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Note

Sorption of primary *n*-alkanols on Tenax

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In a previous paper [1], an empirically modified Langmuir isotherm equation [2]:

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

where V_g (ml/g) is the solute specific retention volume, c_s (mol/g) is the solute sorbent-phase concentration, T is the absolute temperature and a, b, c, d and e are adjustable parameters, was successfully used for the description of *n*-alkane sorption in an *n*-alkane–nitrogen–Tenax system. The assumption of a linear dependence of the thermodynamic functions of sorption on the number of methylene groups in the solute molecule [3] leads to

$$\log V_g = c_1 + c_2n + c_3/T + c_4n/T + (c_5 + c_6n)Y + (c_7 + c_8n)Y/T \tag{2}$$

where n is the number of methylene groups in the *n*-alkane chain, which describes the sorption properties of the whole homologous series. The function Y reflects the extent of the deviation from linearity of the sorption isotherm:

$$Y = \log[1 + (c_9 + c_{10}n)c_s] \tag{3}$$

An average relative deviation of 8.5% was found between the calculated and the experimental values of the specific retention volume (C_5–C_8 *n*-alkanes in the temperature range 19.9–50.3°C and at gas-phase concentrations of $6 \cdot 10^{-12}$–$7.5 \cdot 10^{-7}$ mol/ml) with use of eqn. 2. This was partly due to the systematic deviations at low gas-phase concentration [1]. When the individual sorption isotherm are correlated by eqn. 1, the values of the average relative deviations decrease to 3–4%.

The aim of this work was to demonstrate the correlation capabilities of eqns. 1 and 2 for the description of the sorption isotherms of the homologous series of primary *n*-alkanols in mixture with nitrogen on Tenax.

EXPERIMENTAL

The preparation of standard gaseous mixtures, the measurements and the calculation of the partition coefficients were described previously [4,5]. The purity of the *n*-alkanols (C_2–C_5) (Fluka, Buchs, Switzerland) was better than 99.5% and they were used without further purification. *n*-Alkanol partition coefficients (208 values) were measured at temperatures in the range 13.5–41.7°C and at gas-phase concentrations of $2.1 \cdot 10^{-12}$–$2.7 \cdot 10^{-7}$ mol/ml.

RESULTS AND DISCUSSION

First, eqn. 1 was used to correlate the sets of sorption isotherms of the individual primary *n*-alkanols. The results of the optimization are summarized in Table I.

The values of the average deviations increase with increasing carbon number and the average value of 4.65% corresponds with the estimated experimental error of 4–5%. The increased values in comparison with those for non-polar compounds (benzene, *n*-alkanes) are obviously connected with the experimental method used. As already found with acetone [6], the experimental reproducibility of the data is worse for polar than for non-polar compounds.

The linear dependence of the parameters of eqn. 1 on the number of methylene groups is the basic condition for successful application of the additivity principle[3]. Table I shows a very good linear dependence of the parameters *a, b* and *d* on the methylene number and the lack of a dependence for *c* and *e*. In spite of this, the whole homologous series of *n*-alkanols was correlated by eqn. 2 and the resulting parameters are given in Table II. An average relative deviation of 18.3% was found, double that for *n*-alkanes, as expected. The results are illustrated graphically in Fig. 1 for *n*-propanol. Marquardt's algorithm was used for the calculation of non-linear parameters [7].

CONCLUSION

The modified Langmuir isotherm equation (eqn. 1) was successfully applied for the description of sorption isotherms of primary *n*-alkanols. The description of the whole homologous series of *n*-alkanols by eqn. 2, which follows from the application of the additivity principle, results in an average relative deviation of *ca.* 18%. This is still

TABLE I

SUMMARY OF OPTIMIZED PARAMETERS OF EQN. 1 FOR PRIMARY *n*-ALKANOLS

n is the number of methylene groups between two carbon atoms in the molecule of primary *n*-alkanols $CH_3(CH_2)_nCH_2OH$; *a, b, c, d* and *e* are the parameters in eqn. 1; $\Delta_i(\%) = 100V_{g,calc} - V_{g,exp}/V_{g,exp}$; the average relative error is defined as $\bar{\Delta}_i\ (\%) = \sum_i \Delta_i/i$, where *i* is the number of experimental points.

n	a	b	c	d	e	i	$\bar{\Delta}_i$ (%)
0	−6.5859	2850.1	2.1225	− 799.90	24986.6	56	2.69
1	−7.0647	3249.89	1.8636	−1000.02	20012.7	50	3.28
2	−7.4331	3600.13	1.9747	−1199.95	20965.5	47	5.17
3	−8.0081	3945.26	1.6426	−1397.40	20020.0	55	7.44

TABLE II

SUMMARY OF OPTIMIZED PARAMETERS OF EQNS. 2 AND 3

Parameter	Value	Parameter	Value
c_1	−6.3427	c_6	−0.2069
c_2	−0.5703	c_7	−798.95
c_3	2795.27	c_8	−187.18
c_4	395.33	c_9	23501.06
c_5	2.1276	c_{10}	−1390.41

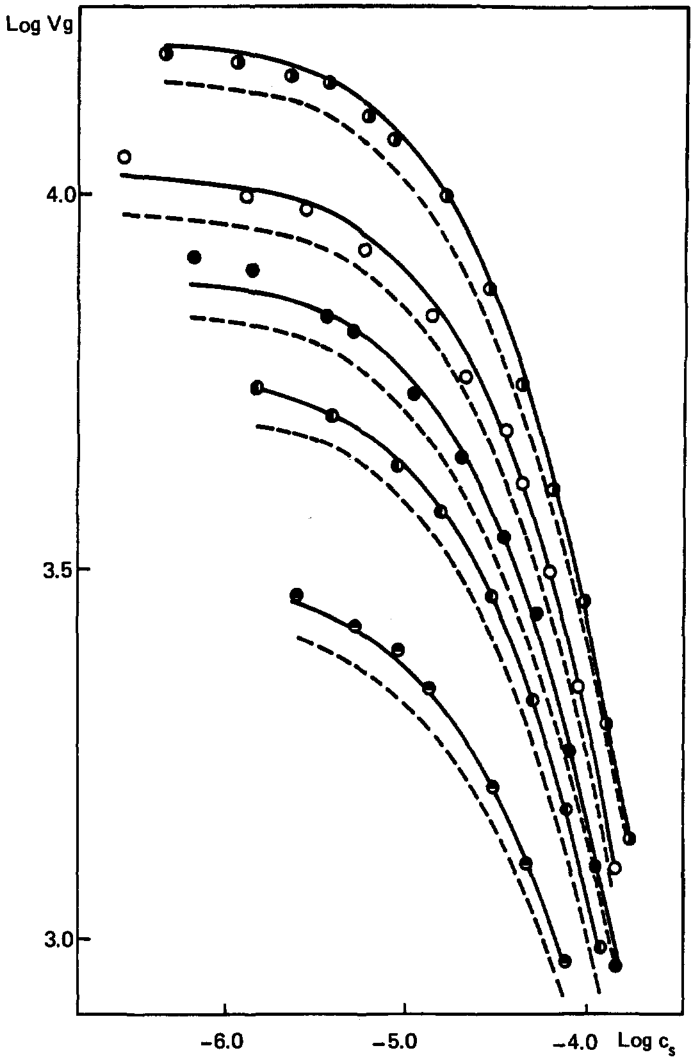

Fig. 1. Relationship between log V_g and log c_s *for* *n*-propanol on Tenax calculated with eqn. 1 (solid lines) and with eqns. 2 and 3 (dashed lines), and experimental points (◑ = 15.2; ○ = 19.9; ● = 23.5; ◐ = 27.1; ⊖ = 35.0°C).

acceptable for the calculation of retention characteristics for trace analysis utilizing preconcentration on Tenax.

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