

## Adsorption behaviour of *N*-haloarene sulphonamides on activated carbon at 303 K

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By batch studies adsorption behaviour of some sodium-*N*-haloarene sulphonamides (NHAS) such as chloramine-B (CAB) and bromamine-B (BAB), chloramine – T (CAT) and its bromo analogue (BAT) on activated carbon (AC) is studied at 303 K. Langmuir adsorption isotherm (LAI), Freundlich adsorption isotherm (FAI) and Temkin adsorption isotherm (TAI) are well obeyed while Harkins Jura adsorption isotherm (HJAI) is poorly obeyed. The constants of these adsorption isotherms have been evaluated and their variation with adsorbate is analysed. The sorption capacity for different NHAS has been arrived and it is more for CAT than for CAB. Similarly it is more for BAT as compared to that of BAB. The specific surface area determined with these four adsorbates is almost the same. The dimensions of the adsorbates have been calculated.

The importance of the *N*-haloarene sulphonamides is evident from the recent literature, viz, the kinetics of oxidation of diazepam<sup>1</sup> and norfloxacin<sup>2</sup> by CAB, oxidation of aspirin<sup>3</sup> by BAB and CAB, pharmacological effects<sup>4</sup> of CAT and oxidation of ethanolamine<sup>5</sup> by CAT. In continuation of our work<sup>6</sup> this present work is undertaken.

### Experimental

Batch adsorption studies were carried out after optimising the conditions. The *N*-bromo analogues of CAT and CAB were synthesized by the well-known reaction of paratoluene sulphonamide with sodium hypobromite followed by salting out. They were characterised by elemental analysis. The concentrations of the different NHAS were

determined iodometrically using standard sodium thiosulphate and starch indicator.

### Results and discussion

#### *Obedience to different adsorption isotherms*

It is evident from Figs 1, 2, 3 and 4 that Langmuir adsorption isotherm (LAI), Freundlich adsorption isotherm (FAI) and Temkin adsorption isotherm (TAI) are obeyed. Figure 5 shows that Harkins Jura adsorption isotherm (HJAI) is only fairly obeyed and it is also seen from poor correlation coefficients.

#### *Constants of different adsorption isotherms*

The constants of different isotherms are presented in Table 1. The constant 'n' in FAI is a correction factor for the mutual interaction among the adsorbed species. If the forces within the surface layers are attractive then 'n' is greater than unity and if repulsive 'n' is less than unity. The fractional 'n' values show repulsive interaction between adsorbed species. This repulsive interaction decreases with decrease in the size of the adsorbate molecule (BAT > BAB > CAT > CAB).

The Freundlich constant 'k' is specific adsorption constant when the equilibrium concentration of the adsorbate tends to zero. These 'k' values decrease with decrease in size of the adsorbed species (Table 1) in the order BAT > BAB = CAT > CAB. This is due to increase in sorption capacity with increase in size or molecular weight of the adsorbate (Table 2).

The LAI is written in the form  $(Ce/a) = (Ce/\gamma) + (1/\gamma\mu)$ , where  
 $Ce$  = equilibrium concentration of the adsorbate,  
 $a$  = specific adsorption,  
 $\gamma$  = constant = number of moles of adsorbate forming monolayer,  
 $\mu$  = temperature dependent constant

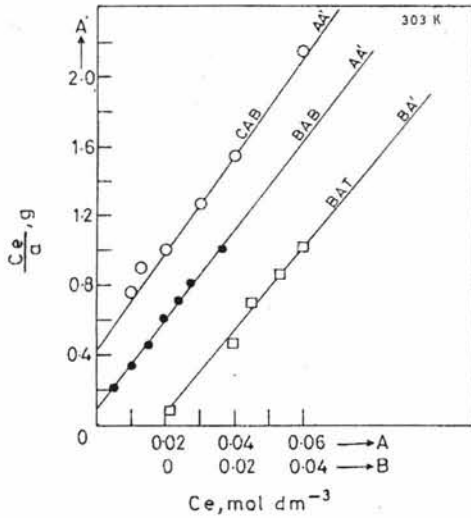


Fig 1 — NHAS-AC system - LAI

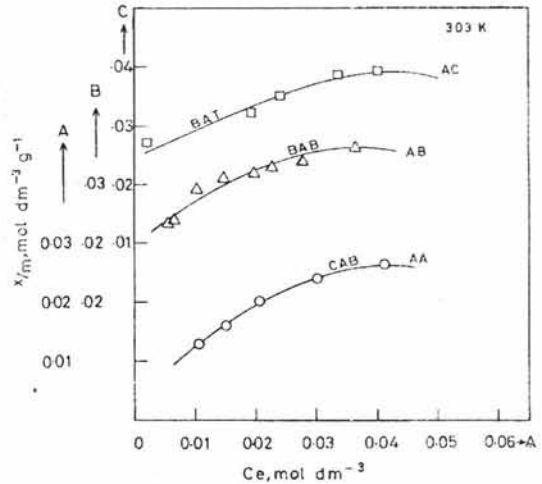


Fig 3 — NHAS-AC system - FAI

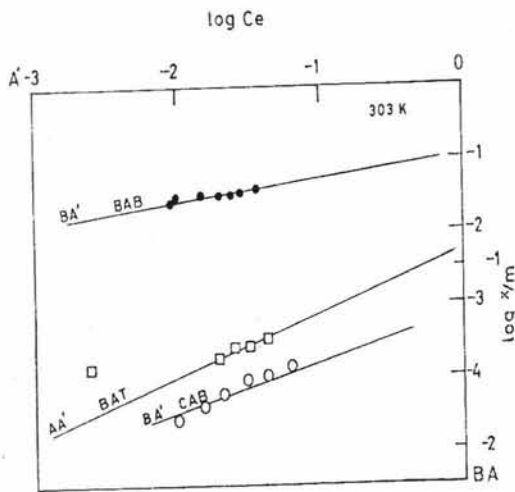


Fig 2 — NHAS-AC system - FAI

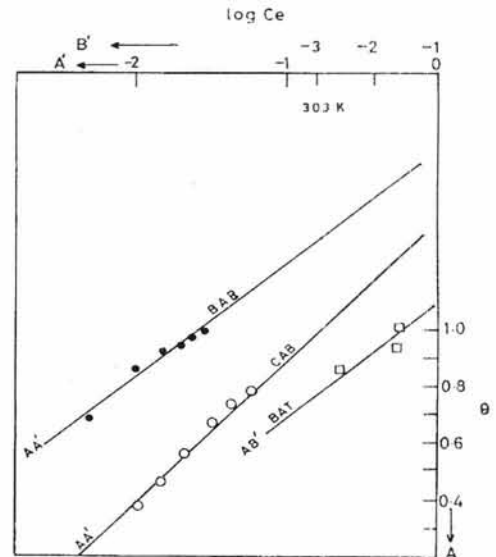


Fig 4 — NHAS-AC system - TAI

As expected  $\gamma$  increases as the size of the adsorbate species decreases. The constant  $\mu$  is adsorption desorption equilibrium constant and the  $\mu$  values suggest that CAT is the best adsorbate on AC while its bromo analogue BAT is fairly adsorbed on AC.

The Harkins Jura adsorption isotherm is given by  $\log C/C_0 = \alpha - \beta/a^2$  where 'a' is the adsorption at the equilibrium relative concentration  $C/C_0$  and  $\alpha$  and  $\beta$  are constants. The negative slope of the linear plot of  $\log C/C_0$  versus  $1/a^2$  must be proportional to the square of the surface area of the adsorbent. Thus  $\beta$  of HJAI can be used to compare specific surface areas of

different adsorbents. The  $\beta$  values are in the order  $10^{-4}$  and can be taken as a constant except with CAB where the obedience to HJAI is very poor.

The fractional coverage,  $\theta$ , is related to the equilibrium concentration of the adsorbate ( $C_e$ ) by Temkin isotherm

$$\theta = C_1 \ln C_2 c$$

where  $C_1$  and  $C_2$  are constants. TAI is based on the assumption that adsorption enthalpy is a linear function of concentration of the adsorbate. But FAI assumes that adsorption enthalpy is logarithmic function of adsorbate concentration. The obedience to

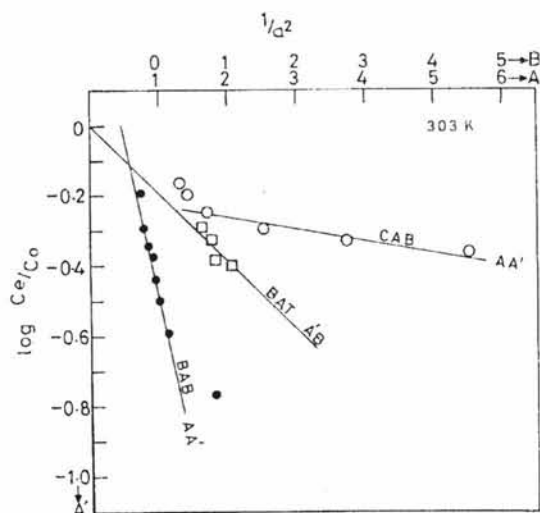


Fig 5 — NHAS-AC system - HJAI

both FAI and HJAI can be due to the small range of chosen experimental concentrations of the adsorbate.

*Effect of anion molecular weight on sorption capacities*

The data presented in Table 2 reveal that as the molecular weight of the adsorbed species increases

sorption capacity increases. The greater sorption capacity of CAT over CAB and BAT over BAB may be attributed to increased negative charge on atom adsorbed due to the presence of paramethyl group with +I effect in CAT and BAT.

*Molecular dimensions of NHAS*

Assuming spherical geometry for the nitrogen atom ( $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2 - \bar{\text{N}} - \text{Cl}$ ) through which the anion of NHAS is attached to the acidic surface of AC and circular surface coverage on the adsorbent, molecular dimensions have been calculated. The radius of the adsorbed species, the circular cross-sectional area occupied by each adsorbate and the length of the molecule are presented in Table 3. All these correlate with the increase in size of NHAS in the order  $\text{CAB} < \text{BAB} < \text{CAT} < \text{BAT}$ .

**Conclusions**

The sorption capacities of BAT, BAB and CAT on AC are almost the same as seen from 'k' values (Table 1) and are greater compared to that of CAB.

Adsorption studies such as these are useful in comparing the molecular weights of structurally

Table 1 – NHAS – AC system  
Constants from adsorption isotherms  
T : 303 ± 0.01 K

Isotherm		BAT	BAB	CAT	CAB
FAI	Intercept	- 0.9000	- 0.9500	- 0.9500	- 1.2500
	n	0.4000	0.2857	0.2308	0.2000
	k	0.1259	0.1122	0.1122	0.0562
LAI	Intercept	0.0500	0.1000	0.0020	0.4000
	Slope	31.2500	29.4100	28.5300	27.7800
	$\mu$	$6.2500 \times 10^2$	$2.9412 \times 10^2$	$1.4265 \times 10^4$	$6.9464 \times 10^1$
	$\gamma$	$3.2000 \times 10^{-2}$	$3.4000 \times 10^{-2}$	$3.5050 \times 10^{-2}$	$3.5990 \times 10^{-2}$
HJAI	$\alpha$	0.0100	0.1300	1.8000	0.0065
	$\beta$	$1.2500 \times 10^{-4}$	$4.0000 \times 10^{-4}$	$1.0000 \times 10^{-4}$	$1.0000 \times 10^{-3}$
TAI	Intercept	1.2500	1.6300	1.6800	1.3800
	Slope	0.1600	0.3600	0.3077	0.4400
	$C_1$	0.0695	0.1563	0.1336	0.1911
	$\log C_2$	7.8125	4.5278	5.4599	3.1364

Table 2 – NHAS – AC system  
Effect of molecular weight on sorption capacities

T : 303 ± 0.01 K		
Adsorbate	Anion molecular weight	a/mol dm <sup>-3</sup> for co = 0.03 M
CAB	190.5	0.0160
CAT	204.5	0.0270
BAB	234.5	0.0271
BAT	248.9	0.0280

Table 3 – NHAS-AC system molecular dimensions of NHAS

NHAS	BAT	BAB	CAT	CAB
$\sigma, \text{A}^2$	10.100	9.502	9.230	8.977
Radius metre $\times 10^{-10}$	1.792	1.739	1.700	1.690
Length of the molecule A <sup>n</sup>	10.380	8.790	10.300	8.740
SA of AC m <sup>2</sup> g <sup>-1</sup> $\times 10^3$	1.950	1.950	1.946	1.950

related adsorbates and in arriving at their molecular dimensions using bond length data from literature (Table 3).

The specific surface area SA (Table 3) arrived for at AC with different adsorbates is the same proving that these adsorbates are held to the surface of AC through the negatively charged nitrogen atom.

### Acknowledgement

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