CHAPTER 2

LITERATURE SURVEY

Analysis of effluent responses to input disturbances has widely been used to study the behavior of process equipment. There have been two rather different objectives in such experiments:

1) determining the dynamic character of processing units so that control strategies could be devised to optimize performance, and

2) determining rate and equilibrium parameters of the system from the experiments themselves.

In the latter case, many of the parameters are independent of the dimensions of the equipment, so that the results from a laboratory-scale apparatus are generally applicable. The nature and operation of the laboratory apparatus are the same as for conventional chromatographic experiments. The difference lies in the treatment of response data. Instead of measuring peak areas, or heights, one uses the retention time and shape of the effluent peak to extract equilibrium and rate parameters.

Chromatographic methods provide an alternative to conventional gravimetric or volumetric methods of determining adsorption equilibrium and rate parameters. The method, using a non-adsorbing carrier gas into which a small trace of an adsorbable component is injected and measuring retention data, is relatively simpler and quicker, making it ideal for preliminary adsorbent screening studies, and it is more easily adapted to the extreme

conditions of high pressure and temperature which are of interest in many catalytic processes.

Recent papers on chromatographic study of adsorption of gases on solid are reviewed as follows:

Kucera [1] derived a model for describing adsorption of gas on porous solid including various rate processes: the longitudinal diffusion in the mobile phase, the finite rate of mass transfer through the boundary, the radial diffusion inside the pore and the adsorption rate on the internal surface of the porous solid. By means of statistical moments, the solution of the model was expressed in terms of the moments of chromatographic peaks up to the fifth order, where the first absolute moment determines the retention time and the second central moment represents the variance of the peak, etc.

Masamune and Smith [2] studied the adsorption of a component in a gas mixture on a solid particle which could be described by a three-step mechanism: diffusion from the main body of the gas phase to the external surface of the particle, diffusion into the particle (for example, through the pore volume, or by migration along the solid surface of the pore in a porous particle, and by a solid diffusion mechanism in an impermeable particle), and adsorption on the pore surface. Based upon reasonable assumptions, analytical solutions (the concentration of the adsorbate in the gas leaving the bed as a function of time) were summarized based on whether the overall rate was determined by one or two or all of the three steps.

Schneider and Smith [3] studied the adsorption of ethane, propane and n-butane on silica gel. By introducing the step and pulse signal through the adsorption column in the experiment, the first

absolute and second central moments of the chromatographic curve were obtained and ultilized to predict the adsorption equilibrium constants, the adsorption rate constants and effective intraparticle diffusivities. These adsorption rate constants were used to show the agreement between the experimental data and predicted breakthrough curve.

Ma and Macel (4) used the gas chromatographic techniques to measure the diffusion coefficients and the isosteric heats of adsorption of CO_2, NO, NO_2, and SO_2 on 5A and 13X molecular sieves, natural mordenites, and synthetic Na- and H-mordenites in the temperature range of 133 to $325^{\circ}C$. Diffusional resistances for all gases studied decrease in the following order: natural mordenites > Na-mordenites > H-mordenites > (13X, 5A) indicating the increased ease of flow in the 3-dimensional network. Isosteric heats of adsorption (range from 3 kcal/mole to 12 kcal/mole) and activation energies (range from 3 kcal/mole to 19 kcal/mole) decrease in the same order. The variations of diffusion coefficients, heat of adsorption, and activation energies are discussed in terms of the interaction between the surface and gas molecules as well as the openings of the pores relative to the size of the diffusing molecules.

Hashimoto and Smith (5) studied the adsorption of nitrogen and n-butane gas on commercial pellets containing a clay binder and 5A molecular sieves. The general adsorption model including macropore and micropore diffusion was derived. The moments of the effluent peaks were evaluated and used to determine the macropore diffusivity, but the micropore (or crystal) diffusivity was difficult to obtain because of some inherent characteristics of the chromatographic method.

Garg and Ruthven (6) studied experimental saturation (adsorption) and regeneration (desorption) breakthrough curves for a molecular sieve adsorption column operated isothermally under conditions of micropore diffusion control. For systems with a linear equilibrium isotherm, column performance may be adequately predicted from Rosen's theoretical analysis. The form of the breakthrough curves is very sensitive to quite small deviations from linearity and, for systems which exhibit a favourable Langmuir type of isotherm, regeneration is much slower than saturation under comparable conditions. These effects can be quantitatively accounted for by the non-linear model of Garg and Ruthven. Equilibrium constants and diffusivities calculated from the breakthrough curves show satisfactory agreement with the values obtained from gravimetric measurements.

Shah and Ruthven (7) used the chromatographic method to study the adsorption and diffusion of methane, ethane, propane and cyclopropane in 5A molecular sieve. The adsorption isotherm and time constants for zeolitic diffusion, obtained from the chromatography peaks, agreed with the values obtained previously by the gravimetric method, thus confirming the validity of the experimental technique. The results obtained in several previously reported chromatographic studies were reviewed, and it was shown that the apparent discrepancies between chromatographic and gravimetric data arose mainly from differences in the way in which the micropore diffusivity was defined. The relative advantages and disadvantages of the gravimetric and chromatographic methods were briefly considered.

Gangwal et al. (8) developed the conditions for the accurate measurement of the mass transfer coefficients, internal

diffusivity and adsorption rate constants using pulse gas chromatography within the limits of the approximation of the Kubin-Kucera model for adsorption in a packed bed. Physisorption rates were shown to be many orders of magnitude higher than those measurable. Thus, pulse chromatography could not be used to determine physisorption rate constants. Mass transfer coefficients at low Reynolds Numbers were shown to be measurable under severely restricted conditions.

Gangwal et al. (9) studied the reproducibility of response characteristics and parameters derived therefrom, and adequacy of the Kubin-Kucera model for pulse chromatography were investigated experimentally using the physisorption of methane and ethane on silica gel. Reproducibility was found to be excellent, while the agreement of predicted and observed effects of velocity, particle size, temperature and bed length on model parameters confirmed the adequacy of the model. Agreement of the pore diffusivity and the adsorption equilibrium constant with values measured by other techniques provided further support for the model. Rearrangement of model terms showed that the rate coefficient for physisorption and the mass transfer coefficient could not be measured using chromatography.

Ruthven and Kumar (10) determined the equilibrium isotherms for Ar, O_2, N_2, CH_4, and CO in 4A molecular sieve and for Ar, O_2, N_2, CH_4, CF_4, C_2H_6, C_2H_4, and C_3H_8 in 5A molecular sieve by a chromatographic method. Both the Henry constants and the full isotherms are in satisfactory agreement with available gravimetric and volumetric data. It is shown that the chromatographic method may be simply extended to allow the

determination of binary isotherms with two adsorbed species. Binary isotherms have been determined for CH_4-N_2, CH_4-Ar, N_2-CO, and CH_4-CO on 4A sieve and for N_2-Ar, N_2-O_2, $C_2H_4-C_3H_8$, $CH_4-C_2H_6$, and $C_2H_6-N_2$ on 5A sieve. This method proved simpler and quicker than the conventional methods of determining binary equilibria. The binary isotherms are in satisfactory agreement with the theoretical curves predicted from a simplified statistical model isotherm using the Henry constants and effective molecular volumes derived from the single component data. Approximate equilibrium data for He are also presented and it is shown that, with weakly adsorbed species such as O_2, Ar, etc., above room temperature, the adsorption of the helium carrier must be considered in the analysis of retention-time data.

Gangwal et al. (11) studied dead volumes present in the measurement of kinetic and transport parameters using pulse gas chromatography (PGC). A set of criterion was derived for the bed volume necessary to make these dead volume effects negligible. Application of this criterion and assumptions to some typical data sets in the PGC literature were discussed.

Hsu and Haynes (12) applied the gas chromatography technique to measurements of diffusion of n-butane in zeolite NaY. The linear chromatography theory failed to explain these results quantitatively, and a significant system nonlinearity was demonstrated. This nonlinearity is likely associated with non-Fickian diffusion. Order of magnitude estimates of the diffusivity could still be obtained, however. Over the range of temperatures 105 to $240^{\circ}C$, the n-butane diffusivities were in the range 10^{-8} to 10^{-6} cm^2/s. Similar results were obtained with n-hexane and

calculated diffusivities were about an order of magnitude smaller than the corresponding n-butane values. In contrast, limited experiments with cyclohexane, 2,2-dimethylbutane, and trans-decalin were entirely consistent with the linear chromatography theory. At the measurement temperatures, the intracrystalline diffusion was too rapid to be detected in any of these systems. Attempts to operate at lower temperatures where diffusion might be significant were frustrated by extensive peak broadening and concomitant loss of detector response.

Chiang et al. (13) studied the adsorption of propane and n-butane in a column packed with Linde 5A zeolite crystals, and methane, propane, n- and iso-butane in a column packed with silicalite crystals. The adsorption equilibrium constant K and crystal diffusivity D_c were obtained at different temperatures in the range 100-300°C, for each sorbate and packing and the heat of adsorption and diffusional activation energy were determined. The results show that in order to separate the effects of K and the pressure drop, the latter must be independently estimated by a suitable correlation. The values of K thus obtained agree well with current literature and are well-determined. Similarly, there is a high correlation between D_c and the axial diffusivity D_{ax}, which may be resolved by fitting the model simultaneously to runs made at both high and low velocities. The values of D_c found are in broad agreement with the results of adsorption rate measurements for the Linde 5A zeolite. For the silicalite lower diffusivities were obtained, which may point to a surface resistance or a concentration-dependent diffusivity.

Haynes et al. (14) studied a gas chromatography pulse dispersion data for the n-butane/zeolite NaY system. The data

analyzed in terms of two models, an intracrystalline diffusion limiting model and a surface barrier model. Both models provided acceptable fits to the pulse dispersion data; however, the temperature dependence of the apparent mass transport parameters strongly suggests that a surface barrier is responsible for the observed transport resistance. The Henry's law constants were independent of choice of model and the isosteric heat of sorption was consistent with literature values.

Choudhary (15) developed a suitable gas chromatographic method for measuring sorption isotherms in narrow-pore zeolites and also for studying sorption of benzene in H-ZSM-5 under catalytic conditions. The sorption data at lower temperatures (373-523 K) could be fitted satisfactorily to the Dubinin-Polanyi equation. The sorption occurred by the volume filling mechanism. The isosteric heat of sorption has been found to be strongly dependent on the sorbate loading, particularly in the lower region. This fact clearly reveals the presence of site energy distribution in the zeolite.