INTERFERENCE EFFECTS IN TRAPPING TRACE COMPONENTS FROM GASES ON CHROMATOGRAPHIC SORBENTS

SORPTION OF BENZENE IN THE PRESENCE OF o-XYLENE

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SUMMARY

  The sorption isotherms of benzene in the presence of o-xylene as a co-sorbate were measured in various chromatographic sorbent–nitrogen systems at 35°C. The benzene gas-phase concentration was kept at 0.5 ppm while that of o-xylene was varied within about 0.025–25 ppm. With Tenax GC, Porapak P and Porapak Q as sorbents the partition coefficients of benzene were substantially decreased due to the presence even of about 0.01 ppm o-xylene in the gaseous phase. With Apiezon K and QF-1 liquid sorbents the partition coefficients of benzene remained practically constant up to about 2.5 ppm of o-xylene in the gaseous phase.

INTRODUCTION

  In trace analysis by gas chromatography (GC), sample enrichment techniques based on the trapping of analytes in a short sorbent-packed column, thermal desorption of the deposit and GC analysis of the concentrate are widely employed. From the viewpoint of quantitation, it is expedient to distinguish between the conservation[1] and equilibration[2] modes of trapping. The analytical aspects of these two modes of trapping have already been discussed[3]. Naturally, with the conservation and equilibration modes of trapping, the maximum possible or minimum necessary sample volumes are dependent on the migration velocities and spreadings of the frontal zones of the most weakly or most strongly sorbed components respectively of the mixture analyzed in the trapping column. As has been shown earlier[1,2,4-6], in order to achieve either conservation or equilibration trapping of an analyte, the sample volume must be either smaller than $V_R - 2\sigma_V$ or larger than $V_R + 2\sigma_V$, V_R and σ_V being respectively the retention volume of the analyte, as measured on the trapping column, and the standard deviation of the differentiated frontal zone of the analyte, the median of which has migrated over the length of the trapping column. Provided that the frontal chromatographic process in the trapping column occurs in a linear Henry-law portion of the corresponding sorption isotherm, V_R refers to the concentration inflection of the frontal zone, and $\sigma_V = V_R/\sqrt{N}$ where N is the number of theoretical

plates of the trapping column under the operating conditions. V_R is related to the partition coefficient, K, by $V_R = V_M + KW_S$ where V_M and V_S are the void volume and the mass of the sorbent in the trapping column, and K is defined as $K = g_S/c_g$ where g_S and c_g are the analyte concentrations expressed respectively in units of amount of analyte substance (moles) per 1 g of the sorbent and per 1 ml of the gaseous phase at the temperature and mean pressure in the trapping column.

Provided that the sorption isotherm is linear and there are in the gas analyzed no components to interfere with sorption of the analyte in the trapping column, the partition coefficient of the analyte in the sorbent bed practically depends only on temperature. However, the sorption isotherm of a pure compound (in non-sorbed gases) on a given sorbent at a given temperature is linear only up to a certain (rather low) concentration of the compound in the gas[3,7]. Beyond this limit the partition coefficient varies markedly on changing the analyte concentration. If interfering co-sorbates are present, the partition coefficient of the analyte may be changed even when the concentration of the analyte in the gaseous phase does not exceed the linearity limit found for the sorption of pure analyte. Apparently, with sorption processes based on dissolution in bulk liquids and on adsorption on the surface of a solid material the effect of interfering substances will be substantially different. With adsorbents, which are used most frequently as trapping materials, the presence of interferents always decreases the analyte gas-phase concentration limit beyond which the sorption isotherm is non-linear. In the conservation mode of trapping, the apparent retention volume of the most weakly adsorbed component is then lowered due to the displacement of it by more strongly adsorbed ones, whereas in equilibration trapping the values of the partition coefficients (necessary to calculate the results) of all the components of the mixture analyzed differ from those found for the pure components. These variations are very difficult to assess, let alone to quantitate, and the literature data on this subject are rather scarce.

An extensive investigation of displacement effects taking place in the sorption of complex mixtures of trace components from gaseous samples on Tenax GC was
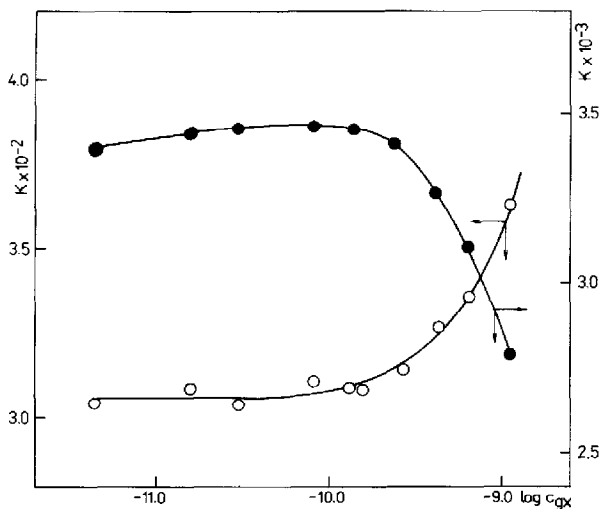

Fig. 1. Partition coefficients, K, of benzene ($\bigcirc$) and o-xylene ($\bullet$) plotted against the gas-phase concentration of o-xylene, c_{gx}. Sorbent: Apiezon K.
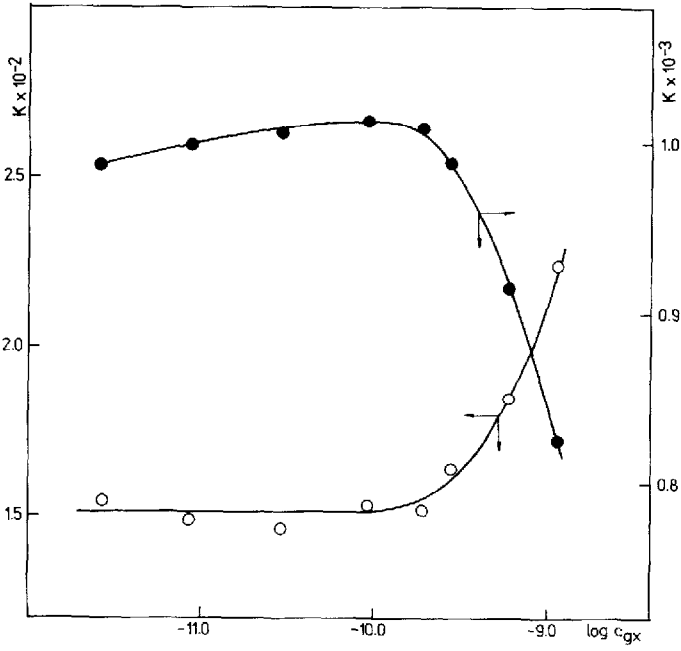
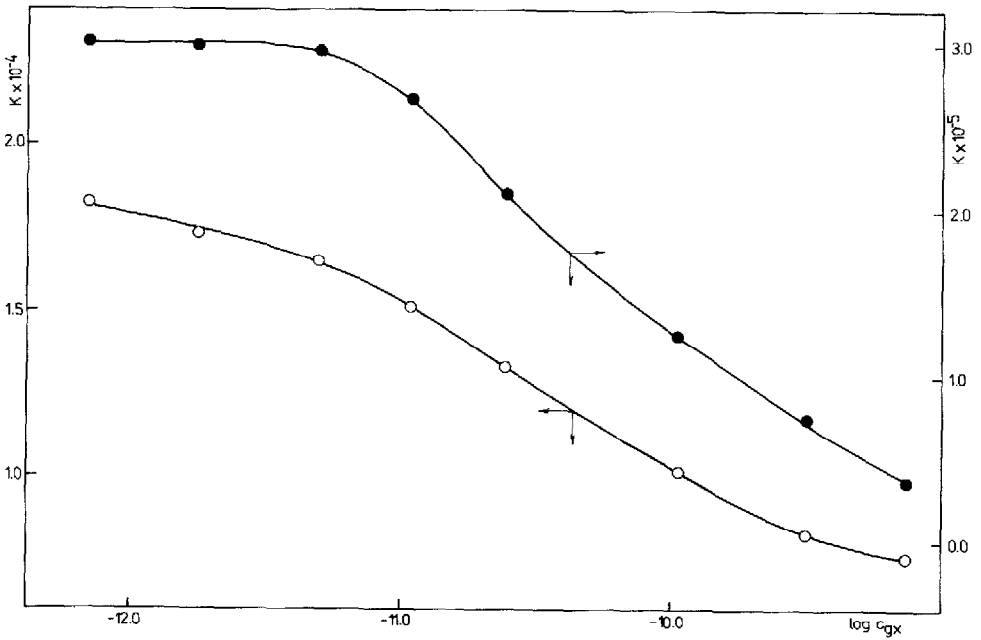Fig. 2. Plots as in Fig. 1 but with QF-1 as sorbent.

Fig. 3. Plots as in Fig. 1 with Tenax GC as sorbent.

performed by Novotný *et al.*[8]. Janák *et al.*[9] studied the effect of water on the retention of model compounds on Tenax GC. Differences amounting to $\pm 10\%$ of the values determined were found between the specific retention volumes measured using pure nitrogen and nitrogen saturated with water vapour as carrier gases. Pellizzari *et al.*[10] found that the water content had no significant effect on the breakthrough volumes of different model compounds on Tenax GC. Gold *et al.*[11] studied the trapping of acrolein from both dry and water-containing model acrolein–air mixtures and found that the breakthrough volumes of acrolein decreased due to the presence of water. Sydor and Pietrzyk[12] investigated the effect of the presence of water and methyl ethyl ketone on the retention of organic compounds of different polarities on the XAD adsorbents. With both water and methyl ethyl ketone as co-sorbates, decreases as well as increases in solute retention were observed, depending on the solute and sorbent polarities. Brown and Purnell[5] measured directly the breakthrough volumes of acetone and acrylonitrile on Tenax GC traps and found differences of $\pm 5\%$ to occur due to the presence of water in the gas analyzed. Bertoni *et al.*[13] found significant differences between the breakthrough volumes measured for sorbates alone in air and for mixtures of them on a column packed with Carbopack B.

In our earlier work[3,7], the sorption isotherms of model compounds alone in nitrogen were measured on different sorbents. The aim of the present work was to provide more data by measuring the isotherms of benzene in the presence of *o*-xylene as a co-sorbate in various sorbent–nitrogen systems, employing both non-volatile liquids and organic adsorbents as sorbent phases.

EXPERIMENTAL

Benzene and *o*-xylene, analytical-reagent grade (Fluka, Buchs, Switzerland), and high-purity nitrogen (Technoplyn, Ostrava, Czechoslovakia) were used as model sorbates and carrier, respectively.

Sorbents: Apiezon K (AEI, Manchester, Great Britain), 9.70% on Inerton AW DMCS, 0.125–0.16 mm (Lachema, Brno, Czechoslovakia); silicone oil QF-1 (Carlo Erba, Milan, Italy) on Inerton AW DMCS (as with Apiezon K); Tenax GC, 0.175–0.25 mm (Applied Science Labs., State College, PA, U.S.A.); Porapak Q, 0.175–0.31 mm, and Porapak P, 0.15–0.175 mm (Waters Assoc., Milford, MA, U.S.A.).

Instruments and procedures

The model mixtures of nitrogen with known trace contents of benzene and *o*-xylene were prepared by the saturation method, employing the apparatus described previously[3,14]. The concentration of benzene was kept constant while that of *o*-xylene was varied over a range of about three orders of magnitude. The gas was drawn through a short column packed with a known amount of the sorbent material investigated, until sorption equilibrium was attained. Then the benzene and *o*-xylene entrapped in the column were thermally desorbed, purged by a stream of pure nitrogen and determined by GC. The construction of the trap as well as the entire procedure of trapping, thermal desorption, GC analysis and the calculation of the results were as described earlier[3]. The concentrates recovered from the trap were analyzed on a modified 402 Hewlett-Packard (Avondale, PA, U.S.A.) gas chromatograph equipped with a Porapak P column and a flame ionization detector. The chromatograph
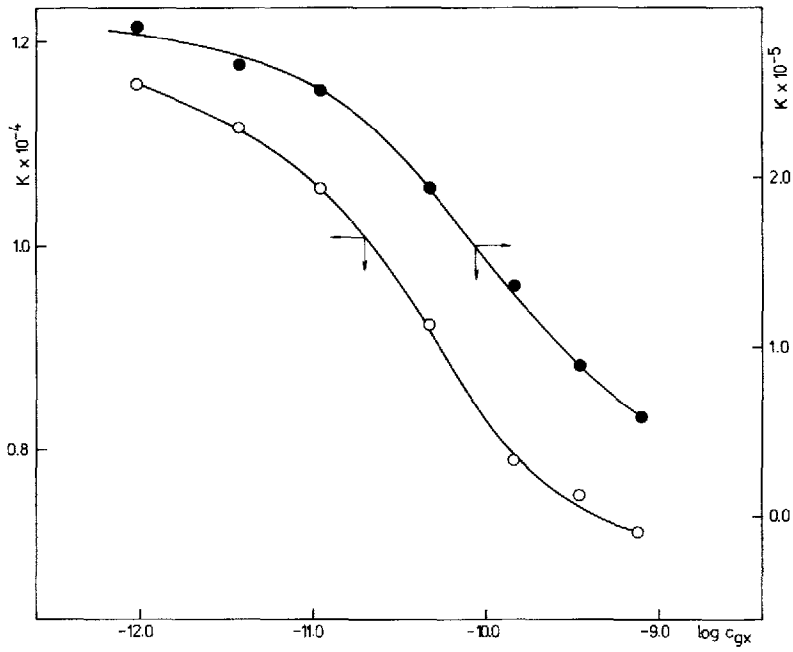
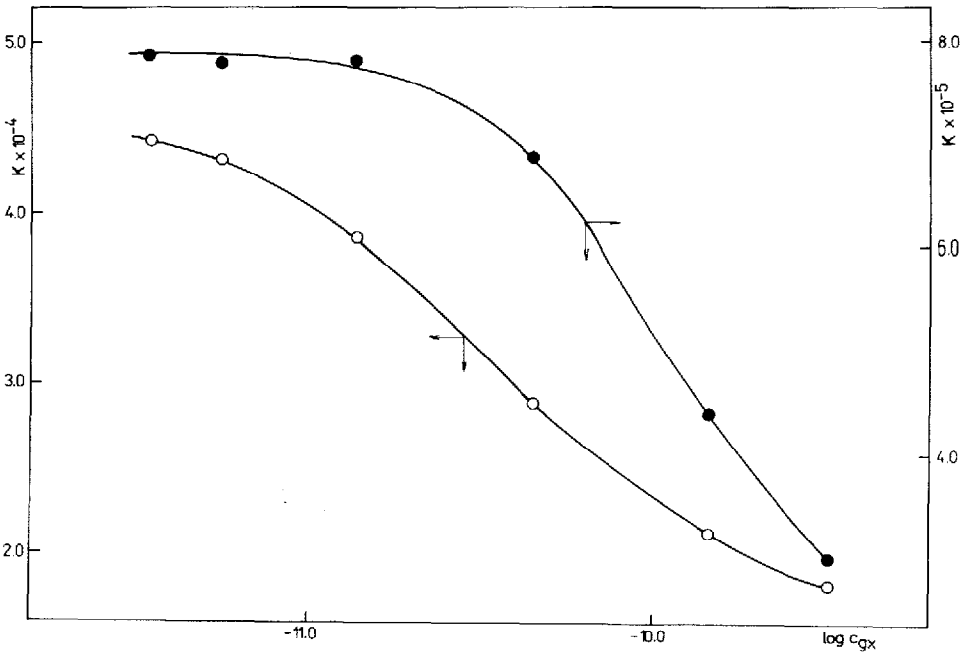Fig. 4. Plots as in Fig. 1 with Porapak P as sorbent.

Fig. 5. Plots as in Fig. 1 with Porapak Q as sorbent.

output data were processed by an Infotronics (Shannon Airport, Ireland) CRS 100 integrator.

RESULTS AND DISCUSSION

With all the systems studied the concentration of benzene in the gas was set to $2 \cdot 10^{-11}$ mol/ml, while the concentrations of o-xylene ranged from about $1 \cdot 10^{-12}$ to $1 \cdot 10^{-9}$ mol/ml at 35°C, the trapping column being kept at 35°C too. For both benzene and o-xylene the partition coefficients, K, defined as solute mass per unit mass of sorbent divided by solute mass per unit volume of gas, were calculated and plotted against the logarithm of the o-xylene concentration, c_{gx}, in the gaseous phase. Figs. 1 and 2 show the results obtained with the two gas–liquid systems studied, *i.e.*, Apiezon K and QF-1, respectively. In both cases the partition coefficient of benzene remains practically constant (linear isotherm) up to an o-xylene concentration of about 10^{-10} mol/ml in the gaseous phase. Beyond this limit the K of benzene increases with increasing concentration of o-xylene while the K of o-xylene decreases. The changes of K with c_{gx} may be due to changes in the solute activity coefficient, gasphase non-ideality and molar volume of the sorbent, of which the first factor is probably most important. No attempt at a more detailed explanation of the courses of the K *versus* log c_{gx} curves obtained has been made at this stage of the investigation.

As expected, completely different behaviours are obtained when using adsorbents as packing materials (Figs. 3–5). Whereas there is an indication of a practically linear isotherm for o-xylene at c_{gx} below about $5 \cdot 10^{-12}$, $1 \cdot 10^{-12}$ and $1 \cdot 10^{-11}$ mol/ml with Tenax GC, Porapak P and Porapak Q, no such course can be observed with benzene. Hence, even at o-xylene gas-phase concentrations as low as 10^{-12} mol/ml the interference effect of o-xylene is large enough to decrease markedly the K values of benzene. In the absence of any interferent the K values of benzene on the adsorbents quoted were found[3] to be practically constant up to about $4 \cdot 10^{-11}$ mol/ml of benzene in the gaseous phase, *i.e.*, about twice as high a concentration as that used in the present work.

CONCLUSIONS

The sorbent/gas partition coefficients measured for 0.5 ppm of gas-phase benzene in the presence of o-xylene as a co-sorbate on Tenax GC, Porapak P and Porapak Q at 35°C are strongly dependent on the o-xylene concentration. Even at o-xylene gas-phase concentrations as low as about 0.01 ppm the partition coefficients of benzene are substantially smaller than those measured in the absence of any cosorbate under the same conditions. With Apiezon K and QF-1 liquid sorbents the partition coefficients of benzene remain practically unaffected by the presence of up to about 2.5 ppm o-xylene in the gaseous phase.

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