature range provides the enthalpy of vaporization $\Delta_l^g H_m$(298.15 K) = (63.0 ± 0.2) kJ·mol^{-1}, and

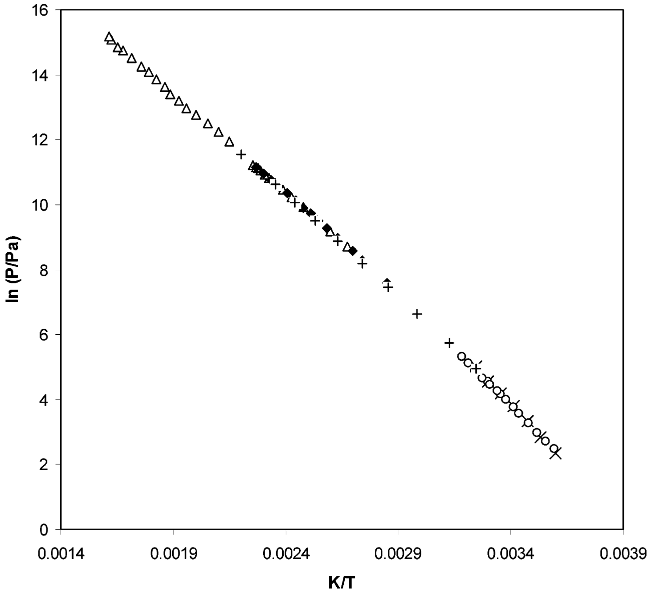

Figure 2. Plot of vapor pressure against reciprocal temperature for dimethyl malonate: ×, ref 5; ◆, ref 26; △, ref 25; +, ref 28; ○, this work.

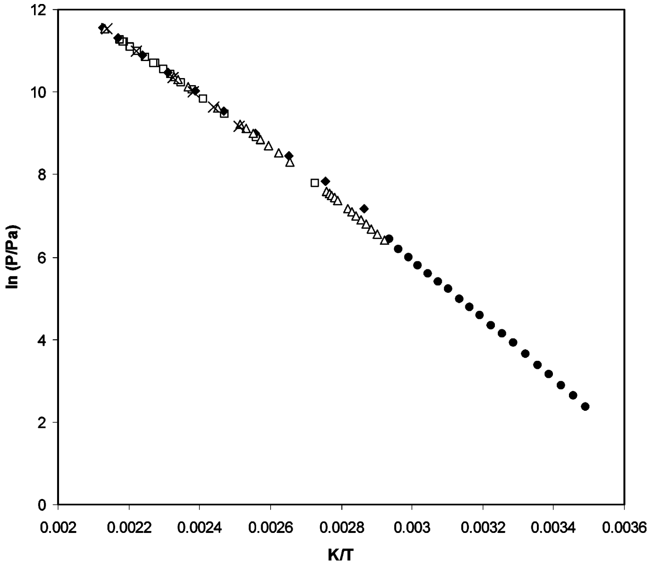

Figure 3. Plot of vapor pressure against reciprocal temperature for dimethyl succinate: △, ref 30; □, ref 38; ×, ref 27; ◆, ref 28; ●, this work.

this value is in disagreement with other available results (see Table 2). The reason for this disagreement is rather in the simplified procedure for long extrapolation of $\Delta_l^g H_m$ to 298.15 K than in the accuracy of the vapor pressures reported in ref 25. Thus, we have treated vapor pressures of dimethyl malonate[25] only in the temperature range of (374.1 to 441.0) K. The value $\Delta_l^g H_m$(298.15 K) = (57.8 ± 0.2) kJ·mol^{-1} (see Table 2) is now in close agreement with another available result.

Katayama[30] reported vapor pressures of dimethyl succinate measured using the static method. Our results are in acceptable agreement with those from the static method within the boundaries of the experimental uncertainties.

Vlasov et al.[27] reported vapor pressures for dimethyl succinate, dimethyl glutarate, and dimethyl adipate using ebulliometry in the temperature range close to the boiling point. In contrast, our data are measured possibly close to the reference temperature T = 298.15 K. Thus, direct comparison with the data from this work is hardly possible; however, their results are in close agreement with other data obtained at the elevated temperatures (see Figures 3 and 4).

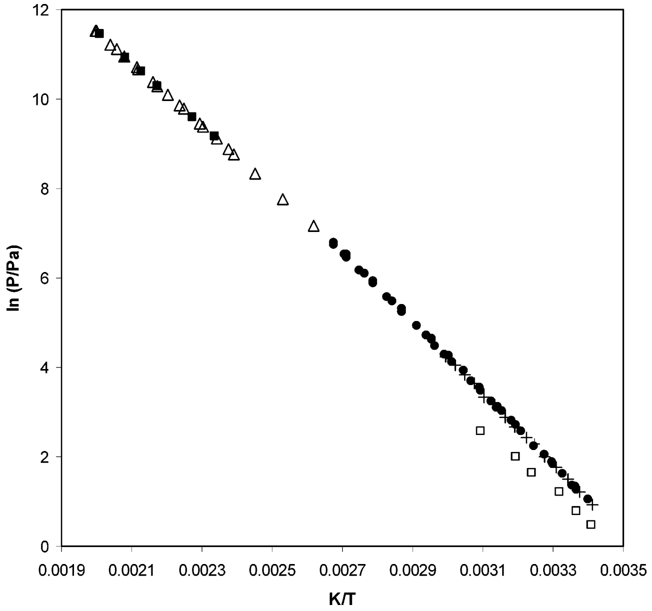

Figure 4. Plot of vapor pressure against reciprocal temperature for dimethyl adipate: □, ref 31; +, ref 32; △, ref 28; ■, ref 27; ●, this work.

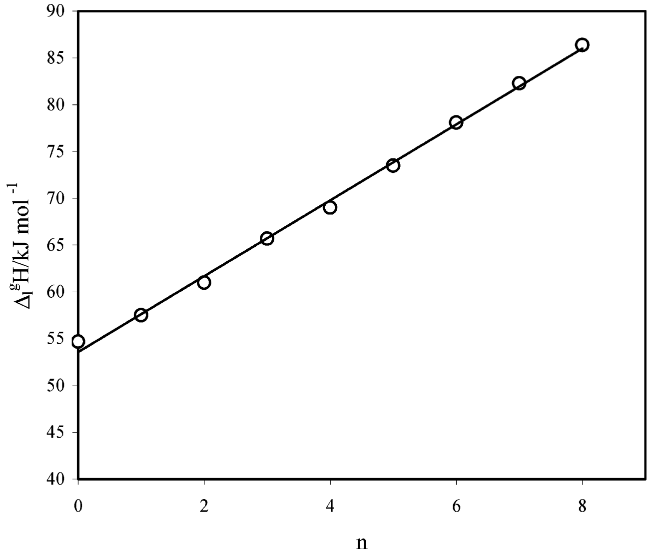

Figure 5. Plot of experimental vaporization enthalpies $\Delta_l^g H_m$(298.15 K) against the number of CH_2 groups in the linear aliphatic dimethyl esters of dicarboxylic acids CH_3-CO_2-$(CH_2)_n$-CO_2-CH_3 with n = (0 to 8).

Dimethyl adipate was already investigated by the method of transference in our previous work.[32] In this work, we have substantially extended the temperature range of investigation of this compound. Vapor pressures measured in this work for dimethyl adipate are in close agreement with the previous results[32] (see Figure 4). However, our results for the vapor pressures at different temperatures are inconsistent with the recent data measured by Chen et al.[31] using a torsion-effusion method in the temperature range of (293.3 to 323.2) K on dimethyl adipate (see Figure 4). Our vapor pressures are systematically higher in comparison with those from ref 31. The enthalpy of vaporization of dimethyl adipate calculated from the Chen et al.[31] data using eq 2 and eq 3 is also in disagreement with other results (see Table 2).

Chickos et al.[23] reported the sublimation enthalpy of dimethyl oxalate, which has been measured by calorimetric and a headspace method. These results along with vaporization enthalpy measured by a correlation GC method and fusion enthalpy measurements suggested that the experimental data

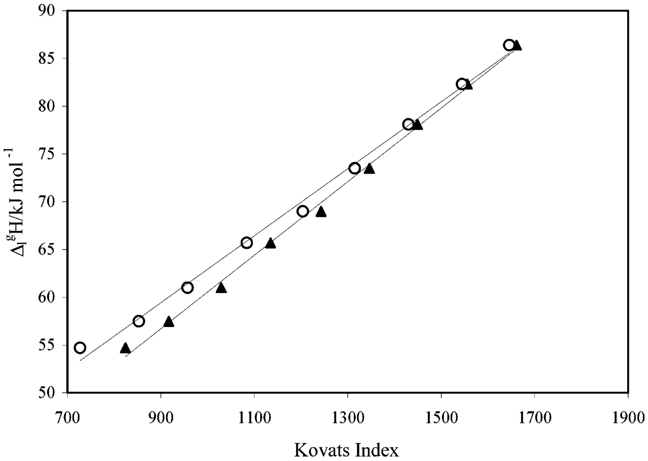

Figure 6. Plot of experimental vaporization enthalpies $\Delta_l^gH_m$(298.15 K) against Kovat's index for dimethyl esters of dicarboxylic acids: ○, SE-54 at 413 K;[36] ▲, SE-30 at 493 K.[37]

Table 3. Critical Temperatures of Dimethyl Esters of Dicarboxylic Acids CH_3-CO_2-$(CH_2)_n$-CO_2-CH_3: Experimental Values and Comparison with Predictive Methods

	T_c/K		
substance	exptl	ref 39	ref 40
dimethyl oxalate	639 ± 6[a]	600.8	592.6
	533[b]		
	533[c]		
	628 ± 7[d]		
dimethyl malonate	649 ± 7[a]	535.9	613.5
dimethyl succinate	662 ± 7[a]	434.0	632.7
dimethyl glutarate	682 ± 7[a]	484.0	651.8
dimethyl adipate	692 ± 7[a]	523.2	669.5
dimethyl pimelate	711 ± 7[a]	555.3	686.0
dimethyl suberate	723 ± 7[a]	582.7	701.3
dimethyl sebacate	742 ± 7[a]	627.4	729.3
AAE[e]/K		114.6	27.9

[a] This work. [b] Data by Regnault.[8] [c] Data by Weger.[8] [d] Data by Stern and Kay.[8] [e] AAE = $(1/N)(\sum |T_c^{exp} - T_c^{calc}|)$, where N is the number of experimental data points, T_c^{exp} and T_c^{calc} are the experimental and calculated values of the critical temperature.

Table 4. Critical Pressures of Dimethyl Esters of Dicarboxylic Acids CH_3-CO_2-$(CH_2)_n$-CO_2-CH_3: Experimental Values and Comparison with Predictive Methods

	p_c/MPa		
substance	exptl	ref 39	ref 40
dimethyl oxalate	4.06 ± 0.12[a]	3.919	3.963
	0.96[b]		
	3.98 ± 0.41[c]		
dimethyl malonate	3.53 ± 0.11[a]	3.472	3.480
dimethyl succinate	3.06 ± 0.09[a]	3.100	3.093
dimethyl glutarate	2.77 ± 0.08[a]	2.787	2.787
dimethyl adipate	2.50 ± 0.08[a]	2.521	2.534
dimethyl pimelate	2.37 ± 0.07[a]	2.293	2.322
dimethyl suberate	2.30 ± 0.07[a]	2.096	2.144
dimethyl sebacate	2.08 ± 0.06[a]	1.776	1.860
AAE[d]/MPa		0.108	0.082

[a] This work. [b] Data by Regnault.[8] [c] Data by Stern and Kay.[8] [d] AAE = $(1/N)(\sum |p_c^{exp} - p_c^{calc}|)$, where N is the number of experimental data points, p_c^{exp} and p_c^{calc} are the experimental and calculated values of the critical temperature.

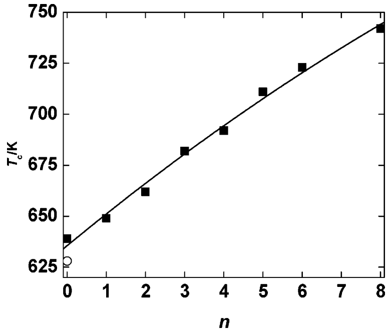

Figure 7. Critical temperature of dimethyl esters of dicarboxylic acids CH_3-$CO_2(CH_2)_nCO_2CH_3$ as a function of the number of CH_2 groups in a molecule: ■, this work; ○, ref 8.

measured by Anthoney et al.[22] using a static Bourdon gauge are seemingly in error. However, as can be seen from Figure 1, the vapor pressures measured using the headspace method by Chickos et al.[23] are in total disagreement not only with those from the ref 22 but with our results as well. In this work, vapor pressures of dimethyl oxalate have been measured at below and above the melting temperature (see Table 1). To test the consistency of experimental data on vaporization and sublimation enthalpies of dimethyl oxalate derived in this work, let us compare their difference with the experimental enthalpy of fusion, $\Delta_{cr}^{l}H_m$, measured by DSC.[23] The enthalpy of fusion can be calculated as the difference $\Delta_{cr}^{l}H_m(298.15\ K) = \Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ (both values referred to $T = 298.15$ K) = (20.4±0.6) kJ·mol^{-1}. The experimental enthalpy of fusion at the melting temperature, $T = 327.6$ K is $\Delta_{cr}^{l}H_m(T_{fus}) = (21.3 \pm 0.4)$ kJ·mol^{-1}. Because of the deviation from $T = 298.15$ K, the experimental enthalpy of fusion of dimethyl oxalate had to be adjusted to the reference temperature. The adjustment was calculated from the equation:[34]

$$\{\Delta_{cr}^{l}H_m(T_{fus}/K) - \Delta_{cr}^{l}H_m(298.15\ K)\}/(J\cdot mol^{-1}) = \{(0.75 + 0.15C_p^{cr}/J\cdot mol^{-1}\cdot K^{-1})[(T_{fus}/K) - 298.15]\} - \{(10.58 + 0.26C_p^{l}/J\cdot mol^{-1}\cdot K^{-1})[(T_{fus}/K) - 298.15]\} \quad (7)$$

where C_p^{l} and C_p^{cr} were calculated (see Table 2) according well-established procedures.[11−13] With this adjustment (the uncertainty of the correlation was not taken into account), the standard enthalpy of fusion at $T = 298.15$ K, $\Delta_{cr}^{l}H_m(298.15\ K) = (20.2 \pm 0.4)$ kJ·mol^{-1} was calculated. Thus, the enthalpy of fusion $\Delta_{cr}^{l}H_m$ calculated from difference $\Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ measured in this work differs from those measured by calorimetry (and adjusted to $T = 298.15$ K) only by 0.2 kJ·mol^{-1}. Thus, our results for vaporization and sublimation enthalpies of dimethyl oxalate have been shown to be consistent. It should be also mentioned that the enthalpy of fusion, $\Delta_{cr}^{l}H_m(T_{fus})$, reported by Chickos et al.[23] for dimethyl oxalate and used in this work, is in close agreement with another value available from the literature:[35] 21.1 kJ·mol^{-1} at 327.6 K.

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 $\Delta_l^gH_m$ appear to be a linear function of the number of carbon atoms of the aliphatic esters[3] and aliphatic nitriles.[33] The plot of $\Delta_l^gH_m$(298.15 K) against the number of C-atoms in the linear aliphatic dimethyl esters of dicarboxylic acids CH_3-CO_2-$(CH_2)_n$-CO_2-CH_3 with n = (0 to 8) is presented in Figure 5. As can be seen in Figure 5, the first representative—dimethyl oxalate—is slightly out of the linear correlation. Such an anomaly has been also observed for aliphatic esters[3] and aliphatic nitriles,[33] and this fact might be caused by the high dipole moment of these species. The dependence of vaporization enthalpy on the number of C-atoms for $n \geq 1$ is expressed by the following equation:

$$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = 52.9 + 4.17n \qquad (8)$$

from which enthalpy of vaporization $\Delta_l^g H_m$(298.15 K) for other representatives of this series with $n > 8$ can be calculated.

Correlation of Enthalpies of Vaporization with Kovat's Indices. The correlation of the enthalpies of vaporization with the 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 the Kovat's index, *n*-alkanes serve as the standards and logarithmic interpolation is utilized defined by

$$J_x = \frac{\lg(t_x) - \lg(t_N)}{\lg(t_{N+1}) - \lg(t_N)} \cdot 100 + 100N \qquad (9)$$

where x refers to the adjusted retention time, N is the number of carbon atoms of the *n*-alkane eluting before the peak of interest, 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 homologues *n*-hydrocarbons.[37] 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 two stationary phases SE-30 and SE-54.

The vaporization enthalpy $\Delta_l^g H_m$ appears to be a linear function of the Kovat's indices in homologous series of alkanes, alcohols, and aliphatic esters.[3,33] We have used Kovat's indices available from the literature[36,37] and own results for $\Delta_l^g H_m$(298.15 K) for dimethyl esters of dicarboxylic acids (see Table 2) in order to test how the results fit into a systematic dependence on the Kovat's indices. It can be seen from Figure 6 that the data for $\Delta_l^g H_m$(298.15 K) fit very well in the linear correlation, again except for dimethyl oxalate. The following empirical equation for the enthalpy of vaporization of the dimethyl esters of dicarboxylic acids for $n \geq 1$ is suggested:

$$\Delta_l^g H_m(298.15\ \text{K})/(\text{kJ}\cdot\text{mol}^{-1}) = 20.8 + 0.039\cdot J_x \text{ for SE-54} \qquad (10)$$

$$\Delta_l^g H_m(298.15\ \text{K})/(\text{kJ}\cdot\text{mol}^{-1}) = 26.1 + 0.036\cdot J_x \text{ for SE-30} \qquad (11)$$

where J_x is the Kovat's index of an ester. This relationship can be used as evidence of the internal consistency of our experimental results for vaporization enthalpies.

Experimental J_x-values for dimethyl esters dicarboxylic acids with the $n = (0 \text{ to } 8)$ used in this work are as follows:[36,37]

from the reference SE-54[36] at $T = 413$ K:
824, 917, 1029, 1135, 1243, 1346, 1449, 1556, 1661

from the reference SE-30[37] at $T = 493$ K:
727, 853, 957, 1084, 1204, 1315, 1430, 1545, 1646

Critical Properties of Dimethyl Esters of Dicarboxylic Acids. The critical temperatures and pressures of dimethyl esters of dicarboxylic acids with $n = (0 \text{ to } 6)$ and 8 are given in Tables 3 and 4 and in Figures 7 and 8. From our knowledge, only the critical properties of dimethyl oxalate have ever been measured.[7] Some very earlier data of Regnault and Weger cited in the ref 8 are apparently of historical interest. Stern and Kay[8] detected that dimethyl oxalate was thermally unstable above 473 K; however, they measured the critical temperature directly from the disappearance of the liquid−vapor interface. The critical pressure was determined by extrapolation of vapor pressures measured at low temperatures to the critical temperature. The disagreement between our data and those by Stern and Kay do not exceed the combined uncertainties. According to the well-known correlation by Lydersen,[20] the quantity $(M/p_c)^{1/2}$ is a linear function of the number of CH_2 groups in a molecule n within a given homologous series. Here M is the molar mass. Indeed, this rule works well for many homologous series, at least for the lower members of the series. However, for the esters studied in this work, the following equation seems to be more accurate:

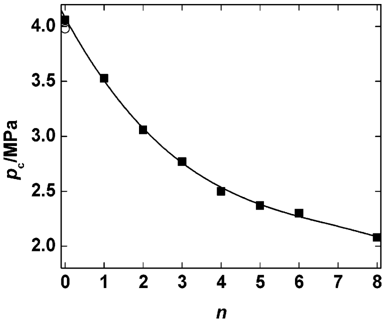

Figure 8. Critical pressure of dimethyl esters of dicarboxylic acids $CH_3CO_2(CH_2)_nCO_2CH_3$ as a function of the number of CH_2 groups in a molecule: ■, this work; ○, ref 8.

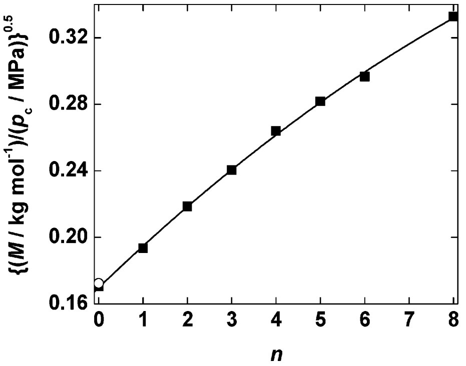

Figure 9. Correlation of the critical pressure of dimethyl esters of dicarboxylic acids $CH_3CO_2(CH_2)_nCO_2CH_3$ as a function of the number of CH_2 groups in a molecule and molar mass: ■, this work; ○, ref 8.

$$\left(\frac{M}{p_c}\right)^{1/2} = 0.016993 + 0.0256n - 6.6866\cdot 10^{-4} n^2 \qquad (12)$$

The solid line in Figure 9 corresponds to this equation.

The critical temperatures and pressures of dimethyl esters of dicarboxylic acids were also estimated using the well-known group contribution methods by Constantinou and Gani[39] and Marrero and Gani[40] (see Tables 3 and 4). The method by Constantinou and Gani considerably underestimates the critical temperatures of the esters studied; the average absolute error (AAE) is more than 114 K whereas the uncertainty of the results of the measurement is equal to from (6 to 7) K. The method by Marrero and Gani underestimates the critical temperatures of the esters too, giving however much better results although the value of AAE exceeds several times the uncertainty of the experimental data. On the other hand, both methods give a reasonable estimation of the critical pressures of the esters, especially the method by Marrero and Gani for which the value of AAE is practically equal to the uncertainty of the measurements. Both methods can be used for predicting the critical pressures of dimethyl esters of dicarboxylic acids, at least, when the number of CH_2 groups in a molecule of a dicarboxylic acid does not exceed eight.

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