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A Gas Saturation Apparatus for Very Low Vapor or Sublimation Pressure Measurements (10^{-3} Pa): Vapor−Liquid Equilibria of *n*-Alkanes (*n*-C_{10}, *n*-C_{24}, *n*-C_{28})

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An apparatus for very low vapor or sublimation pressure measurements (10^{-3} Pa) was designed and built. The principle of the apparatus is based on the saturation by the sample and by a standard compound of an inert gas flowing through a saturator and into a cold GC column used as a trap. This stage is followed by a chromatographic analysis consisting of increasing the temperature of the column. The originality of the present apparatus lies on the use of a supplementary line containing the standard compound. The study of the two substances is carried out simultaneously. This relative method allows reliable measurements of vapor or sublimation pressures. The apparatus was tested by the study of several alkanes. The experimental pressures are in a good agreement with the available literature data.

Introduction

Vapor and sublimation pressures are fundamental data required in several applications, such as in the design of several processes and products in various industries and particularly in petroleum industries where low vapor pressure measurements are essential for the characterization of high petroleum fractions and for the development of thermodynamic models. At the present time, there is enhanced interest in low-pressure measurements ($10^{-4} < P/\mathrm{Pa} < 1$) for characterizing low volatility substances such as pharmaceuticals, agro chemical products, or potentially harmful chemicals. In this work, we respond to the new European law, CE n^{o}1907/2006, called REACH (registration, evaluation, authorization, and restriction of chemicals) concerning chemical substances.

Our laboratory has a long tradition in vapor or sublimation pressure measurements. We have studied various compounds with different chemical structures (alkanes,[1−3] aromatic compounds,[4−6] alcohols,[7] alkanones,[8] esters,[9] sulfides...[10]) in the pressure range between 0.1 Pa and 200 kPa using a static apparatus.

With our static apparatus, we arrived at the limit of measurement of high molecular weight compounds (*n*-C_{30}).[11] For this reason, we have designed and built a new apparatus based on the gas saturation method. The apparatus was tested by determining vapor pressures of three alkanes. The results are in good agreement with those obtained with the static apparatus and with the available literature data.

Experimental Methods for Low Vapor Pressure Measurements

Many methods exist in the literature for low vapor pressure measurements. We retain three techniques widely applied to the study of organic compounds: the static method, the gas saturation method, and the effusion method.

Static Method. The static method consists of direct measurements of pressure. The sample (liquid or solid) is introduced in a cell maintained at the equilibrium temperature. The air is then evacuated, and the pressure is measured by a pressure gauge (Baratron type). This technique provides high precision data in the medium and the low-pressure range (0.1 Pa to 200 kPa),[1−12] but it is not suited for very low vapor pressures for different reasons: there is no commercial Baratron gauge supporting temperatures above 200 °C and capable of measuring pressures below 10^{-2} Pa, because of wall adsorption phenomena or thermal transpiration.

Effusion Method. The effusion method is well adapted for the low-pressure range, down to 10^{-5} Pa. It is based on the determination of the effusion rate of the vapor phase through a small orifice and requires the knowledge of the orifice area. The method with different versions has been used by many authors to measure vapor pressures of different substances.[13−15] This technique presents many difficulties, and the main problem is the uncertainty of the effusion rate determination which leads to a poor precision of the measurements.

Gas Saturation Method. The gas saturation method (known also as the transpiration, transport, or flow method) is a very old method used for the first time by Regnault[16] in 1845. For a long period, the method fell into oblivion due to the poor performance of analytical techniques of that time. This method is recommended for pressures below 200 Pa.[16−20] The sample is introduced into a cell. When the equilibrium temperature is reached, the vapor is swept along by an inert gas and trapped by different methods (liquid nitrogen, chromatographic column...). Different kinds of methods are used to determine the concentration of the trapped sample. The sensitivity and the limit of the pressure measurements depend on the technique used. Among the used methods, we can mention: gravimetric determination of the trapped substance,[21] spectrometric analysis of the trapped compound,[22] infrared analysis of CO_2 produced by the combustion of the saturated gas,[20,23,24] and chromatographic analysis of the collected compound.[18,19,25,26]

The last analysis method is commonly used in a continuous way: the sample is trapped by a cold analytical column and then eluted by increasing the chromatographic oven temperature.

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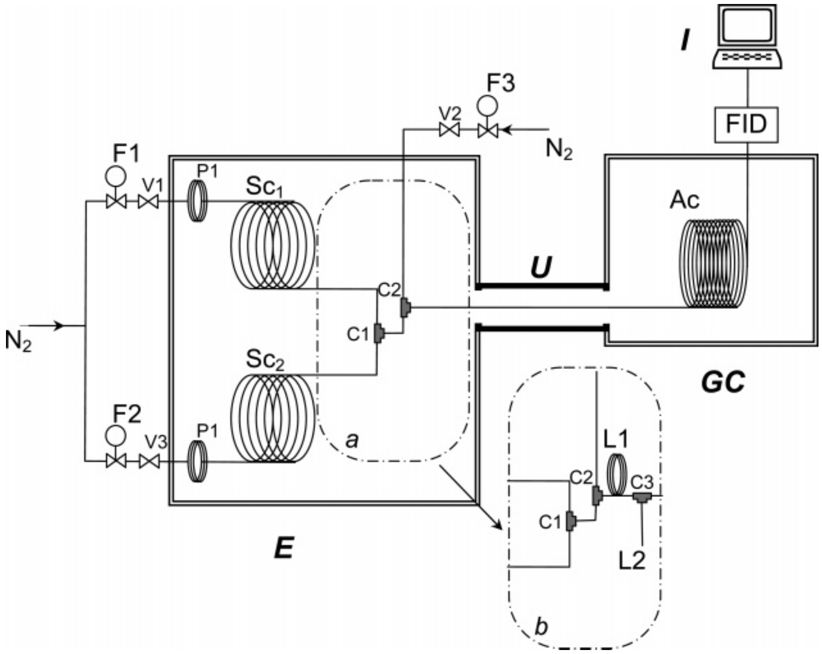

Figure 1. Saturation apparatus: (a) splitless; (b) with split. Ac, analytical capillary column (i.d. 0.53 mm); C1, C2, C3, stainless steel Swagelok connectors; F1, F2, mass flow meters from Bronkhorst (uncertainty of ± 0.01), (0 to 10) $\text{mL}\cdot\text{min}^{-1}$; F3, mass flow meters from Bronkhorst (flow range between (0 and 500) $\text{mL}\cdot\text{min}^{-1}$ or between (0 and 7.5) $\text{mL}\cdot\text{min}^{-1}$ depending, respectively, on if the apparatus is used with the split or splitless); E, equilibrium oven ($30 \leq t\ °\text{C} \leq 300$); I, Chemstation software from Agilent; P1, P2, stainless steel tubing ($L = 3$ m, i.d. $= 0.50$ mm) for saturation gas preheating; Sc1, Sc2, saturation columns (stainless steel tubing with $L = 2$ m, i.d. $= 2.1$ mm) containing, respectively, "Gas Chrom P" support (particle diameter of (147 to 175) μm) impregnated with, respectively, 30 % of the standard and the studied compound; L1, mixing loop constituted of fused silica prior to the split ($L = 2$ m, i.d. $= 0.53$ mm); L2, split tubing made of fused silica (7 cm $\leq L \leq$ 80 cm; i.d. $= 0.53$ mm); U, heated transfer line (to avoid condensation); Vi, electrovalves controlling gas flow.

This "on-line" chromatographic method is the most interesting as it reduces the number of manipulations; however, the method is limited by the accuracy of the calibration procedures. The different calibration methods used in the literature are exponential dilution,[27,28] direct injection,[19,29] and diffusion cell procedures.[27,30]

All these calibrations can cause serious errors due essentially to wall adsorption. Hales et al.[19] described the difficulties encountered in the direct injection of low concentrated samples such as poor reproducibility of peak areas.

Carruth et al.[18] used a steady-state flow method to calibrate the GC. The sample is metered at a known flow rate into a flowing helium carrier gas stream using a micropump (designed and built by the authors), delivering a small flow rate from (0.36 to $8 \cdot 10^{-8}$) $\text{cm}^3 \cdot \text{min}^{-1}$. The sample of known concentrations passes to the detection unit for calibration. The authors carried out measurements only at subambient and close to ambient conditions.

Our method consists of a simultaneous study of a standard compound and the sample: two streams of inert gas saturated with each of the compounds pass through a cold analytical column used as a trap. The elution of the compounds, by increasing the temperature of the analytical column, leads to two chromatographic peaks which permit the determination of the vapor (or sublimation) pressure of the sample. In this way, each vapor pressure determination includes its own calibration. Therefore, it is essential to determine the relative response factor of the FID (sample/standard) which is carried out separately.

Experimental Section

Apparatus. The realized apparatus (Figure 1) is based on the saturation of an inert gas by the studied compound and by a standard, followed by a chromatographic analysis. The vapor pressure of the sample is determined relative to the standard compound submitted to the same measurement conditions as the sample. The two compounds are studied simultaneously. This point constitutes the originality of our apparatus.

The experimental apparatus (Figure 1) is made of two compartments: the sampling part consists of an oven containing two stainless steel columns filled with a porous support, commonly used to prepare GC packed columns and, respectively, impregnated with the sample and the standard compound. These saturators were connected to the gas chromatograph through the GC column. The analysis device was an HP6890 gas chromatograph with an FID detector. On opening valves 1 and 3 (V_2 closed), the inert gas N_2 flowed through the two saturators maintained at the equilibrium temperature to the cold capillary column (type BPX1, length 10 m, diameter 0.53 mm, thickness of the film 2.65 μm). The analytical capillary column was directly connected to C2 or C3 stainless steel connectors (respectively, Figure 1a and Figure 1b). The stationary phase of the capillary column had been previously removed on 20 cm length by alkaline hydrolysis to limit adsorption phenomena in the overheated tubing. In the present case, the capillary GC column was at ambient temperature because this temperature was low enough to trap the compounds, as they had a low volatility. Once the trapped substance was sufficient for analytical measurement, valves V_1 and V_3 were closed and V_2 was opened (carrier gas valve). Simultaneously, the temperature program of the oven was started to heat the GC analysis column and to elute the compounds which were detected by the FID. The nitrogen flow (used for sampling and as a carrier gas) was measured precisely by three computer-controlled mass flow meters from Bronkhorst (uncertainty of ± 0.01). The apparatus is totally automatic as the different valves are controlled by the analogical output of the GC.

The equilibrium temperature in the oven was measured by a copper-constant thermocouple calibrated against a 25 Ω platinum resistance standard thermometer (± 0.001 K, ITS-90) and a Leeds & Northrup bridge (± 10^{-4} Ω). The estimation of the uncertainty is 0.05 K for the temperature range 200 K $< T <$ 420 K and 0.1 K for $T >$ 420 K.

The connection between the analytical column and the saturators remains an important point. For pressures below 150 Pa, the analytical column was directly connected to the C2 connector (Figure 1a) using a graphite rod. For pressures above 150 Pa, it was necessary to limit the trapped quantity to avoid the saturation of the FID. In this case, a split was fitted out between the saturators and the analytical column (Figure 1b). The L1 tubing enables the homogenizing of the vapor prior to the split. The length of the L2 tubing was adjusted according to the split flow necessary to apply.

In both cases (split or splitless), the connection between the saturation oven and the GC was overheated (20 °C above the temperature of the saturation oven).

Impregnation of the Support. The impregnation of the support by the compound was done by batch: 0.5 g of the compound was dissolved in an organic solvent (toluene or dichloromethane); the chromatographic support ("Gas Chrom P" (147 to 175) μm) was added to the solution to have a ratio "compound mass/support mass" equal to 30 %; the flask containing the mixture was subjected to the action of an oscillating stirrer for 24 h before totally evaporating the solvent using a rotational evaporator; and the dry support impregnated with the compound was finally introduced into the saturation column.

The purity of the studied alkanes was 99 %. They were used without further purification.

Saturation Gas Flow Rate and Purge Time. The nitrogen flow (used for sampling and as a carrier gas) was measured precisely by a computer-controlled mass flow meter from Bronkhorst. We studied the effect of the gas saturation flow on the chromatographic peak area ratio (sample peak area/standard peak area). We found that it had no consequence (the ratio was constant with temperature) if the gas flow was between (2 and 8) mL·min^{-1} and if sufficient time was allowed for adsorption equilibrium to be reached in the case of a saturation column of 3.2 mm internal diameter and 2 m length. So the flows were comprised between (2 and 8) mL·min^{-1}, according to the volatility of the compounds. The same collection time was applied for the two compounds. It varied between 30 min and 10 h (10 h for very low vapor pressure measurements, 10^{-4} Pa).

Vapor Pressure Determination. The vapor pressures were calculated using the following equation:

$$\frac{P_1}{P_2} = k\frac{A_1}{A_2}\frac{M_2}{M_1}\frac{F_2}{F_1}\exp\left[\frac{(V_{L_2} - V_{L_1})P_{N_2}}{RT}\right] \qquad (1)$$

where subscripts $i = 1$ and $i = 2$ refer, respectively, to the standard and the sample; P_i is the vapor pressure; A_i is the chromatographic peak area; M_i is the molar mass; F_i is the saturation gas flow rate; P_{N_2} is the inert gas pressure; V_{L_i} is the partial molar volume of the liquid for compound i; T is the equilibrium temperature; R is the ideal gas constant; and k is the relative response factor of the FID.

Equation 1 supposes an ideal behavior of the vapor phase and no solubility of the saturation gas in the liquid phases (sample or reference). The exponential term of eq 1, called the Poynting correction, is a correction factor due to the compression of the liquid. Indeed the equilibrium pressure of a compound in the presence of the saturation gas (N_2) is different from the vapor pressure of the pure liquid compound at the same temperature. At low inert gas pressures, the Poynting factor could be neglected. For example, the exponential factor, for n-C20 with n-C18 taken as a standard compound at 373.15 K and $P_{N_2} = 2$ bar, is 1.002.

Table 1. Mean Relative Response Factor *k* of the GC for Even *n*-Alkanes between *n*-C8 and *n*-C40 Contained in a Standard DRH-004S-5X[a,b,c]

no. of carbons	$k \pm \sigma$ [c]
8	0.71 ± 0.02
10	0.98 ± 0.03
12	0.993 ± 0.002
14	1.014 ± 0.001
16	1.011 ± 0.002
18	1
20	1.0077 ± 0.0004
22	1.007 ± 0.001
24	1.006 ± 0.001
26	1.011 ± 0.001
28	1.000 ± 0.001
30	1.011 ± 0.002
32	1.013 ± 0.002
34	1.006 ± 0.003
36	1.017 ± 0.002
38	0.965 ± 0.003
40	0.978 ± 0.003

[a] From AccuStandard Inc. [b] n-C18 is the reference compound. [c] Standard deviation σ is calculated from four analyses. [c] Analytical conditions: GC (type HP 6890 A) equipped with an on-column injector; analytical column, BPX1, length 10 m, i.d. 0.53 mm, thickness of the film 2.65 μm; carrier gas flow N2, 0.8 mL·min^{-1}; FID temperature, 450 °C; on-column injection, 50 °C to 430 °C, rate 10 °C·min^{-1}.

For this reason, the final equation is then

$$\frac{P_1}{P_2} = k\frac{A_1}{A_2}\frac{M_2}{M_1}\frac{F_2}{F_1} \qquad (2)$$

Determination of the Response Factor k. The response factor k, determined by internal calibration of the GC equipped with an "on-column" injector to avoid discrimination between compounds with different volatilities, was calculated using eq 3

$$k = \frac{m_1/A_1}{m_2/A_2} \qquad (3)$$

where m_1 and A_1 are, respectively, the mass and the chromatographic peak area of the standard; and m_2 and A_2 are, respectively, the mass and the chromatographic peak area of the sample.

The vapor pressure of the standard compound (from the literature or from our static apparatus) and the relative response factor k are sufficient parameters to determine the vapor pressure of the sample.

Results and Discussion

To test the operation of the apparatus, several n-alkanes were studied.

Relative Response Factor k of the GC. It is well-known that the relative response factor k of n-alkanes analyzed by a flame ionization detector is equal to unity. Nevertheless, we have determined k by studying a standard mixture of even n-alkanes (DRH-004S-5X, from AccuStandard Inc.) between n-C8 and n-C40 with a GC (type HP 6890 A) equipped with an on-column injector. As shown in Table 1, n-C18 was chosen as the reference compound. The analytical conditions are as follows: analytical column, BPX1, length 10 m, i.d. 0.53 mm, thickness of the film 2.65 μm; carrier gas flow N2, 0.8 mL·min^{-1}; FID temperature, 450 °C; on-column injection, 50 °C to 430 °C, rate 10 °C·min^{-1}. Except for n-C8, k is equal to unity.

Table 2. Vapor Pressures of *n*-Dodecane (n-$C_{12}H_{26}$) from Viton et al.[2]: Comparison with Literature Data (RD = $(P_{exptl} - P_{lit})/P_{lit}$)

T/K	P/Pa[a]	RD[b]	RD[c]	RD[d]
323.48	123		0.0079	0.014
343.65	433		−0.0052	0.0032
363.78	1277	−0.010	−0.011	−0.0075
382.05	3054	−0.0034	0.0026	−0.0017
402.09	7024	−0.0026		−0.0047

[a] From ref 2. [b] Comparison with ref 12. [c] Comparison with ref 26. [d] Comparison with ref 31.

Table 3. Experimental Vapor Pressure of *n*-Decane (n-$C_{10}H_{22}$) Obtained by the Saturation Apparatus: Comparison with Literature Data (RD = $(P_{exptl} - P_{lit})/P_{lit}$)

T/K	P/Pa	RD[a]	RD[b]	RD[c]	RD[d]	RD[e]
323.94	955,6	0.036	0.043	0.044	0.038	0.038
353.57	4252,2	0.0044	0.025		0.023	
373.15	10050	0.0091	0.051		0.050	
402.36	29482	−0.016	0.069		0.068	
402.48	29357	−0.024	0.060		0.060	

[a] Comparison with ref 2. [b] Comparison with ref 12. [c] Comparison with ref 26. [d] Comparison with ref 31. [e] Comparison with ref 32.

Repeatability of the Measurements and Uncertainty on the Vapor Pressures. The repeatability of the measurements in the entire investigated range (10^{-3} Pa to 400 Pa) was determined (Table 6). The repeatability of the area ratio was satisfactory as the relative standard deviation (RSD) on this parameter was comprised between 0.3 % and 4 %. On the other hand, the repeatability was the same for all the pressure ranges explored: the average RSD was about 1.5 %. It is then reasonable to admit that the relative uncertainty of the area ratio is 3 %. As shown in Table 1, for alkanes above *n*-C8, the average RSD of the response factor of the FID is 0.3 %. Thus, by taking into account the uncertainty on the flow rate of the saturation gas (uncertainty 1 %), we deduce from eq 1 that the relative uncertainty on the pressure ratio was about 3.5 %. If the standard compound was known with a good accuracy (suppose 0.5 %), the relative uncertainty on the vapor pressure of the sample is about 4 %. The estimated relative uncertainty is in a good accord with the results obtained with *n*-C10, *n*-C24, and *n*-C28 presented later on.

Vapor Pressure of n-C10. n-C_{10} was studied using n-C_{12} as a standard compound. The reference values of n-C_{12}, measured in our laboratory by the static method,[2] are in good agreement with those of Morgan et al.,[12] with Allemand et al.,[26] and with the recommended vapor pressures from Ruzicka and Mayer[31] (Table 2).

The experimental results of *n*-C10 obtained in the present study along with the comparison with literature data are presented in Table 3. Our experimental data are slightly higher than the literature values, P_{lit}, as shown by the mean relative deviation $\Delta P/P$ calculated as follows

$$\Delta P/P = \frac{1}{n}\sum_{1}^{n}\frac{|P_{exptl} - P_{lit}|}{P_{lit}} \qquad (4)$$

The mean relative deviation is equal to 0.018 from Viton et al.;[2] $\Delta P/P = 0.050$ from Morgan et al.;[12] and $\Delta P/P = 0.048$ from Ruzicka and Majer.[31] We found only one point of comparison with Chirico et al.[32] (relative deviation 0.038) and with Allemand et al.[26] (relative deviation 0.044).

Table 4. Vapor Pressures of Eicosane (n-$C_{20}H_{42}$) from Viton et al.[2]: Comparison with Literature Data (RD = $(P_{exptl} - P_{lit})/P_{lit}$)

T/K	P/Pa[a]	RD[b]	RD[c]	RD[d]
341.85	0.349	0.039		
361.65	2.030	0.0009		
381.75	9.750	−0.0093		−0.0016
402.25	39.520	−0.011	0.011	0.050
422.35	134.90	0.013	0.0060	0.099

[a] From ref 2. [b] Comparison with ref 31. [c] Comparison with ref 32. [d] Comparison with ref 34.

Table 5. Experimental Vapor Pressures of Tetracosane (n-$C_{24}H_{50}$) Obtained by the Static Method and by the Saturation Method: Comparison with Literature Data (RD = $(P_{exptl} - P_{lit})/P_{lit}$)

	saturation method	static method				
T/K	P/Pa	P/Pa	RD[a]	RD[b]	RD[c]	RD[d]
333.46	0.0043	–		0.13		
353.43	0.0435	–		0.14		
353.97	0.0450	–		0.11		
373.17	0.307	0.296	0.037	0.11		
373.61	0.316	0.322	−0.019	0.097		
379.15	0.524	0.531	−0.013	0.098		
393.20	1.725	1.727	−0.0011	0.092		
393.20	1.721	1.727	−0.0035	0.091		
397.55	2.406	2.432	−0.011	0.075		
414.68	8.430	8.547	−0.014	0.051		
417.75	10.50	10.55	−0.0047	0.056		0.15
433.10	–	28.57	–	0.047		0.096
452.60	–	89.31	–	0.035	0.017	0.047

[a] Comparison with the static apparatus. [b] Comparison with ref 33. [c] Comparison with ref 12. [d] Comparison with ref 34.

Table 6. Row Data of Octacosane (n-$C_{28}H_{58}$) with the Relative Standard Deviation, RSD

			average ratio			
T/K	no. of exptl points	$F_{C_{28}}/F_{C_{24}}$[b]	$A_{C_{28}}/A_{C_{24}}$[c]	100 RSD	$P_{C_{24}}$/Pa	$P_{C_{28}}$/Pa
354.01	4	2	0.1023	2.62	0.0489	0.00214
373.92	3	2	0.1212	2.41	0.342	0.0177
373.92	2	2	0.1232	4.02	0.342	0.01.80
393.65	3	2	0.1547	0.65	1.85	0.122
393.65	4	2	0.1590	1.16	1.85	0.126
413.50	2	1.25	0.1132	1.23	8.19	0.633
413.50	2	1.25	0.1163	0.92	8.19	0.651
413.50	6	1.25	0.1128	1.86	8.19	0.630
433.32	3	1	0.1148	0.28	29.88	2.93
453.28	4	1	0.1499	0.68	99.03	12.642
473.64	2	1	0.1770	1.15	288.09	44.04
494.80	3	1	0.2395	1.47	762.83	155.39
516.89	4	1	0.2627	1.49	1916.79	427.17

[a] Reference compound is n-$C_{24}H_{50}$. [b] $F_{C_{24}}$ and $F_{C_{28}}$ are, respectively, the saturation gas flow rate. [c] $A_{C_{24}}$ and $A_{C_{28}}$ are, respectively, the chromatographic peak area of n-C_{24} and n-C_{28}.

Vapor Pressure of n-C₂₄. The standard compound for n-C_{24} vapor pressure determinations is n-C_{20}. The reference values of n-C_{20}, measured by the static method, are from Viton et al.[2] (Table 4). The data of this author are in good agreement with those of Chirico et al.,[32] with the recommended values of Ruzika and Mayer[31] (mean relative deviation of about 0.014), and with the vapor pressures from TRC Thermodynamics Tables[34] (mean relative deviation of 0.050).

In Table 5, we present the experimental vapor pressures of n-C_{24} obtained by the saturation apparatus and by our static apparatus described in previous papers.[1−11] The two sets of results are original and are in a good accord (mean relative deviation is 0.012). Our data are in disagreement with Chickos and Hanshaw[33] values for pressures below 1 Pa (mean relative deviation 0.11); for pressures above 2 Pa, our values become closer to those of Chickos and Hanshaw[33] (mean relative

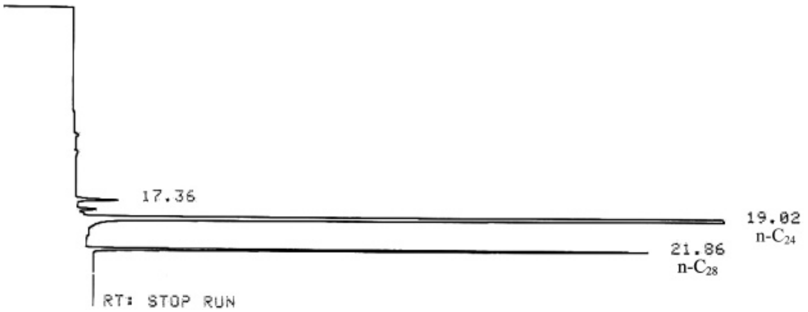

Figure 2. Chromatogram obtained at 354.01 K when studying n-C_{28}. n-C_{24} is the reference compound.

Table 7. Experimental Vapor Pressures of Octacosane (n-$C_{28}H_{58}$) Obtained with the Saturation Apparatus: Comparison with Literature Data (RD = ($P_{exptl} - P_{lit}$)/P_{lit})

	saturation method				
T/K	P/Pa	RD[a]	RD[b]	RD[c]	RD[d]
354.01	0.00214			0.17	
373.92	0.0177			−0.026	
373.92	0.0180			−0.098	
393.65	0.122			−0.077	
393.65	0.126			−0.052	
413.50	0.633			−0.17	
413.50	0.651			−0.14	
413.50	0.630			−0.17	
433.32	2.93			−0.16	
453.28	12.642		−0.11	−0.075	−0.047
473.64	44.04		−0.076	−0.057	−0.065
494.80	155.39	−0.034	0.063	0.074	0.043
516.89	427.17	−0.049	0.033	0.039	0.00

[a] Comparison with ref 12. [b] Comparison with ref 32. [c] Comparison with ref 33. [d] Comparison with ref 34.

deviation 0.053). Our experimental vapor pressures are in quite good agreement with those of TRC Thermodynamics Tables[34] (mean relative deviation 0.098). At 452.60 K, the vapor pressure of n-C24 obtained with the static apparatus is in good agreement with the Morgan et al.[12] single common value (relative deviation 0.017).

Vapor Pressures of n-C_{28}. To determine the vapor pressures of n-C_{28}, we used n-C_{24} as the standard compound. The reference data of n-C_{24} are those obtained with the saturation apparatus. In Table 6, we report the row data obtained when studying n-C_{28}: number of experimental points, relative flow rate of the saturation gas, the relative chromatographic peak areas, and the corresponding vapor pressures of n-C_{28} at different temperatures. An example of a chromatogram obtained at low pressure (T = 354.01 K and $P_{C_{28}} = 2.14\ 10^{-3}$ Pa) after 10 h of trapping the compounds in the analytical column is also given in Figure 2. One can observe some minor impurities, of n-C_{24}, due to the high sensibility of the analysis required for low-pressure measurements. As shown in Table 7, the experimental vapor pressures of n-C_{28} are in quite good agreement with Chirico et al.[32] data (mean relative deviation 0.070), with TRC Thermodynamics Tables[34] (mean relative deviation 0.039), and with the two common points of Morgan et al.[12] (relative deviation 0.041). In general, our data are in good agreement with those of Chickos and Hanshaw[33] in the pressure range between (10^{-3} and 430) Pa.

Vapor Pressure Fits to the Antoine Equation

The Antoine equation was fitted to the vapor pressure data of n-C_{10}, n-C_{24}, and n-C_{28} in the form

$$\log P/\text{Pa} = A - \frac{B}{t/°\text{C} + C} \qquad (5)$$

Table 8. Parameters of the Antoine Equation and the Standard Deviation σ

n-alkane	T/K	A (σ)	B (σ)	C (σ)
n-$C_{10}H_{22}$	323.94 to 402.48	9.687 (0.273)	1844.0 (171.0)	224.11 (14.42)
n-$C_{24}H_{50}$	333.46 to 452.60	10.528 (0.071)	3049.4 (40.6)	176.13 (1.90)
n-$C_{28}H_{58}$	354.01 to 516.89	12.814 (0.338)	4805.2 (257.7)	229.34 (10.11)

Parameters derived from the fits along with the standard deviation are given in Table 8.

Conclusion

The new apparatus permits us to measure pressures down to 10^{-3} Pa with an estimated relative uncertainty of about 0.04 (if the vapor pressure of the reference compound is known with good accuracy). The apparatus has several advantages based on the relative method of vapor or sublimation pressure measurements: the calibration and the pressure measurement of the sample are carried out simultaneously which increases the accuracy of the measurements; the adsorption phenomena are minimized and controlled; the method permits us to monitor the purity of the studied compound and its eventual decomposition; it is possible to measure, as well, sublimation pressures; the quantity of the studied compound is relatively small, about 0.3 g; and except the preparation of the saturation columns, the method is totally automatic. With this method, every kind of molecule could be studied at any temperature, and the main parameter to be determined is the relative response factor of the chromatographic detector.

The principal disadvantage of the present saturation method is the need to dispose of a reference compound in the studied temperature range. The reference compound could be used to study several samples. The sole condition is that the ratio of the vapor pressure (sample/reference) should be comprised between 0.01 and 100.

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