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Langmuirian parameters for Tenax GC adsorption of airborne hydrocarbons and oxygenated compounds

Pau Comes^a, Norbert Gonzalez-Flesca^a, Joan O. Grimalt^{b,*}

^aINERIS, Measurement and Analysis Department, Parc Technologique Alata, BP 2, 60550-Verneuil-en-Halatte, France

^bDepartment of Environmental Chemistry (C.I.D.–C.S.I.C.), Jordi Girona, 18, 08034-Barcelona, Catalonia, Spain

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Abstract

A study of the sampling conditions of diverse volatile aromatic and aliphatic hydrocarbons, ketones, esters (acetates), aldehydes (crotonaldehyde) and alcohols (*n*-butanol) adsorbed on Tenax GC showed that the chromatographic behavior of these compounds can be modeled with a Langmuir isotherm. The equations derived from this model allow a description of the dependence between breakthrough volumes and atmospheric phase concentration of the adsorbates. They also indicate the breakthrough volumes at infinite dilution and the concentration thresholds requiring the application of Langmuir isotherms to avoid important quantitative sampling errors. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

As shown in previous studies, the retention behavior of airborne volatile organic compounds (VOCs) on solid-phase adsorption packings is air concentration-dependent [1–8] and can be described with Langmuir isotherms [9–12]. This adsorption model provides a realistic description of the breakthrough volumes (V_b) for VOCs in the range of 1–500 mg m⁻³ which is the concentration interval of interest for many emission regulations and occupational safety guidelines. In contrast, the linear isotherm is useful for the description of the retention behaviour at low concentrations (<0.5–1 mg m⁻³), such as those encountered in ambient atmospheres.

The Langmuir equation shows a dependence between V_b and analyte concentration (c):

$$V_b = b \cdot m_{\max} / (1 + b \cdot c) \quad (1)$$

where b is the distribution coefficient between the gas and solid-phases and m_{\max} is the maximum mass that can be retained to form a monolayer on the adsorbent surface.

The linear model can, in fact, be described as a specific case of the Langmuir isotherm because V_b becomes independent of c when $b \cdot c \ll 1$.

In any case, the practical use of the Langmuirian model for prediction of adequate sampling conditions requires the knowledge of the constants defining the adsorption isotherms for the analyte-adsorbent systems of interest. Unfortunately, these are rarely available in the literature.

*Corresponding author.

In the present study, the constants corresponding to a group of volatile aromatic hydrocarbons (benzene, toluene, *o*-, *m*- and *p*-xylene, *n*-ethylbenzene, styrene, 1,2,4-trimethylbenzene, *n*-propylbenzene and mesitylene), ketones (methylethylketone, methylisobutylketone, cyclohexanone), esters (ethyl, propyl, *n*-amyl, 2-methoxyethyl acetates), *n*-octane, crotonaldehyde and *n*-butanol adsorbed with Tenax GC are reported.

These constants have been calculated experimentally using a generator of dynamic atmospheres with known VOC composition [11,13]. For each compound, air flows with different concentrations were generated. These air masses were subsequently sampled with cartridges packed with this adsorbent and the breakthrough volumes were determined by direct mass spectrometric measurement of the air eluting from the cartridges. Adequate *m/z* ratios for the compounds under study were selected in each case. The resulting curve fitted lines allowed to calculate the isotherm parameters at 20°C and confirmed that this group of compounds effectively follows a Langmuirian behavior on adsorption on Tenax GC.

2. Experimental

2.1. Generation of atmospheres with known VOC composition

The equipment designed for the generation of dynamic atmospheres containing known amounts of hydrocarbons and oxygenated compounds has been described elsewhere [13]. A circular oven equipped with a natural gas burner and a primary air entrance was used to generate a current of hot air (ca. 1000°C) that was diluted with ambient air. The resulting gas mixture was cooled in a heat exchanger (ca. 200°C) and received known amounts of hydrocarbons and oxygenated compounds that were introduced with a Chromatem 380 high-performance liquid chromatographic pump. The compounds were pumped through a 1-mm I.D. PTFE tubing into a sprayer situated at the base of a vertical 5 m×29 cm I.D. pipe. This pipe homogenized and channeled the air stream (average flow-rate 300 m³ h⁻¹), which was subsequently released to the outside with an extraction fan. The fan was keeping all the system

below atmospheric pressure (600 Pa). The pipe was equipped with three type K thermocouples for the control of the temperature at the top and at the base. The stream flow was measured with a Pitot tube connected to a capacitive electronic micromanometer (Furness Controls FCO-14). This micromanometer was used in a range of 0–10 Pa with time constant fitting. A sampling probe situated at 50 cm below the top of the pipe allowed the introduction of a portion of the spiked air into a glass dilution chamber where it was mixed with nitrogen (1:10). The dilution ratio was controlled with two oxygen analyzers situated before and after the air/nitrogen mixing device. Water condensation was avoided by external heating at 150°C.

2.2. Adsorption and analysis

The adsorption system was composed of 11.5 cm×4 mm I.D. Supelco glass tubes filled with 150 mg of Tenax GC (35–60 mesh, Enka) situated between glass wool plugs. The tubes were kept at 20°C. The air from the diluted stream was passed through the filled tubes (150 ml min⁻¹) by a membrane pump (Charles Austen, Capex 2D) working in impeller mode. The air volumes were measured with a Schlumberger precision volume meter. The analysis of the tube effluent was performed on-line using a mass spectrometer Balzers 420 equipped with a heating capillary for atmospheric sampling. This instrument was focussed on mass fragment ions characteristic of the compounds present in the air-stream for the measurement of the V_b values. The same detection was also used for the direct analysis of the air stream by adequate switching of two three-way valves connected to a bypass tubing.

Repeated measurements of the concentrations of the spiked compounds showed a range of variation of 3–4% with respect to the mean. This dispersion was essentially introduced by the pulses of the chromatographic injection pump. Once the system was in a steady-state condition, the average VOC concentration did not exhibit any significant drift (<1%). The evaluation of the linearity between amount of compound introduced in the air flow and concentration measured at the sampling site showed a straight line with a regression coefficient of 0.999 [13].

3. Results and discussion

3.1. The linear expression of the Langmuir isotherm

Eq. (1) can be linearized by transformation into the reciprocal form:

$$1/V_b = 1/(bm_{\max}) + c/m_{\max} \quad (2)$$

V_b and c are the respectively dependent and independent variables in the experiments of generation and adsorption of atmospheres with known VOC composition. Thus, Eq. (2) can be used to determine the Langmuir constants for the VOC of interest.

Furthermore, this equation provides a useful criteria for the estimation of the suitability of the Langmuirian model. If the compound-adsorbent system can be described with a Langmuir gas/solid isotherm, the experimental points must show a good fitting to Eq. (2). This is illustrated in Fig. 1 where the least-squares straight lines corresponding to several representative cases, e.g. toluene, *o*-, *m*-, and *p*-xylene, 1,2,4-trimethylbenzene, styrene, ethyl and propyl acetate, cyclohexanone, *n*-butanol, are shown. In all cases, the agreement between experimental points and fitted line is good. As shown in Table 1, the regression coefficients corresponding to the fitting of this equation to the experimental V_b values are high in all cases, 0.94–0.9994.

Eq. (2) has been used to calculate the Langmuir constants of the compounds included in this study. The b and m_{\max} constants range between 0.0064–0.12 m³ mg⁻¹ and 0.043–19 mg, respectively (Table 1). Thus, a higher dispersion of values is found among m_{\max} , nearly three orders of magnitude, than among b . In fact, the b parameters exhibit a remarkable uniformity among compounds of similar functionality. Thus, they range between 0.011–0.070 and 0.079–0.12 among the aromatic hydrocarbons and the ketones, involving less than one order of magnitude in both cases. The m_{\max} constants of these two groups of compounds range among 2.3–12 mg and 0.5–5.5 mg per 1 g of Tenax GC in the cartridges. Thus, changes in the degree of alkyl substitution are more reflected in analyte load capacity of the adsorbent than in the distribution coefficients between gas and solid-phases [11,14].

The higher dispersion of b values observed among the acetates, 0.0069–0.11, probably reflects the functional differences of the alkoxy moieties, e.g. ethyl vs. 2-methoxyethyl. In this compound group both Langmuir constants range over similar intervals.

On the other hand, the low m_{\max} and b parameters observed in other compounds, e.g. crotonaldehyde, probably reflect the low chemical affinity, and retention capacity, of Tenax GC for the compound.

3.2. Langmuir vs. linear isotherms

Eq. (1) predicts that at infinite dilution there is a V_b beyond which the retained VOC elute independently of the concentration of the adsorbate in the gas phase. This volume is coincident with the retention volumes currently reported as guidelines for the chromatographic behavior of the VOCs in the diverse adsorbent systems [4,15,16].

The infinite dilution V_b corresponding to the VOCs considered in this study are summarized in Table 2. These volumes range over a wide span, from 0.31 to 430 when they are normalized to 1 g of adsorbent. In this respect, it has to be mentioned that even higher retention volume differences have been predicted for these compounds. Thus, whereas the maximum sampling volumes of Table 2 for toluene and mesitylene are 80 and 170 l, respectively, other studies based on temperature extrapolations predict retention volumes of 65 and 905 l, respectively [17]. On the other hand, these Table 2 volumes are similar to those predicted as safe sampling volumes from heat of adsorption considerations for benzene and *n*-butanol but they are lower in the case of toluene, xylenes and others [2]. Other predicted retention volume values [17], e.g. toluene, are similar to those reported in Table 2.

Current sampling volumes for field analyses are 0.5–5 l. Thus, according to Table 2 values, the Tenax GC cartridges considered in this study could be useful for the analysis of low concentrations of these compounds in all cases except crotonaldehyde. However, these values refer to the single presence of the compounds in the gas phase. As previously reported, in multicomponent VOC mixtures there is a competitive effect for the adsorption sites of the packings which result in a lower retention capacity of the individual compounds [13]. An obvious way

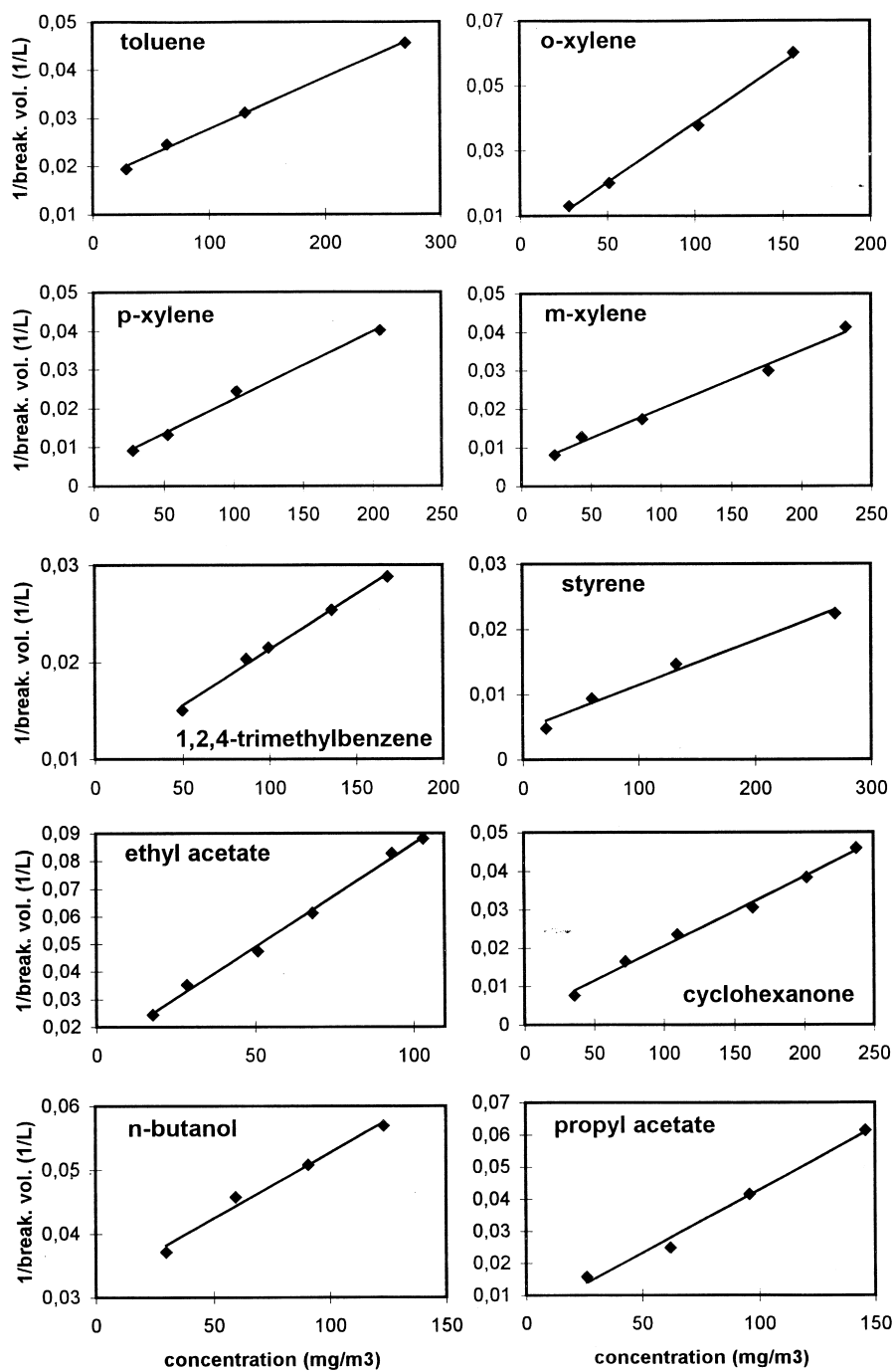


Fig. 1. Straight lines corresponding to least-squares curve fitting of Eq. (2) to the experimental breakthrough volumes determined with the generator of dynamic atmospheres with known VOC composition.

Table 1
Calculated Langmuir constants for the hydrocarbons and oxygenated compounds included in this study

Compound	m_{\max} (mg) ^a	b (m ³ mg ⁻¹)	Regression coefficient	n	Range (mg m ⁻³)
Benzene	2.3	0.011	0.996	5	30–300
Toluene	5.0	0.016	0.9994	4	30–350
<i>o</i> -Xylene	3.6	0.038	0.998	4	20–200
<i>m</i> -Xylene	6.6	0.031	0.995	5	20–250
<i>p</i> -Xylene	5.5	0.041	0.996	4	20–250
<i>n</i> -Ethylbenzene	5.1	0.039	0.993	5	20–250
Styrene	12	0.022	0.991	4	60–350
1,2,4-Trimethylbenzene	8.75	0.012	0.997	5	40–200
Propylbenzene	6.2	0.027	0.999	3	40–150
Mesitylene	2.4	0.070	0.995	5	30–200
<i>n</i> -Octane	1.4	0.0415	0.9997	3	40–100
Methylethylketone	0.5	0.12	0.997	4	10–50
Methylisobutylketone	2.2	0.10	0.999	4	50–250
Cyclohexanone	5.5	0.079	0.997	6	30–250
Crotonaldehyde	0.043	0.0072	0.991	5	10–80
Ethyl acetate	1.35	0.061	0.998	6	10–150
Propyl acetate	2.55	0.11	0.994	4	20–150
<i>n</i> -Amyl acetate	8.7	0.044	0.94	5	90–250
2-Methoxyethyl acetate	19	0.0069	0.97	5	100–300
<i>n</i> -Butanol	4.85	0.0064	0.992	4	20–150

^aThese values are normalized to cartridges filled with 1 g of Tenax GC.

to increase retention efficiency is the use of higher amounts of adsorbent in the cartridge since the m_{\max} parameter depends on the total solid-phase amount. Table 1 and Table 2 values correspond to cartridges normalized to 1 g of adsorbent, a commonly used amount for operational reasons.

Another aspect to be considered is the threshold concentration above which the V_b become affected by the gas phase concentrations of the adsorbate. This is an important parameter to understand whether the chromatographic system behaves according to linear conditions or non-linear isotherms. According to Eq. (1), the system starts to deviate from the linear isotherm when the term $bc > 0$ and contributes significantly to $(1 + bc)$. Obviously, if b is constant the significance of this term depends on the gas phase concentration (c).

Thus, for a relative error of 5%, the ratio $0.05/b$ provides a reference concentration above which non-linear Langmuirian effects become significant. These ratios lie between 0.42 and 7.8 mg m⁻³ (Table 2). These threshold values can easily be lower than the concentrations usually encountered at emission or even occupational safety regulations [18]. Thus, the

sampling strategies for these VOCs must take into account Langmuirian effects which make the V_b smaller than those predicted by the linear theory.

4. Conclusions

The chromatographic behavior of volatile aromatic and aliphatic hydrocarbons, ketones, esters (acetates), aldehydes and alcohols follow Langmuir isotherms when adsorbed on Tenax GC from atmospheres were they are present in concentrations up to 50–350 mg m⁻³. The chromatographic behavior of these compounds on this adsorbent cannot be described with linear isotherms at air concentrations above 0.4–8 mg m⁻³.

These values are easily lower than concentrations usually encountered at emission or in occupational safety regulations and define upper limits for the use of GC retention volume data. The gas-phase distribution coefficients of the compounds with the same chemical functionality are similar. Thus, in the series of aromatic hydrocarbons and ketones considered in the present study these values range within

Table 2
Sampling conditions defined by the Langmuir constants listed in Table 1

Compound	Maximum sampling volume ^a (m_{\max}/b) (l)	Maximum analyte concentration ^b ($0.05/b$) (mg m^{-3})
Benzene	25	4.5
Toluene	80	3.1
<i>o</i> -Xylene	140	1.3
<i>m</i> -Xylene	200	1.6
<i>p</i> -Xylene	230	1.2
<i>n</i> -Ethylbenzene	200	1.3
Styrene	260	2.3
1,2,4-Trimethylbenzene	105	4.2
Propylbenzene	170	1.9
Mesitylene	170	0.71
<i>n</i> -Octane	58	1.2
Methylethylketone	60	0.42
Methylisobutylketone	220	0.5
Cyclohexanone	430	0.63
Crotonaldehyde	0.31	6.9
Ethyl acetate	82	0.82
Propyl acetate	280	0.45
<i>n</i> -Amyl acetate	350	1.1
2-Methoxyethyl acetate	130	7.2
<i>n</i> -Butanol	31	7.8

^aAt infinite dilution. These values are normalized to cartridges filled with 1 g of Tenax GC.

^bConcentrations involving 5% breakthrough errors due to Langmuirian effects.

less than one order of magnitude. In any case, the different chromatographic behaviour of the compounds with different chemical functionalities is more reflected in changes of the m_{\max} than the b constants, indicating a stronger relation with changes in the analyte load capacity of the adsorbent than with changes in gas–solid-phase distribution.

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