CHAPTER - 4

INFLUENCE OF TEMPERATURE

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INFLUENCE OF TEMPERATURE ON THE ADSORPTION OF DYES ONTO OXIDES AND GRAPHITE SURFACES.

4.1 Introduction

Temperature is one of the most important factor which determines the extent of adsorption of a given system. Its influence in deciding the actual alteration is both positive and negative, and depends on the nature of interaction involved. A lowering of temperature is favourable for large adsorption in the case where physical adsorption is predominant; on the otherhand in chemisorption or in activated adsorption, an elevated temperature is preferred. However, the variation is not always predictable except in simple cases, because many times very complicated results are obtained especially when one type of adsorption is followed by or is attended simultaneously by another type of adsorption. In general, the level of adsorption at any particular concentration usually decreases with an increase in temperature, i.e., the over all process is exothermic [1,2]. General examples where a decrease in adsorption has been observed with an increase in temperature include the adsorption of common gases and also of several solutes from solution onto ordinary adsorbents. A decrease in adsorption with temperature was reported by Everett [3] in the study of adsorption of stearic acid in benzene and that of dodecanol in n-haptane onto Graphon. Everett and Findenegg [4] have used graphitized carbon black for the adsorption of n-docosane and decanol in n-haptane and a decrease in adsorption has been reported with an increase in temperature.

A number of dyes also showed diminished adsorption onto various adsorbents as the temperature is raised. Examples include the adsorption of chrome dye onto coal [5] as well as on a mixture of fly ash and coal [6], and adsorption of basic dyes (e.g. methylene blue, crystal violet, malachite green and rhodamine B) onto silica and graphite [7]. A decrease in adsorption with temperature has also been reported in the study of adsorption of safranine T on alumina as well as in the adsorption of crystal violet and orange II on zinc oxide and TiO_2 [8,9]. However in various other cases an enhanced adsorption has been seen with temperature. Mills and Hockey [10,11] have reported an increase in adsorption with temperature of lauric acid and methyl esters of n-fatty acids (C_{10} and C_{14}) from benzene solution onto silica. Such results have also been found in the adsorption of basic dyes onto hardwood [12] and that of active dye onto activated carbon from wastewater [13]. Results indicating no appreciable alteration in the amount adsorbed due to variations in temperature are also known [14,15] i.e., the adsorption of methylene blue onto alumina shows almost constant value over the temperature range of 20° to 60°C. In addition, results showing different behaviour of adsoption of same adsorbent towards different dyes have also been reported. Thus kaolinite which shows enhanced adsorption of crystal violet and malachite green at higher temperatures exhibits relatively no significant variation with the adsorption of methylene blue [16].

Temperature also plays an important role on the rate of the adsorption. Generally rate is found to increase with temperature [17-19]. For processes involving chemisorption, Taylor [20] described that the increase in rate proceeds exponentially. The results [21-23] of the study of adsorption of hydrogen onto nickel powder, oxygen and carbon monoxide onto platinum foil, hydrogen onto magnesium oxide and a number of other gases onto surface of various powdered materials are in agreement with Taylor's finding. An increase in the rate of adsorption has also been reported in the adsorption of the substrate from the liquid phase. Thus with the adsorption of Basic Yellow onto activated carbon [24], methylene blue, crystal violet and malachite green onto iron oxide showed an enhanced adsorption rate with temperature [25].

Study of influence of temperature on the rate of adsorption of dyes has been mostly restricted to the textile fabrics used as the adsorbents. It was of interest therefore, to make such measurement using oxides and graphite as adsorbents. This study is helpful in the determination of the alteration in the extent of adsorption as well as computing the corresponding energy of activation involved in the process [26-28]. The value of energy of activation is a measure of rate of the process which is very important from the standpoint of kinetic study.

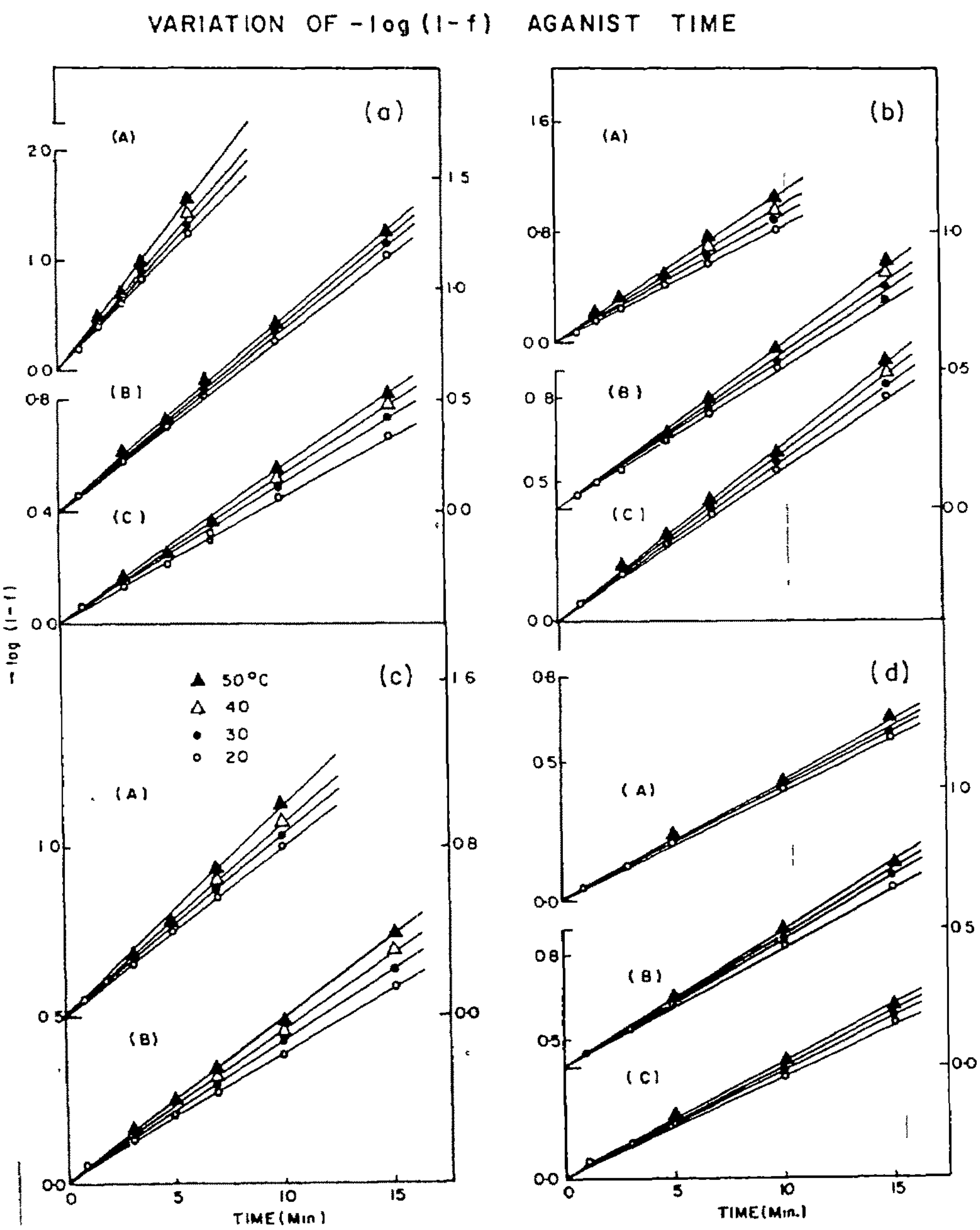


Fig.4 5a Adsorption of (A) Acid Green 25 (B) Ketone Blue A and (C) Acid Black 1 on neutral alumina with temperature.

Fig 4.5b Adsorption of (A) Basic Brown 4, (B) Basic Green 1 and (C) Basic Violet 1 on silica gel with temperature.

Fig 4.5c Adsorption of (A) Basic Brown 4 and (B) Basic Violet 2 on basic alumina with temperature

Fig 4 5d Adsorption of (A)Basic Green 1, and (B) Ketone Blue A and (C) Basic Blue 3 on graphite with temperature

4.2 Experimental

The procedure employed in the present study was the same in principle, as adopted during the time rate study of adsorption and is described in detail in Chapter 3. A known amount of the adsorbent was kept in contact with a fixed volume of the dye solution. The system (consist of adsorbate and adsorbent) was maintained at constant temperature and was shaken continuously till the equilibrium was attained. The sample solutions withdrawn at various time intervals were used (in the same way as described earlier) for measuring the corresponding concentrations remaining in the solution. The values thus obtained were employed for computing the actual amount of dye adsorbed on the surface at that time. The experiments were repeated at various other temperatures in the range of 20^{o} to 50^{o}C. The results for the total amount of dye adsorbed at equilibrium at various temperatures are given in Table 4.1; for the sake of brevity the corresponding values for intermediate time intervals are not given. The time variation of adsorption of dyes for some systems are shown graphically in Figures 4.1 to 4.4. In these the time variation by the use of a given adsorbent is shown by the separate curves for each of the dyes and the temperatures employed. The corresponding plots of - log (1-f) Vs time are given Figures 4.5a to 4.5d.

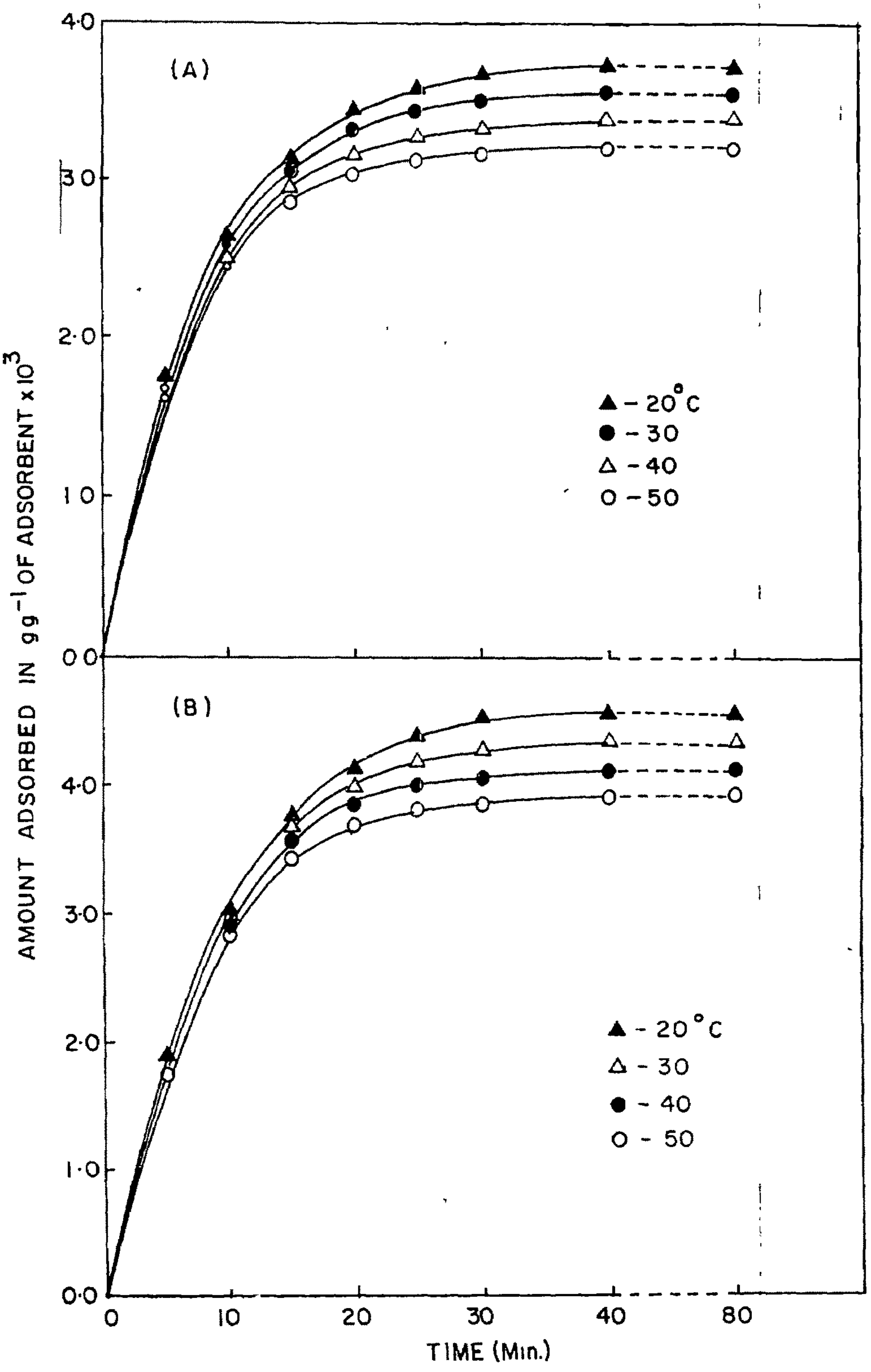


Fig 4 1 Time variation of adsorption of (A) Basic violet 1 and (B) Basic Green 1 onto silica gel with temperature

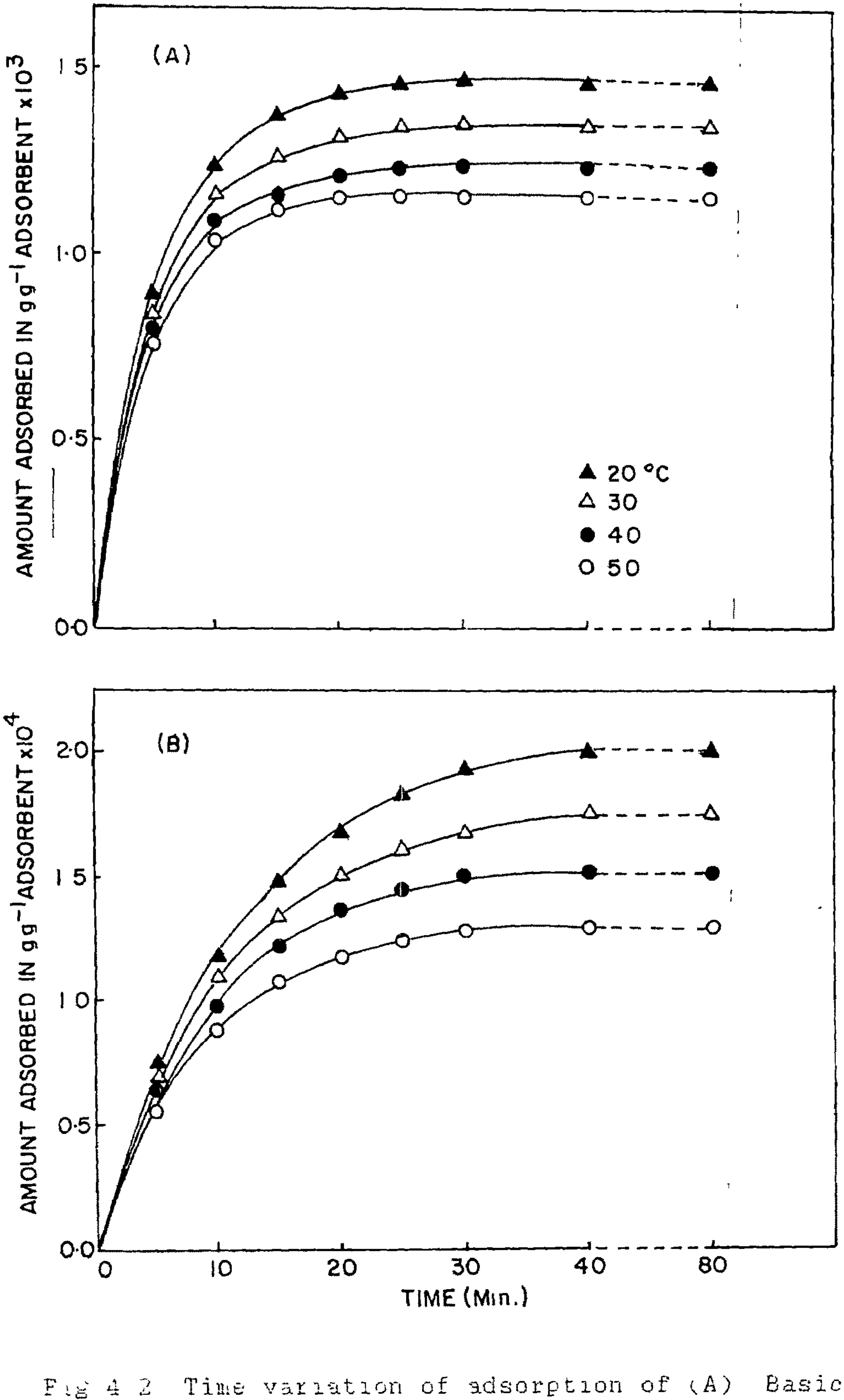


Fig 4 2 Time variation of adsorption of (A) Basic Brown 4 and (B) Basic Violet 2 onto basic alumina with temperatue

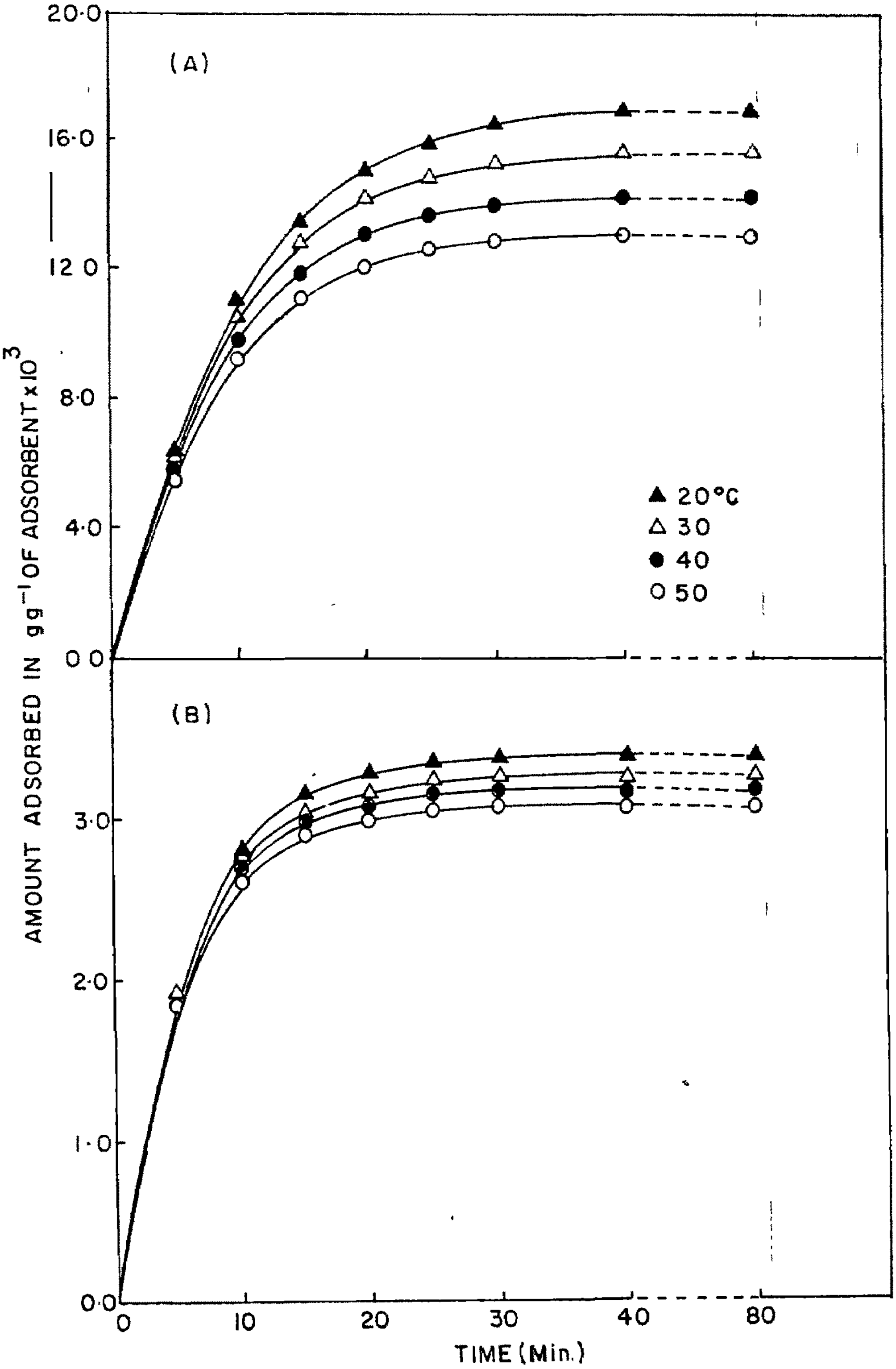


Fig 4.3 Time variation of adsorption of (A) Acid Black 1 and (B) Ketone Blue A on neutral alumina with temperature.

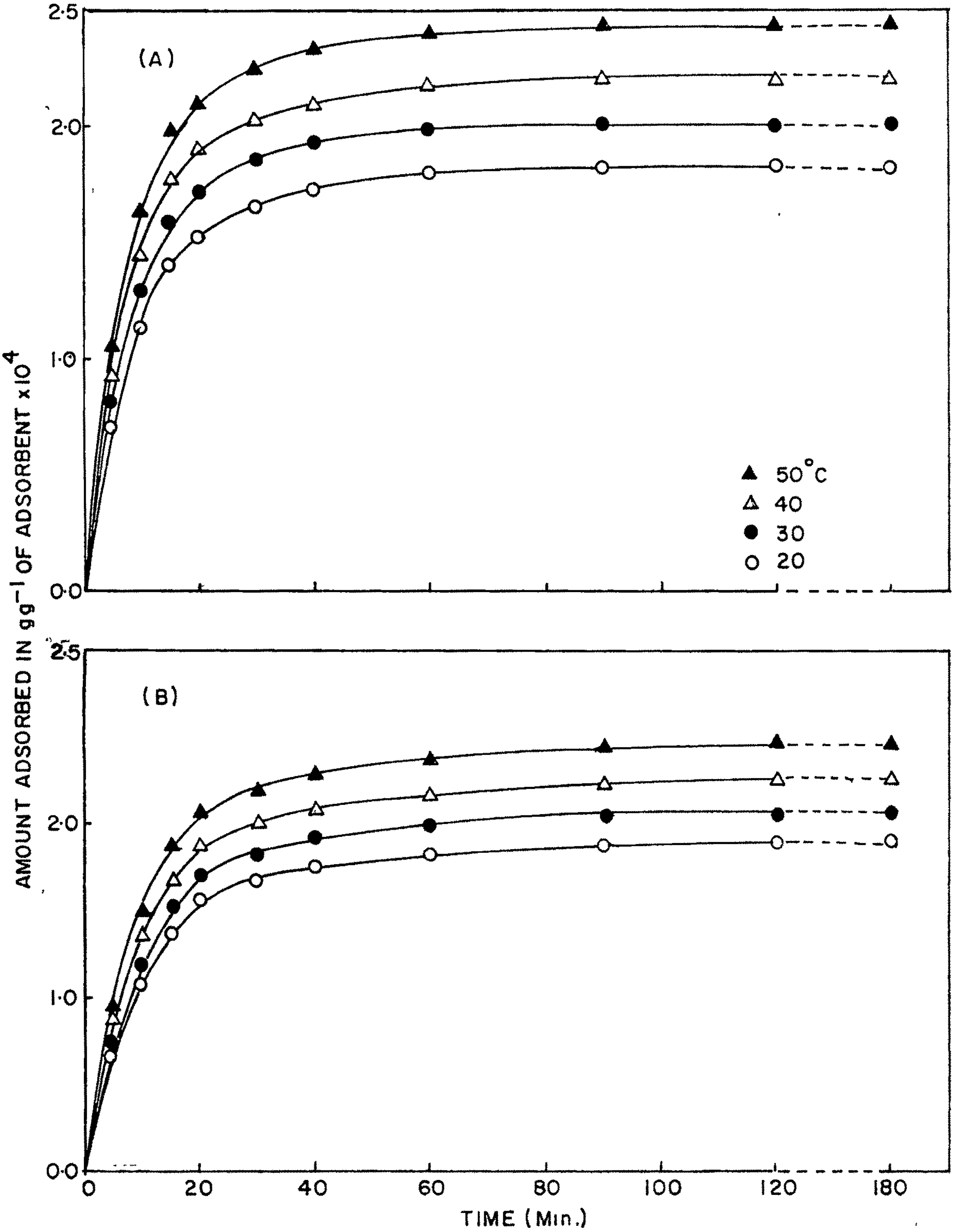


Fig.4.4 Time variation of adsorption of (A) Ketone Blue A and (B) Basic Blue 3 onto graphite with temperature.

VARIATION OF -log (1-f) AGANIST TIME

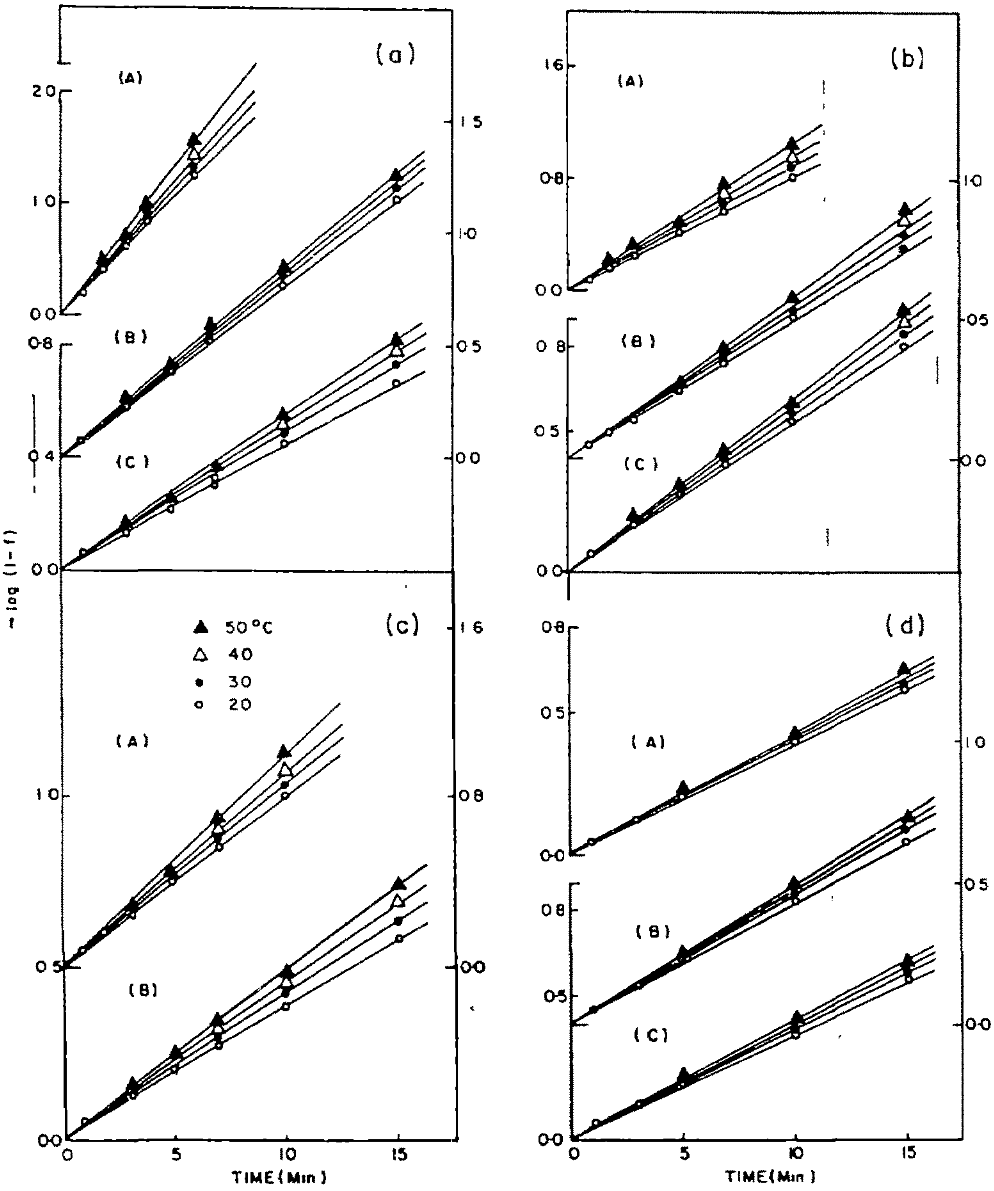


Fig 4.5a Adsorption of (A) Acid Green 25 (B) Ketone Blue A and (C) Acid Black 1 on neutral alumina with temperature

Fig 4.5b Adsorption of (A) Basic Brown 4, (B) Basic Green 1 and (C) Basic Violet 1 on silica gel with temperature.

Fig 4 5c Adsorption of (A) Basic Brown 4 and (B) Basic Violet 2 on basic alumina with temperature.

Fig.4 5d Adsorption of (A)Basic Green 1, and (B) Ketone Blue A and (C) Basic Blue 3 on graphite with temperature

The specific reaction rates obtained from the slopes of these plots are given Table 4.1. The values for the energy of activation calculated from the slopes of the Arrhenius plots (i.e., logk Vs 1/T) are also shown in Figures 4.6a to 4.6d for some systems; others because of being essentially similar in nature, are not given.

4.3 Results and discussion

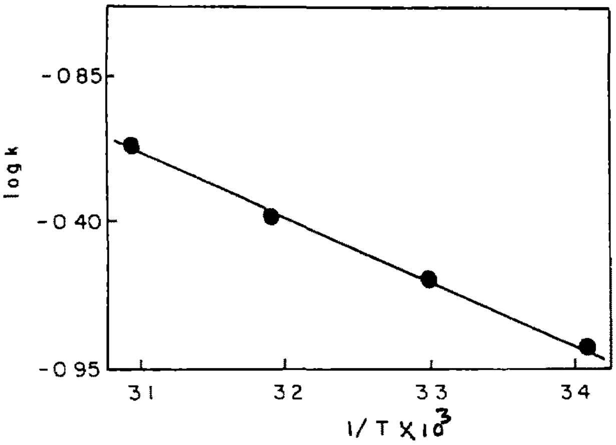
From the curves 4.1 to 4.4 it is seen that the nature of the variation of dye adsorption does not change with change in temperature. This uniformity is found in case of all the systems over the temperature range studied. The actual amount of dye adsorbed due to a change in temperature is however, observed to be affected both at the intermediate stages of adsorption as well as at the equilibrium. In the case of oxides, the adsorption was found to decrease with an increase in temperature. Thus the amount of Basic Brown 4 adsorbed (from 5.0×10^{-5} M solution) onto the surface of silica are 5.47×10^{-3} gg^{-1} and 4.33×10^{-3} gg^{-1} respectively at 20° and 50°C. Using the same adsorbent and a different dye (Basic Violet 1) of different concentration (1.0×10^{-5} M) the corresponding amounts are 3.72×10^{-3} gg^{-1} and 3.21×10^{-3} gg^{-1} respectively. Results with alumina used as adsorbent also show a decrease in adsorption of various dyes with an increase in temperature. The results are given in Table 4.1. From these results it is evident that with the dyes employed in the present work, a diminution in adsorption is observed with rise

Table 4.1 ADSORPTION OF DYES ONTO OXIDES AND GRAPHITE SURFACES AT DIFFERENT TEMPERATURES.

1 System	2 Temperature (°C)	3 Initial concentration (M) × 10^5	4 Quantity of dye solution (ml)	5 Amount of adsorbent (gm)	6 Amount adsorbed in gg^{-1} adsorbent at equilibrium.
Silica-Basic Blue3	20	2.0	300	0.5	4.12×10^{-3}
	30				3.99
	40				3.82
	50				3.68
Silica-Basic Violet1	20	1.0	300	0.3	3.72×10^{-3}
	30				3.56
	40				3.38
	50				3.21
Silica-Basic Brown4	20	5.0	300	1.0	5.47×10^{-3}
	30				5.08
	40				4.67
	50				4.33
Silica-Basic Green1	20	1.0	300	0.3	4.53×10^{-3}
	30				4.33
	40				4.12
	50				3.91
Basic alumina-Basic Brown4	20	5.0	300	2.0	1.46×10^{-3}
	30				1.35
	40				1.24
	50				1.15
Basic alumina Basic violet2	20	1.0	200	2.0	1.99×10^{-4}
	30				1.76
	40				1.53
	50				1.31

Table 4.1 Continuation

1	2	3	4	5	6
Graphite-Acid Green25	20	0.5	200	2.0	1.59×10^{-4}
	30				1.67
	40				1.76
	50				1.85
Graphite-Ketone BlueA	20	1.0	200	2.0	1.81×10^{-4}
	30				2.01
	40				2.20
	50				2.42
Graphite-Basic Blue3	20	1.0	200	2.0	1.90×10^{-4}
	30				2.07
	40				2.26
	50				2.46
Graphite-Basic Green1	20	1.0	200	2.0	3.02×10^{-4}
	30				3.21
	40				3.43
	50				3.66
Neutral alumina Acid Green25	20	1.0	200	1.0	0.89×10^{-3}
	30				0.83
	40				0.76
	50				0.70
Neutral alumina Acid Black1	20	3.0	300	0.3	16.89×10^{-3}
	30				15.60
	40				14.23
	50				13.02
Neutral alumina Ketone BlueA	20	2.0	200	2.0	3.36×10^{-3}
	30				3.24
	40				3.15
	50				3.06



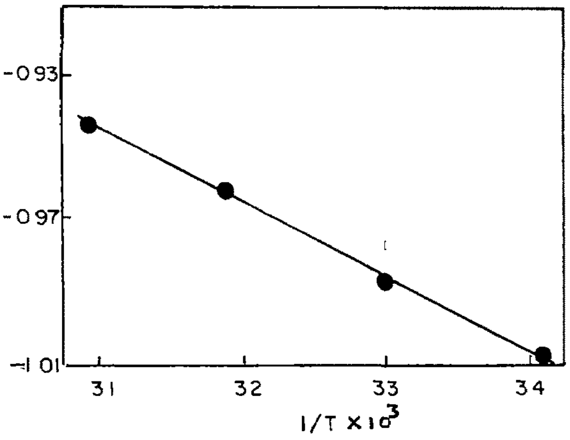
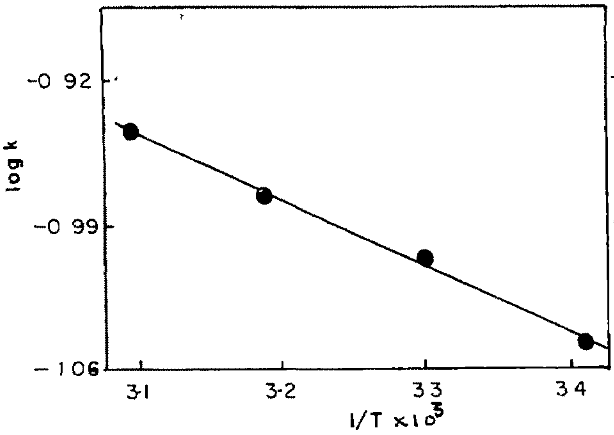


Fig.4.6a Variation of log k with 1/T for the adsorption of Basic Green 1 on silica gel

Fig 4.6b Variation of log k with 1/T for the adsorption of Ketone Blue A on graphite.



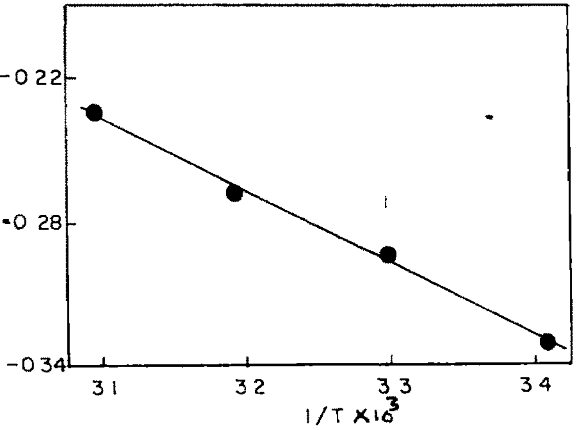


Fig 4 6c Variation of log k with 1/T for the adsorption of Basic Violet 2 on basic alumina

Fig 4.6d Variation of log k with 1/T for the adsorption of Acid Green 25 on neutral alumina in temperature. These results are in agreement with the findings of Gupta et al.[5,6] and various other workers [7,29,30]. On the otherhand an enhanced uptake is observed in the adsorption of both types of dyes (i.e. cationic and anionic) onto graphite surface with an increase in temperature. Thus the amount adsorbed of Ketone Blue A (from 1.0×10^{-5} M solution) onto graphite are 1.8×10^{-4} and 2.42×10^{-4} gg^{-1} at 20^{o} and 50^{o}C respectively; the corresponding values obtained with Basic Green 1 are 3.02×10^{-4} and 3.66×10^{-4} gg^{-1} respectively. An increase in adsorption has been reported by Ram and Prasad [7] in the adsorption of basic dyes onto graphite and by McKay et al. [31] in the adsorption of basic dyes onto activated carbon.

The extent of adsorption depends on the nature of both the adsorbent and adsorbate respectively irrespective of the temperature of the system. Thus the dye adsorption on oxide surface is favoured at lower temperatures whereas the reverse is true with the graphite surface though the rate of adsorption is found to increase with both types of the adsorbents. Thus the specific reaction rate, k for adsorption of Basic Green 1 onto silica increased from 0.114 to 0.134 $min.^{-1}$ when the temperature is raised from 20^{o} to 50^{o}C while with Basic Violet 1 it varies from 0.124 to 0.144 $min.^{-1}$. Similar trends have also been observed in the case of other dye-adsorbent systems. Thus the increase in k for the adsortion of Ketone Blue A onto graphite is from

0.098 to 0.114 $min.^{-1}$ with an increase in temperature from 20^{o} to $50^{o}C$. Similar results have also been described by Perineau et al.[32] with the adsorption of acidic dyes onto carbon particles. Enhancement in the rate has also been observed by other workers using ionic species. Thus Griffin and Jurinak reported a large increase in the rate of adsorption of phosphate ions on calcite with rise in temperature [18].

Temperature has also its impact on the time required to attain equilibrium. It is seen that the equilibrium is attained earlier in case where higher temperature is employed. The time difference is small and in extreme cases its precise determination becomes difficult because the temperature range selected for the study with the solution is limited. In those cases of the present systems where changes in the amount and the rate of adsorption are appreciable, this time difference is seen to be within a range of 5 minutes.

The values of energy of activation calculated from the Arrhenius plots are found to be low for all the systems and is dependent on the nature of the adsorbent-adsorbate pair. The highest value is seen with silica-Basic Brown 4 system, where it is 6.21 kJ $mole^{-1}$ and lowest with neutral alumina-Ketone Blue A system with a value of 2.26 kJ $mole^{-1}$. Other systems show values intermediate between the above two limits (Table 4.2). The such small energy requirements are indicative of fast processes. The quick attainment of

Table 4.2 SPECIFIC REACTION RATE AND THE ENERGY OF ACTIVATION FOR THE ADSORPTION OF DYES ONTO OXIDES AND GRAPHITE AT DIFFERENT TEMPERATURES.

1	2	3	4	5
System with particulars	Initial dye concentration (M)x10^5	Temperature (°C)	Specific reaction rate k (min^{-1}.)	Energy of activation Ea (kJ.mole^{-1})
Silica-Basic Blue 3 (0.5g, 300ml)	2.0	20	0.129	2.85
		30	0.135	
		40	0.140	
		50	0.145	
Silica-Basic Violet 1 (0.3g, 300 ml)	1.0	20	0.124	3.95
		30	0.131	
		40	0.137	
		50	0.144	
Silica-Basic Brown 4 (1.0g, 300ml)	5.0	20	0.187	6.21
		30	0.205	
		40	0.219	
		50	0.238	
Silica-Basic Green 1 (0.3g, 300ml)	1.0	20	0.114	4.17
		30	0.120	
		40	0.126	
		50	0.134	
Basic alumina Basic Brown (2.0g, 300ml)	5.0	20	0.184	5.53
		30	0.196	
		40	0.211	
		50	0.227	
Basic alumina Basic violet 2 (2.0g, 300ml)	1.0	20	0.089	6.18
		30	0.098	
		40	0.106	
		50	0.113	
Graphite-Acid Green 25 (2.0g, 200ml)	0.5	20	0.062	3.88
		30	0.065	
		40	0.068	
		50	0.072	

Table 4.2 Continuation

1	2	3	4	5
Graphite-ketone Blue A (2.0g, 200ml)	1.0	20 30 40 50	0.098 0.103 0.109 0.114	4.04
Graphite-Basic Blue 3 (2.0g, 200ml)	1.0	20 30 40 50	0.083 0.087 0.092 0.096	3.88
Graphite-Basic Green 1 (2.0g, 200ml)	1.0	20 30 40 50	0.089 0.093 0.096 0.100	3.00
Neutral alumina- Acid Green 25 (1.0g, 300ml)	1.0	20 30 40 50	0.467 0.507 0.537 0.583	5.72
Neutral alumina- Acid Black 1 (1.0g, 300ml)	3.0	20 30 40 50	0.104 0.112 0.119 0.126	5.02
Neutral alumina- ketone Blue A (1.0g, 200ml)	2.0	20 30 40 50	0.177 0.183 0.188 0.193	2.26

equilibrium, found in the present study is in harmony with this. The low value of the energy of activation for the dye adsorption on activated carbon has also been reported by McKay [33]. Its value also provides necessary information regarding the nature of the process; the low value indicates that the process involved in the dye adsorption is similar to that of a simple physical adsorption rather than a chemisorption. However, it is necessary to consider that the adsorbate is of ionic type and the adsorbents (in the present experimental environment) also carry surface charges. The interaction under such conditions should be fast even if it is quasi chemical in nature. Such type of the surface product is quite stable and difficult for easy reversal. Studies for the removal of dyes from surface indicate that the adsorption product is sufficiently resistant towards detachment quite distinct from that of the easy reversibility as usually seen in physically adsorbed species.

The values of entropy of activation ($\Delta S^{\ddagger}$) for the present adsorption processes are calculated using the following equation [34],

$$k_r = e \, \frac{kT}{h} \, e^{\frac{\Delta S^{\ddagger}}{R}} \, e^{\frac{-E_{exp}}{RT}}$$

(where k_r is the specific reaction rate, k is the Boltzmann constant, h is the Planck's constant and E_{exp} is the experimental energy of activation) and are found uniformly to be negative and low (Table 4.3). The negative values

Table 4.3 ENTROPY OF ACTIVATION FOR THE ADSORPTION OF DYES ONTO OXIDES AND GRAPHITE.

Temperature : 30 ± 0.1 °C

System	Entropy of activation $-\Delta S^{\ddagger}$ (joule degree$_{-1}$ mole$_{-1}$)
Silica - Basic Blue 3	260.37
Silica - Basic Violet 1	257.23
Silica - Basic Brown 4	246.06
Silica - Basic Green 1	258.78
Basic alumina-Basic Brown 4	248.70
Basic alumina-Basic Violet 2	252.30
Graphite-Acid Green 25	259.49
Graphite-Ketone Blue A	258.95
Graphite-Basic Blue 3	260.87
Graphite-Basic Green 1	263.21
Neutral alumina-Acid Green 25	240.16
Neutral alumina-Acid Black 1	255.01
Neutral alumina-Ketone Blue A	260.04

[18,35] have also been seen with the adsorption of phosphate ions onto calcite, isocil and bromocil onto silica gel and illite clay; the values in the former is usually less than that in the latter. Since $\Delta S^{\ddagger}$ is the entropy change in going from the reactants to the activated complex, and since little can easily be said about the properties of activated complex, the transition-state theory tends to avoid any definite quantitative prediction. Inspite of all ill-defined nature of the transition state, a number of conclusions can be made concerning $\Delta S^{\ddagger}$.

For reactions that occur in solution, a similar but negative $\Delta S^{\ddagger}$ might be expected because the translations and rotations that are lost, and are replaced by vibrations are less free [36]. In addition, the solvent molecules are oriented upto some extent towards the solute which imposes a restriction on the motion of some of the solvent molecules. This solvation is an appreciable factor in determining the entropy of the system. Changes in this solvation entropy must therefore be considered in the formation of the activated complex. From the consideration of the activated complex [37], it may be concluded further, that the final adsorption product is obtained without much change from the activated complex. This is associated with a loss of freedom [36] and decrease in volume than that of the reactants. This therefore implies that the adsorption product should be stable. On the basis of above results i.e., the low value of energy of activation as well as negative value of entropy of activation for adsorption, it is evident that the dye adsorption is rapid and involves simple interaction.

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