

# UNDERLYING MECHANISM OF DR EQUATION FOR ADSORPTION IN ACTIVATED CARBON

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ABSTRACT: The Dubinin-Radushkevich (DR) equation is widely used for adsorption in microporous carbonaceous materials. This equation only yields a macroscopic behaviour of loading for a given pressure. In this paper, we apply our theory (Langmuir, 15, 3608, 1999) to explain the microscopic adsorption behaviour behind the DR equation.

## INTRODUCTION

The Dubinin-Radushkevich (DR) equation is used to describe adsorption of sub-critical fluids in microporous solids such as activated carbon. The DR equation has the form

$$W/W_0 = \exp\left[-(A/E)^2\right], \quad A = RT \ln(P/P_0)$$

This equation provides the macroscopic information of the fraction of the total micropore volume occupied by the adsorbate molecules. It does not give any picture on how adsorption behaves microscopically, that is which micropores are filled and which are partially filled as it is well known that activated carbon has a rather broad pore size distribution. This information of microscopic distribution of adsorbed molecules is important in the study of mobility of adsorbed molecules. Here we apply a new method (Nguyen and Do, 1999) to describe the adsorption process in microporous carbonaceous materials with a pore size distribution. It is a structure based method, where enhancement of adsorption is allowed for due to the proximity of the pore walls. We will use this technique to investigate the adsorption in carbon micropores in an attempt to shed some light to the working mechanism of the DR equation.

## THEORY

In our approach (Nguyen and Do, 1999) we adopt a common mechanism for the adsorption process occurring in carbonaceous pores as a sequence of surface layering followed by pore filling, irrespective of their sizes. The principal feature of this theory is the allowance for the enhancement in adsorption induced by the overlapping of the potential fields of opposite pore walls. This enhancement not only affects the adsorbed phase, but also the gas phase molecules occluded within the pore. The pressure exerted by these occluded molecules is calculated from:

$$p_p(r) = p \exp(-E_{av}/RT)$$

with  $E_{av}$  the average potential energy of the occluded molecules. These occluded molecules will provide source to build up adsorbed layers on the pore walls, following a mechanism akin to BET, but in this theory we take that these layers are enhanced due to the potential energy of interaction with the pore walls. The BET constant in a pore is calculated in terms of the BET constant of a corresponding flat surface as:

$$C_p(r) = C_s \exp[(Q_p(r) - Q_s)/RT]$$

where  $Q_p(r)$  and  $Q_s$  are heats of adsorptions in pore and a flat surface, respectively. Adsorption in pores can be pictured as a process whereby gas phase molecules are drawn into the pore interior. Once inside, they are further pressed against each other as a result of the overlapping potential fields. If the pore pressure is beyond the corresponding vapor pressure, the adsorbed phase turns into liquid (albeit compressed liquid). It is, therefore, understood that in some narrow pores, due to the very large enhanced pressures, the adsorbed phase exists as liquid even at very low bulk pressures. This liquid filling process progresses to pores larger in size as the bulk pressure increases. This is essentially the micropore filling process described in the Dubinin theory (1960). In larger pores, adsorption occurs as a surface layering process, and this layer will grow until the following condition is satisfied:

$$r - t - \sigma_M / 2 = \gamma v_M / [RT \ln(P_0/P_p)]$$

when the complete pore filling will occur. Here  $r$  is the half width,  $\gamma$  is the surface tension and  $v_m$  is the liquid molar volume. The statistical thickness "t" is calculated from:

$$t(r) = t_m \frac{x_p(r)C_p(r)}{(1 - x_p(r))(1 - x(r) + x_p(r)C_p(r))}; \quad x_p(r) = \frac{P_p(r)}{P_0}$$

## RESULTS & DISCUSSION

The fractional loading in the DR equation defined as  $\theta = W/W_0$  accounts for adsorption in micropores only. This means that the contribution of larger pores on the uptake must be removed before they can be used with the DR equation. Furthermore, the DR equation provides only the macroscopic information. For example, when the change in the free energy,  $A$ , is equal to the characteristic energy of the system, the fractional loading is 0.37, meaning 37% of the micropore volume is occupied by the adsorbate molecules. Our approach models adsorption as a process occurring in all pores simultaneously, with the amount adsorbed in a pore dependent on the pore size. At a given pressure small micropores are completely filled, while larger micropores have a layer of adsorbate molecules. Knowing the volume of each pore, the overall fractional loading is calculated from:

$$\theta = \sum_j \theta_j w_j / \sum_j w_j$$

where  $\theta_j$  is the pore fractional loading, and is equal to 1 for filled pores and equal to  $t_j/(r_j - \sigma_{ss}/2)$  for pores having layers of adsorbate. This overall fractional loading is then compared with that calculated from the DR equation.

We illustrate this theory with nitrogen adsorption data at 77 K on an ACF sample. This ACF has a micropore volume of 0.24 cc/g, and a mean micropore half width of 0.66 nm. Fitting the DR equation with the data yields the characteristic energy of 6.9 kJ/mol. The distribution of pores calculated by our method is shown in Table 1 (columns 1 and 2) where we show 24 representative pores with their corresponding pore volumes. Using our theory we calculated the amounts adsorbed in each pore at three levels of pressure:  $6 \times 10^{-5}$ ,  $3 \times 10^{-2}$  and 0.4, and these are shown in Table 1. To distinguish pores already filled, the amount adsorbed in these pores are printed bold. At the very low relative pressure of  $6 \times 10^{-5}$ , adsorption occurs mainly in the smallest micropores. The first three pore sub-ranges are filled completely with adsorbate while larger pores are layered with adsorbate molecules. The overall capacity calculated by our theory is 3.04 mmol/g, compared to 3.06 mmol/g calculated using the DR equation. Our approach provides a detailed distribution of this 3.04 mmol/g capacity. At a relative pressure of  $3 \times 10^{-2}$ , all pores having half width less than 0.588 nm are filled. This pore filling is progressed to pores of larger size when pressure increases. For example, at a reduced pressure of 0.4, the threshold pore size for complete filling is 1.266 nm, which is now in the mesopore range. Table 2 presents the results of the nitrogen adsorption onto the ACF sample at these three pressure levels calculated using the DR and our method. As seen in the table, the amount adsorbed calculated using the DR equation is by and large equal to the sum of the amounts adsorbed in all pores using our technique. The difference is more significant at the higher end of the pressure range, where adsorption in mesopores occurs in addition to that in micropores. This is because the DR equation, unable to deal with mesopores, underpredicts the data at high relative pressures, while our technique describes well the data at all pressure levels.

We now turn to the isosteric heat of adsorption, which can be calculated from the DR equation (Do, 1998) as:

$$-\Delta H = \Delta H_{vap} + E \left( \ln \frac{1}{\theta} \right)^{1/2} + \frac{E\delta T}{2} \left( \ln \frac{1}{\theta} \right)^{-1/2}$$

where  $\delta$  is the coefficient of expansion of liquid adsorbate, which is very small. Figure 1 shows the plot of the isosteric heat of adsorption of nitrogen versus relative pressure at  $-196^\circ\text{C}$  onto the ACF sample calculated from this DR equation. To calculate the heat of adsorption from our method, we assume that the adsorption heat is approximated by the decrease in the potential energy of adsorbate, when moved from the bulk into the interior of the pore. This is shown in Table 1 for all pores. Energy released is larger in smaller pores, and proportional to the pore volume. Since the ACF sample has a distribution of pores mostly in the range from 0.32 to 0.397 nm, most of the heat comes from the pores in that range. The total heat released at any overall loading ( $C_\mu$ ) is obtained by summing all the individual heats released in each pore. This is the cumulative heat produced when the amount of  $C_\mu$  is loaded into a clean sample. For example, from Table 1 the cumulative heat at the relative pressure of  $3 \times 10^{-2}$  is 55 Joule, corresponding to an amount of 6.38 mmol loaded on 1 gram of the ACF sample. The isosteric heat of adsorption

is the heat released at a given loading  $C_\mu$ , i.e. it is the incremental heat produced per unit mole when the loading is incrementally increased from  $C_\mu$  to  $C_\mu + \Delta C_\mu$  ( $\Delta C_\mu \ll C_\mu$ ). This is applied for nitrogen adsorption onto ACF data, and the results are shown in Figure 1. The maximum possible isosteric heat for nitrogen is  $\sim 16.2$  kJ/mol if all pores having half width equal to the solid-fluid collision diameter. The isosteric heat calculated using the DR equation and our technique are quite different. The comparison between the methods and/or the justification of the suitability can be made based on the experimental measurement of the isosteric heat of the system, which is not available at this stage.

We now address the question regarding the validity of the DR equation. Figure 2 shows the isotherms of nitrogen adsorption of representative pore sub-ranges in the form of  $\log(C_\mu)$  versus  $\log^2(1/x)$ . As seen, none of the single pore isotherms can be considered to be a straight line. However, by adding up the individual isotherms, we get the overall isotherm shown as a dotted line, which is practically a straight line, supporting the suitability of the DR equation. It is clear that the DR equation is not applicable for adsorbents having an extremely narrow pore size distribution. Samples having very skewed PSDs can not also be described by DR equation. Thus, for the DR equation to be applicable, the porous solid must have a distribution of micropores, and that distribution must not be very skewed. This explains why the DR equation is not applicable to all microporous materials.

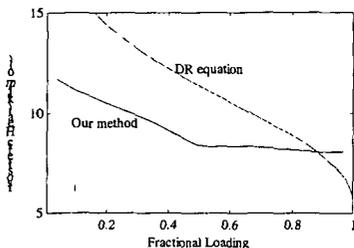


Figure 1: Plot of the isosteric heat versus loading

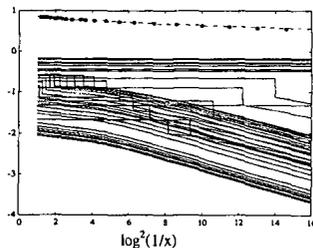


Figure 2: Plot of  $\log(C_\mu)$  versus  $\log^2(1/x)$

#### ACKNOWLEDGEMENT

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**Table 1:** Nitrogen adsorption onto ACF at 77 K at three relative pressures (per gram of sample).

Half width	Volume	$x = 6 \times 10^{-3}$		$x = 3 \times 10^{-2}$		$x \approx 0.4$	
		loading	energy	loading	energy	loading	energy
nm	cc	mmol	J	mmol	J	mmol	J
0.286	0.004	0.1256	1.32	0.1256	1.32	0.1256	1.32
0.320	0.047	1.3611	13.10	1.3611	13.10	1.3611	13.10
0.357	0.041	1.1914	10.84	1.1914	10.84	1.1914	10.84
0.397	0.029	0.2410	2.11	0.2677	2.24	0.2677	2.24
0.439	0.009	0.0367	0.31	0.2653	2.27	0.2653	2.27
0.485	0.007	0.0144	0.12	0.2069	1.74	0.2069	1.74
0.534	0.021	0.0241	0.20	0.6021	4.99	0.6021	4.99
0.588	0.030	0.0219	0.18	0.8551	7.03	0.8551	7.03
0.645	0.026	0.0136	0.11	0.3667	3.00	0.7624	6.23
0.706	0.018	0.0069	0.06	0.2249	1.83	0.5144	4.19
0.772	0.008	0.0018	0.01	0.0674	0.55	0.1688	1.37
0.843	0.005	0.0012	0.01	0.0490	0.40	0.1340	1.09
0.919	0.005	0.0010	0.01	0.0465	0.38	0.1382	1.12
1.001	0.006	0.0011	0.01	0.0516	0.42	0.1663	1.34
1.090	0.004	0.0007	-	0.0328	-	0.1141	-
1.266	0.002	0.0003	-	0.0159	-	0.0637	-
1.683	0.002	0.0002	-	0.0085	-	0.0155	-
2.249	0.002	0.0001	-	0.0066	-	0.0118	-
2.912	0.005	0.0003	-	0.0155	-	0.0278	-
3.805	0.006	0.0002	-	0.0144	-	0.0258	-
4.958	0.006	0.0002	-	0.0117	-	0.0208	-
6.444	0.009	0.0002	-	0.0134	-	0.0240	-
8.361	0.014	0.0003	-	0.0161	-	0.0288	-
9.214	0.007	0.0001	-	0.0071	-	0.0126	-
Micropore	0.254	3.042	28.39	6.240	55.09	7.318	63.87
overall	0.308	3.044		6.382		7.663	

**Table 2:** Nitrogen adsorption onto ACF sample calculated using our method and DR equation.

$P/P_0$	Overall capacity (mmol/g)		Micropore capacity (mmol/g)	
	Experimental	our method	DR eq.	our method
$6 \times 10^{-3}$	3.03	3.04	3.06	3.04
$3 \times 10^{-2}$	6.36	6.38	6.25	6.24
0.4	7.63	7.66	6.9	7.31