

## Adsorption of Solute from the Solutions. V.<sup>1)</sup> Adsorption Rate of Cyanocobalamin on Talc

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For the lubrication of cyanocobalamin preparations in the tablet compression, talc has not been recommended because it adsorbs the vitamin and consequently interferes with its intestinal absorption and assay.<sup>3)</sup> However, there has been no knowledge about the rate at which cyanocobalamin is adsorbed. In the present work, the velocity and activation energies for adsorption and desorption of the vitamin on talc from aqueous solutions are investigated.

The adsorption of cyanocobalamin on talc from buffer solutions has been reported to obey to the Langmuir isotherm equation.<sup>4)</sup> Accordingly, from the assumptions with which the Langmuir equation is derived, the overall adsorption velocity may be shown as

$$dx/dt = k(a-x)(n-x) - k'x \quad (1)$$

where  $a$  is the initial vitamin concentration of the solution,  $x$  the amount of the adsorbed vitamin at the time  $t$  after the start,  $n$  the saturated amount, and  $k$  and  $k'$  are the rate constants of adsorption and the desorption, respectively. The amount of talc was fixed to be 40 g liter<sup>-1</sup>, the and the unit of mole liter<sup>-1</sup> was used for  $a, n$ , and  $x$  for the convenience of calculations. For  $n$ , the value previously obtained<sup>4)</sup> was utilized. In the equilibrium state in which  $dx/dt=0$ ,  $k'$  may be given from Eq. (1) by

$$k' = k(a-x_e)(n-x_e)/x_e \quad (2)$$

where  $x_e$  is the equilibrium amount of the adsorbed vitamin. Substituting Eq. (2) into Eq. (1), and then integrating the resultant equation with the consideration that  $x=0$  when  $t=0$ , we obtain

$$\frac{1}{B} \log \frac{(A-B)(A+B-2x)}{(A+B)(A-B-2x)} = \frac{kt}{2.303} \quad (3)$$

In this equation,  $A \equiv a + n + (a-x_e)(n-x_e)/x_e$  and  $B \equiv (A^2 - 4an)^{1/2}$ .

The plots of  $(1/B) \log \{(A-B)(A+B-2x)/(A+B)(A-B-2x)\}$  against  $t$  at 10° and 30° in

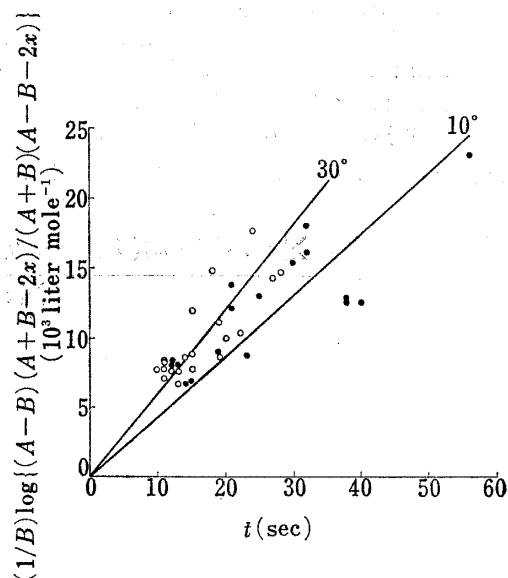


Fig. 1. Plots of  $(1/B) \log \{(A-B)(A+B-2x)/(A+B)(A-B-2x)\}$  vs.  $t$

O: at 30°    ●: at 10°

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- 2) Location: *Hatanodai, Shinagawa-ku, Tokyo.*
- 3) J. Dony and J. Conter, *J. Pharm. Belg.*, **11**, 338 (1956); C. Trolle-Lassen, *Arch. Pharm. Chemi*, **67**, 504 (1960).
- 4) I. Moriguchi and N. Kaneniwa, *Chem. Pharm. Bull.* (Tokyo), **17**, 394 (1969).

0.1M tartrate buffer solution of pH 4.0 with  $10^{-4}\text{M}$  of initial vitamin concentration are shown in Fig. 1. The slopes of the graph were determined by the method of least squares. From the slopes,  $k$  was evaluated by using Eq.(3), and then  $k'$  was obtained from Eq.(2). These values are listed in Table I.

TABLE I. Rate Constants of Adsorption and Desorption of Cyanocobalamin on Talc<sup>a)</sup> at pH 4.0

Temperature (°C)	$k$ liter mole <sup>-1</sup> sec <sup>-1</sup>	$k'$ sec <sup>-1</sup>
10	$1.38 \times 10^3$	$5.91 \times 10^{-2}$
30	$1.01 \times 10^3$	$2.02 \times 10^{-2}$

a) 40 g liter<sup>-1</sup>

From these values and the temperatures, the activation energies for the adsorption and the desorption were evaluated to be 1.16 and 3.98 kcal mole<sup>-1</sup>, respectively, by using the Arrhenius equation. It may be indicated that cyanocobalamin is energetically more stable in the adsorbed state than free in the solution because the activated states for the adsorption and the desorption are considered to be identical.

### Experimental

**Materials**—All the materials used were same as previously described.<sup>4)</sup>

**Adsorption Experiment**—Talc (400 mg) was suspended in 10 ml of  $10^{-4}\text{M}$  cyanocobalamin solution in 0.1M tartrate buffer of pH 4.0, and shaken vigorously in a thermostat at 10° and 30° for various times. Then the solution was immediately filtered, and subjected to measurement. The loss in concentration by the filtration was negligible.

**Determination of Cyanocobalamin**—Cyanocobalamin was determined spectrophotometrically by the method as previously described.<sup>4)</sup>

**Least Square Method Calculation**—The slope ( $m$ ) of the plot of  $(1/B)\log\{(A-B)(A+B-2x)/(A+B)(A-B-2x)\}$  vs.  $t$  was determined so that the value of  $\sum_i [(1/B)\log\{(A-B)(A+B-2x_i)/(A+B)(A-B-2x_i)\} - mt_i]^2$  might be minimized. The actual calculation was made as

$$m = \frac{\sum_i t_i \log\{(A-B)(A+B-2x_i)/(A+B)(A-B-2x_i)\}}{B \sum_i t_i^2}$$