

APPLICATION OF THE DUBININ-ASTAKHOV EQUATION TO THE EVALUATION OF THE
BENZENE AND CYCLOHEXANE ADSORPTION ISOTHERMS ON STEAM GASIFIED
HUMIC ACIDS CHARs FROM BROWN COAL

Teresa Siemieniewska, Kazimierz Tomków, Jan Kaczmarczyk, Andrzej Albinia
Institute of Chemistry and Technology of Petroleum and Coal, Techni-
cal University, Gdańska 7/9, 50-306 Wrocław, Poland

Yves Grillet

Centre de Thermochimie et de Microcalorimétrie du CNRS, 26, rue du
141 RIA, 13003 Marseille, France

Michèle François

Centre de Recherches sur la Valorisation des Minerais, École Natio-
nale Supérieure de Géologie, BP 40, 54501 Vandoeuvre Cédex, France

INTRODUCTION

The Dubinin's theory of volume filling of micropores (1) is ap-
plied to the evaluation of adsorption isotherms to characterize the
capillary structure of microporous carbonaceous solids (2-15). Re-
cently, this theory is frequently represented by the Dubinin-Astak-
hov (DA) equation (16):

$$W = W_0 \exp \left[- (A/\beta E_0)^n \right] \quad (1)$$

where W is the volume of micropores filled with the adsorbate at
temperature T and relative pressure p/p_0 , W_0 is the total volume of
micropores, $A = RT \ln(p/p_0)$ is the differential molar work of adsorp-
tion. The product βE_0 is equal E , where E_0 and E are characteristic
adsorption energies for a standard and a chosen adsorptive, respec-
tively. The coefficient β is a similarity factor, related to the ad-
sorptives (β is usually calculated as the ratio of molar volumes or
parachores of the adsorptives), and it enables the characteristic
curves (plots of W/W_0 versus A) of different adsorptives on the same
solid to be superimposed. The value of the parameter n is chosen so
that the experimental data would fit equation 1.

The proper choice of n may present some difficulties. Also, the
question arises, if the rectilinearity of the plot in the coordi-
nates corresponding to the logarithmic form of equation 1: $\ln W$ ver-
sus $(A/\beta E_0)^n$, even if it should be attained for a given n , can be
considered as a sufficient indication for the physicochemical vali-
dity of the resulting parameters W_0 and βE_0 .

The aim of this work was to establish, for a suite of carbona-
ceous materials, the values of n for which a satisfactory agreement
would be obtained between the experimental adsorption data and the
DA equation, trying also to verify the obtained DA parameters refer-
ring to related results calculated, or obtained experimentally, in-
dependently.

As adsorptives benzene (frequently used as standard) and cyclo-
hexane (to avoid the presence of π - electrons in the molecule)
were chosen. To have a suite of samples characterized by a systema-
tically changing porosity, humic acids steam gasified chars were
prepared with varying burn-offs. Humic acids from brown coals can be
obtained with a low mineral matter content and they are thought to
be representative for the organic substance of low rank coals. Ad-
ditionally, two industrial active carbons, described elsewhere (17)
were investigated.

EXPERIMENTAL

Humic acids (HA) were obtained from a Polish humodetrinitic
brown coal (containing about 70 wt %, daf, HA), by extraction with
diluted NaOH solution, followed by precipitation with hydrochloric

was taken. The lower limit of p/p_0 results from our possibility of accurate adsorption measurements; the higher limit is connected with the fact that at relative pressure above 0.1, before the beginning of the hysteresis loop, capillary condensation might, in some cases, occur, due to the tertiary process of adsorption in wider micropores (20). For each of the assumed value of n , correlation coefficients were calculated, and for each of the adsorbate/adsorbent system the correlation coefficients were closest to unity when $n=2$ (in a few cases $n=1.5$ or $n=2.5$) was chosen (upper part of figure 5). This indicates that the best coincidence of experimental points with the DA equation is achieved, within the considered limits of relative pressures, for $n=2$ (if integrars are to be considered). However, this does not necessarily mean that the values of W_0 and βE_0 corresponding to $n=2$ are of true physicochemical significance.

Applying, for the calculation of the values of n , the method of Dubinin(21), for benzene adsorption on HA 850/10 ... HA 850/85 the following values were obtained: $n=6$, $n=6$, $n=5$, $n=3$ and $n=4$, and on the charcoals 208 C and 264: $n=6$ and $n=4$. Similar values of n were obtained for cyclohexane adsorption on these samples.

To gain some additional information concerning the validity of the values of W_0 obtained for $n=2$ (and also to check the remaining W_0 values), an independently calculated value of the volume of micropores was necessary. We thought this purpose might be served by the volume of micropores, as given in figures 3 and 4 (V_{mic}). We tried also to assess the position of the values of V_m calculated by application of the Brunauer, Emmett and Teller(BET) equation(22) in relation to the respective values of V_{mic} . Because in the BET coordinates practically no straight lines were obtained from the isotherms in figures 3 and 4, a modification of the BET procedure, according to Joyner, Weinberger and Montgomery (23) was applied.

It appears that here the values of V_m (according to the theory of BET, V_m is the monolayer capacity of the adsorbent) are in a very good agreement with respective values of V_{mic} , the correlation coefficient being equal 0.998 (figure 6 a). This means that V_m , in case of the investigated samples, might represent the volume of adsorbate contained in the micropores only, not including the adsorption in the monolayer of the mesopores (V_{Smes}). If to the values of V_m the values of V_{Smes} are added, an approximate position of point B of the isotherms in figures 1 and 2 is reached. This is seen in Table II, where the amounts adsorbed are expressed directly in mmol/g.

Table II. Benzene adsorption (mmol/g) and corresponding p/p_0

Sample	a_{mic} (p/p ₀)	a_m (p/p ₀)	$\{a_m + a_{Smes}\}$ (p/p ₀)	a_0 (p/p ₀)
HA 850 10	1.43 (0.10)	1.43(0.10)	1.53 (0.22)	1.40(0.07)
HA 850 25	2.77 (0.07)	2.73(0.06)	2.92 (0.18)	2.77(0.07)
HA 850 50	4.26 (0.05)	4.27(0.05)	4.76 (0.16)	4.34(0.06)
HA 850 75	4.99 (0.05)	4.93(0.04)	5.71 (0.14)	5.12(0.06)
HA 850 85	4.95 (0.04)	4.94(0.04)	5.81 (0.16)	5.04(0.05)
Charcoals:				
208 C	4.23 (0.08)	4.23(0.08)	4.42 (0.16)	4.27(0.09)
264	3.25 (0.06)	3.40(0.08)	3.90 (0.19)	3.32(0.07)

For all the investigated samples correlation coefficients were calculated for the relationships between W_0 obtained for different values of n and the respective values of V_{mic} and V_m . In all cases

acid. The carbonization was carried out at a rate of 5°C/min to the final temperature of 850°C. The obtained char, designed as HA 850, was gasified, in a thermogravimetric apparatus, with steam at 800°C to following burn-offs: 10, 25, 50, 75 and 85 %. The obtained samples were designed as: HA 850/10..... HA 850/85. Active carbons: charcoal 208 C and charcoal 264, based on coconut shell and on coal, correspondingly, were obtained from the firm Sutcliffe Speakman Ltd. Sorption measurements of benzene and cyclohexane were carried out at 25°C in a gravimetric vacuum apparatus (McBain quartz springs). Mercury porosimetry was used for the determination of macropore volumes of the steam gasified HA chars.

RESULTS AND DISCUSSION

The characteristic of samples is presented in Table I.

Table I. Proximate and ultimate analyses (wt %)

Sample	Proximate analysis			Ultimate analysis		
	Moisture	Ash	Volatile matter	C	H	(O+N+S _o) _{diff}
		dry	daf	daf	daf	daf
Brown coal	52.1 ⁴⁾	9.5	57.1	70.8	6.0	23.2
HA	6.3	0.4	53.2	69.1	6.0	24.9
HA 850	1.1	0.6	1.7	97.1	0.5	2.4
HA 850 10	0.5	0.7	1.8	96.3	0.7	3.0
HA 850 25	0.6	0.8	1.7	96.3	0.7	3.0
HA 850 50	0.6	1.2	1.6	96.4	0.7	2.9
HA 850 75	0.7	2.4	1.6	97.6	0.6	1.8
HA 850 85	0.6	3.0	0.8	98.6	0.7	0.7
Charcoals:						
208 C	6.2	5.4	3.2	96.1	1.2	2.7
264	4.7	14.8	3.0	95.4	1.1	3.5

⁴⁾ Total moisture of raw coal.

Isotherms of benzene and cyclohexane adsorption are given in figures 1 and 2. Basing on the desorption branch of the benzene isotherms, the pore size distributions of mesopores were calculated (18,19). The volume of micropores (V_{mic}) was calculated as the difference between the Gurvitch volume (the amount adsorbed at $p/p_0 = 0.96$, corresponding to the effective radius of 50 nm, was taken) and the volume of mesopores. Within the micropores volumes, the volumes of super- and ultramicropores were distinguished, in which primary and secondary (cooperative) adsorption processes occurred (20). The results are shown in form of bar graphs in figures 3 and 4. For the HA steam gasified chars, also the volumes of macropores are indicated. With increasing burn-offs systematic changes of each kind of considered porosity are visible.

On the basis of standard adsorption isotherms on a non-porous carbon black - Spheron 6-2700, the benzene and cyclohexane isotherms in figures 1 and 2 were corrected, subtracting at successive relative pressures the respective amounts adsorbed on the surface of mesopores (S_{mes}). The values of S_{mes} for the samples HA 850/10HA 850/85 are: 25.3, 51.1, 133.2, 206.6 and 228.8 m²/g, and for the charcoals 208 C and 264: 49.0 and 132.3 m²/g, respectively.

The corrected isotherms were used to calculate the values of W_0 and βE_0 according to the DA equation, assuming different values of the exponent n , from 1 to 6. The results are shown in figure 5. For these calculations the relative pressure region between 0.01 and 0.1

the best correlation was obtained, if W_0 values corresponding to $n=2$ were considered. It follows from figure 6 b, that there exists almost an identity between the W_0 values calculated from the DA equation for $n=2$ and the respective V_{mic} and V_m values. For all the investigated samples, if W_0 is calculated for $n=2$, for benzene adsorption: points of the plots $V_m=f(W_0)$ and $V_{mic}=f(W_0)$, and for cyclohexane adsorption: points of the plot $V_m=f(W_0)$, are placed on a straight line which passes almost through the origin of the coordinate system with a slope very close to 1. This is not the case, if for the calculation of W_0 in the DA equation other values of n are used.

Examples of DA plots for $n=2$, for chosen samples, are presented in figure 7. These plots confirm the proper choice of the upper limit of the relative pressure region ($p/p_0=0.10$) considered for calculations.

An attempt was made to determine the micropore volumes of the samples, employing the α_s -method (20), using Spheron6-2700 as standard. For samples with a low surface area of mesopores (HA 850/10, HA 850/25 and charcoal 208 C) a fairly good agreement was obtained with W_0 values for $n=2$.

To test the validity of the values of βE_0 obtained for $n=2$, the method presented by Stoekli and Kraehenbuehl (6,8) was applied. The enthalpies of immersion in organic liquids ($-\Delta H_{im}$)_{mic} of microporous solids with negligible external and mesopore surface areas can be related to the characteristic energies of adsorption (βE_0) according to the equation:

$$(-\Delta H_{im})_{mic} = \beta E_0 (\sqrt{\pi}/2)(1 + \alpha T) \quad (2)$$

where α is the thermal expansion coefficient of the adsorbate at temperature T ; for benzene and cyclohexane the values of α were taken as 8.87×10^{-4} and $9.80 \times 10^{-4} \text{ K}^{-1}$, respectively, calculated on the basis of their densities at the boiling and critical points (21).

$(-\Delta H_{im})_{mic}$ is expressed in the same units as βE_0 , e.g. in kJ/mol. In order to express the enthalpy per mass unit, e.g. in J/g, it is necessary to take account of the amount adsorbed in the micropores corresponding to this unit of mass, i.e. $a_0 = W_0/d$ (where d is the density of the adsorbate, taken as the density of the adsorbate as liquid at corresponding temperature):

$$(-\Delta H_{im})_{mic} = (-\Delta H_{im})_{mic} \times a_0 \quad (3)$$

These calculations were carried out for the steam gasified HA chars. To the obtained values of $(-\Delta H_{im})_{mic}$ corrections for the evolution of heat on the mesopore surface area were added:

$(-\Delta H_{im})_{Smes}$. These corrections were calculated on the basis of the respective a_{mes} values of the HA chars and the βE_0 values of Spheron 6-2700. The sum: $(-\Delta H_{im})_{mic} + (-\Delta H_{im})_{Smes} = (-\Delta H_{im})$, considered as the calculated total enthalpy of immersion of the char, was compared with the respective enthalpy value determined experimentally by microcalorimetric measurements (24). The results are shown in figure 8, and (with the exception of samples with highest burn-offs) a satisfactory agreement between the calculated and experimentally determined enthalpy values can be stated.

These considerations point to the fact that the values of W_0 and E_0 calculated from the DA equation with $n=2$, represent, in all probability, the real properties of the capillary structure of the investigated samples. Deviations obtained if other values of n are chosen, are shown in figure 9. Values of W_0 and E_0 for $n=2$ are given in Table III (for benzene $\beta=1$; for cyclohexane $\beta=1.22$).

Table III. Parameters W_0 ($\text{cm}^3 \text{g}^{-1}$), βE_0 and E_0 (kJ mol^{-1}) for $n=2$

Sample	Benzene adsorption		Cyclohexane adsorption		
	W_0	E_0	W_0	βE_0	E_0
HA 850 10	0.125	28.6	0.074	24.9	20.4
HA 850 25	0.248	26.6	0.211	26.7	21.9
HA 850 50	0.388	23.0	0.381	21.1	17.3
HA 850 75	0.458	20.1	0.474	17.0	13.9
HA 850 85	0.451	19.9	0.458	14.2	11.6
Charcoals:					
208 C	0.382	29.1	0.350	23.6	19.3
264	0.297	18.6	0.313	13.9	11.4

A comparison of the W_0 values resulting from adsorption of benzene (molecular sizes: 0.37 and 0.70 nm) and of cyclohexane (molecular sizes: 0.48 and 0.68 nm), indicates the presence of slit-like micropores of widths below 0.48 nm in the microporous system of the HA chars of low burn-offs and the charcoal 208 C. In all cases the values of E_0 for benzene are higher from the respective values for cyclohexane.

CONCLUSIONS

- The parameters W_0 and βE_0 , calculated for the considered adsorption data, are in a satisfactory agreement with the independently calculated micropore volumes and calorimetrically determined enthalpies of immersion, if in the DA equation the exponent $n=2$ is assumed.
- These results were obtained for micro- and mesoporous carbonaceous materials, which can be considered as being representative for the majority of active carbons.
- It is very probable that the values of W_0 and βE_0 for $n=2$ are closely related to real properties of the capillary structure - the micropore volume and the integral enthalpy of immersion.

ACKNOWLEDGEMENTS

This work was sponsored by the Technical University of Wrocław and the Polish Academy of Sciences (Scientific Program CPBP 01.16).

REFERENCES

- Dubin, M.M. in Chemistry and Physics of Carbon (P.L. Walker, Jr., Ed.); Dekker: New York, 1966; Vol. 2, pp 51-120.
- Rand, B. J. Colloid Interface Sci. 1976, 56, 337-343.
- Huber, U.; Stoekli, H.F.; Houriet, J.P. J. Colloid Interface Sci. 1978, 67, 195-203.
- Dubin, M.M.; Stoekli, H.F. J. Colloid Interface Sci. 1980, 75, 35-42.
- Walker, Jr., P.L. Phil. Trans. R. Soc. London 1981, A300, 65-81.
- Stoekli, H.F.; Kraehenbuehl, F. Carbon 1981, 19, 353-356.
- Masters, K.J.; McEnaney, B. J. Colloid Interface Sci. 1983, 95, 340-345.
- Stoekli, H.F.; Kraehenbuehl, F. Carbon 1984, 22, 227-229.
- McEnaney, B.; Masters, K.J. Thermochemica Acta 1984, 82, 81-102.
- Stoekli, H.F.; Kraehenbuehl, F.; Lavanchy, A.; Huber, U. J. Chim. Phys. 1984, 81, 785-790.
- Ali, S.; McEnaney, B. J. Colloid Interface Sci. 1985, 107, 355-361.
- Carrott, P.J.M.; Roberts, R.A.; Sing, K.S.W. Carbon 1987, 25, 59-68.

13. Marsh, H. Carbon 1987, 25, 49-58.
14. McEnaney, B. Carbon 1987, 25, 69-75.
15. Barton, S.S. Carbon 1987, 25, 77-80.
16. Dubinin, M.M.; Astakhov, V.A. Izv. Akad. Nauk SSSR Ser. Khim. 1971 No 1, 5, 11.
17. Everett, D.H.; Parfitt, G.D.; Sing, K.S.W.; Wilson, R. J. appl. Chem. Biotechnol. 1974, 24, 199-219.
18. Pierce, C. J. Phys. Chem. 1953, 57, 149-152.
19. Kankare, J.; Jantti, O. Soumem Kemistilehti 1967, B40, 51-53.
20. Gregg, S.J.; Sing, K.S.W. Adsorption, Surface Area and Porosity; Academic Press: London, 1982.
21. Komarov, W.S. Adsorbents and their Properties (Russian language); Nauka i Tech.: Minsk, 1977; pp 231-239.
22. Brunauer, S.; Emmett, P.H.; Teller, E. J. Am. Chem. Soc. 1938, 60, 309-319.
23. Joyner, L.G.; Weinberger, E.B.; Montgomery, C.W. J. Am. Chem. Soc. 1945, 67, 2182.
24. Grillet, Y.; François, M.; Torralvo, M.J.; Guerrero, A.; Siemieniowska, T.; Tomków, K.; Kaczmarczyk, J.; Albinia, A. Proc. IUPAC Symposium on Characterization of Porous Solids, Bad Soden, F.R.G. 26-29 April 1987; Elsevier.

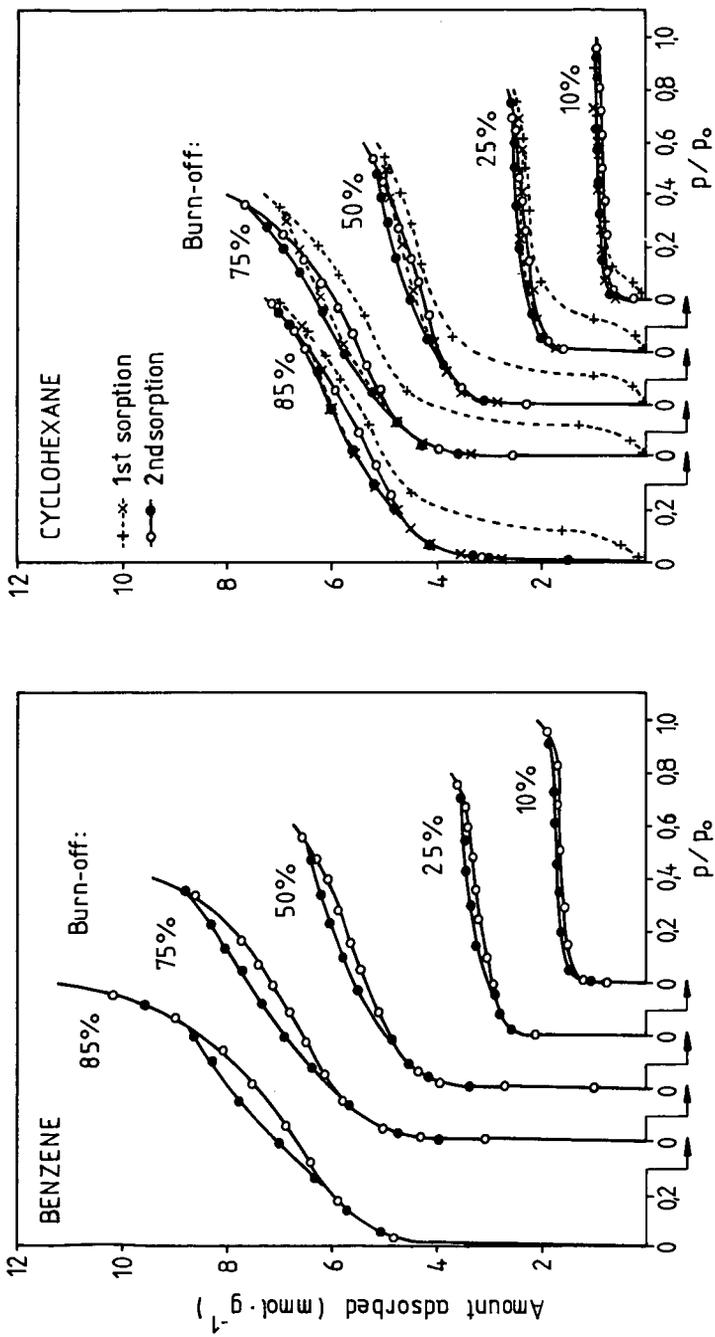


Figure 1. Benzene and cyclohexane sorption isotherms at 25°C on steam gasified (800°C) humic acids char HA 850.

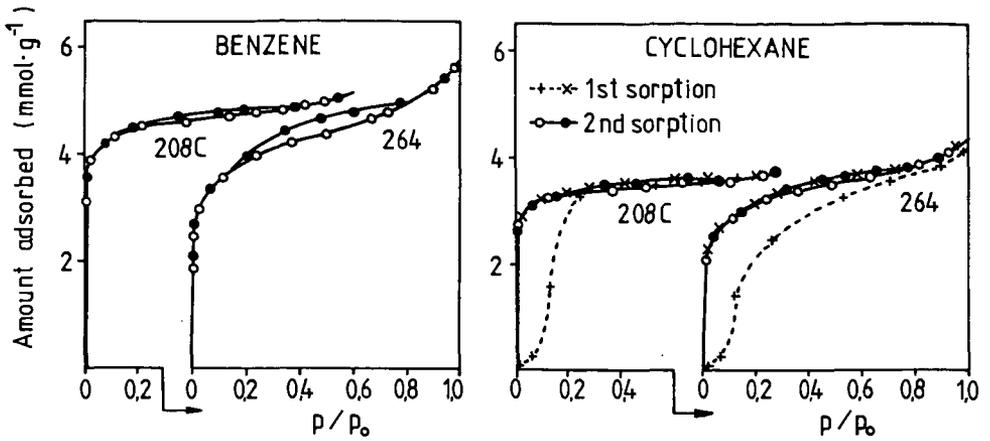


Figure 2. Benzene and cyclohexane sorption isotherms at 25°C on charcoals 208C and 264.

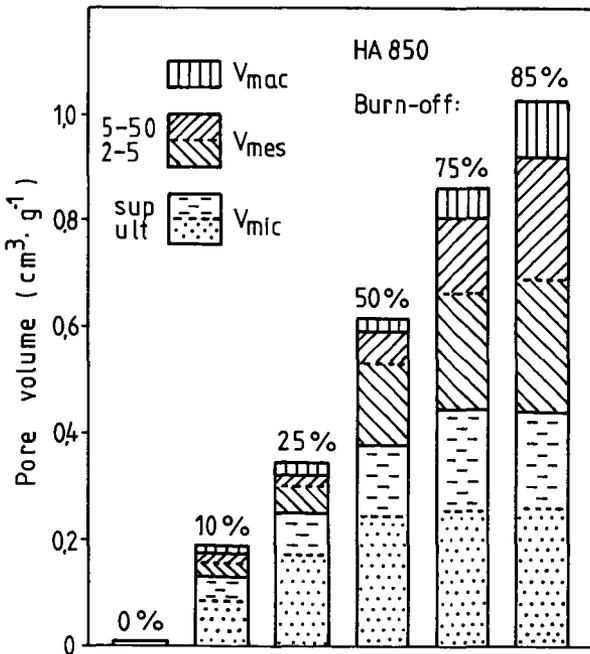


Figure 3. Influence of burn-off on the pore size distribution of steam gasified (800°C) humic acids char HA 850.

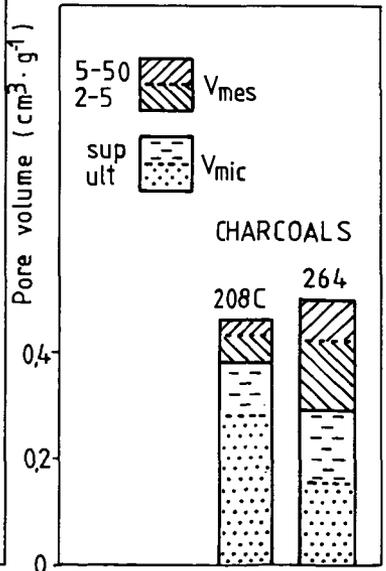


Figure 4. Pore size distribution in charcoals 208C and 264.

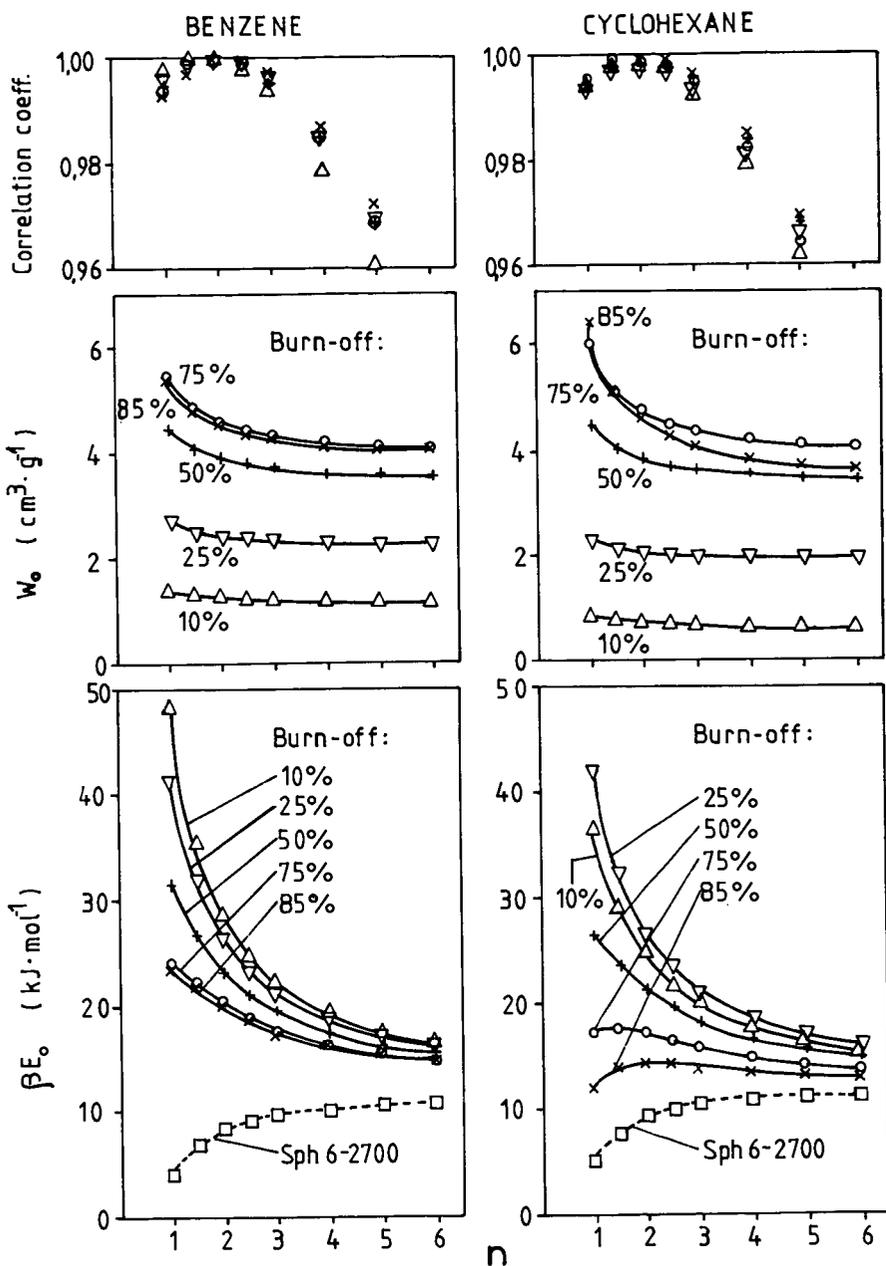


Figure 5. Influence of n used in calculations on the resulting values of W_0 and βE_0 of the DA equation.

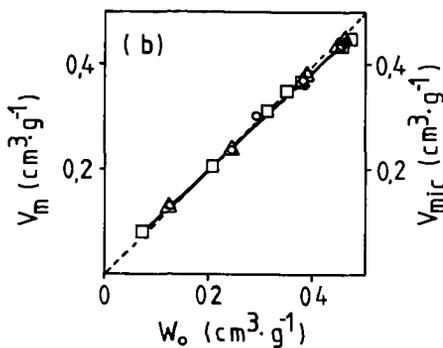
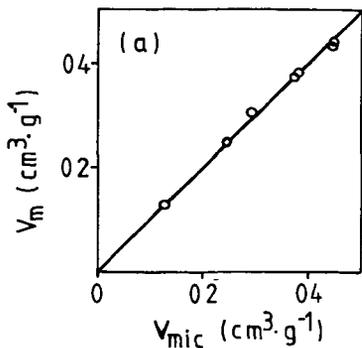


Figure 6. Plots: (a) V_m vs V_{mic} (o, benzene); (b) V_m vs W_o (o, benzene; \square , cyclohexane); V_{mic} vs W_o (Δ , benzene).

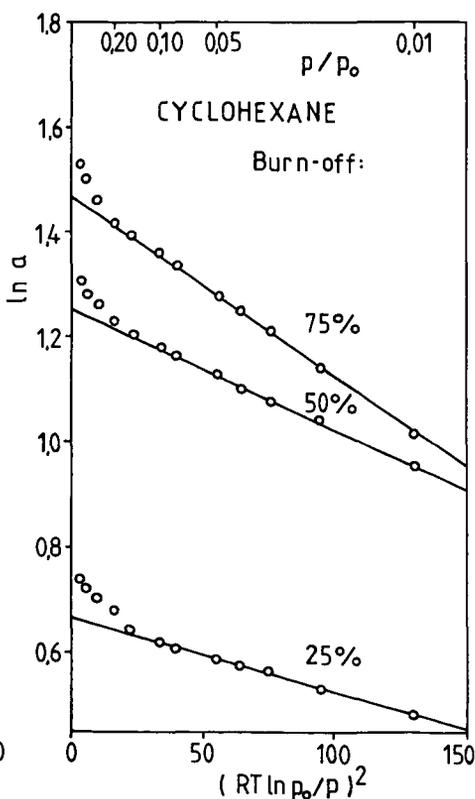
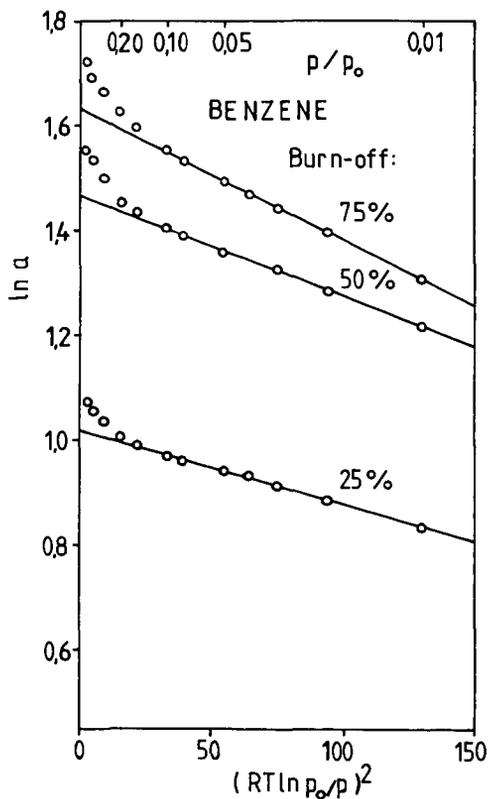


Figure 7. Plots: $\ln a$ vs $(RT \ln p_o/p)$ for steam gasified humic acids char HA050; a in $\text{mmol}\cdot\text{g}^{-1}$, RT in $\text{kJ}\cdot\text{mol}^{-1}$.

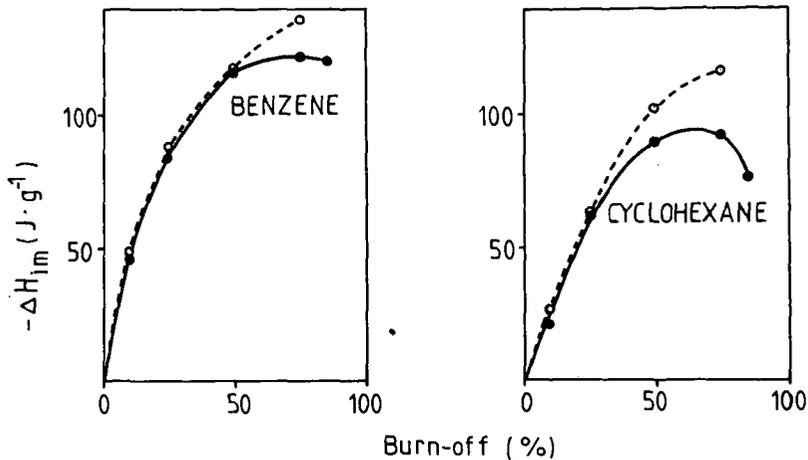


Figure 8. Enthalpies of immersion of steam gasified humic acids char HA850: \circ - experimental and \bullet - calculated from parameters βE_o and W_o of the DA equation for $n=2$.

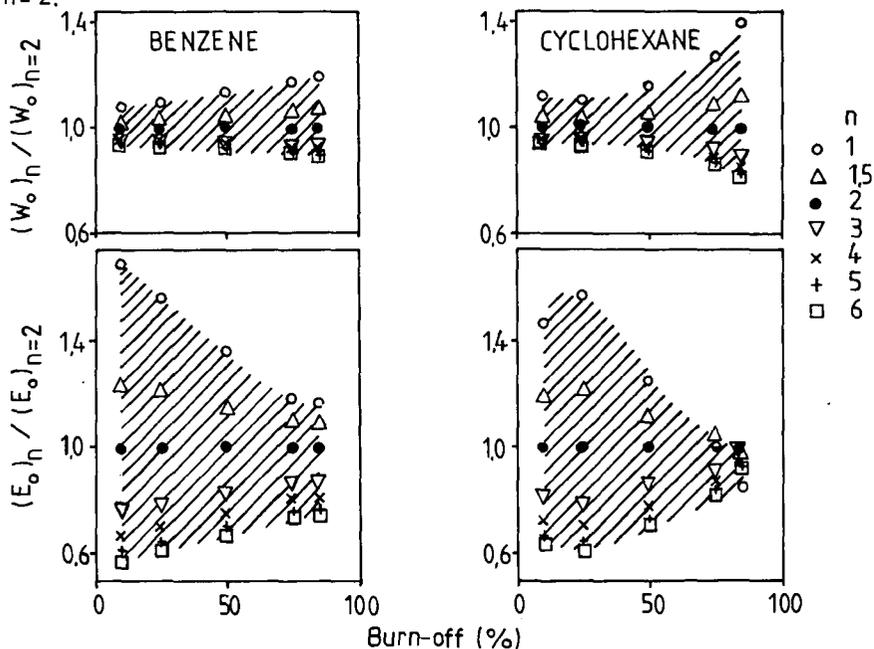


Figure 9. Influence of n in the DA equation on the ratios $(W_o)_n / (W_o)_{n=2}$ and $(E_o)_n / (E_o)_{n=2}$ for steam gasified humic acids char HA850.