Chemical Engineering Science 158 (2017) 462–479

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

On the hysteresis of adsorption and desorption of simple gases in open end and closed end pores

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ARTICLE INFO

Keywords:
Adsorption
Hysteresis
Slit pore
Condensation
Evaporation

ABSTRACT

This paper presents a comprehensive computer simulation study of the microscopic mechanisms of adsorption and desorption in uniform sized pores. Our specific aim is to elucidate the origin of hysteresis, especially in those pores having one end closed to the bulk gas surroundings. These pores, despite their simplicity, capture many fundamental aspects of how molecules adsorb and are restructured in pores, which results from the interplay between a number of fundamental processes: (1) molecular layering, (2) clustering, (3) capillary condensation and evaporation and (4) molecular ordering. We have found that pore size, surface affinity and temperature are the most important parameters influencing these processes. The inter-relationship between them is highly significant in determining the possible existence of a hysteresis loop. Two classes of loop have been identified: (1) a condensation and evaporation loop and (2) a restructuring loop. Our simulations show that the origins of hysteresis stem from the following causes:

(1) Different curvatures of the interface separating the adsorbed layer and the gas-like phase during adsorption and desorption. This always occurs in open ended pores when the temperature is below the critical hysteresis temperature and, most interestingly, is manifested in closed end pores only when the surface affinity is very weak;
(2) Low temperatures, where the adsorbate become solid-like as filling progresses in both open and closed end pores;
(3) Restructuring of the condensed phase in both open and closed end pores of specific pore size where the adsorbate changes from a liquid-like state to a solid-like state.

1. Introduction

Understanding the underlying physics of adsorption and desorption in porous materials has been a subject of great interest to both scientists and engineers for: (1) the purpose of characterization of the structure of porous solids and (2) the application of porous materials for gas separation or purification processes (Gregg and Sing, 1982; Rouquerol et al., 1999). One issue, which continues to be challenging, is the existence of hysteresis, because a strict application of thermodynamics demands that only one equilibrium state can exist for a given set of thermodynamic parameters. However, it is well established experimentally that (1) there exist distinct adsorption and desorption branches of an isotherm over a certain range of pressure, and (2) that the existence of hysteresis is associated with a demarcation between smaller (micropore) and larger (mesopore) pore widths relative to the adsorbate molecule size (Thommes, 2004). Unlike micropores in which adsorption isotherms are reversible because molecular filling and emptying processes occur by the same mechanism (in different directions), hysteresis associated with capillary condensation and evaporation is observed in mesoporous materials at temperatures below a critical hysteresis temperature (T_{ch}) (Morishige and Nakamura, 2004). Experimental studies have shown that the presence of a hysteresis loop and its shape, size and position depend on the porous structure, pore size and temperature, and this dependence is extensively used in the characterization of porous structure and the calculation of pore size distribution (Thommes, 2004; Horikawa et al., 2011). For this reason, attempts have been made to classify the various shapes of the hysteresis loop and this classification has evolved over the past decades as a consequence of: (1) advances in the synthesis of ordered mesoporous materials (Zhao et al., 1998; Kresge et al., 1992), (2) the use of high resolution apparatus for the measurement of physical adsorption and (3) the increasing power of computer simula-

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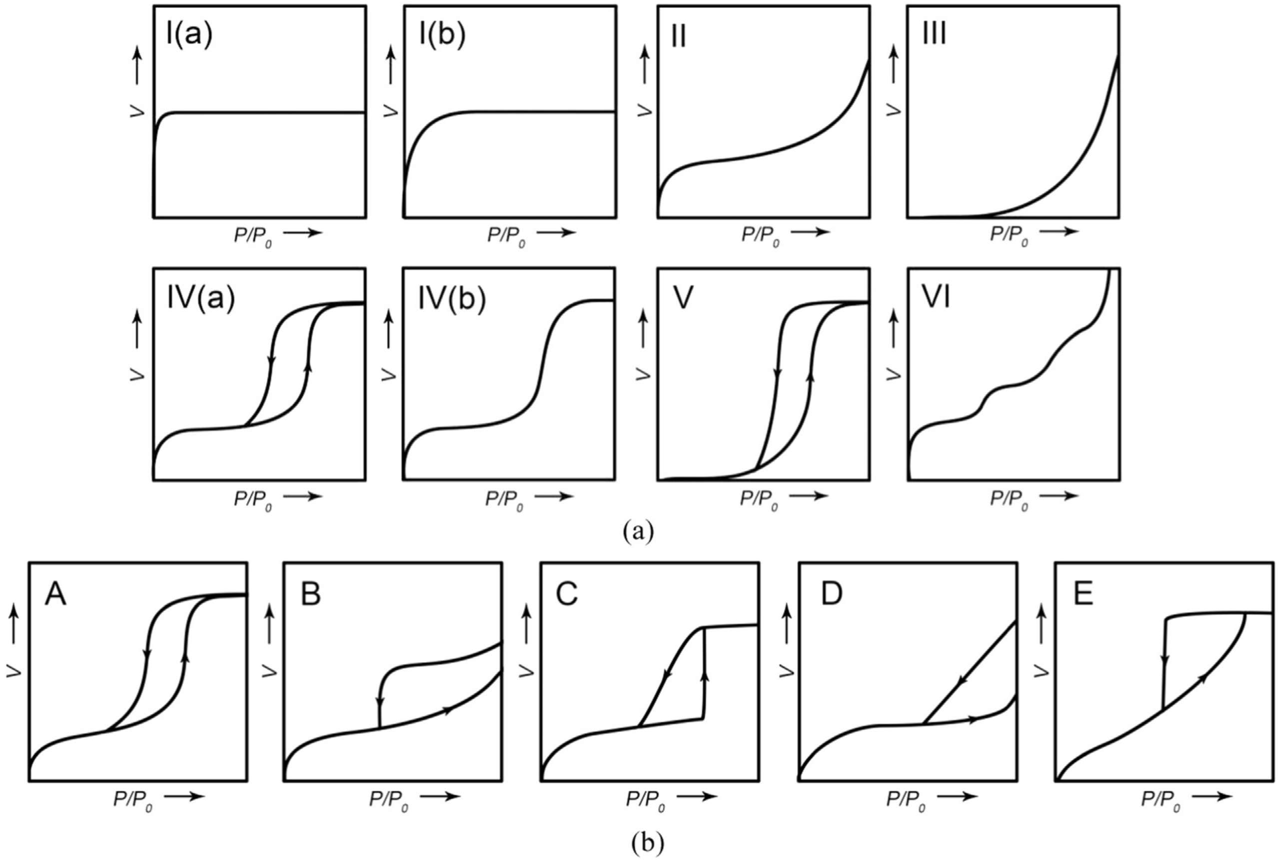
http://dx.doi.org/10.1016/j.ces.2016.10.048
Received 23 June 2016; Received in revised form 30 September 2016; Accepted 27 October 2016



(a)

(b)

Fig. 1. (a) New (2015) IUPAC classification of adsorption isotherms; (b) de Boer's original classification of 1972.

tion (Allen and Tildesley, 1989; Frenkel and Smit, 1996). Recently a new classification, shown in Fig. 1a, has been proposed by IUPAC (Thommes et al., 2015), which encompasses both the earlier (1985) IUPAC classification (Sing et al., 1985) (based on experimental analysis) and the original, 1972, classification by de Boer (De Boer, 1972), shown in Fig. 1b.

Most of the early work on adsorption and desorption mechanisms focus on simple pore models, typically with cylindrical or slit pore geometry with both ends open to the gaseous surroundings (Fig. 2). The classical explanation of pore-filling and emptying in a cylindrical pore was proposed by Cohan, in which both adsorption and desorption follow equilibrium paths, and the hysteresis depends solely on the difference in the curvature (cylindrical on adsorption and spherical on desorption) of the meniscus separating the adsorbed phase and the gas-like region (Cohan, 1938, 1944). However, the derivation of Cohan's equations assumes the validity of macroscopic thermodynamics and does not account for the possibility of an undulating interface separating the adsorbed phase and the gas-like phase in the confined space. Furthermore, it takes no explicit account of the adsorbent potential energy field (despite its dependence on the existence of an annular

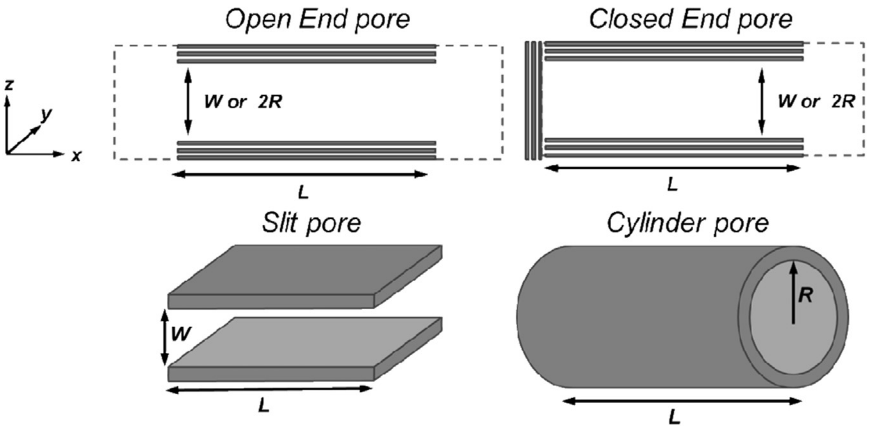


Fig. 2. Schematics of the pore models.