

# diffusion-fundamentals

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## Diffusion Measurement of Chlorinated Hydrocarbons into High-Silica Zeolite by Chromatographic Method

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### 1. Introduction

Diffusion as well as adsorption equilibrium in adsorbent particles are important in designing adsorption processes. The purpose of this work is to experimentally determine the micropore diffusivities and adsorption equilibrium constants of various chlorinated organics in zeolite at wide temperature ranges and to correlate the obtained activation energies of micropore diffusion and isosteric heats of adsorption with the properties of adsorbate gases. Chromatographic measurements were made for this purpose. By introducing the concentration pulse of adsorbate to the carrier gas stream at the inlet of the adsorbent column, the concentration elution curve at the outlet of the column was measured. Adsorption equilibrium constant and micropore diffusivity were determined by means of moment analysis of elution curves.

### 2. Experimental method

The apparatus is a conventional gas chromatograph (GC-9A) (Shimadzu Co., LTD). PQ-USY, USY-6.18, Na-Y Pentasil-2 and Pentasil-1 (crashed and screened to obtain particle size between #20 and #32) were used as adsorbent. These particles were packed in a column. The carrier gas was helium. Dichloromethane (DCM), chloroform (TCM), trichloroethylene (TCE), and tetrachloroethylene (PCE) were used as adsorbate. The adsorbate was introduced as pulse into the carrier gas stream by a 6-way valve. The flow was controlled by mass flow controllers (about 25 cm/sec). The outlet signal from the TCD cell was recorded to a chart-recorder and converted into personal computer as pulse response.

### 3. Result and Discussion

**Table 1** Properties of gases for adsorption

	PQ-USY	USY-6.18	Na-Y	Pentasil-2	Pentasil-1	
	$\Delta H$ [kJ/m <sup>3</sup> ]					
	28.0					
DCM	$q_{st}$ [kJ/m <sup>3</sup> ]	38.6	42.2	43.4	56.3	59.7
	$E$ [kJ/m <sup>3</sup> ]	19.3	23.3	13.7	43.4	33.4
	$\Delta H$ [kJ/m <sup>3</sup> ]	29.4				
TCM	$q_{st}$ [kJ/m <sup>3</sup> ]	35.1	45.2	46.0	34.4	57.2
	$E$ [kJ/m <sup>3</sup> ]	19.0	39.4	30.3	8.7	40.5
	$\Delta H$ [kJ/m <sup>3</sup> ]	31.4				
TCE	$q_{st}$ [kJ/m <sup>3</sup> ]	43.4	49.2	48.2	61.1	62.5
	$E$ [kJ/m <sup>3</sup> ]	17.9	20.1	10.8	30.0	39.0
	$\Delta H$ [kJ/m <sup>3</sup> ]	34.7				
PCE	$q_{st}$ [kJ/m <sup>3</sup> ]	47.5	50.5	56.5	61.5	52.0
	$E$ [kJ/m <sup>3</sup> ]	12.8	21.3	40.1	38.5	34.6

In this study, the isosteric heat of adsorption is obtained with the chromatographic method, so that the estimated values are for zero coverage (the initial isosteric heats of adsorption). Therefore, these values correspond entirely to the interaction between the adsorbate molecule and the adsorbent lattice atoms, excluding the interaction among adsorbate molecules.

Isosteric heat of adsorption  $q_{st}$  for four adsorbates with five adsorbents have been plotted against the heat of vaporization  $\Delta H$  of corresponding adsorbate. The amount adsorbed and isosteric heats of adsorption became low, when  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of zeolite became high. The isosteric heats of adsorption were roughly 1.4 to 2.0 of the heats of vaporization. (Barrer and Lee 1968) showed that the ratios  $q_{st}/\Delta H$  for zeolite L slightly exceeded 2. Adsorption heat of PQ-USY is the lowest on all adsorbate. Adsorption heat of tetrachloroethylene was highest for all adsorbents.

Diffusion in the micropore zeolites is called activated diffusion and is described as a hopping from an adsorption site to another across the energy barrier which separates adjacent sites, which is similar to surface diffusion.

The activation energy was found to be half of isosteric heat of adsorption for the gases examined here.

#### 4. Conclusion

Adsorption equilibrium constants in the Henry's law region and diffusivities in the micropores in zeolite were determined from the first absolute moment and the second central moment where the effects of all the other possible transport processes in the case of bidispersed pore structure and also the log-normal size distribution of the microparticle were taken into account.

The amount adsorbed and isosteric heats of adsorption became low, when  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of zeolite became high. The isosteric heats of adsorption were roughly 1.4 to 2.0 of the heats of vaporization. The activation energies of diffusion in the micropore of zeolite were found to be almost 40% of the isosteric heats of adsorption.

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