

THE COMPENSATION EFFECT FOR THE KINETICS OF ADSORPTION/DESORPTION OF GASES/VAPORS ON MICROPOROUS CARBONS

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Introduction

Activated carbons have many practical applications in organic vapour removal from air streams, as both hydrophilic functional groups and hydrophobic graphene layers are present, acting as primary adsorption sites for polar groups and hydrocarbons respectively. Adsorption isotherms are a function of adsorption site distribution, type of sites, pore structure and experimental conditions such as vapour pressure and temperature. Information regarding kinetics, which are critically important for assessment of active carbon bed performance for effluent specie adsorption are critically important. This work involves the investigation of adsorption and desorption kinetics and compensation effect for a wide range of linear organic molecules, two planar molecules, a bulky planar molecule and water on an activated carbon. These probe molecules vary widely on both shape and functional group characteristics.

Kinetic Model

Adsorption kinetics for the systems studied usually obey the Linear Driving Force (L.D.F.) model¹, which can be described by:

$$M_t/M_e = 1 - e^{-kt} \quad (1)$$

where M_t is the uptake at time t , M_e is the equilibrium uptake and k is the rate constant. The rate constants can be evaluated either from a graph of $\ln(1 - M_t/M_e)$ versus time or by fitting the M_t/M_e versus time graph to the above equation.

Experimental

Carbon BAX950, a wood-based activated carbon with a particle size fraction of 1-2mm obtained from Westvaco Corporation, Virginia was used α -pinene (99%), benzene(99.9%), pyridine (99.9%), methanol, n -octane (purity $\geq 99.5\%$) were supplied by Aldrich Chemical Co. Static vapour adsorption isotherms were recorded using an 'Intelligent Gravimetric Analyser' (I.G.A.) supplied by Hiden Analytical Ltd, which allows the corresponding kinetics of adsorption to be determined.² Vapour isotherms were obtained at constant temperature by setting pressure intervals between vacuum and a pressure just below saturated vapour pressure. The carbon

sample, BAX950, of 100 ± 1 mg, was outgassed until it reached a constant mass at $\sim 10^{-6}$ Pa after which the pressure was gradually increased, to prevent microbalance disruption, to a set point and equilibration established. The operation was repeated for remaining pressure steps to provide an adsorption desorption isotherm.

Results and Discussion

The pore volumes obtained for all the adsorbates agreed well ($0.84 - 0.89 \text{ cm}^3\text{g}^{-1}$) and compared favourably with those previously obtained for nitrogen³ ($0.83 \text{ cm}^3\text{g}^{-1}$). Carbon dioxide adsorption³ gave a micropore volume of $0.18 \text{ cm}^3\text{g}^{-1}$ suggesting BAX950 is predominantly meso/macroporous. There is very limited literature concerning the adsorption / desorption kinetics of gases and vapours on activated carbons due to the complexity of the experimental techniques involved. The isotherms are classified as intermediate between Type I and II for n -octane, α -pinene, benzene and pyridine, Type III for water and Type II for methanol vapour in the IUPAC classification scheme (Fig. 1). Hysteresis was observed for water adsorption/desorption between the relative pressures $p/p^0 = 0 - 0.84$. A very small amount of hysteresis was observed for n -octane and benzene desorption above an uptake of ~ 3.5 and $\sim 6.2 \text{ mmol g}^{-1}$ respectively. Isothermic enthalpies of adsorption, calculated using the van't Hoff isochore, showed a decrease with increasing surface coverage for benzene and pyridine. However an increase is observed up to a surface coverage of 3.3 mmol g^{-1} for α -pinene adsorption followed by a subsequent decrease.

The LDF model is obeyed for methanol, n -octane, benzene desorption and pyridine, benzene adsorption between the relative pressures $p/p^0 = 0 - 0.96$. α -pinene obeys LDF for p/p^0 up to 0.011 above which the kinetics obey a combined barrier-resistance/diffusion model. The variation in rate constants with surface coverage (Fig. 2) shows a change with respect to the hydrophilicity / hydrophobicity of the adsorbate. Peaks were observed at low relative pressures between $p/p^0 \sim 0.003-0.22$. Similar trends in rate constants were observed for, benzene and pyridine.

Activation energies were calculated to investigate the diffusional barriers to adsorption, and as the isotherms were carried out in relative pressure terms the activation energies correspond to changes in surface coverage. The values obtained (Fig. 3) show highest values at low relative pressure and peaks for water, due to agglomeration and clustering of admolecules, as well as both aliphatics, where a barrier causes a maximum at the relative pressure corresponding to a deviation in the D-R plot.⁴ There is good correlation between $\ln(A)$ and the activation energy, E_A for all the systems, indicative of a compensation effect (Fig. 4). These systems also have non-zero isokinetic temperature which indicates that the effect is real.⁵ The results compare well with those obtained for other adsorptives on BAX950.⁶ An explanation of the compensation effect is based on the existence of 2 factors (a) diffusion along the pore to the barrier and (b) diffusion through the barrier at the pore entrance. LDF is obeyed when (b) is rate determining. Essentially high E_A leads to a build-up of adsorbate at the barrier i.e. a high $\ln(A)$ and vice versa.

References

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Acknowledgements

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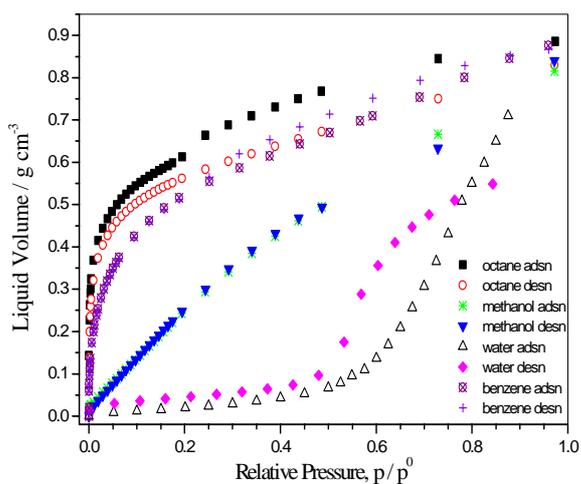


Figure 1. Isotherms for Adsorption/Desorption on BAX950 at 303K

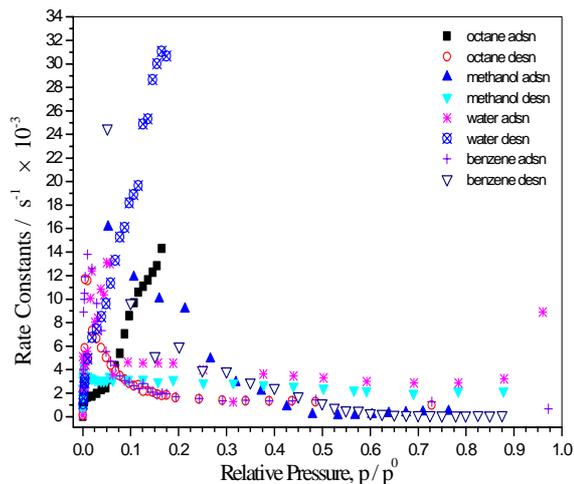


Figure 2. Variation of Rate Constants with Relative Pressure at 303K

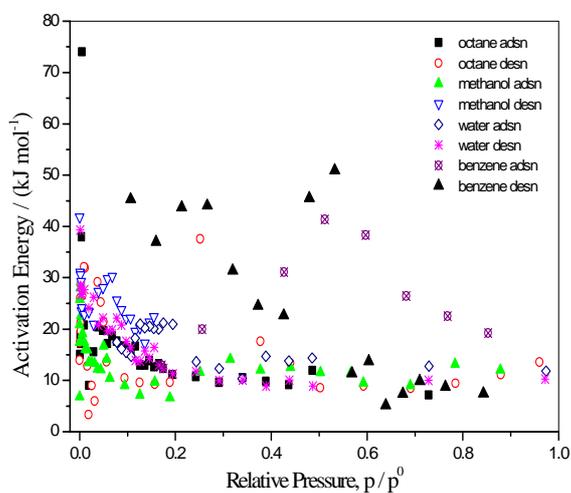


Figure 3. Variation of Activation Energies with Relative Pressure

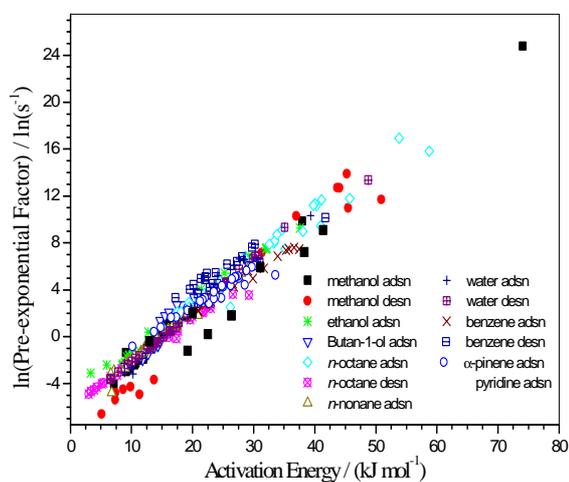


Figure 4. Compensation Effect for Adsorption/Desorption on BAX950