

Empirical mathematical model based on Moisture Diffusion and its Activation Energy in nAg/PVP nanocomposite

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ABSTRACT

An empirical relation to determine effective diffusivity and the activation energy of moisture in nano silver metal/ PVP composite (nAg/PVP) on the cylindrical alumina substrate is reported. nAg/PVP of size 55±10 nm composite is synthesized by in situ chemical reduction AgNO₃ in the presence of 0.001 wt% of PVP matrix. The film of nano composite is coated by drop casting of 2 µl solutions of nAg/PVP. 10, 18, 26, 33, 41 and 49 µm with ±2 µm thicknesses are obtained by layer by layer coating which named as A1, A2, A3, A4, A5 and A6 respectively. To determine the amount of water content, as a function of exposure time, which is essential for determining the effective diffusivity, the resistance is measured as a function of exposure time. A Strobe's formula is used to convert resistance into moisture content, which in turn relates diffusion time to moisture content. Resistance as a function of the diffusion time gives a 3rd order exponential decay. When the decay is divided into 3 terms, the constant shown in the strobe's formula in each region is calculated by measuring water content along with resistance at the center point of each region. The resistance values related to the corresponding moisture content are converted into moisture ratio (MR). The slope of ln (MR) vs. diffusion time gives effective diffusivity. The experiments were carried out at three different temperatures in the range 22-38°C. Activation energy is obtained as a slope of effective diffusivity as a function of (1/ (Temperature)). The activation energies are in different in three different regions of moisture diffusion suggesting three diffusion rates in three different regions. A model is suggested on the bases of these three diffusion rates. The activation energies go on increasing with thickness to a certain extent and then it's saturate.

Keywords: nAg/PVP nanocomposite, effective diffusivity, activation energy and empirical mathematical model.

INTRODUCTION

The reported polymeric resistive humidity sensors are based on either polyelectrolyte or conjugated polymers [1-4]. It is reported that conjugated polymers and their derivatives, when doped with proper dopant, however become sensitive to humidity. Their response is poor, at the most one order of magnitude change in the conductivity, due to their weak hygroscopic nature [5-11]. Therefore, research on polyelectrolytes doped with a particular dopant to enhance the sensitivity becomes a challenging work [12, 13]. Here PVP matrix doped with nAg particles are used.

In humidity sensing, the transfer of moisture is an important factor [14], therefore effective diffusivity value (D_e) and activation energy during drying [15-21] is used to describe the rate of moisture movement. Most of the research related to transfer of moisture is reported on vegetables and fruits for finding effective diffusivity value (D_e) and activation energy during drying [15-21]. A humidity sensor should have high diffusivity and high drying rate for quick response and recovery. The knowledge of water activity (effective diffusivity) and equations that describe their relationship, as a function of moisture content and temperature are important for modeling and predicting film barrier efficiency.

The present paper reports thickness and temperature dependent resistive properties of nAg/PVP nanocomposite as a humidity sensor. To understand the water transport mechanism in the present film a successful attempt is made to explain three different diffusion processes by measuring the effective diffusivity and activation energy as a function of time at a constant humidity. For measurement of effective diffusivity of moisture in the film, it is necessary to know the amount of diffusion of moisture in the film at the particular diffusion time, but it is found to be a very complicated job to measure accurate moisture content in the film with diffusion time by gravimetric method. To overcome above limitation, we tried to use Strobe empirical formula reported by Strobe et. al 2002 [22, 23] for our films by modifying constant.

METHODOLOGY

Synthesis of nAg/PVP composites and film Fabrication

In situ nAg/PVP composite is synthesized by chemical reduction of silver salt [24] in the presence of PVP polymer. The aqueous solution of PVP having concentration of 0.001 wt% of the polymer is prepared in double distilled water. The procedure for synthesis of nAg/PVP nanocomposite is already explained in ref. [24]. The reaction is stopped when a colorless solution becomes pale yellow (≈ 45 min), which is an evidence of formation of Ag nanoparticles [24, 25].

For fabrication of a film, Ceramic rods (length=0.3 cm and Diameter =1.50 mm) with nicrome cap for contact purpose are used. nAg/PVP nanocomposite is coated on a ceramic rod by drop casting of 2 μ l solutions and uniformity in the coated film was trying to achieve by using hand spinning. Further the film dried at room temperature of 32°C. The thickness of film is increased by successive deposition of 2 μ l solution per layer.

Material characterization

Structural, micro structural and electrical characterization of the synthesized nanocomposites was carried out using UV-vis spectroscopy (UV-Vis) and Transmission electron microscopy (TEM) techniques. Absorption spectra of the synthesized nanocomposites were recorded using UV- Vis spectrometer model HP 8452 with a resolution of 1nm and a required quartz cell. The particle size and morphology of nAg nanoparticles were analyzed by using transmission electron microscope (TEM; TECNAI G2 20-TWIN (FEI-NETHERLANDS)). The % water content in films was measured by using an electronic balance (accuracy 0.0001g).

System for studying diffusion of moisture in humidity sensing film

A system used to study the diffusion of moisture in humidity sensing film is shown in Fig.1. The system is same as the one used in our previous work [24]. It consists of a testing glass chamber with a small neck mounted on the glass sheet. The sensing film and the commercially available humidity sensor ((48-EU-05) to monitor/calibrate the chamber humidity) are kept neatly in the chamber.

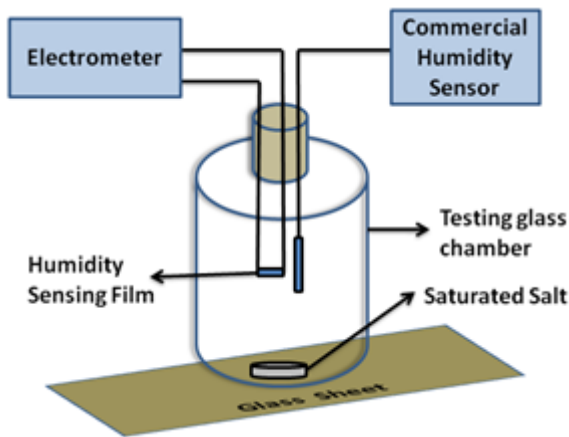


Fig.1. System for diffusion of moisture in humidity sensing film

The resistance of the film was measured using an electrometer (6517B, Keithley, $V = 20V$, $I=200nA$) [24]. For the present work, relative humidity of 95%RH was created in a glass chamber by using KNO_3 saturated salt [26] and make air tight by modeling clay, % RH is continually monitored by commercially available humidity sensors. A dry environment of 1-5%RH is created by using P_2O_5 salt. The film is kept for overnight in a dry environment and then exposed to 95%RH, by introducing it in a glass chamber from the upper neck side then make it air tight. The resistance of film with diffusion time is recorded. This data is used for further analysis of effective diffusivity and activation energy of film with thickness.

Data collection for modeling of RH sensor

The main part of the experimentation relates to the collection of data for diffusion of moisture in the film under study by surface/ bulk diffusion under various conditions via thickness of film, temperature (T), % RH to which film is exposed, with diffusion time (t). To measure moisture content (M) in film continuously as a function of diffusion time, under various conditions, by gravimetric method will be a very tedious job. However, it is easy to measure resistance as a function of exposure time. We have therefore devised a new method by using Strobe's empirical mathematical formula which relates moisture content to resistance. It has a constant term [22, 23]. This strobe's formula is used to convert resistance into moisture content, which in turn relates diffusion time to moisture content. The procedure is as follows,

- 1) The Film is exposed to relative humidity and change in resistance with diffusion time is measured.
- 2) An empirical formula reported by Strobe et. al 2002 [22, 23] for moisture adsorption in wood species, exposed to specific %RH at a given temperature for converting the corresponding resistance into moisture content is available and used here.

$$\text{Log}_{10}(\text{Moisture content}) = C - 2.113(\text{Log}_{10}(\text{Log}_{10}(R))) \quad \text{Eq.(1)}$$

Where: moisture content is the mass ratio in percentage (%) and R is the Ohmic resistance during the corresponding diffusion time in ohm (Ω). The empirical constant C in eq.1 is material dependent and 2.113 might be liquid (water) dependent.

Therefore, we determined the empirical constant C experimentally for nAg/PVP nanocomposite. The following procedure is adapted to determine the constant C.

- 2.1 The data on Resistance vs. Diffusion time is calculated at a specific humidity at a specific temperature for each film. A graph of Resistance vs. Diffusion time tried fitted for exponential relation up to three terms. The data is also subdivided into three regions and corresponding constants (C) are determined separately for three regions to minimize error.
- 2.2 Once the regions are fixed then to calculate constant C, 1st the dry film of weight (M_0) is exposed to specific humidity (say 95%RH) under isothermal environment (at $T= 22.2/ 28.3/ 38.8$ ° C) for a particular diffusion time, which is decided from regions and is weighed again (M_t) by using an electronic balance (accuracy 0.0001g). By knowing the values of M_t and M_0 , the moisture content at any time (time = t sec) was determined from Eq. 2 [27]

$$\text{Moisture content (\%)} = \left(\frac{M_t - M_0}{M_0} \right) \times 100 \quad \text{Eq.(2)}$$

- 2.3 For the same time (t sec), the resistance is also measured under the same isothermal environment at specific %RH. Knowing the value of moisture content and resistance at time (t sec), the empirical constant is determined by using Eq.1 (constant = C for nAg/PVP). Once the constant

(C) is decided for a particular region than resistance in particular region is converted into moisture content by using constant (C) for that region using eq.1.

- 2.4 The same procedure is repeated for every film three times at three different temperatures (22.20, 28.30 and 38.80°C). The constant is dependent on material thickness and environmental temperature (T) and not on time.
- 2.5 To verify the applicability of the above relation, water content at different diffusion times are carefully measured by gravimetric method and these experimental values are compared to the values determined by the above empirical relation with corresponding C (Eq.1). C may be different for different temperatures and different regions of sensitivity curves; hence these variations were studied to minimize error.
- 3) Once all resistance values converted into water content, then the water content is converted into the moisture ratio (MR) by using following equation eq.(3),

$$\text{Moisture ratio (MR)} = \left(\frac{M_t}{M_\infty} \right) \quad \text{Eq. (3)}$$

Where, $M_t = M_t$ is the mass of the moisture after absorption time t , $M_\infty =$ Saturated mass at specific RH.

The saturated mass is different for different region. For 1st and 2nd region, the time for saturated mass is decided from the region length. Approximately the last reading is considered as a saturated mass for the 1st and 2nd region. And for 3rd region saturated mass (M_∞) is the mass at the response time of the sensor where sensor achieves a stable resistance value (≈ 1 to 6 min according to the thickness of the film).

- 4) Once the MR is decided then effective diffusivity (De) and activation energy (Ea) are determined.

RESULTS AND DISCUSSION

1. UV-Visible and TEM analysis

Synthesis of nAg/PVP composite is carried out for 3-4 times and representative results are given here. When solution became pale yellow, then it was collected for study on diffusion of moisture. The UV-Visible peak around 400 nm is the confirmation for formation of

nAg particles. The solutions show same peak position around ≈ 425 nm (Fig.2). In order to find the size and morphology of nAg particles TEM images are taken. TEM image of nanocomposites is shown in insert of Fig. (2).The particle size is found to be of around 50 ± 5 nm with average spherical geometry.

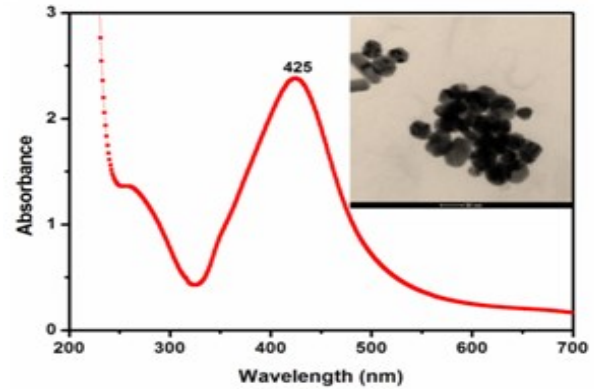


Fig.2. UV-Vis spectra of nAg/PVP nanocomposite

2. Relating measured Resistance to moisture content through mathematical model

Data collection for change in resistance with diffusion time

The change in resistances with diffusion time is measured for various thicknesses (10, 18, 26, 33, 41 and 49 μm). Data on two films of each thickness was taken. The data were also taken at three different temperatures (22.2, 28.3 and 38.8°C) for all the films. All the films showed similar exponential decay for a resistance Vs diffusion time. Representative data for film of thickness 26 μm (film A3) taken at three different temperatures is shown in Fig. 3.

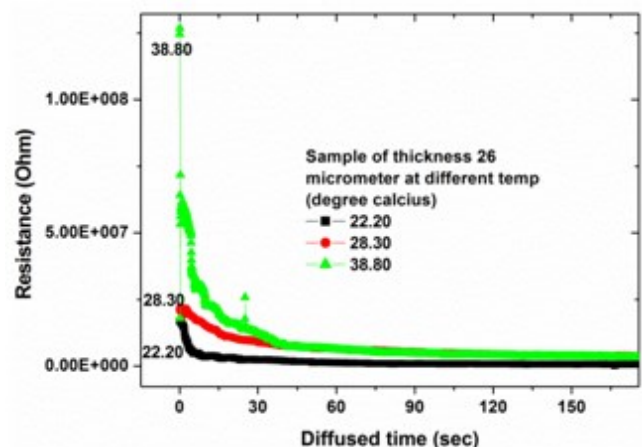


Fig.3. Resistance Vs. diffusion time at 94 %RH for Film A3

As can be seen from Fig.3, there is a slight decrease in resistance with an increase in temperature. This is seen in all the films. This data is used for calculation of activation energy in films required diffusion of moisture.

Curve fitting and Model generation

In this research paper, we tried 1 term, 2 terms and 3terms exponential model fitting to analyse the experimental data of Resistance vs. Diffusion time taken for all the films [28]. Fig.4 shows the representative data for film C at 22.2°C. When one term exponential equation is tried to fit, then regression coefficient is $R^2=0.923$, for two term exponential equation, it is ≈ 0.9482 and for the three term exponential equation is 0.96525 (Fig. 4). The three term exponential decay fitting is carried out for all films having different thicknesses at different temperatures having regression coefficient in the range 0.98-0.99.

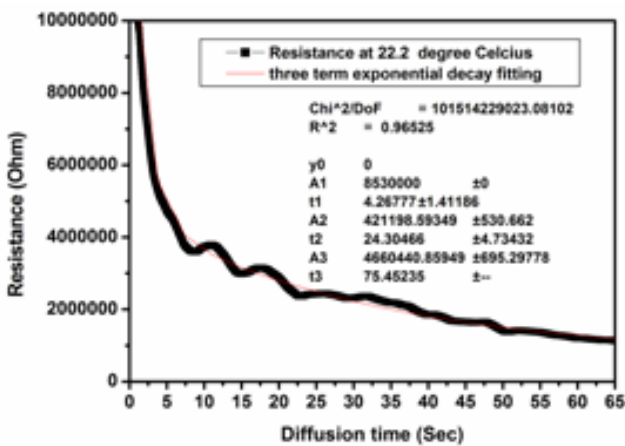


Fig.4. Three term exponential decay equation fitting for resistance vs. diffusion time for the A3 film Curve fitting expression is given in Eq. 4.

$$y = y_0 + A_1 e^{-\frac{x}{t_1}} + A_2 e^{-\frac{x}{t_2}} + A_3 e^{-\frac{x}{t_3}} \quad \text{Eq. (4)}$$

Eq. 4 consists of three different exponential terms having their own different time constants t_1 , t_2 and t_3 with coefficients of exponential terms, i.e A_1 , A_2 and A_3 having unit Ohm/sec. Where, each term corresponds to a different diffusion process. y_0 is the constant which comes out to be zero for the fitted curves where ($R^2=0.98$ to 0.99 for all the curves).

Relating resistance to the moisture content

From fig. 4 and Eq. 4, it can be inferred that, there are three different diffusion rates [29], represented by three different diffusion time regions. The regions are divided in such a way that, the values of exponential coefficient (A) and time constant (t) remain approximately the same as observed in Fig.4. These regions are shown in Fig. 5(a,b,c). Values of A and t are indicated in corresponding figures.

Further recorded resistance as a function of diffusion time is converted into moisture content by using eq. 1 (see section 2.4). The value of constant C in Eq. 1 is calculated for three different regions as explained below. For this conversion, the constant (C) in eq.1, has to be decided for each region separately by using following procedure.

1. To decide the constant for the 1st region in the A3 film Fig.5a, %moisture content (using eq.2) at midpoint of time interval (6 sec) of 1st region is measured by gravimetric method and taken as reference.
2. At the same time the resistance is taken which was measured by using an electrometer under the same temperature (22.2°C).
3. Now substituting the values of resistance and % moisture content in eq.4, constant (C) was determined and taken as constant for whole region, which comes out to be 0.89003 for the 1st region in A3 film at 22.2°C.
4. After getting the constant (C) for that particular region, all the resistances in that region were converted into moisture content by using the empirical relation in Eq. (1).

Next, separation of data (Resistance Vs Diffusion time) into three regions also helps to minimize the error in moisture content. The figure 6, give converted moisture content at three different temperatures for A3 film and their corresponding resistance at same temperature was given in Fig.3. Comparison between fig. 3 and Fig.6 shows that, at low temperature film has high moisture content and their corresponding resistance is also low.

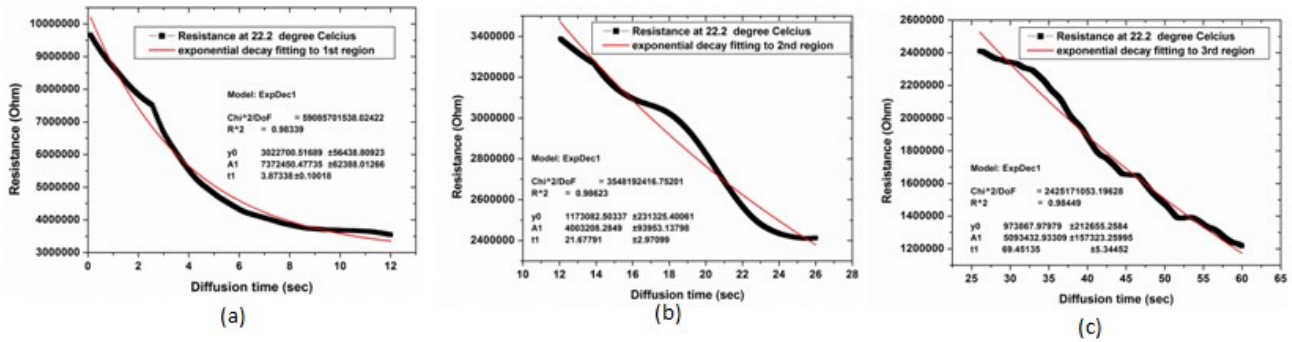


Fig.5. Selection of (a) 1st, (b) 2nd and (c) 3rd region for A3 film at 22.2°C

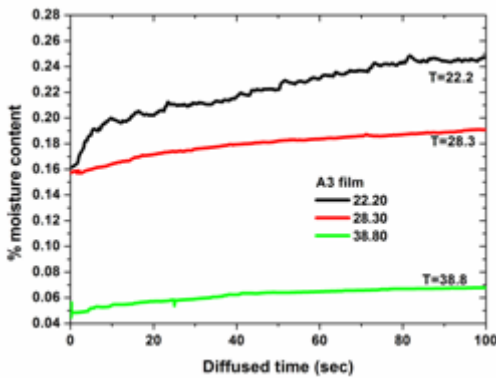


Fig.6. Theoretical % moisture content vs. diffusion time at 95 %RH for a A3 film

To verify the correctness of the theoretical calculated % moisture content from eq.1, the % moisture content at different time (other than mid time) which measured gravimetrically from eq.2 is compared with theoretical % moisture content (Fig.6) and it is given in fig.7.

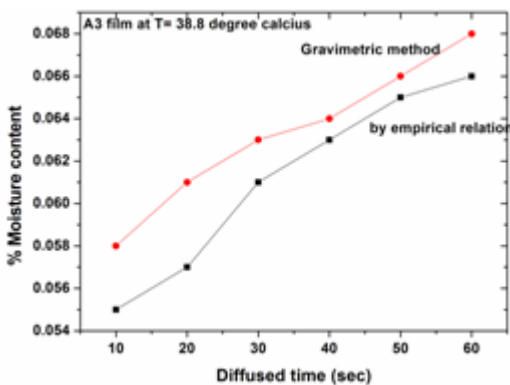


Fig.7. Comparison of % moisture content by empirical relation and gravimetric method at 95 %RH, T= 38.8 °C for A3 film

The comparison shows the correctness of our process, for use in calculating empirical values for that particular region. There is not much of difference in % moisture content by gravimetric (eq.2) and empirical relation (eq.1) though empirical curve shows slightly less moisture content. The maximum error in moisture content is about 5-6% when compared by gravimetric and empirical method.

Once % moisture content with diffusion time is obtained, the effective diffusivity and activation energy can be determined by using further theory.

3. Determination of effective diffusivity and activation energy (step7 of section 2.3)

The mathematical approach to calculate effective diffusion and activation energy is given. To predict the moisture content during the diffusion rate, mathematical models have been proposed using 2nd law of Fickian’s diffusion, as shown in Eq. (5). Here we considered that our film is like an infinite rectangular slab where it has thickness of about 11-49 μm as compared to length of film 0.01m. [30-33, 34]

$$\frac{\partial M}{\partial t} = \nabla[D_e(\nabla M)] \quad \text{Eq. (5)}$$

Where: D_e is the effective moisture diffusivity in m^2/s , t is time in second and M is moisture content in kg.

The calculated data of % moisture content Vs diffusion time follow the Fickian’s law, only when the mass uptake (moisture content) has a linear relation to the square root of diffusion time. The fig. 8 of %Moisture content Vs diffusion time shows linearity with regression coefficient $R^2 = 0.98771$. This shows nAg/PVP films follows the Fickian’s law.

The above expression is integrated over the thickness for the diffusion of moisture in thin film and the solution became [32, 34],

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{D_e(2n+1)^2\pi^2 t}{4L^2}} \quad \text{Eq. (6)}$$

Where, M_t is the mass of moisture after absorption time t , and M_∞ is the mass of moisture saturated film, D_e is the effective water diffusion coefficient in (m^2/s), t is the diffusion time, and L is the length of the film in meter.

In order to determine Fickian's coefficient (effective diffusivity) of diffusion, initial stage of Fickian's equation is simplified with ($n=0$) [31, 32, 33, 35]. There is not large variation in effective diffusivity when we considered next order ($n=1$). So we continued with $n=0$ [35]. Therefore Eq.6 becomes,

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} e^{-\frac{D_e t \pi^2}{4L^2}} \quad \text{Eq. (7)}$$

Here $\frac{M_t}{M_\infty} = MR$ (moisture ratio), then taking the log on both sides of Eq.7. The effective diffusivity of moisture (D_e) is determined from following eq.8 [35]

$$\frac{\ln(MR)}{t} = \frac{\pi^2 D_e}{4L^2} \quad \text{Eq. (8)}$$

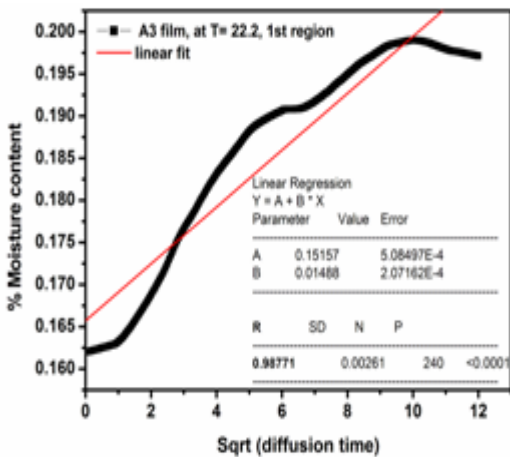


Fig.8. Moisture content Vs sqrt (diffusion time) at 95 %RH, T= 22.2 °C for A3 film

The effective diffusivity is determined from the slope of $\ln(MR)$ vs. diffusion time from simplifying equation. (6),

$$\text{slope of } \ln(MR) \text{ Vs. Diffusion time} = \frac{D_e \pi^2}{4L^2} \quad \text{Eq. (9)}$$

From moisture content, MR is calculated (Equation 5). The effective diffusion diffusivity is determined by plotting $\ln(MR)$ vs. Time (t) (Equation. (8)). Table 1, gives a brief idea about effective diffusivity (D_e) with temperature and thickness. Here D_1 is the effective diffusivity in region1, D_2 is the effective diffusivity in region2 and D_3 is the effective diffusivity in region3.

From table 1, Effective diffusivity of moisture decreases as the diffusion time increases in nAg/PVP. The dependence of the effective diffusivity on temperature can be described by the Arrhenius equation [31, 33]

$$D_e = D_0 e^{-\frac{E_a}{RT}} \quad \text{Eq. (10)}$$

Here, the effective diffusivity is D_e , D_0 diffusion constant = a^2v = product of the square of lattice constant and vibration frequency. It produces the same effect on effective diffusive of film at a particular temperature. So for the sake of simplicity, we neglect it. Our aim is to see trend in activation energy with diffusion time and thickness. E_a is the activation energy in KJ/mol and T is the absolute temperature of the chamber in Kelvin. $K = 1.38 \times 10^{-23}$ J/K is the Boltzmann's constant [32]. The activation energy can be determined from the slope of the Arrhenius plot, $\ln(D_e)$ vs. $1/T$ simplifying eq. (11)

$$\frac{\ln(D_e)}{1/T} = \frac{-E_a}{K} \quad \text{Eq. (11)}$$

The slope of the $\ln(D_e)$ Vs ($1/T$) segments will yield the activation energy for a particular region of diffusion.

From eq.11, Arrhenius plot between effective diffusivity and absolute temperature ($1/T$) gives nearly straight lines and regression parameters show good correlation with R^2 whose values ranging from 0.96 to 0.99 (Fig. 9a and 9b for thickness 26 μm), The slope of the $\ln(D_e)$ Vs $1/T$ plots gives activation energy in each region. The straight line nature and the high R^2 justify the application of the Arrhenius equation [16]. In Fig 9b, the constant B, represent the slope of region 3 for the A3 film. The product of slope and K (Boltzmann's constant) gives activation energy in Joule. For region 1 of A3 film, the activation energy was found to be 7.914×10^{-20} J or 0.49 eV. The same procedure is used for other films. According to Schmidt (1968) activation energy of approximately

0.17-0.22 eV may be assumed for the motion of hydrated ions in bulk water [36]. Table 2, gives a brief idea about activation energy of moisture during diffusion in eV.

Table.1. Effective diffusivity at different thickness and temperature

Thickness (μm)	Temperature (K)	Effective Diffusion (m ² /s)		
		D ₁	D ₂	D ₃
10	295.2	1.12E-7	2.28E-8	5.59E-9
	301.3	8.05E-7	7.69E-8	8.30E-9
	311.8	8.96E-7	1.48E-7	1.18E-8
18	295.2	4.19E-7	4.09E-8	7.48E-9
	301.3	5.42E-7	5.83E-8	9.48E-9
	311.8	1.57E-6	6.23E-8	1.28E-8
26	295.2	1.26E-7	1.39E-8	3.85E-9
	301.3	1.44E-7	1.58E-8	4.85E-9
	311.8	1.56E-7	2.54E-8	6.72E-9
33	295.2	1.26E-7	4.03E-9	7.93E-9
	301.3	1.44E-7	1.58E-8	8.90E-9
	311.8	1.56E-7	2.54E-8	1.39E-8
41	295.2	8.54E-8	1.82E-9	1.72E-9
	301.3	1.22E-7	9.84E-9	2.13E-9
	311.8	1.30E-7	1.02E-8	2.75E-9
49	295.2	3.28E-7	4.13E-8	1.17E-8
	301.3	3.59E-7	1.55E-8	1.24E-8
	311.8	4.94E-7	1.60E-8	2.15E-8

From table 2, E₁ is the activation energy during the sharp fall of resistance due to high adsorption of moisture in Fig.2, E₂ is the activation energy where resistance tries to achieve saturation which is time dependent region and E₃ is the activation energy during which resistance achieved saturation or time independent region (Fig.5). E₂ is higher than E₁ and E₃ i.e. E₃ < E₁ < E₂.

Table: 2. Change in activation energy with thickness and regions

Thickness (μm)	Activation energy (eV)		
	E ₁	E ₂	E ₃
10	0.58	1.20	0.21
18	0.48	1.26	0.25
26	0.49	1.26	0.25
33	0.59	1.31	0.32
41	0.60	1.08	0.25
49	0.24	1	0.20

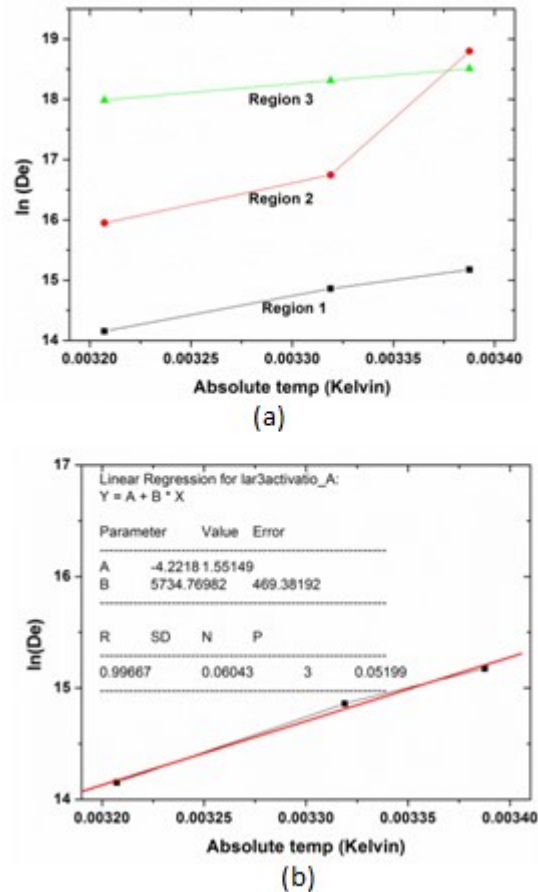


Fig.9. (a) Plot of ln (De) Vs. absolute temperature (1/T) for A3 film with each separate region (b) Linear fit with regression coefficient for the 3rd region to find activation energy

At the initial stages when film is exposed to moisture, resistance of the film falls sharply. With further increase in diffusion time, fall in resistance tends to achieve saturation. At the initial stages when film is exposed to moisture, moisture content in the film is low which increases with increase in diffusion time and achieved saturation [32] (Fig.6). The sharp fall in resistance during 1st region is due to more unsaturated sorption sites available for moisture adsorption. As the diffusion time increased, the sites become occupied, resulting in the reduction of the material capacity to absorb water. As the number of sites becomes fully occupied the moisture content approaches equilibrium [27]. So with the increase in diffusion time, there is a decrease in the diffusion of moisture which is verified by the table. 1. From above results, the diffusivity of moisture taking place in three successive steps. The effective diffusivity decreases continuously with an increase in diffusion

time. The comparison shows that inter Grain Diffusivity > Surface Diffusivity > Volume Diffusivity [34]. If we compared above comparison between grain, surface and volume diffusivity with table 2, then region 1 for surface diffusion, region 2 for the inter grain diffusion and 3rd region for volume diffusion.

When film is exposed to humidity, then sensor surface is the 1st part which comes in contact with humidity (surface diffusivity), as the diffusion time increases the moisture diffusion on the surface will start penetrating inside the film (grain diffusivity). Once all active sites are occupied, then the moisture tends to reach saturation (volume diffusivity). The correlation between effective diffusivity and activation energy shows that, the 3rd region, i.e. volume diffusion requires less amount of energy (0.20-0.32 eV) as compared to 1st and 2nd region. 2nd region, i.e. internal diffusion (grain diffusion) required more energy (1.08 - 6.21 eV) as compared to the energy in the other two regions. The amount of energy required for surface diffusion is an intermediate between intergrain and volume diffusion.

There is an increase in activation energy up to particular thickness, with further increase in thickness, the activation energy decreases. For these, thickness dependent behavior of activation energy, need to be studied further about the surface morphology of the film.

CONCLUSION

The diffusion mechanism of moisture in a nAg/PVP film is studied. It offers an exponential response of resistance as a function of diffusion time. An empirical model is suggested to fit to the data obtained for diffusion. The three orders exponential curve is fitted to data of resistance Vs diffusion time, offering three different rates of diffusion. These three terms exponential equations represent three different diffusion rates via surface, inter grain and volume diffusion. The activation energy needed for the three different diffusion rates is successfully calculated. The effective diffusivity of moisture decreases with increase in diffusion time and each region has its specific trend in activation energies with diffusion

time due to different diffusion rates. The activation energy required for inter grain diffusion is greater than surface and volume diffusion.

Conflicts of interest: The authors stated that no conflicts of interest.

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