

# Determination of Pure and Binary Volatile Organic Compounds (VOCs) Adsorption Equilibria using the Dynamic Method

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## 1. Introduction

Removal of volatile organic compounds (VOCs) is of significant interest in air quality control. Activated carbon adsorption is widely used in the removal of VOCs. To construct adsorption facilities, data on adsorption equilibrium and knowledge on the actual adsorption behavioral patterns are needed. By using the dynamic method for adsorption equilibria experiments these can be derived. Also when developing a mixed VOC component adsorption equilibria model it is difficult to control the experimental conditions such as keeping the total pressure constant and controlling the gas phase ratio especially for other conventional techniques. To overcome these problems the dynamic method was used for the adsorption equilibrium experiments.

In this study an original apparatus for the dynamic method was constructed and experimental studies were made on the adsorption of pure benzene and toluene and their binary mixtures at various concentrations by activated carbon. Also experimental and theoretical correlation of the adsorption equilibrium was also carried out using Toth equation and Dubinin-Radushkevich equation for pure component systems and for theoretical prediction of the adsorption equilibria of binary component systems the Ideal Adsorbed Solution Theory was used.

## 2. Pure Component Adsorption Equilibria Experiment

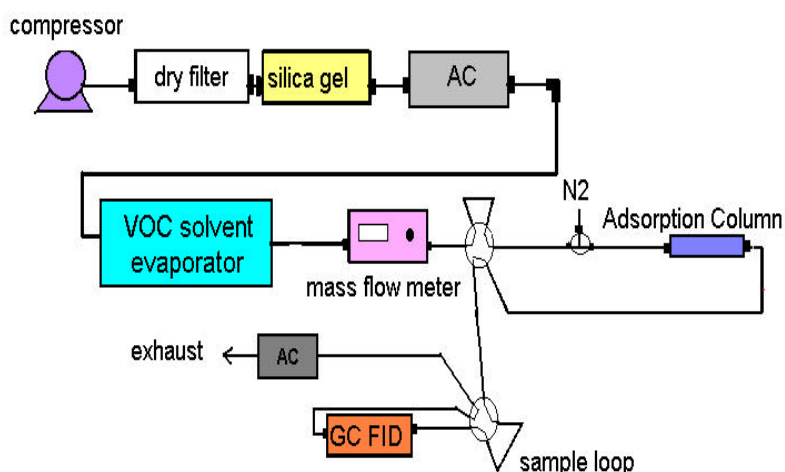
### 2.1 Method

An original apparatus used was constructed and is shown in Fig 1. Diffusion and bubbling were used as VOC evolution methods. The flow of the VOC gas was controlled using mass flow controllers. In the initial stages of the experiment a constant flow and concentration of the VOC gas was confirmed by directing the flow to the sample loop where automatic sampling was carried out and analyzed by Gas Chromatograph equipped with Flame-Ionization Detector (Shimazu GC-17A). At constant flow rate, constant concentration the VOC gas was fed to the adsorption column. About 3 g of activated carbon was packed in a stainless steel column of 1.60 cm ID. The VOC concentration of the outlet gas of the adsorption column was automatically analyzed at constant time intervals of 5 to 10 minutes. On completion of the experiment the activated carbon in the adsorption column was regenerated using flow of pure nitrogen at 403 K for 15 hours.

### 2.2 Results and Discussion

#### 2.2.1 Comparison of Dynamic Method with Headspace Gas Chromatography

The amount adsorbed for the pure component (benzene, toluene) derived from the breakthrough curves were compared to the amount adsorbed from Headspace Gas Chromatography (HS-GC) method<sup>(1)</sup>



**Fig.1 Apparatus used in the Dynamic Method**

used in previously in my laboratory (Fig.2) and shows a slight deviation of -0.6~22 % for benzene and -3~10 % for toluene, the reliability of the apparatus used in this dynamic method was confirmed.

### 2.2.2 Correlation using Toth and Dubinin-Radushkevich Equation

The Toth equation<sup>2)</sup> was used to correlate the experimental adsorption data for pure benzene and toluene.

$$N = mP / (b + P^t)^{1/t}$$

N : amount adsorbed, m : saturated amount adsorbed [mol/g], b : equilibrium constant [(kPa)<sup>t</sup>], t : parameter indicating heterogeneity of adsorbent [-]. The experimental adsorption equilibrium data for pure toluene and benzene were successfully correlated with Toth equation as shown in Fig.2. Also correlation of experimental data with Dubinin-Radushkevich equation<sup>3)</sup> shown below was carried out.

$$W = W_0 \exp\left[-\left(\frac{A}{\epsilon_0}\right)^2\right]$$

W : amount adsorbed [ml/g], W<sub>0</sub> : micropore volume [mL], A : adsorption potential [J/mol], ε<sub>0</sub> : affinity coefficient [-], ε<sub>0</sub> : VOCs standard adsorption potential [J/mol]. Experimental data for pure benzene and toluene showed a good correlation with Dubinin-Radushkevich equation as shown Fig.3.

## 3. Binary Adsorption Equilibrium Experiment

### 3.1 Method

For the binary component adsorption experiments the apparatus used was similar to that used in the pure component adsorption experiment (Fig. 1) except for a few alterations. In the VOC solvent evaporator section, the diffusion method was carried out using the permeator. The two gas lines in the permeator were used in the evolution of benzene and toluene, which were diluted to desired concentrations. The outlet flow of gases were monitored by mass flow controllers and then

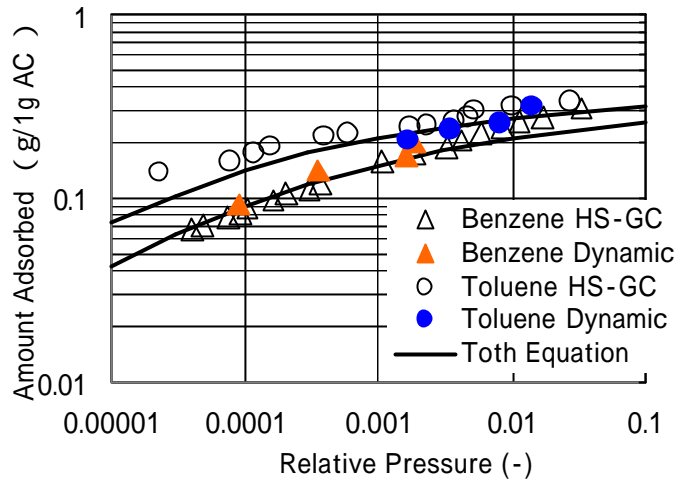


Fig. 2 Pure Benzene and Pure Toluene Isotherms for Dynamic and HS-GC Method

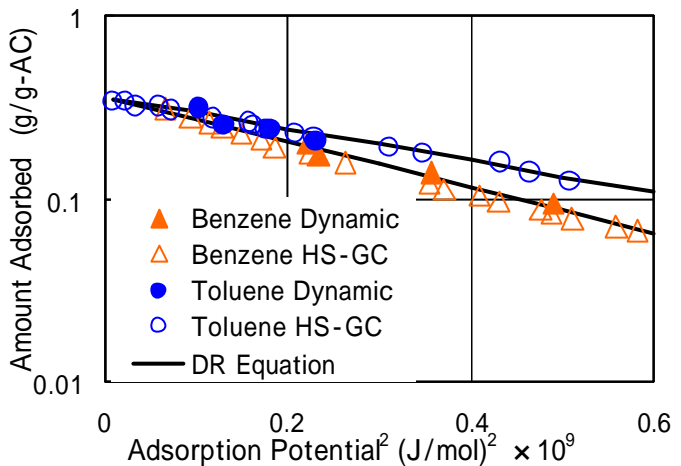


Fig. 3 Pure Benzene and Pure Toluene D-R Plot for Dynamic and HS-GC Method

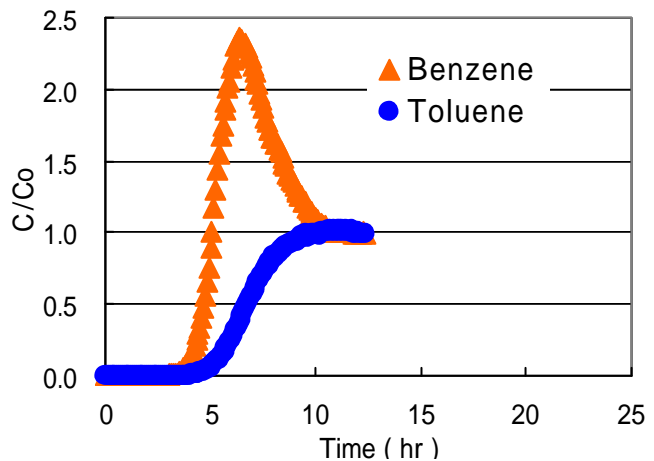


Fig. 4 Breakthrough Curve for Benzene and Toluene Mixture (Bz 2 : To 8)

passed to the mixing chamber. The binary adsorption experiments of benzene and toluene mixtures were carried out at the ratios (0.2 ~ 0.8) with the total concentration fixed at 507ppm.

### 3.2 Results and Discussion

#### 3.2.1 Binary Mixture Adsorption Equilibrium Breakthrough Curves

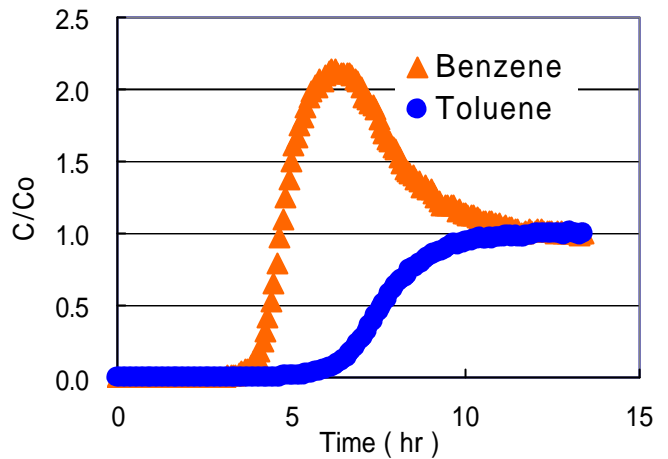
The binary mixture adsorption experiments of benzene and toluene were carried out and breakthrough curves are shown in Fig. 4 ~ Fig. 7. From the breakthrough curves benzene appears earlier and has a steeper slope compared to toluene, regardless of the inlet concentration. The competitive adsorption pattern was observed, benzene was being displaced by toluene, which was more the strongly adsorbed compound causing the benzene curve to display a “roll up phenomenon”. The amounts adsorbed are shown in Table 1. When comparing the amount adsorbed for binary mixtures and the amount adsorbed for the same concentration as a pure component calculated using the Toth Equation; for benzene the amount adsorbed is drastically decreased when being adsorbed in the presence of toluene. This is due to toluene displacing the adsorbed benzene. However the amount of Toluene adsorbed is slightly lower in the presence of benzene because benzene is not completely displaced by toluene.

#### 3.2.2 Correlation using Ideal Adsorbed Solution (IAS) Theory

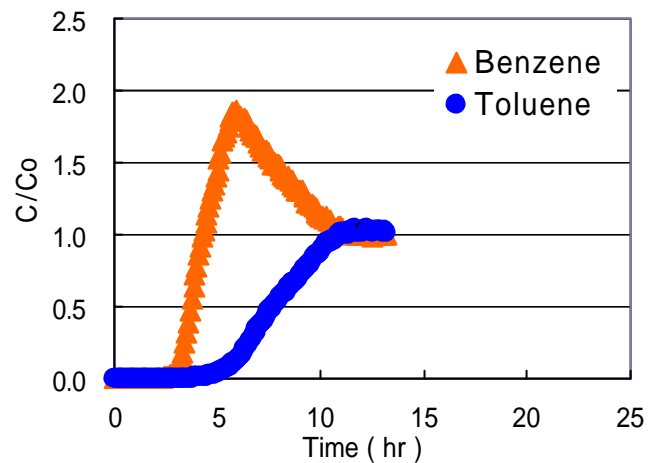
The binary adsorption equilibria experimental results were compared with results derived from the Ideal Adsorbed Solution Theory<sup>4</sup>). The IAS theory model, which is one of the most widely used multicomponent systems models, is uses only pure component isotherms for prediction. In this study, the Toth equation was selected for calculation of IAS theory. The basic equation of IAS theory is similar to Raoult’s law for ideal solutions:

$$Py_i = x_i P_i^o(p)$$

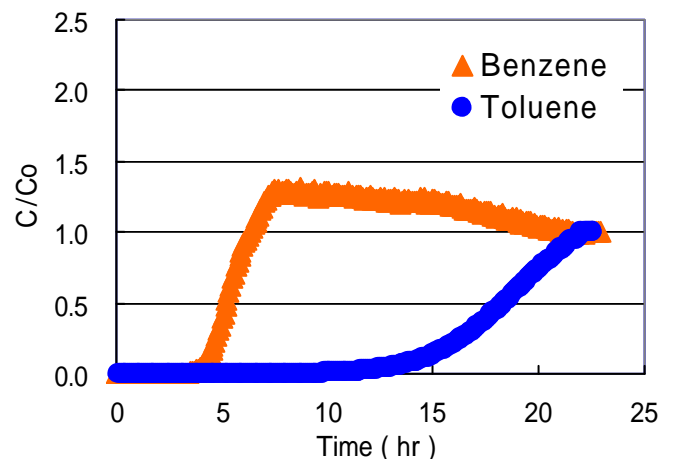
Where P is the total pressure,  $y_i$  is the gas phase mole fraction of component i,  $x_i$  is the



**Fig. 5 Breakthrough Curve for Benzene and Toluene Mixture ( Bz 4 : To 6 )**



**Fig. 6 Breakthrough Curve for Benzene and Toluene Mixture ( Bz 5 : To 5 )**



**Fig. 7 Breakthrough Curve for Benzene and Toluene Mixture ( Bz 8 : To 2 )**

adsorbed phase mole fraction of component  $i$ , and  $p^?$  is the spreading pressure of the mixture. The standard state pressure  $P_i^o(p)$  is defined as the gas pressure when only component  $i$  is present. This corresponds to the spreading pressure of the mixture. From the Gibbs isotherm, the spreading pressure can be given as

$$p_i^* = \frac{p_i A}{RT} = \Pi_i(P_i^o) = \int_0^{P_i^o} \frac{n_i^o(P_i^o)}{P_i^o} dP_i^o$$

**Table 1 Benzene and Toluene Mixture Experimental Results**

	Bz 0.2	To 0.8	Bz 0.4	To 0.6	Bz 0.5	To 0.5	Bz 0.8	To 0.2
Amount Adsorbed (g/g-AC) (Dynamic Method)	0.008	0.258	0.012	0.245	0.016	0.201	0.042	0.170
Amount Adsorbed when Pure (g/g-AC) (Toth)	0.140	0.274	0.164	0.266	0.172	0.259	0.233	0.190

The comparison of experimental and theoretical results is shown in Fig. 8. It can be said that the prediction correlates well with the experimental data for the benzene and toluene mixed adsorption equilibria data. The good correlation is due to both benzene and toluene having similar structures and both being nonpolar compounds, thus the benzene and toluene is considered to be an ideal mixture.

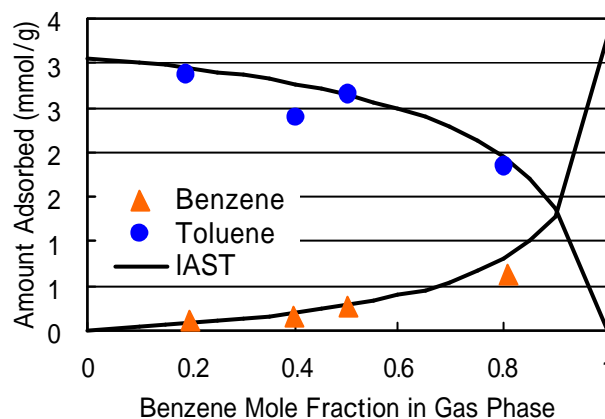
#### 4. Conclusion

The original apparatus constructed and the dynamic method was successfully carried out for both pure component and binary component adsorption equilibria experiments.

Correlation of pure component experimental data with Toth and Dubinin-Radushkevich Equations were in good agreement. From the binary component experiments, competitive adsorption was observed and the adsorption equilibria data was successfully derived using the dynamic method. Prediction using the IAS theory for the binary component was in good correlation with experimental data. It can be concluded that prediction using the IAS theory for the binary component using the pure component adsorption data was in good correlation with experimental data. Therefore the results and findings from this study can be used for designing adsorption facilities.

#### References:

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**Fig. 8 Comparison of Experimental and IAS Theory Results**