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Isotherm Consideration of PAHs Adsorbed on Polymeric Capillary Tubing in an Aqueous Sample Preconcentration

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ABSTRACT

This study examined the isotherm of polycyclic aromatic hydrocarbons (PAHs) adsorbed on capillary concentrating tubing. Equations for common adsorption isotherms, including Langmuir and modified Freundlich, were used to fit the adsorption data obtained from pyrene and acenaphthene samples. Each fitting's correlation coefficient was then used to assess the appropriateness of the isotherm of interest. Experimental results indicate that the modified Freundlich isotherm most aptly accounts for monocomponent PAH adsorption from water onto ethyl vinyl acetate tubing. From the appropriateness of the Langmuir isotherm individually in low- and high-concentration ranges, multilayer adsorption apparently occurs at a higher concentration. In bicomponent adsorption, acenaphthene was highly competitive with pyrene at a higher competition coefficient. In addition,

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the competitive coefficient of an analyte increased with decreasing competitor concentration.

Key Words. Polycyclic aromatic hydrocarbons; Capillary tubing; Adsorption isotherm; Capillary gas chromatography

INTRODUCTION

Capillary plastic tubing has been used to preconcentrate trace organics in aqueous systems with the merits of no restriction on the sample volume pumped through and favorable recovery factors (1, 2). A recent study examined the feasibility of using poly(ethyl vinyl acetate) (EVA) and polyethylene (PE) capillary tubing as alternative media to solid-phase extraction techniques for the removal and preconcentration of residual polycyclic aromatic hydrocarbons (PAHs) in aqueous samples (2).

Adsorption isotherms are highly desired for describing adsorption capacity and adsorbent selection, as well as determining the required amount of adsorbent. Such isotherms have also been used to evaluate theoretically and interpret thermodynamic parameters such as adsorption heat (3). However, to our knowledge the adsorption isotherm of organics in open capillary plastic tubing has not been investigated.

The five adsorption isotherms listed in Table I are frequently used to describe adsorption behaviors under specified conditions (4–6). Generally, if the number of active sites on the adsorbent surface is limited and the multiple layer is insignificant, the adsorption behavior can be described by the following Langmuir adsorption isotherm.

$$\theta_i = \frac{n_i}{n_{mi}} = \frac{K_i C_i}{1 + K_i C_i} \quad (1)$$

where θ_i denotes the fraction of adsorption sites occupied by component i , n_i represents the amount of analyte i adsorbed, n_{mi} is the adsorption capacity, K_i denotes the Langmuir-type constant that characterizes the exchange of solute and solvent molecules between the adsorption phase and the bulk solution, and C_i represents the concentration of solute i . For solid-liquid systems, Eq. (1) is generally written in the form indicated in Eq. (2):

$$q_e = \frac{b q^0 C_e}{1 + b C_e} \quad (2)$$

where q_e denotes the total coverage by component e in terms of adsorbate weight per unit length of tubing, C_e is the equilibrium concentration (mg/

TABLE 1
Adsorption Isotherm Equations

Name	Linear form equation ^a
Henry's law	$q_e = K_h C_e$
Langmuir	$1/q_e = (1/bq^0)(1/C_e) + 1/(q^0)$
Freundlich	$\log(q_e) = (n) \log(C_e) + \log(k_f)$
BET	$C_e/[q_e(C_s - C_e)] = [(B - 1)/(Bq^0)](C_e/C_s) + 1/(Bq^0)$
Modified Freundlich	$\log(q_e) = (n) \log(C_e/C_s) + \log(k_f)$

^a q_e denotes the total coverage by component e in terms of adsorbate weight per unit length of tubing; C_e represents the equilibrium concentration ($\mu\text{g/mL}$) of adsorbate; C_s is the solubility ($\mu\text{g/mL}$) of adsorbate in water; n and K_f denote characteristic constants related to the adsorption energy and the adsorption capacity, respectively; K_h , b , q^0 , and B are constants.

L) of adsorbate, b represents a constant related to the adsorption energy, and q^0 is the limiting adsorption capacity. For small bC_e ($bC_e \ll 1$), q_e is close to bq^0C_e ; that is, the amount adsorbed is proportional to C_e (7). In practice, the amount adsorbed is most likely proportional to C_e^n (where n denotes a real number), as described by the Freundlich adsorption isotherm (8). However, in an aqueous solution the adsorbed amount is related to the analytes' solubilities. This situation can be resolved in the equation by replacing the concentration term with the ratio of concentration to solubility term, resulting in the modified Freundlich equation (9) shown in Table 1. However, the solubility of an analyte remains constant under specified conditions. Hence, the modified Freundlich isotherm closely resembles the Freundlich isotherm in a monocomponent system.

In this study we examine the feasibility of applying five adsorption isotherm equations (including the modified Freundlich isotherm) to the adsorption of PAHs on EVA tubing. The adsorption data obtained from pyrene and acenaphthene samples are used to test these isotherms because of their symmetrical structures. In addition, aqueous samples of a pyrene and acenaphthene mixture are used to study the modified Freundlich bi-component isotherm.

EXPERIMENTAL

Materials

All capillary tubings and glassware were cleaned prior to use. Capillary tubing was prepared by pumping through 30 mL of toluene followed by a rinse with 250 mL of saturated soap solution (Konex) and an additional

rinse with 100 mL of distilled, deionized water. Glassware was soaked in soap solution overnight and then thoroughly rinsed with distilled, deionized water. EVA capillary tubing, with an internal diameter of 0.76 mm, was obtained from Cole-Parmer Instrument Company. PE tubing of 0.25 mm i.d. was acquired from Thomas Scientific. Stock solutions of acenaphthene (306 mg/mL) and pyrene (312 mg/mL) were prepared in acetonitrile. These solutes were purchased from Aldrich with a stated purity exceeding 96%. Standard solutions were prepared by appropriately diluting with distilled deionized water. Acetonitrile and toluene were certified ACS grade solvents obtained from Fisher Scientific.

Instrumentation

A Perkin-Elmer Autosystem Gas Chromatograph equipped with a split injector (split ratio of 50/1) and flame ionization detection was used in this study with a DB-5 capillary column (30 m \times 0.32 mm i.d. of 0.25 μ m film thickness). Helium was used as the carrier gas at a linear velocity of 30 cm/s. Temperatures of the injector and detector were maintained at 280°C. The following temperature program was employed during the investigation: initial column temperature of 130°C for 7 minutes, then increased to 230°C at 5°C/min and held for 8 minutes. Data acquisition was achieved by an IBM AT compatible PC with a Data Translation 2802 board and LabCalc software (Galactic Industries). All chromatograms were digitally smoothed using Savitsky-Golay seven point smoothing.

Procedure

One hundred milliliters of varying concentrations of pyrene and acenaphthene were pumped through the PE (0.254 mm i.d. \times 5 m) and the EVA tubes (0.76 mm i.d. \times 4 m) at a flow rate of 1.0 mL/min with a Perkin-Elmer series 100 pumping system. Next, 10 mL of toluene was used to desorb the sample and then concentrated to 1.0 mL by a rotatory evaporator. A 50- μ L internal standard aliquot (0.1% tridecane in toluene) was spiked into the concentrated solution. A 2- μ L aliquot was then sampled for gas chromatographic analysis. The sample concentration and its relative response to the internal standard were used to determine the isotherm equation's parameters.

In the bicomponent adsorption study, 100 mL of mixture solutions with different pyrene concentrations and a fixed acenaphthene concentration (or vice versa) were pumped through EVA tubes at a flow rate of 1.0 mL/min. The analytes were then desorbed by 10 mL toluene for chromatographic analysis after appropriate treatment as described.

The capillary tubes were assumed to be sufficiently long, and the sampling flow was slow enough for adsorption phenomenon to reach the isotherm equilibrium state from our previous studies (1).

RESULTS AND DISCUSSION

The adsorption of PAHs from aqueous solution on capillary tubing is in the following steps: 1) PAHs migrate from bulk solution to the surface of the tubing by diffusion; 2) PAHs are adsorbed on the active sites of the tubing surface by hydrophobic interaction. Physical adsorption is a dynamic equilibrium that encompasses adsorption and desorption processes. The theory for these processes has been discussed elsewhere (9–11).

For Monocomponent Adsorption Systems

We evaluated the absorbate quantity eluted from the preconcentrated tubes by GC determination with a definite amount of internal standard. The total coverage of an adsorbate is proportional to the relative response of peaks (adsorbate to internal standard) in the chromatogram. In addition, the relative response of the adsorbate and its concentration in the aqueous solution are used for isotherm evaluation throughout the studies.

Table 2 lists the concentrations of pyrene in aqueous solution along with its relative responses in GC analyses after the preconcentrations and elutions. Table 3 displays the isotherm equation parameters for pyrene adsorption on PE and EVA tubings. According to the correlation coefficient square, r^2 , four isotherm equations (except BET, Brunauer-Emmett-Teller) have an acceptable relationship, and the modified Freundlich isotherm (the same as Freundlich) is the most proper one for PE tubes in the 65 to 4140 ng/mL concentration range and for EVA tubes in the 73 to 4680 ng/mL concentration range. In general, the linearity for EVA tubing is better than that for PE tubing as is shown in the log-log plots of Fig. 1. According to this figure, the plot's slope is smaller and the intercept is higher for PE tubing than for EVA tubing. This finding implies that the PE tubing has a higher adsorption energy and a lower capacity than the EVA tubing. However, in the lower concentration ranges of pyrene (65 to 259 ng/mL for PE tubing, and 73 to 293 ng/mL for EVA tubing) or in the higher concentration ranges (259 to 4140 ng/mL for PE tubing, and 293 to 4680 ng/mL for EVA tubing), the Langmuir isotherm equations have an excellent linear relationship with r^2 , exceeding 0.99. Table 4 lists the parameters for Langmuir isotherm equations in these concentration

TABLE 2
The Pyrene Concentrations and the Relative Responses

Polyethylene tubing			Ethyl vinyl acetate tubing		
Concentration (ng/mL)	Relative ^a response	log(RR) ^b	Concentration (ng/mL)	Relative ^a response	log(RR) ^b
4140	0.1766 (3.4) ^c	-0.753 (1.99) ^c	4680	0.2220 (4.5)	-0.654 (2.98)
2070	0.1359 (2.9)	-0.867 (1.50)	2340	0.1834 (5.5)	-0.737 (3.24)
1035	0.0873 (5.7)	-1.059 (2.36)	1170	0.1152 (8.7)	-0.939 (4.03)
518	0.0767 (6.5)	-1.115 (2.51)	585	0.0927 (8.6)	-1.033 (3.61)
259	0.0746 (4.0)	-1.127 (1.51)	293	0.0766 (10.4)	-1.116 (4.04)
129	0.0563 (10.7)	-1.249 (3.68)	146	0.0504 (19.8)	-1.298 (6.62)
65	0.0362 (16.6)	-1.441 (5.00)	73	0.0348 (11.5)	-1.458 (3.42)

^a Peak area ratio of adsorbate to internal standard.

^b RR: Relative Response.

^c The data in parentheses are the relative standard deviations (in %) for three injections.

ranges. The energy-related item, *b*, demonstrates that PE has a higher adsorption energy than EVA. Moreover, a higher adsorption energy is necessary for both tubings to preconcentrate a solute at a high concentration range. This fact also indicates that different adsorption behaviors are carried out at the lower and higher concentration ranges. At lower

TABLE 3
Summary of Isotherm Equation Parameters for Pyrene Adsorption on PE and EVA Tubings^a

Tubing	Henry's law		Langmuir			Freundlich			Modified Freundlich			BET		
	K_h	r^2	q^0	b	r^2	K_f	n	r^2	K_f	n	r^2	q^0	b	r^2
PE	0.0315	0.93	0.122	6.44	0.94	0.1026	.3436	0.95	0.0516	.3436	0.95	0.012	0.9504	0.28
EVA	0.0398	0.95	0.159	3.64	0.97	0.1172	.4400	0.99	0.0471	.4400	1.0	-0.016	0.9643	0.30

^a r^2 is the correlation coefficient square. Concentration range: 65–4140 ng/mL for PE tubing and 73–4680 ng/mL for EVA tubing.

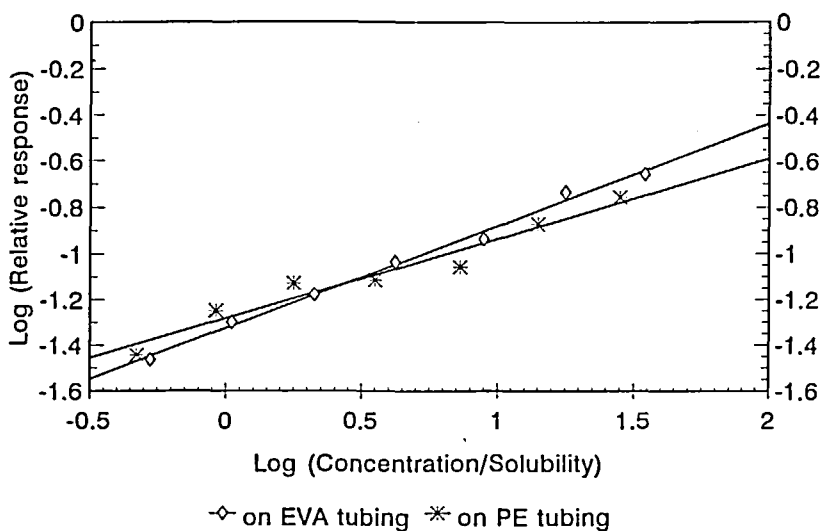


FIG. 1 The log-log plot of modified Freundlich isotherms for pyrene adsorption on EVA tubing. Concentration ranges for EVA tubing = 73–4680 ng/mL, and for PE tubing = 65–4140 ng/mL.

concentrations of PAH, q_e is close to bq^0C_e in Eq. (2), so the amount adsorbed is thus proportional to C_e . However, at a higher concentration the interaction between PAH molecules was significant due to their extremely low solubility in aqueous solution. The PAH molecules may cluster on the surface of tubings. Therefore, a multilayer adsorption of pyrene

TABLE 4
Parameters of Langmuir Isotherm Equation for Pyrene Adsorption on PE and EVA Tubings in Various Concentration Ranges

Concentration range (ng/mL)	Tubing					
	PE			EVA		
	q^0	b	r^2	q^0	b	r^2
65–259	0.262	0.489	1.0			
259–4140	0.100	9.08	0.99			
73–293				0.345	0.434	0.99
293–4680				0.126	5.12	0.99

on both tubes might occur at a higher concentration range. This two-step adsorption phenomenon can be found in plots of the Langmuir isotherm for pyrene adsorption on two tubes as demonstrated in Fig. 2. The large relative standard deviation (RSD) of detection in the lower concentration range in Table 2 may be attributed to the harder to attain ability of adsorption equilibrium in addition to a large system error (such as significant depletion by the glassware used) in a lower concentration determination. However, the RSDs of the detection decrease to less than 5.0% after logarithm transformation in the log-log plot, which is used to linearly fit the isotherms. Thus, an evaluation of the parameters in isotherm equations shows this deviation to be acceptable.

Table 5 lists the isotherm equation parameters for acenaphthene adsorption on EVA (0.76 mm i.d. \times 4 m) tubing. According to the correlation coefficient square, r^2 , the modified Freundlich isotherm is also the most appropriate isotherm for the concentration range 95 to 1530 ng/mL.

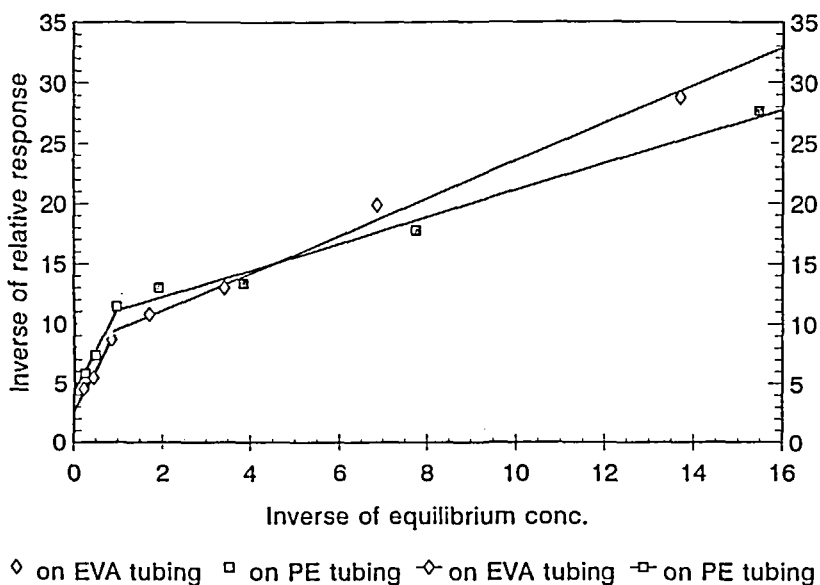


FIG. 2 The two-step adsorption phenomena of Langmuir isotherms for pyrene adsorption. Concentration ranges for EVA tubing = 73–300 and 585–4680 ng/mL, and for PE tubing = 65–260 and 260–4140 ng/mL.

TABLE 5
Summary of Isotherm Equation Parameters for Acenaphthene Adsorption
on EVA Tubing^{a,b}

Henry's law		Langmuir			Freundlich			Modified Freundlich			BET		
K_h	r^2	q^0	b	r^2	K_f	n	r^2	K_f	n	r^2	q^0	b	r^2
2.19	0.99	3.06	2.06	0.95	2.57	.715	0.99	7.39	.715	1	0.376	-0.95 ^c	0.86

^a r^2 is the correlation coefficient square.

^b Concentration range: 95–1530 ng/mL.

The Competition Adsorption in a Bicomponent System

For a bicomponent system, the total coverage of adsorbate i and j can be obtained by an integration procedure (11). Equations (3) and (4) provide the total coverages of adsorbate i and j , respectively. These coverages influenced each other due to competition adsorption.

$$q_i = (K_i/m_i)(C_i/C_{is})[C_i + a_{ij}(C_j/C_{js})]^{n_i-1} \quad (3)$$

$$q_j = (K_j/m_j)(C_j/C_{js})[C_j + a_{ji}(C_i/C_{is})]^{n_j-1} \quad (4)$$

where C_{is} and C_{js} denote the solubilities of solutes i and j in water, respectively. Also, n_i , n_j , K_i , and K_j are constants and can be determined from the monocomponent system. Moreover, K_i/m_i and K_j/m_j are reduced constants. a_{ij} and a_{ji} are competition coefficient and can be determined from their respective bicomponent systems.

The linear form of the two-component modified Freundlich isotherm can be obtained by rearranging Eqs. (3) and (4) to the forms shown by Eqs. (5) and (6):

$$m_i(C_i/C_{is}) + m_i a_{ij}(C_j/C_{js}) = K_i(C_i/C_{is} q_i)^{1/(1-n_i)} \quad (5)$$

$$m_j(C_j/C_{js}) + m_j a_{ji}(C_i/C_{is}) = K_j(C_j/C_{js} q_j)^{1/(1-n_j)} \quad (6)$$

By fitting the $K_i(C_i/C_{is} q_i)^{1/(1-n_i)}$ to C_i/C_{is} , and the $K_j(C_j/C_{js} q_j)^{1/(1-n_j)}$ to C_j/C_{js} with the linear least-squares algorithm, if the concentration of C_j (or C_i) remains constant, the linear equation's slope can be obtained as m_i (or m_j) and the intercept is $m_i a_{ij}(C_j/C_{js})$ [or $m_j a_{ji}(C_i/C_{is})$].

TABLE 6
Summary of Two-Component Modified Freundlich Isotherm Equation Parameters
for Pyrene Adsorption on EVA Tubing

Pyrene concentration range (ng/mL)	Acenaphthene concentration					
	1184 ng/mL		918 ng/mL		612 ng/mL	
	a_{ij}	r^2	a_{ij}	r^2	a_{ij}	r^2
87.8–1450	3.252	0.98	4.352	0.99	11.50	0.99
87.8–702.5	0.2845	0.99	1.827	0.99	2.49	0.99

Tables 6 and 7 provide the competitive modified Freundlich isotherm equation parameters for pyrene and acenaphthene adsorption on EVA tubing, respectively. According to the correlation coefficient parameter, r^2 , the linearity is better for lower concentrations ranging from 87.8 to 702.5 ng/mL for pyrene and 306 to 1184 ng/mL for acenaphthene. The competition coefficient for acenaphthene, a_{ji} , is less than that for pyrene, a_{ij} , because the acenaphthene molecule is smaller and diffuses faster. Theoretically, the competitive coefficient a_{ij} (or a_{ji}) should remain constant. However, as Tables 6 and 7 reveal, each competition coefficient decreases with an increasing concentration for each analyte. This phenomenon is ascribed to the limited number of active adsorbed sites which develop a significant multiple adsorption layer.

TABLE 7
Summary of Two-Component Modified Freundlich Isotherm Equation Parameters
for Acenaphthene Adsorption on EVA Tubing

Acenaphthene concentration range (ng/mL)	Pyrene concentration					
	1405 ng/mL		351 ng/mL		176 ng/mL	
	a_{ji}	r^2	a_{ji}	r^2	a_{ji}	r^2
306–1480	0.0253	0.92	0.0421	0.93	0.0503	0.99
306–1184	0.0176	0.93	0.0231	0.94	0.0391	0.99

CONCLUSION

This study has demonstrated that the modified Freundlich isotherm is the most appropriate isotherm to correlate monocomponent and bicomponent PAHs adsorption on EVA tubing. According to results presented herein, the competition coefficient of acenaphthene is less than that of pyrene due to its small molecular structure. However, in bicomponent PAHs adsorption systems, the competitive coefficient varies with the analyte concentration. This variation is attributed to the limited number of adsorption sites and the formation of multilayers. The multilayer adsorption phenomena can also be observed from the different adsorption behaviors of pyrene in the lower and higher concentration ranges.

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