

KINETICS OF CROSSLINKING REACTION OF PVA MEMBRANE WITH GLUTARALDEHYDE

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Abstract—Prior to investigate the influences of degree of crosslinking on the hydrophilicity and mechanical strength of polyvinyl alcohol (PVA) membrane, the kinetics of crosslinking of PVA membrane with glutaraldehyde was examined. The reaction variables were temperature, hydroxyl group concentration of PVA membrane, and concentrations of glutaraldehyde and sulfuric acid in crosslinking solution. The overall reaction rate of crosslinking was suggested, which agrees well with the experimental results. The crosslinking reaction is approximately first order with respect to the concentration of hydroxyl group of PVA membrane, of glutaraldehyde, and of sulfuric acid. The activation energy was estimated to be about 5.77 kcal/mol. It was also found that the degree of crosslinking of PVA membrane can be easily changed by controlling the reaction variables.

INTRODUCTION

Polyvinyl alcohol (PVA) membranes have been used extensively in industry for separations of organic solvents and many other applications. Especially, pervaporation process through PVA membranes is useful for concentration of ethanol from aqueous solutions in the high ethanol content region. It is known that PVA is a hydrophilic polymer and PVA membrane is highly selective to water [1-3].

The majority of the commercially available membranes are prepared by the so-called phase inversion process. PVA membrane preparation procedure of the phase inversion process consists of casting, precipitation and crosslinking. PVA is dissolved in water, and this solution is cast on a support, i.e., a glass or metal plate or a nonwoven textile fabric. The cast PVA solution is then precipitated by immersing it in an aqueous solution of inorganic salts. The precipitated PVA membrane (PVA polymer film) is still soluble to water, and can not be used for separations of aqueous mixtures. To increase the stability of PVA membrane to water, it should be crosslinked with an aldehyde.

The crosslinking reaction may affect the mechanical strength and hydrophilicity of PVA membranes. Swel-

ling characteristics and surface properties of PVA membranes can be changed according to the degree of crosslinking. As a result, the selectivity and flux of PVA membranes may be influenced. The crosslinking reaction may be important in designing a permselective PVA membrane.

Ogata et al. [4] studied the kinetics of the formation of the formal of PVA. It was reported that the rate was proportional to the product of the stoichiometric concentrations of formaldehyde and the hydroxyl group of PVA. Smets et al. [5] examined the kinetics of acetalization of PVA with acetaldehyde in water-dioxane solution at different temperatures in the presence of sulfuric acid as a catalyst. It was found that the reaction is first order with respect to the each reactant concentration.

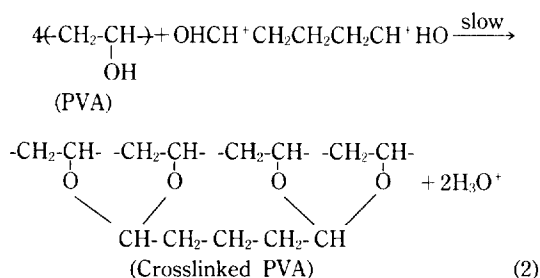
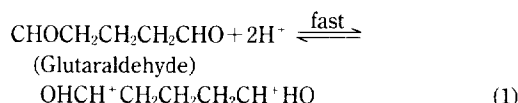
Previous studies on the kinetics of crosslinking of PVA are informative regarding the synthesis of the formal and gelation of PVA. However, It has hardly been done to study the kinetics of crosslinking reaction of PVA polymer film (PVA membrane) with an aldehyde. In this paper, the crosslinking reaction of PVA membrane using glutaraldehyde as a crosslinking agent is investigated. The reaction variables are temperature, hydroxyl group concentration of PVA membrane, and concentrations of glutaraldehyde and sulfuric acid in crosslinking solution. For the optimum

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design and preparation of PVA membrane, the crosslinking reaction should be thoroughly understood.

MECHANISM AND RATE EQUATION OF CROSSLINKING

The reaction mechanism of the crosslinking of PVA with glutaraldehyde can be written as follows [4, 5]:



The crosslinking reaction is carried out in the presence of sulfuric acid as a catalyst. The proposed mechanism for acid catalytic reactions involves the transfer of a proton to or from a substrate molecule. The reaction of Eq. (2) is the rate-determining step in this crosslinking reaction. We will consider only the reaction of Eq. (2) in the following study.

Regarding the reaction of Eq. (2), the general rate equation can be proposed:

$$-\frac{dG}{dt} = k H^\alpha G^\beta S^\gamma \quad (4)$$

where k is the overall rate constant, H is the hydroxyl group concentration of PVA polymer film, G and S are the concentrations of glutaraldehyde and sulfuric acid, respectively, in the crosslinking solution, t is the reaction time, and α , β and γ are the reaction orders with respect to the each reactant concentration. The hydroxyl group concentration of PVA polymer film is defined as the number of moles of a repeat unit $\left(\text{CH}_2-\underset{\text{OH}}{\text{CH}}\right)$ of PVA in the PVA polymer film per the unit volume of the aqueous PVA solution cast on a casting plate. PVA polymer film means the film formed prior to crosslinking. The two terms of PVA polymer film and PVA membrane are used interchangeably in this paper. For the calculation of H , the following equations are used:

$$\begin{aligned} H &= (\rho V_p W_p / M_u) / (V_p / 1000) \\ &= 1000 \rho W_p / M_u \end{aligned} \quad (5)$$

Where ρ and W_p are the density and weight fraction of PVA, respectively, of aqueous PVA casting solution, V_p is the casting volume of casting plate, and M_u is the molecular weight of a repeat unit $\left(\text{CH}_2-\underset{\text{OH}}{\text{CH}}\right)$ of

PVA and equal to 44. We assume that ρ is constant and equal to 1.0 g/cm³.

From the stoichiometric relationship of Eq. (2), Eq. (6) can be obtained:

$$G_o - G = 1/4(H_o - H) V_p / V_c \quad (6)$$

where V_c is the volume of crosslinking solution, and the subscript o denotes the initial concentration.

It is difficult to measure H during the crosslinking reaction. To replace H in Eq. (4) with measurable variables, the following equation, which is derived from Eq. (6), can be used:

$$H = H_o - 4(G_o - G) V_c / V_p \quad (7)$$

EXPERIMENTAL

1. Preparation of PVA Membrane

PVA membranes were prepared by the phase inversion process. PVA obtained from Aldrich Chem. Co. (degree of polymerization 1700, degree of hydrolysis 98%) was used. PVA solution was prepared by dissolving PVA in water at temperature of 70-90°C. PVA concentration varied within the range of 10-18 wt%. The PVA solution was cast on a stainless steel plate as shown schematically in Fig. 1 (a). The effective area and depth of the casting plate were 120 mm W × 250 mm L and 0.5 mm, respectively. Therefore, the casting volume (V_p) is 15 cm³. We assume that for the calculation of hydroxyl group concentration (H) of PVA membrane its volume is equal to the casting volume. The PVA solution was poured onto the plate and spread out with a knife. The plate was kept in air for 10 minutes at ambient temperature of 20-22°C. The resulting system was then placed in the precipitation bath (250 mm W × 400 mm L × 150 mm H) at room temperature. The precipitation solution as given in Table 1 was poured carefully over the PVA solution on the casting plate. The PVA solution remained in contact with the precipitation solution for 60 minutes. As a result, the PVA solution precipitated to form a film. The PVA membrane formed in the precipitation process can be still soluble aqueous solvents.

To increase the stability of the membrane toward aqueous solvents, it must be crosslinked with an alde-

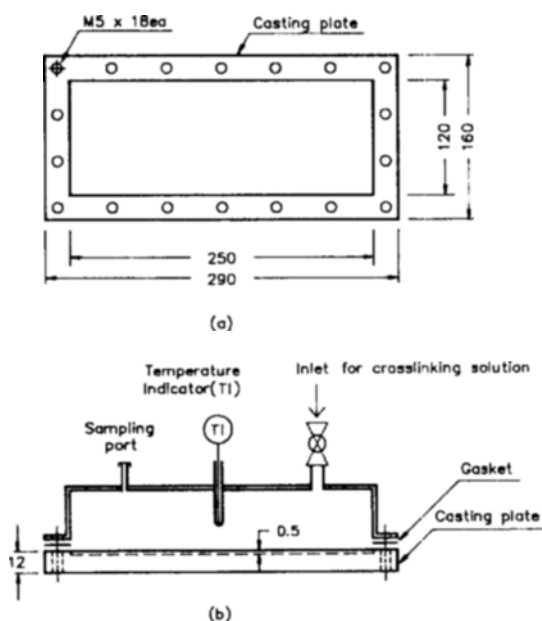


Fig. 1. Casting plate (a) and crosslinking reaction apparatus (b).

Table 1. Composition of aqueous precipitation solution

Component	Concentration (mol/l)
Sodium sulfate	1.41
Sodium hydroxide	0.625

Table 2. Composition of aqueous crosslinking solutions

Component	Concentration (mol/l)
Sodium sulfate	0.96
Sulfuric acid	0.1-0.4
Glutaraldehyde	0.015-0.060

hyde.

2. Crosslinking Reaction

The crosslinking solution consisted of glutaraldehyde, sulfuric acid, sodium sulfate and water as given in Table 2. The PVA membrane obtained was crosslinked by immersing it in the crosslinking solution.

The system used for the crosslinking reaction is shown in Fig. 1 (b). The crosslinking apparatus containing the PVA membrane was immersed in a constant temperature bath. After the apparatus was preheated to a reaction temperature, the crosslinking solution preheated separately to the reaction temperature was introduced into the reaction chamber to prevent the PVA membrane from crosslinking below the reaction temperature. The volume of crosslinking solution (V_c)

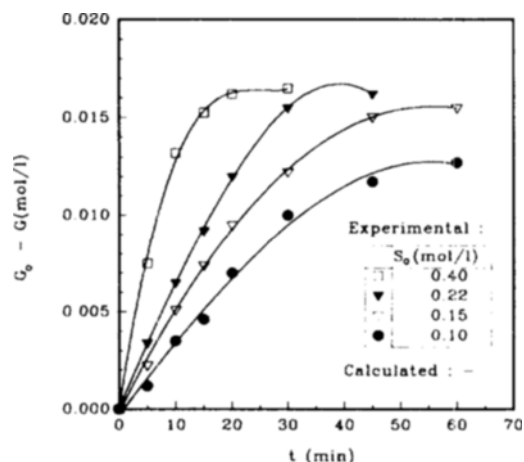


Fig. 2. Effect of sulfuric acid concentration on the crosslinking reaction ($H_0=3.41$ mol/l, $G_0=0.030$ mol/l, $T=313^\circ\text{K}$).

used in our experiments was 400 cm^3 . The crosslinking reaction was carried out without agitation by varying the concentrations of glutaraldehyde and sulfuric acid (Table 2), and the reaction temperature within the range of $20\text{--}60^\circ\text{C}$. During the reaction the crosslinking solution was sampled as a function of time, and the glutaraldehyde concentration in the sample was analyzed by a titration method. The titration method used was the so-called sodium bisulfite method based on the addition reaction of bisulfite salt to aldehydes [6, 7].

RESULTS AND DISCUSSION

1. Effect of Sulfuric Acid Concentration

To find the effect of sulfuric acid concentration on the crosslinking reaction, the crosslinking reaction was performed by varying the sulfuric acid concentration in the range of $0.1\text{--}0.4$ mol/l. The other variables such as PVA concentration, glutaraldehyde concentration and reaction temperature were kept constant. The concentrations of hydroxyl group of PVA and glutaraldehyde were 3.41 and 0.030 mol/l, respectively. The reaction temperature was 40°C .

As the reaction proceeds, the glutaraldehyde concentration decreases. The decrease in glutaraldehyde concentration was measured as a function of time. The results are shown in Fig. 2.

To obtain the reaction rate, $-(dG/dt)$, from Fig. 2, a correlation in the form of $G_0 - G = at + bt^2 + ct^3$ was used. Using this correlation and the experimental data, the coefficients of a , b and c were calculated by a

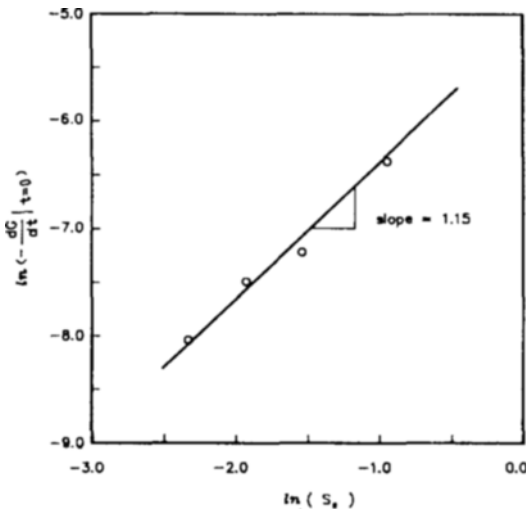


Fig. 3. Determination of the reaction order, γ , with respect to the sulfuric acid concentration ($H_0=3.41$ mol/l, $G_0=0.030$ mol/l, $T=313^\circ\text{K}$).

regression method. The calculated results from the correlation of $G_0 - G = at + bt^2 + ct^3$ are compared with the experimental data in Fig. 2. It can be seen that the correlation is appropriate. The reaction rate can be obtained by differentiating the correlation with t . The initial reaction rate at $t=0$ becomes a .

We will use the initial reaction rate to find the reaction order because it does not need a lot of data. When the concentrations of hydroxyl group of PVA and glutaraldehyde are constant, the initial reaction rate at $t=0$ can be written as follows from Eq. (4):

$$-\left. \frac{dG}{dt} \right|_{t=0} = a = k' S_a^\gamma \quad (8)$$

where k' is equal to $k H_0^\alpha G_0^\beta$, and S_a does not vary throughout the reaction. The reaction order, γ , can be determined from the slope of a straight line which correlates $\ln a$ with $\ln S_a$.

In Fig. 3, $\ln a$ [$= \ln(-dG/dt|_{t=0})$] is plotted against $\ln S_a$, and we see that a linear relationship exists between them. From the slope, the reaction order with respect to the sulfuric acid concentration is found to be 1.15.

2. Effect of Glutaraldehyde Concentration

The variation of the glutaraldehyde concentration was measured at four different glutaraldehyde concentrations within the range of 0.015–0.060 mol/l. The concentrations of hydroxyl group of PVA and sulfuric acid were kept constant and equal to 3.41 and 0.15 mol/l, respectively. The reaction temperature was 40

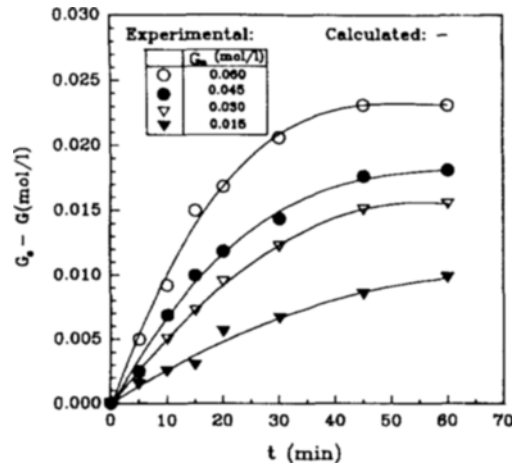


Fig. 4. Effect of glutaraldehyde concentration on the cross-linking reaction ($H_0=3.41$ mol/l, $S_0=0.15$ mol/l, $T=313^\circ\text{K}$).

$^\circ\text{C}$.

The variation of glutaraldehyde concentration measured as a function of time is shown in Fig. 4. A correlation is a function of third order as mentioned above. The glutaraldehyde concentration decreases linearly with time within 20 minutes. After 20 minutes the decreasing rate in the glutaraldehyde concentration becomes lower as the reaction proceeds. This trend appeared consistently throughout the experiments.

When the concentrations of sulfuric acid and hydroxyl group of PVA are constant, the initial reaction rate can be expressed as follows:

$$-\left. \frac{dG}{dt} \right|_{t=0} = a = k'' G_0^\beta \quad (9)$$

where k'' is equal to $k H_0^\alpha S_0^\gamma$.

The reaction order, β , with respect to the glutaraldehyde concentration can be determined as mentioned earlier.

The plot of $\ln a$ against $\ln G_0$ gives a straight line (Fig. 5). The slope of the straight line is the reaction order with respect to the glutaraldehyde concentration and found to be 1.07.

3. Effect of PVA Concentration

The initial rate was measured at four different PVA concentrations of aqueous casting solutions ranging from 10 to 18 wt%. The initial concentrations of glutaraldehyde and sulfuric acid were 0.030 and 0.15 mol/l, respectively, in each experiment. The reaction temperature was 40°C .

As the initial concentrations of glutaraldehyde and sulfuric acid are constant, the initial reaction rate can

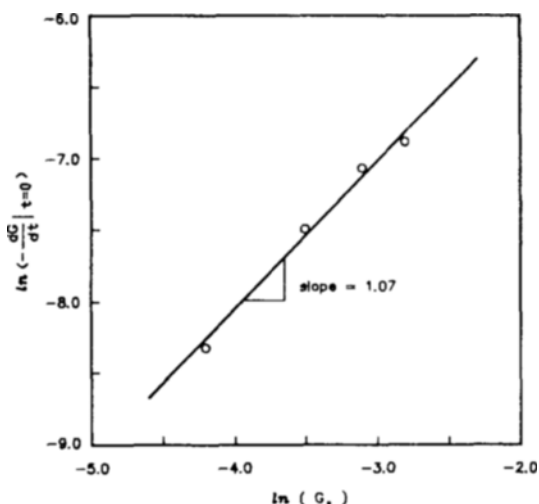


Fig. 5. Determination of the reaction order, β , with respect to the glutaraldehyde concentration ($H_0=3.41$ mol/l, $S_0=0.15$ mol/l, $T=313^\circ\text{K}$).

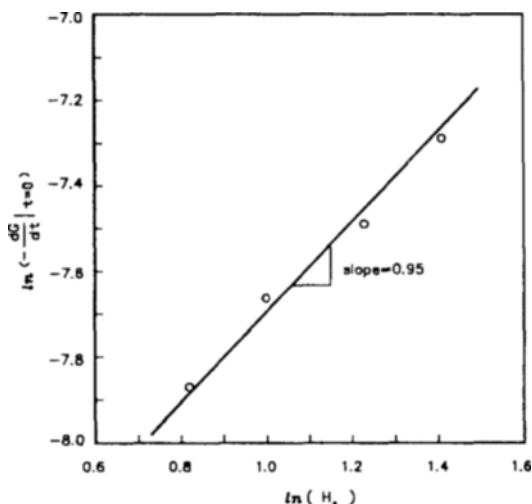


Fig. 6. Determination of the reaction order, α , with respect to the hydroxyl group concentration of PVA ($G_0=0.030$ mol/l, $S_0=0.15$ mol/l, $T=313^\circ\text{K}$).

be expressed as follows:

$$-\frac{dG}{dt} \Big|_{t=0} = a = k'' H_0^\alpha \tag{10}$$

where k'' is equal to $k G_0^\beta S_0^\gamma$.

As can be seen from Fig. 6 the plot of $\ln a$ against $\ln H_0$ gives a straight line. The reaction order with respect to the hydroxyl group concentration of PVA is estimated to be 0.95.

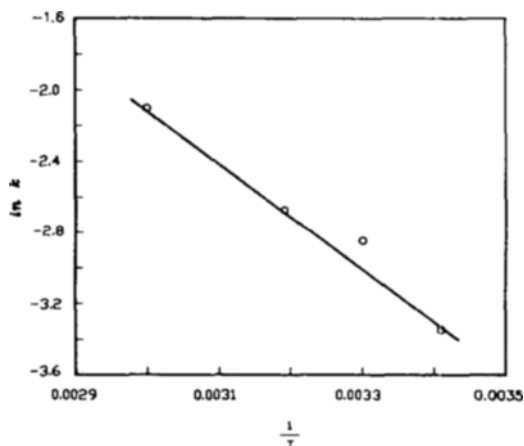


Fig. 7. Arrhenius plot of crosslinking rate constants ($H_0=3.41$ mol/l, $G_0=0.030$ mol/l, $S_0=0.15$ mol/l).

4. Effect of Crosslinking Temperature

From the preceding results the initial rate of crosslinking may be expressed by the following equation:

$$-\frac{dG}{dt} \Big|_{t=0} = k H_0^{0.95} G_0^{1.07} S_0^{1.15} \tag{11}$$

By measuring the initial rate at different temperatures and using Eq. (11), the effect of temperature on the crosslinking reaction can be investigated.

Assuming that the Arrhenius relationship holds between the rate constant and temperature, then

$$k = k_0 \exp(-E/RT) \tag{12}$$

where k_0 is the frequency factor, T is the absolute temperature, R is the ideal gas constant, and E is the activation energy.

The plot of $\ln k$ vs. $1/T$ is shown in Fig. 7. It gives a straight line. The slope and intercept are calculated by the least square method. From the slope and intercept the activation energy and the frequency factor are estimated to be 5.77 kcal/mol and 7.78×10^2 (mol/l·min)/[(mol/l)^{0.95}·(mol/l)^{1.07}·(mol/l)^{1.15}], respectively.

5. Overall Rate Equation of Crosslinking Reaction

From the preceding results the overall reaction rate of crosslinking can be written by Eq. (13):

$$-\frac{dG}{dt} = 7.78 \times 10^2 \exp\left(-\frac{2.90 \times 10^3}{T}\right) H^{0.95} G^{1.07} S^{1.15} \tag{13}$$

It is difficult to measure the hydroxyl group concentration of PVA during the reaction. Combining Eqs. (7) and (13), the overall reaction rate can be expressed with the measurable variables:

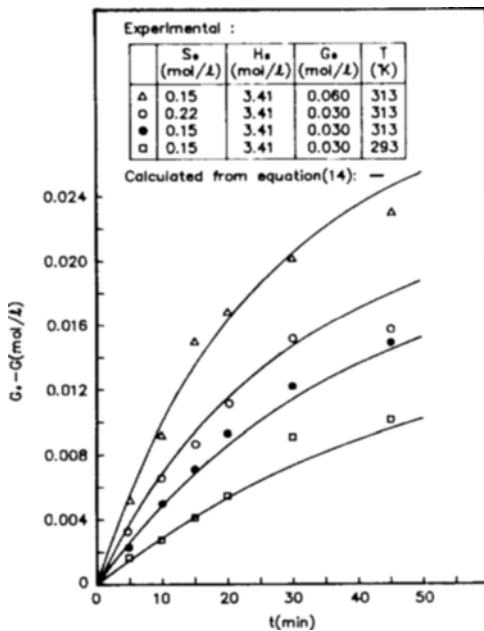


Fig. 8. Comparison of the variation of $(G_0 - G)$ calculated from Eq. (14) with the experimental data.

$$-\frac{dG}{dt} = 7.78 \times 10^2 \exp\left(-\frac{2.90 \times 10^3}{T}\right) (H_0 - 4(G_0 - G)) \left(\frac{V_r}{V_p}\right)^{0.95} \cdot G^{1.07} S^{1.15} \quad (14)$$

In Fig. 8 the experimental data for the decrease in glutaraldehyde concentration during the reaction is compared with the results calculated numerically from Eq. (14). It shows that these two results agree well.

It can be concluded that the overall reaction rate for the crosslinking of PVA polymer film immersed in aqueous glutaraldehyde solution conforms to Eq. (14). This results can be used very importantly for the design and optimization of PVA membranes.

6. Degree of Crosslinking

The degree of crosslinking D_c , can be defined in terms of the hydroxyl group concentration of PVA:

$$D_c (\%) = \frac{H_0 - H}{H_0} \times 100 \quad (15)$$

Introducing Eq. (7) into Eq. (15) gives:

$$D_c (\%) = \frac{4(G_0 - G)}{H_0} \left(\frac{V_r}{V_p}\right) \times 100 \quad (16)$$

In our experiments the maximum degree of crosslinking calculated from Eq. (16) reaches to about 75%. It shows indirectly that the degree of crosslinking of

PVA membrane can be easily changed by controlling the reaction variables. It is expected that the PVA membrane becomes less hydrophilic and more brittle as the degree of crosslinking increases. The degree of crosslinking may play an important role in the hydrophilicity and mechanical strength of PVA membranes. We will further investigate in detail the effect of the degree of crosslinking on the physical properties of PVA membranes in the following research.

CONCLUSIONS

The kinetics of crosslinking of PVA membrane with glutaraldehyde was examined, and the followings were found:

1. The reaction is approximately first order with respect to the concentration of hydroxyl group of PVA, glutaraldehyde and sulfuric acid.
2. The activation energy for the crosslinking reaction is about 5.77 kcal/mol.
3. The overall reaction rate can be expressed as follows:

$$-\frac{dG}{dt} = 7.78 \times 10^2 \exp\left(-\frac{2.90 \times 10^3}{T}\right) H^{0.95} G^{1.07} S^{1.15}$$

4. The degree of crosslinking of PVA membrane can be easily changed by controlling the reaction variables. It is also expected that the hydrophilicity and mechanical strength of PVA membranes can be modified by controlling the degree of crosslinking.

NOMENCLATURE

- a, b, c : coefficients of the correlation of $G_0 - G = at + bt^2 + ct^3$
- D_c : degree of crosslinking [%]
- E : activation energy [kcal/mol]
- G : concentration of glutaraldehyde at time t [mol/l]
- G_0 : initial concentration of glutaraldehyde [mol/l]
- H : hydroxyl group concentration of PVA polymer film at time t [mol/l]
- H_0 : initial hydroxyl group concentration of PVA polymer film [mol/l]
- k : overall rate constant [(mol/l·min)/[(mol/l)^a·(mol/l)^b·(mol/l)^c]]
- k_0 : frequency factor [(mol/l·min)/[(mol/l)^{0.95}·(mol/l)^{1.07}·(mol/l)^{1.15}]]
- k' : $k H_0^a G_0^b$ [(mol/l·min)/(mol/l)^{a+b}]
- k'' : $k H_0^a S_0^c$ [(mol/l·min)/(mol/l)^{a+c}]
- k''' : $k G_0^b S_0^c$ [(mol/l·min)/(mol/l)^{b+c}]

- M_n : molecular weight of a repeat unit $\left[\text{CH}_2-\underset{\text{OH}}{\text{CH}} \right]_n$
of PVA and equal to 44
R : ideal gas constant [1.98 cal/mol \cdot °K]
S : concentration of sulfuric acid at time t [mol/l]
 S_0 : initial concentration of sulfuric acid [mol/l]
T : temperature [K]
t : reaction time [min]
 V_c : volume of crosslinking solution [cm³]
 V_p : casting volume of casting plate [cm³]
 W_p : weight fraction of PVA of aqueous PVA casting solution [-]

Greek Letters

- α : reaction order with respect to hydroxyl group concentration of PVA membrane [-]
 β : reaction order with respect to glutaraldehyde concentration [-]
 γ : reaction order with respect to sulfuric acid concentration [-]
 ρ : density of aqueous PVA casting solution [g/cm³]

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