

Diffusion of nanoparticles in solution through elastomeric membrane

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Abstract. Diffusion phenomena encountered in mass transfer of liquids play an important role in many technological processes of polymer manufacturing and use. In addition and alongside the notable growth of nanoparticles use, particularly when in suspension in liquid solutions, it has become important to pay some attention to their interactions with polymeric structures. The aim of this work is to evaluate some diffusion parameters of gold nanoparticle solutions as well as of their liquid carrier (water) through elastomeric membranes. Gravimetric method was chosen as the main technique to quantify swelling phenomena and to assess kinetic properties. The dynamic liquid uptake measurements were conducted on gold nanoparticles (5 nm and 50 nm in diameter) in aqueous solutions when brought into contact with two types of nitrile material samples. Results showed that diffusion mechanism of the liquids lies between Fickian and sub-Fickian modes. Slight deviations were noticed with the gold nanoparticle solutions. A growth in liquid interaction with the rubbery structure in presence of the nanoparticles was also observed from comparison of K factor (characteristic of the elastomer-liquid interaction). Difference between the characteristics of the two membranes was also reported using this parameter. Besides, diffusion coefficients testified the impact of the membrane thickness on the penetration process, while no significant effect of the nature of the nanoparticle solution can be seen on this coefficient.

Keywords: Diffusion mechanism, gold nanoparticle solutions, nitrile rubber films, gravimetric method.

1. Introduction

The study of sorption and transport of liquids into polymeric systems is an important area of research that finds applications in many processes of industrial relevance [1]. Molecular transport of solutions through dense elastomeric films is found to obey the solution-diffusion model of transport in which, permeants dissolve in the membrane material and then diffuse through the membrane down a chemical potential gradient [2]. The diffusion of molecular species through a polymeric matrix of a membrane is affected by many factors such the liquid properties, the nature of the rubbery structure as well as the types of membrane-penetrant system interactions [3]. On the other hand, colloidal suspensions, particularly gold nanoparticle solutions are increasingly the subject of substantial research for their unique optical, electronic, and molecular-recognition properties [4]. However, there is a lack of information about the mechanisms of their transport through the polymeric structures. Therefore, the aim of this study is to develop a state of knowledge about some kinetic parameters of transport of gold nanoparticle solution through nitrile rubber membranes. The transport phenomenon is often accompanied by the swelling of the polymeric structure under the effect of the chain's relaxation [5].



Hence, the liquid diffusion phenomenon and the processes of material inflation are closely interrelated. Quantitative data of swelling yield valuable information about transport mechanisms [6, 7]. Among several experimental techniques, gravimetric method was adopted in this study to assess swelling of nitrile films brought into contact with two gold nanoparticle solutions of different diameters.

2. Experimental

2.1. Materials

As elastomeric membrane, two common disposable nitrile rubber gloves were used for this study. Both had similar chemical composition but different thicknesses ($73.2 \pm 3.0 \mu\text{m}$ and $117.0 \pm 6.5 \mu\text{m}$). Until the end of this manuscript, both models are labeled as NBR1 and NBR2 respectively.

Regarding nanoparticle suspensions, two commercial gold nanoparticle solutions (5 and 50 nm) in MilliQ water were selected. Both suspensions had the same concentration of 0.05 mg/mL. To ensure their stability, the gold nanoparticles were coated with polyvinylpyrrolidone. Nanoparticle solutions were purchased from NanoComposix (San Diego, CA, USA), and they were labeled as AuNP-5 and AuNP-50 respectively.

2.2. Methods

Rectangular samples ($60 \times 10 \text{ mm}$) were taken from palm section of the protective gloves. Each sample was weighted using digital balance ($\pm 0.1 \text{ mg}$). At ambient temperature, samples were placed in glass bottles containing about 10 mL of gold nanoparticle solution. At regular periods of time, specimens were removed and were gently dried using a filter paper from any adhering liquid and weighted. The tests ended when the weight of the sample reached a plateau (equilibrium state).

Mass uptake data (M_t/M_∞) were represented as a function of the root square of time normalized by the thickness of the sample using the following equations [8]:

$$M_t/M_\infty = (m_t - m_0)/(m_\infty - m_0) \quad (1)$$

Where, m_0 is the initial weight of sample, m_t is the weight at time t and m_∞ is the weight at the equilibrium.

2.3. Theories

Diffusion mechanism:

In order to investigate the type of transport phenomenon and the diffusion mechanism, the dynamic sorption data of all the penetrant-membrane systems have been fitted to the following empirical relation [9]:

$$\log(M_t/M_\infty) = \log K + n \log t \quad (2)$$

Where, n is an index related to the type of the transport mechanism of the penetrant through the membrane structure. Regarding rubbery materials and liquid systems, the values of n are usually located between 0.5 and 1 [10]. For n equal to 0.5, the diffusion follows the Fickian trend in which the rate of the elastomer chains relaxation exceeds the rate of the liquid diffusion. On the other hand, for n equal to unity, the diffusion mode is non-Fickian and the diffusion rate of the permeant molecules is higher than the elastomer segment mobility. K factor depends upon the elastomer-liquid interaction as well as the structural features of the rubbery material [11].

Diffusion coefficients:

With Fickian transport mode, diffusion coefficients of an unidirectional flow of solution through the nitrile membranes can be calculated using the thin-film solution for the second Fick's law of mass transfer given by [12]:

$$\partial C / \partial t = D(\partial^2 C / \partial x^2) \quad (3)$$

Where, C refers to the liquid concentration within the nitrile membrane at a given time t and for a depth x inside the sample, D is the diffusion coefficient of the penetrant through the sample.

An analytical solution of this differential equation defines the liquid concentration during sorption through a given rubber sheet of thickness h, at time t, and a distance x. Equation (3) was solved under suitable initial and boundary conditions using some assumptions; the concentration of the colloidal solution on the membrane surface is supposed to reach equilibrium immediately upon exposure during the immersion test [13]:

$$\begin{aligned} \text{for } t = 0 & & 0 < x < h & & C = 0 \\ \text{for } t \geq 0 & & x = 0, x = h & & C = C_{\infty} \end{aligned} \quad (4)$$

$$C_{(t,x)} / C_{\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \exp\left(-\frac{(2n+1)^2 \pi^2 D}{h^2} t\right) \times \sin\left(\frac{(2n+1)\pi}{h} x\right) \quad (5)$$

Where $C_{(t,x)}$ is the concentration of the solution at time t and distance x from the membrane surface. C_{∞} is the solution concentration at equilibrium and h refers to the thickness of the membrane. Integrating Equation (5) gives the mass of the absorbed penetrant by the film as a function of time. Under these conditions, mass uptake of the penetrant solution can be described by either of the following equations [14]:

$$M_t / M_{\infty} = 4 \left(\frac{D}{\pi}\right)^{0.5} \cdot \left(\frac{\sqrt{t}}{h}\right) \quad (6) \quad \ln(1 - M_t / M_{\infty}) = \ln\left(\frac{8}{\pi^2}\right) - \pi^2 D \cdot \left(\frac{t}{h^2}\right) \quad (7)$$

Equation (6) converges rapidly at short times (where $M_t / M_{\infty} \leq 0.6$), whereas equation (7) converges at long times of immersion (where $M_t / M_{\infty} \geq 0.6$). Both expressions were limited to the first order of iteration (n=0), the error caused by the simplification is less than 0.1% [15].

Concentration profiles:

The determined values of D were incorporated into Fick's law solution equation (5) to generate theoretical sorption curves. Concentration profiles of the solutions at different depths of the nitrile films have been calculated.

3. Results and discussion

3.1. Mass uptake and elongation phenomena

Swelling takes place as liquid is adsorbed. This phenomenon depends upon the solubility characteristics of the elastomer-solution system. At a prolonged period of exposure, the penetrant causes a relaxation of the polymeric chains giving rise to more space to occupy by the liquid. The main change noticed after immersion is the mass uptake and the volume change of the rubbery sample [16]. Figure 1 represents mass uptake over time of NBR2 in contact with MilliQ water, AuNP-5 and AuNP-50. Results showed typical curves of liquid sorption by an amorphous polymeric structure. A gradual increase was noticed until attaining a state of saturation. The saturation was achieved after about 200 hours of immersion. At equilibrium, the nitrile rubber sample gained around 40% of its initial weight with MilliQ water. However, this gain was around 50% with each one of the nanoparticle solutions.

In order to be able to compare swelling behavior of the two materials, reduced sorption data plots were presented in Figure 2 as function of normalized time according to equation (1). Both curves of NBR1 and NBR2 in AuNP-50 were similar in form and exhibited the Fickian feature of linearity up to

about 60% of fractional weight uptake. When comparing the linear parts of the two nitrile films, it is worth noting that the slope the NBR2 curve seems to be slightly higher. It was also remarkable that NBR2 achieved saturation much earlier than NBR1.

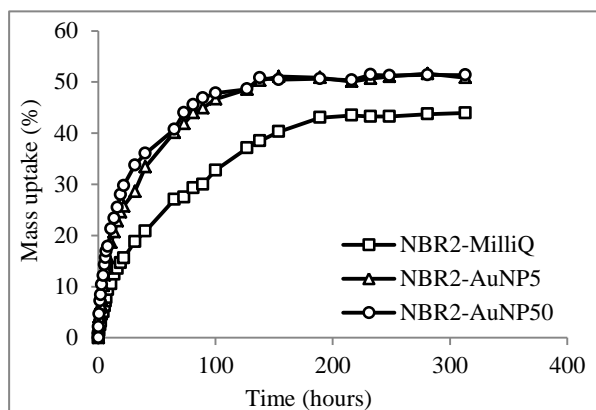


Figure 1 Mass uptake curves as function of time for NBR2 in MilliQ water, AuNP-5 and AuNP-50

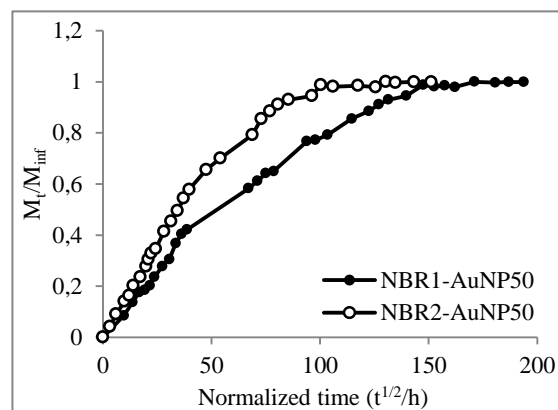


Figure 2. Reduced sorption plots of NBR1 and NBR2 in contact with AuNP-50 (M_{inf} refers to M_{∞})

3.2. Kinetic parameters of diffusion

Power law model expressed under logarithmic form by equation (2) is reported to be the easiest and most common mean to describe sorption results [17]. Using fitting module of MATLAB software, experimental data were fitted to power law curve. Information about the diffusion mechanism of NBR1 and NBR2 in MilliQ water as well as in both nanoparticle solutions are represented in Table 1. The values of n vary from 0.42 to 0.55 for NBR1 and from 0.5 to 0.52 for NBR2 suggesting a slight deviation from Fickian diffusion (accurate to ± 0.01 unit). As a side note, the size of the nanoparticles seems not having a significant effect on the diffusion mechanism for both nitrile rubber films. However, a related point to consider is that n index for NBR1 is 0.05 unit lower than the n index of NBR2, and that for both nanoparticle solutions. This fact is related to the difference in thickness of the two films.

Regarding K factor, there are two noteworthy aspects to consider: Firstly, and for all the liquids, a difference of about five orders of magnitude was noticed between the two membranes. A higher interaction of NBR1 with the solutions can be deduced. This fact may be due to a difference of the chemical composition of the two glove materials. Secondly, and for both films, K factors for nanoparticle solutions are from 2.5 to 3 times higher than the MilliQ water factors. This result highlights a possible effect of the nanoparticles on the membrane-penetrant interaction.

Table 1 Diffusion mechanism index, K factor and first order factor k_1 of the penetration of MilliQ water, AuNP-5 and AuNP-50 through NBR1 and NBR2

	NBR1		NBR2	
	n	K ($\text{g} \cdot \text{g}^{-1} \cdot \text{min}^{-n}$)	n	K ($\text{g} \cdot \text{g}^{-1} \cdot \text{min}^{-n}$)
MilliQ water	0.5572	9.736	0.5236	2.962
AuNP-5	0.4452	25.680	0.5056	5.369
AuNP-50	0.4276	31.01	0.5156	6.115

Sorption data (M_t/M_{∞}) curves were used to determine diffusion coefficients through the relations given by equation (6) and equation (7). Taking into account the change in the mass uptake profile over time, diffusion coefficients should be separately assessed for short and long times. Table 2 displays diffusion coefficients data, at short and long times, of MilliQ water, AuNP-5 and AuNP-50 through NBR1 and NBR2. First of all, it has not escaped our notice that for gold solutions, and less for MilliQ water, the thickness of the membrane is a very important parameter affecting the diffusion coefficients

[10], which also seen in equations (6) and (7). For NBR2 and the both gold suspensions and at short times, D was at least three times higher than the coefficients of NBR1. Nonetheless, no significant effect can be reported regarding the nature of the colloidal solution. In addition, and for NBR2, short diffusion coefficients of the nanoparticle solutions were notably higher than the coefficient of MilliQ water with the same material. This behavior was not seen with NBR1. This effect is consistent with the diffusion mechanism results and may be caused again by a different chemical composition between the two nitrile rubber materials. Moreover, when comparing diffusion coefficients using previously described equations at short and long times of immersion, insignificant differences were mentioned. Therefore, it can be deduced the continuity of the short and long models along the total immersion time.

Table 2 Diffusion coefficients ($\times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$) of MilliQ water, AuNP-5 and AuNP-50 through NBR1 and NBR2 for short and long times at first order of iteration (simplified expression).

	NBR1		NBR2	
	Short times	Long times	Short times	Long times
MilliQ water	4.13	3.96	4.87	5.23
AuNP-5	3.39	3.98	8.27	8.17
AuNP-50	3.33	4.11	10.29	8.95

A graphical representation of the liquid presence inside the polymeric structure was made possible due to equation (5). Fractional concentration of MilliQ water, AuNP-5 and AuNP-50 were plotted all long NBR2 membrane thickness at a fixed immersion time lapse of 50 hours (Figure 3). When the nitrile rubber sample is immersed, the liquid penetrates the structure until reaching the center of the film at a given time t . The concentration (C_t) increases in the core up to the initial concentration ($C_t/C_\infty=1$). It is worth mentioning that the sample absorbed about 15% of MilliQ water in the center. However, and at the same immersion time (50 hours), the concentration ratio of AuNP-5 and AuNP-50 were between 60 and 70% respectively. Membrane structure seems to absorb more nanoparticle solutions than MilliQ water. An important related point to consider was that the colloidal solutions contain additives used as stabilizers for the dispersion of the nanoparticles. These substances may affect considerably the penetration process and be a part of the differences seen in the concentration profiles.

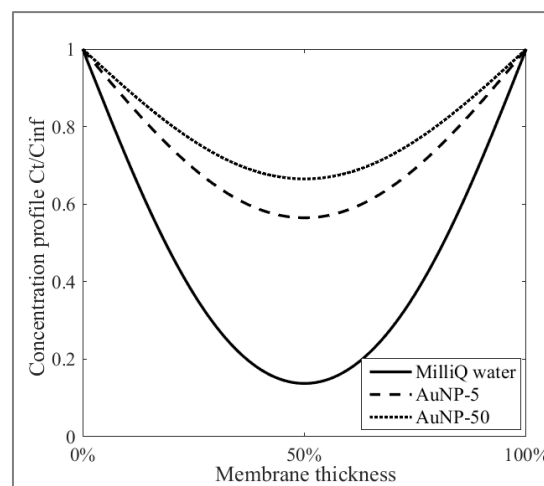


Figure 3 Concentration profiles of MilliQ water, AuNP-5 and AuNP-50 into the structure of NBR2 at 50 hours of immersion (C_{inf} refers to C_∞)

4. Conclusions

Research on sorption and diffusion properties of liquids through polymeric structures was extensively covered, along decades, by numerous studies. In spite of all that, the penetration of nanoparticle solutions through elastomeric membranes has not been well studied yet. Gravimetric method was retained as an effective technique to study penetration kinetics of the nanoparticle solutions through the nitrile rubber membrane structures. This paper presents an analysis of some penetration parameters, through nitrile membranes, of two gold nanoparticle solutions (5 and 50 nm of diameters) as well as of their liquid carrier (MilliQ water). Findings demonstrate that mechanism diffusion of the liquids ranges from sub-Fickian to Fickian diffusion mode. The noticed mode deviation can be explained by the presence of the gold nanoparticles in the solutions. An increase in liquid interaction with the rubbery structure in presence of the nanoparticles was also observed from comparison of K factor. Difference between the characteristics of the two membranes was also reported using this parameter. In addition, diffusion coefficients showed the effect of the membrane thickness on the penetration process, while no significant difference can be seen on this coefficient when adopting a short or long time model. As summary, presence of nanoparticles on the solutions can affect penetration phenomena. Further investigation is required to evaluate the kinetic parameters of these nanoparticles on the process.

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