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Decoding gas-solid interaction effects on adsorption isotherm shape: I. Non-polar adsorptives

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ABSTRACT

A suite of non-polar adsorptives of different kinetic diameters and shape were used to determine adsorption and pore filling mechanism of a well-characterised poly(furfuryl alcohol)-based activated carbon. Triplicate measured Type I adsorption isotherms for each adsorptive were averaged to provide standard deviation in relative pressures and associated amounts adsorbed. Plateau amounts adsorbed for N_2, Ar, CH_4, and C_6H_6, provided Gurvitsch volumes averaged to $0.368 \pm 0.015 \, \text{cm}^3(\text{liq})/\text{g}$. The calculated Gurvitsch volumes were compared with those derived via the Dubinin-Radushkevich (DR) equation. Additional adsorptives were CO_2, iso-butane and SF_6. The results of these 7 adsorptives were used to qualitatively analyse and decode a micropore filling adsorption mechanism. The DR equation was also used for further analysis of the pore filling mechanism. Based on the adsorbate-adsorbate and adsorbate-adsorbent interactions, adsorbates were classified into three groups: (a) Non-polar with non-specific interactions (no dipole, no quadrupole, not readily polarizable: Ar, N_2, CH_4 and iso-butane), adsorbing as a continuous uptake over the observed relative pressure range; (b) Non-polar adsorptives with potential for specific interactions (no dipole, quadrupole moment: CO_2 and C_6H_6), adsorbing as a condensation process over a relatively narrow relative pressure range in a medium pressure range; (c) Halogenated adsorptives (no dipole, no quadrupole, polarizable: SF_6), adsorbing with an S-shaped uptake extending over a relatively broad relative pressure range.

1. Introduction

Preparation, activation, modification, and application of porous carbonaceous materials are the subjects of a variety of researches over the past few decades. Characterization of these materials using gas adsorption techniques is a key step in their application [1]. Kiselev classified adsorptives as two distinct types: non-polar and polar with various sub-categories due to adsorptive chemical properties [2]. Gregg and Sing summarised these, directing non-polar adsorptives towards adsorbent structure characterization and polar adsorptives towards surface chemistry analyses. Maximum information from the latter relies on detailed interpretation of the former [3]. A gap exists in the literature whereby no systematic or detailed study has been reported examining the mechanism of adsorption via various molecules that could provide insight into adsorbent structure and chemistry effects on adsorbate-adsorbent interactions and adsorbate-adsorbate interactions.

The experimental practicalities of liquid nitrogen (77 K) have seen N_2 become the molecule most widely used for adsorbent structure analysis [1]. Its relatively small kinetic diameter of 0.36 nm promotes analysis of micropores and its ready condensation below saturation pressure conditions promotes mesopores analysis. Consequently, N_2 adsorption isotherms are principal for standard adsorption data for isotherm analyses [4] and pore size distribution (PSD) modelling [5]. The low adsorption temperature and kinetic dimension contribute to diffusion limitations to N_2 adsorption equilibrium in pores identified as ultra-micropores, widths ≤ 0.7 nm. An alternative adsorptive for these pores is carbon dioxide, which offers a smaller kinetic diameter, 0.33 nm, and adsorption isotherm temperature typically at 273 K, reducing diffusion barriers. In comparison with N_2, CO_2 has the disadvantage of a relatively high quadrupole moment making it sensitive to surface polar groups; its high saturation vapour pressure at 273 K dramatically narrows the applicable relative pressure range (under

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1 bar pressure limitations), nullifying mesoporosity characterization [6]. Appropriate analysis of adsorption isotherms due to both adsorptives would provide a complementary picture of all micropores and mesopores [7]. In contrast to the shape and modest surface chemistry susceptibility of these two adsorptives, Ar is a non-polar, spherical adsorptive of intermediate kinetic diameter, which has received support as an alternative to N_2; Recent IUPAC recommendations suggest Ar to be the preferred adsorptive [8]. Argon also suffers from the low temperature diffusion problems of N_2 for small micropores [9] and, liquid argon is not readily available to *all* experimentalists, Ar adsorption isotherms tend to be measured using liquid nitrogen at 77 K, at which the adsorbed phase would be solid [6].

Dubinin's research into activated carbon compared and contrasted N_2 adsorption isotherms with C_6H_6 adsorption isotherms [10]. Benzene offers a slightly larger kinetic diameter, 0.37 nm, a planar structure for probing (deduced) parallel surface or slit-shaped pores, and a chemical structure that would suggest non-polar adsorbate-adsorbent interactions. In fact, its relatively high polarizability acts as a disadvantage if the adsorbent should contain polar surface sites leading to π-electron, adsorbent surface-specific interactions. Benzene's highly carcinogenic properties require appropriate handling procedures.

Micropore size distributions have been defined via DFT models [11], and those based on modifications of the Horvath-Kawazoe models [12,13]. Size exclusion or molecular sieve effects have been applied as an alternative hypothesis, exploiting size (and shape) of molecules centred on propane [14]. These include propane, *iso*-butane, and *neo*-pentane, measured at temperatures in the range 273–298 K. These probes offer dispersion force interactions with an adsorbent and negligible polarizability; their shape differences offer marginal increases in kinetic diameter [14–17]. Additional, but infrequently used spherical molecules are CH_4, CF_4, and SF_6. The chemical conformation of each indicates no dipole moment but the high electronegativity of fluorine could lead to specific interactions with appropriately electron-rich surface sites. Despite this shortcoming, Seaton and co-workers modelled adsorption isotherms of these molecules to define pore network connectivity [18,19].

Considering the advantages and disadvantages of the molecules above, we classify some of them in Table 1 as adsorptives with increasing kinetic diameter, no dipole moment (aside from *iso*-butane as 0.1 D [20]), modest polarizability, and subtle shape differences. A comparison of the adsorption isotherms of these adsorptives on the same solid should give qualitative insight into their interaction mechanism with a surface, and provide details of the surface structure and possibly its surface chemistry influence on the isotherm shape. The adsorbent investigated in the work presented below is the previously investigated poly(furfuryl alcohol) (PFFA)-based carbon [21–24]. These adsorptives were contacted, compared, and contrasted as high-resolution, averaged isotherms. Linear-linear axis plots helped define Gurvitsch volume results; inconsistency in these and their sources are

presented and discussed. The calculated Gurvitsch volumes were compared with those obtained *via* the DR method. Isotherms also presented as linear-log (relative pressure) axis plots clarified subtle differences in initial uptake processes and their relative pressure ranges, with each interpreted in terms of adsorptive shape, size, and likelihood for adsorbate-adsorbent interaction specificity. This interpretation was further investigated using DR plots to decode fluid-fluid and fluid-solid interactions and pore filling mechanisms. Although all the isotherms showed a Type I shape based on IUPAC classification, our investigation here shows that Type I isotherms can be further classified based on the fluid-fluid and fluid-solid interaction potentials and pore filling mechanism. Although a quite specific adsorbent and adsorptives have been used in this study, the methodologies and principle concepts used here are quite general and represent a foundational development in the topic of adsorption isotherm measurement and analysis.

2. Materials and methods

The adsorbent used in this work was a synthetic microporous poly (furfuryl alcohol)-based, activated carbon. Its synthesis and activation procedures were discussed before in detail [22]. In summary, distilled furfuryl alcohol was mixed with oxalic acid (100:3, w/w) at room temperature. A continuous argon gas flow during mixture polymerisation (150 °C; 1 h) and subsequent carbonization (800 °C; 2 h) resulted in a char. After grinding and sieving (≈100 μm), the particles were subjected to a repeated, cyclic oxygen-argon activation procedure. Firstly, oxygen chemisorption (250 °C; 8 h) followed by desorption and activation under argon atmosphere (800 °C; 2 h); 9 cycles were determined to be 45% burn-off. The structural evolution of the adsorbent along the activation pathway has been examined in detail [21], along with the chemistry and surface properties of the sample [24].

Table 1 contains a summary of the physical properties of the non-polar adsorptives used in this study. Each is defined as non-polar with *iso*-butane (pedantically) the exception, offering a dipole moment of 0.1 D [20]. For discussion purposes, we regarded this value as negligible and assumed non-specific interactions with the adsorbent surface.

Prior to each experiment, each sample was degassed under the same conditions (250 °C; 4 h; 10^{-5} kPa). Ar and CH_4 gas adsorption isotherms were prepared using an ASAP-2020 apparatus (Micromeritics, Norcross, GA, USA) equipped with a cryostat (Cold Edge Technologies, Allentown, PA, USA). All other adsorption isotherms were obtained using a BELSORP-max gas adsorption apparatus (BEL, Osaka, Japan) equipped with a vapour adsorption kit and a Neslab refrigerated bath circulator controlling temperature ± 0.01 K. Helium was used for all dead-space measurements (> 99.999%, ex. BOC Gases, Australia). Repeatability within and reproducibility from different adsorption apparatus indicated self-consistent timing for equilibrium penetration of this adsorptive, and apposite removal (25 °C; 1 h; 10^{-5} kPa) prior to helium dead-space measurements.

Table 1
Adsorptives, their physical properties, and conditions used for adsorption experiments.

Adsorptive	Molecular Weight (kg/kmole)	Temp. (K) /Temp. control device[a]	Liquid Density at Temp. (kg/m³) [25,26]	Minimum Kinetic Diameter (nm)	Polarizability $\alpha/10^{-30}$ (m³) [27]	Grade /Supplier[b]
CO_2	44.0	273 /CIW	909	0.33 [28]	2.63	> 99.999% /CG
Argon (Ar)	39.9	87 /C	1400	0.34 [28]	1.66	> 99.999% /BOC
Nitrogen (N_2)	28.0	77 /LN2	808	0.36 [28]	1.77	> 99.999% /CG
Benzene (C_6H_6)	78.1	298 /RC	879	0.37 [17]	10.4	HPLC Grade > 99.9% /SA
Methane (CH_4)	16.0	110 /C	422	0.38 [29]	2.60	> 99.999% /BOC
[c]*iso*-butane	58.1	298 /RC	552	0.50 [6]	–	> 99.995% /SA
Sulfur-hexafluoride (SF_6)	146.1	293 /RC	1450	0.55 [30]	6.54 [31]	> 99.75% /SA

[a] CIW = crushed ice-water bath; C = cryostat; LN2 = liquid nitrogen bath; RC = refrigerated circulator.
[b] CG = Coregas, Australia; BOC = BOC Gases, Australia; SA = Sigma-Aldrich, USA.
[c] *iso*-butane dipole moment = 0.1 D [20].