Journal of Chromatography, 547 (1991) 239–245
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 207

Temperature dependence of dead time as determined by methane retention in open-tubular capillary gas chromatography

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(First received September 4th, 1990; revised manuscript received February 13th, 1991)

ABSTRACT

The temperature dependence of the retention time of methane was determined in open-tubular capillary gas chromatography with either nitrogen or hydrogen as the carrier gas. Linear regression according to the equation $t_M = AT^B$ gave smaller standard deviations s for $0.5 < B < 1$ than for $B = 0.5$. However, the equation $t_M = Ae^{B-T}$ may fit almost equally well, the constant B being approximately independent of the column inlet pressure and of the nature of the carrier gas, which facilitates the determination of the theoretically important term $\delta \ln k'/\delta(1/T)$.

INTRODUCTION

Interest has been shown in the use of retention data for qualitative analysis ever since the advent of gas chromatography [1]. Several methods for the determination of the column dead time t_0 are currently in use. The non-coincidence [2] of gas hold-up t_0 and retention time t_M of a "non-interacting" compound such as air [3] or methane [4] has led to the determination of t_0 by a variety of computational methods based on retention data of hydrocarbons, some of which involve a high degree of sophistication [5]. Whereas significant differences between t_M and t_0 were found for packed columns showing methane adsorption [6,7], in gas–liquid chromatography with contemporary open-tubular capillary columns the methane retention time t_M in first order represents a fairly good approximation for t_0, provided that the column temperature is sufficiently high.

The temperature dependence of t_M is of interest in two fields of increasing importance, *viz.*, the determination of thermodynamic parameters of solute–solvent interactions, particularly useful for chiral recognition studies [8–10], and the prediction of retention data under temperature programming [11–14]. Ettre [15] calculated temperature-dependent viscosity data for several carrier gases that were adopted by many workers [11–13,16–19]; however, only a few experimental data on the temperature dependence of t_M have been published [17,18]. This observation prompts us to report on some previous experimental investigations on this subject [20,21].

EXPERIMENTAL

Gas chromatography was performed on a Carlo-Erba Model 2101 gas chromatograph with hydrogen or nitrogen as the carrier gas. The inlet pressure was kept at a set of constant values, as indicated; the splitting ratio was 1:50 and detection was effected with a flame ionization detector. Retention data were measured in triplicate, using a stop-watch. Linear regression calculations were performed according to the method of Deming [22], where each data point is represented by a three-dimensional Gaussian.

Non-deactivated borosilicate glass capillaries were coated with L-Chirasil-Val [23–25], as described [26]. A stainless-steel capillary column was coated with squalane, as described [27].

RESULTS AND DISCUSSION

The capillary column may be compared with an Oswald viscometer; according to the Hagen–Poiseuille law let [28]

$$\eta = C d t_M \tag{1}$$

where η = viscosity of the gas, d = density, C = constant for the given apparatus and t_M = gas hold-up. Neglecting the temperature dependence of C and d, it follows that

$$\frac{\delta t_M}{dT} \propto \frac{\delta \eta}{dT} \tag{2}$$

Hence the effect of the temperature dependence of dead time t_M is reduced to the well known problem of the temperature dependence of the viscosity η. Depending on the gas theory applied, several equations have been established [29]:

$$\eta \propto T^{0.5} \qquad \text{ideal gas theory} \tag{3}$$

$$\eta \propto T^{B} \qquad \text{for real gases} \tag{4}$$

where B varies from *ca.* 0.7 for hydrogen up to 1.0 for less ideal gases, and

$$\eta \propto \frac{T^{0.5}}{1 + C/T} \qquad \text{Sutherland equation} \tag{5}$$

where C is a constant specific for the particular compound, and for $C = 0$ eqn. 5 is reduced to eqn. 3. It is worth mentioning that the temperature dependence of the viscosity played a historical role in establishing a suitable model for gases, *e.g.*, Maxwell erronously predicted an exponent $B = 1.0$ in eqn. 4, assuming that the molecules would repel one another with a force inverse to the fifth power of the distance between them [29]. In contrast, the Sutherland eqn. 5, still in use today [28,30,31], is based on the assumption of a viscous action between successive gas layers.

TABLE I

TEMPERATURE DEPENDENCE OF THE RETENTION TIME OF METHANE ON SQUALANE WITH NITROGEN AS THE CARRIER GAS: COMPARISON OF EXPERIMENTAL AND CALCULATED DATA

Stainless-steel capillary column (100 m x 0.5 mm I.D.), inlet pressure 0.5 bar, splitting ratio 1:50, flame ionization detection; conditions (a) (see Table III).

T(°C)	t_M(s)				
	Experimental, $t_{M_{exp}}$	Calculated			
		t_{M_1}	t_{M_2}	t_{M_3}	t_{M_4}
50	359.3	359.22	359.28	363.42	359.16
60	367.6	367.68	367.68	369.00	367.74
70	376.0	376.02	375.96	374.52	376.08
80	384.2	384.18	384.18	379.92	384.06

In view of this discussion, we decided to determine t_M in a gas chromatographic apparatus at different temperatures. In a first experiment with nitrogen as the carrier gas (see Table I), experimental data $t_{M_{exp}}$ were compared with t_{M_1}, t_{M_2} and t_{M_4} obtained from different regression analyses:

$$t_{M_1} = AT^{0.5} + B \tag{6}$$

$$t_{M_2} = AT^{B} \tag{7}$$

$$t_{M_3} = AT^{0.5} \tag{8}$$

$$t_{M_4} = Ae^{B/T} \tag{9}$$

The one-parameter approximation, eqn. 8, can be ruled out by the fairly poor accordance with the experimental data for $t_{M_{exp}}$ (see Table III). However, all two-parameter approximations examined, eqns. 6, 7 and 9, agree almost equally well with $t_{M_{exp}}$. On the basis of the standard deviations s, 0.06 s for both t_{M_1} and t_{M_2} and 0.15 s for t_{M_4}, a clear distinction between the three different mathematical models is not possible.

The good description of the temperature dependence of the retention time of methane by the exponential approximation, eqn. 9 deserves particular attention. To the best of our knowledge, there is no corresponding equation for the viscosity of gases in literature. However, with respect to the viscosity of liquids, Andrade [32] published eqn. 10, which was later modified by Vogel to give eqn. 11 [33]:

$$\eta \propto e^{B/T} \tag{10}$$

$$\eta \propto e^{B/(T-C)} \tag{11}$$

The underlying model is not too different from that discussed for the viscosity of gases in the way in which a given flux is assumed, and the interaction of one layer of molecules with an adjacent layer of molecules in the liquid is used to derive the viscosity behaviour. The high predictive power of Andrade's eqn. 10 was regarded as "quite astonishing" in view of the imperfections in all the considerations involved [33].

In contrast to this statement, one may argue that an open-minded comparison of the different theoretical approaches may eventually demonstrate the arbitrariness of the multi-parameter regression analyses applied, in view of the limited accuracy of the experimental data. In order to shed some more light on the problem, an extended series of measurements were performed with hydrogen as the carrier gas. For each of four different values of the inlet pressure fourteen data points were taken (see Table II). For $p_i = 0.5$ bar hydrogen, the parabolic approximation t_{M_2}, calculated according to eqn. 7 as published previously [15], was compared with the exponential approximation t_{M_4} as proposed in eqn. 9 (see Fig. 1). No significant advantage of the former approach over the latter can be seen from this plot.

A similar observation is made for the overall set of experimental data, as judged from the standard deviation s. The relative error in the temperature coefficient B is in the range 0.9–2.2% for eqn. 7 and 1.5–2.9% for eqn. 9. However, these deviations are far below the relative errors calculated for the mean values of B, *i.e.*, 3.8% for eqn. 7 and 4.0% for eqn. 9. There is no apparent dependence of B on the inlet pressure p_i. As predicted by the classical kinetic gas theory, η of an ideal gas should be independent of its pressure p [29]. Moreover, there should be no apparent influence of the pressure drop $\Delta p = (p_i - p_0)$ on the temperature coefficient B. This prediction is justified by the

TABLE II

TEMPERATURE AND INLET PRESSURE DEPENDENCE OF THE RETENTION TIME OF METHANE ON L-CHIRASIL-VAL WITH HYDROGEN AS THE CARRIER GAS (EXPERIMENTAL DATA)

Borosilicate glass capillary column (No. H14, 20 m × 0.25 mm I.D.), splitting ratio 1:50, flame ionization detection, conditions (b) (see Table III).

T(°C)	$t_{M_{exp}}$(s)			
	0.3	0.5	0.7	1.0 [bar]
50	52.9_3	32.0_7	23.4_0	17.3_0
60	53.8_0	32.6_7	23.8_3	17.5_3
70	54.8_3	33.2_0	24.2_3	17.9_3
80	55.3_7	34.1_3	24.5_3	18.2_0
90	56.4_8	34.6_3	25.0_7	18.6_0
100	57.5_3	35.1_7	25.4_5	18.8_8
110	58.8_3	35.7_3	25.9_5	19.2_7
120	59.9_3	36.3_0	26.5_0	19.5_5
130	61.2_0	37.0_7	27.2_3	19.9_7
140	62.1_3	37.9_0	27.7_7	20.2_3
150	62.9_3	38.1_7	28.1_0	20.4_7
160	64.1_0	38.5_5	28.3_0	20.7_7
170	65.0_3	39.1_3	28.8_7	21.0_7
180	66.0_7	39.8_3	29.2_7	21.4_0

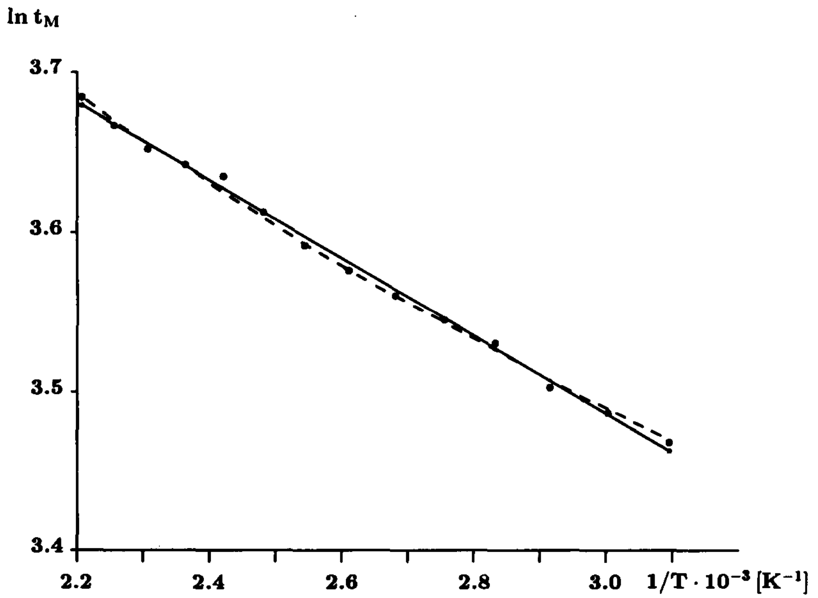

Fig. 1. Comparison of the two approaches, t_{M_2} and t_{M_4}, with the experimental data; conditions (b) (Table III), 0.5 bar H_2. Solid line, $t_{M_2} = 68.2e^{-246/T}$ s; dashed line, $t_{M_2} = 0.80T^{0.64}$ s.

TABLE III

LINEAR REGRESSION ANALYSES

Chromatographic conditions[a]	Theoretical model	Regression equation for t_M (s)	s (s)[b]
(a) 0.5 bar N_2	$t_{M_1} = AT^{0.5} + B$	$t_{M_1} = (30.55 \pm 0.09)\sqrt{T} - (190.0 \pm 1.6)$	0.06
	$t_{M_2} = AT^B$	$\ln t_{M_2} = (0.756 \pm 0.002) \ln T + (1.517 \pm 0.012)$	0.06
	$t_{M_3} = AT^{0.5}$	$t_{M_3} = (20.22 \pm 0.20)\sqrt{T}$	4.46
	$t_{M_4} = Ae^{B/T}$	$\ln t_{M_4} = -(255.2 \pm 2.2) \cdot 1/T + (6.673 \pm 0.007)$	0.15
(b) 0.3 bar H_2	$t_{M_2} = AT^B$	$\ln t_{M_2} = (0.675 \pm 0.011) \ln T + (0.059 \pm 0.063)$	0.24
0.5 bar H_2		$\ln t_{M_2} = (0.640 \pm 0.010) \ln T - (0.227 \pm 0.061)$	0.14
0.7 bar H_2		$\ln t_{M_2} = (0.688 \pm 0.015) \ln T - (0.830 \pm 0.091)$	0.15
1.0 bar H_2		$\ln t_{M_2} = (0.638 \pm 0.006) \ln T - (0.841 \pm 0.038)$	0.05
	Mean value for B	(0.660 ± 0.025)	
(b) 0.3 bar H_2	$t_{M_4} = Ae^{B/T}$	$\ln t_{M_4} = -(261.4 \pm 6.5) \cdot 1/T + (4.762 \pm 0.017)$	0.31
0.5 bar H_2		$\ln t_{M_4} = -(246.0 \pm 4.3) \cdot 1/T + (4.223 \pm 0.011)$	0.04
0.7 bar H_2		$\ln t_{M_4} = -(264.6 \pm 7.6) \cdot 1/T + (3.957 \pm 0.020)$	0.05
1.0 bar H_2		$\ln t_{M_4} = -(245.2 \pm 3.6) \cdot 1/T + (3.600 \pm 0.009)$	0.05
	Mean value for B	$-(255.3 \pm 10.2)$	

[a] As indicated in Tables I and II.

[b] Standard deviation $s = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n}(t_{M_{exp}} - t_{M_j})^2}$

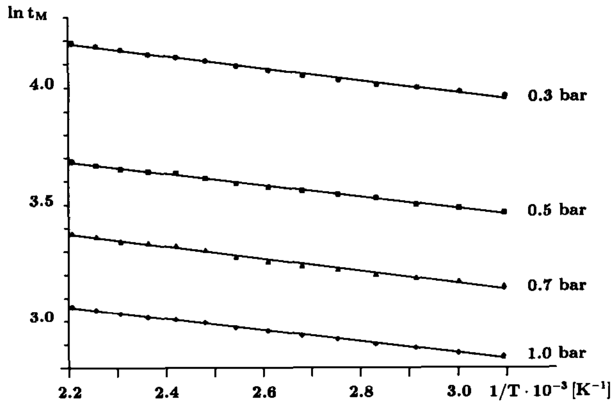

Fig. 2. Comparison of experimental and theoretical data t_{M_4}; conditions (b) (Table III), 0.3, 0.5, 0.7 and 1.0 bar H_2.

data in Table III. The entire data set of conditions (b) is depicted in Fig. 2, together with the regression analyses according to the exponential eqn. 9.

Hence this approach proves to be equally valid for gases, and not only for liquids as originally assumed. Intriguingly, both carrier gases, hydrogen and nitrogen, show a similar temperature coefficient, *i.e.*, $B = -255$. Whether this coincidence is real or an artefact remains open to further investigations. In the equation $t_M = AT^B$, a significant difference in B is found for the different gases, *i.e.*, $B = 0.756$ for nitrogen and $B = 0.660$ for hydrogen. Both values differ only slightly from those used by Ettre [15] for the temperature coefficient of the viscosity $\eta \propto T^B$ with $B = 0.725$ for nitrogen and $B = 0.680 - 0.695$ for hydrogen.

CONCLUSIONS

The temperature dependence of the retention time of methane is in good accord with both eqns. 7 and 9. As judged by the standard deviations s, both approaches are of striking resemblance. The latter, although following a viscosity theory originally established by Andrade [32] for liquids, has the advantage of fitting into the determination of thermodynamic parameters of solute–solvent interaction by gas chromatography. We found it convenient simply to determine the temperature dependence of the net retention t'_R at a constant inlet pressure [9], which yields the theoretically important term

$$\frac{\delta \ln k'}{\delta(1/T)} = \frac{\delta \ln t'_R}{\delta(1/T)} - B \tag{12}$$

where the constant B is approximately independent of the column inlet pressure and of the nature of the carrier gas. Beyond these applications in the realm of chromatography, the exponential equation $\eta \propto e^{B/T}$ proposed for the temperature dependence of the viscosity of gases may be of general interest with regard to model building in kinetic gas theory [29].

ACKNOWLEDGEMENTS

We are indebted to Professors E. Bayer and V. Schurig for helpful support.

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