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Adsorption equilibrium of the mixture of EtOH and TCE on FAU type high silica zeolite

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Abstract In this study, the adsorption equilibrium of the FAU type high silica zeolite was obtained by a gravimetric adsorption experiment device and a molecular simulation. The adsorbate used was ethanol and trichloroethylene, which are the system of azeotropic mixture.

In the course of this study, it became necessary to check whether equilibration was disturbed or not by changing the dosing sequence, that is, whether first adsorbate in the crystal cage could exchange or not by second adsorbate because of each mutual displacement disturbance. Experimental confirmation was done by changing dosing sequence to get the obtained results coincident. Also, molecular simulations by MM and MD were tried to check the possibility of exchange movement of adsorbate in the pore.

Keywords Azeotropic adsorption · Displacement adsorption · Gravimetric method

1 Introduction

In recent years, 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 (Smallwood 1993). Therefore, adsorption operation of binary systems is needed. Furthermore, since azeotropic adsorption may happen, in the case of the design of a solvent recovery system and operation, those adsorption equilibria are required as basic data.

The purpose of this work is to analyze the adsorption phenomenon from both sides of the simulation and the experiment, especially for the removal of the solvent vapors from air by adsorption. The solvents used were trichloroethylene (TCE) and ethanol (EtOH).

The mixture of EtOH and TCE actually has been used in industry (Smallwood 1993) and cause some social and/or environmental problems. This mixture is one of the typical mixture and, hence, azeotropic adsorption equilibria could be typical in many occasion. Therefore, the azeotropic phenomenon should clarify for the design estimation. The related information seems not to be enough up to now.

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2 Experimental

2.1 Adsorbent

Gravimetric method of laboratory-scale was carried out for the adsorption of organic solvent vapors by FAU type high silica zeolite. Experimental results for binary component system, which showed azeotropic mixture systems, could be obtained satisfactorily.

2.2 Gravimetric method

Figure 1 shows experimental apparatus for gravimetric analysis. The zeolite sample (about 0.25 g) 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). The concentration in the tube was determined by gas chromatography with FID, just after sampling from the sampling port.

The experiments were carried out using a batch system with circulation flow of the adsorbate mixture around the adsorbent to prevent the concentration distribution in gas phase, changing the total concentration and composition of ethanol and trichloroethylene, by stepwise dosing of mixed solvent vapor.

2.3 Simulation

Simulation module in Materials Studio (Accelrys Inc.) was used throughout MC simulations. The potential parameters used were cvff that was the corrected Universal. Ratio of the silica alumina (SiO_2/Al_2O_3) of the FAU type zeolite used in the experiment was 460, so that, siliceous model is used in the library of MS. It calculated by the Sorption module, and the adsorption isotherm was obtained.

In MS, density field of ethanol and trichloroethylene that adsorbs zeolite is shown in Fig. 2.

$$qt = \frac{P_0 - P_t}{RT} \times V \times M \qquad (1)$$

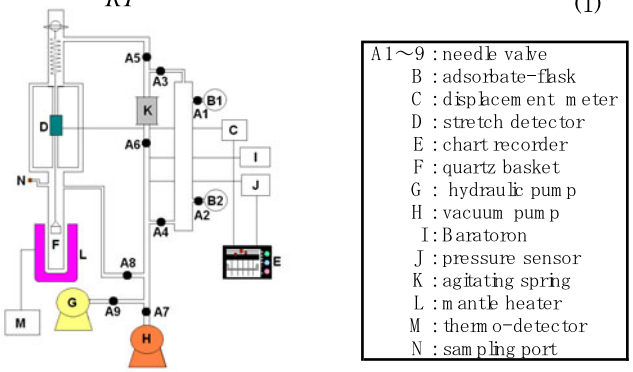

Fig. 1 Experimental apparatus to gravimetric method

3 Result and discussion

3.1 Binary adsorption isotherm

In the gravimetric method, the adsorption isotherm of binary systems was obtained. Figure 3 show adsoption isotherm obtained for EtOH-TCE -Y-type zeolite system. The result of the binary systems experiment and simulation were able to reproduce the result of the binary breakthrough. In Fig. 3, a ratio of EtOH and TCE is 0.185:0.812 on experiment and 0.200:0.800 on simulation. It was seen that amount adsorbed increased as ratios of TCE increased.

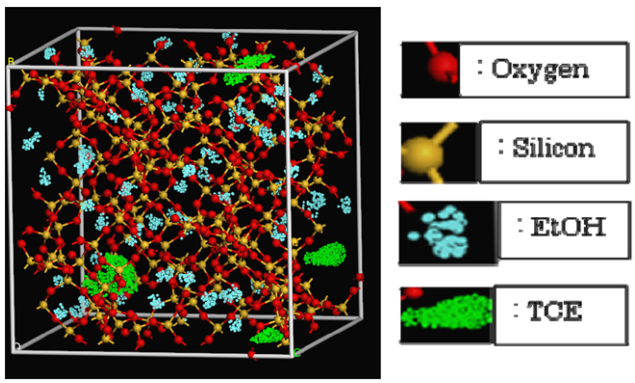

Fig. 2 Density field of ethanol and trichloroethylene that adsorbs zeolite

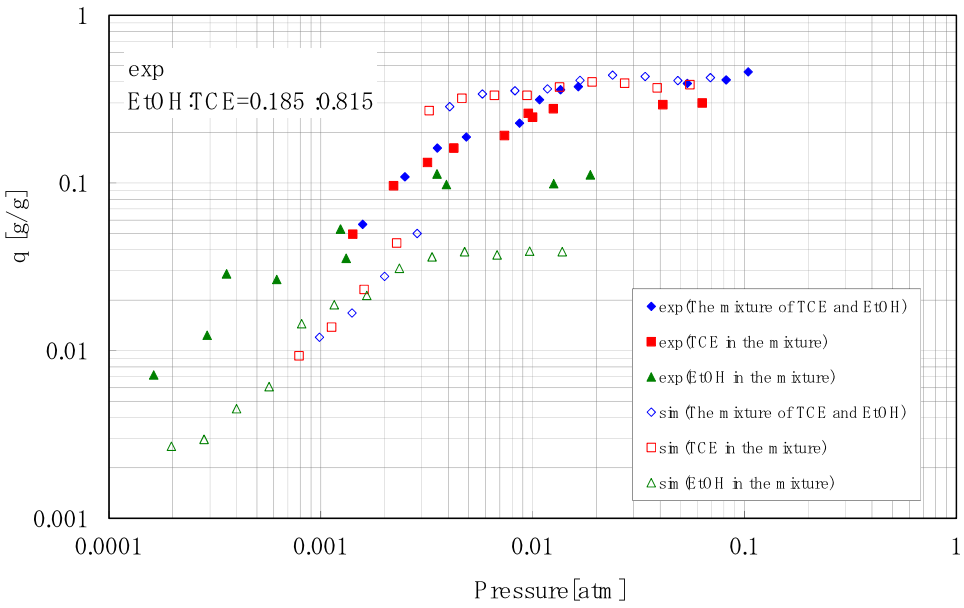

Fig. 3 Adsorption isotherm observed and simulated for EtOH-TCE-FAU-type system

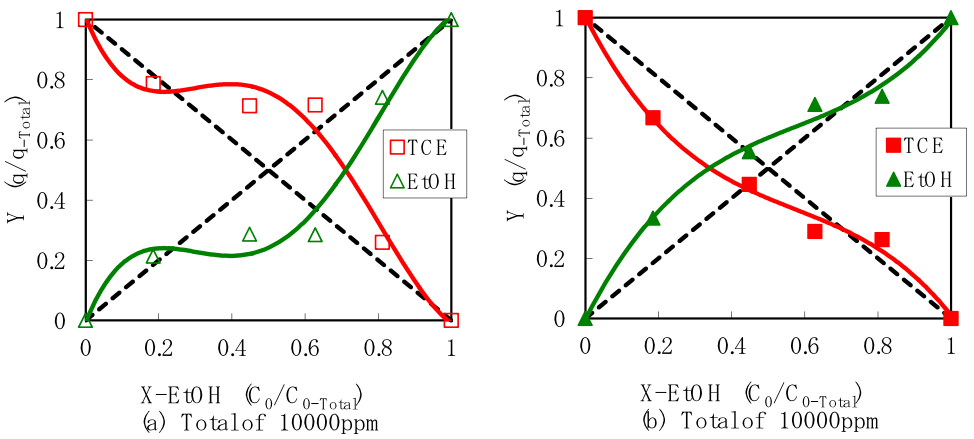

Fig. 4 Comparison of adsorption equilibrium for experimental and simulation ((**a**) Gravimetric method (*left*), (**b**) simulation (*right*))

3.2 Adsorption equilibria

Binary adsorption equilibria for the system of EtOH-TCE of total concentration of 10,000 ppm are shown in Figs. 4(a), 4(b) 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 4a shows the experimental result. Figure 4b shows the Monte Carlo simulation result.

As for the gravimetric method and simulation, azeotropic phenomenon was seen in the concentration (10,000 ppm) and almost the same shape(tendency). For this system, one azeotropic point appeared. The result was compared with the result of the breakthrough experiment obtained in the past in this laboratory to get very good coincidence.

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.

In the course of this study, it became necessary to check whether equilibration was not disturbed by dosing sequence, which is, first adsorbate in the crystal cage could not exchange by second adsorbate by each mutual displacement disturbance. Experimental confirmation was done by changing dosing sequence to get the obtained results coincident.

4 Conclusion

Adsorption of EtOH-TCE vapors onto HSZ was studied. Azeotropic points appeared in the adsorption equilibrium for this EtOH-TCE-Y-type system. As for the gravimetric method, azeotropic phenomenon was seen in the X–Y diagram. It became necessary to check whether equilibration was disturbed or not by changing the dosing sequence, that is, whether first adsorbate in the crystal cage could exchange or not by second adsorbate because of each mutual displacement disturbance. Experimental confirmation was done by changing dosing sequence to get the obtained results coincident. Also, molecular simulations by MM and MD were tried to check the possibility of exchange movement of adsorbate in the pore.

The equilibrium amount of adsorption was able to be calculated as a tendency in MS (Figs. 3, 4). In accuracy, the amount adsorbed of MS is slightly different compared with the gravimetric method experiment. It will be necessary to improve the crystal structure and the calculation condition of MS in the future.

References

Smallwood, I.: Solvent Recovery Handbook. Edward Arnold, London (1993)