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Note

Sorption of *n*-alkanes on Tenax

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In our recent paper[1] an empirically modified Langmuir isotherm equation was derived for the description of the relationship between the gas-phase and the sorbent-phase benzene concentrations in a benzene–nitrogen–Tenax system.

The resulting equation

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

where V_g (ml/g) is the solute specific retention volume, c_s (mol/g) is the solute sorbent-phase concentration and T is the absolute temperature of the system, contains five adjustable parameters a, b, c, d and e. Under the conditions of infinite dilution ($c_s \rightarrow 0$), eqn. 1 reduces to

$$\log V_g = a + b/T \tag{2}$$

which is the usual expression for the temperature dependence of the specific retention volume.

If the gas-phase solute concentration, c_g, has dimensions mol/ml, the following equations apply

$$K = c_s/c_g \tag{3}$$

$$V_g = K \cdot \frac{273.15}{T} \tag{4}$$

where K is the solute partition coefficient.

This work was undertaken to test the applicability of eqn. 1 to a description of non-polar solute sorption on Tenax. A series of *n*-alkanes (C_5–C_8) was chosen because it makes possible verification of the assumption of linear dependence of the thermodynamic functions of sorption on the number of methylene groups for the non-linear part of the sorption isotherm. The validity of this concept for the infinite dilution region was demonstrated by Novák *et al.*[2].

EXPERIMENTAL

The methods for the preparation of the model gaseous mixtures, the measurements and the calculation of the partition coefficients were described earlier[3,4]. The purity of n-alkanes was better than 99.5% (Fluka, Switzerland) and they were used without further purification.

n-Alkane partition coefficients (155 values) were measured at temperatures in the range 19.9–50.3°C and at the gas-phase concentrations $6 \cdot 10^{-12}$–$7.5 \cdot 10^{-7}$ mol/ml.

THEORETICAL

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

$$\Delta G_s^0 = -2.3 \, RT \log (k^0 V_g) \tag{5}$$

where k^0 is a constant dependent on the choice of the standard state[5].

Since

$$\Delta G_s^0 = \Delta H_s^0 - T\Delta S_s^0 \tag{6}$$

where ΔH_s^0 and ΔS_s^0 are the changes in the standard enthalpy and entropy of sorption, respectively, eqn. 5 can be rewritten as:

$$\log V_g = -\frac{\Delta H_s^0}{2.3 \, RT} + \frac{\Delta S_s^0}{2.3 \, R} - \log k^0 \tag{7}$$

From a comparison of eqns. 2 and 5 it follows that:

$$a = (\Delta S_s^0/2.3 \, R) - \log k^0 \tag{8}$$

$$b = -\Delta H_s^0/2.3 \, R \tag{9}$$

Assuming additivity[6] of the contributions of the individual parts of the molecule to the values of ΔH_s^0 and ΔS_s^0, we can write for n-alkanes

$$\Delta H_s^0 = 2 \, \Delta H_s^0(CH_3) + n\Delta H_s^0(CH_2) \tag{10}$$

$$\Delta S_s^0 = 2 \, \Delta S_s^0(CH_3) + n\Delta S_s^0(CH_2) \tag{11}$$

where n is the number of methylene groups in the n-alkane molecule. Combining eqns. 8–11

$$a = c_2 n + c_1 \tag{12}$$

$$b = c_4 n + c_3 \tag{13}$$

where the parameters c_1, c_2, c_3 and c_4 have the following physical meanings

$$c_1 = 2\Delta S_s^0(CH_3)/2.3\ R - \log k^0 \tag{14}$$

$$c_2 = \Delta S_s^0(CH_2)/2.3R \tag{15}$$

$$c_3 = -2\Delta H_s^0(CH_3)/2.3R \tag{16}$$

$$c_4 = -\Delta H_s^0(CH_2)/2.3R \tag{17}$$

and hence we can finally write

$$\log V_g = c_1 + c_2 n + c_3/T + c_4 n/T \tag{18}$$

which is valid under the condition of infinite dilution or, in other words, in the linear parts of the sorption isotherms.

Eqn. 1 can be rewritten with the use of the additivity assumption if we suppose the same linear dependence of parameters c, d and e on the number of methylene groups:

$$c = c_6 n + c_5 \tag{19}$$

$$d = c_8 n + c_7 \tag{20}$$

$$e = c_{10} n + c_9 \tag{21}$$

By combining eqns. 1, 12, 13 and 19–21 we obtain

$$\log V_g = c_1 + c_2 n + c_3/T + c_4 n/T + (c_5 + c_6 n)Y + (c_7 + c_8 n)Y/T \tag{22}$$

which describes the sorption properties of the whole homologous series of n-alkanes. The function Y reflects the extent of the deviations from linearity of the sorption isotherm:

$$Y = \log [1 + (c_{10} n + c_9)c_s] \tag{23}$$

In the case of $c_s \to 0$ the function Y is zero and eqn. 22 is transformed into eqn. 18.

RESULTS AND DISCUSSION

The whole set of experimental data was correlated by eqn. 22 with the use of the simplex method on a Hewlett-Packard 9845 A/S computer. The optimized values of parameters c_1–c_{10} are summarized in Table I. For comparison, the values of parameters c_1–c_4 of eqn. 18 from ref. 2 are also presented. The agreement between these two sets of parameters is only qualitative, obviously as a consequence of the different temperature intervals (75–95°C). In Figs. 1–4 the experimental data are plotted in the coordinates $\log V_g$ vs. $\log c_s$ together with the courses calculated from

TABLE I

SUMMARY OF ADJUSTABLE PARAMETERS

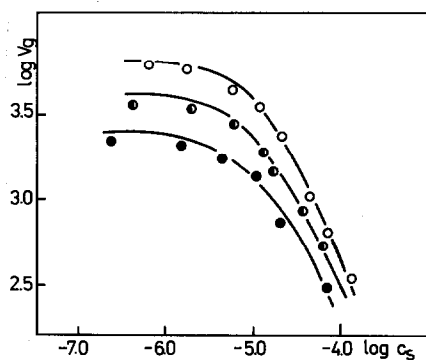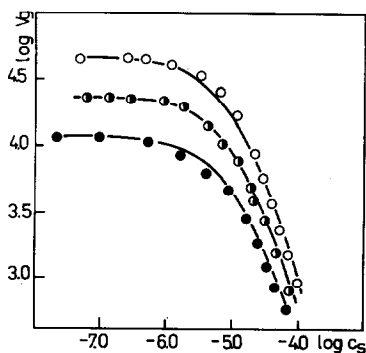| c_i	Eqn. 22	Eqn. 18 from ref. 2
1	−2.614858	−5.4550
2	−1.214159	−0.42981
3	1236.3472	2052.74
4	579.9602	340.363
5	0.480481	
6	0.383629	
7	−253.461	
8	−212.9841	
9	15 309.77552	
10	16 077.803	

Fig. 1. Relationship of log V_g vs. log c_s for n-pentane on Tenax calculated by eqn. 22 (full lines) and experimental points (○ = 19.9; ◐ = 27.1; ● = 34.7°C).

Fig. 2. Relationship of log V_g vs. log c_s for n-hexane on Tenax calculated by eqn. 22 (full lines) and experimental points(○ = 19.9; ◑ = 27.1; ● = 35.1°C).
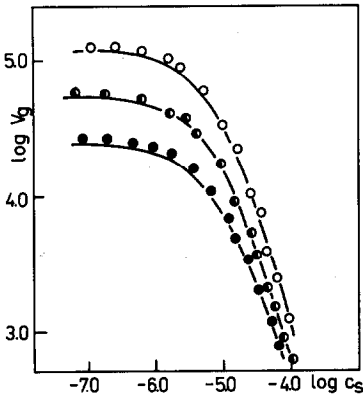
Fig. 3. Relationship of log V_g vs. log c_s for n-heptane on Tenax calculated by eqn. 22 (full lines) and experimental points (O = 27.1; ◑ = 35.0; ● = 43.15°C).
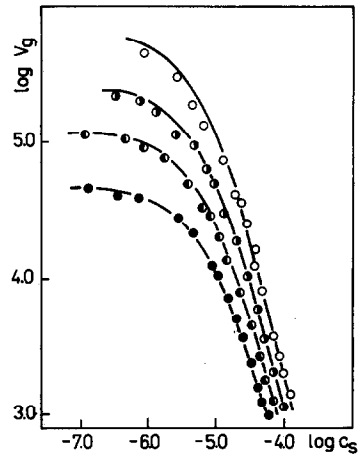
Fig. 4. Relationship of log V_g vs. log c_s for n-octane on Tenax calculated by eqn. 22 (full lines) and experimental points (O = 27.1; ◑ = 35.0; ◑ = 41.7; ● = 50.3°C).

eqn. 22. The average deviation between the calculated and the experimental values of the specific retention volume is 8.5% relative, more than twice that in ref. 1. This is partly due to the systematic deviations in the regions of low gas-phase concentrations.

In the non-linear parts of the sorption isotherms, eqn. 2 can still be used to describe the temperature dependence of the specific retention volume, of course under the condition of a constant c_s value. In this case

$$\log V_g = A + B/T \qquad (c_s = \text{constant}) \tag{24}$$

and the following relationships apply:

$$a = \lim_{c_s \to 0} A \tag{25}$$

$$b = \lim_{c_s \to 0} B \tag{26}$$

$$A = n(c_2 + c_6 Y) + (c_1 + c_5 Y) \tag{27}$$

$$B = n(c_4 + c_8 Y) + (c_3 + c_7 Y) \tag{28}$$

The physical meanings of the expressions in parentheses are the same as those defined by eqns. 14–17.

In Figs. 5 and 6 the dependences of parameters A and B on the sorbent-phase solute concentration, c_s, are shown. They confirm the conclusions about the non-homogeneity of the Tenax surface[1]. These phenomena can also be caused by the
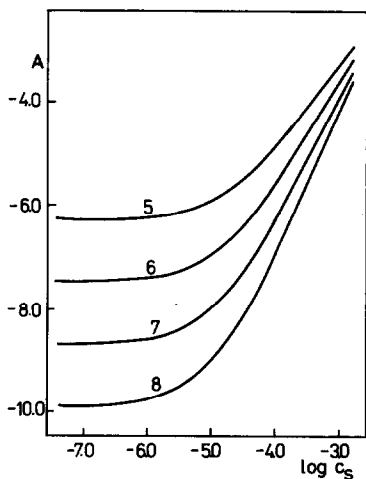
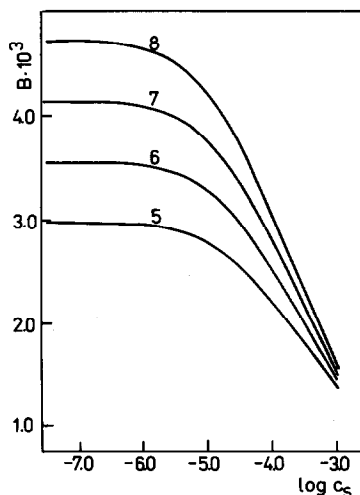Fig. 5. Dependence of parameter A on the sorbent-phase concentration, c_s, for the series of n-alkanes (C_5–C_8).

Fig. 6. Dependence of parameter B on the sorbent-phase concentration, c_s, for the series of n-alkanes (C_5–C_8).

presence of different pores in a porous adsorbent (micropores, transition pores, as well as macropores) and by an unequal use of the internal surfaces of the adsorbent throughout a range of adsorbates possessing different molecular areas.

The values of the gas-phase solute concentrations up to which the courses of the sorption isotherms are linear were determined: n-pentane (9.4), n-hexane (1.0), n-heptane (0.11) and n-octane (0.012 ppm).

CONCLUSION

The applicability of eqn. 1 to the description of the sorption behaviour of non-polar solutes on Tenax was demonstrated. With the use of the additivity concept, eqn. 22 was derived, which permits simultaneous correlation of logarithms of the specific retention volumes of homologous compounds with the number of methylene groups, temperature and sorbent-phase solute concentration. The extrapolated values of the specific retention volumes can also be obtained for other members of homologous series of n-alkanes. The concept was confirmed to be valid also for homologous series of n-alcohols[7].

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