

Thermodynamics of Adsorption of Dyes on Activated Silica Gel

MUHAMMAD JAVED IQBAL* AND MAQSOOD HUSSAIN
Department of Chemistry, Quaid-e-Azam University, Islamabad, Pakistan

(Received 14th March, 1992, revised 14th November, 1992)

Summary: A quantitative treatment pertaining to the study of thermodynamics of adsorption of sulphorhodamine-B, acid red-4 and acid green-25 on activated silica gel through the evaluation of the Gibbs free energy, ΔG , as a function of temperature is presented. The ΔG values are computed by employing the Gibbs adsorption equation by making use of the areas under the m - $\ln C_s$ curves. The enthalpy, ΔH , and the entropy, ΔS , has also been calculated. The results are discussed in terms of the nature of the adsorbates.

Introduction

In order to fully understand the nature of adsorption, the thermodynamic studies on adsorption has played an important role. In particular the statistical interpretation of the adsorption thermodynamic functions have been of considerable value [1-3]. The precise quantitative estimation of the free energy changes (ΔG) associated with adsorbent surfaces and the calculations of allied thermodynamic functions namely the heat of adsorption (ΔH) and the entropy changes (ΔS) help in understanding the various adsorption systems.

The Gibbs free energy changes ΔG for an adsorbate per unit cross-section of the adsorbent is effectively shown to be identical in magnitude to the surface film pressure, π , obtained from the Gibbs adsorption equations (1,4).

$$d\pi = RT (m/M_w A) d \ln C_s \quad (1)$$

where m is the amount adsorbed in grams, M_w is the molecular weight, A is the area of the adsorbent surface, C_s is the equilibrium adsorbate concentration and R and T have their usual meanings. Thus the ΔG at a given adsorbate concentration can be obtained by integrating equation (1).

$$\pi = \Delta G = RT/M_w A \int_0^{C_s} m \ln C_s \quad (2)$$

This paper reports the calculations, of ΔG , ΔH and ΔS from adsorption data of sulphorhodamine-B, acid red-4 and acid green-25 on activated silica gel at different temperatures.

Results and Discussion

The determination of the integral, $\int_0^{C_s} m \ln C_s$, was done by a graphic integration technique [2]. $\ln C_s$ has been plotted against the amount adsorbed, m , at constant temperature, using equation (2). Such plots are shown in Figs. 1-3. The area under the m - $\ln C_s$ curves gives the value of ΔG .

The enthalpy, ΔH , is evaluated by using the Calusius-Clapeyron equation,

$$\ln C_s = -\Delta H/RT + C \quad (3)$$

which would yield a straight line on plotting $\ln C_s$ versus $1/T$. The slope of the line gives the value of ΔH . The value of ΔS can be readily obtained from,

$$\Delta G = \Delta H - T.\Delta S \quad (4)$$

The calculated values of ΔG , ΔH and ΔS are summarised in Table 1.

The magnitude of ΔH (Table 1) indicates that the three dyes studied here are chemisorbed on the surface of silica gel. The possible mechanism of adsorption of these dyes has been reported elsewhere [6].

The changes of the free energy of liquid-gas, liquid-liquid, liquid-solid and gas-solid interfaces has been described [7-10] in terms of 'film pressure' assuming that the adsorption leads to a mobile layer of two-dimensional fluid similar to a water film [11] where molecules freely move about and interact laterally on the surface. For the interpretation of adsorption forces, a thermodynamic viewpoint has

*To whom all correspondence should be addressed.

Table 1: The calculated values of the Gibbs free energy (ΔG), heat of adsorption (ΔH) and entropy of adsorption (ΔS) on activated silica gel at different temperature

Adsorbate	$-\Delta H/\text{kJ mol}^{-1}$	$-\Delta G/10^{-7} \text{ kJ mol}^{-1} - \Delta S/\text{J K}^{-1} \text{ mol}^{-1}$							
		283 K	293 K	303 K	313 K	283 K	293 K	303 K	313 K
Acid Green-25	37.78 ± 4.85	6.44	5.13	3.46	2.16	133.5	128.9	124.7	120.7
Acid Red-4	43.68 ± 0.10	-	7.29	3.49	1.67	-	149.1	144.2	139.6
Sulphorhedamine-B	30.50 ± 2.64	7.63	5.97	4.35	3.08	107.8	104.1	100.7	97.4

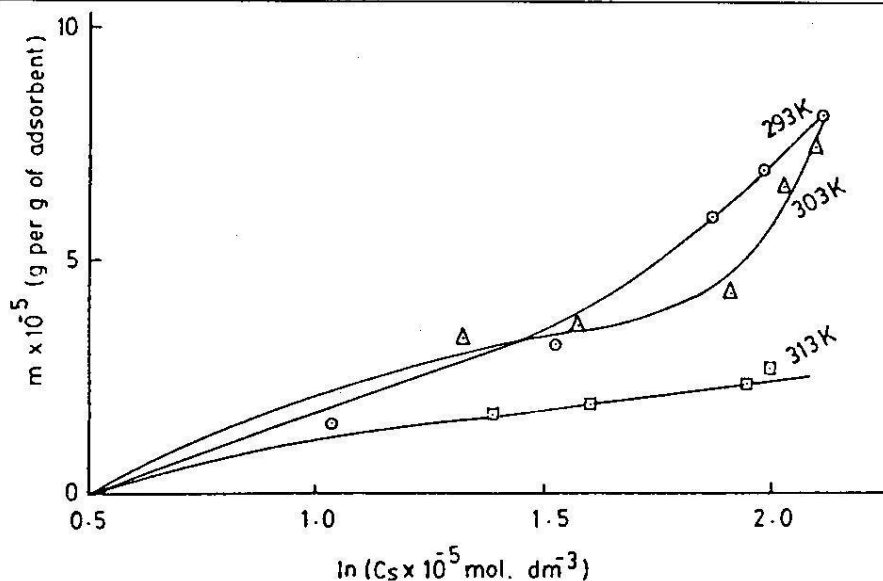


Fig. 1: Plots of the amount of Acid Red-4 adsorbed per g of adsorbent (m) versus concentration of the adsorbate.

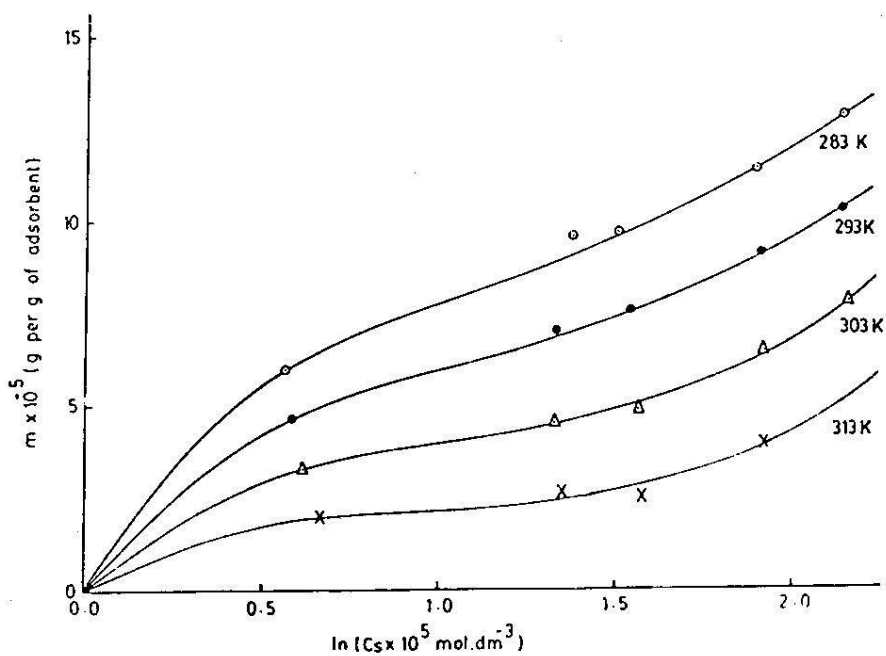


Fig. 2: Plots of the amount of Acid Green-25 adsorbed per g of adsorbent (m) versus concentration of the adsorbate.

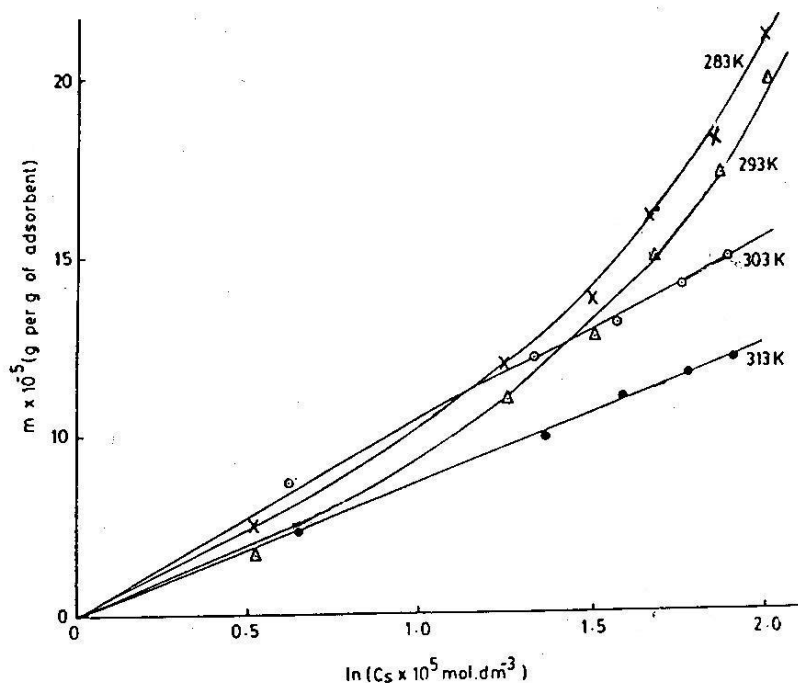


Fig. 3: Plots of the amount of sulphorhodamine-B λ per g of adsorbent (m) versus concentration of the adsorbate.

been employed here. The forces involved in adsorption are looked at as tendency of an adsorbate to decrease the surface free energy.

It is evident from Table 1 that the surface free energy is reduced on adsorption i.e. ΔG is negative. At any temperature, for example at 293 K, the reduction in the surface free energy by acid red-4 is greater ($\Delta G = -7.29 \times 10^{-7} \text{ kJ mol}^{-1}$) compared with acid green-25 and sulphorhodamine-B where ΔG is -5.13×10^{-7} and $-5.97 \times 10^{-7} \text{ kJ mol}^{-1}$, respectively. This shows that the former interacts (adsorb) more strongly with the adsorbent surface as compared to the latter dyes. The extent of the adsorbate-adsorbent interaction in acid red-4 is also manifested in a higher ΔS value ($-43.68 \text{ kJ mol}^{-1}$) and higher ΔS value ($-149.1 \text{ J mol}^{-1}\text{K}$) for acid red-4 at 293 K as compared to the other two adsorbates. The order of the strength of adsorption in the case of the three dye adsorbates is found to be as follows:

acid red-4 > acid green-25 > sulphorhodamine-B

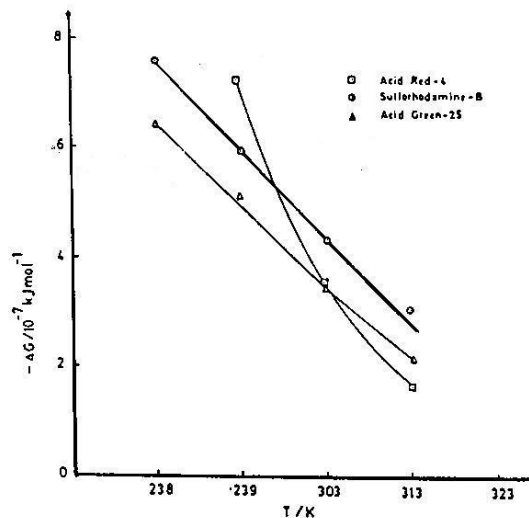


Fig. 4: Plot of ΔG versus temperature of adsorption.

An increase in temperature causes a decrease in the values of ΔG for the three dye adsorbates investigated here (Fig. 4). As the temperature is increased extent of adsorption is decreased owing to

the fact that adsorption is an exothermic process therefore surface free energy at higher temperature would be lesser.

Experimental

Sulphorhodamine-B, obtained from Exiton (USA), acid red-4 and acid green-25, supplied by Janssen Chemica (Belgium), were high purity chemicals (Laser grade) and were used as received. Silica gel (60-120 mesh; pore radius of 8×10^{-16} cm [5] and surface area of $307 \text{ m}^2 \text{ g}^{-1}$) was supplied by BDH (Germany) which was activated before adsorption studies by heating at 473 K.

Stock solutions of the dyes sulphorhodamine-B, acid green-25 (10^{-4} mol) and acid red-4 (10^{-3} mol) were prepared by dissolving weighed amounts in conductivity water and their necessary dilutions to various concentrations in the range $10^{-5} \text{ mol.dm}^{-3}$ were made in the same solvent. Weighed amounts of activated silica gel (1 g) in a test tube containing 50 ml of a dye solution was shaken for 50 minutes [6] in a Yamato BT-47 water bath incubator at a particular temperature, i.e. 283, 293, 303 and 313 K. The solutions were filtered and the absorption spectra were recorded on a Shimadzu UV-120-02 spectrophotometer at the respective λ_{max} of each dye [6].

Since the pre-equilibrium concentrations of dye molecules in all the solutions are extremely low

(i.e. $10^{-5} \text{ mol dm}^{-3}$) the aggregation of the dye molecules was not believed to have taken place. For the same reason the adsorption of dyes on the glass surface and on the filter paper was considered to be negligibly small and therefore no corrections were applied.

References

1. M. Afzal and J. Ahmed, *Colloid Polymer Sci.*, **253**, 635 (1975).
2. M. Afzal and M. Jaffar and S. Yasmin, *Colloid Polymer Sci.*, **255**, 252 (1977).
3. M. Afzal, M. Jaffar and N. Perveen, *Colloid Polymer Sci.*, **256**, 356 (1978).
4. D. H. Bangham, *Trans. Faraday Soc.*, **33**, 805 (1937).
5. M. Khan, Ph.D. Thesis, Quaid-e-Azam University, Islamabad, Pakistan (1987).
6. M. J. Iqbal and M. Hussain, *J. Chem. Soc. Pak.* (submitted).
7. J. Jasper and B. L. Housman, *J. Phys. Chem.*, **67**(7), 1548 (1963).
8. D. Graham, *J. Phys. Chem.*, **68**(10), 2788 (1964).
9. A. W. Czanderna, *J. Phys. Chem.*, **68**(10), 2765 (1964).
10. P. Y. Hsieh, *J. Phys. Chem.*, **68**(5), 1068 (1964).
11. N. K. Adam, *The Physics and Chemistry of Surfaces*, Oxford University Press, 1941, Chapter 2.