

## COLUMN ADSORPTION OF THE MIXED ORGANIC-SOLVENT BY Y TYPE ZEOLITE

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## ABSTRACT

Fixed-bed adsorption experiments of laboratory-scale were carried out to remove organic solvent vapors by Y-type zeolite adsorbent. Some of binary adsorption equilibria of azeotropic mixture-HSZ systems showed one or two azeotropic points. Breakthrough curve could be simulated using the Stop & Go method for these systems.

## INTRODUCTION

Discharge of organic substances into air has been strongly prohibited since some decades ago, to preserve comfortable natural environment. Though hydrocarbons, alcohols and chlorinated hydrocarbons had been used as the degreasing agent in industries, these solvents may also affect to our environment, and it is necessary to remove them from air as much as possible. This study was performed aiming at presenting useful data for the design of adsorption processes, especially the removal of the solvent vapors, as above, from air by adsorption. The solvents used were trichloroethylene (TCE), iso-propanol (IPA) and ethanol (EtOH).

## EXPERIMENTAL

### Adsorbent

Y-type of high silica zeolite (HSZ) (from TOSOH Corp.,Ltd JAPAN.) were used. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was 460.

### Experimental Procedure

Solvents used were *iso*-propanol (IPA), trichloroethylene (TCE) and ethanol (EtOH). Adsorbents were packed in a glass column of 0.10m length and 0.0156m i.d. Experimental conditions were as follows: linear flow rate; 0.2 m/s, influent concentration; in the range of 0.004~0.2 mol/m<sup>3</sup>, and temperature; 298 K. (Figure 1)

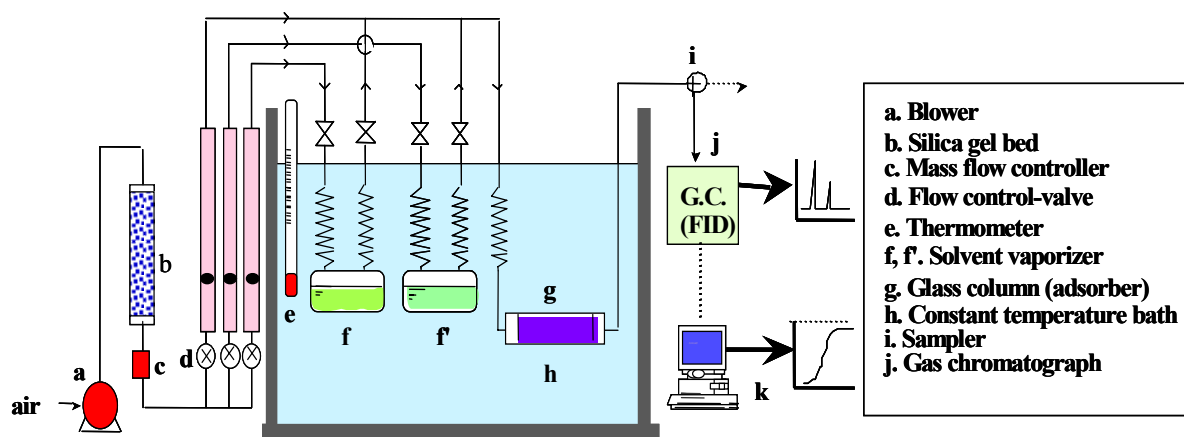


Figure 1. Schematic diagram of experimental apparatus for adsorption

## RESULT AND DISCUSSION

### Breakthrough Curves

Figure 2 and Figure 3 show several types of breakthrough curves obtained for IPA-TCE -Y-type zeolite system. There, the range of the total concentration of IPA and TCE shows 2000~4000ppm and 5000~5500ppm, respectively. For this system, reversal of the order of break (turn over) occurred twice at concentrations of 0.25 and 0.75 mole fractions of IPA. When the mole fractions were 0.25 and 0.75, the mixture of two components

behaved as if it was a single component system as shown in Figure 2 (B) and (D). For other azeotropic mixture systems, the turnover occurred only once. The breakthrough curves for other systems always showed so-called constant pattern behaviour for the whole concentration range [1]. Figure 4 show several types of breakthrough curves obtained for EtOH-TCE -Y-type zeolite system. The range of the total concentration of EtOH and TCE shows 5500~6500ppm. For this system, reversal of the order of break (turn over) occurred once at concentrations of about 0.25 mole fractions of EtOH. When the mole fractions were 0.25 , the mixture of two components behaved as if it was a single component system as shown in Figure 5 (B).

### Adsorption Equilibria

Binary adsorption equilibria for the system of IPA-TCE of several concentrations are shown in Figure 5 in form of X-Y diagram (X and Y are the mole fractions of feed concentration and the amount adsorbed at equilibrium, respectively). For this system, it is reported that the azeotropic point of vapor-liquid equilibrium is only one, but two azeotropic points were observed in the adsorption equilibrium. When the saturation vapor pressures of each component were almost the same, appearance of two azeotropic points were reported for vapor-liquid equilibrium. It is thought, therefore, that the phenomenon occurred in adsorption equilibrium for these systems can be ascribed to the fact that the saturation vapor pressure and the boiling points of each component were almost the same. The same thing can be said about the system of EtOH and TCE, which are shown in Figure 6. For example, in the case of Figure 5, (B) and (D), and in the case of Figure 6, (B) are azeotropic points.

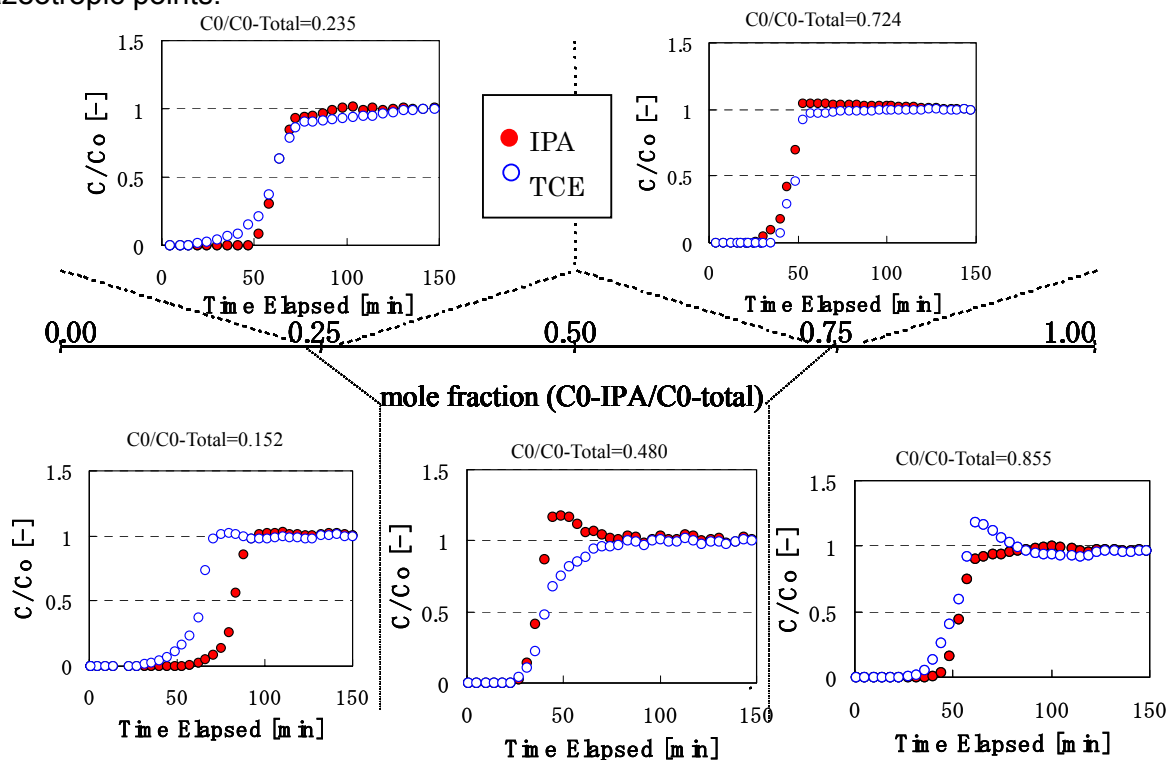


Figure 2. Several types of breakthrough curves observed for IPA-TCE- system (2000~4000ppm)

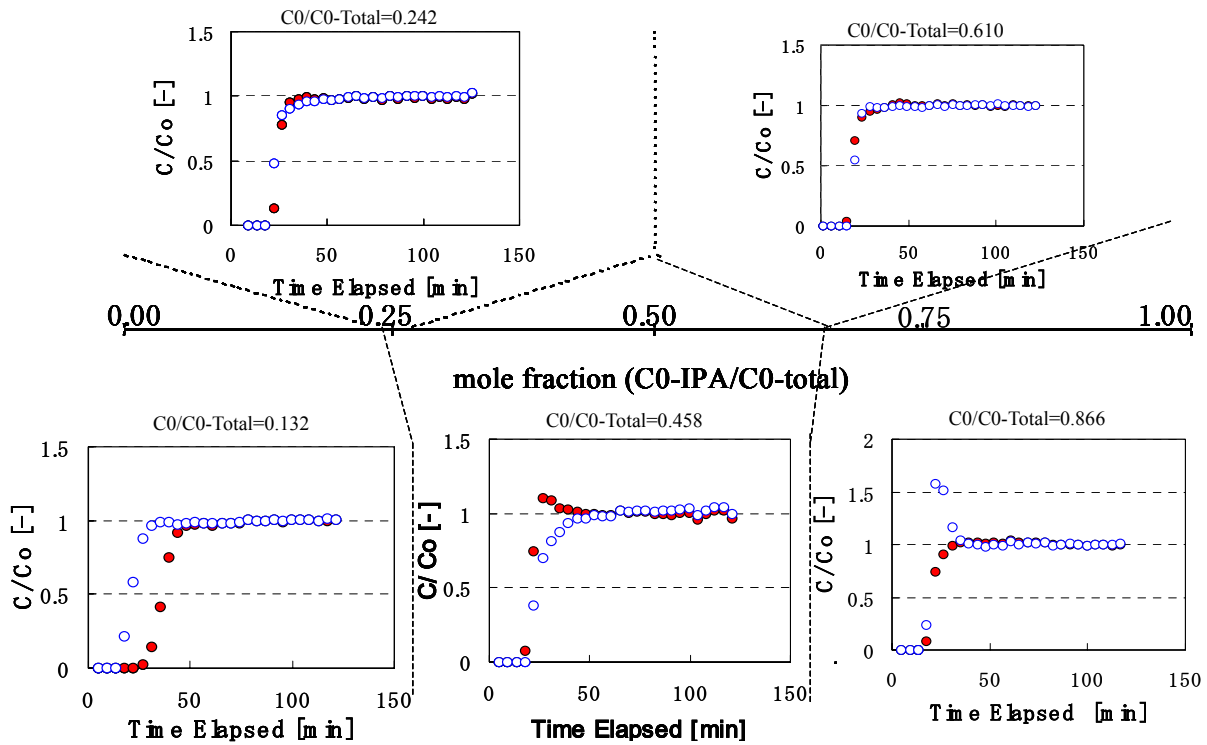


Figure 3. Several types of breakthrough curves observed for IPA-TCE- system (5000~5500ppm)

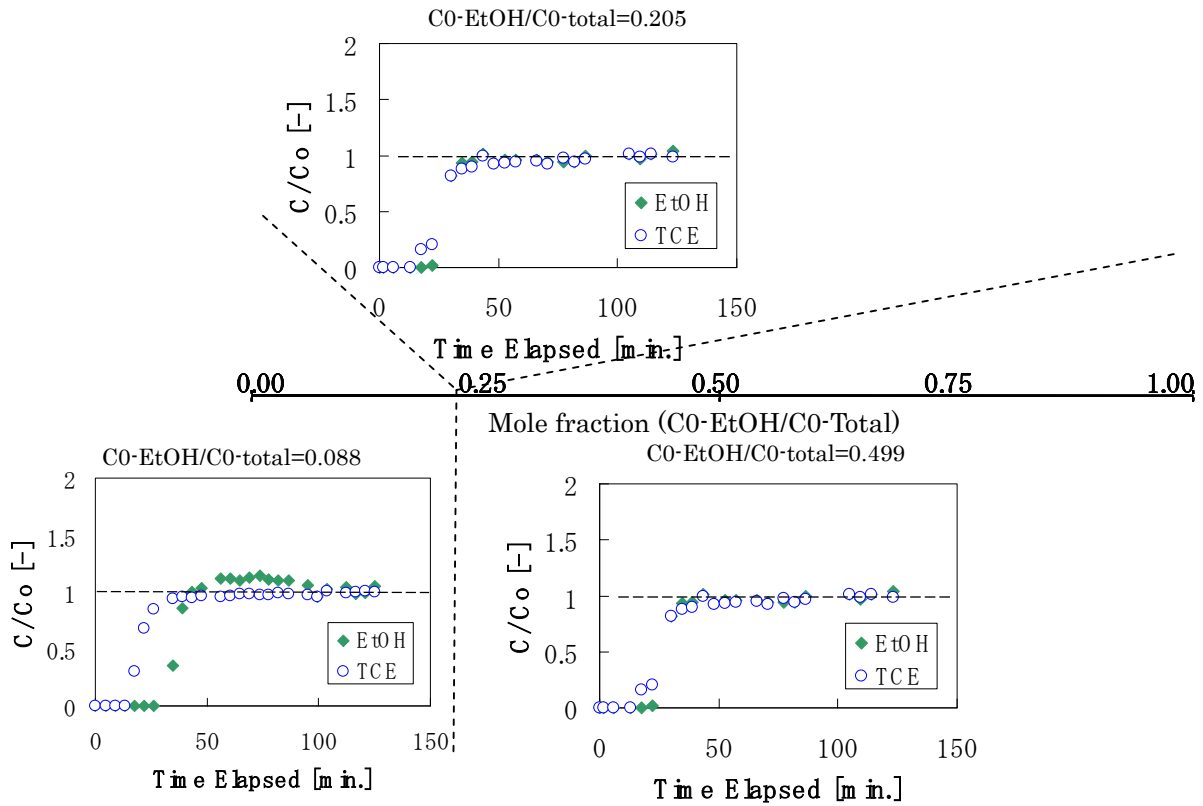
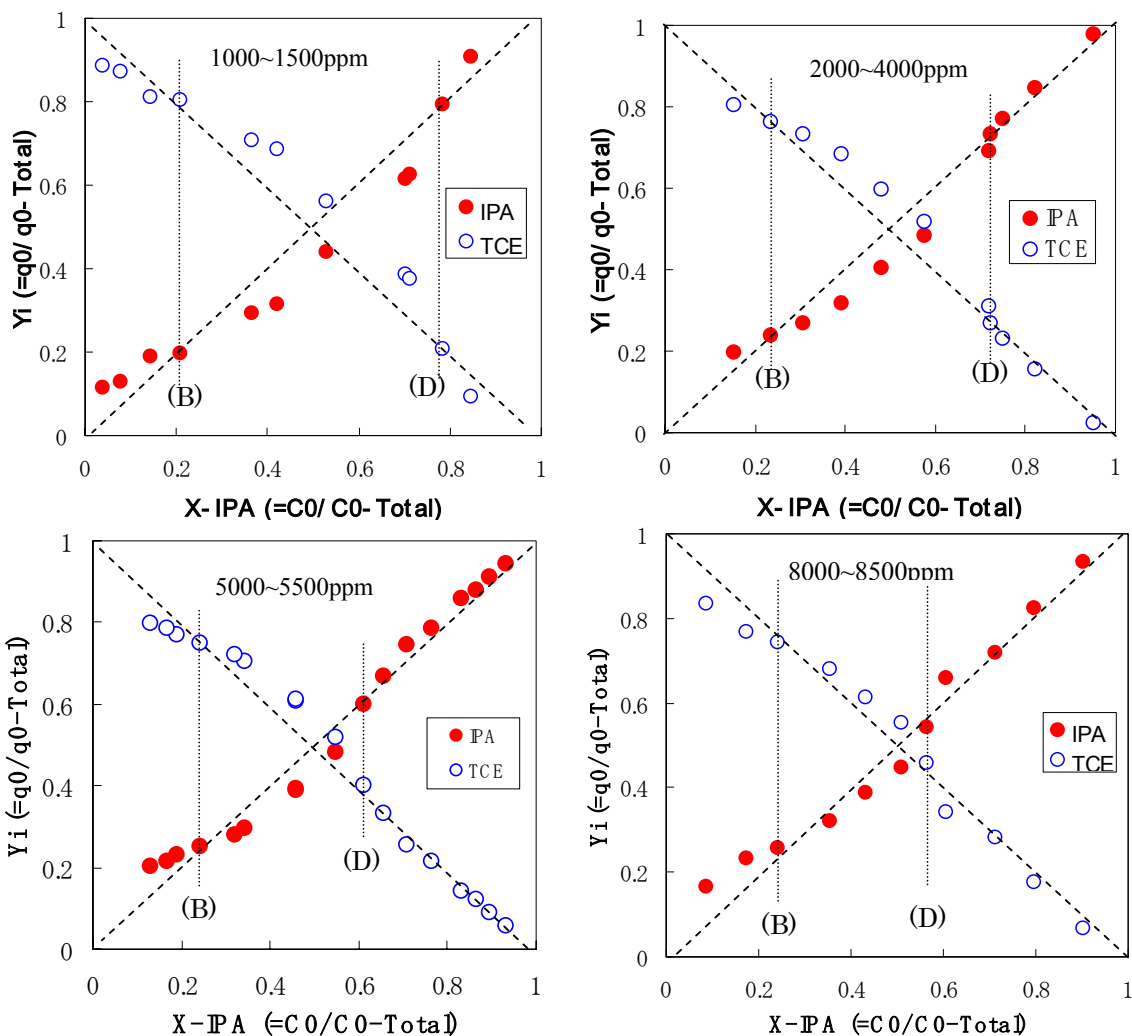
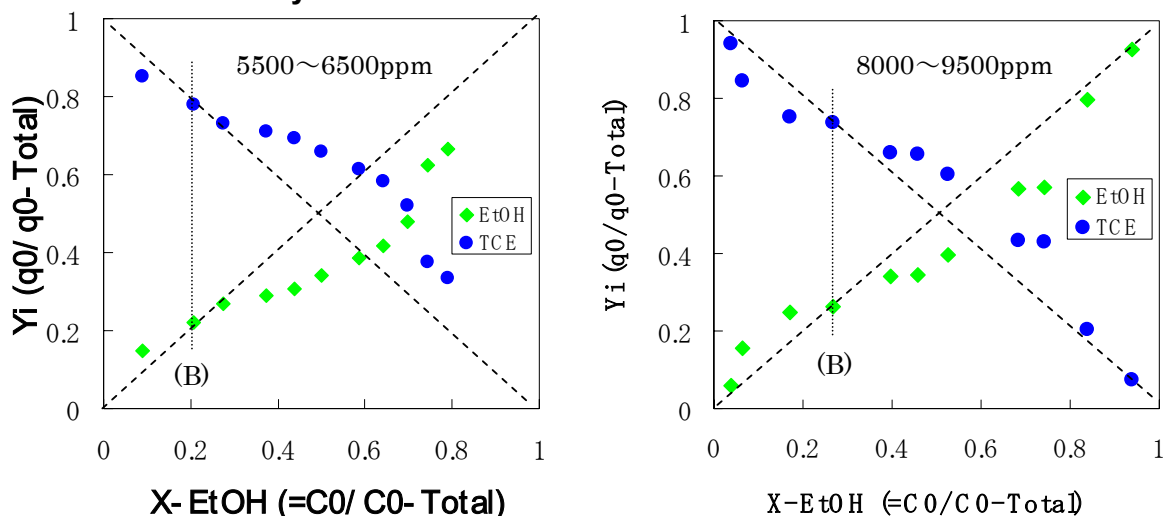


Figure 4. Several types of breakthrough curves observed for EtOH-TCE system (5500~6500ppm)



**Figure 5. Comparison of adsorption equilibrium for experimental concentration 1000~1500,2000~4000,5000~5500,8000~8500ppm on IPA-TCE-Y-type zeolite system**



**Figure 5. Comparison of adsorption equilibrium for experimental concentration 5500~6500, 8000~9500ppm on EtOH-TCE-Y-type zeolite system**

## Stop & Go Method

(1) Stop & Go Method: Figure 7 shows a concept of Stop & Go method. The Stop & Go method used in this study can be explained briefly as follows. Each column is divided to N complete mixed cells in axial direction. While the flow between cells is stopped for a certain short time (dt), the adsorbed or desorbed amount of the adsorbate within this time interval is calculated (Stop calculation). After this Stop calculation, the flows between cells are calculated by using inflow, remain gas amount and column pressure for dt time (Go calculation). These Stop and Go calculations within dt are repeated alternatively to get the breakthrough curve.

(2) Simulation Result: Since Langmuir equation was not able to be used for this binary systems, in which adsorption equilibrium data, two azeotropic points were observed, the following equation (1) was used. The equation of the azeotropic theory in a liquid-vapor azeotropic equilibrium was applied instead of Langmuir equation.

$$Y_i \gamma_i P_i^* = X_i P \quad (1)$$

where  $P_i^*$  is the vapor pressure and  $\gamma_i$  the activity coefficient of component i.

The activity coefficient was first calculated from experimental data. The relation between a gaseous phase molar fraction and the activity coefficient are shown in Fig.7.  $\gamma$  vs. X equation was obtained by curve fitting of this figure. This equation was substituted into Eq. (1) to get equation two correlations between a gaseous phase molar fraction and an adsorbed phase molar fraction as shown in Figure 7. Stop & Go method [2] for simulation of breakthrough curve with these correlations (Figure 7, 8 and 9) was applied to get Figure 8 and 9. Substitution of the order of breakthrough was seen twice in the simulation as well as the experiment. Also, breakthrough curves were almost simulated in all cases.

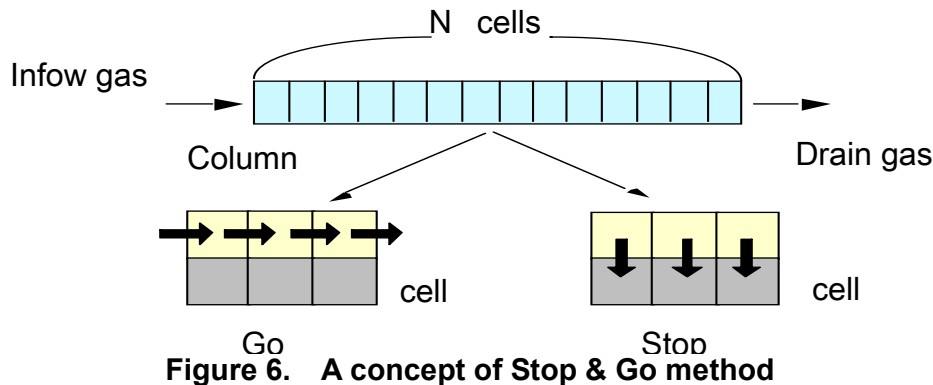


Figure 6. A concept of Stop & Go method

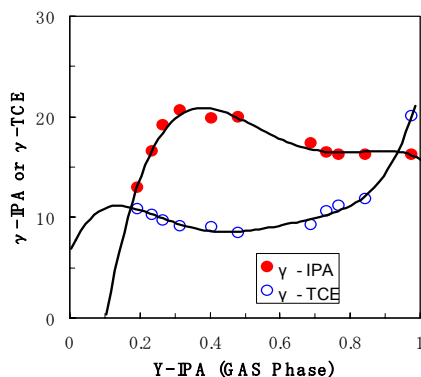


Figure 7. The relation between a gaseous phase Molar fraction and the activity coefficient

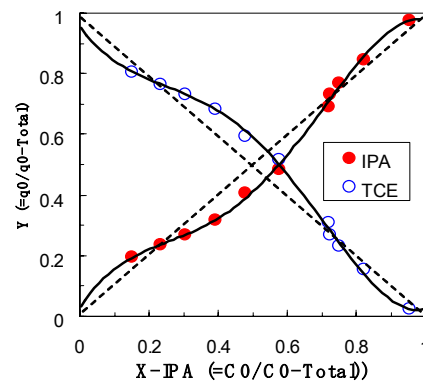


Figure 8. Comparison of the actual measurement of adsorption equilibrium data and estimated value

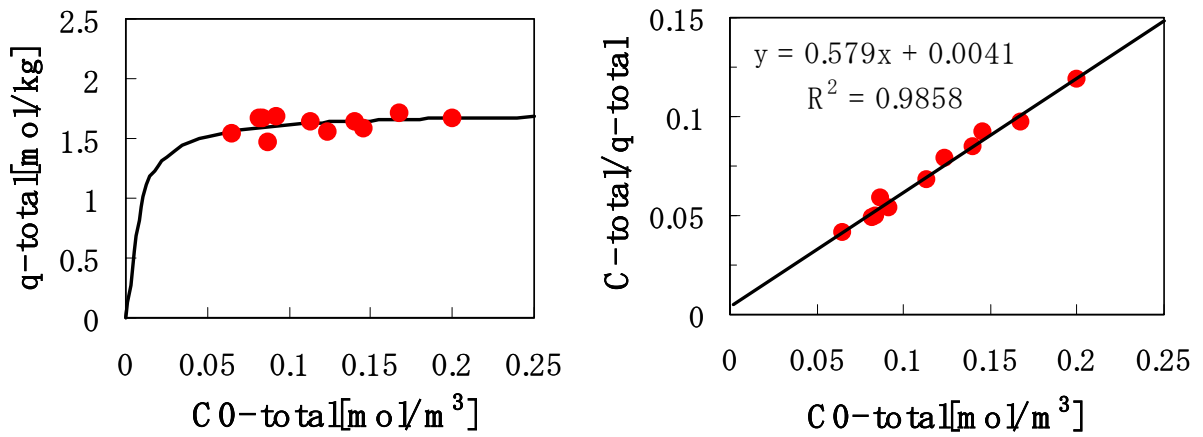


Figure 9. Adsorption isotherm as the total of IPA and TCE and Langmuir plot

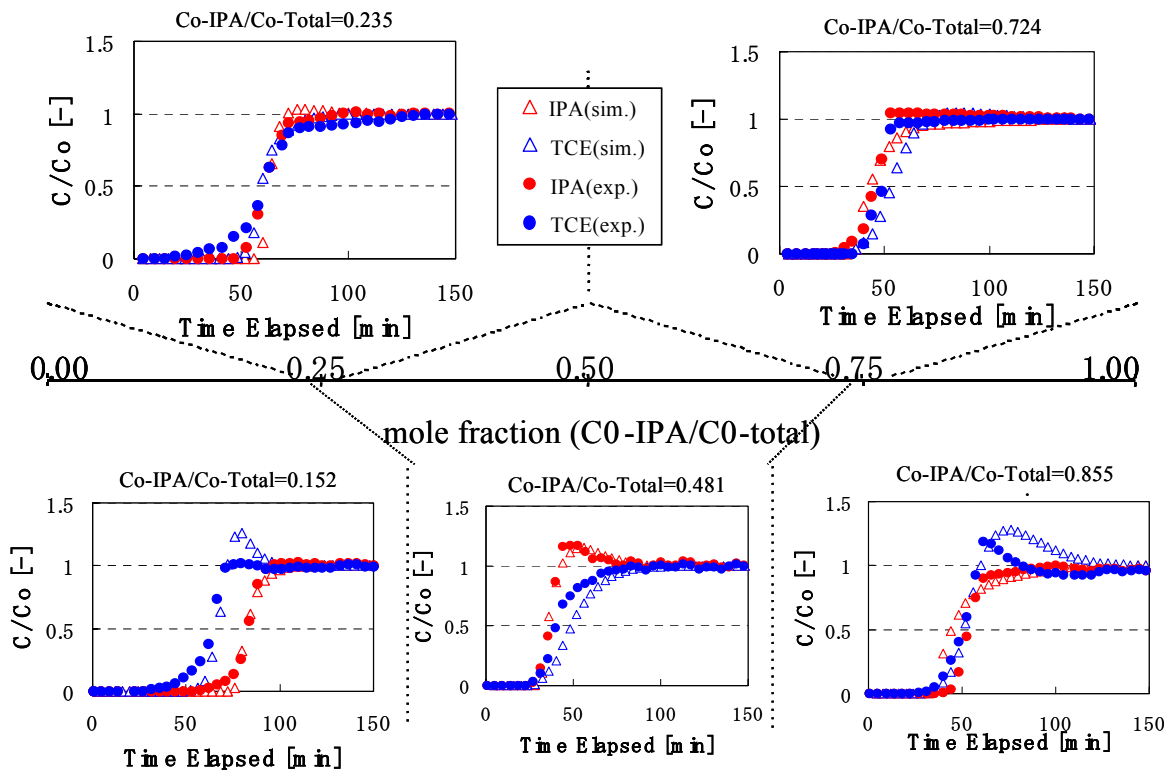


Figure 10. Comparison of the breakthrough curves for experiments and simulations (2000~4000ppm)

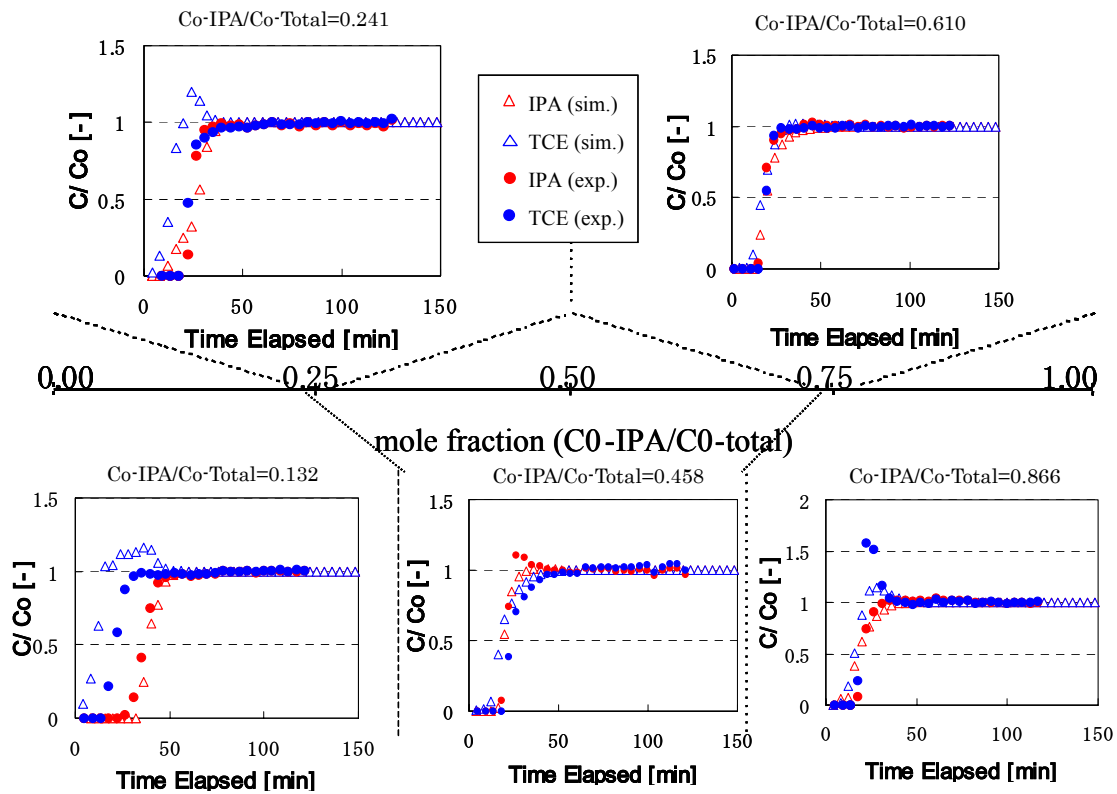


Figure 11. Comparison of the breakthrough curves for experiments and simulations (5000~5500ppm)

## CONCLUSION

Adsorption of some organic solvent vapors onto HSZ was studied. Usually, binary adsorption equilibrium except azeotropic mixture-HSZ systems could be correlated by Markham-Benton equation for the whole concentration range. Two azeotropic points appeared in the adsorption equilibrium for IPA-TCE -Y-type system. For this binary systems, adsorption equilibrium data could be expressed by proposed equation, similar to liquid-vapor azeotropic equilibrium equation. Breakthrough curve could be simulated using the Stop & Go method in the whole range for azeotropic mixture systems as well as for zeotropic systems. Comparison of simulated single adsorption isotherm of IPA and TCE with the experimental value, respectively, and brought a good result. One azeotropic point appeared in the adsorption equilibrium for IPA-TCE -Y-type system.

## REFERENCE

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- [2]Chihara. K., and Kondo. A.; "SIMULATION OF PRESSURE SWING ADSORPTION -Three gas components and three adsorption columns-," 2nd Inst. Conf. on Fundamentals of Adsorption, USA (1986)