Thermodynamics of Adsorption of Rhodamine B and Nile Blue Sulphate on Alumina from Aqueous Solutions

M. SALEEM*, M. AFZAL, F. MAHMOOD, A. HAMEED
Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

(Received June 7, 1993)

Summary: Adsorption of the cationic dyes: Rhodamine B and Nile Blue Sulphate, from their aqueous solutions, on alumina was investigated. The adsorption of the dyes was found to decrease with the increase in temperature of the solutions. The adsorption isotherms obtained at different temperatures were found to obey the Langmuir isotherm equation. Free energy, entropy and enthalpy of the adsorption were calculated from the isotherms and the values, obtained for these thermodynamic parameters, were interpreted. The thermodynamic data indicate that the adsorption of these dye molecules on alumina is more favourable at high temperature.

Introduction

Metal hydroxides and hydrated oxides have been widely used as adsorbents and ion exchangers for the separation and preconcentration of trace amount of ions present in solutions [1-3]. Oxides of aluminum are extensively employed to remove the toxic and health hazardous particles and ions from gases and solutions [2,4,5]. Alumina is extensively used as an adsorbent in many processes of industrial or environmental importance because of its large surface area and good adsorption capacity.

In recent years the requirements of monitoring different pollutants in water system have increased due to uncontrolled release of heavy metals and colorants (dyes) into the surface and under ground water resources. The present communication describes the study carried out for the removal of dyes: Rhodamine B and Nile Blue Sulphate from their aqueous solutions by adsorption on alumina. Adsorption isotherms were obtained at different temperatures and used for the calculation of values of such thermodynamic parameters as free energy, entropy and enthalpy. The calculated values have been interpreted and discussed.

Results and Discussion

Adsorption of Rhodamine B and Nile Blue Sulphate was studied as a function of amount of adsorbent. The results of the dependence of dye adsorption on the amount of alumina are shown in Fig. 1. The concentration of 25 ml of solution and shaking time were fixed at 5×10^{-5}M and 30 minutes respectively, while the amount of alumina was

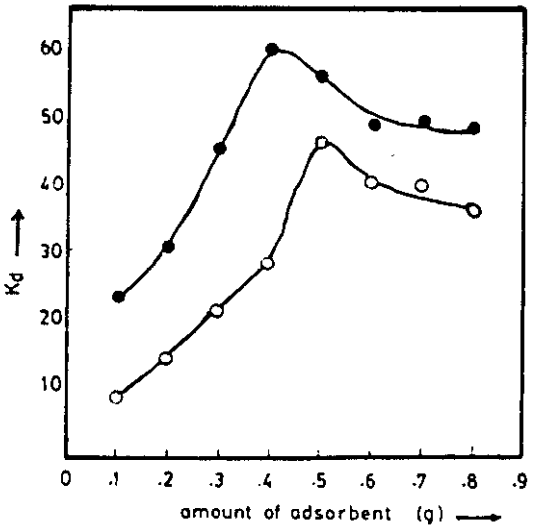

Fig. 1: Plots of the amount of alumina necessary for Rhodamine B (O); Nile Blue Sulphate (●)

increased from 0.1 g to 0.8 g. The adsorption of dye increases with increasing amount of the adsorbent upto 0.5 and 0.4 for Rhodamine B and Nile Blue Sulphate respectively. Therefore these amounts of alumina were used for studying adsorption of the respective dyes at different temperatures.

Adsorption of Rhodamine B and Nile Blue Sulphate was also studied as a function of shaking time 25 ml of 5×10^{-5}M aqueous solution of each dye was shaken with 0.5 grams of alumina for different intervals of time ranging from 5 to 60 minutes. Figure 2 shows the variation of amount adsorbed with

*To whom all correspondance should be addressed.

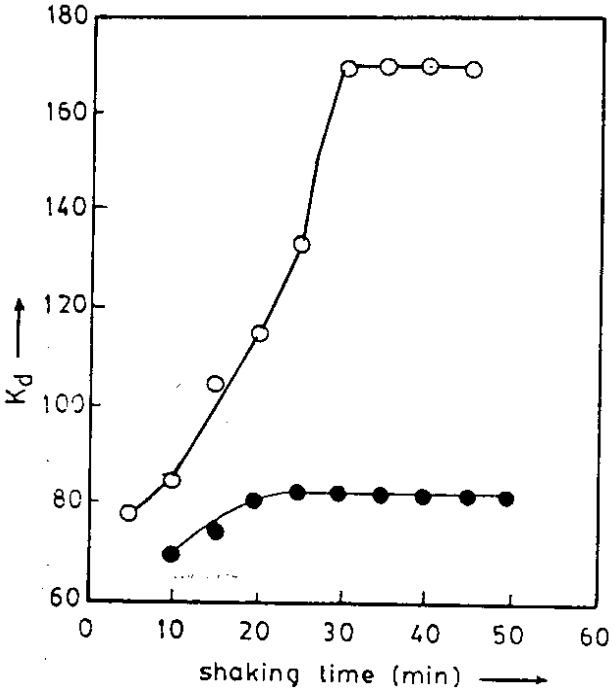

Fig. 2: Plots of shaking time versus K_d values Rhodamine B (●); Nile Blue Sulphate (O)

shaking time, indicating that the adsorption increases with time and then attains a constant value when adsorption equilibrium is established. Therefore, time required for equilibrium was selected for all further adsorption studies.

The adsorption isotherms for Rhodamine B and Nile Blue Sulphate obtained at different temperatures (Figs. 3 and 4) are L_3 and S_1-type respectively according to Giles classification [6]. In L-type isotherms, the initial sharp rise in adsorption shows that it becomes increasingly difficult for a bombarding solute molecules to find a vacant site available as more and more sites in the adsorbent are filled. In S-type isotherm, the adsorption becomes easier as concentration of adsorbate increases. This implies a side by side association between molecules helping to hold them to the surface. This is called co-operative adsorption.

The effect of temperature shows that the adsorption of Rhodamine B and Nile Blue Sulphate decreases with the increase in temperature. The decrease in adsorption with temperature may be due to a positive temperature coefficient of real adsorption of solvent [7].

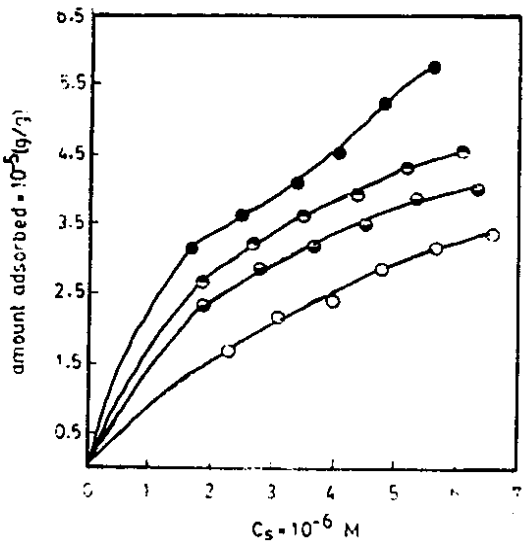

Fig. 3: Adsorption isotherms for Rhodamine B at 323 K (O); 313 K (◒); 303 K (◓); 293 K (●).

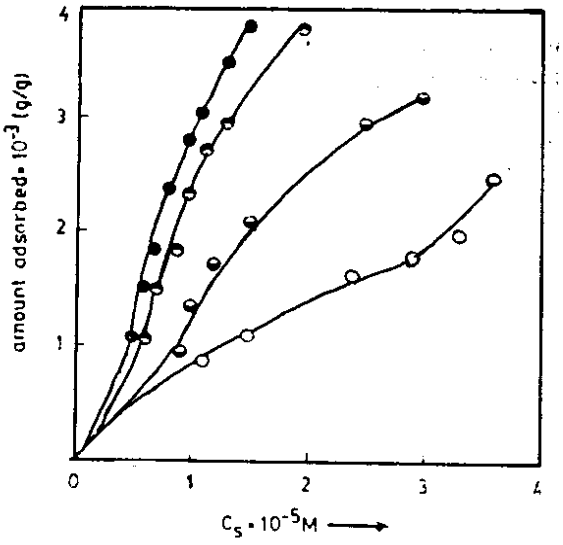

Fig. 4: Adsorption isotherms for Nile Blue Sulphate B at 323 K (O); 313 (◒); 303 K (◓); 293 K (●).

The adsorption of Rhodamine B and Nile Blue Sulphate at all temperature fitted the linear form of Langmuir isotherm equation [8].

$$C_s/x/m = 1/K_1V_m + Cs/V_m$$

where C_s, x and m stand for residual concentration, mass of the dye and mass of alumina respectively. V_m

is the volume required to form the monolayer and K_1 is related to the heat of adsorption by the relation of $K_1 = K_o \exp(-q/RT)$ where q is the heat of adsorption [9]. The values of V_m and K_1 are given in Table 1. Typical plots of these isotherms are shown in Figs. 5,6. It is evident that the values of V_m decrease with the rise of temperature indicating that adsorption of these dyes is less favourable at elevated temperatures. The values of K_1 decrease with temperature for the adsorption of Rhodamine B and Nile Blue Sulphate.

Table 1: Langmuir parameters for the adsorption of Rhodamine B and Nile Blue Sulphate

Temperature (K)	K_1(mol/g)	V_m(g/g)
Rhodamine B		
283	3.4×10^5	9.31×10^{-5}
303	3.3×10^5	6.82×10^{-5}
313	3.1×10^5	6.13×10^{-5}
323	2.6×10^5	5.86×10^{-5}
Nile Blue Sulphate		
293	2.3×10^5	2.43×10^{-4}
303	2.1×10^5	1.26×10^{-4}
313	1.9×10^5	8.82×10^{-5}
323	1.7×10^5	5.41×10^{-5}

Thermodynamic parameters such as free energy, entropy and enthalpy of adsorption were calculated from the binding constant (K_1) obtained from Langmuir equation using the following relation:

$$-\Delta G = RT \ln K_1$$
$$\ln K_1 = \Delta S/R - \Delta H/RT$$

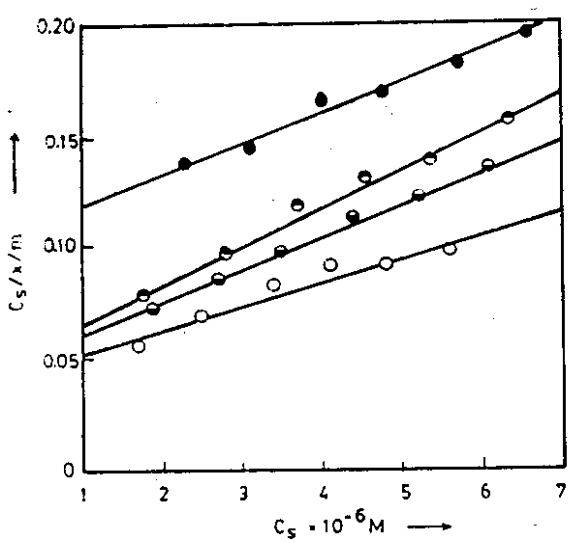

Fig. 5: Langmuir Plots for Rhodamine B at 323 K (●); 313 K (◓); 303 K (◒); 293 K (O)

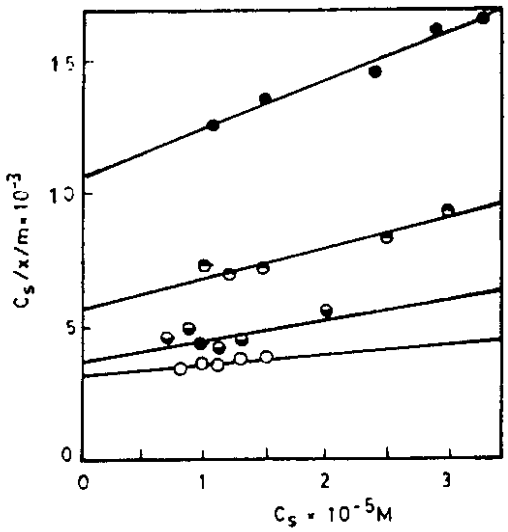

Fig. 6: Langmuir Plots for Nile Blue Sulphate at 323 K (●); 313 K (◓); 303 K (◒); 293 K (O)

The values of ΔH and ΔS were calculated from the slopes of the linear variation of $\ln K_1$ with reciprocal of temperature and are given in Table 2. The results show that the value of ΔH are positive i.e., endothermic, which is quite contrary to usual observation. One possible explanation of endothermicity of heat of adsorption is that on adsorption, the environment of the dye ions is less aqueous than it was in the solution state [10].

Table 2: Values of free energy, enthalpy and entropy of adsorption for Rhodamine B and Nile Blue Sulphate on alumina

Temperature	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol.K)
Rhodamine B			
293	7.373	-30.36	0.0251
303	7.373	-31.90	0.0243
313	7.373	-33.08	0.0235
323	7.373	-34.27	0.0228
Nile Blue Sulphate			
293	12.33	-26.65	0.0420
303	12.33	-30.36	0.0406
313	12.33	-31.68	0.0393
323	12.33	-32.90	0.0361

The values of ΔG of adsorption at different temperature for both the systems are negative as expected for spontaneous process such as adsorption. The rise in ΔG values with increasing temperature shows that adsorption of dye molecules is more favourable at high temperature. This may be due to

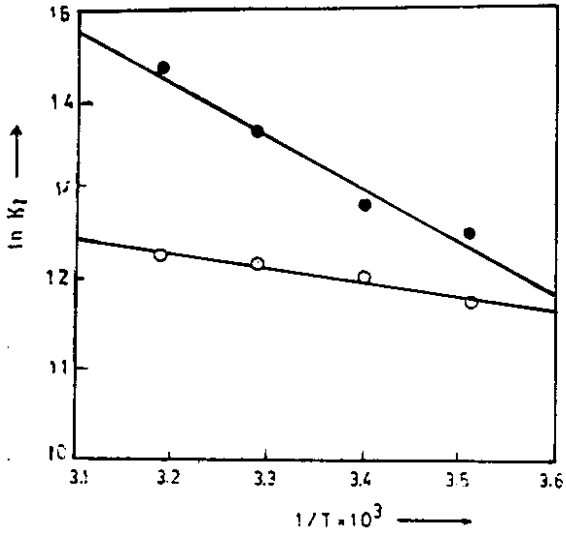

Fig. 7: Plots of $\ln K_1$ versus 1/T for Rhodamine B(●) and Nile Blue Sulphate (O).

desolvation of dye molecules at higher temperature as explained earlier. The values of enthalpy of adsorption for both dyes lie in the range of 8-18 kJ/mol which is within the range of ion-exchange reaction [11].

Experimental

E. Merck alumina 80 G neutral (Item No. 2316260). Rhodamine B (99.5%) and Nile Blue Sulphate (99.5%) were used as received. Table 3 shows the experimental values of the physical parameters of the sample of alumina used in the present study.

Table 3: Experimental values of the physical parameters of alumina.

S.No.	Parameter	Value
1.	Moisture contents	22.0%
2.	Bulk density	0.570 g/cm^3
3.	Tap density	1.210 g/cm^3
4.	True density	2.12 g/cm^3
5.	BET surface area	116 m^2/g
6.	% porosity	68.0 %
7.	Pore volume	0.76 cm^3/g
8.	Average pore radius	17 + 0.5 μm

Adsorption of Rhodamine B and Nile Blue Sulphate from aqueous solutions on alumina have been carried out by a batch technique in the temperature range of 293 to 303 K except where otherwise specified. A known amount of alumina was added to 250 ml reagent bottles containing 25 ml dye solutions of known concentration and the bottles were shaken for a specified time period. Solutions were then filtered and first 5-10 ml of the filtrate was discarded becuase of the adsorption of dye solution by filter paper. The concentration of dye solutions was determined by Shimadzu spectrophotometer, (Model No. UV-120-01). The amount adsorbed per unit mass of adsorbent was calculated and plotted against equilibrium concentration.

References

1. M. Afzal and M. Khan, *J. Chem. Soc. Pak.*, **8**, 489 (1986).
2. M. Afzal, M. Khan and H. Ahmad, *Colloid Polym. Sci.*, **269**, 483 (1991).
3. H. Ahmad, M. Afzal, S. M. Hassany and F. Mahmood, *J. Radioanal. Nucl. Chem.*, **170**(2), 309 (1993).
4 M. Afzal, M. Khan and H. Ahmad, *J. Chem. Soc. Pak.*, **13**, 157 (1991).
5. M. Saleem, M. Afzal, F. Mahmood and A. Ali, *Adsorp. Sci. Technol.*, **9**, 17 (1992).
6. C. H. Giles, T. H. MacEvan, S. N. Makhwa and D. Smith, *J. Chem. Soc.*, 3973 (1960).
7. J. J. Bikermann, "Surface Chemistry; Theory and Applications p-294. Academic Press Inc. New York 1958.
8. I. Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1971).
9. M. Afzal, M. Saleem, U. Rasul and J. Iqbal, *Islamabad, J. Sci.*, **4**, 18 (1977).
10. E. A. Belovsov and N. P. Kolobov, *Izv. Vysshikh. Uchebn. Zavednii, Khim-i-Khim Technol.*, **8**, 1026 (1985).
11. F. Helferich "Ion-exchange" McGraw Hill, New York, 1962.