

A GLC-method for the Determination of Low Vapour Pressures Applied to 1-Chloroalkanes

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A high-precision gas chromatographic apparatus coupled on line to a computer has been used for the determination of the vapour pressure of 1-chlorotetradecane, 1-chlorohexadecane, and 1-chlorooctadecane in the temperature range 40–120 °C. The chloroalkanes were used as stationary phases and the vapour pressures were calculated from the loss of the stationary phase, when a known volume of carrier gas had passed through the column. Frequent measurements were made of the retention volume for a test solute. The decrease in the volume of the stationary phase was calculated from the decrease of the retention volume for the test solute. Values of the enthalpy of vaporization were calculated from the variation of the vapour pressure with the temperature. These values were in good agreement with those determined from calorimetric measurements.

At carrier gas flow rates normally used in gas-liquid chromatography the carrier gas leaving the column is saturated with the vapour of the stationary phase.¹ The loss of stationary phase as a function of carrier gas volume can be used to calculate the vapour pressure of this phase at the column temperature. According to equations developed earlier¹ the vapour pressure p of the stationary phase is given by eqn. (1), where V_N is the net

$$p = -\frac{dV_N}{dV_{acc}} \times \frac{w_1^B}{V_N^B} \times \frac{RT}{M} \quad (1)$$

retention volume for a solute. V_{acc} is the carrier gas volume that has passed through the column from the start of the experiment. The retention volume at the start V_N^B is the intercept of the regression line for V_N versus V_{acc} . dV_N/dV_{acc} is the

slope of this line, w_1^B is the mass of the stationary phase at the start of the experiment, R is the gas constant, T the column temperature, and M the molecular weight of the stationary phase. Eqn. 1 is valid if contributions of adsorption effects to the retention volume can be neglected. This can easily be achieved by proper selection of solute. Use of silanized support and a high stationary phase loading (e.g. 20% w/w) also minimize adsorption effects.

In this paper the vapour pressures for three chloroalkanes were determined. Chloroalkanes have previously been investigated at the Thermochemistry Laboratory in Lund, where the enthalpies of vaporization for several haloalkanes have been determined from calorimetric measurements.²

EXPERIMENTAL

All measurements were performed using a high-precision gas chromatograph coupled on line with a mini-computer. This system developed by Jönsson and co-workers^{3,4} is described elsewhere.

1-Chlorooctadecane and 1-chlorohexadecane, *puriss.* grade (Fluka AG, Buchs SG, Switzerland) and 1-chlorotetradecane, technical grade (Eastman Kodak Co, Rochester, N.Y. USA) were further purified according to the procedure described in Ref. 2, i.e. adsorption chromatography on a column of silica gel with hexane as eluent and evaporation of the solvent. Three V-shaped columns (700 × 4 mm I.D.) were used, each containing ca 3 g of packing loaded with about 20% w/w of one of the long-chain chloroalkanes as stationary phase. Chromosorb W-AW DMS 80–100 mesh (Johns-Manville, USA) was used as the support. The carrier gas was hydrogen and methane was used for

the determination of the void volume. The carrier gas flow rate was about 50 ml/min in all experiments. This flow rate is low enough to yield complete saturation with the vapour of the stationary phase.¹

The column temperature was kept within ± 0.05 °C by means of an oil thermostatic bath.

It is necessary to keep the temperature of the carrier gas at column inlet and outlet the same as the column temperature. The amount of stationary phase was carefully determined by weighing at the time of the preparation of the column packing. After an experiment at one temperature, the loss of stationary phase was calculated and the remaining weight was used as the start weight (w_1^B) in the next experiment.

RESULTS AND DISCUSSION

For each temperature the net retention volume of the solute, V_N , was plotted *versus* the accumulated carrier gas volume, V_{acc} . Linear relationships were obtained. In Fig. 1 an example of such a plot is shown. Experimental conditions and results are given in Table 1 with the vapour pressures calculated according to eqn. (1).

The main cause of uncertainty in the calculation of p from eqn. (1) arises from the uncertainty in the slope dV_N/dV_{acc} of the regression line. The other contributions to uncertainty are neglected so the

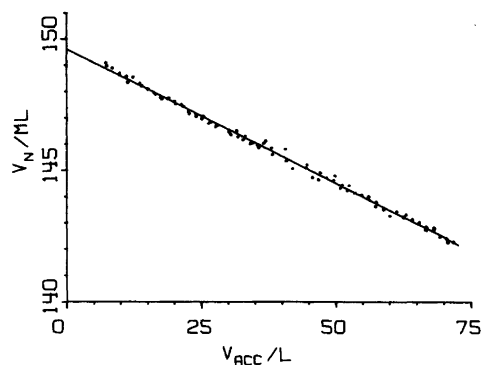


Fig. 1. Net retention volume for 1-chloropentane on a 1-chlorohexadecane column at 80.0 °C *versus* the total accumulated carrier gas volume.

relative uncertainty of p and dV_N/dV_{acc} is the same. The uncertainties for p in Table 1 are given as twice the standard deviation. Boublik, Fried and Hala⁵ have calculated Antoine equations for 1-chlorotetradecane and 1-chlorohexadecane based on measurements by Kemme and Kreps⁶ in the temperature intervals 142–297 and 165–327 °C, respectively. Vapour pressures calculated with these equations are given in Table 1. They show good agreement with our values keeping in mind that extrapolations over about 100 °C are involved.

Table 1. Experimental conditions and results. a=1-chlorobutane, b=1-chloropentane. Uncertainties are given as twice the standard deviation.

Stationary phase	$t/^\circ\text{C}$	Solute	No. of inj.	w_1^B/g	V_{acc}/l	p/Pa^a	p/Pa^b
$\text{C}_{14}\text{H}_{29}\text{Cl}$	40.1	a	100	0.4021	195	0.66(1)	0.55
	60.0	a	130	0.5024	65	4.06(6)	3.72
	80.0	b	43	0.4803	20	19.3(5)	18.6
	100.0	b	42	0.4480	8	74.0(10)	73.2
$\text{C}_{16}\text{H}_{33}\text{Cl}$	40.1	a	113	0.4190	270	0.069(7)	0.062
	60.0	b	88	0.5080	143	0.56(1)	0.55
	80.0	b	97	0.4500	73	3.61(7)	3.45
	100.0	b	61	0.5368	20	16.8(5)	16.4
	120.0	b	58	0.5007	10	63.3(8)	62.1
$\text{C}_{18}\text{H}_{37}\text{Cl}$	60.0	b	129	0.5781	463	0.111(3)	
	80.0	b	129	0.5559	290	0.78(1)	
	100.0	b	51	0.5727	44	4.10(12)	
	120.0	b	56	0.5293	33	17.0(5)	

^aThis work. ^b Calculated with the Antoine equations in Ref. 5.

For each column the different temperatures were run in random sequence as can be seen from the w_1^B values in Table 1. In this way it was possible to minimize systematic errors due to long-term drift and possible error in the w_1^B -calculations. The w_1^B -calculation from one temperature to the other was checked by repeating the measurements at 60 °C on the 1-chlorohexadecane column after using the column at three other temperatures. The partition coefficient K for the distribution of the solute between the liquid and the gas phase was then calculated from $K = V_N^B \delta / w_1^B$ where δ is the density of 1-chlorohexadecane. The K -values at the two measurements were 554.1 and 553.9 and the vapour pressures 0.56 and 0.55 Pa. The value of $\delta = 0.8582 \text{ g/cm}^3$ for 1-chlorohexadecane was obtained from the value at 25 °C (Ref. 7) assuming the same volume expansion with temperatures as for 1-chlorooctadecane in Ref. 8. The validity in the procedure above of obtaining w_1^B has previously been established by combustion experiments of octadecane columns.¹ The influence of impurities on the vapour pressures of the chloroalkanes is different for impurities with considerable higher or lower vapour pressure than the investigated chloroalkane. Those with lower vapour pressure will give only small errors in the vapour pressure since the vapour pressure will be proportional to the mol fraction of the main component according to Raoult's law. Thus the relative error will be approximately the same as the impurity concentration. Impurities with higher vapour pressure will affect the slope of the line of V_N versus V_{acc} only in the beginning of the first experiment on a column. Consequently the experiment should be run long enough for a straight line to be obtained, which may not be the case for a completely new column. However, in the systems described in this work, such effects were not observed.

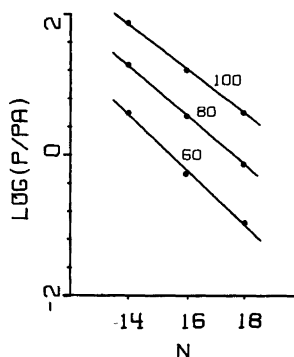


Fig. 2. The logarithm of the vapour pressure for 1-chloroalkanes with N carbon atoms.

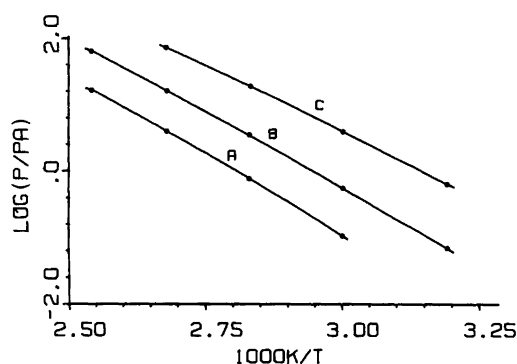


Fig. 3. The logarithm of the vapour pressure for 1-chloroalkanes versus the reciprocal temperature. A = 1-chlorooctadecane; B = 1-chlorohexadecane; C = 1-chlorotetradecane.

Plots of $\log p$ at certain temperatures versus the number of carbon atoms, N , in the chloroalkanes are given in Fig. 2. As expected, these plots are linear. Plots of $\log p$ versus the reciprocal temperature appear as slightly curved lines (Fig. 3).

Table 2. Enthalpies of vaporization, ΔH_{vap} (in kJ mol^{-1}), for 1-chloroalkanes.

$t/^\circ\text{C}$	1-chlorotetradecane	1-chlorohexadecane	1-chlorooctadecane
25	81.8 ^a	91.5 ^a	101.2 ^a
40	80.2	91.2	—
60	78.0	92.7	96.9
80	74.4	87.0	93.4
100	72.9	81.5	88.4
120	—	82.1	86.7

^a From Ref. 2.

The enthalpy of vaporization is calculated according to the Clausius-Clapeyron equation⁹ which can be written:

$$\frac{\Delta H_{\text{vap}}}{R} = - \frac{d \ln p}{d(1/T)} \quad (2)$$

To calculate ΔH_{vap} it is necessary to numerically differentiate the relations represented in Fig. 3. To accomplish this, spline functions (with a knot at every data point)¹⁰ were fitted to the experimental data. The slightly curved lines in Fig. 3 are obtained from these functions. The vaporization enthalpies were then calculated from these functions according to eqn. (2) and are given in Table 2 and Fig. 4.

ΔH_{vap} -values for some chloroalkanes at 25 °C were determined at the Thermochemistry Laboratory.² An empirical equation of ΔH_{vap} at 25 °C as a function of the number of carbon atoms in the chloroalkanes was given. Values calculated by this equation are shown in Table 2 and Fig. 4. Regression lines for ΔH_{vap} versus temperature were calculated from the ΔH_{vap} -values determined by us for 1-chlorotetradecane and 1-chlorooctadecane. For 1-chlorohexadecane no regression line was calculated because of the large scatter of the points (see Fig. 4). The regression lines gave values of ΔH_{vap} at 25 °C in good agreement with those in Ref. 2. Including these literature values new regression lines were calculated. The change of heat capacity ΔC_p is the slope of the respective line. Table 3 contains ΔC_p values for 1-chlorotetradecane and 1-chlorooctadecane together with the

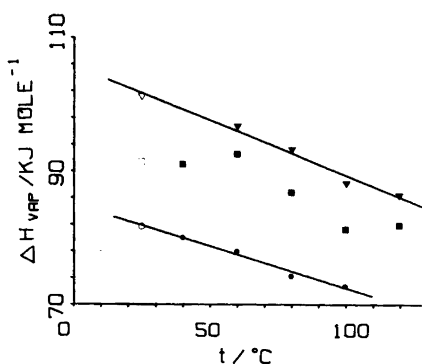


Fig. 4. Heat of vaporization for 1-chloroalkanes versus temperature.

○, ● = 1-chlorotetradecane; □, ■ = 1-chlorohexadecane; △, ▲ = 1-chlorooctadecane; Filled symbols: This work; Unfilled symbols: Ref. 2.

Table 3. ΔC_p values for the vaporization of chloroalkanes and normal alkanes.

Substance	$\Delta C_p/\text{kJ mol}^{-1} \text{K}^{-1}$
1-Chlorotetradecane	0.12
1-Chlorooctadecane	0.16
n-Tetradecane	0.11 ^a
n-Octadecane	0.15 ^a

^a Extrapolated from Ref. 11.

values for the corresponding n-alkanes as a comparison. These were obtained by linear extrapolation from literature data for lower homologs.¹¹

The method developed above is best suited for the determination of vapour pressures in the range 0.1–100 Pa. For higher vapour pressures the fast bleeding of the stationary phase gives rise to disturbances in the detector function, especially when using a flame ionization detector. At very low vapour pressures the long-time stability of the equipment will be a problem. The use of an on-line computer has of course facilitated the measurements but we think that similar experiments can be performed on a commercial chromatograph equipped with a good timer provided the carrier gas flow is well-known at each injection of solute.

Acknowledgements. We thank Dr. Lars Haraldson and Dr. Margret Månsson for valuable discussions concerning this work.

REFERENCES

- Olsson, A. M., Mathiasson, L., Jönsson, J. Å. and Haraldson, L. *J. Chromatogr.* 128 (1976) 35.
- Månsson, M., Sellers, P., Stridh, G. and Sunner, S. *J. Chem. Thermodyn.* 9 (1977) 91.
- Jönsson, J. Å. and Jönsson, R. *J. Chromatogr.* 111 (1975) 265.
- Jönsson, J. Å., Jönsson, R. and Malm, K. *J. Chromatogr.* 115 (1975) 57.
- Boublik, T., Fried, V. and Hala, E. *The Vapour Pressure of Pure Substances*, Elsevier, Amsterdam 1973, p. 555.
- Kemme, H. and Kreps, S. *J. Chem. Eng. Data* 14 (1969) 98.
- Coursey, B. M. and Heric, E. L. *J. Chem. Eng. Data* 14 (1969) 426.
- Mathiasson, L. *J. Chromatogr.* 114 (1975) 39.
- Guggenheim, E. A. *Thermodynamics*, 5th Ed., Nord-Holland, Amsterdam 1967, p. 121.
- Reinsch, C. H. *Num. Math.* 10 (1967) 177.
- Shaw, R. *J. Chem. Eng. Data* 14 (1969) 461.

Received August 22, 1979.