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Determination of Vaporization Enthalpies of the Branched Esters from Correlation Gas Chromatography and Transpiration Methods

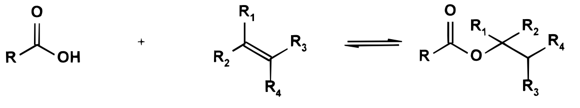
Sergey P. Verevkin* and Andreas Heintz

Department of Physical Chemistry, University of Rostock, Hermannstrasse 14, 18051 Rostock, Germany

The temperature dependencies of retention indices of a set of 80 esters with branched molecular structures were measured on a nonpolar gas chromatographic column. The correlation gas chromatography method and reliable data set of 16 esters selected from the literature were used to derive a correlation for the prediction of the standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ at the temperature $T = 298.15$ K. Experimental values of $\Delta_l^g H_m^\circ$ for 64 branched esters were obtained with the help of this correlation. The vaporization enthalpies of isopentyl acetate, ethyl hexanoate, and neopentyl pivalate were additionally obtained by the transiration method from the temperature dependence of the vapor pressure measured in a flow system and used for checking the validity of the correlation gas chromatography method.

Introduction

Vaporization enthalpies are indispensable for the assessment of the environmental fate and behavior of environmental contaminants. Volatilization from soil and vegetation is largely controlled by the compound's vapor pressure. Vaporization enthalpy is also an important parameter in the prediction of partitioning properties; for example, its value can be used to calculate the temperature dependence of solubility parameters, frequently used in relationships to predict solubility behavior (Krop et al., 1997). While diverse group-additivity methods (Chickos et al., 1981) give excellent correlations between observed and calculated values for linear homologues, deviation may arise, especially for the branched members of the series. Because the distribution of the bulky molecules in the liquid and their intermolecular interactions seem to be unique for the branched molecules, for reliable predictions of the vaporization enthalpies of such species, a more detailed study is required. A very few systematic investigations of vaporization enthalpies of branched compounds are known from the literature (Chickos et al., 1995b; Verevkin et al., 1996). We report here a systematic determination of the vaporization enthalpies of a series of branched esters. Some years ago we started the investigation of the chemical equilibrium of reaction I:



(I)

where R and R_1-R_4 are alkyl substituents of different chain length. The structures of the carboxylic acids and olefins involved in this study are presented in Figure 1. The products of reaction I are branched esters, but the reaction mixtures are strongly associated due to the presence of carboxylic acid. Our preliminary studies have demonstrated that activities rather than concentration are necessary to obtain thermodynamic equilibrium constants for these reactions. The equilibrium constants of the reactions carboxylic acid + olefin ↔ ester in the liquid phase were systematically studied, and the enthalpies of reaction were derived from the temperature dependencies of the equilibrium constants. The activity coefficients in the liquid mixtures were estimated by the UNIFAC and ERAS (Heintz, 1985) models. However, the validity of activity coefficients of strongly associated species calculated by these methods remains questionable. Therefore, it is desirable to possess a criterion to check the consistency of our experimental results and estimates for the liquid state. An independent way to obtain such criterion are enthalpies of the same reaction (carboxylic acid + olefin ↔ ester) but calculated from standard enthalpies of formation $\Delta_f H_m^\circ$(liq) of the reaction participants in the liquid state. Concurrence between measured and estimated enthalpies can be a valuable test to establish the ability of the UNIFAC and ERAS models to predict the deviation from ideal behavior in the reactive associated mixtures. Liquid-state standard enthalpies of formation $\Delta_f H_m^\circ$(liq) of carboxylic acids and

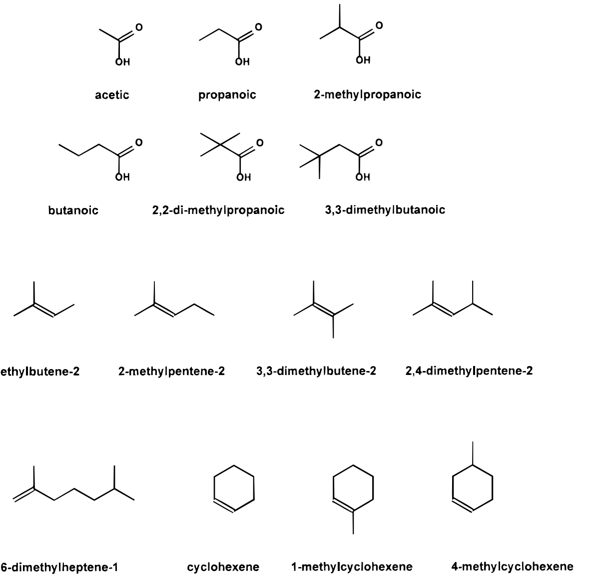


Figure 1. Structures of carboxylic acids and olefins involved in the investigation of chemical equilibrium.

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* To whom correspondence should be addressed. E-mail: sergey.verevkin@chemie.uni-rostock.de.

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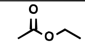
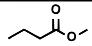
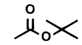
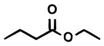
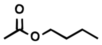
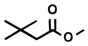
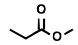
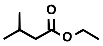
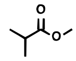
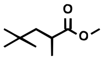
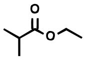
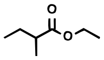
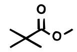
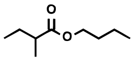
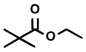
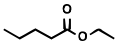
Table 1. Data Set of $\Delta_l^g H_m^\circ$ of the Reference Esters and the Results from GC Correlation Measurements on These Compounds

	$\ln(1/t_r) =$ a	a + b/(T/K) -b	$\Delta_{sol}^{g}H_m^\circ$ / kJ·mol^{-1}	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1}		$\ln(1/t_r) =$ a	a + b/(T/K) -b	$\Delta_{sol}^{g}H_m^\circ$ / kJ·mol^{-1}	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1}
	-4.43	79.82	0.30	35.56		-3.32	543.1	4.51	39.28
	-3.40	500.1	4.16	38.03		-1.76	1180	9.81	43.18
	-1.50	1280	10.6	43.62		-1.38	1340	11.1	44.39
	-3.32	484.2	0.60	35.82[a]		-0.17	1810	15.1	43.90
	-3.86	324.3	2.69	37.42[b]		2.52	2960	24.6	48.39
	-2.45	888.4	7.38	39.80		-0.28	1770	14.7	44.31
	-2.95	676.8	5.62	39.20		4.19	3690	30.7	50.57
	-1.53	1250	10.4	41.25		0.86	2240	18.6	47.11

[a] Data from Sunner et al., 1979. [b] Data from Majer and Svoboda, 1985.

olefins are available from the literature (Verevkin and Heintz, 1999; Verevkin et al., 1999). Experimental data for the branched esters are scarce, but the MM3 force field calculation method (Allinger et al., 1992) has claimed to predict the gaseous standard enthalpies of esters with acceptable accuracy. Knowledge of the vaporization enthalpies of the appropriate branched ester could provide the possibility to estimate the enthalpies of formation of the participants of the reactions studied in the liquid state. The part of our work concerning equilibrium studies will be reported separately. In this study, the enthalpies of vaporization of a number of branched esters are measured using correlation gas chromatography.

Correlation gas chromatography has several advantages over other methods. It is a fast and easy method where low concentrations are used and relatively impure substances are tolerated. A detailed description of the method used can be found elsewhere (Chickos et al., 1995a,b). In short, a plot of $\ln(1/t_r)$ versus $1/(T/\mathrm{K})$, where t_r is the retention time (in seconds) corrected for the dead volume, results in the straight line whose slope when multiplied by the gas constant affords $\Delta_{sol}^{g}H_m^\circ$. It was found (Chickos et al., 1995a) that, in cases where compounds are properly selected with regard to the analogy of their molecular structures, plotting $\Delta_{sol}^{g}H_m^\circ$ versus the known standard molar vaporization enthalpy $\Delta_l^g H_m^\circ$ also affords a linear relationship. This relationship can subsequently be used to evaluate the unknown vaporization enthalpy of any structurally related species, provided that the unknown species is analyzed at the same conditions as the standards. To our knowledge, methods capable of reflecting the effect of minor structural differences in the position and configuration of substituents on $\Delta_l^g H_m^\circ$ better than correlation gas chromatography have not existed up to now.

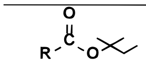
Experimental Procedure

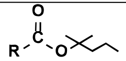
Materials. Samples of the reference esters were available from the collection of chemicals synthesized in the Chemical Departments of the Universities of Freiburg and Rostock. Other samples of branched esters were synthesized via alkylation of an appropriate carboxylic acid with an olefin or an alcohol (Verevkin et al., 1992; Kashkarova et al., 1995) and were purified by distillation in a vacuum. The structures of the esters used were established by NMR spectroscopy. The purities of all samples determined by GC were better than 0.99 mole fraction, but this is not of concern, since capillary gas chromatography allowed separation even of minor contaminations from the major peak.

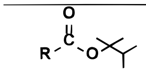
GC Correlation Method. Measurements were made with a Hewlett-Packard Series 5890 gas chromatograph, equipped with a FID, an autosampler, and a Hewlett-Packard Integrator 3390A. GC runs were done isothermally on a DB-1 capillary column of length 50 m and diameter 0.32 mm packed with the film thickness 0.25 μm. Nitrogen was used as the carrier gas with the flow rate of 0.333 $\mathrm{cm^3{\cdot}s^{-1}}$. At each temperature corrections of retention times with the value for the nonretained component (propane) were made. The temperature was maintained constant within ±0.1 K. All substances were dissolved in acetonitrile. Five separate mixtures of esters were prepared because of the large differences in retention times. Experiments on each mixture at six temperatures within 333−378 K were performed twice to ensure reproducibility. By using an autosampler, retention times were generally reproducible within 1−3 s. The enthalpies of transfer from solution to the gas phase $\Delta_{sol}^{g}H_m^\circ$ were obtained for each compound by plotting $\ln(1/t_r)$ versus $1/T$ (see Tables 1 and 2). The slope of this linear correlation $\ln(1/t_r) = a + b{\cdot}T^{-1}$, when multiplied by the gas constant R, affords $\Delta_{sol}^{g}H_m^\circ$. The method used correlates the gas chromatographical behavior (retention time) of a compound of interest with the net retention times of some standard compounds with the known enthalpies of vaporization (Chickos et al., 1995a,b). The linear relationship between $\Delta_{sol}^{g}H_m^\circ$ and $\Delta_l^g H_m^\circ$ for the structurally related compounds suggests an easy possibility for obtaining the vaporization enthalpy of an unknown compound. The accuracy of the results depends on the accuracy of the $\Delta_l^g H_m^\circ$ of the reference standards. The best results are usually obtained when the reference compounds are structurally similar and from the same chemical family. We used our own experimental results for $\Delta_l^g H_m^\circ$ of branched esters as well the data available from the literature (Table 1), which were compiled recently (Verevkin et al., 1996).

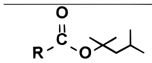
Transpiration Method. The enthalpies of vaporization of isopentyl acetate, ethyl hexanoate, and neopentyl piv-

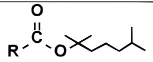
Table 2. Results for Esters Synthesized from Carboxylic Acids and Olefins from Measurements of the Enthalpy of Transfer from Solution to Vapor $\Delta_{sol}^{g}H_m^\circ$ by Correlation Gas Chromatography and Vaporization Enthalpies $\Delta_l^{g}H_m^\circ$ Derived from These Measurements

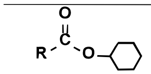
	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	-1.08	1440	12.0	42.8
R = CH_3 - CH_2 -	0.54	2130	17.7	45.7
R = $(CH_3)_2$ - CH -	1.67	2610	21.7	47.8
R = CH_3 - $(CH_2)_2$ -	2.48	2862	23.8	48.9
R = $(CH_3)_3$ - C -	1.74	2660	22.1	48.0
R = $(CH_3)_3$ - CH_2 -	4.45	3860	32.1	53.2

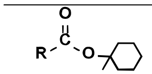
	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	0.46	2100	17.5	45.6
R = CH_3 - CH_2 -	2.77	3070	25.5	49.8
R = $(CH_3)_2$ - CH -	3.62	3450	28.7	51.4
R = CH_3 - $(CH_2)_2$ -	4.65	3910	32.5	53.4
R = $(CH_3)_3$ - C -	4.09	3660	30.4	52.3
R = $(CH_3)_3$ - CH_2 -	6.43	4740	39.4	57.0

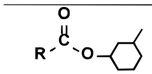
	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	0.67	2190	18.2	46.0
R = CH_3 - CH_2 -	2.81	3100	25.8	49.9
R = $(CH_3)_2$ - CH -	37.73	3510	29.2	51.7
R = CH_3 - $(CH_2)_2$ -	4.85	4010	33.3	53.8
R = $(CH_3)_3$ - C -	4.34	3780	31.4	52.8
R = $(CH_3)_3$ - CH_2 -	6.47	4770	39.7	57.1

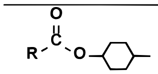
	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	1.74	2650	22.0	47.9
R = CH_3 - CH_2 -	3.72	3520	29.3	51.7
R = $(CH_3)_2$ - CH -	4.61	3920	32.4	53.4
R = CH_3 - $(CH_2)_2$ -	5.82	4460	37.1	55.8
R = $(CH_3)_3$ - C -	4.98	4100	34.1	54.2
R = $(CH_3)_3$ - CH_2 -	7.03	5070	42.2	58.4

	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	6.13	4590	38.2	56.4
R = CH_3 - CH_2 -	7.56	5290	44.0	59.4
R = $(CH_3)_2$ - CH -	8.24	5620	46.7	60.8
R = CH_3 - $(CH_2)_2$ -	8.98	6000	49.9	62.5
R = $(CH_3)_3$ - C -	8.42	5720	47.6	61.3
R = $(CH_3)_3$ - CH_2 -	10.2	6630	55.1	67.4

	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	3.90	3590	29.9	51.7
R = CH_3 - CH_2 -	6.43	4690	39.0	56.8
R = $(CH_3)_2$ - CH -	6.80	4900	40.7	57.7
R = CH_3 - $(CH_2)_2$ -	8.19	5520	45.9	60.0
R = $(CH_3)_3$ - C -	7.49	5210	43.3	59.0
R = $(CH_3)_3$ - CH_2 -	8.74	5920	49.2	62.1

	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	4.08	3680	30.6	52.4
R = CH_3 - CH_2 -	5.77	4470	37.2	55.8
R = $(CH_3)_2$ - CH -	6.46	4800	39.9	57.2
R = CH_3 - $(CH_2)_2$ -	7.22	5180	43.1	58.9
R = $(CH_3)_3$ - C -	6.77	4960	41.2	57.9
R = $(CH_3)_3$ - CH_2 -	8.27	5760	47.9	61.4

	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	4.69	3960	32.9	53.6
R = CH_3 - CH_2 -	6.65	5039	41.9	58.3
R = $(CH_3)_2$ - CH -	7.00	5280	43.9	59.3
R = CH_3 - $(CH_2)_2$ -	7.95	5881	48.9	61.9
R = $(CH_3)_3$ - C -	6.90	5557	46.2	60.5
R = $(CH_3)_3$ - CH_2 -	9.21	6242	51.9	63.5

	$\ln(1/t_r)$ =	a + b/(T/K)	$\Delta_{sol}^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$	$\Delta_l^{g}H_m^\circ$ / $kJ\cdot mol^{-1}$
	a	-b		
R = CH_3 -	5.41	4230	33.9	54.1
R = CH_3 - CH_2 -	6.90	5172	43.0	58.9
R = $(CH_3)_2$ - CH -	7.13	5376	44.7	59.7
R = CH_3 - $(CH_2)_2$ -	8.51	5990	49.8	62.4
R = $(CH_3)_3$ - C -	7.02	5653	47.0	60.9
R = $(CH_3)_3$ - CH_2 -	9.96	6374	53.0	64.1

alate were determined using the method of transference in a saturated N_2-stream (Chickos et al., 1995b). About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The amount of condensed product was determined by GC analysis using an internal standard (hydrocarbon n-C_9H_{20}). The vapor pressure p at each saturation temperature was calculated from the amount of product collected within a definite time period, and the small value of the residual vapor pressure at the temperature of condensation was added. The latter was calculated from a linear correlation between ln(p) and T^{-1} obtained by iteration. To derive the standard molar enthalpy of vaporization $\Delta_l^{g}H_m^\circ(T)$ at the mean temperature $\langle T\rangle$ of the experimental temperature range, the integrated form of the linear Clausius−Clapeyron equation

$$\ln(p/\mathrm{Pa}) = a - b\cdot(T/\mathrm{K})^{-1} \qquad (1)$$

where $b = \Delta_l^{g}H_m^\circ(T)\cdot R^{-1}$, was used. The observed enthalpies of vaporization $\Delta_l^{g}H_m^\circ(T)$ at the temperature T obtained by this procedure are listed in Table 3. The experimental data were approximated with the linear equation $\ln(p) = f(T^{-1})$ (see Table 3) using the method of least squares. The error in the enthalpy of vaporization was defined as the deviation of the experimental ln(p) from this linear correlation. Because of the deviations from T = 298.15 K, the observed values of the enthalpies of vaporization of esters measured by transpiration had to be adjusted to the reference temperature. The corrections were estimated with the help of the correlation

$$\{\Delta_l^{g}H_m^\circ(\langle T\rangle) - \Delta_l^{g}H_m^\circ(298.15\ \mathrm{K})\}/(\mathrm{kJ\cdot mol^{-1}}) = -(5.44 \times 10^{-2})\{(\langle T\rangle/\mathrm{K}) - 298.15\}$$

following the recommendation of Chickos et al. (1993). With these corrections and the measured values, the standard molar enthalpies of vaporization at T = 298.15 K were calculated (Table 3).

Results

The experimental results for the temperature dependence of the corrected retention time in the form of the equation $\ln(1/t_r) = a + b/T$ for a series of 16 reference esters and their derived values of $\Delta_{sol}^{g}H_m^\circ$ are listed in Table 1. From the correlation of the selected data set, the following equation for the estimation of vaporization enthalpies was obtained:

$$\Delta_l^{g}H_m^\circ/\mathrm{kJ\ mol^{-1}} = (36.50 \pm 0.23) + (0.520 \pm 0.021)\Delta_{sol}^{g}H_m^\circ \qquad (r = 0.971) \quad (2)$$

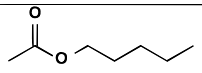
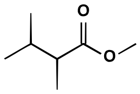
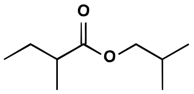
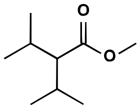
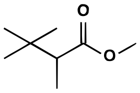
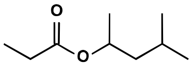
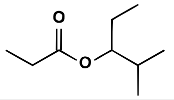
The uncertainty of $\Delta_l^{g}H_m^\circ$ obtained from this equation is assessed to be ±0.5 kJ mol^{-1}. With this correlation and measured values of $\Delta_{sol}^{g}H_m^\circ$ for esters which are products of reaction I, the values of the enthalpies of vaporization for the 57 compounds of interest were derived (see Tables

Table 3. Results from Measurements of the Vapor Pressure *p* by the Transpiration Method

T^a/K	m^b/ mg	$V(N_2)^c$/ dm^3	p^d/Pa	T^a/K	m^b/ mg	$V(N_2)^c$/ dm^3	p^d/Pa
Isopentyl Acetate; $\ln(p/\text{Pa}) = (25.45 \pm 0.07) - (5624 \pm 19)\cdot(T/\text{K})^{-1}$							
278.4	6.97	0.742	188.9	293.2	7.89	0.289	529.2
281.2	7.36	0.634	231.1	296.2	7.14	0.217	635.7
284.2	7.95	0.543	288.7	299.2	7.14	0.180	764.3
287.2	8.11	0.451	352.4	302.2	7.04	0.145	933.5
290.2	7.98	0.362	429.7	305.2	6.32	0.108	1124.0
$\Delta_l^g H_m^\circ(291.8\ \text{K}) = (46.76 \pm 0.16)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H_m^\circ(298.15\ \text{K}) = (46.41 \pm 0.16)\ \text{kJ}\cdot\text{mol}^{-1}$							
Ethyl Hexanoate; $\ln(p/\text{Pa}) = (25.78 \pm 0.16 - (6104 \pm 45)\cdot(T/\text{K})^{-1}$							
279.4	6.75	2.32	51.93	297.4	9.92	0.923	186.5
282.4	6.71	1.84	64.63	300.4	10.5	0.769	236.5
285.4	7.41	1.61	80.97	303.2	9.12	0.558	282.6
288.4	7.66	1.33	1.009	306.2	8.86	0.435	351.9
291.4	8.75	1.23	1.242	309.2	6.06	0.245	426.6
294.4	8.97	1.03	151.6				
$\Delta_l^g H_m^\circ(294.3.0\ \text{K}) = (50.75 \pm 0.37)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H_m^\circ(298.15\ \text{K}) = (50.55 \pm 0.37)\ \text{kJ}\cdot\text{mol}^{-1}$							
Neopentyl Pivalate; $\ln(p/\text{Pa}) = (25.42 \pm 0.18) - (5907 \pm 63)\cdot(T/\text{K})^{-1}$							
279.5	10.2	2.160	70.62	297.7	13.1	0.756	252.5
282.5	10.9	1.790	90.10	300.7	11.6	0.550	307.4
285.5	11.3	1.510	110.4	303.6	10.6	0.412	371.8
288.5	12.0	1.290	136.7	306.6	8.95	0.274	472.7
291.6	13.8	1.250	162.1	309.6	6.80	0.171	574.2
294.7	12.6	0.911	201.5				
$\Delta_l^g H_m^\circ(294.5\ \text{K}) = (49.11 \pm 0.52)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H_m^\circ(298.15\ \text{K}) = (48.92 \pm 0.52)\ \text{kJ}\cdot\text{mol}^{-1}$							

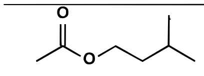
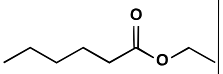
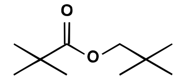
[a] Temperature of saturation, N_2 gas flow 0.26−0.52 cm$^3\cdot$s^{-1}. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at $T = 243$ K.

Table 4. Results from Measurements of the Enthalpy of Transfer from Solution to the Vapor $\Delta_{sol}^g H_m^\circ$ by Correlation Gas Chromatography for Some Branched Esters and Vaporization Enthalpies $\Delta_l^g H_m^\circ$ Derived from These Measurements

	$\ln(1/t_r) =$ a	$a + b/(T/K)$ -b	$\Delta_{sol}^g H_m^\circ$ / kJ·mol^{-1}	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1}
	1.28	2658	22.1	48.0
	0.52	2050	17.0	45.3
	1.16	2380	19.8	46.8
	2.85	3110	25.9	50.0
	2.53	2970	24.7	49.3
	2.81	3127	26.0	50.0
	2.87	3200	26.6	50.3

2 and 5). In the same manner, the enthalpies of vaporization of 7 other branched esters were derived (see Table 4).

Table 5. Comparison of Vaporization Enthalpies $\Delta_{sol}^g H_m^\circ$ of Isopentyl Acetate, Ethyl Hexanoate, and Neopentyl Pivalate Derived from the Correlation Gas Chromatography and Transpiration Method

	$\ln(1/t_r) =$ a	$a + b/(T/K)$ -b	$\Delta_{sol}^g H_m^\circ$ / kJ·mol^{-1}	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1} [a]	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1} [b]
	0.18	2197	18.3	46.0	46.41±0.16
	1.53	3192	26.5	50.3	50.55±0.37
	2.76	3070	25.5	49.8	48.92±0.52

[a] Vaporization enthalpy derived by GC correlation method. [b] Vaporization enthalpy derived by transpiration method.

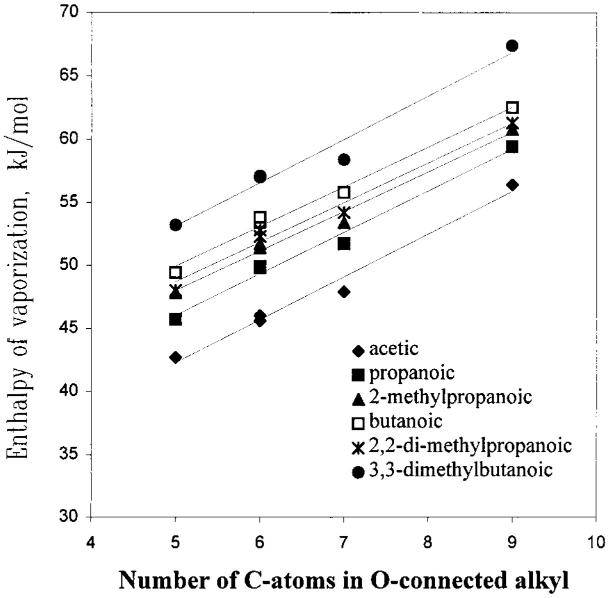


Figure 2. Experimental vaporization enthalpies of the branched esters of carboxylic acids as a function of the number of carbon atoms in the oxygen-connected alkyl chain of the esters.

To prove the ability of eq 2 to predict the vaporization enthalpies correctly, the values of $\Delta_l^g H_m^\circ$ of isopentyl acetate, ethyl hexanoate, and neopentyl pivalate were also measured by the transpiration method and were excluded from being obtained by eq 2 deliberately. The results for these three compounds derived from the GC correlation method and the transpiration method are indistinguishable within the limits of their experimental uncertainties (Table 5). Additionally, we used for checking of eq 2 a small set of reliable $\Delta_l^g H_m^\circ$ of some branched esters measured by transpiration in previous work (Verevkin et al., 1996) and those from correlation gas chromatography (see Table 2). The values derived from transpiration and GC correlation methods are as follows (in kJ mol^{-1}): *tert*-amyl acetate, 42.7 and 42.8; *tert*-amyl butyrate, 49.4 and 48.9; cyclohexyl acetate, 52.0 and 51.7; cyclohexyl butyrate, 60.4 and 60.0. Our value for the vaporization enthalpy of amyl acetate is 48.0 kJ mol^{-1} (Table 4), being in good agreement with those measured by ebulliometry (48.56 ± 0.37) kJ mol^{-1} recently (Steele et al., 1996).

Previous determination of the standard molar enthalpy of vaporization of isopentyl acetate was made by using ebulliometry (Usanovich and Dembitskii, 1959). Their value of $\Delta_l^g H_m^\circ = 45.29$ kJ·mol,$^{-1}$ derived from Antoine coefficients recalculated by Afeefy et al. (1998), is in a very close agreement with ours (Table 3).

Nilson et al. (1986) determined the enthalpy of vaporization of ethyl hexanoate $\Delta_l^g H_m^\circ = (51.72 \pm 0.10)$ kJ·mol^{-1} using calorimetry. Wiberg et al. (1991) reported $\Delta_l^g H_m^\circ = (51.6 \pm 1.6)$ kJ·mol^{-1} for this compound. Our value (Table 3) is in close agreement within the limits of the experimental uncertainties.

The correlation of the enthalpies of vaporization with the number of C atoms of the esters is a valuable test to check the consistency of the data derived from gas correlation chromatography. Vaporization enthalpies $\Delta_l^g H_m^\circ$ appear to be a good linear function of the number of carbon atoms of the alkanes (Chickos et al., 1997) or aliphatic esters (Koutek et al., 1998). A similar trend was observed for the branched esters studied in this work, as is shown in Figure 2.

An application of values of the vaporization enthalpies of branched ester for the development of theoretical models for prediction of activity coefficients in real associated mixtures will be reported in forthcoming papers.

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