CHAPTER - VII

Effect of Temperature on the Adsorption of Dyes by Aluminosilicates.

According to thermodynamic principles the adsorption process should be exothermic since it is associated with decrease in entropy and free energy. In fact evolution of heat had been observed by gas adsorption on clean surfaces and on other substrates. Yung Fang and Yu Yao (1) have observed that adsorption of n-propyl, n-butyl, n-amyl amines, tridecyl amine and water in their Vapour states on oxidised and reduced iron surfaces is exothermic.

The adsorption of sphere-like molecules on graphitised carbon black (2), benzene on Cr-Al-K Catalyst (3) is similarly exothermic. The heat of adsorption varies in some cases with the amount of adsorbate, while in others it does not. By plotting the heat of adsorption against the percentage of surface covered Kevorkian et al (4) obtained irregular graphs which they accounted by assuming surface heterogeneity. The adsorption study of neopentane and carbon tetrachloride on carbon black graphitised at 3000^{o}C, shows similar results. The heat of adsorption plotted against amount adsorbed shows a maximum. This has been explained by suggesting that the molecules are adsorbed in a non-localised fashion and that they interact strongly with each other in the adsorbed layer.

Yung Fang and Yu Yao (1) have also observed that the graph of heat of adsorption against the amount of amines adsorbed on reduced and oxidised iron surfaces consists of two plateaus. The first one corresponds to the heat of chemsorption and second one to physical adsorption. But the results of adsorption of Cyclohexane on Cr-Al-K catalyst at 20°, 50° and 150° (5) show that the heats of adsorption are of the order of 10.3 k cals/mol and independent of surface coverage. The differential heats of adsorption of n - C_5H_{11} and n - C_6H_{14} on $BaSO_4$ (6) have been found to be almost constant till the surface is half filled, then they gradually decrease with increase on adsorption because of surface heterogeneity.

In the solution phase, however, endothermic adsorption processes have often been encountered. The adsorption of crystal violet by hydrated ferricoxide (7) and Chromic oxide Sol (8) and that of Congored and fucshine by hydrated thorium oxide Sol (9) are endothermic.

Giles, Eastone, and McKay (10) have observed that certain dyes e.g. magenta and ethyl violet are adsorbed on alumina with absorption of heat, while safranine T and Rhodamine 6B are adsorbed with evolution of heat. No heat change was however, obwerved with methylene blue, rhodamine 3B and rhodamine B. Again with victoria pure blue, negative heat of adsorption has been noticed at low coverage while at high coverage heat has been evolved.

Giles et al (11) found that the values of heat of adsorption of dyes from their aqueous solution on inorganic surfaces ranged between -1.00 and -10.00 Kcal/mole. In the adsorption of some dyes on cellulose acetate the successive heat changes were examined quantitatively by Majury (12). De (13) studied the effect of temperature on the adsorption of methylene blue, malachite green and Crystal violet in aqueous solution of Na-Kaolinite and Na-Bentonite. They found the process to be endothermic for malachite green and crystal violet whereas no appreciable difference was noticed in the case of methylene blue. Narine and Guy (14) recorded a decrease in adsorption of methylene blue by Na-Bentonite from 69.3 $\pm$ 3.0 to 64 $\pm$ 3.0 to 64 $\pm$ 2.0 meq per 100 gm of the clay, when temperature was changed from 3 ^{o}C to 55 ^{o}C . In the study of the effect of temperature of some thiazine dyes with clay minerals by Sunwar (15) it has been noticed that adsorption process of the thiazine dyes on montmorillonite and kaolinite is exothermic in nature but in case of vermiculite the exothermic nature of the curves are altered with change in temperature and concentration. At low concentrations the sorption isotherms at 23 ^{o}C and 40 ^{o}C show exothermicity but at higher concentration these curves exhibit endothermicity.

According to the idea of Bartell, Tudor and Yung Fu (16) though the adsorption process itself is exothermic the solubility of the adsorbate and its temperature dependence are the significant factors which control the resultant heat of adsorption. Thus, according to them, if the solubility of a substance is inversely related to temperature, the amount adsorbed would increase with rise in temperature, and if the solubility increased with temperature the effect would be the opposite. They observed the adsorption of some low molecular weight aliphatic substances on carbon to be exothermic at low concentration while endothermicity was found at higher concentration. At higher concentrations the effect of temperature on solubility was supposed to be more influenced.

Mundhara etal (17) on the study of adsorption of brilliant cresyl blue and safranine-T on Tin oxide substrats at 30-60^{o}C found the adsorption process to be exothermic at lower concentration but endothermicity at higher concentration of the dyes. They also attributed the endothermic bonding to an increase in the number of available sites with temperature as a consequence of dissociation of the dye aggregates in the substrates. The heat of adsorption values were 23-80 KJ/mole for brilliant cresyl blue and 17-26 KJ/mole for safranine-T. They suggested that concurrence of more than one reaction was responsible for these variable heats of adsorption values.

According to Giles et al (10) the apparent endothermic nature of the adsorption is a result of aggregation of the dye molecules (18) in the solution. They found the adsorption of janus red and lassamine green from their aqueous solution on inorganic surfaces to be an endothermic reaction. Hajela and Ghosh (7) have also remarked that association of dye molecules in aqueous medium affects the heat of adsorption. According to them, as the disassociated dye molecules are gradually taken up by the adsorbate, more and more of the aggregated dye molecules in solution are dissociated into simpler forms. At each stage the heat of dissociation of the aggregated dye molecules is included in the experimental heat of adsorption. The heat of adsorption is, therefore, controlled by several factors such as solubility, association and actual process of adsorption itself.

From the values of the heat of adsorption, the nature of bonding namely, whether chemical or physical both of the adsorbed species with the substrate surface can be judged (3). Very little data are available in the literature on the heat of adsorption of the dyes by alumino silicate minerals in the form of suspension. In order, therefore, to provide some information on this subject adsorption measurements were carried out at different temperatures with montmorillonite and kaolinite in suspension and RG and RB as adsorbates. The experimental procedure has already been described in Chapter III page 55.

Sorption on Dyes or Na-Montmorillonite and Na-Kaolinite

The temperature dependence of adsorption of RG^+ and RB^+ on Na-montmorillonite and Na-kaolinite is represented graphically by drawing the respective isotherms. The heat of adsorption was calculated using the equation:

$$Q = \frac{RT_1T_2}{T_1-T_2} \times \ln \frac{C_1}{C_2}$$

where C_1 and C_2 are the concentrations of the dye in solution phase at temperature T_1 and T_2 for the same amount of dye adsorbed.

Sorption of RG^+ on Na-montmorillonite:

Fig. 59 represents the adsorption isotherms of RG on Na-montmorillonite at 23^o, 38^o and 68^oC and the inset shows the plot of heat values against the amount of dye adsorbed. The nature of the curves remains unchanged with increase in temperature and the amount adsorbed decreases with increase in temperature indicating the process to be exothermic. All the isotherms are of Langmuir type. Introducing the values of C_1 and C_2 for temperature 23^o and 68^oC from the graph the heats of adsorption were calculated according to the above mentioned equation. The results are shown in table 12. It is found that there is variation of the amount of dye adsorbed with the heat of adsorption so it is not a constant quantity. It shows a minimum at a certain value of the dye adsorbed indicating probably to a situation when the monolayer or when the adsorption value approaches the cation exchange capacity of the mineral. From the sorption isotherm it is apparent that the slope gradually decreases with rise in solute concentrations. This is because of the fact that the adsorption first takes place on the higher energy sites of the adsorbent and with the progress in adsorption, the vacant sites become more difficultly accessible. As a consequence the heat of adsorption decreases. The heterogeneity of the montmorillonite surface and the complications in actual systems cause a progressive diminution in the heat of adsorption as the surface coverage increases, long before the monolayer is complete (19). It has been pointed earlier that the experimental heat of adsorption is the net result of several processes such as solubility, association of the dye molecules etc. Where heat may be evolved or adsorbed. In the present study the heat of adsorption is positive. Whereas in the earlier work reported by De (13) this value has been found to be negative. The sorption isotherms have been drawn at equilibrium concentrations that fall mostly within the monomolecular range of the dye. The values of heat of adsorption in this case lie between + 1.25 to + 2.59 K cal per mole and calculated values are shown in Table 12.

Sorption of RB^+ on Na-montmorillonite

The adsorption isotherms of RB on Na-montmorillonite at 23^o, 38^o and 68^o are shown in Fig. 60. The change in temperature does not cause any change in the nature of the curves. It is observed that the amount adsorbed decreases with rise in temperature as in the case of RG sorption. From the plot of heat of adsorption in Kcal/mole vs amount adsorbed in meq/100g a minimum is obtaining at a particular value of the dye adsorbed and this can be explained in similar manner as in the case of sorption ofi RG considering the equilibrium concentrations of the isotherms to be in the monomolecular range. Also the heat of adsorption lies in the range of + 1.91 to + 4.25 Kcal/mole (Table 12) which is higher than that observed in Na-montmorillonite. RG, suggesting a stronger binding of the former to the clay. The desorption studies of the dyes from their clay mineral complexes with various electrolytes also confirm this conclusion.

Sorption of Dyes on Na-kaolinite

Sorption of RG^+ and RB^+

Isotherm of RG^+ and RB^+ on Na-kaolinite at 26^o, 46^o, 70^o are displayed in Fig. 61 and 62 respectively. All the isotherms are of Langmuir type. The values of C_1 and C_2 for temperatures 26^oC and 70^oC are found out from the graph from which the heat of adsorption was calculated according to the equation given in page 138 (Table 13). It is found that the heat of adsorption changes with quantity of dye adsorbed but the nature of the sorption remains unchanged at different temperature and the adsorption process in exothermic.

It is interesting to note that in kaolinite the plot of heat of adsorption values against the amount of RG adsorbed does not show a distinct minimum as has been obtained in montmorillonite but increases progressively with adsorption. This is probably due to the adsorption of the dye in the form of aggregated species, which results in the sorption of dye beyond the c.e.c. of the mineral at an early stage when the equilibrium concentration is till quiet low.

The heat of adsorption of RB is greater than that of RG which suggests higher affinity of the former than of the latter to the mineral systems. The desorption studies of the dyes also support this view which have been discussed in the previous chapters.

TABLE - 12

Heat of adsorption when various quantities of dyes are sorbed onto aluminosilicates.

(Sorption of Na-montmorillonite)

Name of the Dye	Amount and dye sorbed in meq/100 gm	Concentration C_1 at temperature $T_1=23^{o}C$	Concentration C_2 at temperature $T_2=68^{o}C$	Heat of adsorption in Kcal/mol
RG	75	$0.95\ x10^{-5}$ (M)	$1.7\ x10^{-5}$ (M)	2.59
	80	$1.8\ x10^{-5}$ (M)	$2.85\ x10^{-5}$ (M)	2.04
	85	$2.9\ x10^{-5}$ (M)	$4.1\ x10^{-5}$ (M)	1.53
	90	$4.3\ x\ 10^{-5}$ (M)	$5.7\ x10^{-5}$ (M)	1.25
	95	$6\ x10^{-5}$ (M)	$8.1\ x10^{-5}$ (M)	1.33
	97.5	$7\ x10^{-5}$ (M)	$9.6\ x10^{-5}$ (M)	1.40
RB	65	$1\ x10^{-5}$ (M)	$2.6\ x10^{-5}$ (M)	4.25
	70	$1.7\ x10^{-5}$ (M)	$4\ x10^{-5}$ (M)	3.80
	75	$3\ x10^{-5}$ (M)	$5.5\ x10^{-5}$ (M)	2.69
	80	$4.6\ x10^{-5}$ (M)	$7.4\ x10^{-5}$ (M)	2.11
	85	$6.5\ x10^{-5}$ (M)	$1\ x10^{-4}$ (M)	1.91
	87.5	$8\ x10^{-5}$ (M)	$1.4\ x10^{-4}$ (M)	2.48

TABLE - 13

Heat of adsorption when various quantities of dyes are sorbed onto aluminosilicates

(sorption on Na-Kaolinite)

Name of the Dye	Amount of dye sorbed in meq/100g	Concentration C_1 temperature $T_1=26\,^{o}C$	Concentration C_2 at temperature $T_2=70\,^{o}C$	Heat of adsorption in Kcal/mol
RG	4.5	0.5×10^{-5} (M)	0.7×10^{-5}	1.55
	5	0.9×10^{-5} (M)	1.3×10^{-5}	1.70
	5.5	1.65×10^{-5} (M)	2.5×10^{-5}	1.92
	6	2.78×10^{-5} (M)	4.8×10^{-5}	2.49
	6.25	3.7×10^{-5} (M)	6.6×10^{-5}	2.67
RB	4	0.2×10^{-5}	0.3×10^{-5}	1.87
	4.5	0.8×10^{-5}	1.1×10^{-5}	1.47
	5	1.28×10^{-5}	1.9×10^{-5}	1.82
	5.5	1.95×10^{-5}	3.25×10^{-5}	2.35
	6	3.3×10^{-5}	6×10^{-5}	2.76

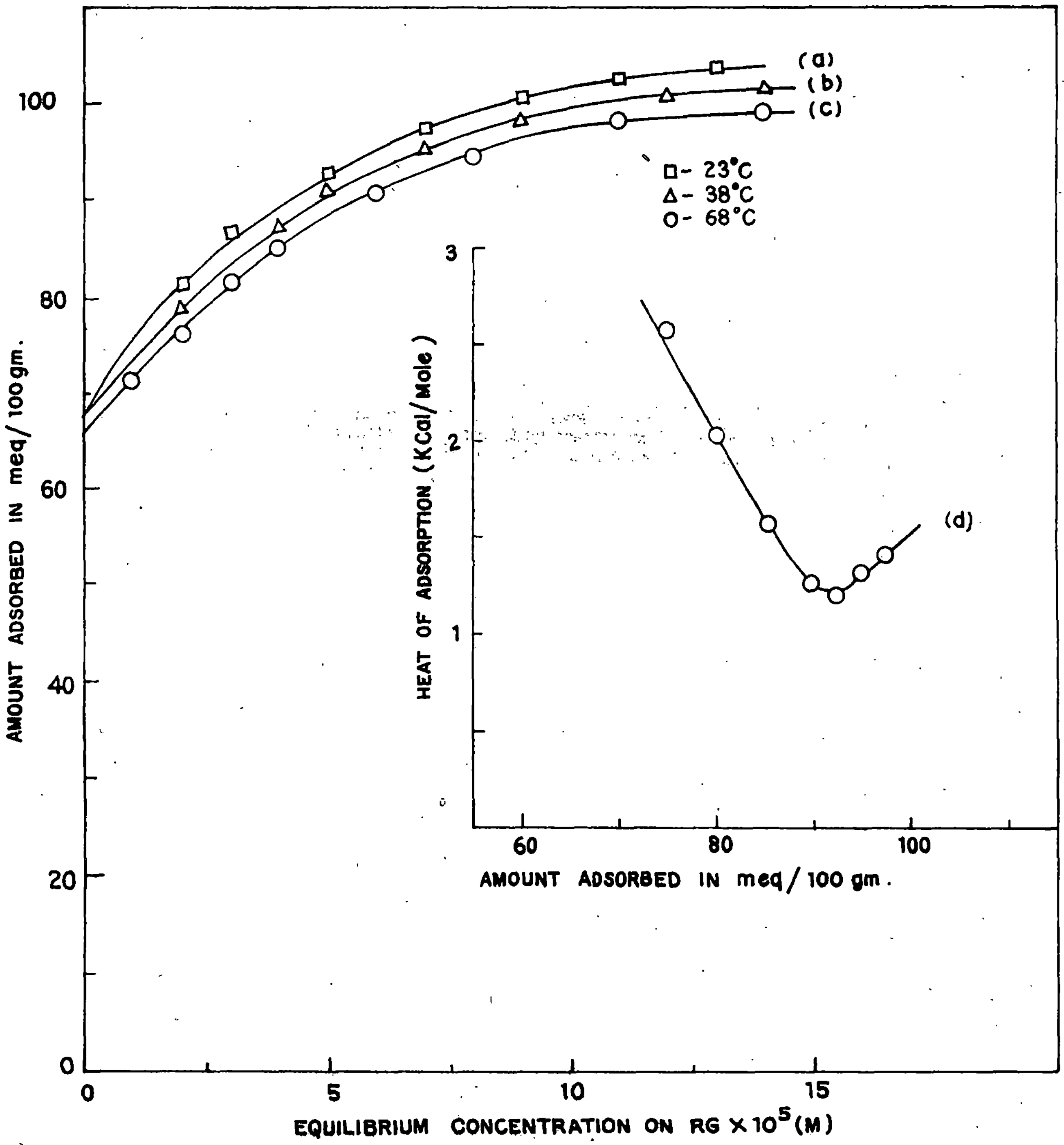

FIG. 59. ADSORPTION ISOTHERMS OF RG ON Na-MONTMORILLONITE AT DIFFERENT TEMPERATURES (a,b,c) AND RELATION OF HEAT OF ADSORPTION WITH THE AMOUNT OF DYE-ADSORBED (d).

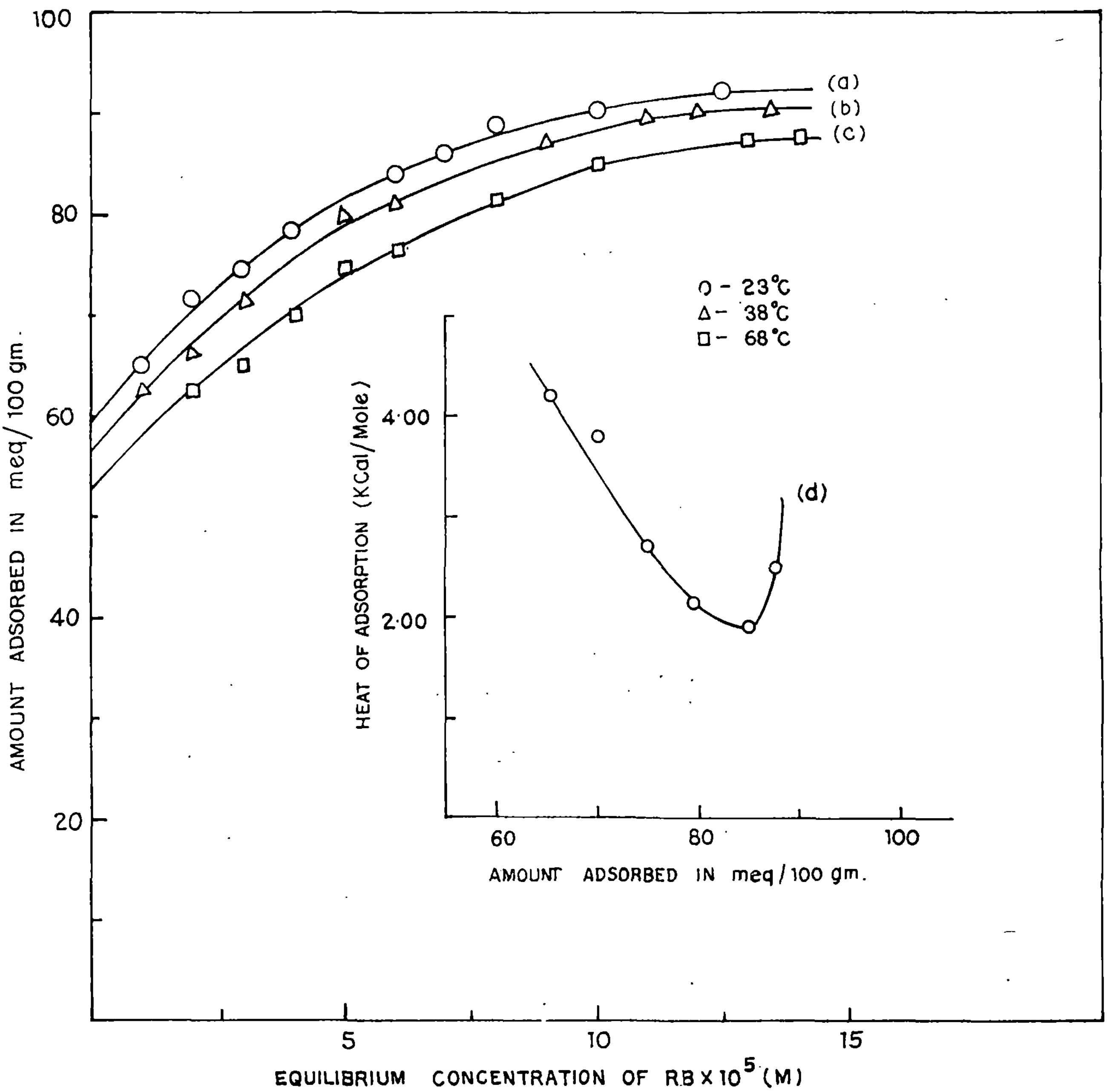

FIG. 60. ADSORPTION ISOTHERMS OF RB ON Na- MONTMORILLONITE AT DIFFERENT TEMPERATURES (a.b.c) AND RELATION OF HEAT OF ADSORPTION WITH THE AMOUNT OF DYE ADSORBED (d).

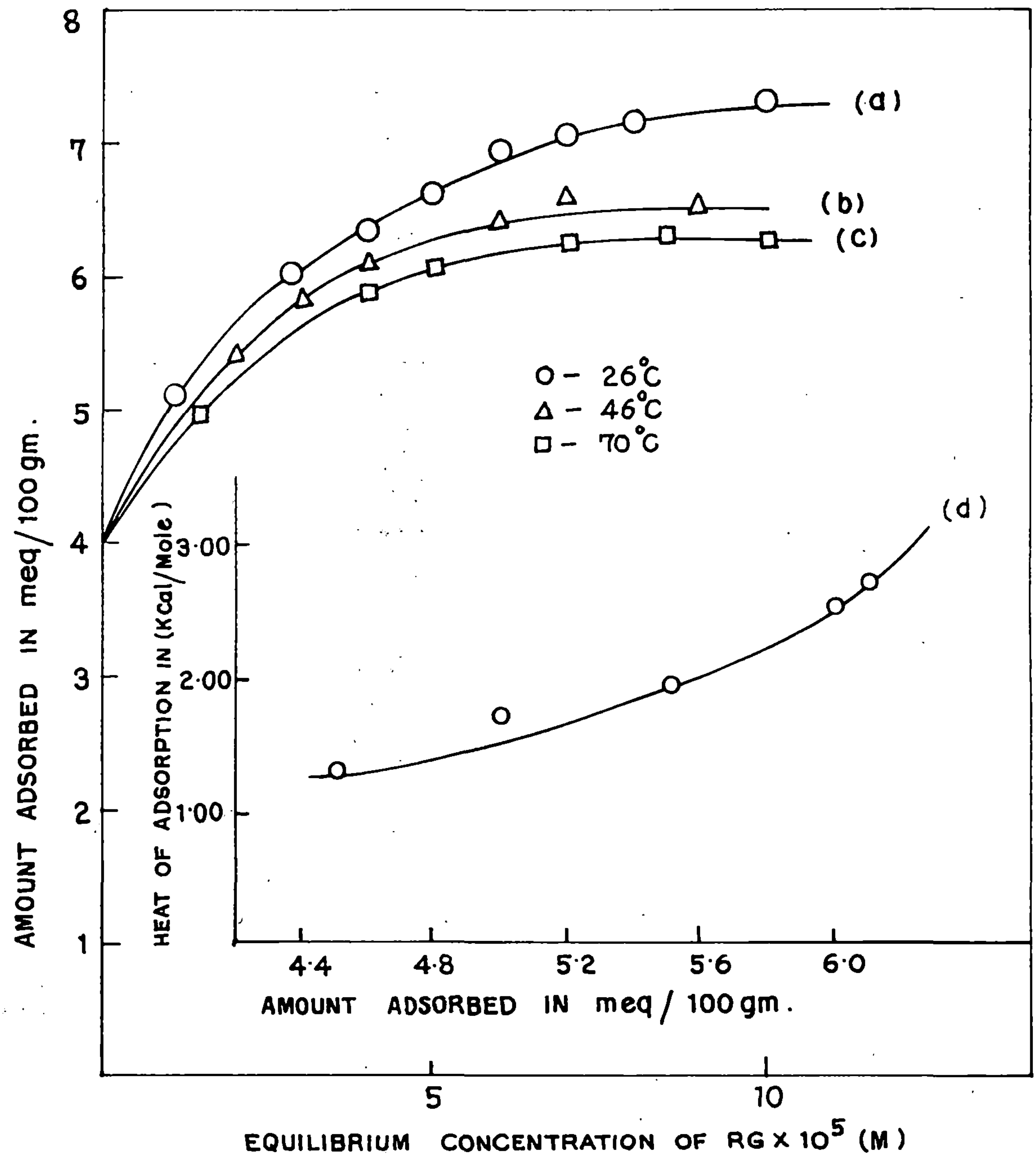

FIG. 61. ADSORPTION ISOTHERMS OF RG ON Na-KAOLINITE AT DIFFERENT TEMPERATURES (a, b, c) AND RELATION OF HEAT OF ADSORPTION WITH THE AMOUNT OF DYE ADSORBED.

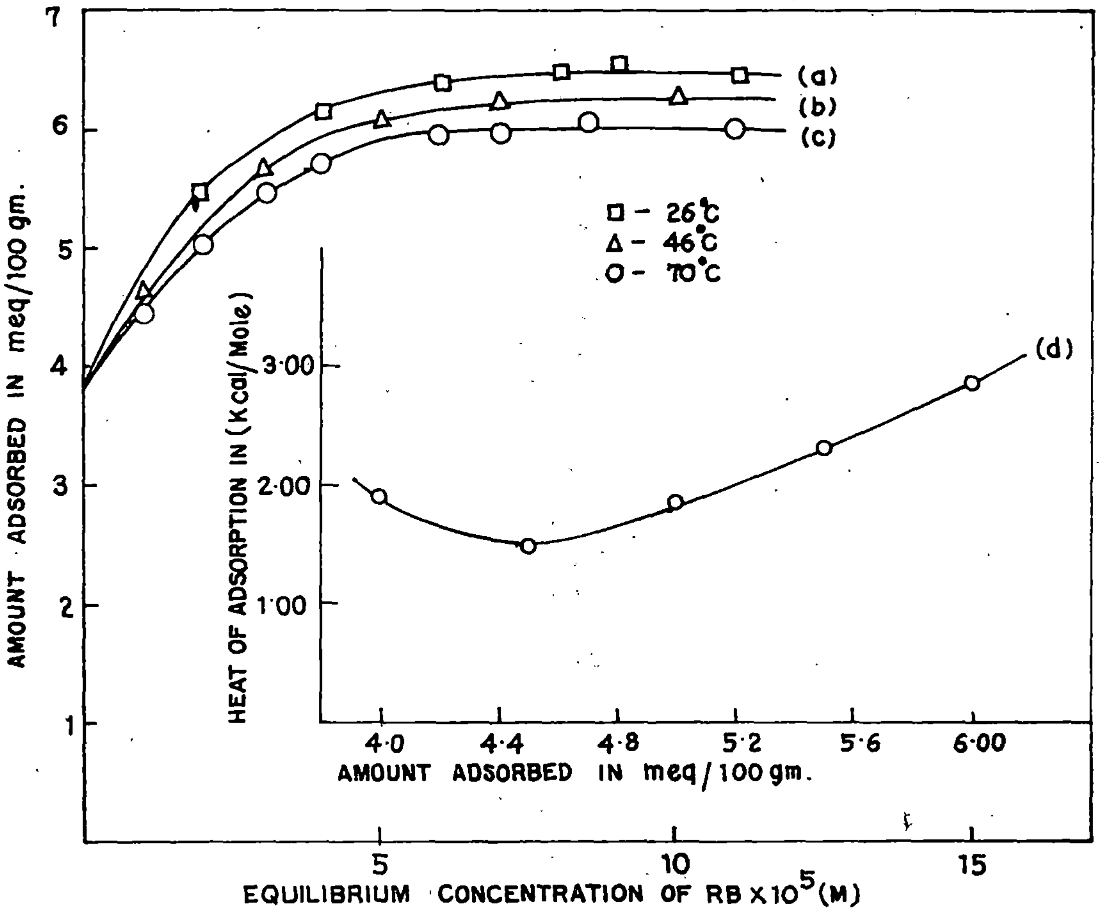

FIG. 62. ADSORPTION ISOTHERMS OF RB ON Na-KAOLINITE AT DIFFERENT TEMPERATURES (a, b, c) AND RELATION OF HEAT OF ADSORPTION WITH THE AMOUNT OF DYE ADSORBED (d).