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Diffusion of Vitamin B12 Across a Mesoporous Metal Organic Framework

Veronica Valencia

University of South Florida, veronica8@mail.usf.edu

Advisors:

Thomas Bieske, Mathematics and Statistics


Shengqian Ma, Chemistry

Yao Chen, Chemistry

Scott Campbell, Chemical & Biomedical Engineering

Problem Suggested By: Shengqian Ma

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Diffusion of Vitamin B12 Across a Mesoporous Metal Organic Framework

Abstract

We measure the rate of uptake and the rate of release of a Vitamin B12 solution (dissolved in water) at 2 different temperatures (room temperature and 37°C) by the mesoporous metal organic framework TbMOF-100 at 1-hour intervals using a spectrophotometer. Using the Beer-Lambert law, we calculate the concentration of the stock solution based on the absorbance values obtained with the spectrophotometer. These values allow for the quantification of the initial rate of uptake and the rate of uptake at a random incubation time of the Vitamin B12 by the TbMOF-100. We also calculate the value of the coefficient of diffusion for this 2-phase system using Fick's laws of diffusion.

Keywords

Diffusion, Fick's Laws of Diffusion, Beer-Lambert Law

PROBLEM STATEMENT

Study the kinetics of diffusion of biomolecules into new types of porous materials at different temperatures. Consider the initial rate of uptake, the diffusion rate, and the coefficient of diffusion for a 2-phase system consisting of TbMOF-100 and Vitamin B12 solution.

MOTIVATION

Porous metal–organic frameworks (MOFs) are highly crystalline inorganic–organic hybrids, and they are constructed by assembling metal ions or metal-containing clusters known as secondary building units (SBUs) with multidentate organic ligands via coordination bonds into a three-dimensional structure. The research experiment conducted dealt with the applications of MOFs for biocatalysis, which according to the New Zealand Institute of Chemistry, can be broadly defined as the use of biological molecules usually enzymes to catalyze specific chemical reactions (Chowdhury, Hill and Whittaker). Due to their high porosity and nanospace inside the framework, MOFs show great promise in the field of biocatalysis as these mesoporous complexes can encapsulate proteins, enzymes, and vitamins within the framework. A study of the diffusion of vitamins into metal-organic frameworks is relevant, because it provides information that is necessary to determine the efficiency of encapsulating the vitamin within the mesoporous structure. A calculation of the diffusion coefficient of this two-phase system provides conclusive data on the rate of diffusion of the vitamin into the MOF structure.

MATHEMATICAL DESCRIPTION AND SOLUTION APPROACH

To calculate the initial rate of uptake and the diffusion rate, the absorbance values calculated experimentally, were converted to actual concentrations according to the Beer-Lambert Law:

$$A = \epsilon lc \quad (1)$$

Where A is the absorbance, l is the path length (equal to 1cm), ϵ is the molar absorptivity constant ($2.65 \times 10^4 \frac{L}{\text{Mol}\cdot\text{cm}}$), and c is the concentration in Moles. Table 1 below provides both the absorbance values collected during the experiment, as well as the concentration of the solution calculated using the Beer-Lambert Law.

Incubation Time (in hours)	Vitamin B12 Solution Absorbance	Vitamin B12 Solution concentration (in mM)
0	0.5919	2.23
1	0.5057	1.91
2	0.5061	1.91
3	0.4715	1.78
4	0.4684	1.77
5	0.4406	1.66
6	0.4350	1.64
19.3	0.3451	1.3

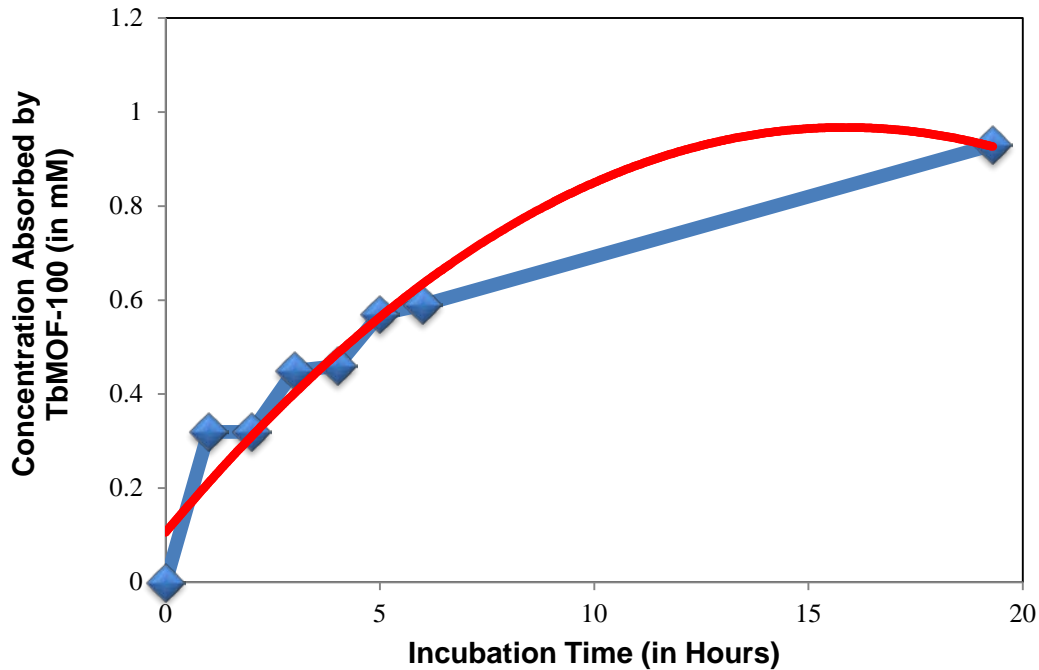
Table 1: Vitamin B12 Solution Absorbance and Concentration

Incubation Time (in hours)	Concentration absorbed by TbMOF-100 (in mM)
0	0
1	0.32
2	0.32
3	0.45
4	0.46
5	0.57
6	0.59
19.3	0.93

Table 2: Concentration Absorbed by TbMOF-100

Moreover, it was necessary to calculate the concentration absorbed by the TbMOF-100 at each time interval. The results are summarized in Table 2.

We plot the data in Table 2 and determine a polynomial approximation for the line of best fit.



Plot 1: Measured (blue) TbMOF-100 uptake profile of Vitamin B12 and best-fit parabola (red)

The equation for the best-fit parabola pictured in Plot 1 is given by:

$$F(x) = -0.0034 x^2 + 0.1086 x + 0.1063 \quad (2)$$

where x is incubation time in hours. Using (2) it is now possible to determine both the initial rate of reaction and the instantaneous reaction rate at any given time. The shape of the above graph suggests that initial reaction rate is fairly constant over the first few hours; therefore the initial rate of the reaction can be calculated by differentiating (2) and evaluating $F'(x)$ at one of the initial data points. Differentiating (2) yields:

$$F'(x) = -0.0068 x + 0.1086 \quad (3)$$

For our purposes we used the data point (3,0.45), thus the initial rate of uptake is given by:

$$F'(3) = 0.0881 \text{ mM/hour} \quad (4)$$

The reaction rate at a given point in the uptake profile can be calculated in a similar manner. For example, the reaction rate at 7 hours of incubation time is determined by:

$$F'(7) = 0.0607 \text{ mM/hour} \quad (5)$$

According to the book *Transport Phenomena in Biological Systems*, “the diffusion coefficient of a molecule diffusing through a mesoporous structure can be found from measurements of the concentration of the solution as a function of time” (Chowdhury, Hill and Whittaker). The measurements are fit to a model for diffusion from a well-mixed bath into a sphere of radius R . In this model, we assume that the geometrical structure of the TbMOF-100 is a sphere, which in reality is not, as can be seen from Figure 1 below.

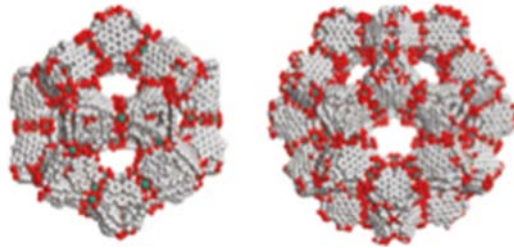


Figure 1: Molecular structure of TbMOF-100

An approximation of the true value of the diffusion coefficient for this 2-phase system can be calculated through the use of the following formula:

$$\theta_t = \frac{\beta}{\beta+1} + \sum_{i=1}^{\infty} \frac{6\beta e^{-\lambda_i^2 \tau}}{9(1+\beta) + \beta^2 \lambda_i^2} \quad (6)$$

In this model, the equation has been cast in dimensionless form through the use of Laplace transforms. The variables in this equation are defined as follows:

$$\theta_f = \frac{C_t}{C_0}, \quad \beta = \frac{V_f}{\phi V_b}, \quad \text{and} \quad \tau = \frac{t D_{eff}}{R^2} \quad (7)$$

where C_t is the concentration in the solution in water at time t , C_0 is the initial concentration of the Vitamin B12 solution, V_f is the volume of the solution, V_b is the volume of the TbMOF-100

crystals, D_{eff} is the diffusion coefficient of the solution, and R is the radius of the crystal structure. In this case we assume Φ , the partition coefficient, is equal to 1. Furthermore, in this model, λ_i are the solutions to the equation:

$$\tan \lambda_i = \frac{3\lambda_i}{3+\beta\lambda_i^2}. \quad (8)$$

Once β is determined, λ_i can be found as the zeros of the function

$$G(s) = \tan(s) - \frac{3s}{3+\beta s^2}. \quad (9)$$

From (6) and (7) we get

$$\frac{C_t}{C_o} = \frac{V_f/V_b}{V_f/V_b+1} + \sum_{i=1}^{\infty} \frac{6\left(\frac{V_f}{V_b}\right) e^{(-\lambda_i^2 \frac{tD_{eff}}{R^2})}}{9\left(1+\frac{V_f}{V_b}\right) + \left(\frac{V_f}{V_b}\right)^2 \lambda_i^2}. \quad (10)$$

and as $t \rightarrow \infty$, $e^{-\lambda_i^2 \frac{tD_{eff}}{R^2}} \rightarrow 0$, thus when the system reaches equilibrium the infinite sum on the right hand side tends towards zero, so $\theta_t \approx \frac{\beta}{\beta+1}$. We assume that the concentration after 19.3

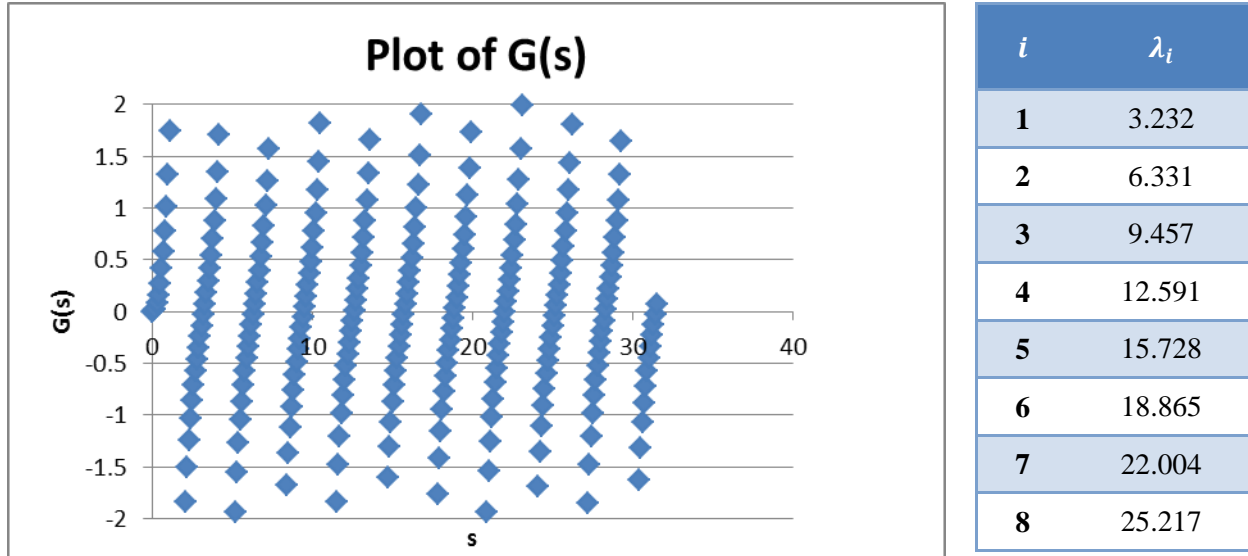
hours of incubation is the same as the concentration at equilibrium. This gives:

$$\frac{1.3mM}{2.23mM} = \frac{\beta}{\beta+1}. \quad (11)$$

And we conclude that

$$\beta = 1.39785 \quad (12)$$

which allows us to use $G(s)$ from (9) to find the values of λ_i . The plot of $G(s)$ shows the different values for λ_i and the values are given in Table 3.



Plot 2: Numerical plot of $G(s)$ as defined by Equation (9) and table of the first few approximations of $G(s) = 0$.

Now with the value of β we are in position to use (10) to calculate D_{eff} . Substituting for the known constants in (10) and using the data collected after 3 hours of incubation we have:

$$\frac{1.78 \text{ mM}}{2.23 \text{ mM}} = \frac{1.39785}{1.39785+1} + \sum_{i=1}^{\infty} \frac{6(1.39785)e^{(-\lambda_i^2 \frac{(3)D_{eff}}{(100 \text{ nm})^2})}}{9(1+1.39785)+(1.39785)^2 \lambda_i^2}$$

$$0.79821 = 0.58296 + \sum_{i=1}^{\infty} \frac{(8.3871)e^{(3 \cdot 10^{-4})(-\lambda_i^2)D_{eff}}}{(21.58065)+(1.95398)\lambda_i^2} \quad (13)$$

$$0.21525 = \sum_{i=1}^{\infty} \frac{(8.3871)(1.0003)^{(-\lambda_i^2)D_{eff}}}{(21.58065)+(1.95398)\lambda_i^2}$$

To calculate the true value of the coefficient of diffusion we used the known λ_i s to approximate the value of the infinite sum. Thus (13) gives:

$$D_{eff} = 66 \text{ nm}^2/\text{hr} \quad (14)$$

The results of this method are summarized in the appendix.

DISCUSSION

The objective of this project was to calculate the initial rate of uptake, the rate of uptake at a random incubation time, and the coefficient of diffusion for this 2-phase system. The objectives of this project were met. The initial rate of uptake was calculated to be 0.088 mM/hr using the first derivative of the best-fit line for the data. The rate of the uptake at the random incubation time (at 7 hours of incubation) was calculated to be 0.061 mM/hr . These calculations were expected, since rates of diffusion are always highest at the beginning of the uptake profile and decrease, until the system reaches equilibrium. This characteristic is also supported by the graphical representation of the data. In addition, the coefficient of diffusion for this 2-phase system was found to be $66 \text{ nm}^2/\text{hr}$, which was also expected, since this positive value confirms that diffusion of the Vitamin B12 into the mesoporous material did indeed occur.

CONCLUSION AND RECOMMENDATIONS

In this experiment, the initial rate of uptake, reaction rate, and coefficient of diffusion were calculated for the diffusion of a Vitamin B12 solution into a mesoporous crystal called TbMOF-100. As expected, the initial rate of uptake was higher than the rate of uptake at later incubation times. In addition, the coefficient of diffusion was calculated to be $66 \text{ nm}^2/\text{hour}$ which confirms the diffusion of the Vitamin B12 into the TbMOF-100. This indicates that the TbMOF-100 is a porous material as its value for the coefficient of diffusion can be explained by its porous structure, which allows for the capture of the Vitamin B12 inside its cages.

Considering that the model used to calculate the coefficient of diffusion is only an approximation, several recommendations could be given to provide a more accurate result for the

value of the coefficient of diffusion for this system. Since the model is designed to measure the coefficient of diffusion of a well-mixed bath into a spherical structure, it would be useful to conduct the experiment to measure the uptake profile on a sonicator to keep the Vitamin B12 solution constantly mixed. Another recommendation would be to construct a new model to compute the coefficient of diffusion, which takes into account the non-spherical structure of TbMOF-100.

NOMENCLATURE

Symbol	Definition	Units
A	Absorbance	N/A
ϵ	Molar absorptivity constant	$\frac{L}{Mol \cdot cm}$
l	Path Length	cm
c	Concentration	mM
C_t	Concentration of solution at time t	mM
C_0	Initial concentration of the solution	mM
V_f	Volume of the solution	mL
V_b	Volume of the TbMOF-100 crystals	mL
D_{eff}	Diffusion coefficient of the solution	nm ² /hour
R	Radius of the crystal structure	nm
t	Incubation time	hours

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APPENDIX

From (13) we have:

$$0.21525 = \sum_{i=1}^{\infty} \frac{(8.3871)(1.0003)^{(-\lambda_i^2)D_{eff}}}{(21.58065) + (1.95398)\lambda_i^2}$$

Thus:

$$\begin{aligned} 0.21525 = & \frac{8.3871(0.99687)^{D_{eff}}}{41.99158} + \frac{8.3871(0.98805)^{D_{eff}}}{99.89922} + \frac{8.3871(0.97353)^{D_{eff}}}{112.96848} \\ & + \frac{8.3871(0.95356)^{D_{eff}}}{331.35151} + \frac{8.3871(0.92849)^{D_{eff}}}{504.93665} + \frac{8.3871(0.89875)^{D_{eff}}}{716.97912} \\ & + \frac{8.3871(0.86482)^{D_{eff}}}{967.65090} \end{aligned}$$

Dividing 8.3871 from both sides gives:

$$\begin{aligned} 0.025664 = & \frac{(0.99687)^{D_{eff}}}{41.99158} + \frac{(0.98805)^{D_{eff}}}{99.89922} + \frac{(0.97353)^{D_{eff}}}{112.96848} + \frac{(0.95356)^{D_{eff}}}{331.35151} \\ & + \frac{(0.92849)^{D_{eff}}}{504.93665} + \frac{(0.89875)^{D_{eff}}}{716.97912} + \frac{(0.86482)^{D_{eff}}}{967.65090} \end{aligned}$$

The best value for D_{eff} was found to be 66nm²/hr. We checked this value with the data obtained from the fifth hour of incubation to test the quality of our solution. Thus:

$$\frac{1.66 \text{ mM}}{2.23 \text{ mM}} = \frac{1.39785}{1.39785 + 1} + \sum_{i=1}^{\infty} \frac{6(1.39785)e^{(-\lambda_i^2 \frac{(5)D_{eff}}{(100 \text{ nm})^2})}}{9(1 + 1.39785) + (1.39785)^2 \lambda_i^2}$$

$$0.74439 = 0.58296 + \sum_{i=1}^{\infty} \frac{(8.3871)e^{(5 \cdot 10^{-4})(-\lambda_i^2)D_{eff}}}{(21.58065) + (1.95398)\lambda_i^2}$$

$$0.16143 = \sum_{i=1}^{\infty} \frac{(8.3871)(1.0005)^{(-\lambda_i^2)D_{eff}}}{(21.58065) + (1.95398)\lambda_i^2}$$

Plugging in seven of the first λ_i (the contribution to the sum is negligible for $i > 7$) the sum on the right hand side becomes:

$$\frac{5.94214}{41.99158} + \frac{2.23521}{99.89922} + \frac{0.43871}{112.96848} + \frac{0.044887}{331.35151} + \frac{0.0023948}{504.93665} + \frac{0.000066742}{716.97912} + \frac{0.00000096888}{967.65090} \approx 0.167906$$

Hence the error is small so we conclude our value is accurate.