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RETENTION VOLUME IN HIGH-PRESSURE GAS CHROMATOGRAPHY

II. COMPARISON OF EXPERIMENTAL DATA WITH THE PREDICTION OF A PSEUDO-BINARY MODEL

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SUMMARY

The specific retention volume of isooctane, tetrachloromethane and toluene were measured in the Apiezon K–hydrogen, nitrogen and carbon dioxide systems at temperatures of 50 and 75°C and at pressures of 10–100 atm for hydrogen and nitrogen and 10–50 atm for carbon dioxide. By comparing the results with the predictions derived from the concept of a pseudo-binary model, it was possible to assess the effect of the carrier gas dissolved in the stationary phase on the specific retention volume. The largest deviations from the pseudo-binary model were found with the isooctane–Apiezon K–carbon dioxide system.

INTRODUCTION

In Part I[1], relationships were derived that describe the pressure dependence of the specific retention volume on the column with a negligible pressure drop. A model concept reducing the system in the column to a ternary liquid solute–carrier gas–stationary phase system and a binary gaseous solute–carrier gas system was the basis of the derivation, *i.e.*, the volatility of the stationary phase was neglected. Except for the latest papers by Cruickshank *et al.*[2] and Gainey and Pecsok[3], however, previous papers dealing with the thermodynamics of the retention volume were based on a pseudo-binary model with the liquid phase formed by a binary solute–stationary phase system and the gaseous phase constituted by a binary mixture of the solute and carrier gas. Hence, in addition to the volatility of the stationary phase, the solubility of the carrier gas in the stationary phase was also neglected.

Under the assumptions discussed in Part I[1], the expressions for the specific retention volume derived by virtue of the above two models differ from each other by the factor

$$\frac{\exp - [(\alpha - \beta) x_2 + \beta x_2^2]}{1 - x_2} \tag{1}$$

where α is a coefficient that characterizes dilute binary liquid solute–carrier gas and solute–stationary phase systems at the column temperature T and a reference pressure Pr, β is a coefficient that characterizes the dilute binary liquid carrier gas–stationary phase system at T and Pr and x_2 is the molar fraction of the carrier gas dissolved in the stationary phase. If the significance of the above correction factor in a particular chromatographic system is to be appreciated, it is possible to use two approaches. One approach consists in measuring direct equilibrium data for the ternary solute–carrier gas–stationary phase system, from which the factor can readily be calculated, while the other is based on a comparison of the experimentally obtained pressure dependence of the specific retention volume with the prediction of the pseudo-binary model. In the latter case, it is necessary to know with sufficient precision the behaviour of the binary gaseous solute–carrier gas mixture within the required temperature and pressure limits and the partial molar volumes of the solute in the stationary phase. In accordance with eqn. 27 in Part I[1], the differences will be due to the solubility of the carrier gas in the stationary phase.

In order to carry out the above comparison, systems of tetrachloromethane, isooctane and toluene with Apiezon K and three carrier gases (hydrogen, nitrogen and carbon dioxide) were studied at temperatures of 50 and 75 °C. The measurements were carried out within a pressure range of 10–100 atm with the systems that contained hydrogen and nitrogen and within the range 10–50 atm with the systems that contained carbon dioxide.

The behaviour of the gaseous binary systems of tetrachloromethane, isooctane and toluene with hydrogen, nitrogen and carbon dioxide at the same temperatures and within approximately the same pressure limits is known from the work of Prausnitz and Benson[4]; these data were obtained from the measurement of the solubility of liquids in compressed gases.

EXPERIMENTAL

The measurements of the specific retention volumes were carried out on a home-made high-pressure gas chromatograph consisting of the following three main parts: a high-pressure manostat, a hot-air column oven with the column and a sample introduction port, and a detection system.

Manostat

The manostat was constructed for operating pressures up to 150 atm (Fig. 1) and consisted of two pressure vessels of total volume 4 l, a bellows-type differential pressure controller (DPC) and a high-pressure solenoid valve (SV). The entire pressurized space of the manostat was placed in a heat-shielding jacket made of foamed polystyrene. The compressed gas from a pressure cylinder passed through a shut-off valve (V_1) and a solenoid valve (SV), controlled by the pressure regulator DPC, into the pressurized space of the manostat. From the manostat, the gas was led via a filter (F) filled with glass-wool, silica gel and charcoal and a shut-off valve (V_2) into the sample inlet port of the chromatograph.

The heart of the differential controller DPC (*cf.*, Fig. 2) was a series of phosphor-bronze bellows soldered together and placed in a pressure jacket. The free end of the bellows bore on to a microswitch connected to a transistor relay controlling

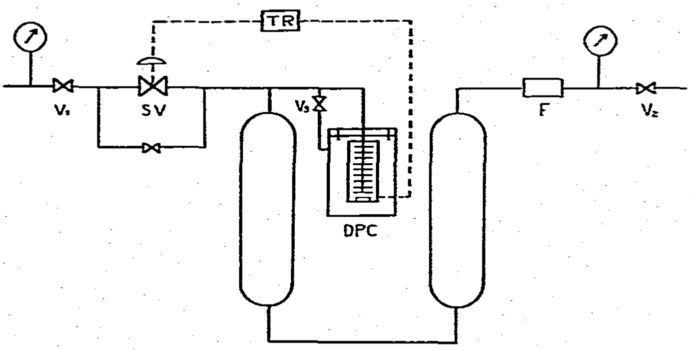

Fig. 1. Flow diagram of the high-pressure manostat. V_1, V_2 = Shut-off valves; V_3 = needle valve; SV = solenoid valve; DPC = differential pressure controller; TR = transistor relay.

the solenoid valve. The inner space of the bellows communicated directly with the pressurized space of the manostat. The space between the bellows and the pressure jacket of the controller communicated with the inner space of the bellows (*i.e.*, with the manostat) through a needle valve (V_3). If the valve V_3 was open, the microswitch at the bottom of the controller DPC was disconnected and the valve SV opened, and the pressure in the manostat gradually increased. As soon as the required pressure level was established, valve V_3 was closed and the bellows actuated the microswitch upon which the solenoid valve SV was closed. When the pressure decreased, the shrunk bellows released the microswitch, thus opening the solenoid valve. If the valve V_3 was closed, the gas in the space between the bellows and the jacket of the controller was held under a constant pre-set pressure, and the controller adjusted intermittently the pressure in the manostat to the pre-set value.

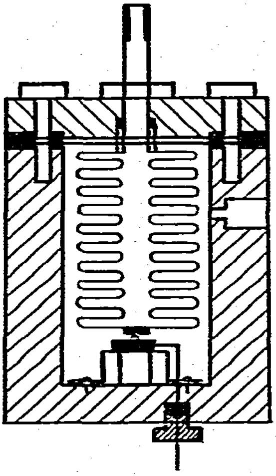

Fig. 2. Differential pressure controller.

The seat of the solenoid valve SV (*cf.*, Fig. 3) was formed by exchangeable jets, the inner diameter (0.1–0.8 mm) of which could be selected such that the charges of gas supplied in the individual pulses did not cause pressure fluctuations greater than about 10 mmHg in the manostat. The jet was closed with a thrusting ring of silicone rubber fastened to the core of the valve. In the work with carbon dioxide, the silicone rubber was replaced with plasticized polyvinyl chloride, as the former showed significant swelling in contact with carbon dioxide under higher pressures.

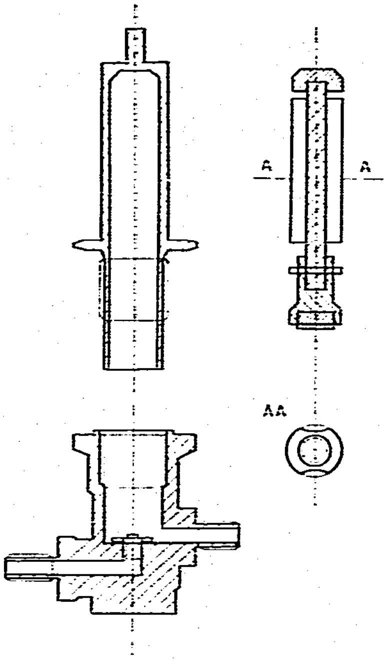

Fig. 3. Solenoid valve.

The manostatting unit also accommodated filters and stabilizing and controlling elements for the low-pressure supply of hydrogen and air into the flame ionization detector.

Column oven and detector

A hot-air column oven of conventional construction, with forced circulation of heated air, was used. The temperature was controlled by means of a contact thermometer graduated in 0.2 C intervals. The input power into the heaters was set roughly by an autotransformer according to the temperature required. The temperature in the oven was measured with a mercury thermometer graduated in 0.1 C intervals.

The detection system consisted of a flame ionization detector of ordinary construction, an electrometer and an EZ 3 line recorder (Laboratory Equipment, Prague, Czechoslovakia).

Column

The column was an 85-cm long U-shaped stainless-steel tube of 10 mm O.D. and 6 mm I.D., packed with Chromosorb W AW, 100–120 mesh, coated with 10% (w/w) of Apiezon K. The percentage of the Apiezon K coating was checked by extracting part of the material with chloroform.

The sample inlet port, supplied with the pressurized carrier gas from the manostat, was suspended in the oven and provided with a silicone rubber septum, which was tightly compressed by a nut furnished with a telescopic guide for the syringe needle[5]. The sample charges were injected with a high-pressure Hamilton HP 305 5-μl syringe (Hamilton, Whittier, Calif., U.S.A.). The pressure in the inlet port was measured with a set of tube manometers of a precision class of 1% (Chirana, Stará Turá, Czechoslovakia). The column effluent passed through a throttling copper capillary of 0.1 mm I.D. and about 10 cm in length into a splitter: part of the effluent was led via the capillary into the detector burner jet and the remainder was discharged into the atmosphere via a needle valve. For each pressure level, a suitable flow-rate of the carrier gas through the column was set by gripping the capillary with pliers.

PROCEDURE AND RESULTS

After setting the desired pressure level in the manostat, the flow-rate of carrier gas through the column was adjusted by means of the throttling capillary so as to achieve a separation efficiency of not less than of 600 theoretical plates. After the temperature in the column oven had been established, the flow-rate of carrier gas was measured repeatedly with a Mariotte flask as long as the differences between the subsequent values exceeded 1% of the values measured. Then part of the effluent was conducted into the detector, and two chromatographic runs were carried out under each set of the conditions. About 0.5-μl charges of the mixture of isooctane and toluene, filled up to 5 μl with methane in the syringe, and of tetrachloromethane, also with methane, were injected into the chromatograph. At the end of the measurement, the flow-rate of carrier gas was checked again by replicate measurements. The retention times of the solutes studied were calculated from the distances measured in the chromatographic records by means of a ruler graduated in millimetres; the chart speed was chosen such that the lengths of the line segments measured were not less than 25 cm. The specific retention volumes in each pair did not differ from each other by more than 1% and were averaged.

The experimental values of the specific retention volumes, V_g^{373}, are summarized in Table I and, for the sake of clarity, are plotted against pressure in Figs. 4, 5 and 6. The values of V_g^{373} were calculated (*cf.* Part I[1], eqn. 4) by the relationship

$$V_g^{373} = \frac{v_0}{w_3}\cdot\frac{z_2^{373}}{z_2^0}\cdot\frac{373.2}{T_0}\cdot\frac{P_0}{\bar{P}}\cdot(t_{R1} - t_m) \tag{2}$$

where v_0 is the volume flow-rate of the carrier gas at the column outlet, *i.e.* after its expansion at temperature T_0 and pressure P_0, w_3 is the weight of the stationary phase in the column, z_2^{373} is the compressibility factor of the carrier gas at the column mean pressure $\bar{P}$ and a reference temperature of 373.2°K, z_2^0 is the compressilibity factor of

TABLE I

EXPERIMENTAL VALUES OF THE SPECIFIC RETENTION VOLUME

$\bar{P}$ (atm)	V_g^{373} (ml/g) CCl_4–N_2		CCl_4–H_2		Isooctane–N_2		Isooctane–H_2		Toluene–N_2		Toluene–H_2		CCl_4–CO_2		Isooctane–CO_2		Toluene–CO_2	
	50°C	75°C	50°C	75°C	50°C	75°C	50°C	75°C	50°C	75°C	50°C	75°C	50°C	75°C	50°C	75°C	50°C	75°C
10,6	225	100	233	105	266	110	280	118	635	249	662	264	202	93,3	231	99,9	535	219
15,5													191	86,9	209	90,6	480	197
20,3	202	91,5	228	102	231	98,4	269	112	556	223	641	252	172	80,7	186	84,1	423	181
25,2													155	74,8	164	75,0	370	162
30,0	181	84,1	219	98,1	200	88,4	255	106	490	202	611	240	145	67,7	151	67,9	337	145
34,8													132	65,2	131	63,3	291	136
39,7	164	78,7	212	95,7	180	80,5	248	104	441	188	595	235	118	58,3	119	56,9	257	120
44,5													103	53,5	98,9	50,3	218	108
49,3	148	72,0	204	92,4	157	73,0	233	99,4	392	170	562	225	93,2	49,4	86,0	45,3	189	97,2
59,0	135	66,4	200	91,5	137	65,5	222	96,9	348	154	537	220						
68,7	123	61,5	190	87,6	124	59,3	212	91,6	318	141	512	210						
78,3	115	57,3	185	84,8	109	53,8	204	89,0	285	129	491	204						
88,0	104	53,5	181	83,0	96,7	49,1	195	87,0	255	118	477	196						
97,7	94,8	50,0	173	81,0	87,4	44,5	187	83,5	231	109	456	191						

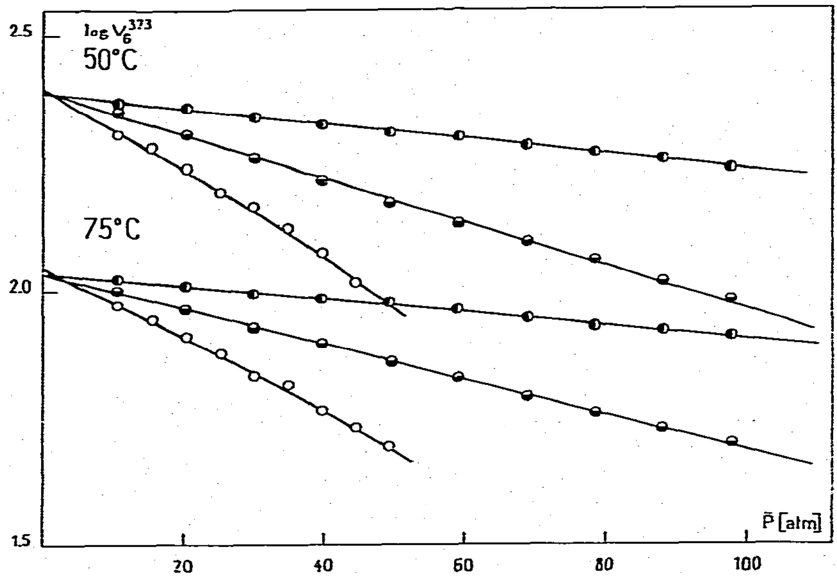

Fig. 4. Dependence of the logarithm of the specific retention volume on Apiezon K of tetrachloromethane on the column mean pressure at 50 and 75°C with hydrogen (◐), nitrogen (⊖) and carbon dioxide (○) as carrier gases.

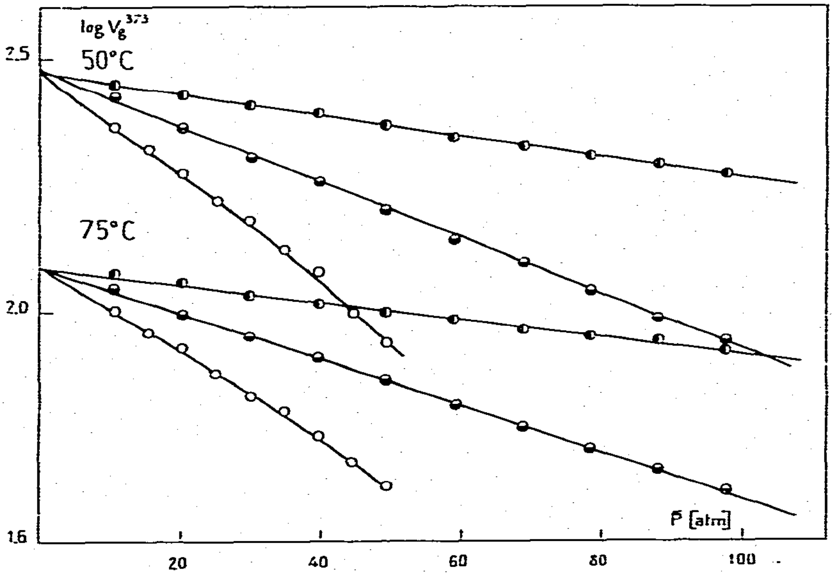

Fig. 5. Dependence of the logarithm of the specific retention volume on Apiezon K of isooctane on the column mean pressure at 50 and 75°C with hydrogen (◐), nitrogen (⊖) and carbon dioxide (○) as carrier gases.

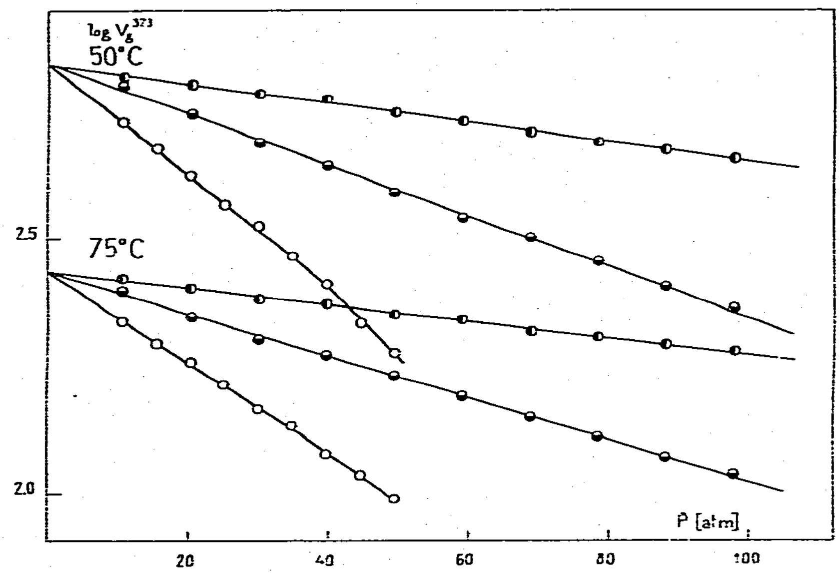

Fig. 6. Dependence of the logarithm of the specific retention volume on Apiezon K of toluene on the column mean pressure at 50 and 75 °C with hydrogen (◐), nitrogen (◒) and carbon dioxide (○) as carrier gases.

the carrier gas at pressure P_0 and temperature T_0, t_{R1} is the retention time of the solute and t_m is the dead retention time. The compressibility factors of the individual carrier gases were calculated from a virial equation with the third virial coefficient according to the recurrent equation

$$z^{(i+1)} = \frac{PV^{(i+1)}}{RT} = 1 + \frac{B}{V^{(i)}} + \frac{C}{V^{(i)2}} \tag{3}$$

the calculation being terminated when two consecutive values of the molar volume did not differ from each other by more than 0.1 %. The values of the virial coefficient

TABLE II

EMPLOYED VALUES OF THE VIRIAL COEFFICIENTS OF THE CARRIER GASES

Carrier gas	*T (°K)*	*B (ml/mole)*	*C (ml²/mole²)*	*Reference*
Nitrogen	298.16	−4.71	1315	6
	323.16	−0.28	1219	6
	348.16	3.20	1257	6
	373.16	6.56	1079	6
Hydrogen	298.16	14.12	405	7
	323.16	14.55	397	7
	348.16	14.90	393	7
	373.16	15.16	384	7
Carbon dioxide	298.21	−123.56	4931	9
	323.16	−102.63	4390	8
	348.42	−86.68	4429	9
	373.16	−71.85	3165	8

TABLE III

CALCULATED VALUES OF THE COMPRESSIBILITY FACTORS OF THE INDIVIDUAL CARRIER GASES

Carrier gas	*P (atm)*	*z (25, 1)*	*z (100, P)*	*z (75, P)*	*z (50, P)*
Nitrogen	10.6	1.000	1.002	1.001	1.000
	20.3		1.005	1.003	1.000
	30.0		1.007	1.005	1.001
	39.7		1.010	1.007	1.002
	49.3		1.013	1.009	1.004
	59.0		1.016	1.012	1.005
	68.7		1.020	1.015	1.007
	78.3		1.023	1.018	1.010
	88.0		1.027	1.021	1.012
	97.7		1.031	1.025	1.015
Hydrogen	10.6	1.001	1.005	1.006	1.006
	20.3		1.010	1.011	1.011
	30.0		1.015	1.016	1.017
	39.7		1.020	1.021	1.022
	49.3		1.025	1.026	1.028
	59.0		1.030	1.031	1.033
	68.7		1.035	1.037	1.039
	78.3		1.040	1.042	1.044
	88.0		1.045	1.047	1.050
	97.7		1.050	1.053	1.056
Carbon dioxide	10.6	0.995	0.975	0.967	0.958
	15.5		0.963	0.952	0.938
	20.3		0.951	0.937	0.907
	25.2		0.939	0.921	0.896
	30.0		0.928	0.905	0.875
	34.8		0.916	0.890	0.852
	39.7		0.903	0.873	0.829
	44.5		0.891	0.857	0.805
	49.3		0.879	0.841	0.780

used in the calculation are given, together with the corresponding references, in Table II. Table III contains the calculated compressibility factors.

DISCUSSION

Table IV gives the values of the second cross-virial coefficient for the system studied, taken from a paper by Prausnitz and Benson[4]. By employing these data, it was possible to eliminate the effect of the fugacity coefficient on the pressure dependence of the specific retention volume and to check the relationship derived for the pseudo-binary model with the second cross-virial coefficient (cf. Part I[1], eqn. 27):

$$\ln \frac{z_2}{z_2^{Tr}} \cdot V_g'^{Tr} - \frac{2B_{12}}{z_2 RT} \cdot \bar{P} = \ln \frac{R\,Tr}{M_3\,H_1^{Pr}} - \frac{\bar{V}_1^{L}}{RT} \cdot \bar{P} \qquad (4)$$

The measured data are plotted in Figs. 7, 8 and 9. The straight lines were obtained by linear regression of the experimental data. Table V shows a comparison of

TABLE IV

VALUES OF THE SECOND CROSS-VIRIAL COEFFICIENTS OF THE STUDIED BINARY SOLUTE-CARRIER GAS MIXTURES AT 50 AND 75 °C

System	*Temperature (°C)*	B_{12} *(ml/mole)*
H_2–CCl_4	75	34.9
H_2–isooctane	50	37.6
	75	55.7
H_2–toluene	50	19.0
	75	37.2
N_2–CCl_4	50	− 58.5
	75	− 49.6
N_2–isooctane	50	− 82.3
	75	− 60.3
N_2–toluene	50	− 98.1
	75	− 88.1
CO_2–CCl_4	50	−205
	75	−163
CO_2–isooctane	50	−303
	75	−252
CO_2–toluene	50	−254
	75	−215

the effective partial molar volumes of the solutes in the stationary phase, calculated from the slopes of the individual straight lines, together with the molar volumes of the pure solutes. The data on the density were taken from Timmermans monograph[10].

If the solubility of the carrier gas in the stationary phase had a negligible effect on the retention volume, all of the experimental points for each binary solute–stationary phase system at a given temperature would lie, according to eqn. 2, on a single straight line, regardless of the kind of carrier gas. The slope of this common straight line would be determined by the partial molar volume of the solute in the stationary phase, *i.e.*, by a quantity independent of the carrier gas according to the above assump-

TABLE V

COMPARISON OF THE EFFECTIVE PARTIAL MOLAR VOLUMES OF TETRACHLOROMETHANE, ISOOCTANE AND TOLUENE, CALCULATED FOR THE INDIVIDUAL KINDS OF CARRIER GAS FROM EQN. 4 WITH THE MOLAR VOLUMES OF THE PURE COMPOUNDS AT THE SAME TEMPERATURES

Compound	*t (°C)*	V^0	$(\overline{V}_{H_2})_{eff}$	$(\overline{V}_{N_2})_{eff}$	$(\overline{V}_{CO_2})_{eff}$
Isooctane	50	171.3	195.3	182.2	−67.2
	75	176.9	216.6	181.9	− 8.54
Tetrachloromethane	50	100.2		150.0	53.7
	75	103.5	151.5	134.0	101.5
Toluene	50	109.8	150.4	116.9	98.9
	75	113.0	175.3	101.3	94.8

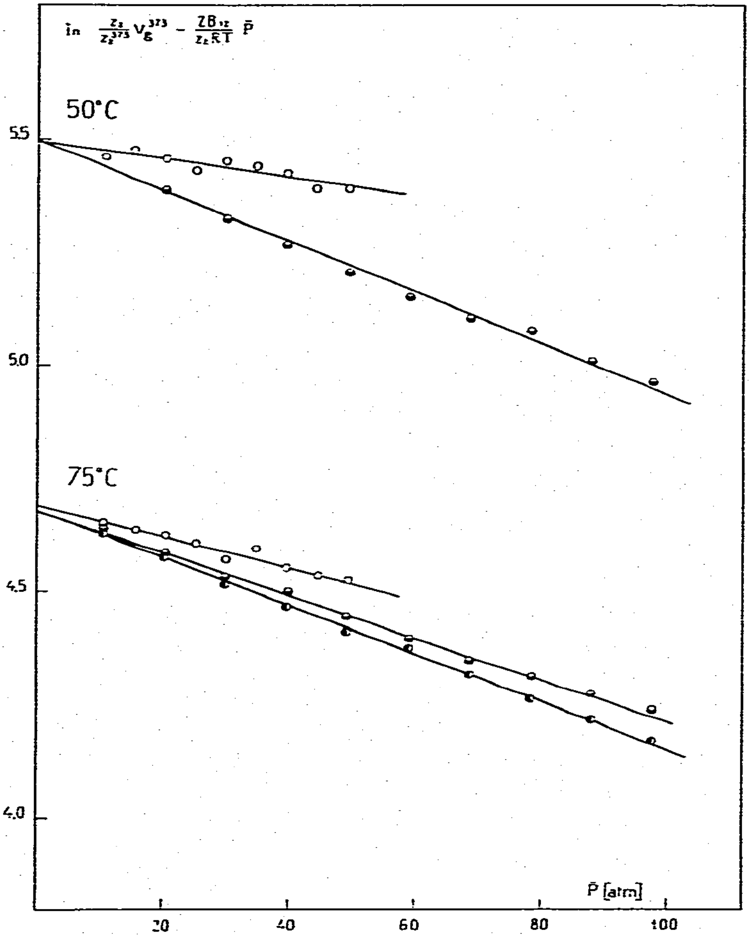

Fig. 7. Graphical check of eqn. 4 for tetrachloromethane. Carrier gas: ◐, hydrogen; ◒, nitrogen; ○, carbon dioxide.

tion. The necessity for taking into account further terms of the virial expansion would be substantiated if the systematic deviations of the data from the common line occurred only at higher pressures. In fact, the experimental data, corrected for the real behaviour of the gaseous phase, for the given solute and stationary phase at a given temperature are grouped around a family of straight lines that pass, within experimental error, through a single point at $\bar{P} = 0$.

Let us now discuss the systems with carbon dioxide, which has a significant solubility in non-polar liquids[11], whereas hydrogen has only a very low solubility. Therefore, the angle formed by the isotherms of a given solute with carbon dioxide and hydrogen can be considered to be at least a rough measure of the quantity a in the correction factor, *i.e.*, a measure of the change in the activity coefficient of a given solute in the liquid phase, caused by the presence of the dissolved carbon dioxide.

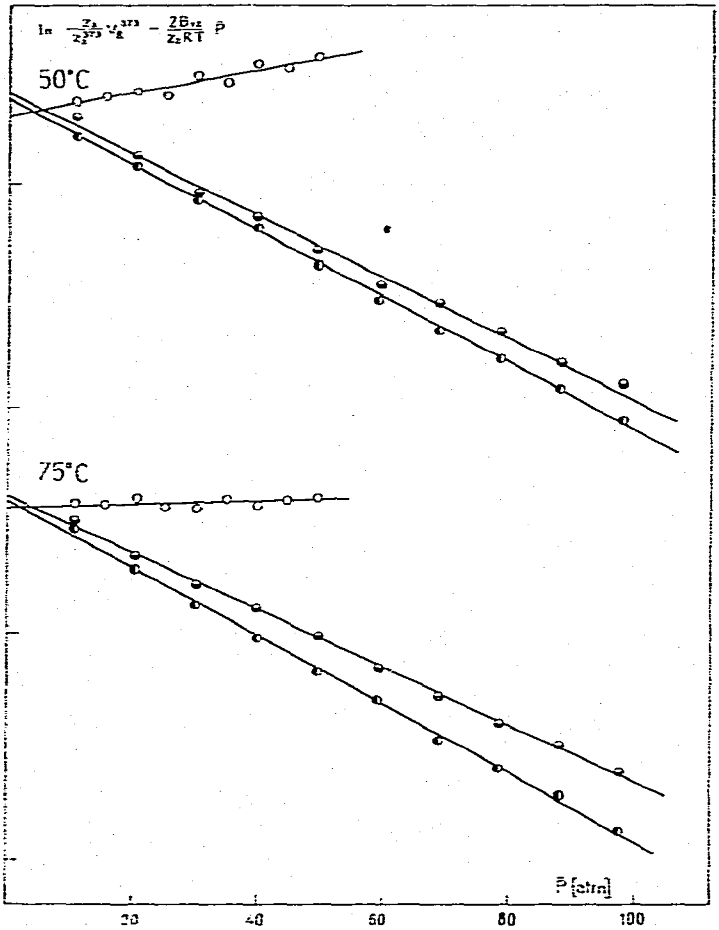

Fig. 8. Graphical check of eqn. 4 for isooctane. Carrier gas: ◐, hydrogen; ◒, nitrogen; ○, carbon dioxide.

The other quantities in the correction factor, such as β and x_2, are independent of the solute. Of the solutes studied, isooctane is the most sensitive to the presence of carbon dioxide in the stationary liquid, tetrachloromethane is less sensitive and toluene is the least sensitive.

It is not necessary to emphasize the failure of the pseudo-binary model in the description of the behaviour of the systems studied: this failure is apparent from Figs. 7, 8 and 9. However, it is worth mentioning that the dependence of log V_g^{373} on pressure is linear (the correlation coefficient does not exceed 0.997) over the whole of the pressure range studied with systems with nitrogen and hydrogen (0–100 atm), and even with those with carbon dioxide at 50°C up to at least 35 atm. Similarly, the dependence of ln $(z_2 V_g^{373}/z_2^{373}) - (2\ B_{12}/z_2RT)\ \bar{P}$ *versus* $\bar{P}$ is linear over the whole of the pressure

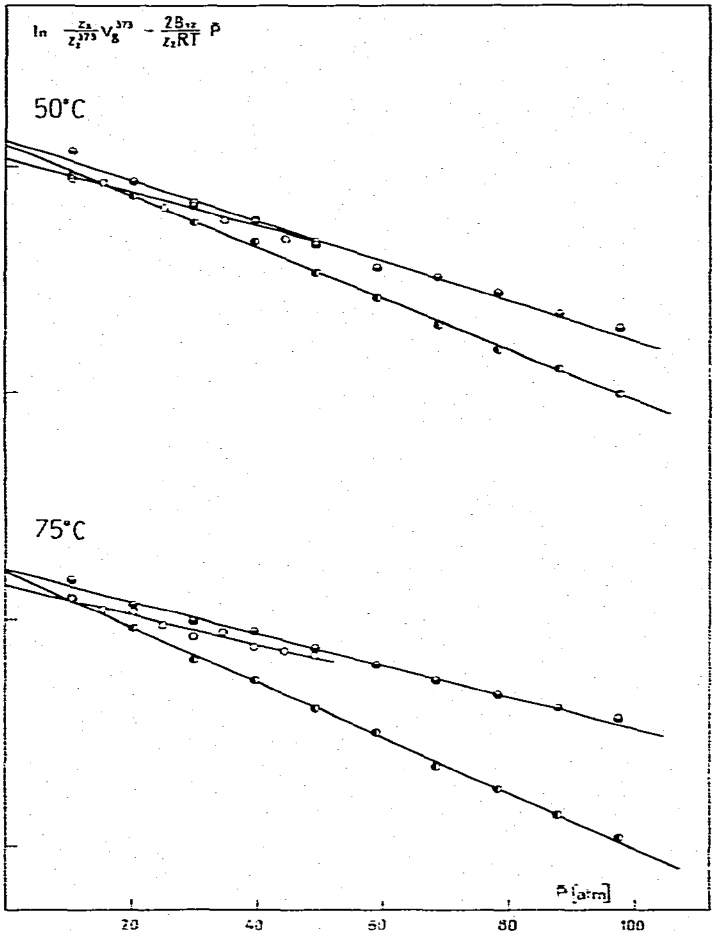

Fig. 9. Graphical check of eqn. 4 for toluene. Carrier gas: ◐, hydrogen; ◒, nitrogen;   , carbon dioxide.

range studied. Hence, if the failure of the pseudo-binary model is due to a significant solubility of the carrier gas in the stationary liquid, the same relative error will also apply to low-pressure, currently performed measurements of retention data.

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