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VAPORIZATION ENTHALPIES AND ENTROPIES OF SOME *n*-ALKANES

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ABSTRACT

The vapour pressure of tetracosane, pentacosane, hexacosane and octacosane were measured by the transpiration method. The values fit the following equations:

Tetracosane, $\log p(\text{kPa}) = (8.76 \pm 0.50) - (4501 \pm 250)/T$

Pentacosane, $\log p(\text{kPa}) = (9.16 \pm 0.60) - (4745 \pm 300)/T$

Hexacosane, $\log p(\text{kPa}) = (9.93 \pm 0.50) - (5168 \pm 200)/T$

Octacosane, $\log p(\text{kPa}) = (10.02 \pm 0.40) - (5385 \pm 150)/T$

From these equations the vaporization enthalpies and entropies of the *n*-alkanes studied were derived. Both values indicate a trend with the molecular weight.

INTRODUCTION

A reliable knowledge of the thermodynamic parameters associated with the vaporization or sublimation of organic compounds is very important in relation to their application in chemical and technological fields. The vaporization enthalpy can also be derived from measurements of the temperature dependence of the vapour pressure of the compound studied as well as from direct calorimetric determinations. At present, the vaporization enthalpies and vapour pressures for a large number of organic compounds are either not known, or the data available are based on old experimental determinations [1,2] and merit further investigation.

In this work, the vaporization enthalpies and entropies of a homologous series of four molten *n*-alkanes, tetracosane, pentacosane, hexacosane and octacosane (C_nH_{2n+2} where $n = 24$, 25, 26 and 28 respectively), have been derived by measuring their vapour pressures using the transport method. For these compounds, Antoine's equations from the TRC Thermodynamic Tables—Hydrocarbons [2] and a few vapour pressure values reported by Grenier-Loustalot et al. [3] represent the only apparent literature data.

RESULTS

The hydrocarbons used were commercial materials (about 99.5% pure, supplied by Aldrich-Chemie) where the small amount of impurities present, principally homologous species, should not appreciably affect the vapour pressure measurements.

The vapour pressure p of the n-alkanes studied was determined by the transport method using the well-known relation [4]

$$p = m/\{m + (p_0 \Phi t M / R T_0)\} \qquad (1)$$

where m is the mass of material transported and condensed on a cooled collector in the time t, M is the vapour molar mass, R the gas constant and Φ the flow rate of the carrier gas measured by a flowmeter at T_0 and p_0. In this work, p_0 and the total pressure over the sample were taken as equal to 1 atm.

The experimental apparatus used for the measurements is shown in Fig. 1. The sample temperature was taken as the average of two values, practically equal, measured with calibrated Fe–Cost thermocouples inserted in two different positions of the steel container of the sample boat, made of pyrophillite. At about 400 K, the two temperatures agree to within 0.5 °. The furnace was made in two sections (A and B in Fig. 1) separately fed in order to counterbalance, when operating on section A, the slight cooling of the assembly occurring when the collector, at room temperature, is introduced

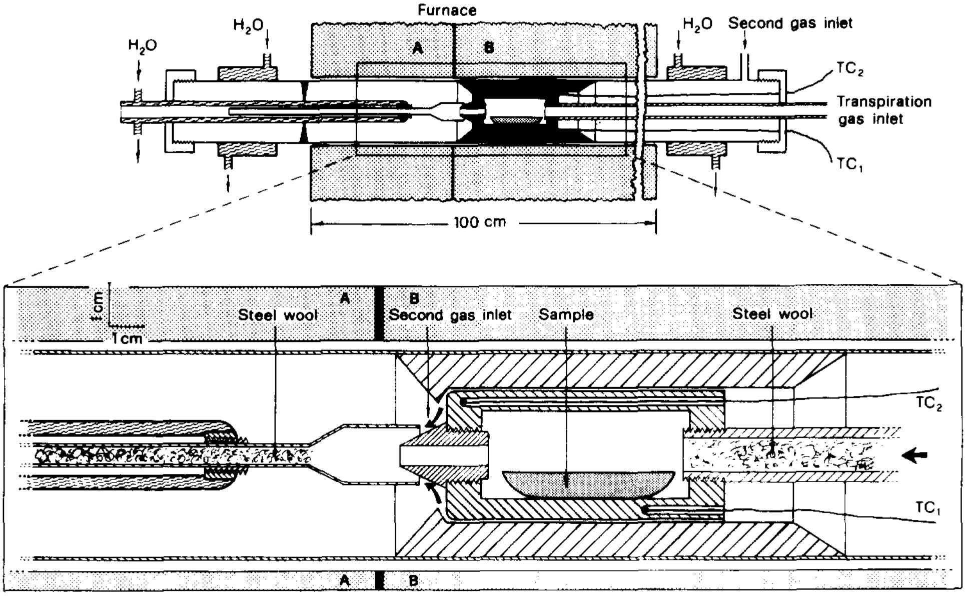

Fig. 1. Transport apparatus.

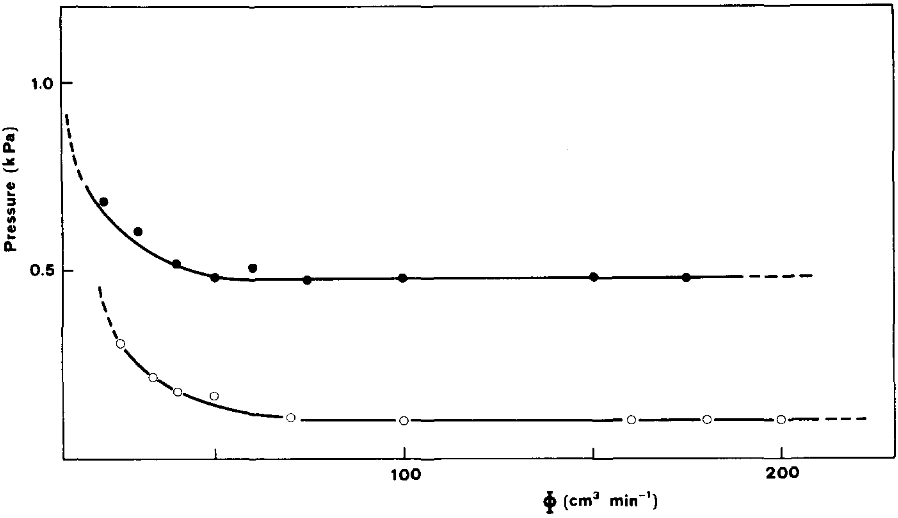

Fig. 2. Dependence of the vapour pressure on helium flow rate: ●, cadmium (at 705 K); ○, tetracosane (at 465 K).

into the furnace. The flow rate of the carrier gas, very pure helium, was measured by a combined Matheson mass flowmeter and controller that ensured a flow constant within ±0.1 cm^3 min^{-1}. In order to minimize

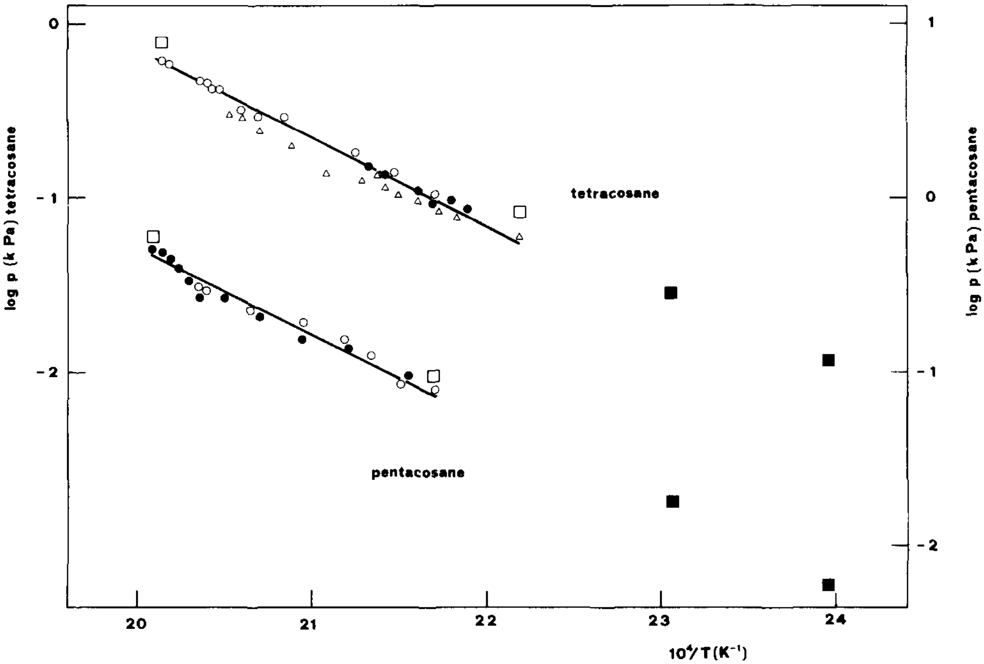

Fig. 3. Vapour pressure of tetracosane: ●, run A; ○, run B; △, run C. Vapour pressure of pentacosane: ●, run A; ○, run B. □, ref. 2; ■, ref. 3.

TABLE 1

Experimental data and vapour pressure values of tetracosane, pentacosane, hexacosane and octacosane

Compound	Run	T ($\pm$0.5) (K)	Φ ($\pm$0.1) (cm^3 min^{-1})	Δt ($\pm$0.1) (min)	m ($\pm$1) (mg)	$-\log p$ (kPa)
Tetracosane	A	457	80	14.0	13	1.07
		459	100	16.0	22	1.00
		461	100	14.0	19	1.01
		463	90	12.0	20	0.97
		467	160	8.0	19	0.87
		469	70	12.0	17	0.82
	B	461	100	7.0	10	0.98
		466	100	9.0	17	0.86
		471	80	10.0	20	0.74
		480	80	13.5	43	0.54
		483	90	12.0	44	0.53
		485.5	70	12.0	37	0.50
		489	70	8.0	33	0.37
		490	70	10.0	42	0.36
		490.5	80	20.0	98	0.35
		491	80	13.0	66	0.34
		495.5	70	4.0	23	0.23
		496.5	70	4.0	24	0.21
	C	451	100	9.5	8	1.21
		458	100	10.0	11	1.10
		460.5	100	12.0	14	1.07
		463	100	17.0	23	1.01
		465.5	100	12.0	17	0.99
		467	100	21.0	34	0.93
		468	90	16.0	28	0.85
		470	90	6.5	10	0.91
		474.5	90	7.5	13	0.85
		479	90	12.0	30	0.70
		483	80	11.0	30	0.61
		485.5	80	11.5	37	0.54
		487	80	9.5	32	0.52
Pentacosane	A	465	90	5.0	6	1.03
		472	90	4.0	7	0.87
		478	90	4.0	8	0.81
		483	80	7.0	17	0.68
		488	70	7.0	19	0.57
		491	70	5.0	13	0.59
		493	70	7.5	25	0.48
		494	70	2.5	10	0.40
		496	70	7.0	33	0.36
		497	70	5.0	24	0.32
		498	70	7.0	35	0.30
	B	461	90	7.0	7	1.11
		465	90	7.0	8	1.05
		469	90	11.0	17	0.92
		472	80	13.0	22	0.83

TABLE 1 (continued)

Compound	Run	T (±0.5) (K)	Φ (±0.1) (cm^3 min^{-1})	Δt (±0.1) (min)	m (±1) (mg)	−log p (kPa)
Pentacosane (continued)	B	478	70	11.0	21	0.72
		484.5	70	7.0	17	0.62
		490.5	80	10.0	33	0.54
		492	70	37.0	113	0.52
Hexacosane	A	461	90	10.5	9	1.19
		467.5	90	13.0	13	1.13
		470.5	90	14.0	17	1.04
		471	80	32.0	38	1.00
		471.5	80	13.0	15	1.01
		473	70	7.0	8	0.96
		476	70	9.0	12	0.89
		479	70	7.0	11	0.82
		482	70	6.5	11	0.79
		485	70	8.0	17	0.60
		488	70	8.0	22	0.58
	B	475.5	90	6.0	8	1.00
		482.5	80	6.5	10	0.89
		489	70	8.0	14	0.78
		494	70	10.0	28	0.57
		498	70	8.5	26	0.53
		500.5	70	7.0	24	0.48
		502.5	70	10.0	43	0.39
		508	70	8.0	38	0.34
	C	455.5	90	8.0	4	1.43
		462	90	9.5	7	1.26
		466.5	90	9.5	9	1.15
		470	90	10.0	12	1.05
		473	90	15.0	21	0.98
		475.5	90	12.0	20	0.91
		477	80	16.0	25	0.88
		478	80	6.0	8	0.95
		480	80	7.5	12	0.87
		484	80	6.5	14	0.74
		488.5	80	7.0	19	0.64
		492	70	8.0	22	0.58
		495	70	9.5	31	0.51
		496.5	70	10.0	36	0.46
		516.5	70	3.0	23	0.14
		519	70	5.5	47	0.09
Octacosane	A	473	100	24.0	15	1.41
		473	100	9.0	6	1.38
		477	130	21.0	25	1.24
		479	150	10.5	17	1.17
		496	100	22.0	46	0.87
		506	80	13.0	39	0.63
		508.5	80	9.0	31	0.57
		513	90	15.0	83	0.42
		514	70	21.0	87	0.44

TABLE 1 (continued)

Compound	Run	T (±0.5) (K)	Φ (±0.1) (cm^3 min^{-1})	Δt (±0.1) (min)	m (±1) (mg)	−log p (kPa)
	B	474	90	6.0	4	1.34
		481	90	11.0	11	1.16
		491	90	14.5	21	1.00
		496	80	17.0	32	0.83
		500	80	17.0	40	0.74
		502.5	80	17.0	43	0.71
		505	70	7.0	19	0.62
		510	70	8.0	24	0.57
		512.5	70	5.0	16	0.55
		515	70	12.5	53	0.42

vapour loss through the interspace between the tube and the collector, an additional helium flow (see Fig. 1) circulates around the transpiration tube into the same collector. As observed in preliminary experiments using cadmium and tetracosane (see Fig. 2), errors in the apparatus due to vapour diffusion are negligible in a reasonable flow rate range, with the lower limit

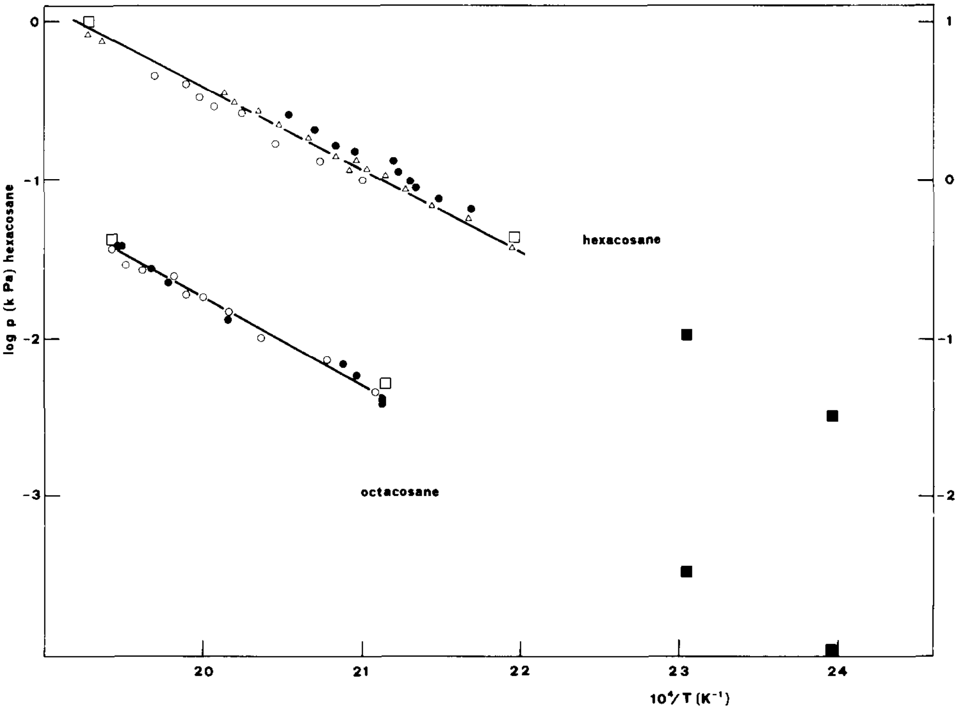

Fig. 4. Vapour pressure of hexacosane: ●, run A; ○, run B; △, run C. Vapour pressure of octacosane: ●, run A; ○, run B. □, ref. 2; ■, ref. 3.

TABLE 2

Experimental temperature–vapour pressure equations of tetracosane, pentacosane, hexacosane and octacosane

Compound	Run	ΔT (K)	No. of points	$\log p$ (kPa) $= A - B/T$	
				A	B
Tetracosane	A	457 –469	6	8.17 ± 0.98 [a]	4221 ± 453
	B	461 –496	12	9.53 ± 0.27	4843 ± 132
	C	451 –487	13	8.31 ± 0.45	4314 ± 211
Pentacosane	A	465 –498	11	9.71 ± 0.67	5008 ± 324
	B	461 –492	8	8.41 ± 0.48	4383 ± 231
Hexacosane	A	461 –488	11	10.40 ± 0.42	5355 ± 198
	B	475.5–508	8	10.09 ± 0.64	5289 ± 315
	C	455.5–519	16	9.53 ± 0.21	4979 ± 103
Octacosane	A	473 –514	9	10.29 ± 0.37	5516 ± 180
	B	474 –515	10	9.77 ± 0.38	5267 ± 189

[a] The quoted errors are the standard deviations.

set at about 70 $\text{cm}^3\ \text{min}^{-1}$. Nevertheless, some high pressure values were determined at this limit in order to avoid condensation of too much vapour in the cool collector which would cause obstruction during the measurement. The amount of vapour condensed in the collector was determined from its weight gain, particular care being taken to ensure dry conditions during the manipulation and weighing operation. The assembly was tested with pure cadmium and the results obtained (vapour pressure values and second- and third-law standard sublimation enthalpies) were in good agreement with those selected by Hultgren et al. [5].

The vapour pressures of the *n*-alkanes are reported in Table 1 and in Figs. 3 and 4. The small experimental temperature ranges do not permit reliable Antoine's elaboration of our data so that for each run the linear equation for $\log p$ vs. $1/T$ was calculated and reported in Table 2, the results being treated by the least-squares method. From these equations, the following final expressions were obtained by selecting weighted slopes and intercepts proportional to the number of the points:

$$\text{Tetracosane, } \log p(\text{kPa}) = (8.76 \pm 0.50) - (4\,501 \pm 250)/T \tag{2}$$

$$\text{Pentacosane, } \log p(\text{kPa}) = (9.16 \pm 0.60) - (4\,745 \pm 300)/T \tag{3}$$

$$\text{Hexacosane, } \log p(\text{kPa}) = (9.93 \pm 0.50) - (5\,168 \pm 200)/T \tag{4}$$

$$\text{Octacosane, } \log p(\text{kPa}) = (10.02 \pm 0.40) - (5\,385 \pm 150)/T \tag{5}$$

where the errors are estimated. These equations are plotted in Figs. 2 and 3 with the values at the extremes of our temperature range calculated using the selected Antoine's equation [2] and those of Grenier-Loustalot et al. [3].

TABLE 3

Thermodynamic parameters associated with the vaporization of the *n*-alkanes studied

Compound	T_{average} (K)	$\Delta H_T^{\ominus}$ (kJ mol^{-1})	$\Delta S_T^{\ominus}$ (J K^{-1} mol^{-1})	$S_T^{\ominus}$ (J K^{-1} mol^{-1})	
				Liquid [a]	Gas
Tetracosane	474	86 ± 5	129 ± 10	–	–
Pentacosane	480	91 ± 6	137 ± 11	1320	1457
Hexacosane	488	99 ± 4	152 ± 10	1370	1522
Octacosane	495	103 ± 3	153 ± 8	–	–

[a] Calculated from thermodynamic data reported by Domalski et al. [6].

CONCLUSIONS

The second-law vaporization enthalpies and entropies from the middle of the experimental temperature range of tetracosane, pentacosane, hexacosane and octacosane were derived from the slopes and intercepts of our selected equations (eqns. (2)–(5)) and are reported in Table 3. Both values show a trend with the molecular weight. In particular, the results show that for each $-CH_2-$ group, there is an increase in the vaporization enthalpies of about 5 kJ mol^{-1} for the compounds studied, while the large uncertainties associated with the entropic changes lead to the conclusion that these thermodynamic parameters have a range of values centred around 140 ± 10 J K^{-1} mol^{-1}.

Using the standard entropies, heats of transition and heat capacities of liquid pentacosane and hexacosane reported by Domalski et al. [6], the entropies of these compounds in liquid and gaseous phases in the middle of the temperature range were derived and are also reported in Table 3.

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