

## Adsorption studies of acetic acid dimers on activated charcoal from organic solvents

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**Abstract.** Acetic acid exists as dimers in organic solvents like benzene, toluene and xylene. Adsorption of dimeric acetic acid on activated charcoal (AC) at various temperatures from benzene, toluene and xylene solutions have been studied. The system obeys Langmuir isotherm, thus signifying a monolayer adsorption of dimers. Corrections on AC-solvent pore volume fillings, molecular cross sectional surface area of acetic acid dimers, the adsorption equilibrium constants, the free energy change and the enthalpy change values are computed at different temperatures for the three solvents. The adsorption process has been found to be physisorption type. The FTIR measurements show that the adsorbed acetic acid dimer seems to retain the cyclic structure against the open chain non-cyclic structure.

**Keywords.** Physisorption of acetic acid dimer; adsorption from non-aqueous solvents; adsorption on activated charcoal; enthalpy and free energy changes of adsorption.

### 1. Introduction

Adsorption of carboxylic acids from aqueous solutions on activated charcoal (AC) has been well studied and rationalised by several others in the past (Yoshinobu *et al* 1990; Afzal *et al* 1991). In low dielectric non-aqueous solvents it is known that carboxylic acids exist as dimers (Glasstone 1984). From the theories of adsorption, it may be envisaged that the mechanism of adsorption would differ from aqueous to non-aqueous type of solvents and from a monomeric to a dimeric form of the solute (Oscik 1992). Adsorption studies of acetic acid (AA) on AC from aqueous solutions are well documented (Rakshit and Pradeep 1987). Very few others have described AA adsorption on carbon blacks from certain non-aqueous solutions (Parkash 1973). Several proposals on a monolayer and multilayer adsorptions are being made especially in non-aqueous solvent systems and reports on the nature of adsorbent-adsorbate complex show spurious inferences.

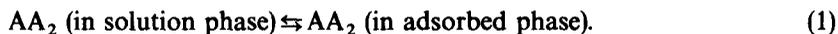
In our laboratory the association factor of AA in benzene, toluene, and xylene solvents has been determined and checked to be 2.0. The literature survey reveals that the adsorption characteristics of AA dimer (AA<sub>2</sub>) from aromatic solvents has not been thoroughly reported. We undertake here to report investigations on the adsorption characteristics of (AA<sub>2</sub>) on AC from various aromatic solvents. AC has the largest specific surface area among the other types of carbon solids, ie, 816.94 m<sup>2</sup>/g (by low temperature N<sub>2</sub> adsorption using BET method). Also AC belongs to the

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porous adsorbent class with the average mesopores radii falling within 50 Å range and with a specific pore volume equal to 0.1 cc/g (Joyner *et al* 1951). The adsorption from solutions involves excess solvent compositions, filling the adsorbent pore volumes due to the small sized solvent molecules and which results in an increase in the initial bulk solute concentration. Subsequently the surficial adsorption equilibrium of the solute with or without the concomitant solvent adsorption would depend on the altered initial solute concentration. Hence pore volume corrections are being made in evaluating the adsorption parameters on porous AC. The results obtained are analysed to befit the various isotherms such as Langmuir, Freundlich and BET. Various adsorption mechanisms have been suggested and verified to suit the isotherm. Thermodynamic parameters like energy change ( $\Delta G_{\text{ads}}$ ) and enthalpy change ( $\Delta H_{\text{ads}}$ ) values of the overall adsorption process are determined from the temperature effects. FTIR spectra of the AA<sub>2</sub>-AC samples from the three solvents seem to emphasise the proposed mechanism.

## 2. Theory

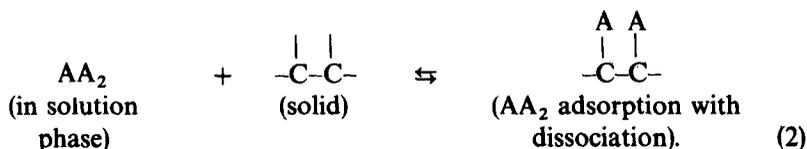
The dimeric acetic acid (AA<sub>2</sub>) adsorption on AC can be visualised to occur via any one of the following mechanisms,



This mechanism is analogous to monomeric AA in solution equilibrating with adsorbed AA. If  $C_o/2$  and  $C_e/2$  are the concentrations of AA<sub>2</sub> in solution before and after adsorption and if 'm' is the weight in grams of the adsorbent used, it may be derived from equilibrium (1) that  $x_d/m = K(C_e/2)^{1/n}$  where K and n being Freundlich parameters and  $x_d$  refers to the weight in gram of the adsorbed dimer obtained from  $C_o$  and  $C_e$  values. Therefore the plot of  $\log(x_d/m)$  vs  $\log(C_e/2)$  should linearly vary with unit slope. By doing so, when the value of 'n' deviates from unity other isotherms may be utilised to analyse the data. In case of Langmuir type of adsorption the linear relation,

$$\frac{1}{x_d} = \frac{K}{x_{d,m}(C_e/2)} + \frac{1}{x_{d,m}},$$

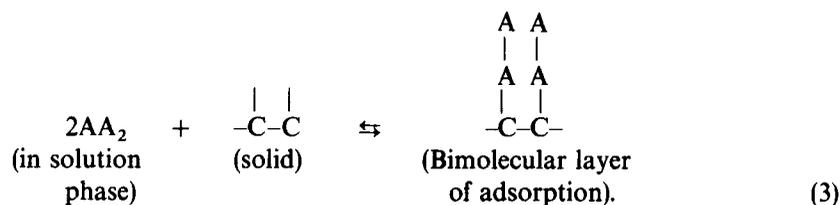
may be derived for equilibrium (1), where  $x_{d,m}$  is the amount of adsorbate (mol/g) covering the surface area of the adsorbent via a monomolecular film. The value of  $x_{d,m}$  is determined from the plot of  $1/x_d$  vs  $1/C_e/2$  (Barrow 1988). By knowing the number of molecules of dimers adsorbed (which is derived from  $C_o/2$  and  $C_e/2$  values) and the specific total surface area of charcoal, the surface area occupied by AA<sub>2</sub> molecule in the monolayer adsorption is known. By correlating this value to the theoretical value of the surface area of the AA<sub>2</sub> the orientation of AA<sub>2</sub> either in the horizontal or in the vertical type of stackings on the adsorbent may be rationalised,



In this scheme of adsorption the dimer requires two sites of adsorption. Under equilibrium conditions  $k_1(C_e/2)(1-\Theta)^2 = k_{-1}\Theta^2$  where  $k_1$  and  $k_{-1}$  are the adsorption and desorption rate constants,  $\Theta$  is the surface area occupied. This condition may be converted to the linear relation

$$\frac{1}{x_d} = \frac{1}{x_{d,m}K^{1/2}(C_e/2)^{1/2}} + \frac{1}{x_{d,m}}$$

and be used to obtain  $x_{d,m}$  and  $k$  values and compared with those of (1).

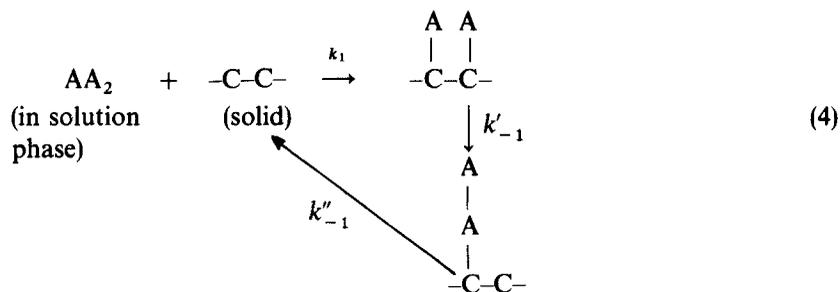


At equilibrium,  $k_1(1-\Theta)(C_e/2) = k_{-1}\Theta$  from which the linear relation,

$$\frac{1}{x_d} = \frac{1}{K(C_e/2)x_{d,m}} + \frac{1}{x_{d,m}}$$

may be derived and analysed with the data.

$AA_2$  adsorption with stepwise desorption process can also be proposed as follows:



The linear expression that follows this scheme would be

$$\frac{1}{x_d} = \frac{1}{KC_e x_{d,m}} + \frac{1}{x_{d,m}}$$

Consequently, the plot  $1/x_d$  vs  $1/(C_e/2)$  would be used to analyse (1) and (3) while  $1/x_d$  vs  $1/(C_e/2)^{1/2}$  and  $1/x_d$  vs  $1/C_e$  plots may be used for (2) and (4) respectively.

The various linear empirical equations are checked and analysed for benzene, toluene and xylene systems at constant temperature.

The BET treatment may also be applied for adsorption on a porous solid for finite  $n$  layers of adsorption stacked one on top of the other. The BET treatment leads

to the equation (Adamson 1990)

$$V = \frac{V_m C x' \{1 - (n + 1)x'_n + n x'^{n+1}\}}{(1 - x') \{1 + (c - 1)x' - C x'^{n+1}\}}$$

where  $x' = C_e/C_o$ ,  $C = \text{BET constant}$  and  $V = x'_d/m$ . The BET plot may be compared with any one of the five standard BET types along with other isotherms (Brunauer 1945).

### 3. Experiments

Glacial acetic acid (GR) and the solvents like benzene (GR), toluene (GR) and xylene (Extra pure) obtained from E Merck (India) were used. The organic solvents were distilled with anhydrous sodium sulphate and the middle fraction of the distillate was used in each case. Activated charcoal (E Merck, India) was preheated at 100°C for 5–6 hours, cooled and stored in a vacuum dessicator. The amount of acetic acid before and after adsorption was estimated by titrating against standard NaOH using phenolphthalein as the indicator. The error in titration was found to be less than 0.03%.

Exactly 2 g of activated charcoal was taken into each of a series of clean bottles. Different concentrations of glacial acetic acid prepared in benzene were pipetted into the bottles. The concentration range lies between 0.05 to 0.5 M. The bottles were shaken using a shaker for 3 hours and thermostatted at the required temperature. The solutions were then centrifuged quickly under cover to prevent evaporation of the solvent. The amount of AA unadsorbed was estimated quantitatively. This procedure has been repeated with other organic solvents and at various temperatures.

FTIR spectra were taken for the activated charcoal adsorbed samples as KBr pellets using a Perkin-Elmer (Model 1706) instrument. Spectral corrections such as the background subtractions from clean (unadsorbed) and only solvent-treated samples have also been included.

### 4. Results and discussion

The adsorption results obtained after the applications of pore volume corrections and concomitant solvent adsorptions, such as the amount of dimer adsorbed ( $x_d$ ) and the equilibrating concentration of the dimer ( $C_e$ ) in solution at various temperatures and solvents are furnished in table 1. When the Freundlich isotherm is verified, the value of  $n$  has been found to be greater than unity. When the data are analysed for the Langmuir type of adsorption corresponding to mechanisms (1) and (3), best fit linear plots are obtained and from the intercept values the amount of dimer molecules for the monomolecular coverage ( $x_{d,m}$ ) are determined. The cross-sectional surface area (van der Waal radii concept) of the single AA dimer molecule ( $\sigma$ ) has been determined to be 150 Å<sup>2</sup> based on MMX calculations (Serena Software 1988). The total surface area covered by the monolayer dimers on AC was determined to be 992.0 m<sup>2</sup>/g. This value agrees well with the reported surface area value of AC. Hence the AA<sub>2</sub> adsorption on AC can be visualised as monolayer adsorption of cyclic dimers with one site per dimer molecule (figure 1). In table 2 values of the  $x_{d,m}$  and  $\sigma$  in the

Table 1. Adsorption data of acetic acid dimers in benzene, toluene and xylene solvents on activated charcoal at various temperatures.

Solvent	20 (°C)		30 (°C)		40 (°C)		50 (°C)	
	$C_e \times 10^2 (M)$	$(x_d/m) \times 10^2$	$C_e \times 10^2 (M)$	$(x_d/m) \times 10^2$	$C_e \times 10^2 (M)$	$(x_d/m) \times 10^2$	$C_e \times 10^2 (M)$	$(x_d/m) \times 10^2$
Benzene	9.35	6.85	8.92	6.36	10.52	4.84	11.03	4.85
	19.69	6.95	15.39	8.01	17.21	6.32	18.04	5.94
	25.10	7.96	22.09	9.48	22.47	6.53	25.56	6.57
	32.98	8.50	29.23	10.68	29.65	6.70	32.58	7.68
	42.34	7.72	34.13	13.50	29.17	7.74	41.10	7.37
Toluene	3.94	3.83	4.45	3.70	4.30	3.79	5.26	2.65
	10.34	5.44	10.70	5.95	10.52	5.71	11.48	4.43
	15.75	7.98	17.53	7.58	17.21	7.54	18.17	5.79
	22.64	9.14	23.77	9.79	22.47	10.49	25.34	6.72
	32.49	7.68	30.88	11.18	29.65	11.71	32.04	8.08
Xylene	35.44	12.37	37.51	13.02	29.17	19.03	37.30	10.72
	2.46	5.09	3.45	4.21	3.83	2.62	2.87	3.48
	7.88	7.52	8.86	6.64	9.08	3.94	9.08	3.93
	15.26	8.18	14.77	8.64	15.30	4.40	15.78	3.97
	23.63	7.96	20.67	10.63	21.99	4.46	20.08	6.17
32.98	6.85	28.06	11.27	28.21	4.90	29.64	3.61	
37.90	9.73	—	—	33.47	6.24	26.30	12.68	

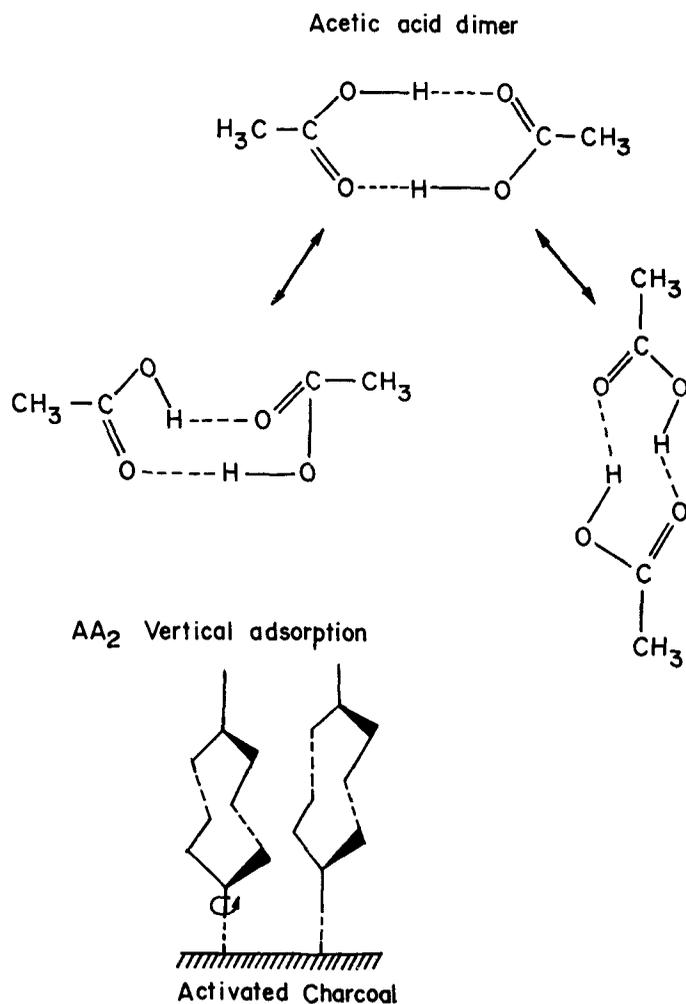


Figure 1. A schematic illustration of acetic acid dimer adsorption on activated charcoal.

Table 2. Values of the amount of acetic acid dimers coverage ( $x_{d,m}$ ) on AC and the molecular cross sectional surface area ( $\sigma$ ) in different solvents at 30°C.

Solvent	$x_{d,m}$ (g)	$\sigma$ (Å <sup>2</sup> )
Benzene	0.1253	130.00
Toluene	0.1504	108.31
Xylene	0.1368	119.08

three aromatic solvents are included. Among the mechanisms (2) and (4), unlike (2), agreeable results are obtained for (4). But in the horizontal stacking of AA<sub>2</sub> molecules which involves a multisite adsorption after the first stage of desorption the system can still be described as AC with AA<sub>2</sub> adsorbed vertically in the cyclic or non-cyclic

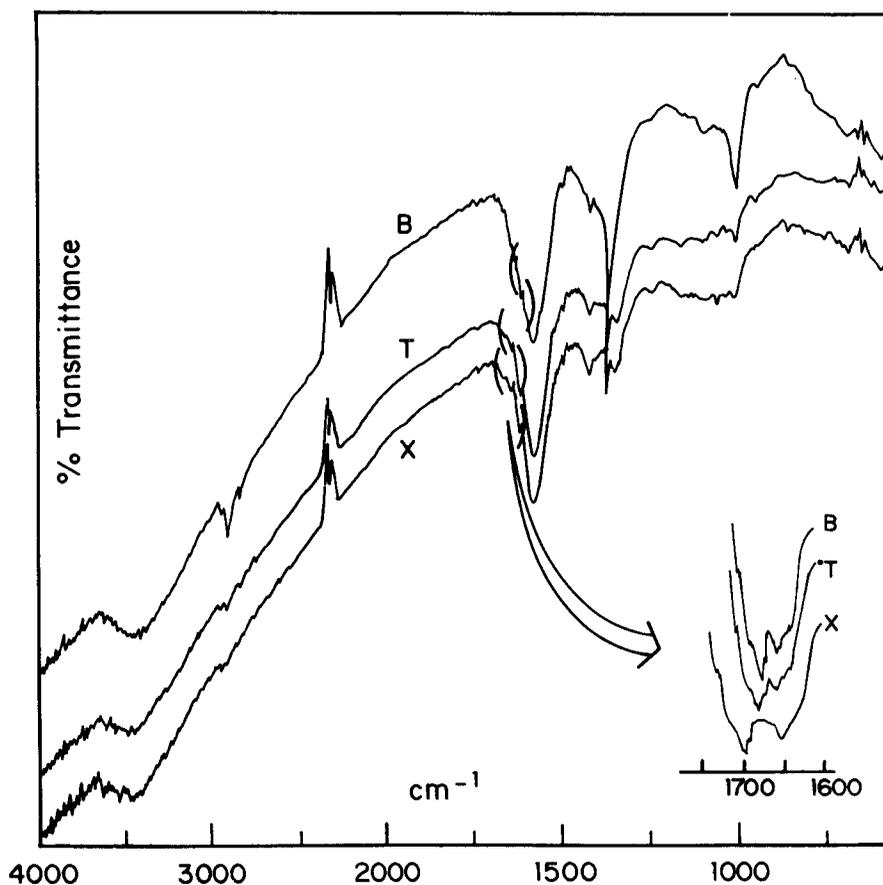


Figure 2. FTIR spectra of AA<sub>2</sub> adsorbed activated charcoal in KBr: (B) benzene, (T) toluene and (X) xylene.

form. The changes in the fine structure of adsorbed AA<sub>2</sub> molecules may be observed by FTIR spectra of the AC on which AA<sub>2</sub> is adsorbed (Dunken and Flink 1962; Kipling and Wright 1963; Silverstein 1981). The valence vibrations of carbonyl group exhibited peaks at 1758 cm<sup>-1</sup> if the form is monomer and at 1668 cm<sup>-1</sup> or at 1713 cm<sup>-1</sup> and 1727 cm<sup>-1</sup> in the case of cyclic dimer or open chain non-cyclic dimer respectively. Regarding the -OH group (figure 2) presence of peak around 3500 cm<sup>-1</sup> and absence of peaks around 3600-3800 cm<sup>-1</sup> indicate that there are no free-OH which when present would correspond to an open chain non-cyclic structure in dimer. However, analyses of BET isotherms show that type I BET curves are obtained (figure 3) signifying a Langmuir type adsorption process i.e. in presence of non-aqueous solvents the AA<sub>2</sub> adsorbs on AC in a monolayer manner and the adsorption process can be described by equilibrium (1). In a non-aqueous solvent environment, only a dissolved solute like acetic acid will exhibit pronounced interactions with activated charcoal due to the hydrophobic nature of carbon. The  $\sigma$  values of AA<sub>2</sub> in various solvents also seem to agree with the  $\sigma$  value of the vertically stacked AA<sub>2</sub> molecule. These aspects make the solid-solution interface appropriate for dimer adsorption

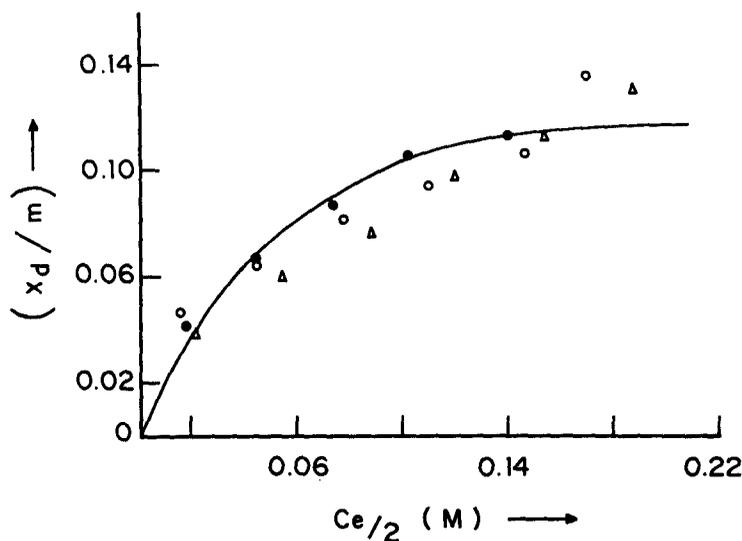


Figure 3. Langmuir plots of acetic acid dimers on activated charcoal from benzene (○), toluene (△) and xylene (●) solutions at 30°C.

leading to vertical stackings. It is noted that, the pore volume corrections range within 0.5% of the original solvent volume and within 0.1% in the concentration range. Hence, pore volume filling has negligible effect on the solute adsorptions. As the  $\sigma$  values of  $AA_2$  are larger than those of the pores, pore fillings by solute molecules are unlikely to occur. The free energy change of adsorption can be determined by the relation  $\Delta G_{\text{ads}}^0 = -RT \ln K_{\text{ads}}$  where the equilibrium constant  $K_{\text{ads}}$  is known from the  $C_o/2$  and  $C_e/2$  values. At different temperatures the changes in the adsorption process are reflected from the variations in the  $C_e/2$  values for similar  $C_o/2$  values. Hence  $\Delta G_{\text{ads}}^0$  values can be calculated from  $K_{\text{ads}}$  as a function of temperature. Applying the regression on the linear variation of  $\Delta G_{\text{ads}}^0$  with temperature the value of  $(\partial \Delta G_{\text{ads}}^0 / \partial T)$  is computed. Using the relation  $\Delta H_{\text{ads}}^0 = \Delta G_{\text{ads}}^0 - T(\partial \Delta G_{\text{ads}}^0 / \partial T)$  the enthalpy change of adsorption may be known. The free energy change and the enthalpy change values are given in table 3.

Studies on the effect of temperature on the net adsorption process have been carried out in the increase in temperature mode. Increase in temperature generally affects the equilibrium solute concentrations with negligible effect on the pore volume fillings. Hence the overall enthalpy change for adsorption will be low and decreases with increase in temperature. Considering the  $\Delta H_{\text{ads}}^0$  under normal conditions the values show that the exothermicity of the process is very low. The energy of physical adsorption which is due to the van der Waals' forces is typically around 5–10 kcal/mol which should not efficiently perturb the bonding structure of the adsorbate before and after adsorption (Adamson *et al* 1966; Pauling 1991). As the actual observed value lies around the lower range of van der Waals' interaction energy vertical adherence of  $AA_2$  on AC surface may be proposed. In case of horizontal stacking, multi-neighbouring sites are required for adsorption which would involve some orders of magnitude of physisorption energy. Hence equilibrium (1) may be taken as the mode of adsorption process.



## 5. Conclusion

Adsorption studies of AA<sub>2</sub> on AC from benzene, toluene and xylene solvents are carried out here. The system obeys Langmuir-type of adsorption with a monolayer of dimers that are stacked vertically. Such a mode of adsorption has been proposed to include the retention of cyclic structure against the open chain non-cyclic structure of the dimer. Free energy change and enthalpy change values of the adsorption equilibrium are evaluated.

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