Journal of Chromatography, 447 (1988) 170–176
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 580

Note

Sorption of benzene on Tenax

J. VEJROSTA*, M. MIKEŠOVÁ, A. ANSORGOVÁ and J. DROZD
Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Leninova 82, 611 42 Brno (Czechoslovakia)

(First received November 27th, 1987; revised manuscript received April 11th, 1988)

The trapping of organic admixtures from gaseous mixtures on solid sorbents is mostly carried out by the method of conservation trapping[1]. Equilibration trapping was introduced[2] as an alternative and both methods were discussed in detail in earlier papers[3,4]. The wide use of the conservation method results from its relative simplicity and the possibility of easy experimental estimation of the safe sampling volumes.

The rôle played in both methods of interference (or displacement) effects arising from the competitive sorption of solutes on the sorbent surface was described in ref. 5. In the equilibration mode, the values of the resulting solute partition coefficients are necessary for the calculation of the solute concentrations in the mixture analyzed. The problems connected with the calculation or reasonable estimation of the relative changes in the partition coefficients at equilibrium and those in the absence of the interferents are probably the main reason for the rare use of the equilibration method.

Previously[6], the extent of the displacement effect on the benzene partition coefficient was investigated for three interferents, *n*-pentane, *o*-xylene and *n*-butanol.

The sorbent-phase concentrations of the interferents that bring about the same change in the partition coefficient of benzene do not differ much from each other. With benzene alone, the same decrease in its partition coefficient is achieved also at practically the same sorbent-phase concentration.

Under these circumstances, it is possible to assess the change in the solute partition coefficient from the known overall concentrations of the interferents in the sorbent, which is very important in view of the equilibration mode of trapping.

We suggested the following procedure: the known overall sorbent-phase concentration, easily determined from an analysis of the contents of the enrichment tube, is taken as the concentration of the model solute, for which the sorption isotherm equation is known. The change in the value of its partition coefficient relative to that at infinite dilution is calculated. The same relative changes are then supposed for the partition coefficients of solutes in the mixture analyzed.

The aim of this work is to find the form of the sorption isotherm equation, describing the sorption of non-polar and slightly polar compounds on Tenax. We chose benzene as a typically non-polar model compound and a set of its partition coefficients were measured over a wide range of concentrations and at four temperatures. An attempt was made to find the isotherm equation correlating the data obtained, which can be used in the equilibration method in the way mentioned above.

0021-9673/88/$03.50

THEORETICAL

If the solute partition coefficient is defined as

$$K = c_s/c_g \tag{1}$$

where c_s is the solute concentration in the sorbent phase in mol/g and c_g the corresponding concentration in the gaseous phase in mol/ml, the relationship between the specific retention volume of the solute, V_g, and its partition coefficient is given by

$$V_g = K \cdot \frac{273.15}{T} \tag{2}$$

where T is the absolute temperature.

The specific retention volume, unlike the partition coefficient, is a quantity the value of which does not reflect the dependence of the volumes of the sorbent and the mobile phase on temperature.

The change in the standard Gibbs function of sorption, ΔG_s^0, is related to the specific retention volume, V_g, by

$$\Delta G_s^0 = -2.3\ RT \log\,(k^0 V_g) \tag{3}$$

where k^0 is a constant dependent on the choice of the standard states[7] and R and T are the universal gas constant and the absolute temperature of the chromatographic column at the measurement of V_g, respectively. As $\Delta G_s^0 = \Delta H_s^0 - T\Delta S_s^0$, where ΔH_s^0 and ΔS_s^0 are the changes in the standard enthalpy and entropy of sorption, eqn. 3 can be rewritten as

$$\log V_g = -\frac{\Delta H_s^0}{2.3\ RT} + \frac{\Delta S_s^0}{2.3\ R} - \log k^0 \tag{4}$$

or

$$\log V_g = A + B/T \tag{5}$$

where $A = (\Delta S_s^0/2.3\ R) - \log k^0$ and $B = -\Delta H_s^0/2.3\ R$. Within certain temperature limits the quantities A and B are virtually constant.

Eqns. 2–5 apply exactly to infinite dilution ($c_s \rightarrow 0, c_g \rightarrow 0$) and the relationship between the solute concentrations is given by Henry's law

$$c_s = K_0 c_g \tag{6}$$

where K_0 is the solute partition coefficient. The interval of the solute concentrations in which eqn. 6 is valid defines the linear part of the sorption isotherm. Outside it the course of the sorption isotherm is generally non-linear and the values of the quantities K, A and B depend on the sorbent-phase concentration, c_s. The use of eqns. 2–5 is restricted to a constant value of c_s.

Since c_s and c_g are interconnected through K, the dependence of the partition coefficient on c_s is easily transformed to a dependence of c_g and *vice versa*. If the isotherm equation describing the relationship between c_s and c_g is available, the determination of the temperature dependence of its adjustable parameters will lead to the equation from which the partition coefficient can be determined at any temperature and any solute concentration (c_s or c_g). With the use of eqns. 2–5, the concentration dependence of the standard thermodynamic functions for the sorption process can be determined.

EXPERIMENTAL

The method of preparation of the model mixture, the measurements and calculation of the partition coefficients as well as the chemicals used were described earlier[3,8]. The partition coefficients of benzene were determined as a function of its concentration at four temperatures: 19.9, 27.1, 35.0 and 41.7°C. The interval of gas-phase concentrations was $6.8 \cdot 10^{-12}$–$7.0 \cdot 10^{-7}$ mol/ml.

RESULTS AND DISCUSSION

The Langmuir isotherm was successfully used for the description of benzene sorption on different sorbents[3] as follows.

Let the fraction of the active sites occupied by sorbed molecules of the solute be defined as $\alpha = c_s/c_s^*$ where c_s and c_s^* are the actual solute concentration in the sorbent and the concentration at which all available sites are occupied, respectively.

The significance of α is analogous to that of the parameter θ in Langmuir's model. The rates of desorption and sorption are defined as $r_d = k_d\alpha$ and $r_s = K_s(1 - \alpha)c_g$, respectively, where k_d and k_s are the respective rate constants. At equilibrium, $r_d = r_s$ and we can write

$$c_s = k_e c_s^* c_g/(1 + k_e c_g) \tag{7}$$

where $k_e = k_s/k_d$. Thus:

$$\frac{c_s}{c_g} = K = \frac{k_e c_s^*}{1 + k_e c_g} \tag{8}$$

Eqn. 8 can be rearranged as

$$\frac{1}{c_g} = \frac{k_e c_s^*}{c_s} - k_e \tag{9}$$

which is a linearized form of the Langmuir isotherm.

The solute partition coefficient at infinite dilution is given by:

$$\lim_{c_g \to 0} K = k_e c_s^* = K_0 \tag{10}$$

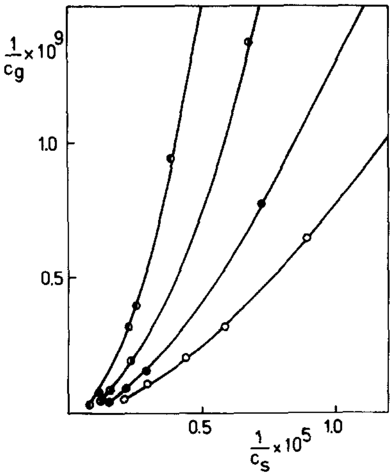

Fig. 1. The relationship $1/c_g$ *vs.* $1/c_s$ at high benzene concentrations: ◐, 19.9; ◑, 27.1; ●, 35.0 and ○, 41.7°C.

By plotting $1/c_g$ against $1/c_s$, a straight line having the slope

$$\frac{\mathrm{d}\,(1/c_g)}{\mathrm{d}\,(1/c_s)} = k_e c_s^* = K_0 \tag{11}$$

will be obtained if the Langmuir isotherm is appropriate for a given system.

We have treated our data in this way and graphical representation of the sorption isotherms in the coordinates $1/c_g$ *versus* $1/c_s$ is illustrated in Fig. 1. Significant deviations from linearity occur at higher benzene concentrations as already indicated elsewhere[3]. The maximum benzene gas-phase concentration up to which the Langmuir isotherm is applicable is approximately $5 \cdot 10^{-9}$ mol/ml.

The regression criterion, R_s, was defined by

$$R_s = \sum_i \frac{|K_{i,\mathrm{exp}} - K_{i,\mathrm{calc}}|}{K_{i,\mathrm{exp}}} \tag{12}$$

and its value for the Langmuir isotherm was used to test further isotherms. About twenty isotherm equations previously described in the literature have been tested and for a surprisingly low number of equations the value of R_s was significantly lower than in the case of the Langmuir isotherm.

Even if a very good correlation was obtained, such as in the case of the Freundlich[9], Temkin[10] and especially Dubinin–Astachov[11] isotherm equations in the non-linear parts of the sorption isotherms, the condition for the transition to the Henry law in the low concentration range was not fulfilled.

Simultaneously we tested several modifications of eqns. 8 by adding one adjustable parameter. Of these

$$K = K_0/(1 + k_1 c_g)^{k_2} \tag{13}$$

where K_0 is the partition coefficient at infinite dilution and k_1, k_2 are adjustable parameters, appeared to be the most suitable. The lowest values of R_s were obtained from all the isotherm equations tested and this equation permits the transition to the Henry law if $c_g \to 0$.

The individual isotherms were correlated by eqn. 13 with the following average deviations between the calculated and experimental values of the partition coefficients: 1.2, 2.6, 1.0 and 2.2% relative in the direction of increasing temperature.

The solute sorbent-phase concentration, c_s, is of much greater importance if one keeps in mind the aim of this work. Eqn. 13 was therefore used with variable c_s

$$K = K_0/(1 + k_3 c_s)^{k_4} \tag{14}$$

and due to the interconnection of c_g and c_s through K it is not surprising that the correlation of the individual isotherms was as good as that obtained with the use of eqn. 13.

With the relationships between K and c_s which followed from the fitting of the data by eqn. 14, an attempt was made to find the dependence of the parameters A, B of eqn. 5 on the sorbent-phase concentration, c_s. The partition coefficients were calculated from the individual isotherms for a number of selected concentrations, c_s. With the use of eqns. 2 and 5, the values of A and B were calculated by linear regression of four V_g values obtained for each concentration, c_s. The resulting dependences of A and B on c_s, obviously as a consequence of the insufficient number of points for the linear regression, exhibited irregular courses with local extremes.

It was clear that the only way to proceed further was to determine the temperature dependence of the adjustable parameters, k_3 and k_4, in eqn. 14. Their values obtained from the fitting of the individual isotherms by eqn. 14, indicated that k_3 was almost independent of temperature and parameter k_4 was linearly dependent on $1/T$.

The partition coefficient, K_0, at infinite dilution is given by

$$K_0 = \lim_{c_s \to 0} V_g \frac{T}{273.15} \tag{15}$$

and its temperature dependence is that of the specific retention volume in this range (eqn. 5).

Based on these results, eqn. 16 was proposed

$$K = \frac{T}{273.15} \cdot \frac{10^{a+b/T}}{(1 + ec_s)^{-(c+d/T)}} \tag{16}$$

with five adjustable parameters a, b, c, d, e. With the use of eqn. 2, the relationship log $V_g = \mathrm{f}(T, c_s)$ is obtained:

$$\log V_g = a + \frac{b}{T} + c \log(1 + ec_s) + \frac{d}{T} \cdot \log(1 + ec_s) \tag{17}$$

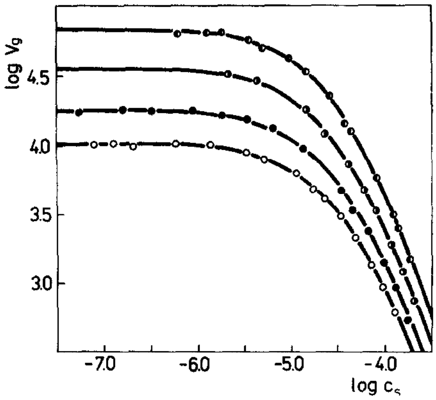

Fig. 2. The relationship log V_g *vs.* log c_s calculated by use of eqn. 17 (full lines) and experimental points (see Fig. 1).

From the correlation of the whole set of experimental data by eqn. 17, the following values of the adjustable parameters were obtained: $a = -7.0618$, $b = 3486.69$, $c = 1.42312$, $d = -1019.63$ and $e = 28964.9$; V_g (ml/g), c_s (mol/g).

In Fig. 2 the experimental data and the data calculated according to eqn. 17 are plotted in the coordinates log V_g *vs.* log c_s. An average deviation of 2.67% relative was found between the calculated and experimentally determined values of the partition coefficients.

It is evident that, at a constant temperature, eqn. 16 is reduced to eqn. 14. The values of parameters a and b are identical with the values of parameters A and B at infinite dilution, usually determined by elution gas chromatography

$$a = \lim_{c_s \to 0} A, \; b = \lim_{c_s \to 0} B$$

Our values of a and b are in a very good agreement with parameters A and B in eqn. 5 determined previously[3] for the system nitrogen–benzene–Tenax ($A = -6.9629$, $B = 3455.25$).

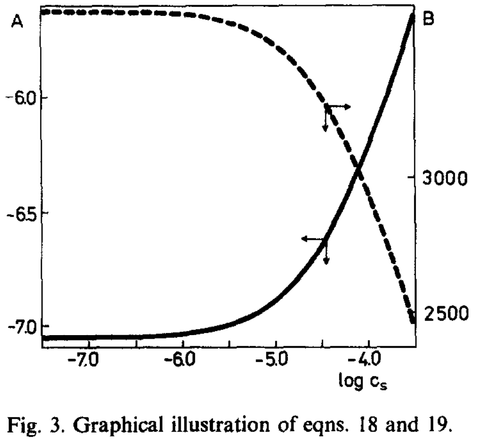

Fig. 3. Graphical illustration of eqns. 18 and 19.

The dependence of parameters A and B on the sorbent-phase solute concentration is expressed by

$$A = a + c \log (1 + ec_s) \tag{18}$$

$$B = b + d \log (1 + ec_s) \tag{19}$$

from which the standard thermodynamic functions of sorption can be calculated for any sorbent-phase solute concentration. These dependences are illustrated in Fig. 3.

CONCLUSIONS

The equation of the Langmuir isotherm modified empirically was proposed for the description of the relationship between gas-phase and sorbent-phase solute concentrations. A simple temperature dependence of the adjustable parameters was found and the resulting eqn. 17 describes well the whole set of experimental data with an average deviation of 2.67% relative, which is in agreement with the estimated experimental error (<3% relative).

Eqn. 17 can be used to calculate relative changes in the partition coefficients of the solute in the equilibration method of trapping under the above mentioned assumption.

The absolute values of the partition coefficients of benzene are of importance in the conservation method of trapping.

The surface of Tenax contains a relatively low portion of the active sites with a virtually constant value of the change in the standard Gibbs function of sorption, ΔG_s^0. The concentration necessary for a complete coverage of this part is approximately 10^{-6} mol of benzene per gram of Tenax. With increasing sorbent-phase concentration the active sites with lower values of ΔG_s^0 become available. This leads to a strong dependence of the parameters A and B of eqn. 5 on the sorbent-phase solute concentration, with consequences for both methods of trapping.

REFERENCES

1 F. R. Cropper and S. Kamiński, *Anal. Chem.*, 35 (1963) 735.
2 J. Novák, V. Vašák and J. Janák, *Anal. Chem.*, 37 (1965) 660.
3 J. Vejrosta, M. Roth and J. Novák, *J. Chromatogr.*, 217 (1981) 167.
4 J. Vejrosta, M. Roth and J. Novák, *J. Chromatogr.*, 265 (1983) 215.
5 J. Vejrosta, M. Mikešová and J. Novák, *J. Chromatogr.*, 324 (1985) 269.
6 J. Vejrosta, M. Mikešová and J. Novák, *J. Chromatogr.*, 354 (1986) 59.
7 M. R. James, J. C. Giddings and R. A. Keller, *J. Gas Chromatogr.*, 3 (1965) 57.
8 J. Vejrosta and J. Novák, *J. Chromatogr.*, 175 (1979) 261.
9 H. Freundlich, *Trans. Faraday Soc.*, 28 (1932) 195.
10 M. J. Temkin, *Zh. Fiz. Khim.*, 14 (1940) 1153.
11 M. M. Dubinin and V. A. Astachov, *Adv. Chem. Ser.*, 102 (1971) 59.