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Adsorption Isotherms of Benzene and Its Derivatives by RPLC Frontal Analysis

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The adsorption behaviour of solute is one of the most important factors to design a batch and a continuous liquid chromatographic separation process. In liquid chromatography, these behaviours are based on the adsorption equilibrium between a liquid mobile-phase and a solid stationary-phase. However, almost of the retention models were developed under linear adsorption isotherm only few researchers have investigated the relationship between the adsorption parameters and the mobile phase composition and some empirical models were introduced. In this work, the adsorption isotherms were obtained by the frontal analysis for 4 low-molecular compounds (benzene, toluene, chlorobenzene and 1,2-dichlorobenzene) on a commercial C_{18} bonded column. The absorption based on the linear and Langmuir models was investigated according to the changes of the composition of methanol high-enriched eluent. The calculations and analysis of the coefficients obtained for both models confirm that the adsorption data for solutes are best modeled with the linear approach. Langmuir isotherm model couldn't satisfactorily describe mechanism and provide the objective information on the physical nature of the absorption in spite of the acceptable accuracy.

Key Words: Adsorption isotherm modeling, Benzene derivatives, Frontal analysis, Mobile phase composition.

INTRODUCTION

An early reversed-phase liquid chromatography (RPLC) retention model was based on the assumption that the formation of a suitable cavity in the mobile phase to accommodate the analyte molecule was the key step in the retention mechanism[1]. Accordingly, this model assumed that the retention of a compound depended essentially on its size and on the surface tension of the mobile phase. The limit of this model became obvious when experimental data showed that retention also governed by the density and the length of the alkyl chains bonded to the silica surface[2-4]. The differences observed were unambiguously interpreted as originating from variations of the phase ratio[5-8]. Long ago, it was suggested that the structure of the bonded

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layer is such that it could explain the simultaneous presence of adsorption and partition sites[9,10]. Thus, new models, which include the characteristics of both the mobile and the stationary phases, were elaborated. The partitioning model[11,12] in which the analyte is transfered from the mobile phase to the stationary phase accounted far better for the experimental data than earlier models. The retention factors of analytes were successfully correlated with their partition coefficients between water and *n*-octane (log P), shown to be proportional to the molecular size of the solute and to be directly affected by their solubility in the mobile phase. However, the driving force for solute adsorption that was measured appeared smaller than predicted by the partitioning model. So, an adsorption model was proposed instead. These two models of the actual retention mechanism, the adsorption and the partition models are certainly the 2 extremities of a broad spectrum of possible retention modes in RPLC. This frame of understanding of the retention mechanisms in RPLC is justified by the heterogeneous nature of the adsorption layer and by the complex organization of the interphase layer. It has been demonstrated that alkyl bonded phases are made of ordered and disordered regions, which are observed in fourier transform infrared spectroscopy (FTIR)[13,14] and in nuclear magnetic resonance (NMR)[15,16]. Accordingly, the overall retention of an analyte in RPLC is more the result of a complicated convolution of many different interactions happening simultaneously.

In this work, the adsorption isotherms were obtained by the frontal analysis for four low-molecular compounds (benzene, toluene, chlorobenzene and 1,2-dichlorobenzene) on a commercial C_{18} bonded column. The experimental adsorption data acquired were fitted to the equations of the linear and Langmuir. One is forced to accept the fact that selected solutes is well examined. But without any doubt, obtained frontal analysis profiles may be of utility to the optimization of the experimental variables in preparative and simulated moving bed isolations of these compounds and their more complex analogs.

Theory

Frontal analysis: Frontal analysis (FA) in the staircase mode requires 2 pumps, one connected to a bottle with mobile phase and other connected to a bottle with the analyte to be investigated dissolved in the mobile phase. Initially, only mobile phase is present in the column and the staircase is obtained by successive abrupt step changes at the inlet of the column. In each step the analyte concentration in the mobile phase is increased and the stationary phase will consequently adsorb successively more analyte[17].

The concentration in the stationary phase is:

$$q_{i+1} = Q_{i+1}/V_s = [Q_i + (C_{i+1} - C_i)(V_{R,i+1} - V_T)]/V_s \qquad (1)$$

where Q_i and Q_{i+1} are the amounts of compound adsorbed by the column packing after the ith and the (i+1)th step, when in equilibrium with the concentrations C_i and C_{i+1}, respectively. $V_{R,i+1}$ is the total dead volume (including column void volume, V_0) and V_s is the volume must be determined, namely the traditional column hold-up volume, V_0, which is used to calculate the volume of the stationary phase, V_s. The other dead volume is the total one, V_T, *i.e.*, the entire volume after the T-connector (including V_0) and the frontal analysis raw-data should be corrected for V_T.

Linear isotherm: The linear isotherm model the adsorbent concentration is a power function of the adsorbate concentration as follows:

$$q = nC + m \qquad (2)$$

where n and m are the constants and C is the equilibrium concentration of dyes in solution. The coefficient n represents the quantity of dye sorbed in adsorbent for a unit equilibrium concentration of the compound under test. The sorbed amount increases indefinitely with the concentration in solution. The linear isotherm indicates a partioning process of the solute onto the sorbent.

Langmuir isotherm: The data points $(q, C)_i$ (i is the number of frontal analysis concentration steps) were fitted to Langmuir isotherm model for liquid-solid equilibrium. This is the model most frequently used in the study of liquid-solid chromatographic processes, in spite of its empirical nature. At equilibrium the rates of desorption kinetic constant (k_d) and adsorption kinetic constant (k_a) of the adsorbate molecules are equal and assuming a first order kinetic equation:

$$q = aC/(1+bC) \qquad (3)$$

where a is the specific saturation capacity of the adsorbent or total number of adsorption sites per unit volume of the adsorbent and $b = k_a/k_d$ is the adsorption-desorption equilibrium constant on the solid surface.

EXPERIMENTAL

The different mobile phases used in this work, whether for the determination of the adsorption isotherms data or for the elution of large size bands were mixtures of distilled water and HPLC-grade methanol, purchased from Duksan Pure Chemical Co. (Ansan, South Korea). The distilled water was filtered with a vacuum pump (Division of Millipore, Waters, USA) and a filter (HA-0.45, Division of Millipore, Waters, USA) prior to use. All the solutes (analytical grade), benzene, toluene, chlorobenzene and 1,2-dichlorobenzene, were obtained from Oriental Chemical Industries (Incheon, South Korea). Each analyte was dissolved in a mixture of water and methanol at concentration 10 % (v/v). These solutions were then sonicated for 0.5 h and stored at 277 K. The working standards were prepared every 2 d to avoid the potential errors from decomposition.

Apparatus and HPLC procedure: The chromatography system consisted of a Waters 600s Multi solvent Delivery System and a Waters 616 liquid chromatography (Waters Associates, Milford, MA, USA), a Rheodyne injector (Cotati, CA, USA) valve with a 20 µL sample loop and a variable wavelength 2487 UV dual channel detector. Millenium software (Ver. 3.2 Interface Eng., South Korea) on a PC was used as a data acquisition system. Experiments were performed with a commercially available Optimapak C_{18} (alkyl-) bonded phase column (4.6 mm × 150 mm i.d. 100 Å pore sizes and 5 µm particles) from Rs-Tech Co. (Daejeon, South Korea). Analyses were performed at temperature 308 K at a flow rate of 1.0 mL/min flowed in isocratic mode and the elution profiles were monitored at λ of 280 nm. The mobile phases were composed from water with different concentrations of organic modifier methanol. The retention times used in this study were the averages of at least 3 determinations. Evaluation of the results of the chromatographic experiments was carried out by mathematical statistic techniques. The relative error of a single measurement did not exceed ± 5 %.

Isotherm measurements: The measurements were carried out at a constant temperature of 308 K. Ten concentration points are acquired, uniformly distributed within the concentration range investigated. The non-linear calibration data are fitted to a third-degree polynomial.

All isotherm data were obtained by frontal analysis. One reservoir of the chromatographic instrument delivered a stream of the mobile phase, another reservoir the sample solution. The desired concentration of the studied compound is obtained by selecting the concentration of the mother sample solution and the flow-rate fractions delivered by the 2 pumps. The breakthrough curves are recorded successively at a flow-rate of 1.0 mg/mL, with a sufficiently long time delay between each breakthrough curve to allow sufficient time for the reequilibration of the column with the pure mobile phase. The injection time of the sample depends on the time required to reach the plateau concentration at the outlet of the column. All the overloaded profiles needed for the validation of the fitted isotherms were recorded during the frontal analysis experiments.

In this work, 4 low-molecular hydrophobic solutes were used to measure the isotherm parameters on the C_{18} adsorbent that is the representative adsorbent of the RPLC. In this case 2 different multi-step single-component frontal analyses were carried out. First case was carried out with the connection of the column, but the other case was carried out without the connection of the column. With the breakthrough curves without the connection of the column, the system volume including dwell time is excluded from the breakthrough curve with the connection of the column by deducting the area of the breakthrough curve without connection from the area of breakthrough curve with connection. Fig. 1 shows the overlapped breakthrough curves with and without connection of the column of benzene. The difference of area in each step means the accumulated amount of solute in the column. Therefore, the adsorbed amount of solute is easily calculated by the volume fraction of the mobile phase and the stationary phase.

RESULTS AND DISCUSSION

An adsorption isotherm is a measure of the relationship between the concentration of bound and sample in a given system and by fitting the experimental adsorption isotherm to a mathematical model. It is possible to estimate the binding properties of the system using the corresponding fitting coefficients. However, the selection of the guest molecule could have direct influence on the characterization of the system.

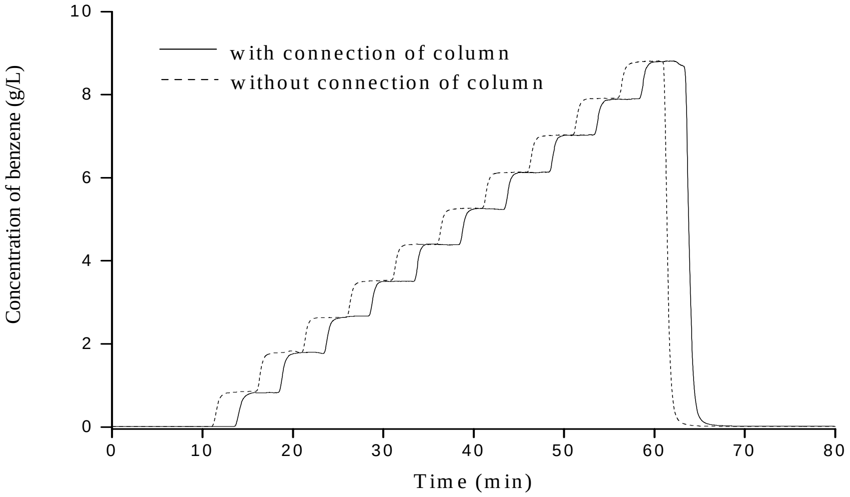

Fig. 1. The overlapped breakthrough curves of benzene with and without connection of column (Solid line is the breakthrough curve with the connection of the column and dash line is the breakthrough curve without the connection of the column)

To this study, solutions of each sample at different concentrations of organic mobile phase modifier ranging from 85 to 94 % were carried out and q was calculated according to the procedure described in the experimental section. Subsequently, the experimental adsorption isotherms were fitted to the linear and well-known Langmuir models. This was accomplished using the solver function in OriginPro 7.5 software by varying the fitting parameters to reach a value of 1 for the squared correlation coefficient (R^2).

This study has chosen 4 similar-shaped hydrophobic molecules *i.e.* benzene, toluene, chlorobenzene and 1,2-dichlorobenzene. The molecules are not homogeneous isomers. Benzene actually is more stable than might be expected for a system of 6 carbon-carbon single bonds and 3 carbon-carbon bonds. The molecule is planar, the carbon atoms are at the corners of a regular hexagon and the delocalization of the electrons is complete. Toluene (methylbenzene) just has a methyl group attached to the benzene ring-replacing one of the hydrogen atoms. It is a bigger molecule and so the van der Waals dispersion forces will be bigger. Chlorobenzene and 1,2-dichlorobenzene are the chloro-substituted benzenes. Some physico-chemical properties for solutes are listed in Table-1[18,19]. We are studying 2 non-polar solutes (benzene and toluene) and 2 low polar solutes (chlorobenzene and 1,2-dichlorobenzene). Comparisons of aqueous solubility of benzene with reference to their structural influence by polarity one can conclude that van der Waals dispersion forces between benzene molecules are quite strong. Toluene has a small permanent dipole, so there will be dipole-dipole attractions as well as dispersion forces. The dipole is due to the CH_3 group's tendency to "push" electrons away from itself. This also affects the reactivity of toluene. Both chlorobenzene and 1,2-dichlorobenzene

TABLE-1
THE PARTITION COEFFICIENTS BETWEEN WATER AND *n*-OCTANE (log P), DIPOLE MOMENTS (μ) AND AQUEOUS SOLUBILITY OF INVESTIGATED SOLUTES

Solute	log P[a]	μ (D)[c]	Aqueous solubility (at 298 K)
Benzene	2.79	0.00	1750 mg/L[d]
Toluene	3.33	0.31	0.052 % [b]
Chlorobenzene	3.66	1.54	0.49 mg/L[d]
1,2-Dichlorobenzene	4.52	2.00	147 mg/L[d]

[a] Data from the http://pubs.acs.org/subscribe;
[b] Data from the http://macro.lsu.edu/howto/solvents.htm
[c] Data from reference 19; [d] Data from reference 20.

possess a dipole moment that is oriented in the plane of their benzene ring. For these solutes the calculations indicate that the lowest energy configuration corresponds to the ring lying flat on the surface. In this orientation the dipole moment lies perpendicular to the radial electric field, which minimizes the polarization. Mobile phase components (water or methanol) do not share this property; however, its response may be muted by competing adsorption on the adjacent hydrophobic C_{18} surface and by intermolecular interaction that cause the modifier molecules.

The empirical adsorption-equilibrium isotherm models most frequently used in liquid-solid chromatography are the Langmuir and the so-called Langmuirian-type (Freundlich, Langmuir-Freundlich, *etc.*) isotherm models[20,21]. The shapes of the Langmuirian isotherms are always convex upward, indicating that there are no significant attractions between molecules of adsorbate and the adsorption capacity of the adsorbent is finite.

The experimental adsorption isotherms of benzene obtained at the different conditions are reported in Fig. 2. The shape of the adsorption isotherm is slightly concave upward on the C_{18} surface, as demonstrated by the plot of q as a function of C which increases constantly within the range of concentrations accessible to measurements. For instance, if the mobile phase was methanol 90 % (v/v) and water 10 % (v/v) chromatograms reported in Fig. 1 - two concentrations, the maximum concentration recorded at the column outlet and the maximum uploaded concentration, were 63.25 and 87.80 mg/mL, respectively. These values define "zones" of the isotherm. For the data measured at the lowest methanol amount (85 %, v/v) this becomes especially important. In fact, because of the noticeably higher time spent by molecules in the column in these conditions (q = 84.87 against q = 47.05 at methanol 94 %, v/v), dispersive phenomena become apparent. The extrapolated value for q in these conditions is, accordingly, the most critical parameter. This is probably also the reason for the isotherm crossing observed in Fig. 2.

Analogous experimental isotherms were obtained for other investigated solutes (Figs. 3-5). It is evident that in case of toluene the intersection is clearly expressed. It is not too difficult to see from Fig. 3 that the discrimination of q values it becomes

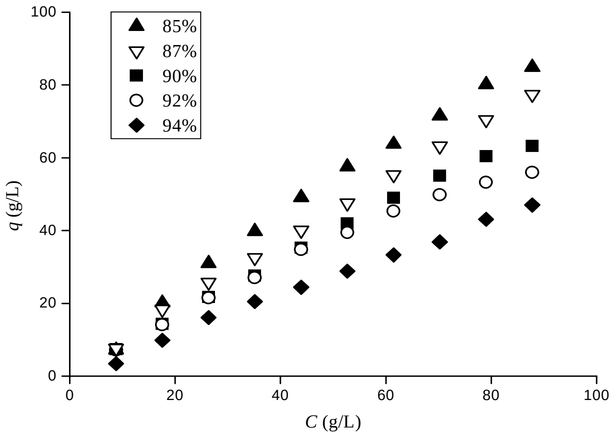

Fig. 2. Experimental isotherms of benzene on the C_{18} column with different concentrations methanol in mobile phases

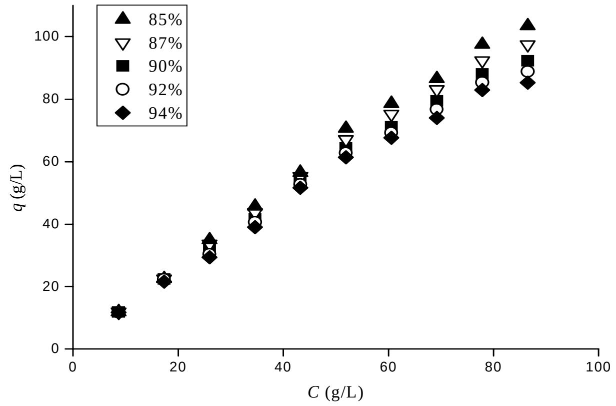

Fig. 3. Experimental isotherms of toluene on the C_{18} column with different concentrations of methanol in mobile phases

expressed with the relatively high C values (more than 60 mg/mL). On comparing toluene and benzene isotherms, these results suggest that the position of the methyl group on the benzene skeleton does have a critical influence on the shape of the equilibrium isotherm. Nevertheless, the introduction of methyl groups in the benzene ring affect q values positively. Similar tendencies demonstrated the experimental chlorobenzene and 1,2-dichlorobenzene isotherms showed in Figs. 4 and 5. It is worthwhile to say that the isotherms approach intersection in the region of low uploaded concentrations. Without doubt, the polar chloride ion handle the absorption result in a positive growth q values. In these cases, the shapes of the adsorption isotherms are also unissentially concave upward on the C_{18} surface. For the data measured at the lowest methanol amount (85 %, v/v) the highest q value calculated for 1,2-dichlorobenzene (q = 214.97 against q = 141.35 for chlorobenzene).

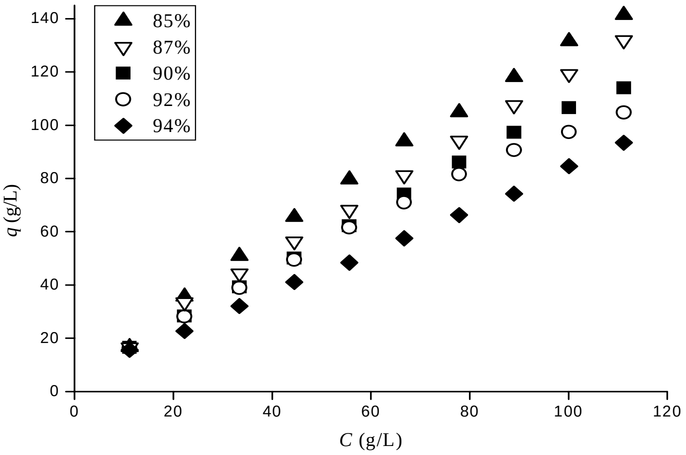

Fig. 4. Experimental isotherms of chlorobenzene on the C_{18} column with different concentrations of methanol in mobile phases

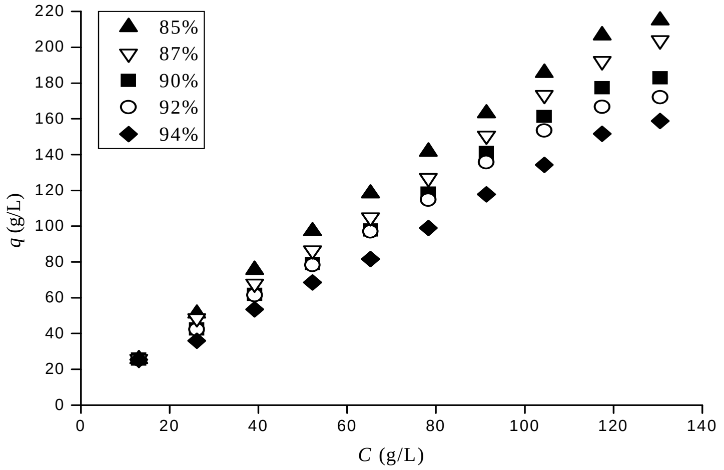

Fig. 5. Experimental isotherms of 1,2-dichlorobenzene on the C_{18} column with different concentrations of methanol in mobile phases

An additional point to emphasize that the benzene derivatives are sorbed in the following modifier concentration order: 94 % < 92 % < 90 % < 87 % < 85 % on a hydrophilic C_{18} surface (Figs. 2-5). Thus, as the concentration of methanol in the mobile phase increases at the liquid-solid interface, the saturation capacity of the adsorbent for solutes decreases.

In general, any adsorption isotherm models relate the analyte concentration in the bulk mobile phase to the apparent solid phase concentration. They assume that the solution contains only two components, the solute and the solvent, so they are really single-component isotherms. However, in present experimental case, the mobile phase is made of an organic modifier (methanol) dissolved in water. This makes used adsorption systems ternary. Theoretically, binary isotherms should be used, accounting for the competition between the solute and the organic modifier for adsorption. But in this case, the simplification of replacing the binary isotherm by a single-component isotherm the coefficients of which depend on the concentration of the modifier is valid. This assumption was proposed originally by Guiochon *et al.*[22]. This is because the adsorption of the organic modifier is weak compared to that of the analyte and the competition for adsorption between the analyte and methanol is negligible. The variation of the concentration of the organic modifier essentially affects the Gibbs free energy of the analyte in the bulk mobile phase. But the situation becomes more complex if the content of the organic modifier in eluent is high as in present experiments. In this case, the modifier the molecules of which tend to aggregate at the interface with the bonded layer, causing the formation of micro-environments (in most cases is monolayer) in which the mobile phase properties are different from those in the bulk.

Despite being aware of the risk of oversimplification, the only possible choice for studying the frontal analysis profiles were the simple linear and Langmuir isotherms. As a partial support for this fact, we mention that, in some isolations (*e.g.* in preparative scale chromatography or simulated moving bed), adsorption isotherms are sometimes considered as 'working-curves' for describing the separation process under well-specified conditions and for the optimization of the experimental variables, without being too concerned with their physical meaning. The experimental adsorption data acquired were fitted to the equations of the linear and Langmuir. The parameters were shown in the Tables 2 and 3. The R^2 values (goodness of fit criterion) computed the 2 types of isotherms are presented in these tables also.

A well-used empirical isotherm is the linear relationship (eqn. 2), which also applicable for a heterogeneous surface that is more often seen in natural systems. Unfortunately, the linear isotherm is, in contrast to the Langmuir isotherm, purely empiric and does not give any estimate of an adsorption maximum. The linear isotherm parameters are reported in Table-2. According to the experimental isotherms presented in Figs. 2-5, the obtained trends are quite linear within the limits of investigated concentrations. In the circumstances, simple linear approach was most suitable for the data. Table-2 indicate that the linear isotherm is appropriate for sorption of benzene, toluene, chlorobenzene and 1,2-dichlorobenzene on a C_{18} surface. When the isotherm data were fit using the linear isotherm model, R^2 values for all isotherms fell between 0.9918 and 0.9996. The analysis of values n (Table-2) showed that their changes in dependence on the composition of mobile phase did have systematic character. Smallest the values of the coefficients n were found for the benzene (0.5329), toluene (0.9883), chlorobenzene (0.7793) and 1,2-dichlorobenzene (1.1980) with 85 % (v/v) of methanol in the mobile phase. The higher values of n were established with 94 % (v/v) of modifier for the all solutes. In most cases, the linear equation (eqn. 2) provides the highest value of the correlation coefficient (R^2) and thus is the model to which the experimental data fit best.

TABLE-2
PARAMETERS OF LINEAR ISOTHERM OBTAINED WITH DIFFERENT METHANOL CONTENT IN THE MOBILE PHASE

Solute	Mobile phase (% methanol/water, v/v)	n	m	R^2
Benzene	94/6	0.9678	3.7649	0.9947
	92/8	0.8660	2.0149	0.9993
	90/10	0.7334	2.2096	0.9970
	87/13	0.6311	4.3917	0.9918
	85/15	0.5329	0.6333	0.9976
Toluene	94/6	1.2045	3.5217	0.9971
	92/8	1.1304	4.4145	0.9965
	90/10	1.0658	4.9464	0.9959
	87/13	1.0245	5.3228	0.9949
	85/15	0.9883	5.4509	0.9933
Chlorobenzene	94/6	1.2326	8.4070	0.9977
	92/8	1.1339	5.9402	0.9996
	90/10	1.0004	6.2544	0.9988
	87/13	0.8981	9.0180	0.9971
	85/15	0.7793	5.9350	0.9996
1,2-Dichlorobenzene	94/6	1.6551	9.1880	0.9977
	92/8	1.5562	6.3103	0.9988
	90/10	1.4223	6.7198	0.9970
	87/13	1.3189	10.0675	0.9964
	85/15	1.1980	6.6495	0.9982

By analyzing the data (Table-3) obtained with the Langmuir model, two aspects can be exploited: (1) the notable agreement among q estimates at the different mobile phase compositions; (2) the a (or b) dependence inversely proportional to the monolayer capacity. The Langmuir isotherm (eqn. 3) represents a case where the binding of the analyte can be described by a finite number of identical surface sites. It is often assumed that if data follows the Langmuir isotherm, it is indicative of a specific interaction between the compound and a surface. The Langmuir isotherm can be used to determine the maximum adsorption capacity of this specific site and also include a constant related to the saturation capacity.

The Langmuir equation (eqn. 3) also provides the suitable value of the correlation coefficient. The coefficients a of Langmuir isotherm for benzene are significantly different. Smallest the values of coefficient a were found for the benzene ($0.05861 < a < 1.2537$). The values of the specific saturation capacity of the adsorbent were quite close for toluene, chlorobenzene and 1,2-dichlorobenzene. This result is consistent with the similarity of the 3 compounds in structure and binding sites onto the stationary phase. For all investigated sorbates, value of coefficients 'a' increase with the decrease of an amount of methanol in the mobile phase. Comparing solutes, the value of coefficient 'a' with 94 % (v/v) of methanol in mobile phase increases

TABLE-3
PARAMETERS OF LANGMUIR ISOTHERM OBTAINED WITH DIFFERENT METHANOL CONTENT IN THE MOBILE PHASE

Sample	Mobile phase (% methanol/water, v/v)	a	b	R^2
Benzene	94/6	0.5861	0.0010	0.9964
	92/8	0.9413	0.0044	0.9926
	90/10	0.8834	0.0019	0.9974
	87/13	0.9807	0.0011	0.9989
	85/15	1.2537	0.0028	0.9971
Toluene	94/6	0.6586	0.0020	0.9976
	92/8	0.8941	0.0052	0.9986
	90/10	1.3955	0.0028	0.9974
	87/13	1.9807	0.0021	0.9987
	85/15	2.0537	0.0028	0.9968
Chlorobenzene	94/6	0.9856	0.0020	0.9937
	92/8	1.3305	0.0040	0.9988
	90/10	1.2702	0.0022	0.9981
	87/13	1.3601	0.0016	0.9977
	85/15	1.6451	0.0029	0.9996
1,2-Dichlorobenzene	94/6	1.7135	0.0015	0.9958
	92/8	1.7163	0.0026	0.9956
	90/10	1.6678	0.0015	0.9948
	87/13	1.7551	0.0011	0.9923
	85/15	2.0386	0.0021	0.9982

in the order: 1,2-dichlorobenzene > chlorobenzene > toluene > benzene, showing increased polarity of these compounds (log P and μ) in the same order. Relative higher value of coefficient 'a'. for 1,2-dichlorobenzene (1.7135) is in accordance with its dipole moment (2.00 D). With the lowest modifier content (85 %, v/v), this order become: toluene > 1,2-dichlorobenzene > chlorobenzene > benzene. As the aqueous solubility of a hydrophobic compound decreases (Table-1), the specific saturation capacity of the adsorbent increases, probably from entropy driven interaction with the surface. In present experiment, the modifier are water soluble organic solvent. Organic modifier can decrease the 'q' by increasing the apparent solubility. The presence of dissolved organic modifier commonly reduces the adsorption of a chemical. This may be due to the increased solubility of the chemical in such a solution or to competitive adsorption. Comparing 1,2-dichlorobenzene and chlorobenzene, the value of coefficient a decreases from 2.0386 to 1.6451 showing decreased polarity that is supported by comparing values of log P and μ from Table-1. For the same reasons, the 'a' values for toluene, chlorobenzene and 1,2-dichlorobenzene should more than that for the benzene. Also, for 1,2-dichlorobenzene, the positive relation of two chloride groups in the ring affects the specific interaction energy between the two similar molecules.

The values of coefficient 'b' of Langmuir isotherm are small and are distinguished weakly for all investigated solutes. Although this model accounts for data obtained with a given compound on a variety of mobile phases, the numerical values of the coefficients of this adsorption isotherm are not sensitive to these conditions. It is suggested that at high concentrations of the organic modifier (85-94 %, v/v) and low solute concentrations, as in present case, the Langmuir isotherm model cannot satisfactorily describe absorption mechanism in spite of the high correlation coefficients. It is conceivable that there are significant new experimental constraints linked to this approach, arising from a limited solubility of the analyte in water and methanol high-enriched eluent, possible adsorbate-adsorbate interactions and solute-solute association. Even though this Langmuir isotherm model provides the satisfactory accuracy, it cannot give much information on the physical nature of the absorption in this case.

Conclusion

The adsorption isotherms of benzene, toluene, chlorobenzene and 1,2-dichlorobenzene were acquired by frontal analysis on commercial C_{18} bonded column with 5 different mobile phases, aqueous solutions of methanol (85, 87, 90, 92 and 94 %, v/v). The adsorption isotherms are always strictly convex upward in methanol/water solutions. Linear and Langmuir adsorption isotherm models were fitted to the plot of the experimental adsorption isotherm. The calculations and analysis of the coefficients obtained for both models confirm that the adsorption data for solutes are best modeled with the linear model. We supposed that at the high concentrations of organic modifier (85-94 %, v/v) and over the range of solute concentrations, the Langmuir isotherm model couldn't satisfactorily describe mechanism and provide the objective information about the physical nature of the absorption despite its acceptable accuracy. Thus, the linear model is more appropriate to describe absorption of hydrophobic solutes on the C_{18} surface at investigated sorbate concentrations using the data obtained by frontal analysis.

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