Abstract – Most of the solids used in adsorption processes are heterogeneous and most isotherm models are not derived to use information about the solid structure and energy heterogeneity. A possible alternative is to use molecular simulation techniques, which turn the thermodynamic model more microscopic. Then, starting from information on the solid structure, it is possible to develop appropriate solid models for each type of real system. Therefore, the objective of this work is to use the grand canonical Monte Carlo technique of molecular simulation for correlating pure-component data and predicting adsorption of multicomponent mixtures. To decrease the computational effort, we use a simplified solid model that is represented by a two-dimensional square lattice. The solid heterogeneity is represented by a random distribution of different kinds of sites, characterized by distinct energy levels. The methodology developed by Cabral et al. (2003a) is used here to correlate pure components and for predicting binary mixtures of ethane, ethylene, isobutane, and carbon dioxide on zeolite 13X with good results.

Keywords – Monte Carlo Simulation, Adsorption, Heterogeneous Solids.

I. INTRODUCTION

Most solids existing in nature are inevitably heterogeneous, i.e., they have a distribution of pores with different shapes and sizes. The heterogeneity of an adsorbent is characterized by an energy distribution of active sites with distinct values for interactions between adsorbent and adsorbate. This energetic heterogeneity plays a major role in adsorption equilibrium, as in the selective adsorption of propane from a propane-carbon dioxide mixture on H-mordenite (Talu and Zwiebel, 1986). In this way, techniques or methodologies capable of taking this feature into account can be important for a better understanding of adsorption phenomena. Recently, adsorption of chain-like molecules on heterogeneous surface has been studied in the framework of the lattice gas model and molecular simulations (Nitta et al., 1997; Ramirez-Pastor et al., 1999, 2000; Borowko and Rzysko, 2001, 2003; Cabral et al., 2003a, 2003b). In fact, the use of molecular simulation has increased because of progresses in computer science and in hardware technology. For example, Ramirez-Pastor et al. (2000) used Monte Carlo simulations to study the adsorption of non-interacting homonuclear k-mer molecules on heterogeneous surfaces. These authors modeled the heterogeneous surface by using two kinds of sites. Sites were formed by square patches randomly distributed (or in a chessboard-like domain) on a two-dimensional square lattice. Grand canonical Monte Carlo simulations were used by Borowko and Rzysko (2003) to study the phase behavior of heteronuclear dimers adsorbed on heterogeneous surfaces. The dimers were composed of two types of segments. These authors considered a surface composed of alternating strips of non-interacting and attractive sites arranged on a square lattice. Rzysko and Borowko (2003) estimated the adsorption isotherms, phase diagrams and critical parameters. It is shown that surface heterogeneity markedly affects the adsorption and phase behavior of the films. The impact of surface topography on critical characteristics was also analyzed. Of special interest was the finding that these systems do not belong to the two-dimensional Ising class of universality. Cabral et al. (2003a) proposed a new methodology for correlating the adsorption of pure components and for predicting the adsorption of binary and ternary mixtures on homogeneous and heterogeneous solids. The methodology proposed by the authors uses the algorithm of molecular simulation in the grand canonical ensemble as an equation of state for the adsorbed phase. The results obtained for the adsorption of the binary mixtures of propane-CO₂ and propane-H₂S, which are strongly non-ideal, were quite satisfactory showing the potential of this technique for the description of real systems. A historical review of application of computer simulation to adsorption phenomena, especially for two-dimensional systems, has been published elsewhere (Steele, 2002).

In this paper, we use the methodology of Cabral et al. (2003a) to correlate the adsorption of pure components and for predicting the adsorption of binary mixtures of ethane, ethylene, isobutane and carbon dioxide on zeolite 13X (experimental data are taken from Hyun and Danner, 1982). Here, the simulations are performed on a two-dimensional square lattice in which the solid heterogeneity is represented by the existence of three kinds of sites, characterized by distinct adsorption energies. For a specific fraction of active sites, several topologies can be generated, each of them characterized by a random distribution of square grains of specific sizes.