Commentary on the paper “On the adsorption affinity coefficient of carbon dioxide in microporous carbons” by E.S. Bickford et al. (Carbon 2004; 42: 1867–71)

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The recent letter to the editor by Bickford et al. [1] discusses the uses of the CO₂ affinity coefficient in microporous carbons, βCO₂, and its physical significance. The paper points out the lack of having absolute β values and attempts to give answer to the question of the suitability of the value of βCO₂ = 0.35 in microporous carbons. The authors conclude that this cannot be considered a “classical” value and that much more work is needed to clarify its physical significance, in order to maintain the well-deserved popularity of the Dubinin–Radushkevich equation.

We welcome the effort of the authors to address – and even challenge – the use of βCO₂ to characterize microporous carbons. However, we cannot agree with their conclusions. Firstly, because we feel that the importance and relevance of β has been overestimated in the paper.

Secondly, because, on the basis of our own research, a suitable classical value of βCO₂ near 0.35 appears to exist. Thus, we have reported excellent agreements on the characteristic curves of different carbons, obtained with many couples comparing CO₂ and benzene and or N₂ adsorption. In all the cases, values near 0.35 for CO₂ and 0.33 for N₂ have been used. We wish to address the following three issues.

1. The concern about βCO₂ and Dubinin’s theory

The uncertainties claimed by the authors should not introduce unsupported concerns about the popularity and general use of Dubinin’s theory for the volume filling of micropores (TVFM). The so-called affinity coefficient β is only an experimental shifting factor, which allows the superposition of the characteristic curves of various adsorbates with the curve of benzene. This scaling factor is only a parameter among other parameters found in Dubinin’s theory. The authors’ concern about β makes sense, but does not differ from that associated with other parameters used in adsorption, such as real adsorption equilibrium, choice of the linear range of the DR and hence micropore volume assessment, density, molecular cross section, etc. To support their concern about βCO₂, the authors present Fig. 1 stating that “If it is indeed an affinity coefficient, it should be able, for example to account for the published results (Bickford’s Ref. [4,5]) compiled in Fig. 1”. This figure is not a suitable example because the use of βCO₂ should always correspond to the basic concepts of Dubinin’s theory:

(i) Dubinin’s fundamental equation expresses a distribution of the filled volume of the adsorption space with respect to the differential work of adsorption and it is only valid, in principle, at adsorption temperatures below $T_c$ (there exists an expression for the limiting pressure or fugacities, but in a limited temperature range above $T_c$).

(ii) The constant value of the parameter β (or that of the ratio of the differential molar work of adsorption of a given vapor to the differential molar work of adsorption of the standard) is only true for equally filled volumes of the adsorption space. Moreover, significant differences in the accessibility of the PSD and/or activated diffusion lead to unrealistic characteristic energies $E$ and consequently to meaningless values of $β = E/E₀$. It follows, that the
characteristic curve of two adsorbates should only be compared for the same range of micropore filling \( \theta \) the adsorbate being in a liquid-like form and preferably at temperatures below \( T_c \). Carbons with strong molecular-sieve effects must be analyzed separately.

None of these points can be applied to Fig. 1 of Bickford et al.’s paper. In addition, the way used to express the results and the experimental conditions used for nitrogen and methane are not the most suitable for comparison purposes because (i) the adsorption uptake is expressed in mmol g\(^{-1}\) (for comparison purposes it should be in liquid volumes) and (ii) methane and nitrogen are adsorbed at a temperature above their critical temperature hence the saturation pressure has to be calculated using different approaches. As a result, this figure is not the most suitable way for reaching conclusions about \( \beta_{CO_2} \). Instead of Fig. 1, a DR (or DA) plot would look much nicer and it might reveal that these adsorbents do not necessarily consider the same degree of pore volume filling \( \theta \). Our Fig. 1 shows the reliable case of \( C_6H_6 \) (293 K) and \( CO_2 \) (273 K) adsorbed under similar conditions, as far as \( \theta \) is concerned. Using molar volumes of 88.9 and 42.8 cm\(^3\) mol\(^{-1}\), one obtains an excellent overlap of the DR plots with \( \beta_{CO_2} = 0.35 \) \((E_o = 31 \text{ kJ mol}^{-1})\).

2. Regarding a suitable value for \( \beta_{CO_2} \) to characterize microporous carbons

A careful analysis of the data quoted by the authors in their Table 1 reveals interesting features as far as the origin of the various \( \beta_{CO_2} \) values is concerned.

Firstly, Bickford’s Refs. [8,11,21,30] are based on the direct comparison of \( CO_2 \) and \( C_6H_6 \) isotherms, so that the definition \( \beta_{CO_2} = E_{CO_2}/E_o \) clearly applies. For all these carbons, including oxidized samples given in Bickford’s Ref. [21], one obtains

\[ \beta_{CO_2} = 0.37 \pm 0.03 \] (standard deviation; 14 values)

Moreover, the data of Bickford et al. leads to 0.35.

Secondly, the authors express their concern about a possible influence of the surface chemistry of the adsorbent on \( \beta_{CO_2} \). However, as shown in Bickford’s Ref. [16], and supported by our own data for \( CO_2 \) adsorption on carbons [2], as well as zeolites [3] and MCM-41 [4], the surface chemistry does not affect \( \beta_{CO_2} \). (Obviously, this is not the case for other adsorptives such as water [5], alcohols [2], etc.). Some authors use \( \beta_{CO_2} \), taken from the literature, which cannot be considered as separate evidence in the present study. Others base their calculations on secondary standards, instead of benzene, which may lead to problems depending on the \( \beta \) values used for these references. In this context, it must be pointed out that in Bickford’s Ref. [14] (Cazorla-Amorós et al.), the \( \beta_{CO_2} \) value was not taken from the literature, but was calculated so that the characteristic curves for \( CO_2 \) and \( N_2 \) adsorption coincided. As no activated diffusion was present for \( N_2 \), the value \( \beta_{CO_2} = 0.35 \) may be regarded as a reliable and independent experimental value.

3. Empirical evaluations of \( \beta \)

As pointed out by Dubinin, there exists an empirical correlation between \( \beta \) and the ratio of properties such as parachor, polarizabilities, molar volumes, etc. of the adsorptives (Wood [6]). However, as there exists no theory relating them, their correlation must be regarded as coincidental and treated with care. This means that a prediction based on these ratios may not be used in the assessment of \( \beta \) itself an experimental quantity (see above). In the present case, this is illustrated by the unrealistic values of \( \beta_{CO_2} \) between 0.53 and 0.69, based on the molar volumes of the free liquid. It is known that the molar volume \( V_m \) (\( CO_2 \)) is be significantly smaller in the adsorbed state, which decreases the expected value of \( \beta_{CO_2} \) accordingly.

References

Authors’ reply to the above commentary

The readers of CARBON will now have the wherewithal to assess the relative merits of the arguments presented in the two papers; and the path for further research in this area is now clear. The main point of our paper is that the parameter $\beta$ is hopefully not “only an experimental shifting factor”. It is intriguing that Dubinin himself was ambiguous regarding the appropriate terminology: he has used both ‘affinity’ and ‘similarity’, the former implicating adsorbate/adsorbent interactions and the latter invoking the properties of the adsorbate only. If $\beta$ is relegate to a similarity coefficient or an experimental shifting factor, Dubinin’s ‘theory’ is arguably reduced to a convenient statistical distribution function, with no physical significance. There is increasing evidence that gas-phase physisorption phenomena are not the exclusive consequence of non-specific (e.g., dispersion) adsorbate/adsorbent interactions, and that both the surface chemistry and the nature of the adsorbate play an important role in determining the adsorption potential (and thus the affinity of the surface for the adsorbate). If $\beta$ can somehow reflect these effects, then Dubinin’s theory has a bright future, side by side with the already very popular approaches based on density functional theory.