

The Adsorption of Cholesterol and Egg-Lecithin from Solutions on Active Carbon

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Synopsis. The adsorption isotherms of cholesterol from ethanol and cyclohexane (at 25 and 35°C), and of egg-lecithin from ethanol and ethanol-water mixed solvent (at 25°C) onto active carbon have been determined. The isotherms can be represented by Dubinin-Radushkevich equation. The results indicate that the adsorption of cholesterol and lecithin from solutions onto active carbon can be explained by the mechanism of micropore filling.

The model biological membrane is of great theoretical and practical importance. The model lipid monolayer formed on solid surface by adsorption method has been studied by Poltorak and Chukhrai,¹⁾ Kamyshnyi et al.,²⁾ Benko et al.³⁾ Tamamushi⁴⁾ studied the adsorption of lipids from solutions. The adsorbents used in these studies were mostly nonporous or had macro-pores. In the present work the adsorption of cholesterol and lecithin from ethanol, cyclohexane, and ethanol-cyclohexane mixtures on active carbon has been studied. The effect of solvents on the adsorption and the mechanism of the adsorption are discussed.

The egg-lecithin was extracted from egg yolk. The MS analysis showed that the molecular weight of the egg-lecithin obtained was 701. The purity of the egg-lecithin was examined by means of thin-layer chromatography. Pure cholesterol was supplied by E. Merck Co. The melting point was 148.5°C, in agreement with literature.⁵⁾ The granular active carbon GH was supplied by Guang Hua Wood Factory and was treated further with acetic acid and hydrofluoric acid repeatedly. The excess acids were washed out with hot water and finally the active carbon was dried in air at 120°C. The BET surface area from the N₂ adsorption method was 1410 m²·g⁻¹, the pore volume was 0.609 cm³·g⁻¹ by the saturated CCl₄ vapor adsorption method, and the average pore radius was 8.6 Å.

The adsorption experiments were carried out with a shaker-bath, at 25 or 35°C (±0.5°C), using 25 cm³ flasks, with 0.1g active carbon samples, 10.0 cm³ solution and a 24 h shaking time (previous experiments showed that equilibrium was achieved within 12 h). After settling, the supernatant liquid was analyzed by UV absorption. The adsorbed amount (a g·g⁻¹) was calculated according to

$$a = \frac{V\Delta C}{m},$$

where ΔC (g·dm⁻³) is the change in concentration of solute caused by adsorption, V is the total volume of solution, and m is the mass of adsorbent.

The adsorption isotherms of cholesterol from the solution of ethanol and cyclohexane (both at 25 and 35°C), and of lecithin from ethanol and mixed solvent

of ethanol-water (volume ratio 4:1) (at 25°C) are plotted in Figs. 1 and 2, respectively. Figure 1 shows that the adsorbed amount of cholesterol from ethanol is smaller than that from cyclohexane in the experimental concentration range. Figure 2 shows that the adsorbed amount of lecithin from the mixed solvent is smaller than that from ethanol when the concentration is higher than 2 g·dm⁻³.

For porous adsorbents, particularly active carbon with micropores whose radius is smaller than 1 nm, the effect of increasing adsorption potentials as a result of overlapping of the fields of opposite walls of the pores is prominent. The characteristic adsorption isotherm due to Dubinin and Radushkevich,⁶⁾ which

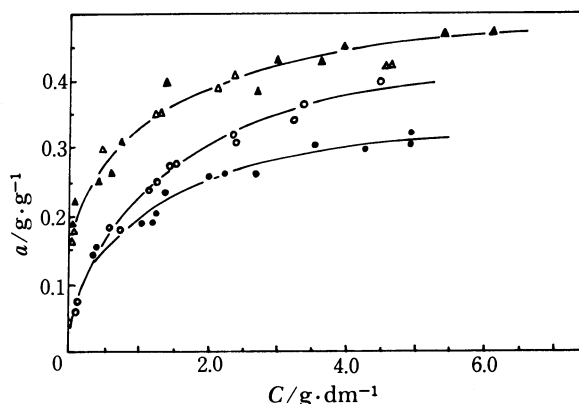


Fig. 1. Adsorption isotherms of cholesterol from ethanol (○, 25°C; ●, 35°C) and cyclohexane (Δ, 25°C; ▲, 35°C) on active carbon GH.

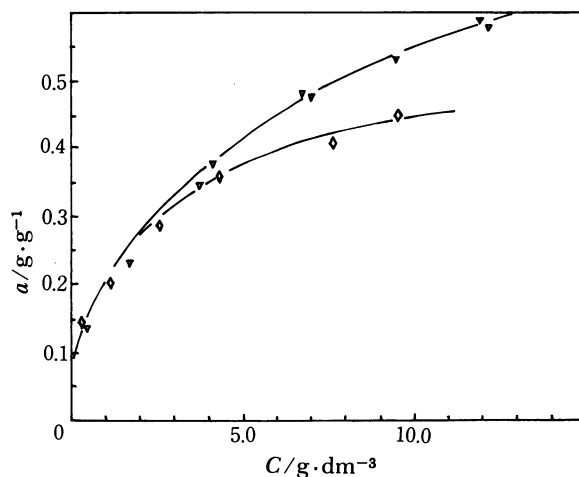


Fig. 2. Adsorption isotherms of egg-lecithin from ethanol (▽, 25°C) and ethanol-water (volume ratio 4:1) mixed solvent (◇, 25°C) on active carbon GH.

Table 1. Adsorption of Cholesterol and Lecithin on Active Carbon GH

Adsorbate	Cholesterol				Lecithin	
	Ethanol		Cyclohexane		Ethanol	Ethanol-water
Solvent						
Temperature/°C	25	35	25	35	25	25
Pore volume of the adsorbent, $W_0/\text{ml} \cdot \text{g}^{-1}$	0.609	0.609	0.609	0.609	0.609	0.609
Maximum volume of adsorbed solute, $W_m/\text{ml} \cdot \text{g}^{-1}$	0.439	0.356	0.498	0.492	0.573 ^{a)}	0.454
W_m/W_0	0.72	0.58	0.82	0.81	0.94	0.75

a) This value is calculated from maximum adsorbed amount, as the solubility data are not available.

was later modified by Dubinin and Zaverina,⁷⁾ can be written in the form,

$$\ln W - \ln W_0 = -A\varepsilon^2, \quad (1)$$

where W is the volume of adsorbed substance, W_0 is the total volume of adsorption space that represents the volume of micropores of the active carbon, parameter the A is a kind of distribution function of volume of the pores according to sizes, and ε is the Polanyi potential. According to the Polanyi theory of adsorption, ε is the work required to transfer a molecule from the gas phase at pressure P to the liquid phase at saturated pressure P_0

$$\varepsilon = kT \ln(P_0/P), \quad (2)$$

and k is the Boltzmann constant. Relationship 1, which is known as the DR equation,⁸⁾ together with its extension,⁹⁾ is used to describe pore filling as pressure increases. When dealing with the adsorption from solutions, the DR equation can be written as

$$\log a - \log a_m = -B \left(\log \frac{C_0}{C} \right)^2, \quad (3)$$

where a and a_m are the amount and maximum amount of the adsorbed substance, respectively, C and C_0 are the equilibrium concentration and saturated concentration of adsorbate, respectively, and B is a constant. A plot of $\log a$ against $(\log C_0/C)^2$ should give a straight line with an intercept $\log a_m$ and a slope $-B$, from which the two constant a_m and B can be evaluated.

Figure 3 gives the plots illustrating the applicability of the DR equation to the adsorption of cholesterol and lecithin from solution on active carbon. It should be noted that the constant B in Eq. 3 depends not only on the adsorbent but also on the solute and solvent. The maximum volume of the adsorbed solute, W_m , can be calculated from a_m and the density of the solute. Table 1 shows that the maximum adsorbed volume of cholesterol and lecithin from solutions are 58–82% and 75–94% of the total pore volume of the adsorbent, respectively. Obviously, the rest of the pore volume should be filled with the solvent. Similar results have been obtained by Koganovskii and Levchenko¹⁰⁾ for the adsorption of 1-propanol, 1-butanol, and 1-hexanol from aqueous solution onto active carbon.

It is well-known that the adsorption of the solute must be accompanied by a displacement of the solvent.

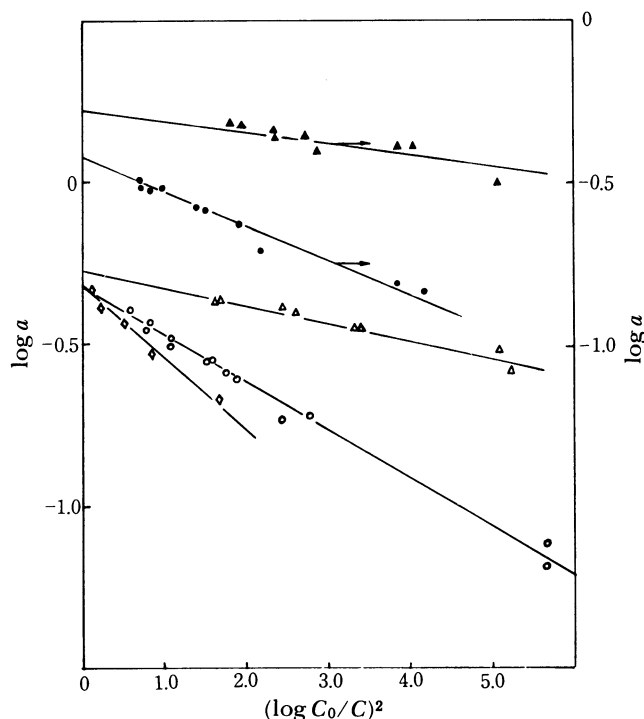


Fig. 3. Adsorption isotherms of cholesterol and lecithin from solutions on active carbon GH, Legend as in Figs. 1 and 2.

Based on the thermodynamics, the free energy of this displacement becomes progressively greater as the interface interaction and the number of solvent molecules on the surface and in the pore space becomes less.¹¹⁾ In other words, the solvent molecules cannot be completely displaced from the solid surface (pore space).

It should be noted that one of the main reasons for the failure of attempts to predict W_m has been the failure to account for solvent remaining in the adsorbed phase. Only when the solubility of the solute in solvent or the miscibility of the solute with solvent is very low and the interaction between the solute and solid surface is very strong, the maximum adsorption volume of solute should be approximately equal to the pore volume of adsorbent. An example is the adsorption of *p*-chlorophenol, *p*-chloroaniline, nitrobenzene, chloroform, and benzene from aqueous solution onto active carbon by Koganovskii et al.¹²⁾

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