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THERMOANALYTICAL STUDY OF ACTIVATED CARBON REGENERATION PART IV. ADSORPTION EQUILIBRIA FOR PHENOL, ANILINE AND THEIR NITRO-DERIVATIVES ON GRANULAR ACTIVATED CARBON *

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ABSTRACT

A linear correlation between adsorptive affinity and acidic properties of adsorbates is evidenced when phenol, aniline and their *o*-, *m*-, and *p*-nitro-derivatives are adsorbed on granular activated carbon. Thermodesorption energies appear to be empirically related to adsorptivity.

INTRODUCTION

Activated carbon (AC) exhausted in water treatment is usually regenerated thermally in the temperature range 900—1000°C under controlled gas conditions. This costly, non-specific regenerative procedure greatly reduces AC application potentialities.

A systematic investigation of the adsorption—thermodesorption mechanism of some common pollutants (phenol, aniline and nitro-derivatives) from a commercial AC has been undertaken to obtain the process energies for each class of pollutant. Subsequently, information on individual adsorbent—adsorbate interactions will be exploited for specific regeneration procedures where mild thermal treatments can occasionally be followed by more drastic conditions to remove strongly adsorbed pyrolitic materials, as described by Hernandez and Harriott [1].

Some data on the thermal behaviour of AC exhausted by the two series of compounds have already been collected [2—4]. In this paper, equilibrium adsorptivities from dilute solutions and thermodesorption energies are discussed.

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TABLE 1

Main characteristics of compounds investigated

Compound	Max. absorption wavelength (nm)	Solubility * (mole l^{-1})	ΔH ** (kcal $mole^{-1}$)	pK_a ***	$14 - pK_b$ ***
P	270	0.998	—25	9.96	
ONP	280	0.014	+114	7.22	
MNP	230	0.101	+134	8.30	
PNP	314	0.122	+105	7.16	
A	230	0.397	—15		4.60
ONA	234	0.007	+65		0.50
MNA	224	0.007	+113		2.50
PNA	380	0.004	+117		1.00

* From ref. 9. ** From refs. 2—4. *** From ref. 10.

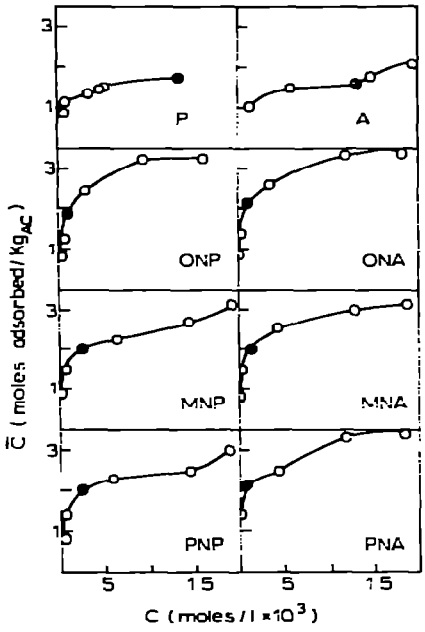
EXPERIMENTAL

Activated carbon Filtrasorb 400 (Calgon Corp., Pittsburg, Pa.) was used for the equilibrium study. Carbon was dry-sieved and the 16—25 (U.S.) mesh fraction collected. This was washed in boiled distilled water to remove fines and dust and then dried to constant weight at 105°C. The equilibrium study was done by adding to 200-ml Erlenmeyer flasks, each containing a variable amount (10—250 mg) of dry carbon, 100 ml of aqueous solution at a concentration of 300 mg l^{-1} of each compound. Carbon plus distilled water was used as blank for each system. All samples were vigorously shaken in a thermostatic Dubnoff shaker at 25 ± 1°C, for five days, which was sufficient time to reach equilibrium. All compounds were spectrometric grade. After filtration, the residual solute concentrations were measured with a double beam Model 1750 spectrophotometer (Pye-Unicam, Cambridge, U.K.) at the wavelength of maximum absorption. Thermodesorption energies (see Table 1) were obtained with a Mettler TA 1 thermoanalyzer as described elsewhere [2].

RESULTS AND DISCUSSION

Previous thermoanalytical investigations showed that both the presence and position of the NO_2 group modify the gravimetric (TG, DTG) and energetic (DTA) behaviour of the thermodesorption of these compounds. Exothermic effects were associated with nitro-isomer release, while endo-effects occurred for the unsubstituted products. Furthermore the highest values were found for *o*-nitrophenol and *m*-nitroaniline.

The experimental adsorption isotherms of phenol, aniline and their three



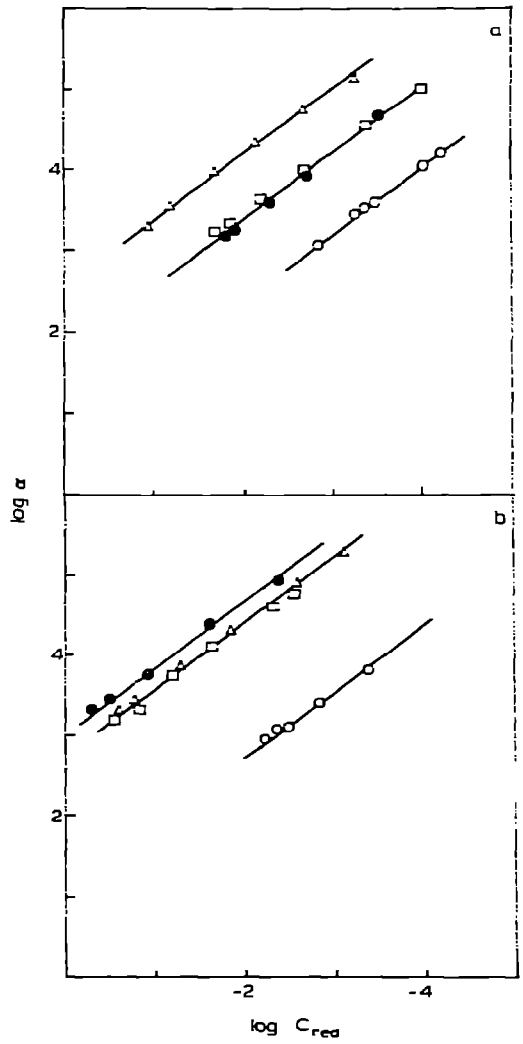
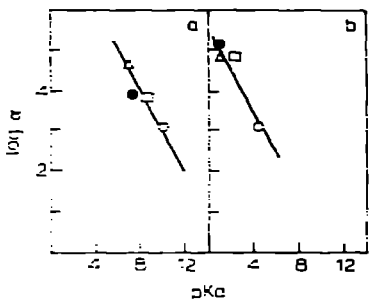


Fig. 1. Adsorption isotherms of phenol, aniline and their nitro-derivatives. Filled circles refer to samples submitted to thermoanalysis.

Fig. 2. Partition coefficient vs. reduced equilibrium concentration for phenolic (a) and aminic (b) compounds. (○) P, (△) ONP, (□) MNP, (●) PNP, (○) A, (△) ONA, (□) MNA and (●) PNA.

nitro-isomers, in the range 5—2000 μmole l^{-1}, are shown in Fig. 1. According to Giles et al. [5], appreciably higher surface coverages can be derived from the initial slopes for nitro-compounds than for unsubstituted adsorbates. In order to normalize the energy requirements to remove each solute from bulk solution to interface, reduced equilibrium concentrations ($C_{red} = C/S$) can be introduced [6]. The solubility value, S, for each compound is listed in Table 1.

When the isotherm slopes, expressed by the partition coefficient ($\alpha = \overline{C}/C$), are plotted versus C_{red} (see Fig. 2), an adsorptivity increase is invariably associated with the NO_2 introduced under the conditions investi-



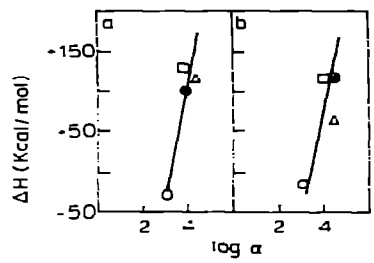


Fig. 3. Partition coefficient vs. acidic character (pK_a) for phenolic (a) and aminic (b) compounds. All α values taken at C_{red} = 0.003. (○) P, (△) ONP, (□) MNP, (●) PNP. (○) A. (△) ONA. (□) MNA and (●) PNA.

Fig. 4. Thermodesorption energies vs. partition coefficients for phenolic (a) and aminic (b) compounds. (○) P, (△) ONP, (□) MNP, (●) PNP, (○) A, (△) ONA, (□) MNA and (●) PNA.

gated. This clearly confirms this group as a major contributor to the adsorptive π electron donor—acceptor interactions as shown by Mattson et al [7].

Moreover a definite influence of the NO_2 position on the aromatic ring is also evident, thus suggesting that the acidic character of the adsorbate also contributes to the adsorption mechanism. As shown by Fig. 3, a striking linear correlation between α and pK_a is obtained for both the phenol and aniline series of compounds. By the least-squares method, the following empirical equation was found to give a best fit to the experimental points:

$$\log \alpha = A pK_a + B \quad (1)$$

where $A = -0.51$, while B equals 8.1 and 5.6 for phenol and aniline derivatives, respectively. This suggests that the physical meaning of "substituent" (NO_2 group) and "substrate" (phenol or aniline) constants could be associated with the A and B parameters.

Finally, a linear correlation between α and the overall thermodesorption energies, ΔH, has been found (Fig. 4), although with a less obvious physical meaning. Quite unexpectedly, indeed, favourable energy requirements are associated in both series with the introduction of a nitro-group with corresponding higher adsorptivities. As already pointed out [3], this seems to confirm that the measured ΔH values are not representative of desorption energies per se, in that they include other thermolytic interactions (such as pyrolysis, NO_2 oxidative effects, etc.).

CONCLUSIONS

A remarkable dependence of the adsorptivity of phenol, aniline and their derivatives on the presence and position of the NO_2 group seems to be derived from the experimental data, in partial disagreement with the literature [8].

From experimental results it is seemingly possible to anticipate the adsorption affinity of a given compound once the substituent and substrate parameters (A and B) are known according to eqn. (1).

There is thus a need for further research to be carried out on the energy interactions of various substituents (—CHO, —COOH, —SO_3H, etc.) in aromatic matrices.

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