Instead of the chlorofluorocarbon specified as the ozone-depleting substance, a chlorinated organic compound, hydrocarbon, alcohol, etc. are used as an alternative washing solvent, and they are used as a mixed solvent in many cases. Therefore, adsorption operation of binary systems is needed. Furthermore, since azeotropes may happen, in the case of the design of a solvent recovery system and operation, those adsorption equilibrium are required as basic data. This study considered the adsorption equilibrium relation used as basic data required in order to adsorb various binary mixture solvent vapor by high silica zeolite.

Keywords
azeotropic adsorption, breakthrough curves, gravimetric method

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) and ethanol (EtOH).

EXPERIMENTAL

2.1 Adsorbent
Fixed-bed adsorption experiment and gravimetric method of laboratory-scale were carried out to remove organic solvent vapors by Y type high silica zeolite. Experimental results for binary component system, which showed azeotropic mixture systems, could be correlated satisfactorily.
2.2 Fixed-bed Adsorption Experiment

Solvents used were ethanol (EtOH) and trichloroethylene (TCE). 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/m³, and temperature; 298 K. Experimental apparatus are shown in Figure 1.

2.3 Gravimetric Method

Figure 2 shows experimental apparatus for gravimetric analysis. The zeolite sample (about 0.25g) was placed in a quartz basket (F). Then the adsorbate in flask (B) was fed to adsorption tube (H). The whole apparatus was in a constant temperature air bath. The temperature range was 293-298 K. The amount adsorbed was measured corresponding to the pressure of the vapor in the tube. The pressure was measured by pressure sensor (J) at higher pressure range (> 0.013 atm) and baratron (I) at lower pressure range (<0.013 atm). Gravimetric Method is an experiment that inputs the adsorption quality like the pulse in the faction of the low pressure, and measures the change in the weight in that case. It predicts it from the working curve that measures the amount of adsorption from a pressure decrease in the device by the adsorption phenomenon beforehand. The weight change was used for the curve fitting and the adsorption curve. The prediction of the amount of adsorption by pressure calculates decrease pressure ΔP by adsorption from amount q of adsorption when the adsorption quality is first input. The difference of Pt at P0 and each time to reaching to equilibrium happens because of adsorption. Amount qt of adsorption at each time was requested by the following expressions.

\[
qt = \frac{P_0 - P_t}{RT} \times V \times M
\]  
(1)
RESULT AND DISCUSSION

3.1 Breakthrough Curves

Figure 3 show several types of breakthrough curves obtained for EtOH-TCE-Y-type zeolite system. In Figure 3, the range of the total concentration of EtOH and TCE are 2500~3500ppm. For this system reversal of the order of breakthrough (turn over) occurred once at concentrations of 0.222 mole fractions of EtOH. When the mole fractions were 0.222, the mixture of two components behaved as if it was a single component system.

Figure 3: Several types of breakthrough curves observed for EtOH-TCE-Y-type system (2500~3500ppm)
3.2 Adsorption Isotherm

In the gravimetric method, the adsorption isotherm of binary systems was obtained. Figure 4 show several types of adsorption isotherm obtained for EtOH-TCE-Y-type zeolite system. The result of the single element experiment was able to reproduce the result of the flow method. In Figure 4, a ratio of EtOH and TCE is 0.587:0.413 and 0.756:0.244. It was seen that amount of adsorption increased as ratios of TCE increased.

![Figure 4: Several types of adsorption isotherm observed for EtOH-TCE-Y-type system](image)

3.3 Adsorption Equilibria

Binary adsorption equilibria for the system of EtOH-TCE of several total concentration are shown in Figure 5 and Figure 6 in form of X-Y diagram (X and Y are the mole fractions of gas phase concentration and the amount adsorbed at equilibrium, respectively). Figure 5 is a result of the fixed-bed adsorption experiment, and figure 6 is a result of the gravimetric method. As for the gravimetric method, azeotropic phenomenon was not seen in the low concentration (3000 ppm, 6000 ppm). However the high concentration region that was not able to be measured by the fixed-bed adsorption experiment was able to be measured. Those equilibria have one azeotropic point, which attribute to the reversal of breakthrough order.

For vapor-liquid equilibrium, when the saturation vapor pressures of each component were almost the same, appearance of one azeotropic points were reported. 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.
Figure 5: Comparison of adsorption equilibrium for experimental concentration (Fixed-bed adsorption experiment)
Figure 6: Comparison of adsorption equilibrium for experimental concentration (Gravimetric method)

CONCLUSION

Adsorption of EtOH-TCE vapors onto HSZ was studied. One azeotropic point appeared in the adsorption equilibrium for this EtOH-TCE -Y-type system. As for the gravimetric method, azeotropic phenomenon was not seen in the low concentration (3000 ppm, 6000 ppm). However, the high concentration region that was not able to be measured by the fixed-bed adsorption experiment was able to be measured.

REFERENCE