

Kinetic and thermodynamic aspects of chloramine – T adsorption on different adsorbents at different temperatures

Jaya Ramachandran, S Vivekanandan & S Lakshmi*

Department of Chemistry, Sri Sarada College,
Salem 636 016, India.

Received: 3 May 2000; revised 5 September 2000

The rate constants for the attainment of adsorption equilibria at 298, 303, 308 and 315.5K have been determined for the adsorption of chloramine-T (CAT) on solid adsorbents such as activated carbon (AC), rice husk carbon (RHC), Salem bentonite (SB) silica gel (SG) and acidic alumina (AA). The energy of activation for chemisorption and Elovich parameters have been evaluated. The calculated pore and film diffusion coefficients have been used to ascertain the rate determining step in each case. The thermodynamic activation parameters for the adsorption of CAT on the different matrices have been evaluated. The calorimetric enthalpies have been experimentally determined. The isosteric, isochoric and Semenov Shilov enthalpies have been calculated. The probable causes for the difference in the different enthalpy values and the variation of free energy of adsorption with temperature have been discussed.

In continuation of our earlier work¹ on adsorption, the kinetics of adsorption of chloramine-T on different adsorbents is studied at different temperatures and kinetic, thermodynamic and Elovich parameters have been evaluated. The calorimetric enthalpy of adsorption is determined and the other enthalpies have been calculated.

Experimental

All chemicals used were of quality AR and Fluka grades. A thermostat of accuracy $\pm 0.01^\circ\text{C}$ with a contact thermometer was used to maintain the temperature during kinetic studies. To 500 ml of a dilute but accurately known concentration of a solution of CAT, thermostated at a definite temperature, 5 g of the adsorbent was added and simultaneously a stop watch was started. 5 ml aliquots or 1 ml aliquots were withdrawn at regular

time intervals through a special pipette (with a glass wool plug at the tip) and then concentration of CAT was determined by iodometry.

The calorimetric enthalpies of adsorption of CAT on different chosen matrices are determined by the standard procedure using the equation

$$\Delta H_{ad} = \Delta T \times V \times 4.186/a \text{ (J mol}^{-1} \text{ dm}^3\text{g)}$$

where ΔT = increase in temperature of the contents due to adsorption, V = volume of CAT solution, and a = specific adsorption of CAT on a given solid matrix in $\text{mol}^{-3}\text{dm}^{-1}\text{g}^{-1}$

From the slopes of the plots of $\log c$ versus $1/T$ the differential, isothermal and isosteric enthalpies have been evaluated. Enthalpy of adsorption at constant value of specific adsorption (x/m = amount adsorbed per unit mass) is isosteric enthalpy of adsorption. It is determined from isotherms using the Clausius Clapeyron equation. Hence, such heats are called isothermal enthalpies.

Semenov Shilov² enthalpies have been calculated using the equation $Ea = 11.5 - 0.25 \Delta H_{ad}$ for which the energy of activation (Ea) from kinetic studies have been used.

Using vant Hoff isochore, ΔH^0 or standard enthalpies of adsorption have been arrived at.

From the ($K'e$) equilibrium constants, ΔG° values ($\Delta G^\circ = -RT \ln K'e$) and from ΔG° values ΔH° and ΔS° values have been evaluated.

Results and discussion

Adsorption comes under the category of complex reactions, namely, the reactions approaching equilibrium. For a typical system viz CAT-AC the rate constant is shown to be independent of the initial concentration of the adsorbate. With three different initial concentrations ($[\text{CAT}]_i$) the rate constants obtained are the same. With all other systems studied,

Table 1 — Equilibrium constants for the adsorption of CAT on different adsorbents at different temperatures

Adsorbent	Equilibrium constant K at temperature			
	298	303	308	315.5K
AC	43.000	24.000	11.350	2.889
RHC	1.643	1.435	1.200	1.041
SB	2.31	0.352	0.242	0.120
SG	0.1598	0.0497	0.0331	0.0256
AA	0.0650	0.0600	0.0450	0.0400

Table 2 – Rate constants

System		Temperature K			
		298	303	308	315.5
CAT-AC	k	3.38×10^{-3}	1.69×10^{-3}	7.94×10^{-4}	3.55×10^{-4}
	k_a	3.30×10^{-3}	1.62×10^{-3}	7.30×10^{-4}	2.64×10^{-4}
	k_d	0.77×10^{-4}	6.77×10^{-5}	6.43×10^{-5}	9.00×10^{-5}
CAT-RHC	k	3.78×10^{-3}	2.10×10^{-3}	1.26×10^{-3}	4.94×10^{-4}
	k_a	2.35×10^{-3}	1.23×10^{-3}	6.87×10^{-4}	2.52×10^{-4}
	k_d	1.43×10^{-3}	0.86×10^{-3}	5.73×10^{-4}	2.42×10^{-4}
CAT-SB	k	3.50×10^{-3}	4.71×10^{-4}	3.98×10^{-4}	2.01×10^{-5}
	k_a	3.36×10^{-3}	1.23×10^{-3}	7.75×10^{-5}	2.10×10^{-6}
	k_d	1.45×10^{-4}	3.49×10^{-4}	3.20×10^{-4}	1.80×10^{-5}
CAT-SG	k	1.23×10^{-3}	2.15×10^{-5}	1.86×10^{-5}	1.33×10^{-5}
	k_a	1.69×10^{-4}	1.00×10^{-6}	0.50×10^{-6}	0.30×10^{-5}
	k_d	1.06×10^{-3}	2.05×10^{-5}	1.77×10^{-5}	1.30×10^{-5}
CAT-AA	k	3.77×10^{-5}	3.64×10^{-5}	1.72×10^{-5}	1.56×10^{-5}
	k_a	2.30×10^{-6}	2.00×10^{-6}	0.70×10^{-6}	0.50×10^{-6}
	k_d	3.54×10^{-5}	3.44×10^{-5}	1.65×10^{-5}	1.51×10^{-5}

k (s^{-1}) = rate constant; k_a ($\text{mol dm}^{-3} s^{-1}$) = adsorption rate constant k_d ($\text{mol dm}^{-3} s^{-1}$) = desorption rate constant

the rate of attainment of adsorption equilibrium³ follows first order kinetics.

Effect of temperature

From the knowledge of equilibrium constant (Table 1) and over all rate constant the adsorption and desorption rate constants have been calculated and presented in Table 2. The adsorption rate constants

decrease and desorption rate constant increase with increase in temperature, as adsorption is an exothermic process. For the same reason the log A (Arrhenius factor A) decreases and $t_{1/2}$ increases with increase in temperature.

The temperature dependent constants of different isotherms reflect the same. The temperature effect on adsorption can be well understood from the

Table 3 — Elovich parameters

System	Temperature K			
	298	303	308	315..5
CAT-AC				
α	1.2954	3.6848×10^2	4.6060×10^2	5.9896×10^2
a	1.5444×10^{-1}	5.427×10^{-4}	4.3420×10^{-4}	3.3390×10^{-4}
CAT-RHC				
α	1.7715	3.189	3.543	4.252
$10^{-4} \times a$	1.128	0.6270	0.5640	0.4900
CAT-SB				
α	8.053	8.858	1.611	9.596
a	2.480	2.250	1.241	2.080
CAT-SG				
α	2.559×10^3	18.42×10^3	22.12×10^3	27.65×10^3
$10^{-5} \times a$	7.810	1.080	0.9000	0.7200
CAT-AA				
α	2.764	3.685	4.146	4.606
$10^{-5} \times a$	7.230	5.420	4.820	4.340

α mol dm⁻³ g⁻¹
a mol dm⁻³ g⁻¹ S⁻¹

Table 4 — Activation parameters

System	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$ J mol ⁻¹ $\times 10^4$			
	Jmol ⁻¹ $\times 10^3$	JK ⁻¹ mol ⁻¹	at T (Kelvin)			
CAT-AC	- 108.08	- 620.72	298.0	303.0	308.0	315.5
			7.7	8.0	8.3	8.8
CAT- RHC	- 91.45	- 602.43	8.8	9.1	9.4	9.9
CAT-SB	- 207.85	- 755.41	1.7	2.1	2.5	3.0
CAT-SG	- 33.26	- 796.15	20.0	21	21.2	21.8
CAT-AA	- 49.88	- 734.63	16.9	17.3	17.6	18.2

variation of temperature dependent constant of various isotherms obtained for CAT on chosen matrices. Usually both 'k' and 'n' of FAI decrease with increase in temperature. The constant 'k' denotes specific adsorption when c_e tends to zero. The decrease in values of 'k' and 'n' with temperature may be attributed to the depleted adsorption as a result of increased thermal motion with increase in

temperature which opposes and disturbs the more ordering exothermic process of adsorption.

The constant 'n' in FAI is actually a correction factor for the mutual interaction among the adsorbed species. If the forces within the surface layers are attractive 'n' is greater than unity and if repulsive, n is less than unity. The experimental values of 'n' are generally less than unity except for CAT-SG system

Table 5 — Enthalpies of adsorption

Adsorbent	Calorimetric ΔH (kJ mol ⁻¹)	Semenov Shilov ΔH (kJ mol ⁻¹)	Isosteric ΔH (kJ mol ⁻¹)	Isochoric ΔH (kJ mol ⁻¹)
AC	- 209.30	- 483.70	- 478.70	- 119.70
RHC	- 144.70	- 428.90	- 114.90	- 191.50
SB	- 176.80	- 684.20	- 134.10	- 215.40
SG	- 51.60	- 811.70	- 68.40	- 59.84
AA	- 20.60	- 275.80	- 31.00	- 28.16

for which 'n' values are greater than unity while for CAT-AA system these 'n' values are unity.

This means that the forces between the adsorbed species are repulsive with all matrices (except SG and AA) while it is attractive with SG. The attractive interaction of CAT adsorbed on AA is marginal as the 'n' value is unity.

The values of temperature dependent constant ' μ ' of LAI increases with temperature for AA, increases with slight deviation for SB and AC and the μ values remain constant equal to unity with RHC. Hence it is quite probable that the temperature dependence varies with the nature of the adsorbent.

Energy of activation

The high values of energy of activation (CAT-AC:109.40, CAT-RHC:95.74, CAT-SB:159.60, CAT-SG:191.50 and CAT-AA:55.44 kJ mol⁻¹) show that adsorption of CAT is an activated process. Except CAT-SG where multilayer adsorption takes place and CAT-AA where pore diffusion is the rate determining step, for the rest the energy of activation is in the order for adsorbents SB>AC>RHC.

Equilibrium constants

The data in Table 1 show that the equilibrium constant for the adsorption of CAT on AC is the maximum and hence AC is the best adsorbent for CAT. As the temperature is raised the equilibrium constant decreases because of exothermic nature of adsorption. The order of equilibrium constants at lower and higher temperatures are different due to difference in the nature of the adsorbents.

The Langmuir contours for CAT-SG are found to be similar to the type III of Brunauers' system of classification of adsorption isotherms suggesting multilayer adsorption of CAT on SG. Hence the data in Tables 1-5 for CAT-SG are unique and different and cannot be compared with the rest with Langmuir monolayer adsorption.

Elovich constants

For a wide variety of activated adsorption the variation of velocity with the amount adsorbed obeys the Elovich⁴ equation. One of the different forms of this equation

$$q = (2.3/\alpha) \log(t+t_0) - (2.3/\alpha) \log t_0 + q_0$$

where

α = deceleration constant of the process,

t_0 = an arbitrary constant chosen for the linearisation of q versus $\log(t+t_0)$ plots

$$t_0 = 1/a\alpha$$

a = initial rate of uptake at $t = 0$

q_0 = amount adsorbed at $t=0$

The applicability of Elovich equation is well demonstrated by the Elovich plots and the evaluated Elovich parameters α and a (Table 3). The Elovich constant ' a ' is the initial rate of uptake of adsorbate, it is proportional to $e^{-E_a/RT}$. Hence ' a ' values for all the systems show roughly exponential dependence on temperature.

The Elovich α shows temperature dependence which can be attributed to different sets of sites on the surface of adsorbent as proposed by Tayler and Thon⁵.

The rate determining step

According to Michelsen⁶ for the film diffusion to be rate determining process the value of film diffusion coefficient D_f

$$\left(D_f = \frac{0.23 r_0 \delta}{t_{1/2}} \frac{c'}{c} \right)$$

(where r_0 = average radius of the sorbent assuming spherical geometry for the particle adsorbed $t_{1/2}$ = half life period in seconds; c'/c equilibrium loading of the sorbent ($c_0 - c/c_0$); c_0 = initial concentration of adsorbate; c = equilibrium concentration of the adsorbate; δ film thickness in cm.) should be between 10^{-6} to $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ($D_p = 0.03 r_0^2 / t_{1/2}$) while for CAT-AA pore diffusion ($D_p = 10^{-11}$) is the rate determining step, for other systems film diffusion is the ($D_f = 10^{-9}$) rate determining step.

Thermodynamic activation parameters

The thermodynamic parameters are given in Tabl 4. From Eyring plots the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ obtained are negative and $\Delta G^\ddagger$ positive for the activated chemisorption process represented by a simple scheme



where A = adsorbate S = substrate or adsorbent $AS^\ddagger$ adsorbent adsorbate activated complex AS adsorbed state.

The increase in the value of $\Delta G^\ddagger$ with increase in temperature is in agreement with the decreased rates of attainment of adsorption equilibrium with increase in temperature.

The slightly higher values of $\Delta G^\ddagger$ for CAT-RHC prove that among the carbons AC is a better adsorbent than RHC. Salem bentonite (SB) is better adsorbent compared to the carbons. Since multilayer adsorption of CAT takes place on SG and the rate determining step is different for CAT adsorption on

AA these systems cannot be directly compared with the rest.

Enthalpies of adsorption

The magnitude of the heat of adsorption is the most significant single property of adsorption and the determination of reliable heats is therefore of considerable importance.

The results are presented in Table 5. There is no correlation among the different enthalpies and no correlation may be expected as Semenov Shilov enthalpy is based on energy of activation which in turn depends on surface coverage, theta while calorimetric enthalpy is the integral heat of adsorption, isosteric enthalpy is the differential heat of adsorption and the isochoric enthalpies are the standard enthalpies of adsorption.

Since CAT adsorption on SG is shown to be multilayer adsorption the observed enthalpy values are higher compared to true values.

The integral heat of adsorption can be taken as a measure for adsorbing capacity and hence AC is a good adsorbent for CAT while AA is a poor adsorbent.

Acknowledgement

The authors gratefully acknowledge the UGC, New Delhi for the assistance given under FIP.

References

- 1 Vivekanandon S, Jaya S & Lakshmi S, *Indian J Chem*, 38A (1999) 708.
- 2 Semenov N & Shilov A E, *Kinet. Katal.* 6 (1965) 3.
- 3 Bhattacharya A K & Venkobachar C, *J environ. Engrg Div. AS CE*. 110 (1984) 110.
- 4 Bhattacharya S K & Samantray B K, *J Indian chem Soc*, LI (1974) 73.
- 5 Taylor H A & Thon N, *J Am. chem. Soc*, 74 (1952) 4169.
- 6 Michelson L D, Gideon P G, Pace E G & Kutal L H USDI, *Office of Water Research and Technology Bull*, 74 (1975).