Adsorption Isotherms of Pigments from Alkali-Refined Vegetable Oils with Clay Minerals

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Adsorption isotherms of pigments from alkali-refined oils (rapeseed, soybean, wheatgerm, safflower, corn, cottonseed and sunflower) were measured to investigate the applicability of the Langmuir and Freundlich equations and to elucidate the adsorption characteristics of pigments on sepiolites and standard activated clay. The Freundlich equation was more applicable to the experimental adsorption isotherms. The equilibrium amount adsorbed, acidity, pore size distribution and inflection of the Freundlich isotherms could be explained by assuming that pigments were adsorbed on the stronger acid sites in smaller pores at low concentration, and then in the larger ones when the concentration increased. The amount adsorbed increased with a rise in adsorption temperatures from 70 to 110°C, and the heat of adsorption was below 10 kcal/mol. The results indicate that pigments were physically adsorbed on the acid sites activated at higher adsorption temperatures.

KEY WORDS: **Adsorption isotherm, alkali-refined oil, clay, Freundlich equation, heat of adsorption, physical adsorption, pigments.**

Pigments are removed from vegetable oils by adsorption on bleaching earth. Proctor and Snyder (1) reported that the adsorption of lutein as pigment from soybean oil on silicic acid occurs according to a Freundlich isotherm. The applicability of Freundlich and Langmuir equations to guide bleaching of vegetable oils was examined for rubber and melon seed oils (2). The relation between the amount of coloring matter removed on the bleaching medium and the equilibrium concentration showed good agreement with Freundlich and Langmuir adsorption isotherms (2). Physical adsorption of pigments on bleaching earth is believed to predominant because of enthalpy changes obtained in the extraction of rubber and melon seed oils (3).

Bleaching efficiencies of bentonites, montmorillonites and sepiolites for alkali-refined rapeseed, soybean, wheatgerm, safflower, corn, cottonseed and sunflower oils were investigated (4). The purpose of this investigation was to study the applicability of the Langmuir and Freundlich equations for adsorption of pigments from these alkali-refined vegetable oils with montmorillonite, sepiolite and standard activated clay. In addition, the isosteric heat of adsorption of pigments on sepiolite and standard activated clay was calculated from a Clausius-Clapeyron equation (5) to the adsorption isotherms from rapeseed and soybean oils at 70°C, 90°C and 110°C.

MATERIALS AND METHODS

Materials. Alkali-refined rapeseed oil was donated by Ajinomoto Co. Inc. (Tokyo, Japan). Alkali-refined soybean, corn and sunflower oils were donated by Honen Oil Co. Ltd. (Shimizu, Shizuoka Prefecture, Japan). Alkali-refined wheatgerm, safflower and cottonseed oils were donated by Summit Oil Mill Co. Ltd. (Chiba Prefecture, Japan). The fundamental properties of the alkali-refined oils were previously reported (4). The oils were stored in a dark cooler at 4°C until used. Adsorbents employed to remove pigments from alkali-refined oils were: Montmorillonite No. 1 (powder), sepiolite No. 2 (powder, native of Turkey), sepiolite No. 3 (spherule, native of Turkey), sepiolite No. 5 (fiber, 5000 × 1 μm, native of China) and standard activated clay (powder, certificated by The Japan Oil Chemists' Society, Wako Pure Chemical Ind. Ltd., Osaka, Japan). Montmorillonite No. 1, sepiolites No. 2, No. 3 and No. 5 were donated by Fuji Talc Ind. Ltd. (Osaka, Japan). The five kinds of adsorbents were identical to those identified in the previous paper (4). The adsorbents were dried at 110°C for 15 hr before use.

Procedure for adsorption isotherms. Alkali-refined oil (10.0 g) was stirred and heated to a constant temperature (70°C, 90°C or 110°C) within 5 min under a vacuum of 18 mm Hg in a suction bottle of 50 mL capacity. The adsorbent (0.05, 0.10, 0.15, 0.20, 0.25, 0.40, 0.50 or 0.70 g) was each added to the heated oil, and the mixture was agitated with a magnetic stirrer for 15 min at a constant temperature, since this was previously determined to be sufficient time to ensure adsorption equilibrium. The mixture was allowed to cool to 25°C under vacuum before being filtered through a glass funnel (TOP, 3G4) covered with glass fiber paper (Whatman, GF/F). Filtered oil was added to benzene (8 mL) in a measuring flask to a total volume of exactly 10 mL. Residual pigment content was measured at maximum wavelength 457 nm (4) in a Shimadzu spectrophotometer UV-120-02 (Shimadzu Corp., Kyoto, Japan). The relative amount of pigment adsorbed, X, and the residual relative amount at equilibrium, X_e, were obtained from the equations $X = (A_o - A_x)/A_o$ and $X_e = A_x/A_o$, where A_o is the absorbance of unbleached oil and A_x is the absorbance of bleached oil. The relative amount adsorbed per g of adsorbent, X/m, is X divided by the weight of adsorbent (m) used. Adsorption isotherms were plotted as X/m *vs.* X_e for each amount of adsorbent used.

Pore size distribution. Pore size distribution of adsorbent was determined by the method of Dollimore and Heal (6) from the nitrogen adsorption isotherm up to a relative pressure of 0.95.

RESULTS AND DISCUSSION

Relative amounts of pigments adsorbed on clay minerals. Table 1 shows the relative amounts of pigments adsorbed on clay minerals at lower (X_e=0.1) and higher (X_e=0.5) relative equilibrium concentrations of pigments. The relative amounts adsorbed on standard activated clay from alkali-refined oils were considerably larger than those on montmorillonite and sepiolites. Acid strength, acidity and specific surface area of the adsorbents used in this work were previously reported (4). The specific surface area of sepiolite No. 2 (281.1 m²/g) was about equal to that of standard activated clay (286.9 m²/g). The acidity of standard activated clay at $-5.6 > H_o \geqslant -3.0$ was six times higher than sepiolite No. 2 (4). The amounts adsorbed,

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TABLE 1

Relative Amount of Pigments Adsorbed on Clay Minerals at Relative Equilibrium Concentrations 0.1 and 0.5[a]

	Rapeseed		Soybean		Wheatgerm		Safflower		Corn		Cottonseed		Sunflower	
Adsorbent	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
Montmorillonite No. 1	0.2	0.8	0.1	0.3	0.1	0.3	0.2	0.7	0.1	0.5	0.1	0.4	0.1	0.5
Sepiolite No. 2	2.0	6.4	0.9	5.0	0.7	2.3	2.6	7.7	0.7	3.4	0.8	4.2	1.8	5.9
Sepiolite No. 3	2.0	4.0	1.8	3.5	1.5	4.7	2.8	9.1	0.8	7.0	1.4	6.9	2.4	8.8
Sepiolite No. 5	1.0	2.8	0.3	1.0	0.3	0.9	0.7	2.0	0.3	1.1	0.3	1.4	0.6	1.7
Standard activated clay	13.0	19.8	13.7	20.8	9.0	21.1	17.0	38.2	2.3	31.0	7.0	26.9	11.0	35.8

[a] Relative amounts of pigments adsorbed per gram of adsorbent were obtained at relative equilibrium concentrations, $X_e = 0.1$ and $X_e = 0.5$ from adsorption isotherms at 110°C.

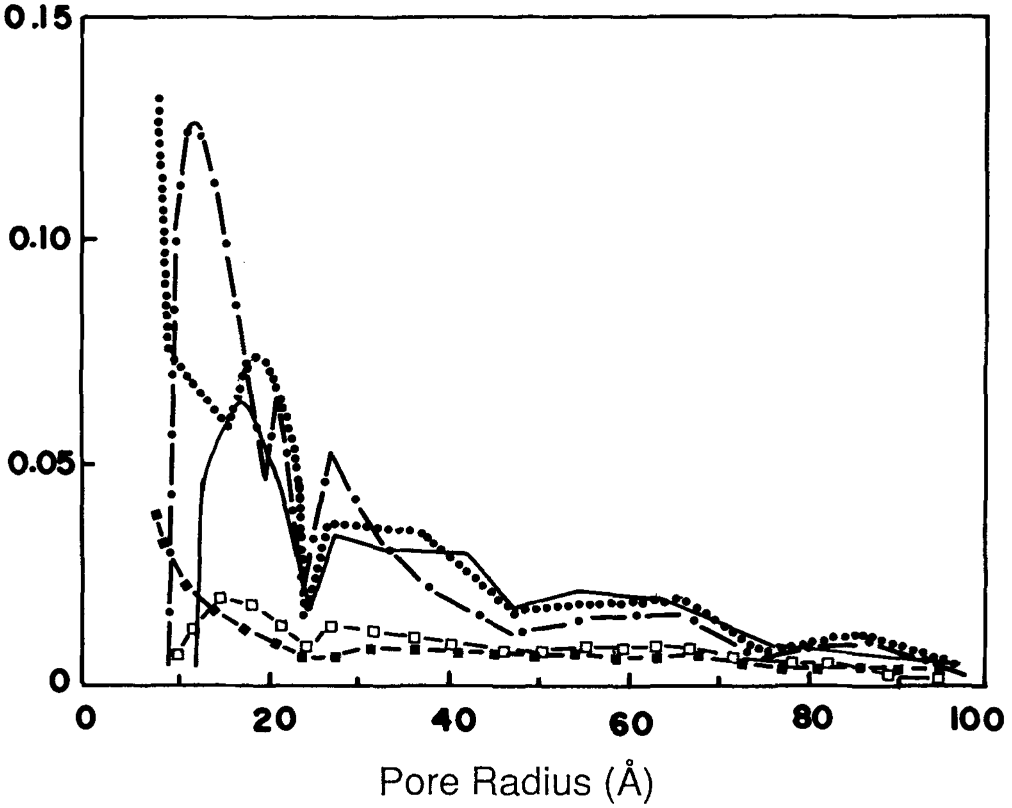

FIG. 1. Pore size distribution curves of adsorbents: □—□, Montmorillonite No. 1; ● ● ● ● ●, sepiolite No. 2; —, sepiolite No. 3; ■—■, sepiolite No. 5; and ●—●, standard activated clay.

specific surface area and acidity data suggest that amounts adsorbed on sepiolites and standard activated clay were mainly dominated by acidity rather than by specific surface area.

Figure 1 shows the differential pore volume *vs.* pore radius of adsorbents used. The fact that the cross-sectional dimensions of monomeric carotene and chlorophyll contained as pigments in the alkali-refined oils are *ca.* 7 × 31 Å and 12 × 15 Å, respectively (7), indicates that carotene and chlorophyll molecules can partially or wholly enter the pores with radii of 10 Å or less, as shown in Figure 1. However, the relation between amounts adsorbed on sepiolite No. 2 and standard activated clay and their pore volumes in the region up to 10 Å does not support the above indication. According to Taylor *et al.* (7), the restricted pore volume in the region of radii 25–100 Å is responsible for adsorption of the pigments. Adsorption in pores is dependent on the ratio of the pore diameter to the molecular diameter of the adsorbate (8). The desirable ratio for adsorption is *ca.* 2 to 10 because of the steric effects of adsorbate (9). According to the desirable ratio, the pores' radii suitable for adsorption are 7–31 Å to 35–155 Å for carotene or 12–15 Å to 60–75 Å for chlorophyll. From our results of amounts adsorbed, differential pore volume and the desirable ratio, the pore volume in the region of pore radii 25–100 Å reported by Taylor *et al.* (7) seems to be responsible for adsorption of the pigments. However, the large differences in amount adsorbed on sep-

TABLE 2

Langmuir Isotherm Constants for Adsorption of Pigments on Bleaching Media at 110°C

	Rapeseed		Soybean		Wheatgerm		Safflower		Corn		Cottonseed		Sunflower	
Adsorbent	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Montmorillonite No. 1	—	—	0.31	−14.09	—	—	—	—	—	—	—	—	—	—
Sepiolite No. 2	14.29	1.40	—	—	7.14	1.00	14.29	2.33	—	—	—	—	14.29	1.40
Sepiolite No. 3	5.56	6.00	4.76	5.25	11.11	1.50	20.00	1.67	—	—	—	—	—	—
Sepiolite No. 5	2.38	2.80	3.57	0.78	1.59	2.52	3.57	2.55	3.33	1.03	2.70	1.95	2.50	4.00
Standard activated clay	20.00	0.00	—	—	—	—	—	—	—	—	—	—	—	—

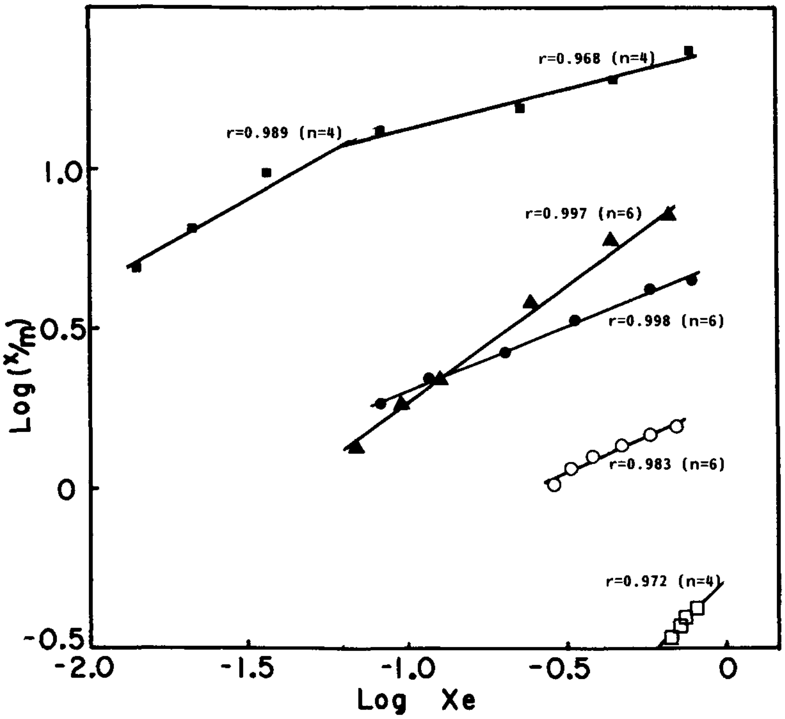

FIG. 2. Freundlich isotherms for adsorption of pigments on adsorbents for rapeseed oil at 110°C: □—□, Montmorillonite No. 1; ▲-▲, sepiolite No. 2; ●—●, sepiolite No. 3; ○—○, sepiolite No. 5; and ■—■ standard activated clay.

iolites and standard activated clay seem to be largely caused by the number of acid sites of the highest acid strength (−5.6 ∿ −3.0) distributed within the restricted pores.

Adsorption isotherm. The constants in Langmuir and Freundlich equations are useful in the design of adsorption process equipment (2). The Langmuir equation is $X_e/(X/m) = 1/ab + X_e/a$, where a and b are constants. The constants are shown in Table 2. The data were obtained from the adsorption isotherms, for which the correlation coefficient of Langmuir plots was 0.917 or higher (n=6, $p < 0.01$). The Langmuir equation could not be applied easily to the isotherms on montmorillonite and standard activated clay.

The Freundlich equation is $\log(X/m) = \log k + 1/n \log X_e$, where k and n are the constants calculated from the intercept and the slope, respectively, of the Freundlich isotherm. Figures 2–8 show the Freundlich isotherms for adsorption of pigments on clay minerals from rapeseed, soybean, wheatgerm, safflower, corn, cottonseed and sunflower oils, respectively, at 110°C. The Freundlich constants are summarized in Table 3. The adsorption isotherms of pigments on standard activated clay had an inflection, whereas the others formed a straight line. The inflection points of standard activated clay for the alkali-refined oils were in the range of $\log X_e = -1.0 \sim -0.5$. The equilibrium concentration (X_e) of the inflection points for rapeseed, soybean and wheatgerm were 0.061, 0.080 and 0.134, respectively, as shown in Figures 2–4. The higher the relative content of pigments in alkali-refined oils (4), the more dilute the equilibrium concentration was at the inflection point. Kulkarni and Jatkar (10,11) reported that the inflection in the Freundlich adsorption isotherm of coloring matter by Fuller's earth in safflower oil was attributed to physical adsorption at low color concentration and chemical adsorption chiefly at higher levels. According to the potential theory of Polanyi the

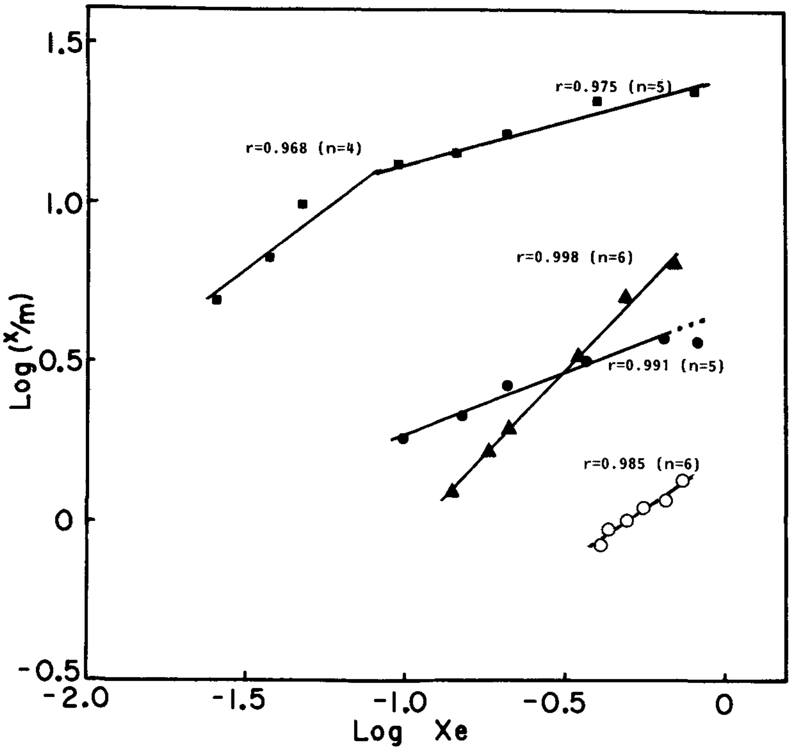

FIG. 3. Freundlich isotherms for adsorption of pigments on adsorbents for soybean oil at 110°C: ▲-▲, Sepiolite No. 2; ●-●, sepiolite No. 3; ○-○, sepiolite No. 5; and ■-■, standard activated clay.

TABLE 3

Freundlich Isotherm Constants for Adsorption of Pigments on Bleaching Media at 110°C

	Rapeseed		Soybean		Wheatgerm		Safflower		Corn		Cottonseed		Sunflower	
Adsorbent	n	k	n	k	n	k	n	k	n	k	n	k	n	k
Montmorillonite No. 1	1.03	0.52	—	—	1.23	0.51	1.71	1.09	1.32	0.87	1.61	0.72	1.64	0.77
Sepiolite No. 2	1.37	10.27	0.93	10.25	1.41	3.86	1.41	13.06	1.11	6.30	1.00	8.56	1.39	9.75
Sepiolite No. 3	2.50	5.10	2.56	4.59	1.41	7.99	1.28	16.65	0.74	17.62	0.93	16.97	1.14	16.82
Sepiolite No. 5	2.17	1.89	1.43	1.62	2.38	1.18	1.75	3.11	1.54	1.77	1.85	1.93	2.44	2.21
Standard activated clay	1.79 4.09[a]	55.82 23.31[a]	1.33 3.75[a]	81.65 24.09[a]	0.81 2.51[a]	147.68 27.31[a]	0.98	159.56	0.29	3310.39	0.72	170.07	0.80	188.23

[a] The constants were calculated in the ranges of about log $X_e = -1.0 \sim 0$ in Figures 2, 3 and 4.

filling of adsorbent pores with adsorbate takes place in the smallest pores first and then sequentially in larger ones. In the adsorption of sodium dodecylbenzene sulfonate on activated carbon, the pores with 10 Å, 15 Å and 20 Å radii were successively filled with dodecylbenzene sulfonate in that sequence as the adsorption proceeded (13). It is also suggested that adsorption takes place in small pores at low concentrations and that adsorption is accelerated in larger pores after the smaller ones are saturated as the concentration increases (13). Our results of deviation from Freundlich isotherms on standard activated clay can also be explained by assuming that the pigments were eccentrically adsorbed into the smaller pores at low equilibrium concentration and then into the larger pores at a higher concentration. A possible explanation for the fact that a larger relative amount of pigments contained in the alkali-refined oils results in a more dilute equilibrium concentration at the inflection point could be that the pore volume of smaller pores of standard activated clay responsible for adsorption is restricted. The value of the slope, 1/n, which gives a measure of the intensity of adsorption (14), was larger in the low-concentration region rather than in the higher-concentration region. The fact that no inflections were observed in the Freundlich isotherms for montmorillonite and sepiolites may be interpreted as being due to the adsorption in the narrow restricted region of pores.

The adsorption isotherms on sepiolites No. 2 and No. 3 interesected at log $X_e = -0.9$ for rapeseed oil and at log $X_e = -0.5$ for soybean oil. Amounts adsorbed on sepiolite No. 2 were larger than those on sepiolite No. 3 at concentrations above each intersection for rapeseed and

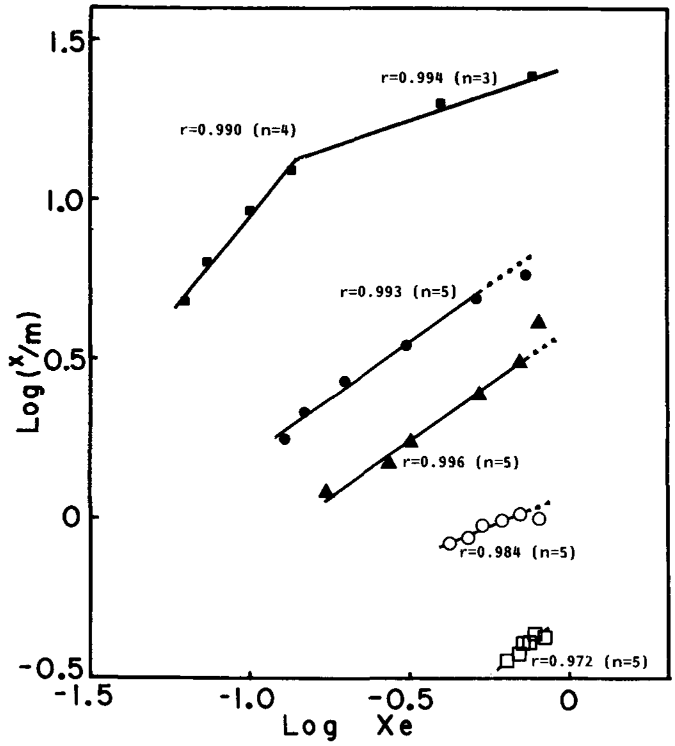

FIG. 4. Freundlich isotherms for adsorption of pigments on adsorbents for wheatgerm oil at 110°C: □-□, Montmorillonite No. 1; ▲-▲, sepiolite No. 2; ● - ●, sepiolite No. 3; ○-○, sepiolite No. 5; and ■-■, standard activated clay.

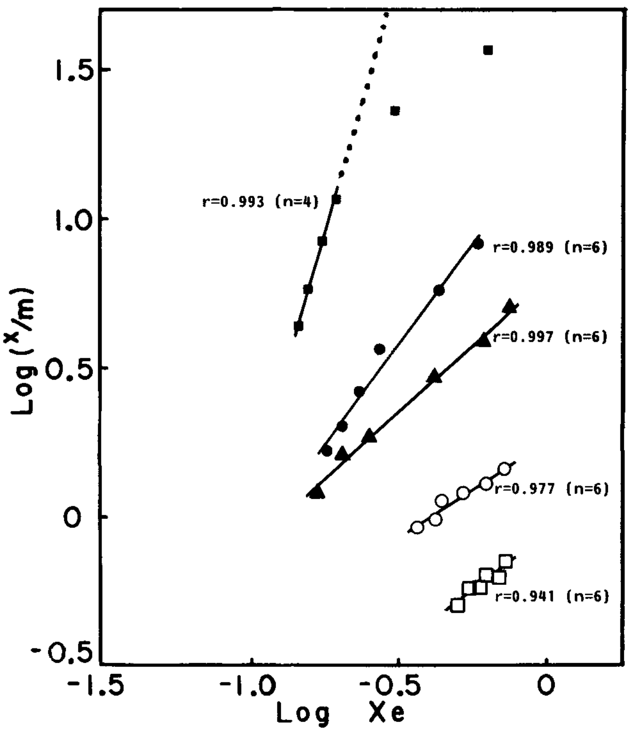

FIG. 6. Freundlich isotherms for adsorption of pigments on adsorbents for corn oil at 110°C. Key as in Figure 4.

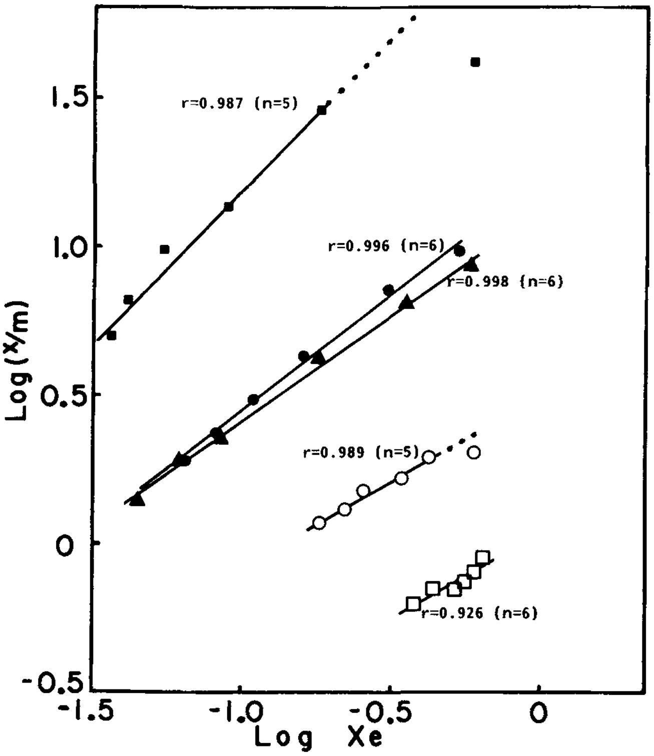

FIG. 5. Freundlich isotherms for adsorption of pigments on adsorbents for safflower oil at 110°C. Key as in Figure 4.

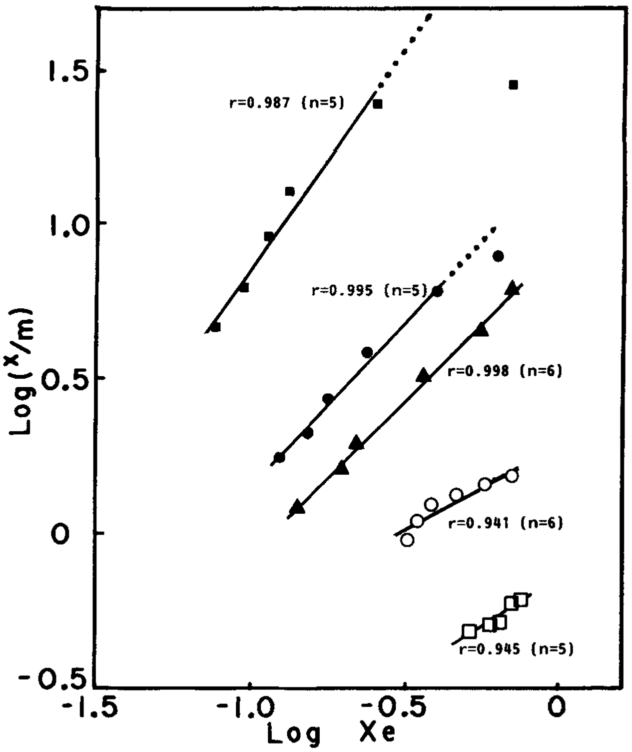

FIG. 7. Freundlich isotherms for adsorption of pigments on adsorbents for cottonseed oil at 110°C. Key as in Figure 4.

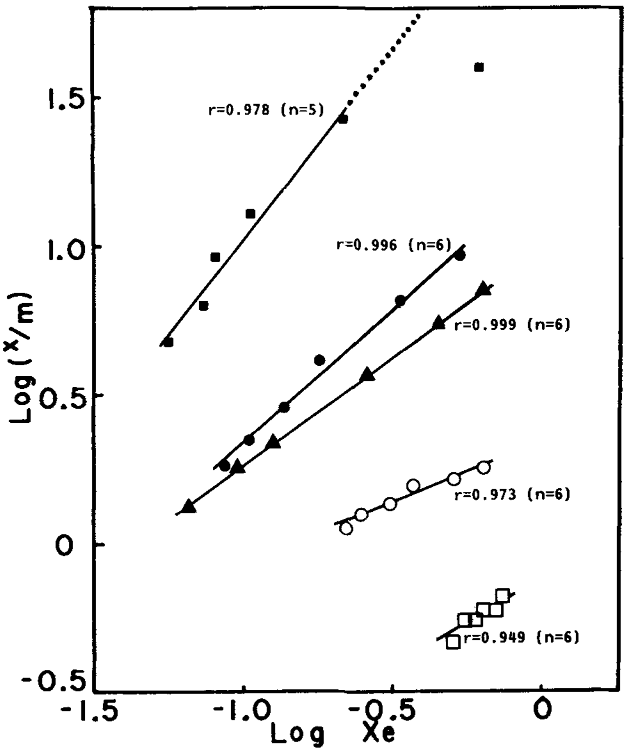

FIG. 8. **Freundlich isotherms for adsorption of pigments on adsorbents for sunflower oil at 110°C. Key as in Figure 4.**

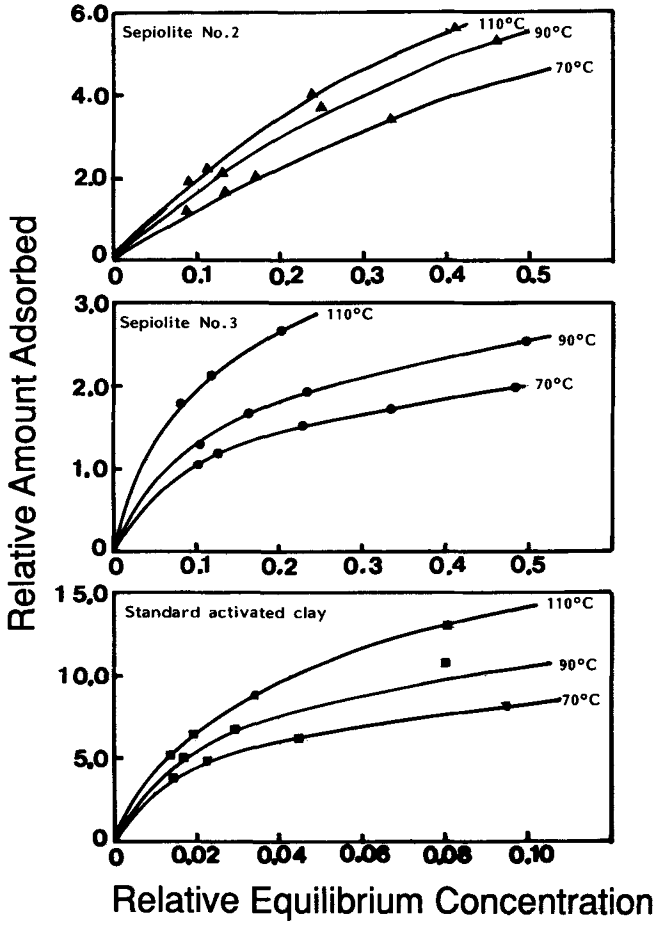

FIG. 9. **Adsorption isotherms of pigments on adsorbents for rapeseed oil at different temperatures.**

TABLE 4

Isosteric Heat of Adsorption of Pigments on Adsorbents for Rapeseed and Soybean Oils

	Isosteric heat of adsorption (kcal/mol)	
Adsorbent	Rapeseed	Soybean
Sepiolite No. 2	2.3–3.2	6.5–7.2
Sepiolite No. 3	3.1–8.6	7.6–9.2
Standard activated clay	2.6–7.8	1.7–2.5

soybean, while the inequality of amounts adsorbed on them were reversed for other oils. The isotherms on sepiolites No. 3 and No. 2 were parallel to each other for wheatgerm and cottonseed oils. The isotherms on sepiolites No. 3 and No. 2 for safflower, corn and sunflower intersected at lower equilibrium concentrations. The intersection and parallel direction of isotherms and the reversal of amounts adsorbed on sepiolites No. 2 and No. 3 for different kinds of alkali-refined oils may be attributed to triglyceride competition (1), oil molecule interference (2) or free fatty acid occupation (4,15).

Effect of temperature on adsorption. Adsorption isotherms of pigments from rapeseed oil and soybean oil on sepiolites No. 2 and No. 3 and on standard activated clay at 70°C, 90°C and 110°C are shown in Figure 9 and Figure 10, respectively. A substantial increase in relative amount adsorbed on the adsorbents was observed as the temperature was increased from 70°C to 110°C. This can be attributed to activation of more adsorption sites on the adsorbents at higher temperatures (2). According to the adsorption of gas, the amount adsorbed physically decreases and chemical adsorption increases with rise in temperature (14). The isosteric heat of adsorption was calculated to elucidate the adsorption nature of pigments on the clays by applying a Clausius-Clapeyron equation (5) [$\partial \ln(X/m)/\partial(1/T)$] $\sim$ Q/R to the data of Figures 9 and 10, where T is the absolute temperature, R is 1.987 cal/deg•mol and Q is the heat of adsorption. The fact that heats of adsorption were below 10 kcal/mol (Table 4) suggests that pigments were physically adsorbed on sepiolites No. 2 and No. 3 and on standard activated clay at temperatures from 70°C to 110°C. It was previously reported that there was no shift in the absorbance maximum of pigments in the alkali-refined oils at continuous absorbance of 400 nm to 700 nm when mixed with the clay minerals (4). No shift in the absorbance indicates purely physical adsorption (16). The results of heat of adsorption were consistent with our previous results (4). Enthalpy changes in the extraction of rubber and melon seed oils were in the range of 4–13.5 kJ/mol, indicating the physical nature of pigment extraction by a solvent (3). It was therefore concluded that pigments were physically adsorbed on the stronger acid sites in the restricted pores of the clays through the bleaching process.

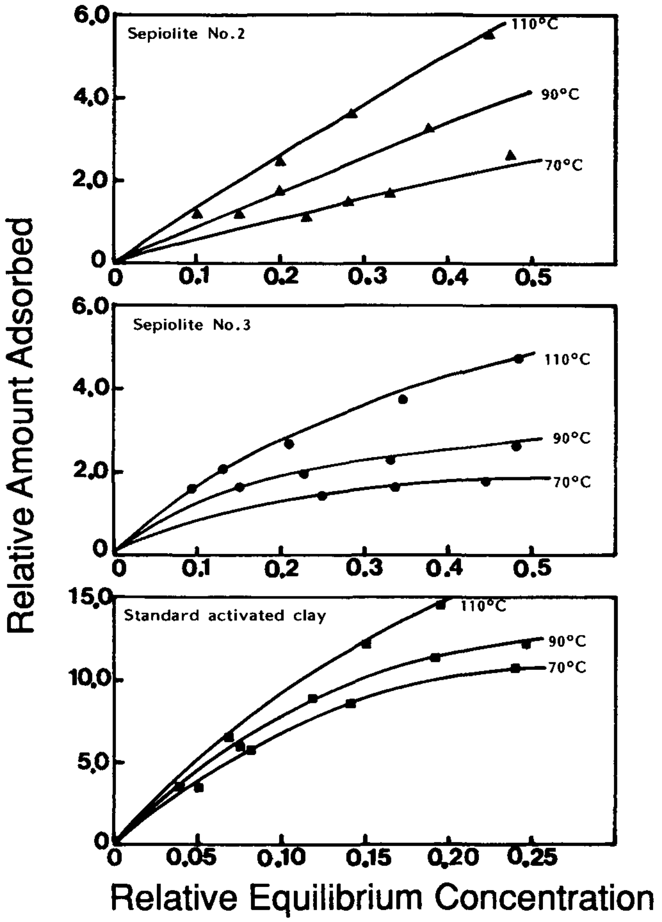

FIG. 10. Adsorption isotherms of pigments on adsorbents for soybean oil at different temperatures.

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