Journal of Chromatography, 219 (1981) 37–44
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,152

COMPARISON OF THE DISTRIBUTION CONSTANTS OF ACETONE IN DIFFERENT CHROMATOGRAPHIC SORBENT–GAS SYSTEMS, DETERMINED BY DIRECT MEASUREMENT OF SORPTION EQUILIBRIA AND CALCULATED FROM GAS CHROMATOGRAPHIC RETENTION DATA

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(Received July 3rd, 1981)

SUMMARY

The distribution constants of acetone in different chromatographic sorbent–nitrogen systems were determined by direct measurement of sorption equilibria at gas-phase concentrations of acetone ranging from tens of ppb (10^9) to hundreds of ppm. Tenax GC, Porapaks P and Q, Apiezon K and silicone oil QF-1 were employed as sorbents. With Tenax GC and Porapak P, the sorption isotherms were almost linear up to concentrations of about 4 ppm of acetone in the gaseous phase, whereas with the other sorbents the isotherms were non-linear over the whole range of concentrations investigated. With the Tenax GC and Porapak P systems, the distribution constants determined at concentrations corresponding to the linear sections of the corresponding isotherms agreed with those calculated from gas chromatographic retention data within about 15% of the values determined.

INTRODUCTION

The concentration of trace components of gaseous and/or liquid materials by trapping them in columns packed with chromatographic sorbents can be carried out in conservation[1] or equilibration[2] modes. In both these modes, it is expedient to know the retention volume of the analyte on the trapping column, from which the so-called breakthrough volume and/or the equilibration (saturation) volume can be calculated. The retention volume, V_R, is given by

$$V_R = V_{M,t} + KW_S$$

$V_{M,t}$, K and W_S being the void volume of the trap, the analyte distribution constant (volume/mass) in the given system and the mass of sorbent in the trap, respectively.

In our previous work[3], the sorption of benzene was studied in different nitrogen–chromatographic sorbent (Tenax GC, Porapaks P and Q, Apiezon K, silicone oil QF-1, Reoplex 400) systems at benzene concentrations in the gaseous phase ranging from tens of ppb (10^9) to hundreds of ppm. The concentration limits of the linearity

0021-9673/81/0000–0000/S02.50

of the sorption isotherms of benzene in the individual systems were determined, and the limiting distribution constants of benzene were compared with those calculated from gas chromatographic (GC) retention data.

In order to assay systems with a polar analyte, the sorption behaviour of acetone on the same sorbents (except Reoplex 400) has now been studied. The concentrations of acetone in the gaseous phase were again varied from tens of ppb to hundreds of ppm.

EXPERIMENTAL

The sorbent materials as well as the instrumentation and procedures employed for the preparation of model gaseous mixtures and the measurements of sorption equilibria and retention data were as described earlier[3,4]. Acetone of analytical-grade purity (Lachema, Brno, Czechoslovakia) was used to prepare the model mixtures.

RESULTS AND DISCUSSION

The distribution constants of acetone, obtained by direct measurement of sorption equilibria in systems with Apiezon K, silicone oil QF-1, Porapaks Q and P and Tenax GC, are plotted against the logarithm of the acetone concentration in the gaseous phase in Figs. 1–5, respectively. Figs. 1 and 2 show that in the systems with liquid sorbents, *i.e.*, Apiezon K and QF-1, the sorption isotherms are non-linear over the entire range of acetone concentrations employed. This is contrary to what has been found for the sorption of benzene on the same sorbents. The non-linearity of the acetone isotherms is probably due to a significant adsorption of acetone at the gas–liquid and/or liquid–solid interfaces which occurs in addition to its dissolution in the bulk liquid[5]. Owing to the small surface areas of these interfaces (about 0.5 m^2/g), the

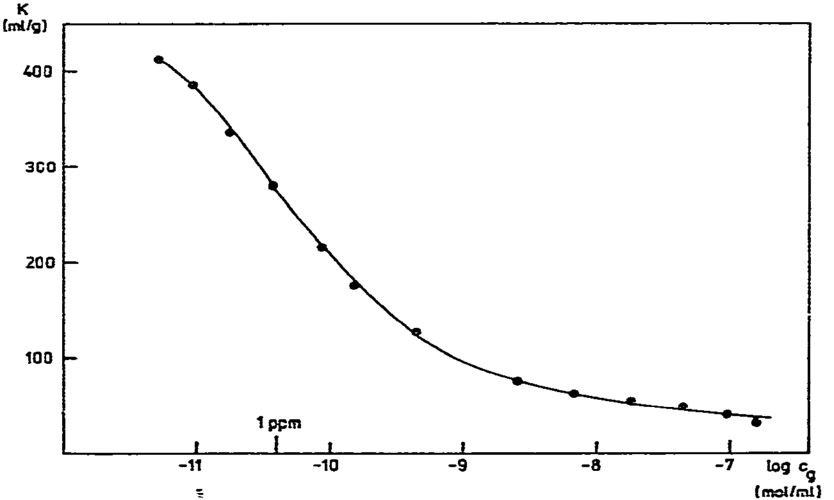

Fig. 1. Dependence of the distribution constant of acetone in the nitrogen–Apiezon K system on the logarithm of the concentration of acetone in the gaseous phase.

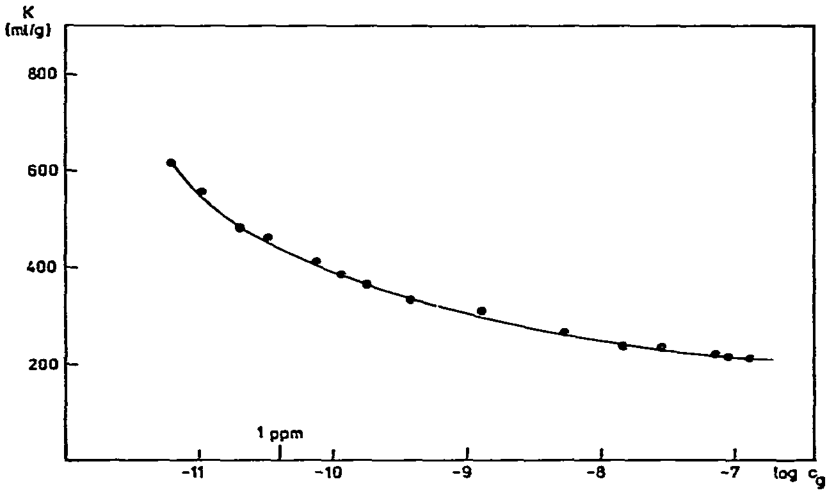

Fig. 2. Dependence as in Fig. 1 for the nitrogen–QF-1 system.

isotherms would probably become linear only at extremely low acetone concentrations.

From Figs. 4 and 5 it is seen that the sorption isotherms of acetone in the systems with Porapak P and Tenax GC are approximately linear up to several ppm of acetone in the gaseous phase. With Porapak Q there is no flat section on the *K versus* log c_g curve within the range of acetone concentrations examined, although for benzene on the same sorbent the corresponding curve was almost flat up to about 1 ppm benzene in the gaseous phase[4]. The cause of this different behaviour of acetone and benzene, on the Porapak Q employed, is not clear.

The acetone distribution constants obtained by direct measurement of sorption equilibria (K_s, K_L) are compared with those calculated from GC retention data (K_r) in

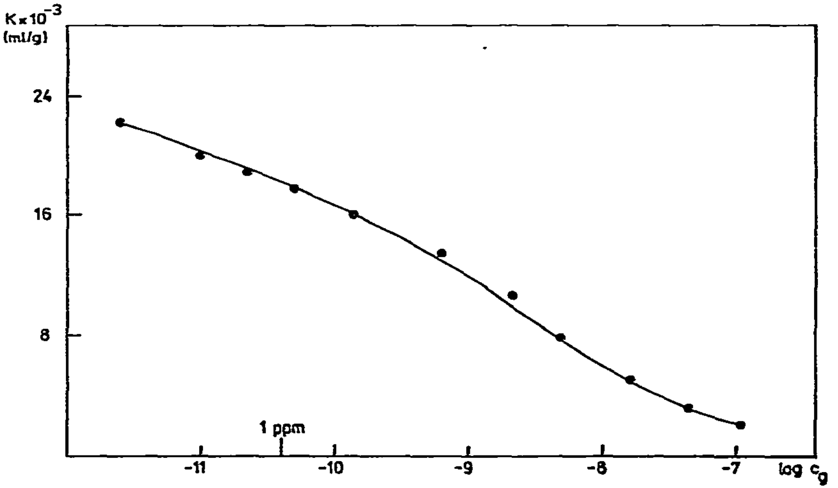

Fig. 3. Dependence as in Fig. 1 for the nitrogen–Porapak Q system.

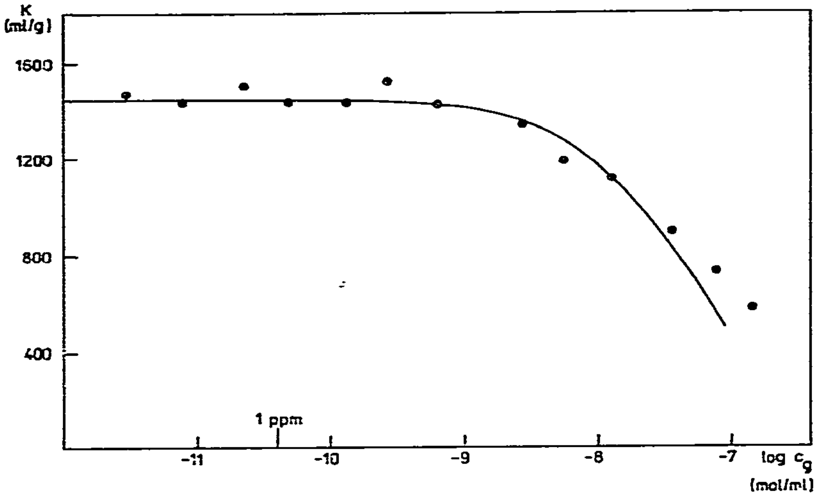

Fig. 4. Dependence as in Fig. 1 for the nitrogen–Porapak P system.

Table I. The K_s values were obtained by simply averaging the K_s values corresponding to the flat sections of the respective K *versus* log c_g curves, and the K_L values were obtained by processing the experimental c_g and c_s data (equilibrium concentrations of acetone in the gaseous phase and in the sorbent, respectively) in terms of Langmuir's isotherm. The K_r values were calculated from the specific retention volumes. The procedures used to calculate K_L and K_r were described in detail in our previous paper[4]. The specific retention volumes, V_g^0, of acetone used to calculate the K_r values were correlated with temperature by:

$$\log V_g^0 = A + B/T$$

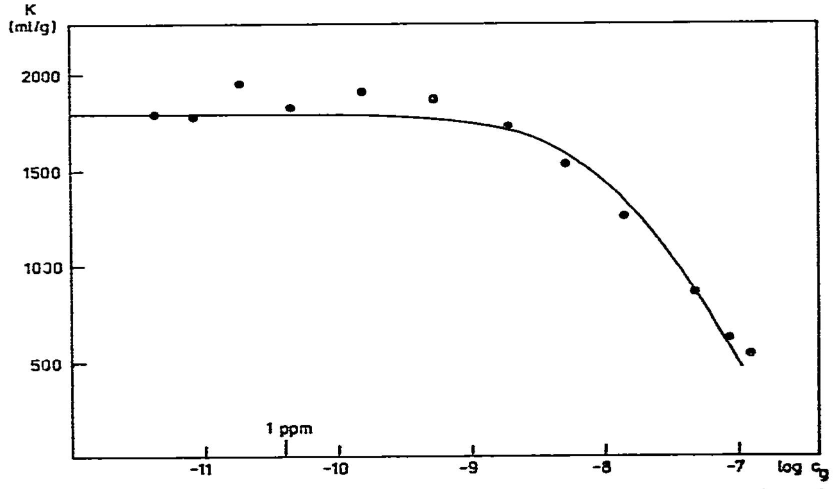

Fig. 5. Dependence as in Fig. 1 for the nitrogen–Tenax GC system.

TABLE I

CHARACTERISTICS OF THE SORPTION ISOTHERMS OF ACETONE

Sorbent	*Linearity limit (ppm)*	K_s *(ml/g)*	K_L *(ml/g)*	K_r *(ml/g)*
Tenax GC	*ca.* 4	1853.0	1787.4	1999.0
Porapak P	*ca.* 4	1462.2	1437.4	1257.9
Porapak Q	<0.1	–	–	13,803
Apiezon K	<0.1	–	–	93*
QF-1	<0.1	–	–	278.3

* The V_g^0 value was dependent on the size of the sample.

The constants A and B, together with the V_g^0 values at 35°C, are summarized in Table II.

With systems in which benzene was used as a model sorbate[4] there was a very good agreement between K_s, K_L and K_r, the maximum difference being less than 2.5%. However, for acetone, differences as large as 15% occur (*cf.*, Table I). It might have been thought that the larger differences between K_s and K_L, relative to benzene, are due to interactions between adsorbed acetone molecules, implying that Langmuir's model is invalid in this case. Upon closer inspection, however, this interpretation is found not to be the case. Thus, Table III shows the coefficients at r^{-6} for the orientation, induction and dispersion contributions to the intermolecular interaction energy[6], calculated for a temperature of 35°C from tabulated data on the polarizabil-

TABLE II

CONSTANTS IN $\log V_g^0 = A + B/T$ AND VALUES OF V_g^0 AT 35°C

Sorbent	A	B	V_g^0 *(35°C) (ml/g)*
Tenax GC	−6.372277	2964.62	1771.9
Porapak P	−5.640364	2677.10	1115.1
Porapak Q	−6.260764	3188.86	12,235.6
Apiezon K	−4.153805	1870.96	82.8
QF-1	−3.942671	1952.33	247.2

TABLE III

COEFFICIENTS AT r^{-6} FOR CONTRIBUTIONS (AT 308.15°K) TO THE INTERMOLECULAR INTERACTION ENERGY OF BENZENE AND ACETONE

Solute	*Coefficient at* r^{-6} $(J \cdot m^6 \times 10^{-79})$		
	Orientation	*Induction*	*Dispersion*
Benzene	0	0	1222.4
Acetone	1056.0	105.8	503.9

ities, ionization potentials and dipole moments of acetone and benzene[7]. It is seen that the sums of the coefficients for benzene are commensurate with those for acetone.

Let us suppose that the surface of the sorbent is homogeneous, that all its parts are equally accessible to the sorbate and that there is no diffusion of the sorbate into the bulk polymer. Then the area of the polymer surface available to each sorbate molecule is

$$A_1 = S/Kc_g N_A$$

where S is the specific surface area of the sorbent, N_A is the Avogadro constant and K and c_g are the distribution constant and the solute concentration in the gaseous phase, respectively. Values of A_1 (mm^2) for acetone and benzene at $c_g = 10^{-10}$ mole/ml and at assumed specific surface areas of Tenax GC, Porapaks P and Q equal to 15, 150 and 550 m^2/g, respectively, are shown in Table IV. The data in Tables III and IV indicate that, for acetone, the processing of c_g and c_s data in terms of Langmuir's model is at least as justifiable as for benzene. The relatively large scatter of the experimental points about the flat parts of the K *versus* log c_g curves for acetone suggests that the larger differences between the K_s and K_L values are probably due to errors incidental to the direct determination of K_s at very low c_g.

TABLE IV

SURFACE AREAS OF SORBENT AVAILABLE TO EACH MOLECULE OF SORBATE

The gas-phase concentration of sorbate was 10^{-10} mole/ml.

Sorbent	*A_1 (nm^2)*	
	Benzene	*Acetone*
Tenax GC	12.8	139.2
Porapak P	200.9	1706.1
Porapak Q	200.7	571.0

However, the most important differences are those between the K_s and K_r values. These differences may have several causes, of which the following appear to be most relevant:

(1) The specific retention volumes were measured at concentrations in the migrating chromatographic zone that exceeded the limit of linearity of the corresponding respective sorption isotherm

(2) Slower sorption mechanisms, such as dissolution in bulk polymer, become operative during long contacts of the solute with the sorbent, but are not manifested significantly in the measurement of retention data

(3) Errors due to the extrapolation of retention data at lower temperatures from those measured at higher temperatures.

A result of the non-linearity of the sorption isotherm is illustrated in Table V, for determinations of acetone in model gaseous mixtures by equilibration trapping on Tenax GC; the values were calculated by means of GC retention data. The data for acetone concentrations of up to 3.5 ppm have been taken from a paper by Janák *et*

TABLE V

DETERMINATION OF THE CONCENTRATION OF ACETONE IN MODEL GASEOUS MIXTURES BY EQUILIBRATION TRAPPING ON TENAX GC[8]

Acetone present in model mixture		*Acetone found*		*Relative error (%)*
g/l	*ppm*	*g/l*	*ppm*	
4.8	2.0	5.0	2.1	+4
5.8	2.4	5.5	2.3	−5
7.8	3.3	7.2	3.0	−8
8.4	3.5	8.0	3.4	−5
15	6.3	11	4.6	−27
19	8.0	14	5.9	−26
53	22	22	9.2	−58
720	302	260	109	−64
1800	754	470	197	−74

al.[8], and those at higher acetone concentrations are unpublished results from the same work. The concentration limit beyond which the results become grossly inaccurate complies with the concentration limit of the linearity of the corresponding sorption isotherm (*cf.*, Fig. 5).

As discussed earlier[9], the sorption properties of different batches of a given sorbent can differ appreciably. For instance, the following values are available for V_g^0 (ml/g) of acetone on Tenax GC at 20°C: 5505 (this work); 5385 (ref. 10); 4215 (ref. 8) and roughly 4900 (ref. 11, calculated from a value of 3200 at 25°C).

CONCLUSIONS

In the absence of compounds capable of competitive sorption, the retention volumes and, consequently, also the breakthrough volumes of acetone on Porapak P and Tenax GC are practically independent of the acetone concentration in the gaseous phase up to several ppm. With Tenax GC, this conclusion is in accord with the results[8] of the determination of acetone in model gaseous mixtures by a method involving equilibration trapping on Tenax GC and with the findings by Brown and Purnell[10]. The error of the calculation of breakthrough volumes from GC retention data is appreciably larger with acetone (about 15%) than with benzene (about 2%).

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